Green Synthesis of NanoMaterials for BioSensing

Juan José García-Guzmán, David López-Iglesias, Dolores Bellido-Milla, José María Palacios-Santander, and Laura Cubillana-Aguilera

Contents

J. J. García-Guzmán · D. López-Iglesias · D. Bellido-Milla
J. M. Palacios-Santander (✉) · L. Cubillana-Aguilera (✉)
Faculty of Sciences, Department of Analytical Chemistry, Campus de Excelencia Internacional del Mar (CEIMAR), Institute of Research on Electron Microscopy and Materials (IMEYMAT), University of Cadiz, Puerto Real, Cádiz, Spain
e-mail: juanjo.garciaguzman@uca.es; david.lopeziglesias@uca.es; dolores.milla@uca.es; josem.palacios@uca.es; laura.cubillana@uca.es

Inamuddin, A. M. Asiri (eds.), *Nanosensor Technologies for Environmental Monitoring*, Nanotechnology in the Life Sciences,
https://doi.org/10.1007/978-3-030-45116-5_7

1 Introduction

"Chemophobia" (Mckinnon 1981; Kauffman 1991; Chalupa and Nesměrák 2018) (or chemphobia or chemonoia) (Ropeik 2015), an irrational panic or preconception against chemical compounds or chemistry, is a relatively very new term quite widespread, with rather repercussions in food chemistry mainly in both the Western world and Asia (Gribble 2013) but founded in conceptions and apprehensions that have been coming for centuries. This mistrust, fed in part by news media's one-sided stories, natural and technological disasters of different magnitude (Cherry et al. 2018; Liu and Wang 2019) and current environmental problems of anthropogenic origin, such as extreme plastics pollution (Eriksen et al. 2014; Bergmann et al. 2017; Belontz et al. 2019), the greenhouse effect (Stephens et al. 2016; Büntgen et al. 2019), global warming (Trenberth et al. 2014), the erosion of ozone layer (Kuttippurath et al. 2018), and the proliferation of emerging pollutants and wastes (Gavrilescu et al. 2015; Calvo-Flores et al. 2018), among many others, has spread to industry, in general, and to chemical industry, in particular.

Arriving at this point, someone may wonders, would it be possible to imagine a life without chemicals or without things manufactured with them? Would it be possible to imagine our life without the enormous amount of goods generated by Chemical Industry? The answers to these questions are very simple: absolutely not and there would be no life at all, at least as we know it now, respectively. This is due to most manufactured goods involve at least one and in most cases many chemical processes. Chemistry and chemical industry have always had a central role in the provision of food and energy, materials, and medicines. Hence, they form part of our daily life (Fortineau 2004; Roy 2016). Nevertheless, chemical industry must follow a pathway that allows it to recuperate the lost confidence, to claim itself as an essential part of the engine that makes the world go round. The sustainability of these industries and hence of our planet depends on strategic choices made by governments. These entities intend to speed up the development and growth of industries to the transition towards a low-carbon economy by implementing green and strategic industrial policies (Cosbey 2013; Schmitz et al. 2015). That is why during the past few decades, scientific community and industry have been cooperating to make it possible, transmitting a new conception based on concerns that are more positive: that of a much greener, ecological, and sustainable chemical industry that generates environmentally benign products, which would be rather more appreciated by Governments, ONGs, and society in general.

For this purpose, the philosophy of "Green Chemistry" saw the light in the 1980s (Clark 2005). Anastas and Warner defined this term at the end of 1990s as "the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" (Anastas and Warner 1998). This term was reformulated and completed by Manley et al. 10 years later as "the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of toxic compounds to human health and the environment" (Manley et al. 2008). The Green Chemistry idea was accepted and worldwide

extended as an essential development of chemistry and chemical industry. Despite the general acceptance of this philosophy for the sustainable development, its application, not only in developed countries but also in India and China, was fragmented at the beginning, representing only a small part of the chemistry done in the past decades. Currently this concept has influenced education, research, and industrial practice in such a manner that an increasing and significant part of the most environmentally aware society daily demands greener and sustainable products, processes, and methodologies. In fact, Green Chemistry is understood now as a group of actions and attitudes rather than being constrained to chemical analyses based on nontoxic solvents; in other words, it must be considered as multidimensional (Kogawa and Salgado 2015). It is thinking about the process as a whole and reducing steps, energy, reagents, and costs to the minimum (de Marco et al. 2019). This sustainability even reaches Academia, since it is responsible for teaching new university students to gain knowledge on how to safeguard the earth for future generations (Płotka-Wasylka et al. 2018). However, as these authors state, there exist several false "greenness" in chemical literature and teaching practices, what suggests that this proper knowledge must be carefully obtained through what we call a "sustainable and green education," "environmental education" as United States Environmental Protection Agency reports (U.S. Environmental Protection Agency 1992), or "education for sustainable development" as UNESCO calls (Leicht et al. 2018).

As it is well known, the increasing industrialization process was a keystone for world economic evolution. During the second half of the twentieth century, social movements promoted a revolution in Green Chemistry and provoked changes that affected all the industry and its processes, trying making them more sustainable. As a consequence of this, environmental impact and companies and population awareness increased. That is why Paul Anastas and John Warner in the 1990s (Anastas and Warner 1998; Anastas and Eghbali 2010) listed the 12 Green Chemistry principles (Table 1), mainly based on the reduction or rejection of toxic solvents and the non-generation of residues in analyses and chemical processes.

In fact, the core of Green Chemistry can be understood as a set of reduction processes (Fig. 1). The reductions shown in the figure lead to many economic, environmental, and social benefits (ENDS 2003; European Commission 2003). Costs can be saved by reducing by-products and energy use, as well as increasing the efficiency of the whole process due to decreasing materials consumption. The abovementioned reductions also drive to environmental profit in terms of both feedstock depletion and end-of-life disposal. Moreover, the growing employment of renewable resources will make the manufacturing industry more sustainable (ENDS 2004). The minimization of hazardous events and the handling of dangerous substances offers additional social benefits to plant operators and local communities (Clark 2005).

Figure 2 summarizes the main important aspects about Green Chemistry and the role that all actors play for reaching global sustainability.

One of the most important documents regarding industrial sustainability is the Green Industry Initiative, where sustainable industrial development was tried to be

Table 1 The 12 principles of green chemistry (Anastas and Warner 1998; Anastas and Eghbali 2010)

N°	Description
1	**Prevention.** It is better to prevent waste than to treat of clean up waste after it is formed
2	**Atom economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product
3	**Less hazardous chemical synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment
4	**Designing safer chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity
5	**Safer solvents and auxiliaries.** The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary whenever possible and, when used, innocuous
6	**Design for Energy Efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure
7	**Use of renewable Feedstocks.** A raw material of feedstock should be renewable rather than depleting whenever technically and economically practicable
8	**Reduce derivatives.** Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste
9	**Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
10	**Design for Degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment
11	**Real-time analysis for pollution prevention.** Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances
12	**Inherently safer chemistry for accident prevention.** Substances and the form of a substance used in chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires

placed in the context of new global sustainable development challenges through Green Industry (UNIDO 2011). In fact, in this document the main points in which this initiative is based are highlighted.

In this declaration, firstly the need for Green Industry is discussed; later, Green Industry as a tool for implementing sustainable development is exposed; then, the benefits of Green Industry are described: economic, social, and environmental; in fourth place, the opportunities that Green Industry entails regarding mitigation of climate change and chemical pollution are presented. Finally, the existing hindrances towards the evolution of Green Industry in developing countries are outlined.

As previously affirmed, most goods and products that industry, especially Chemical Industry, manufactures and people use involve one or more chemical processes. Our life without them would not be the same for sure. However, Green

Fig. 1 "Reducing" as the core of green chemistry

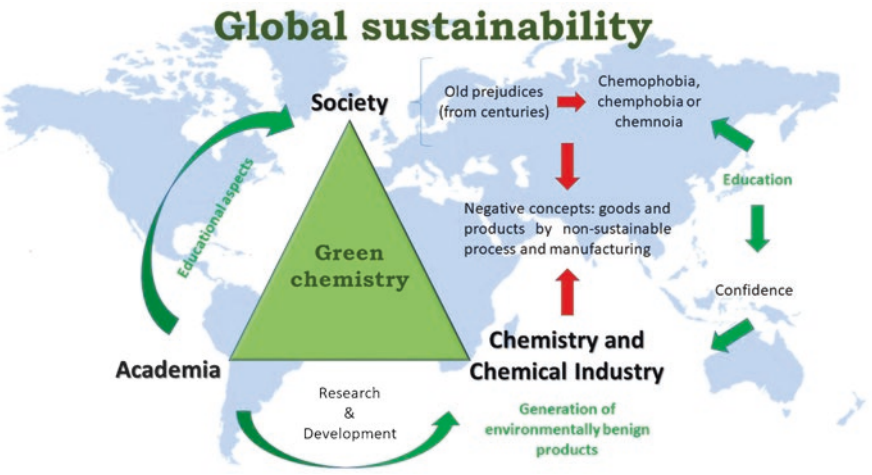


Fig. 2 Concepts related to green chemistry: philosophical aspects

Chemistry helps industry to become more ecological and sustainable, generating in this way environmentally benign products. Green Chemistry is considered as a multidisciplinary field that encompasses many areas like catalysis, solvents, synthesis, raw materials, products, and efficient processes (Song and Han 2015). Green synthesis constitutes one of the pillars of Green Chemistry and that is why the search

for efficient synthetic routes is of vital relevancy to achieve the sustainable industrial production, like in healthcare industry (Morgon 2015). Generation of chemists, mainly organic chemists, have been trained to formulate synthetic reactions in order to maximize yield and purity. Nevertheless, many chemical production processes lack efficiency in the employment of feedstocks and generate large amount of side products. A crucial point to reduce both is increasing atom economy, premise that would satisfy 4 out of the 12 Green Chemistry principles, particularly, principles of Prevention, Atom Economy, Less Hazardous Chemical Synthesis, and Use of Renewable Feedstocks (see Principles 1, 2, 3, and 7 in Table 1). Ideally, all the atoms in reactants should be turned into the desired products. The perfect synthesis, according to Green Chemistry, can be represented in Fig. 3.

Despite that in all industrial chemical processes 100% of atom economy is an utopia. Another form of minimizing the formation of secondary products is the integration of different reactions and processes, being the by-product in a certain reaction the feedstock of another (Song and Han 2015). Of course, yield, product isolation easiness, and purity needs, among other factors, should not be replaced by the concept of atom economy when implementing a chemical synthesis; in fact, it should be considered as an additional aspect (Lancaster 2002). It is noteworthy to mention that there are some reaction types that, due to their nature, would probably minimize waste because of being inherently atom efficient. A3 coupling (Alkyne, Aldehyde, and Amine) (Wei and Li 2002; Wei et al. 2004) and mainly Diels-Alder reaction are two typical and excellent examples of atom-economical reactions (Trost 1991, 1995) (Fig. 4).

Other either well-known or new efficient synthetic tools can be found in Anastas and Eghbali's work (Anastas and Eghbali 2010): cycloadditions, rearrangements, cascade or tandem reactions, multicomponent coupling reactions, metathesis, C-H

Fig. 3 Scheme and features of the perfect synthesis

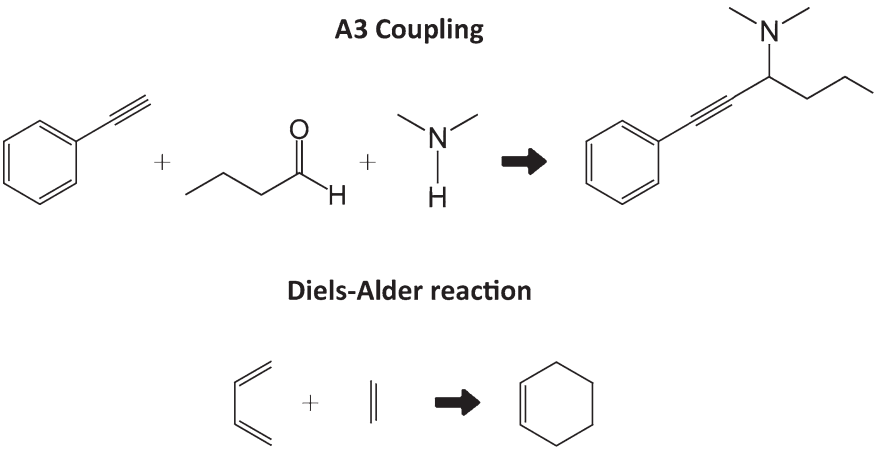


Fig. 4 Examples of two atom-economical reactions

activation, and enzymatic reactions, for citing some examples. Hence, these reaction types are necessary to be taken into account when implementing a synthetic strategy. However, other elements must obviously be considered as responsibles of the most competitive, efficient, and eco-friendly route: cost and feedstocks availability; toxicity/hazardous nature of feedstocks; yield; product isolation and purification easiness; energy, solvent, and cost-effective equipment exigencies; process times; and waste materials nature (Lancaster 2002).

On the other hand, green synthesis cannot be only circumscribed to organic chemistry, as it is formerly suggested, but to other disciplines as well, such as inorganic chemistry, materials science, or even analytical chemistry. In the latter area, it is also possible to point out Green Analytical Chemistry (De la Guardia and Garrigues 2012; Koel and Kaljurand 2019). This recent discipline focuses on the elaboration of new, green, and sustainable analytical procedures for organic and inorganic compounds determination in different kinds of samples characterized by complex matrices composition (Płotka-Wasylka and Namieśnik 2019). In fact, according to experts, the attention should be focused on making sample-pretreatment and analytical methods much greener thanks to the development of new strategies and tools (Armenta et al. 2008). To these ones, other complementary practices can be added, such as minimization of wastes, recovery of reagents, on-line decontamination of wastes, and the use of reagent-free methodologies. Hence, it is mandatory to fix a group of clear and concise reccomendations constituting the principles of Green Analytical Chemistry, susceptible to be applied in laboratory practices. In this way, the 12 principles of Green Analytical Chemistry were proposed in 2013 (Gałuszka et al. 2013) (see Table 2). They supposed a reformulation of the existing principles of Green Chemistry and Green Engineering since they did not fully fulfill the needs of analytical chemistry. From the 12 principles of Green Chemistry, only four can be directly made suitable for analytical chemistry: (1) residues prevention

Table 2 The principles of green analytical chemistry expressed as the mnemonic significance

S	Select direct analytical technique.
I	Integrate analytical processes and operations.
G	Generate as little waste as possible and treat it properly
N	Never waste energy.
I	Implement automation and miniaturization of methods.
F	Favor reagents obtained from renewable source.
I	Increase safety for operator.
C	Carry on in situ measurements.
A	Avoid derivatization.
N	Note that the sample number and size should be minimal.
C	Choose multi-analyte or multi-parameter method.
E	Eliminate or replace toxic reagents.

(principle 1); (2) environmentally friendly solvents and reagents (principle 5); (3) energetically efficient designs (principle 6); and (4) minimization of derivatization (principle 8). These four principles constitute the core of synthesis in some areas of analytical chemistry. Besides, two more key goals should be considered to achieve sustainability in analytical synthesis: (5) removing or reducing chemical substances whatever the purpose they are used for and (6) increased safety for the operator. As it can be seen, most of these topics demand reductions (Clark 2005) (see Fig. 1). However, the necessity of reaching an agreement between the performance parameters and Green Analytical Chemistry exigencies constitutes one of the disadvantages of green laboratory practices. Most of the strategies for analytical chemists projected in the 12 principles collected in Table 2 may worsen some quality analytical parameters: sensitivity, precision, accuracy, selectivity, detectability, or representativeness (Gałuszka et al. 2013). Regardless, the fast technological advance and knowledge about current problems will lead to an enhancement of green analytical methods.

According to Gałuszka et al. (2013), many green alternatives existing in different fields of analytical chemistry versus conventional methods imply the use of sensors and biosensors, i.e., bisphenol A or 17β-estradiol determination in urban wastewater (instead of gas chromatography/mass spectrometry); folic acid determination in medicines, blood glucose or atrazine in water (instead of spectrophotometry); and lead in water (instead of graphite furnace/atomic absorption spectrometry). (Bio) sensors show several advantages versus other commonly used analytical techniques like chromatography or mass spectrometry, including no or simple sample treatment, non-complex instrumentation, low-cost, high specificity, sensitivity, fast response, relatively compact size, multiparameter analysis, in situ determination, and ease of implementation to detect biomolecules (Bahadir and Sezgintürk 2015; Amine et al. 2016; García-Guzmán et al. 2019; Vogiazi et al. 2019). All these advantages are in agreement with the principles of Green Chemistry and Green Analytical

Chemistry (Arduini et al. 2019). Hence, (bio)sensors are a good and serious alternative to determine different kinds of analytes from biomedical, agrifood, or environmental interest versus other typical analytical techniques, which require expensive instrumentations, laboratory setup, skilled personnel, and usually the employment of organic solvents, producing hazardous waste. Due to the aforementioned advantages, (bio)sensing devices are being recently considered of great importance for being used in industry (Siontorou 2019), mainly in food processing industry (Murugaboopathi et al. 2013; Thakur and Ragavan 2013; Mehrotra 2016; Mustafa and Andreescu 2018; Neethirajan et al. 2018a), and also in pharmaceutical (Macdonald 2019), environmental (Patil et al. 2019), and biomedical industries (Cifric et al. 2020).

Nevertheless, most times these (bio)sensors are employed in combination with different kind of materials and nanomaterials in order to enhance analytical quality parameters, like sensitivity, limit of detection, and selectivity, among others, and, thus, their analytical performance (Attar et al. 2015; Bernardo-Boongaling et al. 2019; Shafiei-Irannejad et al. 2019), which make them quite competitive versus other analytical techniques. Among the materials and nanomaterials employed in (bio)sensing, metal (Cubillana-Aguilera et al. 2011; Franco-Romano et al. 2014; Zarzuela et al. 2018; Shukla and Iravani 2019) and metal oxide nanoparticles (González-Álvarez et al. 2016; Henam et al. 2019; Sundaresan et al. 2019), nanowires (Liu et al. 2012; Luo et al. 2019), nanocarbon-based materials (Roh et al. 2019), graphene (Chang et al. 2019; Dong et al. 2019; Hafeez et al. 2019) and magnetic nanostructured molecularly imprinted polymers (Lahcen et al. 2019), among others (Kumar 2007; Merkoçi 2009), as well as new electrode materials stand out (Cordero-Rando et al. 2002; Hidalgo-Hidalgo de Cisneros et al. 2003; Cubillana-Aguilera et al. 2006; López-Iglesias et al. 2016, 2018; Palacios-Santander et al. 2017). There are many different technologies for preparing them, but in this chapter special attention will be paid to two of the most commonly used environmentally friendly technologies, from the energy cost savings point of view: microwave and ultrasound (Strauss 2002; Timothy and Cintas 2002; Chatel 2016). Both techniques are based on the use of focused radiation that reduces reaction times, increases product yields, and also makes reactions more selective (Clark 2005); that is why ultrasound and microwave can be considered the base of the most powerful, ecological, and interesting technologies developed for green analytical synthesis (Lodeiro and Capelo-Martínez 2009). Their advantages versus other synthetic routes can be summarized as follows: (1) environmentally friendliness, (2) very low energy requirements, (3) drastically reduced time of synthesis: from days/hours to few minutes, and (4) simple and (5) low cost instrumentation compared to other technologies.

Moreover, synthesis routes of functional materials and nanomaterials through biomineralization and biotemplating, typically known as biosynthetic routes, by using biopolymers (Khomand and Afsharpour 2019), plant extracts (Agarwal et al. 2019) and other biomolecular structures (bacteria and fungi, among many others) (Gahlawat and Choudhury 2019) play also an important role in Green Analytical

Chemistry and attract tremendous amount of interest. The reason for this attention is the promise to achieve enhanced control over positioning and linking different functional nanostructures to give place to complex nanodevices (Padalkar et al. 2010). In the last decade, the exploitation of natural biopolymers fibers, like cellulose, and plant extracts (olive, geranium, *Aloe vera*, and a much wide etcetera) for synthesizing inorganic nanoparticles, nanoparticle chains, and nanowires has increased a lot. The advantages of using these biostructures in synthetic routes of (nano)materials are evident. For example, in the case of cellulose or other biopolymers-based materials, they are relatively inexpensive, renewable, abundant in many different forms, and have hydroxyl and other functional groups that are accessible for chemical modification (Azizi Samir et al. 2005). With respect to plant extracts (Makarov et al. 2014; Shah et al. 2015), the enormous diversity of reactive chemical compounds possessing different functional groups (alcohols, ketones, esters, etc.) may also offer, in some cases, other advantages, such as abundancy, long lifetime, low or zero-cost requirements for their culture, the easiness of extract preparation, antioxidant activity, antimicrobial properties, and bacterial growth inhibition of some compounds present in the extracts of most plants (Franco-Romano et al. 2014). That is why biosynthesis routes for obtaining (nano)materials will also be paid special attention in this work.

This chapter intends to provide a summary of the most relevant green synthesis or biosynthesis routes, mainly based on the clean ultrasound and microwave technologies, or even in hybrid techniques (Sect. 2), and how they can be employed to synthesize nanomaterials or materials for building (bio)sensing devices (Sect. 3). Currently some of these materials are directly or can be susceptible of being produced by industry, due to scaling-up processes and employed in the industry itself for detection and/or determination purposes and/or for quality control, among other applications in different kinds of industrial companies: food, environmental, biopharmaceutical, and biomedical industries (Sects. 4 and 5). Finally, a critical discussion about the abovementioned topics and their relationships with sustainable development of chemical industry is reported.

2 Green Synthesis Routes

Synthesis routes followed by Green Chemistry principles were given particularly relevance in the last decades. Many research efforts are focused on their development for many reasons, such as short reaction times, low cost, easy workup, and low energy requirements.

Three main synthetic routes can be distinguished: microwave-assisted, ultrasound-assisted, and biosynthesis. A schematic representation is shown in Fig. 5.

In addition to their importance in Green Chemistry, a brief overview for each one will be discussed.

2.1 Ultrasound-Assisted Method

Nowadays, sonochemistry constitutes a broad research field with a growing interest, especially for synthesis purposes. Thus, the employment of ultrasound has been developed as an emergent powerful tool for obtaining an extensive set of organic and inorganic compounds.

2.1.1 Basic Aspects of Ultrasound: Cavitation Process

Sonochemical reactions involves the ultrasonic cavitation, phenomenon based on the formation, growth, and implosion of air bubbles in the liquid phase (Cravotto and Cintas, 2006). Several theories concerning the cavitation phenomena have been proposed: electrical, plasma discharge, supercritical, and hot spots. According to the last one mentioned, high local pressures and temperatures are produced inside the air bubbles and at their interfaces after collapsing, reaching values around 5000 K (Leong et al. 2011). Under these extreme conditions, short-live species from solvent and/or substrate molecules pyrolysis are produced. Hydrogen peroxide and oxygen are generated as by-products by coupling of radical species ($H^{\bullet}$ and $OH^{\bullet}$). This process, known as sonolysis (Torres-Palma and Serna-Galvis 2018), is represented as follows.

Decomposition of water molecules by ultrasound

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet}$$

Formation of secondary radicals

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$$

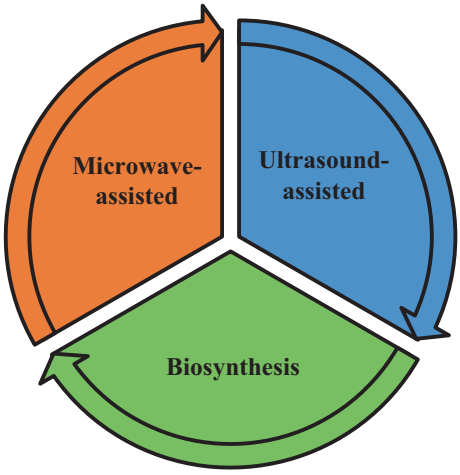


Fig. 5 Schematic representation of the major green synthetic routes

Generation of hydrogen peroxide by radical coupling

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

The radical species derived from ultrasonic waves can react with other reagents, following a single-electron transfer pathway (SET). A representative example is the alkylation of 4-nitrobenzylbromide, which led to a different product under sonication with respect to the one obtained under silent conditions (Fig. 6a). This result can be explained with the involvement of radicals species from reagents' cleavage under sonication (sonochemical switching), as shown in Fig. 6b (Dickens and Luche 1991).

The ultrasound approach has been extensively applied to assist the synthesis of inorganic and organic compounds. In Sects. 2.1.2 and 2.1.3, numerous examples are exposed.

2.1.2 Ultrasound-Assisted Synthesis of Organic Compounds

There are several reviews in the bibliography related to the synthesis of organic compounds assisted by ultrasound, providing a detailed discussion including the reaction pathways proposed for each case (Baig and Varma 2012; Banerjee 2017). Ando's reaction is an illustrative example of organic synthesis in which different product was obtained under ultrasound. The reaction between benzylbromide, potassium cyanide, and alumina in toluene gave the benzylcyanide under sonication, instead of the diphenylmethane derivative obtained under mechanical stirring conditions. The authors proposed the inactivation of the acidic sites on the alumina

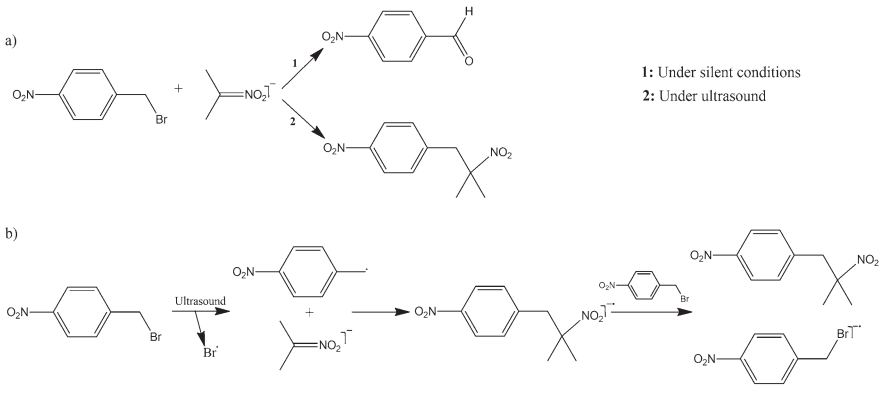


Fig. 6 (**a**) Products obtained by alkylation of benzylbromide under sonication and silent conditions; (**b**) Kornblum-Russell reaction mechanism under ultrasound

surface by the strong adsorption of potassium cyanide under ultrasound conditions (Ando and Kimura 1990).

Not all the ultrasound-assisted organic reactions involve the sonochemical switching phenomena. Despite this fact, two important advantages are ascribed to the use of ultrasound: high yields and low reaction times, among others. All of them lead to several features in terms of Green Chemistry, summarized in Gregory Chatel's work (Chatel 2018): reduction of waste products, easy synthesis workup, and minimization of energy requirements.

Table 3 shows the reaction time and yield obtained for different organic products obtained synthesized under silent conditions and assisted by ultrasound.

As shown in the previous table, shorter reaction times, as well as higher yields were achieved under ultrasound conditions. This demonstrates the benefits of ultrasound in organic synthesis.

Other important aspect in some conventional organic syntheses is the use of toxic reagents, harmful for the environmental and human health. By using ultrasound, organic hazardous solvents can be replaced by greener ones or totally removed (solvent-free conditions). The selective oxidation of sulfides to sulfoxides can be carried out by using hydrogen peroxide as solvent (Mahamuni et al. 2006), instead of methanol. Polymerization can also be mediated by ultrasound, taking place by polymer or solvent-derived radical processes. Several examples of these types of reactions are reported by McKenzie and coworkers (McKenzie et al. 2019).

2.1.3 Ultrasound-Assisted Synthesis of Inorganic Compounds

Inorganic synthesis can also be ultrasound-assisted, leading to several advantages with respect to conventional routes. Suslick and coworkers summarized the influence of chemical and physical effects of ultrasound in the synthesis of nanostructured materials (Bang and Suslick 2010; Xu et al. 2013). Among all of them, metallic and metallic-oxide nanoparticles have received wide attention in the past few decades due to their optical properties, as well as their unique reactivity, very useful in many applications (Christian et al. 2008).

For noble metals, radical species generated by sonolysis of the water ($H^{\bullet}$ and $OH^{\bullet}$) can act as reducing agents, avoiding the use of any additional reducing compound in the synthesis. However, secondary species can be added to produce secondary radical species, promoting the rate of the process.

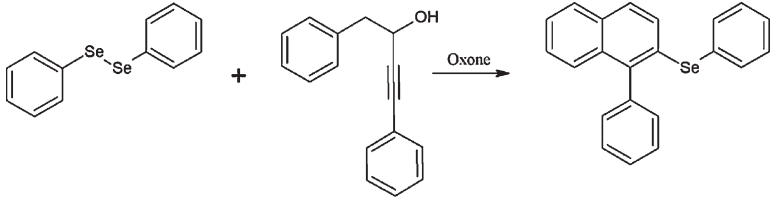
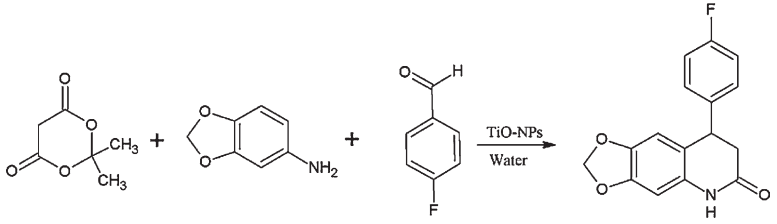
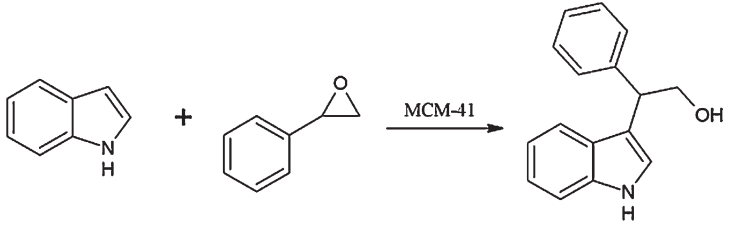
The overall process was detailed in Suslick and coworkers' work (Xu et al. 2013) and can be summarized as follows (recombination of radicals derived from the sonolysis of water was not included).

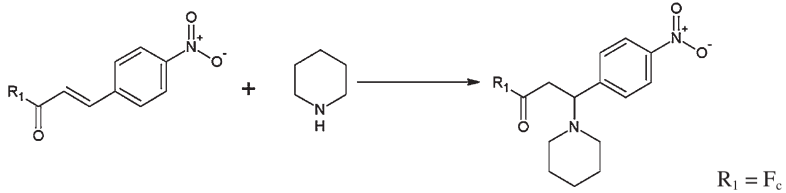
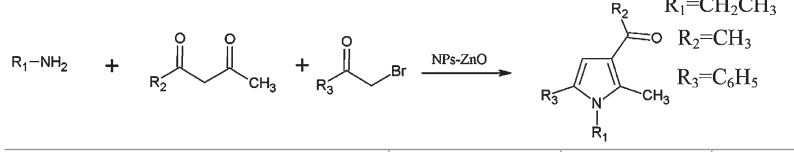
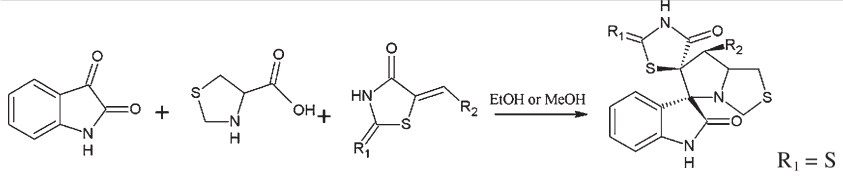
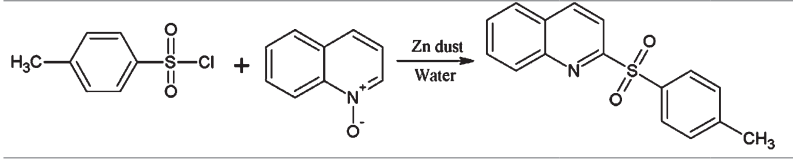
Decomposition of water molecules by ultrasound

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet}$$

Formation of secondary radicals ($R^{\bullet}$)

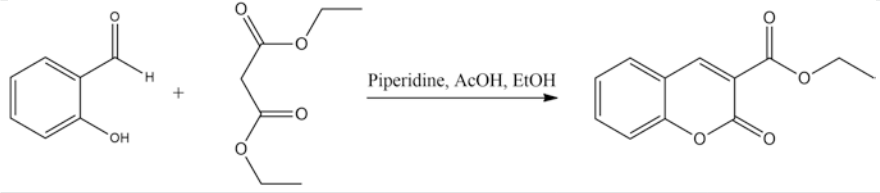
Table 3 Reaction times and yields of different organic compounds obtained under silent conditions and assisted by ultrasound

Synthesis process	Solvent	Silent conditions		Ultrasound-assisted		References
		Time	Yield (%)	Time	Yield (%)	
Synthesis of 2-organoselanyl-naphthalene	EtOH	72 h	78	50 min	84	Perin et al. (2018)
						
Synthesis of quinolone derivative	Water	160 min	60	15 min	90	Bhardwaj et al. (2019)
						
Opening of ring epoxide	Free	150 min	72	60 min	80	Nasef et al. (2016)
						

Aza-Michael reaction	Water	16 h	73	30 min	98	Yang et al. (2005)
 $R_1 = F_c$						
Multicomponent reaction of N-substituted pyrrole	Free	6–9 h	74	30 min	90	Shahvelayati et al. (2017)
 $R_1{=}CH_2CH_3$ $R_2{=}CH_3$ $R_3{=}C_6H_5$						
Cycloaddition reaction	EtOH	13 h	87	5 h	93	Hu et al. (2012b)
	MeOH	15 h	80	6 h	85	
 $R_2 = C_6H_5$ $R_1 = S$						
Synthesis of 2-sulfonylquinoline derivative	Water	8 h	67	25 min	86	Xie et al. (2017)
						

(continued)

Table 3 (continued)

Synthesis process	Solvent	Silent conditions		Ultrasound-assisted		References
		Time	Yield (%)	Time	Yield (%)	
Synthesis of coumarin (Knoevenagel condensation)	EtOH	7 h	80	40 min	88	Da Silveira Pinto and De Souza (2017)
						

$$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O$$

$$RH + H^{\bullet} \rightarrow R^{\bullet} + H_2$$

Chemical reduction of noble metallic salt (M)

$$M^{n+} + nH^{\bullet} \rightarrow M^0$$

$$M^{n+} + nR^{\bullet} \rightarrow M^0$$

Formation of noble metallic salt nanoparticles (M_m)

$$mM^0 \rightarrow M_m$$

By using this approach, gold (Okitsu et al. 2007), platinum (Mizukoshi et al. 1999), silver (Elsupikhe et al. 2015), and palladium (Nemamcha et al. 2006) nanoparticles were synthesized.

The sonochemical method provides mainly spherical nanoparticles, although other nanomaterial shapes can be obtained under ultrasound. Different gold nanoparticles morphologies were formed from the reduction of the gold salt under ultrasound by setting the sodium dodecyl sulfate concentration and the ultrasonic intensity. According to this research work (Park et al. 2006), sodium dodecyl sulfate concentration values lower than critical micelle concentration drove to the obtention of nonspherical nanoparticles. With respect to the influence of the ultrasonic power, low ultrasonic irradiation produces lesser radical species in comparison with those produced at higher values, and hence the generation of nanodisks, nanoprisms, and nanorods, among other structural shapes, is promoted due to the slow reduction rate of the gold salt. Other examples about the obtaining of nonspherical gold nanoparticles from the chemical reduction of the gold salt by ultrasound can be stated. Gold nanorods were obtained when using cetyltimethylammonium bromide as stabilizing agent and ascorbic acid. In this report, the pH of the solution plays a significant role in the aspect ratio of nanorods (length/width ratio): the average aspect ratio decreases as pH value increases (Okitsu et al. 2009). Gold nanobelts were formed in the presence of α-D glucose by using a green, nonhazardous, and rapid synthesis method. The effect of the concentration of α-D glucose was discussed in this research work. Furthermore, the use of ultrasound was proposed to accelerate the process, as well as to enhance the reorganization of the molecules of glucose on gold crystals (Zhang et al. 2006).

Nonspherical nanoparticles constituted by other metals were synthesized following the sonochemical route. Cubic silver nanoparticles were formed by self-arrangement of dodecylbenzenesulfonic acid sodium salt as surfactant. The nanoparticle morphology was also influenced by the concentration of poly(vinylpyrrolidinone), the ripening time, and the ultrasound (Moghimi-Rad

et al. 2011). The formation of copper nanowhiskers was reported in Min Xu and coworkers' report (Xu et al. 2015). According to this work, ultrasound plays an essential role in the synthesis of nanowhiskers: low ultrasonic power favors the growth of the particles in one dimension, while higher values lead to irregular particles.

Gold nanoparticles can also be synthesized using sodium citrate as reductant under high-power ultrasound conditions (Cubillana-Aguilera et al. 2011). Their characteristic features, optical properties and size, can be easily characterized by analytical routine techniques, dynamic light scattering, and UV–vis spectrophotometry. The characterization of nanoparticles' size by dynamic light scattering, considered as a no complex and low-time consuming methodology, was also performed in the silicon oxide nanoparticles synthesis by ultrasound (González-Álvarez et al. 2016), as an alternative versus the classical Stöber method, and successfully correlated to the results obtained with transmission electron microscopy, the most used technique for evidencing particle shape and size. Thus, the utility of routine analysis in the monitoring of optical properties and sizes of metal or metal oxide nanoparticles is demonstrated.

Therefore, the development of ultrasound-assisted syntheses as an alternative to conventional methods is demonstrated. The production of radical species by ultrasonic irradiation enhances the reaction rate, as well as reduces the formation of by-products in some cases by sonochemical switching phenomena. Thus, shorter reaction times, higher yields, and high selectivity were ascribed to the employment of ultrasound, leading to several improvements in terms of Green Chemistry. Furthermore, the role of ultrasound in the formation of shape-controlled nanomaterials can also be stated, allowing tailor-made structures to reach unique and useful properties for sensing and catalysis, among other applications.

2.2 Microwave-Assisted Synthesis

In Sect. 2.1, ultrasound has been exposed as an interesting approach towards Green Chemistry, although it is not the only one. In this section, microwaves assistance will be discussed as an excellent alternative to conventional synthesis routes.

2.2.1 Microwave Heating: Fundamentals and Mechanisms

Microwaves is a kind of electromagnetic radiation comprised between radio waves and infrared, with a wavelength range from 1 mm to 1 m (0.3–300 GHz). The interaction between this radiation and the matter has different physical effects, such as mobilizing the electric charges in liquids or conducting ions in solids. The electromagnetic energy produced by microwave irradiation is transformed into heat, promoting the conversion of reagents to products. As an example, a schematic

representation of a reaction assisted by microwaves radiation appears in Fig. 7. The heating mechanism of this phenomena will be explained deeply later (Sekhon, 2010).

Regarding the interaction between microwave and the compound, three different situations can be established:

1. Microwaves have no effects in the system, e.g., sulfur. The radiation travels through the species without altering it.
2. Microwave is reflected by the system, e.g., metals such as copper. The radiation cannot travel through it and it is reflected.
3. Microwaves are absorbed by the system, e.g., water. The absorption leads to an increase of the temperature.

Based on the previous classification, compounds which absorb the microwaves will be considered in this section due to their predominance in microwave chemistry. However, the other materials have interesting application as well; some of them will be explained later.

There are three main mechanisms about the role of the microwave radiation in the heating process: dipolar polarization, conduction mechanism, and interfacial polarization. All of them will be described in this section.

Dipolar Polarization

A polar molecule, which is affected by a varying electric field (microwave radiation), try to reorientate itself. The molecular friction effect causes a release of heat to the system. Thus, it is necessary to possess a dipole to cause heat with this mechanism. In this sense, it is possible to take advantage of this phenomenon by using polar solvent, such as ethanol, methanol, and water, among others, or polar solutes such as ammonia or formic acid. The most notorious factor is the application of a nonconstant field with a suitable frequency, which facilitates the interaction of the particle. This frequency must not be too high because the molecule will not be fast enough to follow the changes in the field, leading to a premature stop of the

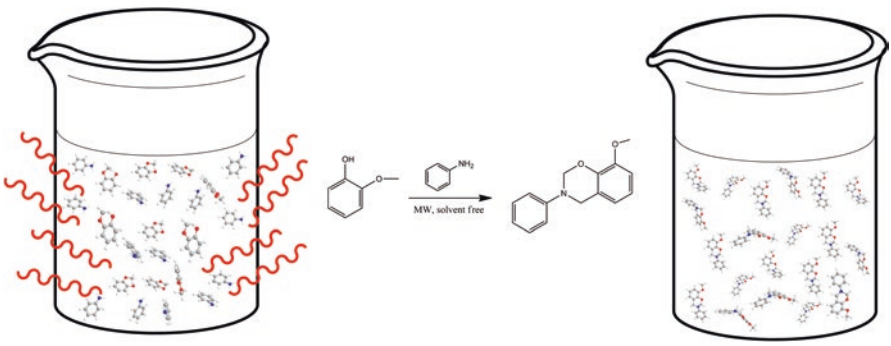


Fig. 7 Example of reaction promoted by microwave

molecule. In another way, if the frequency is too low, the molecule will have enough time to realign itself with no effective interaction between molecules. By using the microwave radiation (frequency 0.3–30 GHz) it is possible to provoke an effective particle interaction (Lidström et al. 2001). An example of dipolar polarization can be observed in Fig. 8a.

Conduction Mechanism

Electrons moved throughout a resistance provide heat to the system. This principle is the basis of the conduction mechanism. A conductor submitted into an electric field generates a flow of electron, or ions, which is against the internal resistance, leading to the heating of the conductor. Therefore, charge carriers (electrons, ions, etc.) in a sample can be moved using an electric field. The inner resistance will heat the sample due to the induced currents formed. It is important to clarify that high conductive materials will not be heated in this way due to the reflective properties of these ones (Wathey et al. 2002). A scheme of the conduction mechanism is presented in Fig. 8b.

Interfacial Polarization

The combination of the previous mechanisms gives, as a result, a third heating mechanism. It is relevant when a conducting material is dispersed in a non-conductive medium such as metal powder in sulfur. Even if the sulfur does not absorb the radiation and the metal reflects it, the whole system is an appropriate microwave absorbing material. This heating mechanism is based on the dipolar polarization but it is slightly different. In this case, the metal powder limits the movement of the ions by forces that are similar to the cases of polar solvents. The

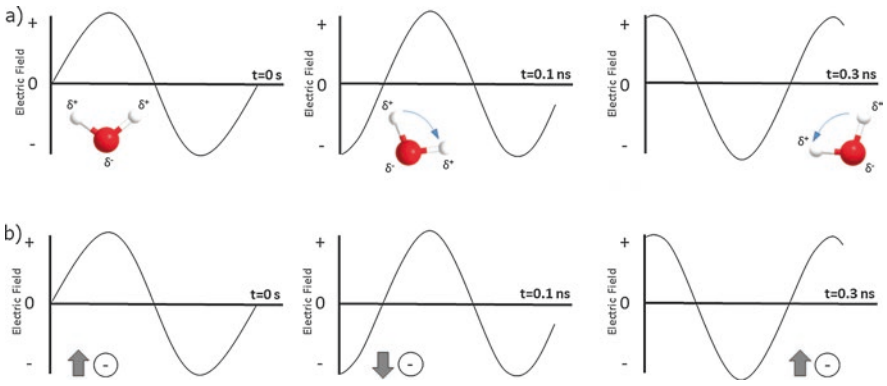


Fig. 8 Heating mechanism of microwave radiation: (**a**) dipolar polarization and (**b**) conduction mechanism

restriction of these ions results in a random motion and, afterwards, the heating of the sample (Gabriel et al. 1998).

2.2.2 The Use of Microwaves as a Green Approach in Organic and Inorganic Syntheses

Classically, the heating methods used in organic and inorganic reactions were based on convection, which involves complex workup, such as oil baths, Bunsen burner, or furnace, among others. Other drawbacks in relation with green terms can be ascribed to conventional synthesis methods. They involved petrochemical ingredients, several catalyst and separation and purification processes. Furthermore, organic synthesis implied many health issues and risk for workers, long reaction times, high cost, and inefficiency to heat the system. The last one is based on the convection mechanism, leading to energy losses due to the heat dissipation phenomena. Microwave assistance is proposed as a suitable alternative to conventional routes. The microwave radiation affects only target molecules or solvent molecules, involving less energy. Thus, the heating procedure is more focused and effective.

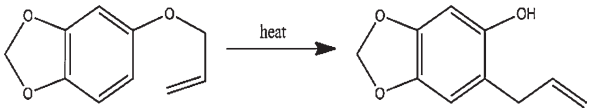
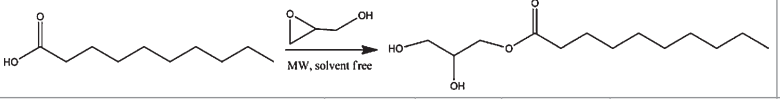
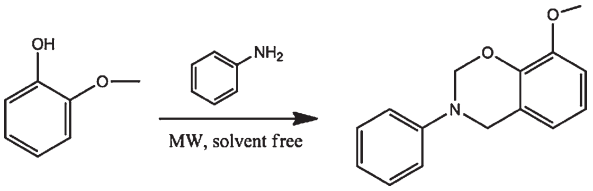
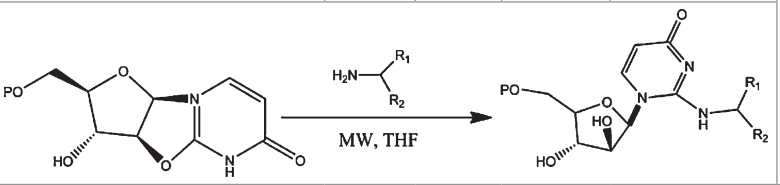
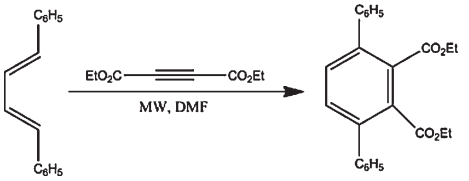
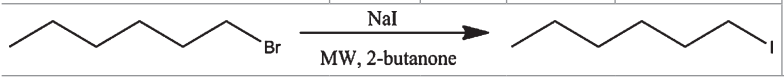
Besides, the microwave provides other advantages like higher reaction rates, fast and easy optimization, and more reproducible syntheses. In addition to the more efficient heating mechanism, the microwave also reaches higher temperatures, decreasing even more the time needed for certain syntheses. For example, the fluorescein synthesis lasts 10 h with conventional procedures; otherwise, it can be performed in 35 min using a microwave approach (Charde et al. 2012). Moreover, in this kind of synthesis higher final yields of the desired product were reached, minimizing the formation of side products. Thus, the purification procedure is easier and takes shorter times.

In Table 4, the synthesis parameters obtained for synthesis procedures assisted by microwaves and by conventional heating are exposed.

In the previous table the reduction in the time reaction and the general increase in yields are demonstrated. It is also established that the microwave approach is highly versatile in organic synthesis. On the other hand, as it has been mentioned previously, there are several reactions where the organic solvents are minimized or completely removed (solvent free). A mineral support is used instead of the non-eco-friendly solvent and the microwave is adjusted to focus only on the sample (Mordini and Faigl 2005; Algul et al. 2008; Gaba and Dhingra 2011). These reactions will be much greener than their conventional analogous process due to saving in toxic solvents. Other aspect that can be stated is the possibility to carry out several reactions at the same time by using a multimode microwave device.

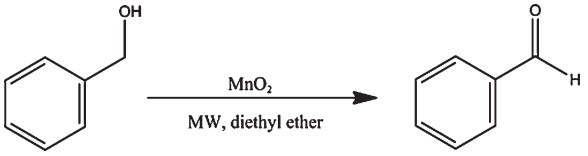
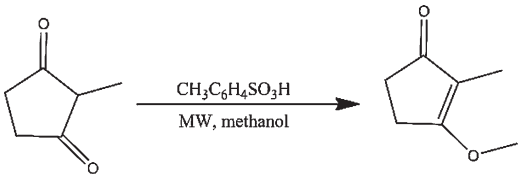
Microwave approach is also used in polymer syntheses. The energy saving in these procedures and the heating efficiency make this technique an economic and suitable option. In addition, the employment of microwave radiation in the curing process has greatly shortened the reaction time. It has been established that this process is strongly dependent on how the pulse is applied; on the contrary, the power applied is not so important. A higher volume of product can be produced by using

Table 4 Reaction promoted by microwaves and their time and yield in comparison with the ones obtained by using conventional heating

Reaction promoted	Microwave-assisted		Conventional heating		References
	Time	Yield (%)	Time	Yield (%)	
Synthesis of 6-allylbenzo[d][1,3] dioxol-5-ol	5 min	97	36 h	72	Majetich and Hicks (1995)
					
Synthesis of 2,3-dihydroxylpropyl decanoate	1 min	100	100 min	77	Mhanna et al. (2018)
					
Synthesis of benzoxazines	6 min	55–82	90–180 min	55–75	Oliveira et al. (2017)
					
Synthesis of a protected *keto*-Lysidine	1 h	68	72 h	71	Sweeney et al. (2019)
					
Diels-Alder reactions	20 min	58	6 h	67	Majetich and Hicks (1995)
					
Finkelstein reactions	4 min	83	40 min	85	Majetich and Hicks (1995)
					

(continued)

Table 4 (continued)

Reaction promoted	Microwave-assisted		Conventional heating		References
	Time	Yield (%)	Time	Yield (%)	
Oxidation reactions	7 min	52	8 h	20	Majetich and Hicks (1995)
					
Esterifications	2 min	86	90 min	84	Majetich and Hicks (1995)
					

large reactors and a controlled solvent-free synthesis with microwave heating. For instance, it has been reported that the peptides production leads high yields and purity. This process implies the assembly of peptide chains of about 30 amino acids carried out only in one night with an automated microwave system (Nayak et al. 2016).

Despite its wide use in organic syntheses, there is a growing increase in the use of microwave in inorganic compound syntheses (Darvishi et al. 2017; Zhao et al. 2017; Li et al. 2019; Rossini et al. 2019; Xu et al. 2019), especially in the nanomaterial field. In these cases, the microwave radiation provides advantages, such as narrow particle size distribution, energetic efficiency, particle size controllability, and fast crystallization rate, among others. The use of microwave was proposed for generating some inorganic compounds by hydrothermal and solvothermal method, leading to some improvements in terms of yields and reaction times, in comparison with the conventional method (Gaikwad and Han 2019). Zhou et al. (2014) proposed a microwave-assisted hydrothermal method to obtain CuO spheres, which are wrapped and linked by graphene nanosheets. Furthermore, it is possible to combine a redox system with a microwave-assisted hydrothermal method. Chen et al. (2013) obtained polymorphic MnO_2, being able to grow the material with different crystallographic phases (α, β and γ) modifying the synthesis parameters. Zhang et al. (2019) have obtained $CoFe_2O_4$ nanoparticles, by a microwave-assisted solvothermal method, which even possess better properties than the nanoparticles resulting from a conventional solvothermal method. Palma-Goyes et al. (2018) provide a facile and rapid microwave-assisted solvothermal method to synthesize RuO_2 nanoparticles employing citric acid in ethylene glycol as stabilizing agent, H_2O_2 as oxidizing agent, and the metallic precursor.

Moreover, it is also possible to use the microwave radiation to assist a sol-gel process. A great number of studies have been carried out in this direction. Ghule et al. (2011) informed the synthesis of zinc oxide nanorods taking advantage of the microwave radiation employing zinc, nitrate, ethylene glycol, and sodium hydroxide as precursors. Shrike et al. (2011) synthesized pure anatase TiO_2 nanoparticles with a particular porous structure by employing a sol-gel microwave-assisted method. Garadkar et al. (2013) developed an easy procedure to synthesize $ZnWO_4$ nanoparticles controlling successfully their size by using a microwave-assisted procedure. This approach can also be used to synthesize magnetic nanoparticles as well. Obaidullah et al. (2019) reported an easy and fast method to make Fe_2O_3 nanoparticles coated by a shell of SiO_2 retaining their magnetic properties even at high temperatures. Thus, the microwave radiation has greatly supported conventional materials syntheses methods enlarging the possibilities in this field. Consequently, the number of green process has been considerably increased over the last few years.

Therefore, it is noteworthy to mention some aspects regarding the use of microwave as green approach in synthesis. Unlike the monotonous conventional heating, which is very time consuming, microwave chemistry opens a wide range of new possibilities for the development of new methods of synthesis. The time saving, replacing the toxic solvents to greener ones, greater selectivity, enhancement of reaction yields, and easier setup are also highlighted. For all these reasons, microwaves assistance is widely considered as a very effective and promising tool in Green Chemistry (Ravichandran and Karthikeyan 2011).

2.3 Biosynthesis

The use of biological compounds is currently considered by the scientific community as an attractive way to synthesize complex molecules by one-pot method (Shamaila et al. 2016). In this manner, biosynthesis constitutes an environmental-friendly, economic, and low-time consuming synthesis route. In this chapter, the main groups used in biosynthesis are presented, providing some information about their role in syntheses.

2.3.1 Plant Extracts

Plants are a rich source of chemical compounds, commonly known as phytochemicals, such as polyphenols, terpenoids, alkaloids, and proteins, for instance. They can be easily extracted by using different solvents, such as water, methanol, ethanol, and dimethylformamide, among others (Altemimi et al. 2017). To follow the green rules, water-based and low-toxicity solvents are required for extraction purposes. Concerning the extraction method, microwave and ultrasound constitutes economic, low cost, low time-consuming, and viable tools in the extraction of phytochemicals (Tiwari 2015; Dhanani et al. 2017), and hence their use is encouraged in Green Chemistry.

The phytochemical compounds from plant extracts contain functionalized groups able to reduce, as well as to stabilize, the final product. Based on this dual role, plant extracts are excellent candidates to synthesize metallic nanoparticles, allowing controlling many properties, e.g., size and morphology. The influence of several parameters to obtain tailor-made nanoparticles, such as temperature, pH, and type of extract, will be commented in Sect. 3.4.1 of this chapter.

Plant extracts are very complex matrices; therefore, a detailed study about the bioreduction mechanism is required. Several research groups investigated the reducing role of flavonoids, proteins, and amino acids available in plant extracts (Makarov et al. 2014). In the case of flavonoids, the reactive hydrogen was released by keto-enol tautomerism, leading to the keto-form. As an example, A. K. Singh and coworkers summarizes a possible mechanism for the synthesis of metallic nanoparticles mediated by the keto-enol tautomeric process of eugenol, shown in Fig. 9 (Singh et al. 2010).

The participation of amino acids and proteins in the reduction process was also reported owing to the existence of functionalized amino groups. Based on the above, the overall process of metal nanoparticles formation implies reducing the metal precursor, followed by the nucleation and growth processes.

2.3.2 Biopolymers

Biopolymers can be obtained via microbial synthesis from biological resources as starting products (Ahmad et al. 2015). Among all of them, polysaccharide biopolymers have some excellent properties, enabling the development of advance functionalized materials for several applications (Wróblewska-Krepsztul et al. 2019). Figure 10 shows some representative polysaccharide biopolymeric structures.

The high reducing properties of metallic salts, together with their ability to coordinate metal ions, make them promising compounds for the biosynthesis of metallic nanoparticles. The reducing/stabilizing dual role enables the formation of metal nanoparticle with specific features, such as tailored sizes, biocompatibility, and nontoxicity, among others (Wang et al. 2017).

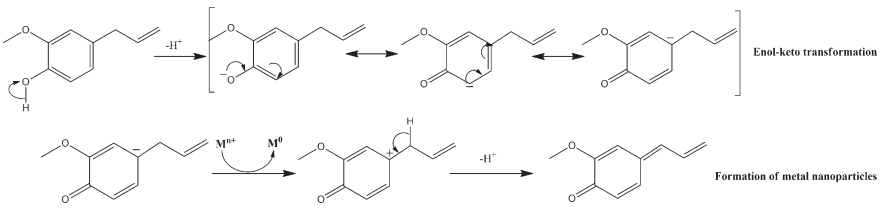


Fig. 9 Schematic representation of the reducing role of eugenol in the bioreduction process

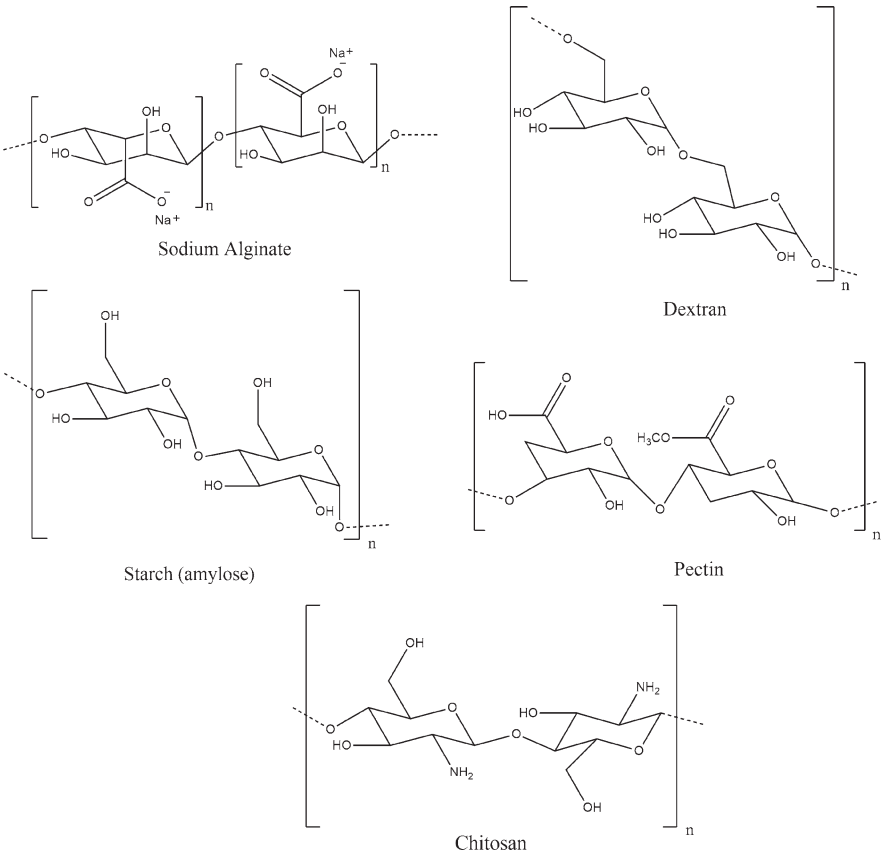


Fig. 10 Representative polysaccharide biopolymers

As happened with plant extracts, the influence of some synthesis parameters on the size and morphology of the generated nanoparticles, as well as more details about the synthesis approaches, will be given in Sect. 3.4.2.

2.3.3 Microorganisms

Living microscopic organisms are involved in several synthesis routes, usually performed at mild conditions (Wang et al. 2016). The use of several microorganisms, such as algae, bacteria, and fungi, should be highlighted for biosynthetic purposes (Schmid et al. 2015; Dahoumane et al. 2017; Skellam 2019).

The metabolic engineering constitutes a powerful tool in biosynthetic routes using microorganisms, by enhancing endogenous metabolic pathways or by introducing exogenous pathways (Grunwald 2012). R. Kumar and S. Prasad summarized the fundamentals of metabolic engineering of bacteria, including three steps

required in the metabolic process: understanding the metabolic pathway, use of a computational approach, and its application at experimental level using different engineering approaches (Kumar and Prasad 2011).

Thus, biosynthesis of several compounds mediated by engineered microorganisms was recently reported. Biodiesel was produced using oleaginous microorganisms from organic wastes by cost-effective approaches (Cho and Park 2018). The production of biofuels and biofuel feedstocks was reported using engineered microorganisms, such as yeasts, cyanobacteria, bacteria, and microalgae (Majidian et al. 2018). The synthesis of 2-phenylethanol, an important aromatic compound, was performed by metabolic engineering in yeast and bacteria, reducing the formation of toxic by-products, usually obtained by chemical synthesis route (Wang et al. 2019b). Lycopene was synthesized from cytosolic isoprenoid precursors using a viral vector (Majer et al. 2017). Biosynthesis of polyhydroxyalkanoate (PHA) seems to be improved by engineered microorganisms (Chen and Jiang 2018). Competing pathways of PHA were minimized, channeling the resources to the PHA biosynthesis pathways.

Microorganisms are also entailed in the synthesis of metal nanoparticles (Ovais et al. 2018). However, the biosynthesis of metal nanoparticles using plants and biopolymers will be presented in Sects. 3.4.1 and 3.4.2.

2.4 Hybrid Green Synthetic Routes

In Sects. 2.1, 2.2, and 2.3, several green approaches have been overviewed individually. However, a new generation of assisted green methods is recently arising based on the combination of some of the advance methods previously discussed. Therefore, new tandems have been proposed as green synthesis advances, such as microwave-ultrasound, microwave-biosynthesis, and ultrasound-biosynthesis assisted methods. These new methodologies take advantages of the synergistic effect involved using different techniques. In this section, they will be briefly presented, discussing some of the most notorious and promising results already available, and exposing their high potential applicability in the green synthesis.

2.4.1 Microwave-Ultrasound-Assisted Methods

The use of ultrasound and microwave radiation has been extensively commented in Sects. 2.1 and 2.2, respectively. Regarding ultrasound, the cavitation phenomena are the core of this approach, which implies physical-chemical process and the generation, growth, and collapse of bubbles. With respect to the microwave radiation, the high effective transference of heat (creation of "hot spots") leads to higher yields and faster processes than those obtained in conventional heating. However, the limitations of this approach with respect to the use of nonpolar compounds should be mentioned (Martina et al., 2016).

Despite microwaves and ultrasounds are based on two different phenomena, their combination leads to better results than the ones provided by the individual use of each technique. In this way, synergistic effect should be remarkable by using the hybrid approach. This synergistic effect is mainly explained by two different contributions: the highly effective heating of the system and the efficient temperature stimulation supplied by the cavitation process. Besides, the microwave heating prevents the loss of energy and the thermal pollution of the environment. In addition, ultrasounds allow the suitable mixing of substrates, even if they are found in different phases, avoiding the need of any additives, such as surfactants (Pawełczyk et al. 2018).

Many researchers have tried to exploit this binomial in order to develop even more efficient and fast synthesis of organic and inorganic compounds (Cravotto et al. 2015). According to the organic synthesis reactions, several kinds of processes have been improved by this approach. Firstly, the transesterification reactions, Martinez-Guerra et al. reported a protocol to convert waste vegetable oil into biodiesel with a yield of 98% in only 82 min (Martinez-Guerra and Gude 2014). The Heck reaction has also been improved with the simultaneous microwave/ultrasound irradiation. Saaco et al. have performed one of the most recent advances: the creation of carbon-carbon bonds by olefin metathesis under microwaves/ultrasound with 86% of yield (Sacco et al. 2015). The microwave/ultrasound irradiation approach has also provided very good alternatives in the C-Heteroatom Bond formation reactions, such as the ethers synthesis and aromatic azo compounds, among others. For instance, the hydrazinolysis of methyl salicylate has greatly improved investing 40 s instead of 9 h with a yield of 84% (Wu et al. 2008). On the other hand, the inorganic synthesis has been a matter of interest from the point of view of microwave/ultrasound irradiation approach, especially in the case of nanoparticles and nanomaterials (Cravotto and Boffa 2014). It is noteworthy to mention that in the case of metallic nanoparticles the application of microwave irradiation has no dangerous implication due to excessive metal dilution in the solution. Following the microwave/ultrasound irradiation methodology, copper nanoparticles has been successfully generated reducing $Cu(OAc)_2$ with hydrazine in ethylene glycol. Transmission electron microscopy and X-ray diffraction were used to characterize the nanoparticles, resulting in a highly pure and spherical nanomaterial. The yields and reaction time were 97% and 4.5 min, respectively, in comparison with those obtained by using the conventional method: 52% and 12 h, respectively (Feng et al. 2014). Cherkasov et al. obtained a solid supported Pd catalyst. In this case, the irradiation was applied sequentially. Palladium was firstly reduced by ultrasound radiation, and after then, it was deposited on the solid surface by microwave irradiation; the clusters obtained were around 100 nm. One of the most notorious milestone of this method is the absence of any surfactants, which make the process much greener than the previously made (Wu et al. 2015). The surface morphology of the nanoparticles can be selected altering the conditions of the synthesis. Mesoporous hydroxyapatite nanoparticles were obtained by Liang et al. through microwave/ultrasound irradiation. However, the most relevant results were the change of the porous structure given for different synthesis conditions. A flake-like non-mesoporous structure

was generated at low temperature (10–50 °C) and microwave power. On the other hand, a clear mesoporous derivative was obtained by using higher temperatures (50–90 °C). Besides, if the microwave is increased until 200 W, a more mesoporous structure is found (Liang et al. 2013). Thus, due to all the reasons previously mentioned, the microwave/ultrasound irradiation approach can be established as an alternative route in order to obtain greener and more efficient procedures.

2.4.2 Microwave-Assisted Biosynthesis

The next approach to discuss is the employment of microwave radiation in a synthesis performed using biological extracts. Both methods have been widely discussed in Sects. 2.2 and 2.3, respectively. In this case, the synergistic effect is more evident than in the previous case. On the one hand, hazardous reagents were replaced to more ecofriendly reducing agents. On the other hand, the microwave radiation highly increases the efficiency and greatly reduces the time necessary for the synthesis process.

This approach has been employed to synthesize majorly metallic nanoparticles. Bhagavanth et al. described a gold nanoparticles synthesis employing an extract of *Annosa Squamosal* L. assisted with microwave radiation. In this work, the synthesis was carried out in 5 min, obtaining spherical-shaped forms and a distribution size of 11 ± 2 nm. In addition, the nanoparticles generated possess good stability due to the carbonyl and hydroxyl groups, which surround the nanoparticles (Reddy et al. 2018). Jahan et al. used an extract of *Rosa Santana* and the microwave radiation to generate silver nanoparticles. It should be noticed that the stability of the nanoparticles was outstanding, being able to maintain their characteristics during 9 months. The size distribution of the nanoparticles provided an average of 14.48 nm with a roughly spherical shape (Jahan et al. 2019). Other researchers have also reported their results in the silver nanoparticles synthesis employing this approach (Eshghi et al. 2018; Francis et al. 2018; Ukkund et al. 2019). Besides, metallic oxide nanoparticles can also be obtained by this hybrid technique. Chankaew et al. reported the synthesis of ZnO nanoparticles and their application in solar cell technology. They used a crude water extract of *Dimocarpus longan* as biological component. The nanoparticles were obtained in about 30 min using cycles of 1 min-off 1 min-on. The distribution size was about 10–100 nm and amorphous shape was observed. However, it is noteworthy to mention that the final nanoparticles possessed a pure hexagonal phase (Chankaew et al. 2019). SnO_2 quantum dots have been obtained using this approach as well. In this case, the extract of *Parkia speciosa* was employed with a microwave program consisting in 30 shots of 10 s each one. Highly pure crystalline and tetragonal rutile polycrystalline structure was observed. Besides, morphology of this nanoparticles was spherical with an average diameter of 1.9 nm (Begum and Ahmaruzzaman 2018). Biopolymers can be employed in the metallic nanoparticles synthesis assisted by microwave as well. Torabfam et al. described the silver nanoparticles generation by using chitosan and microwave radiation. Experimental design was carried out to study the best

conditions for the chitosan solution. The final synthesis was performed in 100 s leading to an average size of 37 nm. In addition, a spherical shape was noted. The high zeta value obtained (+50 mV) indicated the high stability of the nanoparticles obtained (Torabfam and Jafarizadeh-Malmiri 2018). Naggar et al. performed similar process for the obtention of gold and bimetallic gold/silver nanoparticles. The biopolymer used in this work was curdlan, firstly reported for this purpose. The synthesis of both nanomaterials was done in 10 min with microwave assistance. AuNPs with 52 nm as average size were synthesized. Concerning the nanoparticles built as silver core and gold shell, lower size was appreciated, around 45 nm. Furthermore, despite the fact that no important differences were observed in Ag and Au X-ray diffraction patterns due to their close lattice constant, the structure face-centered cubic was confirmed (El-Naggar et al. 2016). Thus, as it can be noticed, this tandem seems to offer good stability, fast reaction times, and good distribution size of the nanomaterials obtained.

2.4.3 Ultrasound-Assisted Biosynthesis

The use of ultrasound as support in the biosynthesis will be briefly discussed in this section. Each individual component has been exposed in Sects. 2.1 and 2.3, respectively. As it has been commented in Sect. 2.4.1, the interest of these hybrid techniques lays in the synergistic effect gained through their simultaneous use. In this case, the cavitation phenomena creates nano-reactors and aids the chemical reaction, meanwhile the selected biological material will interact with the precursor, stabilizing afterwards the final product formed. This is translated into an easier formation of highly stable nanoparticles, much reduced reaction times, and higher yields. As in Sect. 2.4.2, this approach has been mainly exploited in the synthesis of nanoparticles. Manjamadha et al. have informed the synthesis of Ag nanoparticles using an extract of *Lantana camara* and the assistance of ultrasounds. The spherical AgNPs obtained had an average size of 33.8 nm. The process was done in 10 min obtaining pure crystalline phases. However, the nanoparticles obtained exhibit a wide size distribution (Manjamadha and Muthukumar 2016). The synthesis of gold nanoparticles was performed by Franco-Romano et al. They employed geranium extract (*Pelargonium zonale*) and a high-power ultrasound probe. The whole process was done in 3.5 min obtaining nanoparticles of 12 ± 3 nm. In this study, the synthesis conditions were optimized by means of an experimental design, demonstrating that higher volume of reducing agent and precursor led to better synthesis process. On the other hand, it was also exposed that higher volumes of the metallic precursor were related with nonspherical-shaped nanoparticles. The nanoparticles stability was also assessed, showing 8 weeks of lifetime (Franco-Romano et al. 2014). Gu et al. reported the ultrasound-assisted generation of CuO nanoparticles using an alga extract (*Cystoseira trinodis*). The process was performed in 90 min, obtaining a mean size of 9 nm, and a pure nanocrystalline phase was observed too. Nevertheless, several agglomeration were exposed in transmission electron microscopy analysis; these agglomeration increased the range of the size distribution (Gu

et al. 2018). Bayrami et al. synthesized another metal oxide nanoparticle, ZnO_2, by using a leaf extract of *Vaccinium arctostaphylos*. The ultrasound application lasted 15 min, obtaining nonspherical nanoparticles with a size about 100 nm. A hexagonal wurtzite with a high grade of crystallinity was checked in X-ray diffraction assays. In addition, assays for the medical applications of these nanoparticles were done, exposing the improvement in their characteristics, antidiabetic and antibacterial, in comparison with the conventional chemical route of synthesis (Bayrami et al. 2019). Not only can nanoparticles be made employing this approach, but also biopolymers. Zhu et al. described the synthesis of chitosan employing a biological agent (*Ganoderma lucidum* spore powder) and the assistance of ultrasound. This synthesis was based on the ultrasound-assisted deacetylation approach, which reduce the temperatures required, diminish the time needed, and lesser severely the depolymerization risk. X-ray diffraction, thermogravimetric analysis, and Fourier transformed infrared spectroscopy characterization confirmed the successful generation of this polymer. Finally, the antibacterial properties were examined and the chitosan prepared via ultrasound-assisted deacetylation showed better antibacterial properties (Zhu et al. 2018a). Therefore, all the data previously exposed indicates that the ultrasound-biosynthesis binomial is an interesting approach which can offer several advantages over the traditional methods.

3 Trends in the Green Synthesis of (Nano)Materials

The development of (nano)materials with specific features has received much attention in the last decades. Many researchers have made great efforts on the modification of bare devices in order to improve their (bio)sensing properties following the Green Chemistry rules. In addition to the properties of the resulting material, other characteristics, such as low cost, easy setup, low toxicity, and high scalability, are desirable to obtain competitive materials with high applicability in several fields.

In this section, the obtention of diverse materials following green approaches will be summarized, while their application in (bio)sensing will be discussed in Sect. 4. Furthermore, the green synthesis of electrode materials used as bare electrochemical transducers is also reported.

3.1 Graphene-Based Materials

Graphene is a two-dimensional material constituted by a single or few layers of carbon atoms comprised in hexagonal rings. Its promising optical, magnetic, electric, and thermal properties, such as high electrical and thermal conductivity, tunable band-gap, and high tensile strength, are suitable for sensing purposes (Rao et al. 2009). According to all these remarkable reasons, the modification of bare

electrodes by graphene layer deposition was performed to constitute electrochemical devices with excellent analytical features (Kim et al. 2010).

Bottom-up and top-down approaches can be used to obtain pristine graphene. It is noteworthy to mention that only liquid-phase exfoliation, chemical reduction of graphene oxide (top-down approaches), and chemical vapor deposition (bottom-up approach) will be considered due to their high scalability, allowing obtaining graphene layers at industrial scale (Backes et al. 2017; Zhu et al. 2018b).

3.1.1 Graphene Layer by Liquid-Phase Exfoliation

Graphene flakes were produced via liquid-phase exfoliation of graphite by sonication or shear forces mixing. Figure 11 shows a schematic representation of this process.

Xu and coworkers summarized the main aspects regarding the exfoliation process, highlighting the use of solvents as dispersing agents of graphite and the subsequent graphene sheets (Xu et al. 2018). In their work, the selection of the solvent constitutes major relevance, since the dispersibility of the solid in the liquid strongly depends on their interfacial tension: high values lead to poor dispersibility, favoring the agglomeration of the graphene flakes. Organic solvents with surface tension values from 40 to 50 mJ m^{-2} seem to be the best choices for obtaining stable graphene dispersions by liquid-phase exfoliation (Du et al. 2013). In Table 5 common organic solvents employed in exfoliation, together with their surfaces tension values reported in the literature, are summarized.

Various research papers were devoted to the replacement of organic solvents to water-based systems. The use of a wide variety of surfactants in the liquid-phase exfoliation of graphite was tested, since surface tension of water could be reduced, making feasible the exfoliation of graphite (Narayan and Kim 2015). A recent work regarding the role of surfactant in liquid-phase exfoliation of graphite could be highlighted, demonstrating its current research interest (Sukumaran et al. 2019).

The employment of ionic liquids was reported as promising solvents for liquid exfoliation of graphite in some research works owing to their extraordinary thermal stability, low vapor pressure, and low flammability (Bari et al. 2014; Godoy et al.

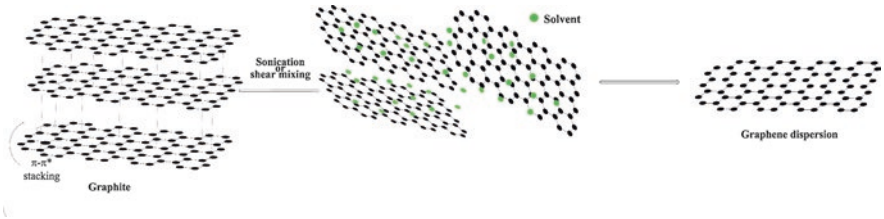
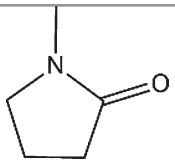
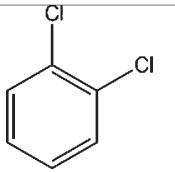
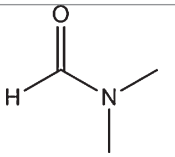
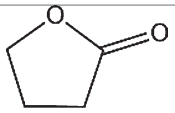


Fig. 11 Liquid-phase exfoliation of graphite

Table 5 Common organic solvents employed for liquid-phase exfoliation of graphite

Organic solvent	Chemical structure	Surface tension, γ^a (dyn·cm^{-1})	Method	References
N-methyl-2-pyrrolidone (NMP)		44.6	Tip-sonication	Khan et al. (2012)
			Bath sonication	Bracamonte et al. (2014)
			High shear mixing	Tran et al. (2016)
Ortho-dichlorobenzene (O-DCB)		35.7	Bath sonication	Sahoo et al. (2013)
N,N-Dimethylformamide (DMF)		34.4	Tip-sonication	Durge et al. (2014)
γ-Butyrolactone (GBL)		53.2	Bath sonication	Hernandez et al. (2008)

[a]Values reported at 25 °C from (Yaws 2009)

2019). However, their toxicity constitutes a high controversy nowadays (Bystrzanowska et al. 2019).

The use of natural extracts was also proposed for the exfoliation of graphene. Chitosan and alginate were studied by Uysal and coworkers as alternatives to organic solvents in the exfoliation of graphite (Uysal Unalan et al. 2015). In their work, the stability of the graphene dispersion was higher when chitosan-assisted, which can be explained in terms of the affinity between the biopolymer and the graphene sheets. Regarding the use of chitosan, the nonpolar segments have a solid affinity with the graphene surface. Moreover, the ionic repulsion between the amine groups and the sheets prevents their agglomeration, leading to stable graphene dispersion. In the case of alginate, the compatibility with the graphene sheets is thermodynamically unfavorable, leading to the restacking and precipitation of the graphene sheets. Black tea was employed to produce graphene in one-step exfoliation method by using a kitchen mixer (Ismail et al. 2017). Other research work reported the use of instant coffee to produce few-layer graphene by ultrasound, proposing the chlorogenic acid as the chemical active component for the graphene functionalization (Abdullah et al. 2019).

The manufacturing of graphene nanoplatelets by high temperature vapor exfoliation of graphite should be mentioned. In this work, no chemicals or surfactants were

required for the exfoliation or dispersion of graphene, reaching good dispersibility even at higher concentrations (Ding et al. 2018).

3.1.2 Graphene Layer By Chemical Reduction of Graphene Oxide

The reduction of graphene oxide (GO) constitutes another scalable top-down approach to get graphene flakes for mass production (Lavin-Lopez et al. 2017). The first step consists of the oxidation and exfoliation of graphite to graphene oxide, which forms a stable colloid dispersion in water due to the presence of hydroxyl groups. The reduction of graphene oxide leads to reduced-graphene oxide (r-GO) by removing these groups, restoring partially the π-π∗ conjugation (Chua and Pumera 2014) (Fig. 12).

The graphene oxide has poor electrical conductivity due to the presence of high content of hydroxyl groups on the edge and basal planes. After the reduction process, some residual oxygen groups still remain in the structure, leading to lower electrical conductivity in comparison with the pristine graphene layer (Pei and Cheng 2012).

C/O ratio should be a critical parameter to evaluate the electrical conductivity, since lower content of oxygen should lead to graphene sheets with higher electrical conductivity. However, this factor is also affected by other parameters, such as sheet orientation or percolation effects (Guex et al. 2017). In spite of this fact, C/O ratio could be used to evaluate the efficient removal of oxygen in resulting graphene sheets, by comparing this value with the one obtained for the initial GO.

The chemical GO reduction involves the addition of a reductant, which plays a key factor in the obtention of graphene layers with the desirable properties for sensing purposes. Several research works were focused on the generation of reduced-graphene oxide by employing diverse reductants, evaluating their C/O ratio. In this sense, hydrazine, hydrazine hydrate, and sodium borohydride were employed for obtaining high-quality graphene layer (Luo et al. 2011; Guex et al. 2017). Due to their toxicity for the living organisms and the environment, their replacing to greener ones is well studied in the last years. With this purpose, less hazardous chemicals and plant extracts, among others, were proposed as alternative reducing agents (De Silva et al. 2017). In Table 6 some examples reported in literature are summarized.

As observed in the previous table, the C/O ratio values of r-GO were higher than the one obtained for GO, indicating the removing of oxygen after reduction.

Chemical reduction of GO can also be assisted by microwave irradiation. Hassan and coworkers performed the chemical reduction of GO assisted by microwave

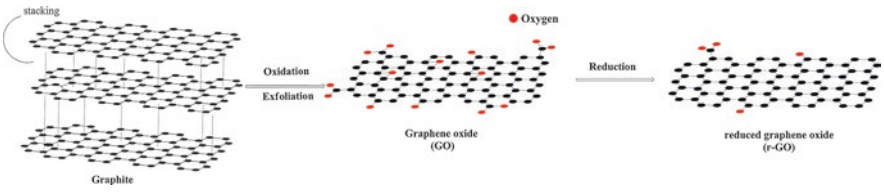


Fig. 12 Chemical reduction of GO to generate reduced-graphene oxide

Table 6 Compounds employed in the chemical reduction of graphene oxide

Reducing agent	C/O ratio	References
GO		
n.a.	1.80–2.37	Peng et al. (2016)
rGO-chemicals		
Ascorbic acid	4.70	De Silva et al. (2018)
Sodium sulfite	4.80	Yin et al. (2019)
Caffeine	6.50	Vu et al. (2015)
rGO-peel extract		
Lemon extract	4.66	Dandan et al. (2017)
rGO-plant extract		
Artemisin	11.7	Hou et al. (2018)
Phaseolusaureus L	6.60	Jana et al. (2014)
Ocinum sanctum	3.10	Mahata et al. (2018)
Colocasia esculenta	7.11	Thakur and Karak (2012)

GO graphene oxide, *rGO* reduced graphene oxide

employing hydrazine hydrate as reductant, obtaining r-GO in few minutes (Hassan et al. 2009), in comparison with the one required by conventional method, about 24 h (Stankovich et al. 2007). Hence, shorter reaction times seem to be endorsed to the application of microwave due to the effective transference of energy to the precursors (Hu et al. 2012a).

The sequential chemical reduction and microwave irradiation of GO was performed by Wen and coworkers (Wen et al. 2014). The electrical conductivity of the rGO after microwave treatment was higher than those obtained by using either single microwave-assisted or chemical reduction of GO. Besides, defects of the rGO obtained by chemical reduction seem to be repaired by microwave.

Microwave-assisted GO reduction was performed with ascorbic acid as reductant under N_2 atmosphere, leading to rGO in 3 min (Iskandar et al. 2017). The flow of nitrogen was found to be more effective, since gases formed as side products during reduction process were removed. Furthermore, the electrical conductivity of the resulting graphene flakes was increased after performing the annealing treatment. Another recent work shows novel approach to obtain graphene patterns onto graphene oxide film by using an rGO template assisted by microwave. This method provides shape-controlled graphene patterns with excellent electrical conductivity (Zhao and He 2019).

Therefore, microwave can be employed as a green powerful tool to obtain graphene flakes from the chemical reduction of GO at short reaction times. However, this technique is yet to be explored, since oxygen and some structural defects are still retained, disrupting the electronic conjugation and, hence, decreasing the electrical conductivity in comparison with pristine graphene (Xie et al. 2019).

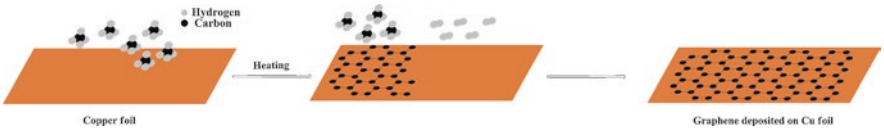


Fig. 13 Chemical vapor deposition of graphene

3.1.3 Chemical Vapor Deposition

Chemical vapor deposition has attracted huge attention for the obtention of uniform and large area graphene layers with low defects. The first step involves the decomposition of the carbon precursor, carried in the vapor phase with an inert gas, e.g., argon. Afterwards, carbon was deposited and grown on a metal substrate surface, such as copper, nickel, palladium, or iridium, among others, which plays a catalytic role in the nucleation and growth process (Zhang et al. 2013a) (Fig. 13).

The first industrial chemical vapor deposition process of graphene deposited on copper foil was reported by Ruoff and coworkers using methane as carbon source. The graphene film can be moved to another substrate, like SiO_2/Si (Li et al. 2009).

The employment of high temperatures in the synthesis of graphene via chemical vapor deposition, around 1000 °C, is usually required (Zhang et al. 2013a). Other chemical vapor deposition derivatives, such as plasma enhanced (Li et al. 2016), inductively coupled plasma (Pekdemir et al. 2017), microwave plasma (Fang et al. 2016), and photo-induced, can be excellent alternatives to reduce the working temperature. Son and Ham summarized the recent progress in the employment of these techniques for synthesis of graphene, highlighting its application in electronic devices (Son and Ham 2017).

New alternative carbon sources were investigated as green precursors. The deposition of graphene on a copper substrate via microwave plasma-chemical vapor deposition using a camphor precursor was reported by Uchida and coworkers (Hideo Uchida et al. 2016). In their work, graphene sheets using camphor showed superior qualities in terms of lower sheet resistance than those obtained using methane. Other natural resources, such as palm oil (Salifairus et al. 2016) and tea tree extract (Jacob et al. 2015), were also employed as green carbon sources due to its high availability and low cost.

A recent work reported a new chemical vapor deposition method using a solid waste plastic as carbon solid precursor (You et al. 2017). A waste material was transformed into a functional material by following a green and sustainable approach at atmospheric pressure, since no chemicals and reagents were used. Therefore, this method seems to be a promising way to obtain high-quality monolayer graphene flakes at industrial scale.

3.2 Carbon and Graphene-Quantum Dots

Carbon-based dots are fluorescent particles with high applicability in analytical and biomedical fields. Cayuela and coworkers summarized the three main types, carbon nanodots, graphene-quantum dots, and carbon-quantum dots, defining their properties and providing a detailed discussion about their applications (Cayuela et al. 2016).

Carbon quantum dots are small carbon particles lower than 10 nm. Graphene quantum dots are constituted by graphene disks from 2 to 20 nm. Both materials have promising applications in sensing and bioimaging owing to their tunable fluorescent properties, small sizes, and low toxicity. Regarding the sensing applications, their deposition onto bare surfaces improves the electrochemical features of the resulting devices (Sun et al. 2013; Algarra et al. 2018).

Carbon-quantum dots can be doped or co-doped with heteroatoms to improve their fluorescence efficacy in terms of quantum yields. Hence, the doping with boron, nitrogen, sulfur, phosphorous, and fluorine was reported in literature (Kandasamy 2019). Regarding graphene-quantum dots, the doping with heteroatoms is also reported (Feng et al. 2018; Kaur et al. 2018).

Several ecofriendly methods have been recently developed for the obtaining of carbon-quantum dots and graphene-quantum dots and their doped derivatives by using different carbon precursors, including waste products and low-toxic chemical reagents (Das et al. 2018). In this sense, microwave and hydrothermal methods emerged in the production of carbon-quantum dots and graphene-quantum dots from green precursors. In Table 7 some recent examples found in the literature are summarized.

Graphene-quantum dots can also be obtained from bulk carbon sources. They were synthesized using different carbon precursors by hydrothermal route (De Xie et al. 2007). In this work, hydrogen peroxide was used as oxidizing reagent, instead of harsh chemicals used in conventional hydrothermal route, such as nitric acid and sulfuric acid. Another hydrothermal method using graphene oxide as carbon source and hydrogen peroxide was reported (Tian et al. 2016). The acid-free synthesis of graphene-quantum dots by sonochemical method with intermittent microwave heating was performed using graphene oxide as carbon source. The resulting graphene-quantum dots exhibited a high quantum and product yields (Nair et al. 2017). Other acid-free approach by microwave was performed to obtain boron-doped graphene-quantum dots from graphene oxide (Hai et al. 2015).

3.3 Multi-Walled Carbon Nanotubes

Carbon nanotubes are carbon allotropes consisting of rolled-up sheets of carbon atoms. Their outstanding optical, mechanical, thermal, and electrical properties make them suitable candidates in gas sensing (Mao et al. 2014) and electrochemical biosensing (Du et al. 2017), among other applications.

Table 7 Obtention of C-QDs and G-QDs assisted by microwave and hydrothermal methods using different precursors

Method	Precursors	Size (nm)	References
Carbon-quantum dots			
Microwave	Lysine	5–10	Park et al. (2017)
	Xylan	≈7.9	Yang et al. (2018)
	Phthalic acid and triethylenediamine	≈3.5	Yu et al. (2018)
	Chitosan and lysine	≈5.5	Janus et al. (2019)
Hydrothermal	Cabbage	2–6	Alam et al. (2015)
	Fresh lemon Ethanol	≈3.1	He et al. (2018)
	Citric acid	2–4	Shen et al. (2018)
	Glucose	3–6	
	Tofu yellow serofluid and Sodium hydroxide	3.5–5.5	Zhang et al. (2017)
Microwave-assisted hydrothermal	Arginine and glycerin	≈4.4	Huang et al. (2019)
Graphene-quantum dots			
Hydrothermal	Citric acid and thiourea	≈2.69	Qu et al. (2013a)
Microwave	Aspartic acid and ammonium bicarbonate	1.8–2.4	Zhang et al. (2016)
	Glucose and urea	<15	Fresco-Cala et al. (2018)
Microwave-assisted hydrothermal	Citric acid and urea	≈5	Nguyen et al. (2019)
	Glucose and urea	≈3	Hou et al. (2016)

Regarding the synthesis of carbon nanotubes, chemical vapor deposition, arc discharge, and laser ablation constitute the most popular methods for production of MWCNTs nanotubes (Rahman et al. 2019). Several drawbacks are ascribed to them, such as high temperatures required, low energy efficiency, and low yields. Furthermore, fossil carbon sources were employed, e.g., methane (Li et al. 2004) and ethylene (Weizhong et al. 2003). Several green attempts using biomass and other ecological products as raw precursors were carried out. In this section, chemical vapor deposition and microwave pyrolysis will be considered.

3.3.1 Carbon Nanotubes Production by Chemical Vapor Deposition from Ecological Sources

As previously commented, chemical vapor deposition raised as a well-established synthesis method of carbon nanomaterials at both laboratory and industrial scale (Pang et al. 2016).

The conventional carbon sources used in chemical vapor deposition were replaced to green precursors in the last decade. An environmental-friendly hydrocarbon, namely camphor, was reported in the obtention of carbon nanotubes via chemical vapor deposition (Pandey et al. 2013). This precursor was also used as carbon source using rice straws hydrothermally treated by a carbonization hydrothermal method with either ferrocene or ferrocene mixed with nickel nitrate (Fathy 2017). Neem oil was also employed in the synthesis of carbon nanotubes by spray pyrolysis-assisted chemical vapor deposition using ferrocene as catalyst (Kumar et al. 2011).

The use of catalysts, commonly transition metals, was required for the catalytic chemical vapor deposition of carbon nanotubes (Rashid et al. 2015). New alternative catalysts obtained from natural sources were proposed over metallic ones. The catalytic role of several plant leaves extracts, garden grass, rose, kaner, and walnut was proposed in the carbon nanotubes growth on silicon substrate (Tripathi et al. 2017). In this work, nontoxicity, high availability, low temperature, and low cost, among other advantages, are highlighted. Natural laterite powder was also recently employed as a catalyst source for the carbon nanotubes growth through chemical vapor deposition, proposing a growth mechanism involving the fragmentation of the pristine iron-containing material (Kumar et al. 2018). The minerals present in natural resources were reported to play a catalytic role in the carbon nanotubes grown process. The minerals obtained from bamboo charcoal, especially calcium silicate and magnesium metasilicate, were found to be responsible of the nucleation and growth of carbon nanotubes carried out by chemical vapor deposition (Zhu et al. 2012). Another work reports the participation of minerals present in the coconut shell in the growth of carbon nanotubes using radio frequency plasma-enhanced chemical vapor deposition (Araga and Sharma 2017).

Thus, new carbon sources and catalysts were investigated for carbon nanotubes production by means of a chemical vapor deposition process. The green methodologies proposed aimed to reduce the overall costs, energy requirements, reaction times, and the formation of toxic side products.

3.3.2 Carbon Nanotubes Production by Microwave Pyrolysis of Biomass

The carbon nanotubes production by microwave pyrolysis of the biomass has attracted huge attention nowadays. This method involves the decomposition of biomass by microwave heating, leading to higher yields of pyrolytic products in comparison with those obtained by conventional heating (Dhyani and Bhaskar 2018). The principles and mechanisms of pyrolysis by microwave were reported in the bibliography (Nomanbhay et al. 2017; Nizamuddin et al. 2018).

Gumwood was used as carbon source in the carbon nanotubes synthesis via microwave pyrolysis (Shi et al. 2014). The decomposition rate of the biomass by using microwave was found to be greater than the one obtained by means of conventional heating, leading to higher yields of pyrolytic products, as commented before.

The microwave pyrolysis of bagasse was performed by using iron and cobalt as metal susceptors (Debalina et al. 2017). Another recent work reported the use of palm kerner shell as raw material, obtaining carbon nanotubes in mild conditions and without adding any catalyst (Omoriyekomwan et al. 2019). The role of cellulose in the synthesis and growth of carbon nanotubes was also reported.

Therefore, microwave heating of biomass constitutes a promising synthesis method in terms of Green Chemistry. However, the mechanism of formation and growth of carbon nanotubes are not fully understood, and hence further investigations are required.

3.3.3 Functionalization of Carbon Nanotubes

Although this subsection is focused on the obtention of carbon nanotubes by green methodologies, their functionalization is also relevant, since their sensing properties seem to be enhanced (Setaro 2017). Among all the functionalization approaches, the decoration of carbon nanotubes with metal nanoparticles constitutes one of the most important methods (Kharisov et al. 2016).

Several decoration procedures were reported in the bibliography. A cost-effective and ecofriendly method using focused solar irradiation over metal precursor and carbon nanotubes dispersion was reported. Different metal, metal oxide, and metal alloy nanoparticles, such as Au, Pt, Ag, NiO, ZnO, and Pt_3Co, were successfully attached on carbon nanotubes surface by using this approach (Baro et al. 2013). Palladium nanoparticles were deposited onto the multi-walled carbon nanotubes surface by drop casting of palladium salt precursor, followed by ultraviolet irradiation (Yoo et al. 2019). The decoration of carbon nanotubes with bimetallic nanoparticles was mediated by aqueous plant extracts (Mendoza-Cachú et al. 2018). Silver nanoparticles were deposited on carboxylated and hydroxylated carbon nanotubes by using a modified Tollens process, which involves the chemical reduction of $[Ag(NH_3)_2]^+$ complex with sugars (Dinh et al. 2015). A one-pot microwave synthesis of copper oxide nanoparticle-carbon nanotubes was performed in a solvent-free system using copper acetate as precursor (Rudd et al. 2019). Figure 14 represents a scheme of each functionalization procedure described.

3.4 Metal and Metal Oxide Nanoparticles-Supported Materials

The one-pot synthesis of metallic nanoparticles mediated by biological compounds is currently considered by the scientific community (Shamaila et al. 2016). A brief overview of the metallic nanoparticles synthesis using natural extracts and biopolymers will be stated in this section.

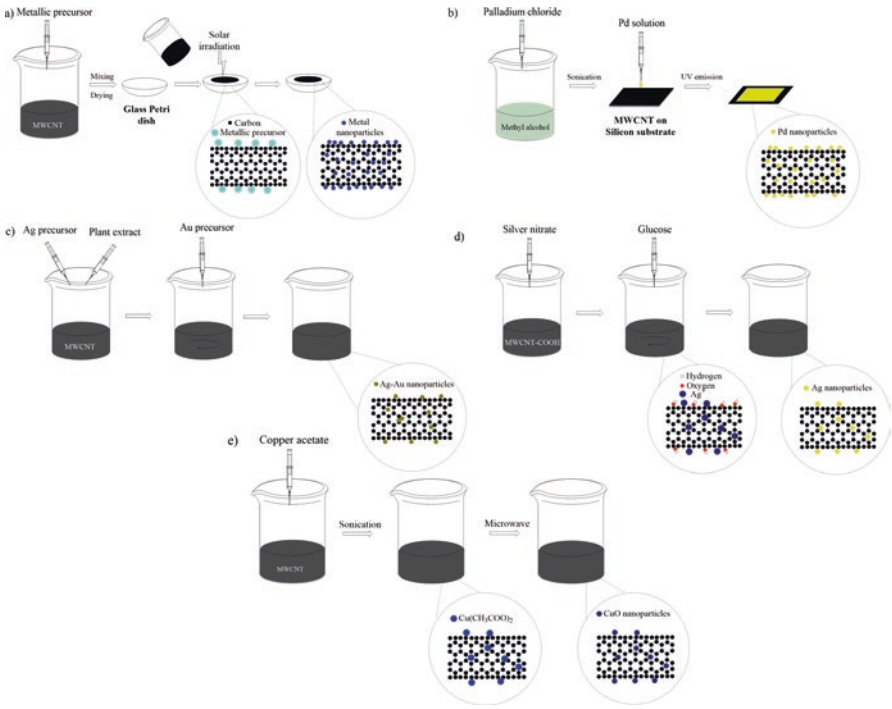


Fig. 14 Different decoration methods of carbon nanotubes with metal nanoparticles: (**a**) Deposition of metal/metal oxide NPs by solar radiation, (**b**) deposition of PdNPs by drop casting on MWCNT/Si substrate, (**c**) deposition of Ag-AuNPs mediated by plant extract, (**d**) deposition of AgNPs by using a modified Tollens method, and (**e**) deposition of CuONPs mediated by the sonication and subsequent microwave treatment of copper acetate

3.4.1 Synthesis of Metal Nanoparticles Mediated by Plant Extracts

The employment of several organisms, such as fungi (Vágó et al. 2016; Gudikandula et al. 2017), bacteria (Ahmad et al. 2017), and plants (Makarov et al. 2014), for one-pot metal nanoparticles synthesis has been extensively studied. Among all of them, plant leaf extracts seems to be a good choice based on green terms: scalable process, lower time required, and eco-friendly waste products (Mittal et al. 2013; Yadi et al. 2018).

The last one is a crucial point to reduce the presence of pollutants, improving the human health. Furthermore, the synthesis procedure is very easy, allowing the generation of metal nanoparticles by direct mixing of the plant extract and the metal solution at room temperature (Fig. 15). Thus, high temperatures and additives are not required for the synthesis step.

The synthesis mechanism of metal nanoparticles using plant extracts is very complex owing to the high amount of phytochemicals able to reduce the metal salt, as well as to avoid the aggregation of the resulting nanoparticles. These compounds,

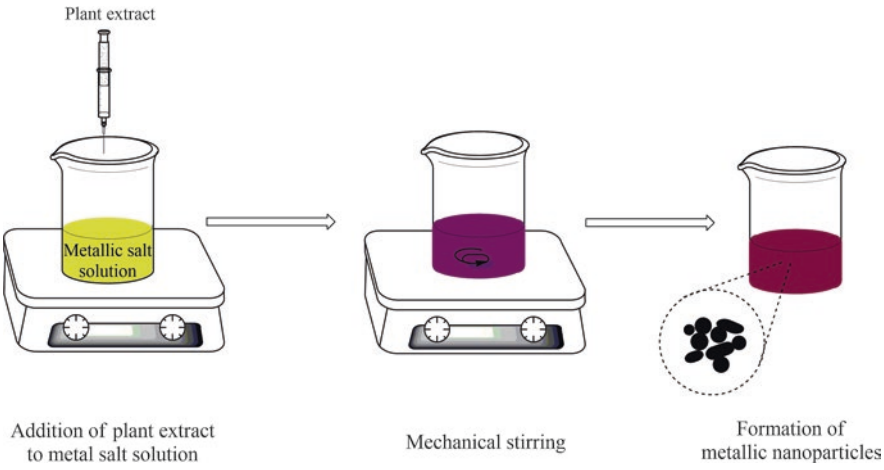


Fig. 15 Synthesis of metal nanoparticles mediated by plant extracts

like flavonoids, sugars, and amino acids, among others, contain functionalized groups responsible for the bioreduction and the subsequent stabilization processes (Rai et al. 2013; Jain and Mehata 2017; Zarzuela et al. 2018).

According to the biochemical reduction mechanism proposed in several reports, the plant extract composition is a key factor in the shape and size of the metal nanoparticles obtained. Table 8 summarizes several examples reported in the bibliography in the last years.

As observed in Table 8, the morphology of AuNPs is strongly dependent on the composition of the extract. Particularly, Lee and coworkers carried out a detailed study about the reducing role of the phytochemicals contained in the extract for the gold nanoparticles synthesis (Lee et al. 2016). This research work revealed different morphologies depending on the fraction of the extract considered. The crude extract led a heterogeneous mixture of gold nanoparticles, while hexane fraction displayed spherical gold nanoparticles with a few proportion of anisotropic nanoparticles. Regarding the chloroform fraction, gold discs lower than 200 nm were mostly obtained. The aqueous and *n*-butanol extracts led to Au platelets and irregular nanoparticles, respectively. A similar study was performed for gold nanoparticles synthesized using *Zostera noltii* extract (an aquatic plant). The buthanolic extract led to mostly spherical nanoparticles with bimodal bell-shaped distribution, while the aqueous/dimethylsulfoxide flavone fraction of buthanolic extract led to nanoparticles with triangular, spherical, and polyhedral shapes (Zarzuela et al. 2018).

The concentration of the phytocompounds present in the extract can influence the shape and size of metal nanoparticles. Smitha and coworkers reported higher proportion of gold anisotropic particles at lower volumes, while spherical shape dominates at higher ones (Smitha et al. 2009). The change in the AuNPs shape by varying the concentration of the extract can be stated on the biosynthesis of gold using other sources. Gold nanotriangles were obtained at low concentration of *Aloe*

Table 8 Size and shape of several metal and metal oxide nanoparticles obtained by using different plant extracts

Metal nanoparticle	Plant specie	Origin of the extract	Size (nm)	Morphology	References
Gold nanoparticles (AuNPs)	*Pelargonium zonale*	Leaf	8–20	Spherical	Franco-Romano et al. (2014)
	Ocimum sanctum	Leaf	10–300	Spherical triangular hexagonal platelets	Lee et al. (2016)
	Coleus aromaticus	Leaf	<20	Spherical triangular hexagonal	Boomi et al. (2019)
	Solanum nigrum	Leaf	5–35	Spherical	Muthuvel et al. (2014)
	Sanseviera roxburghiana	Leaf	5–31	Spherical triangular hexagonal rod	Kumar et al. (2019)
	Croton caudatus Geisel	Leaf	20–50	Spherical	Vijaya Kumar et al. (2019)
	Pueraria lobata	Root	5–36	Spherical	Zhou et al. (2019)
	Chenopodium aristatum L.	Stem	7–19	Spherical Triangular Pentagonal Hexagonal	Golinska et al. (2017)
	Zostera noltii	Leaf	<11; 20–35 (Buthanolic extract)	Spherical	Zarzuela et al. (2018)
			25–65 (flavonoid fraction)	Spherical Triangular	
Silver nanoparticles (AgNPs)	*Ocimum basilicum*	Leaf	≈23	Spherical	Pirtarighat et al. (2019)
	Satujera hortensis	Leaf	2.9–3.4	Spherical	Rasaee et al. (2018)
	Artemisia vulgaris	Leaf	≈25 nm	Irregular	Rasheed et al. (2017)
	Capparis spinosa	Leaf	5–30	Spherical	Benakashani et al. (2016)
	Beberis vulgaris	Leaf	30–70	Spherical	Behravan et al. (2019)
	Cynara cardunculus	Leaf	<45	Semi-spherical	Ruíz-Baltazar et al. (2018)

(continued)

Table 8 (continued)

Metal nanoparticle	Plant specie	Origin of the extract	Size (nm)	Morphology	References
	Ocinum sanctum	Roots	10	Spherical	Ahmad et al. (2010)
	Ocinum sanctum	Stem	5	Spherical	
	Avicennia marina	Leaf roots stem	20–40	Spherical	Abdi et al. (2018)
Zinc oxide nanoparticles (ZnONPs)	*Cassia fistula*	Leaf	5–15	Irregular	Suresh et al. (2015)
	Aloe barbadensis miller	Leaf	25–55	Spherical Hexagonal	Sangeetha et al. (2011)
Palladium nanoparticles (PdNPs)	*Camellia sinensis*	Leaf	6–18	Spherical	Azizi et al. (2017)
	Catharanthus roseus	Leaf	≈38	Spherical	Kalaiselvi et al. (2015)
Copper nanoparticles (CuNPs)	*Tilia extract*	Leaf	4.7–17.4	Spherical	Hassanien et al. (2018)
	Plantago asiatica	Leaf	7–35	Spherical	Nasrollahzadeh et al. (2017)

vera, while spherical nanoparticles were obtained at higher values (Chandran et al. 2006). Anisotropic gold nanoparticles were also obtained using low concentration of *Magnolia kobus* (Song et al. 2009).

The nanoparticle's morphology is influenced by other elements, like pH, reduction time, and temperature, all of them summarized in Baranwal and coworkers review (Baranwal et al. 2016).

3.4.2 Synthesis of Metal Nanoparticles Mediated by Polysaccharide-Based Biopolymers

The green synthesis of metallic nanoparticles also includes the use of biopolymers, mainly characterized by their biodegradability, biocompatibility, and nontoxicity (Hernández et al. 2014). Among all of them, polysaccharides are mainly used for biosynthesis (Wang et al. 2017).

As in the case of the plant extracts use, the metallic nanoparticles synthesis using biopolymers is of great interest from the Green Chemistry point of view. The role of the biopolymer as reducing and/or capping agent avoids the use of any additive, reducing the employment of hazardous reagents. Furthermore, the formation of metal nanoparticles can be reached at short times, minimizing the energy requirements (Balachandran et al. 2015). The main synthesis approach consists of the

direct mixing of the biopolymer and the metal solution, obtaining the metal nanoparticles after stirring in one-step.

The gold nanoparticles synthesis using pectin was investigated by Ahmed and coworkers (Ahmed et al. 2016). In their report, the fragmented units of pectin obtained after alkali treatment reduce Au^{3+} to Au^{0} and promote the nucleation process. In addition, the binding between the reducing sugar units and the gold nanoparticles was proposed, preventing their agglomeration. Consequently, small nanoparticles distribution was obtained.

The chemical bonding metal-biopolymer was also proposed in other reports related to the synthesis of metal nanoparticles using polysaccharide biopolymers. Guibal and coworkers summarized the mechanisms involved in metal ion binding on chitosan, proposing the formation of different metallic chitosan complexes (Guibal et al. 2014). The employment of this biopolymer in the synthesis of copper nanoparticles is reported, leading to improvements in their stability (Muthukrishnan 2015). Gold and silver nanoparticles with high stability were also mediated by chitosan (Wei and Qian 2008). The chelating role of soluble starch was also reported by the linkage between the aldehyde terminal of amylose units and silver in the silver nanoparticles synthesis (Yakout and Mostafa 2015).

Table 9 shows some examples of silver nanoparticles' size and morphology synthesized using biopolymers.

The synthesis of metallic nanoparticles can also be mediated by biopolymeric nanostructures using two approaches, according to several research works (Preiss et al. 2014): incorporation of metallic nanoparticles into a polymeric matrix (ex situ) and the synthesis of metallic nanoparticles in the biopolymeric matrix (in situ).

Boury and Plumejeau summarized the main aspects concerning the in situ synthesis of metal oxide nanocomposites (Boury and Plumejeau 2015). The combination between metal precursor and the biopolymer lead to biopolymer-metallic composite. Afterwards, the biotemplate was removed by thermal treatments, obtaining the metallic oxide nanocomposite. A general scheme is shown in Fig. 16.

The metal oxide nanoparticles can be formed and included into the polymeric scaffold using the sol-gel process, controlling their morphology. Catalytic effects in the sol-gel kinetics are ascribed to the bipolymer, as well as a strong chemical affinity with metals due to the presence of hydroxyl and amine groups (Plumejeau et al. 2015). Zlotski and Uglov reported the synthesis and immobilization of different oxide nanoparticles on cellulose fibers template by sol-gel process (Zlotski and Uglov 2017). A flake-like structure was observed after calcination with irregular

Table 9 Size and morphology of silver nanoparticles using different polysaccharide biopolymers

Biopolymer	Size(nm)	Morphology	Ref
Starch	4–14	Spherical	Božanić et al. (2007)
Sodium alginate	3–12	Spherical	Chunfa et al. (2016)
Chitosan	10–60	Spherical	Kalaivani et al. (2018)
Pectin	5–10	Spherical	Zahran et al. (2014)
Dextran	5–10	Spherical	Bankura et al. (2012)

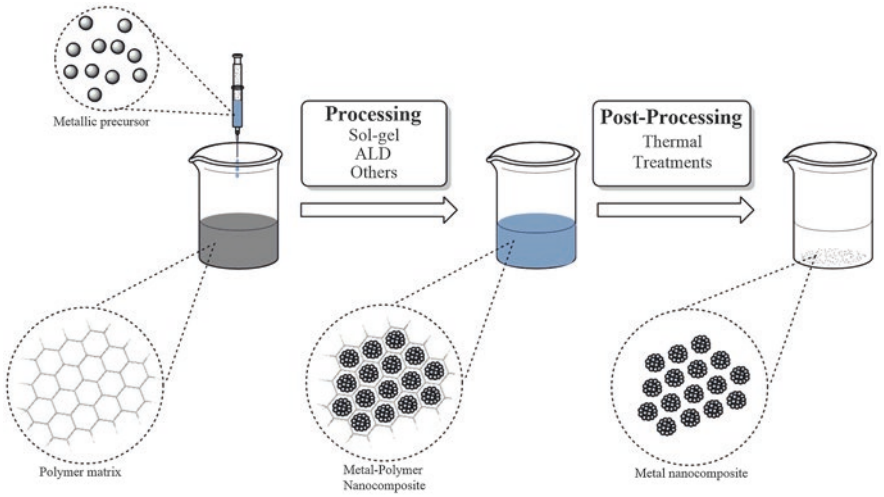


Fig. 16 Synthesis of metallic nanocomposites assisted by biopolymer templating

pores, testifying that cellulose fibers provided seeding points of metal oxide nanoparticles nucleation and growth. Calcium alginate is also used as biotemplate for the synthesis of titanium oxide beads by sol-gel route (Kimling and Caruso 2012).

β-Cyclodextrin, chitosan, and starch were used for the synthesis of titanium oxide nanoparticles by Bao and coworkers using a simple mineralization process (Bao et al. 2013). In their work, the polysaccharide biotemplate plays a key role on the final nanostructure: small rods for β-cyclodextrin, chestnut-like for chitosan, and small nanoparticles for soluble starch. The influence of the polysaccharide on the crystalline structure is also discussed. The rutile phase was obtained mediated by chitosan, while anatase was obtained mediated by starch and β-cyclodextrin.

Therefore, the biosynthesis of metal and metal oxide nanoparticles was carried out by plant extracts and biopolymers, obtained from renewable and clean sources. Their reducing and capping agent role can be highlighted, reducing the waste products. Furthermore, the nanoparticles shape and size can be monitored by the synthesis conditions, such as phytocompounds composition and concentration of the extract and the nature of the polysaccharide, among others.

3.5 Polymers

Polymers are compounds constituted by several monomeric units linked by covalent chemical bondings. They can be employed as immobilization matrices of several enzymatic compounds, increasing the selectivity of the system with respect to a target analyte (García-Guzmán et al. 2018; Bilal and Iqbal 2019). Their use as bulk

transducers in some electronic devices should also be highlighted, improving their electronic transference and, hence, their electrochemical performance (Gautam et al. 2018).

Polymers can be ordered into two groups: intrinsic conducting polymers and nonconducting polymers. Several synthesis routes to produce some of them will be shown in this subsection.

3.5.1 Intrinsic Conducting Polymers: Polythiophene Derivatives, Polyaniline, and Polypyrrole

Conducting polymers have emerged in the last decade due to their high electrical properties, among others. Their high conductivity, attributed to the π-conjugation and electronic doping, enables their use in electrochemical sensing (Kenry and Liu 2018).

Moreover, their redox properties make them suitable for the fabrication of electrochromic and sensing devices (Naveen et al. 2017). Figure 17 shows the chemical structure of the most representative intrinsic conducting polymers, poly-(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), and polypyrrole (Ppy).

The chemical polymerization is a high-scalable approach based on the chemical oxidation of the monomer. Many oxidizing agents and dopants were investigated to control the electrical properties of the resulting polymer and increase their oxidation degree (Nguyen and Yoon 2016). Several synthesis strategies were investigated as alternative polymerization routes.

The **ultrasound-assisted synthesis** led to high polymerization rates, as well as an improvement in the electrical features of the resulting polymer in comparison

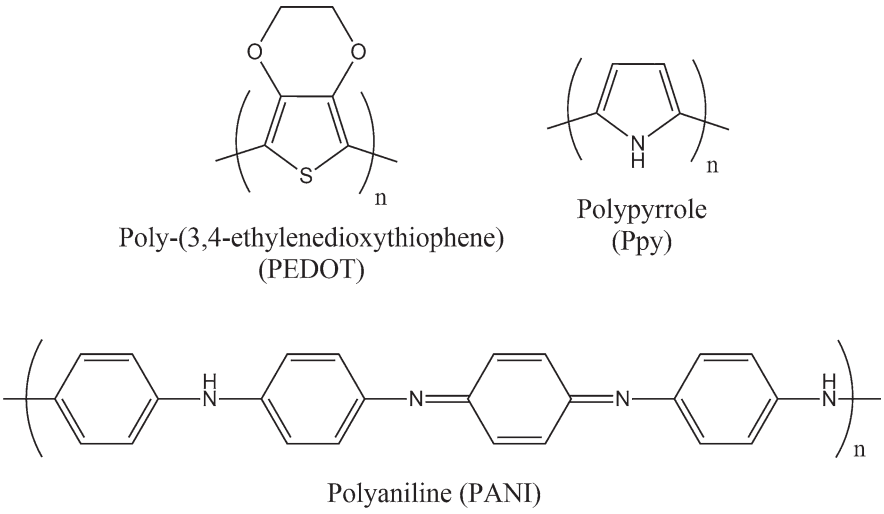


Fig. 17 Chemical structure of PEDOT, PANI, and Ppy

with conventional route (Ali Mohsin et al. 2016). The influence of frequency waves was studied in the acid polymerization of aniline with ammonium persulfate (Husin et al. 2014). PANI nanofibers' diameter decreased when ultrasonic frequency takes higher values. Thus, the role of the ultrasound in the morphology of PANI was demonstrated. Uniform spherical PEDOT nanoparticles were produced under ultrasound, in contrast with irregular-shaped nanoparticles obtained by conventional stirring (Zhong et al. 2010). PEDOT microspheres with controlled morphology were obtained via ultrasonic spray polymerization by using different oxidants and solvents (Zhang and Suslick 2015). The **microwave-assisted synthesis** of conducting polymers was also proposed as an alternative to conventional synthesis, reducing significantly the reaction time and leading to improvements in product yields. Polyaniline was obtained under microwave in 5 min, with a similar yield value than the one obtained under conventional synthesis at 5 h, around 76%. In addition to the reaction time, the morphology was also affected by microwave heating. Nanofibrillar morphology was observed under microwave, while granular morphology was obtained under conventional conditions (Gizdavic-Nikolaidis et al. 2010). A more recent work shows the influence of the concentration of hydrochloric acid in the morphology of PANI, synthesized by oxidative microwave-assisted polymerization: low acid concentration values provided oligomeric chains with flat structure, while high acid concentration led to nanofibers (Qiu et al. 2017). It should be noted that longer oligomeric chains were observed in microwave-assisted polymerization with respect to those obtained under conventional synthesis at same reaction times, demonstrating the role of microwave heating in the improvement of reaction rates and yields.

Enzyme-catalyzed synthesis is another environmental friendly route to produce conducting polymers with desirable electrical and morphological features at mild conditions. The enzymatic polymerization of thiophene, aniline, and pyrrole with embedded glucose oxidase was performed (German et al. 2019). Several synthesis parameters, such as pH, monomer concentration, and ratio enzyme/substrate, were investigated by spectrophotometric assays. Laccase produced by *Aspergillus oryzae* was used as biocatalyst in the polymerization of aniline (De Salas et al. 2016). The polymerization of EDOT was achieved mediated by horseradish peroxidase with high efficiency, by using hydrogen peroxide as clean oxidant (Wang et al. 2014). Two *Aspergillus niger* strains were employed in the polymerization of pyrrole with hydrogen peroxide (Apetrei et al. 2018).

Therefore, biosynthetic routes provide several advantages with respect to the conventional polymerization process, like improvements in product yields, reduction of reaction times, tailored morphological features, and high electrical conductivities. However, some instrumental parameters required a specific control in order to obtain conducting polymers with the desired electrical properties and nanosized morphology.

3.5.2 Nonconducting Polymers: Polysaccharide Biopolymers

Polysaccharide biopolymers are obtained by natural resources. Several pieces of research were focused on their biosynthesis in order to understand the different mechanism pathways. The metabolic engineering offers some improvements in the green synthesis of tailored biopolymers, and thus different synthetic biologic strategies were reported in the literature (Anderson et al. 2018). The biosynthetic routes for three relevant polysaccharide biopolymers are listed in this subsection.

Chitosan and chitin are located in the shell of crustaceans, exoskeleton of mollusks, and fungi's cell walls. For industrial applications, crustacean shells constitute the main source for the production of chitosan and chitin. The chemical extraction procedure to obtain the pure product, shown in a recent review (Abo Elsoud and El Kady 2019), involves five steps: demineralization, discoloration, deproteinization, acid reflux, and deacetylation. The fungal biosynthesis of chitosan was also proposed in the same work for industrial applications over crustacean sources due to several reasons: simple extraction procedure, low cost waste management, and high availability, among others.

Alginate was initially isolated from farmed brown seaweeds for commercial production. However, these algal alginates suffer from heterogeneity in composition and material properties. Other alternative biosynthetic route is the microbial synthesis, summarized in the following review (Hay et al. 2013).

Two types of bacteria, pseudomonas and azotobacter, were used in the alginate biosynthesis (Hay et al. 2013). In this way, the production of alginate was reported using *Pseudomonas mandelii* (Vásquez-Ponce et al. 2017), *aeruginosa* (McCaslin et al. 2015), and *fluorescens* (Maleki et al. 2017). Regarding azotobacter, *Azotobacter vinelandii* was widely employed for alginate biosynthesis (Saeed et al. 2016). Starch is mainly located in the endosperm of cereal grains. Its biosynthesis via ADP-glucose pathway involves the use of sucrose as carbon source, imported from leaves, and the participation of three primary enzymes, ADP-glucose pyrophosphorylase, starch synthase, and starch branching (Thitisaksakul et al. 2012). The starch biosynthesis was investigated in the last decade by using different cereals, such as rice (Fujita 2014), wheat (Chen et al. 2016), maize (Jiang et al. 2013), and grass (Tetlow and Emes 2017). The starch biosynthesis in plants, such as *Cassava* (Tappiban et al. 2019) and *Arabidopsis thaliana* (Malinova et al. 2018), was also investigated.

3.6 Bare Electrochemical Devices and Their Modifications: Carbon Ceramic Materials

Although the majority of reports related to chemical sensors were based on the deposition onto glassy carbon, metallic or ITO surfaces, the development of silicon and carbon ceramic materials by using sol-gel technology and assisted by high-power ultrasound was carried out by some research groups (Hidalgo-Hidalgo-de-Cisneros et al. 2001).

The sol-gel process has been extensively applied to obtain silicon oxide and silicon oxide-derived monolithic substrates at room temperature from silane alkoxides or metallic precursors (Kajihara 2013). The employment of organic solvents, like methanol or ethanol, is required due to the immiscibility of the silane/metallic precursors in aqueous solution. Their use can be suppressed by high-power ultrasound, leading to a new type of silica monolith with higher density matrix. This also implies the reduction of waste products. The structural and mechanical properties of these new materials, namely Sonogels, were extensively studied (Blanco et al. 1999).

The addition of carbon powder after the sonication process leads to a conducting material able to be used as electrochemical device. In the first formulations, Sonogel-Carbon, graphite powder was employed owing to its low cost and high availability, as well as its high electrical conductivity (Cordero-Rando et al. 2002; Cubillana-Aguilera et al. 2006). Figure 18 shows a schematic representation of the fabrication of the Sonogel-Carbon electrodes.

The synthesis process of Sonogel-Carbon is characterized by its high versatility, allowing the obtention of new bare electrode materials. The graphite powder added to the sonosol after sonication can be replaced totally by multi-walled carbon nanotubes and nanocarbon (Palacios-Santander et al. 2017) or partially by 1-furoylthiourea (Cubillana-Aguilera et al. 2010), β-cyclodextrin (Izaoumen et al. 2009), and

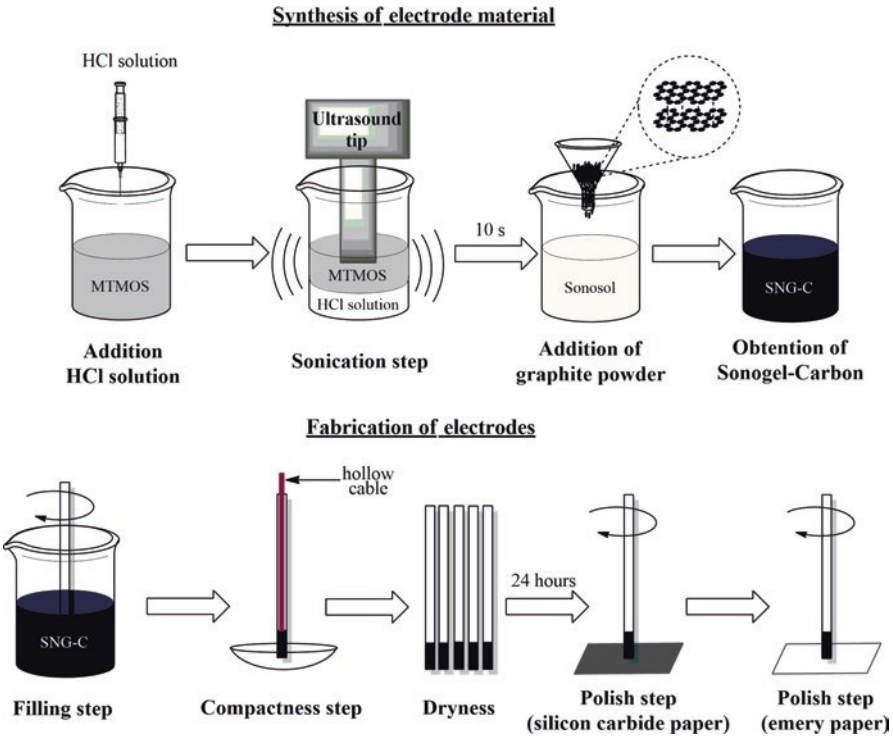


Fig. 18 Fabrication of Sonogel-Carbon electrodes

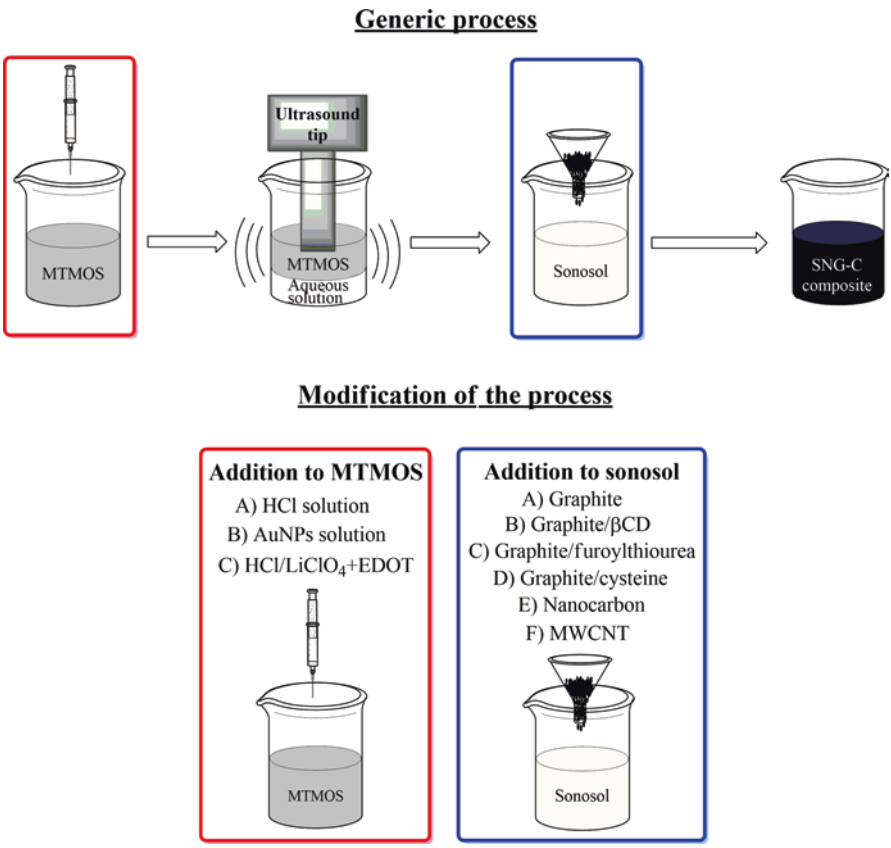


Fig. 19 Different synthesis routes for the fabrication of Sonogel-Carbon derived composites

L-cysteine (El Bouhouti et al. 2009), among other modifiers (Bellido-Milla et al. 2013). The substitution of the acid solution used as catalyst by gold nanoparticles colloidal solution obtained from a green route is under investigation (Franco-Romano et al. 2013). Based on their acid pH, they can catalyze the formation of the silicon oxide network from the silane precursor. Finally, the inclusion of a conducting polymer in the silicon oxide network by using high-power ultrasound was reported in other work (López-Iglesias et al. 2018). Figure 19 summarizes all the synthesis routes mentioned in this subsection.

Therefore, the synthesis of several conducting ceramic materials assisted by high-power ultrasound in one-step was reported in the bibliography. The easy, low-cost and low-time consuming methods are highlighted, together with the use of high-power ultrasound, allowing decrease in the reaction time, as well as minimize the use of hazardous solvents. Moreover, the versatility and greenness of the synthesis scheme, as shown in Figs. 18 and 19, may increase, in the near future, the number of materials susceptible of being employed in the fabrication of ceramic-based electrode devices (López-Iglesias et al. 2016).

4 Application of Green (Nano)Materials in Analytical (Bio)Sensing

The applications of the different (nano)materials obtained by a green synthetic route for (bio)sensing are the main focus of this section. In order to clarify the structure that will be followed, several tables collecting the different materials by type have been included.

In Table 10, a representative collection of ionic liquids used in sensor systems are shown. Some of them correspond to enzymatic biosensors used either as amperometric sensors or in colorimetric tests. The half of them employs nanomaterials to enhance sensitivity, such as graphene and carbon nanotubes.

The amount of analytes that can be detected by these devices based on ionic liquids is quite diverse, including analytes of interest in food industry (like ascorbic and caffeic acid), medical and healthcare industry (i.e., cholesterol and neurotransmitters), and environmental applications (pesticides). They were determined in biological and agrifood matrices such as water, juices, human serum, and blood. The performance of ILs-based sensor systems can be evaluated by several quality analytical parameters, i.e., limit of detection and reproducibility. In general, the figures of merits are quite good in most cases for the linear ranges indicated.

The original interest and applications of ILs in (bio)sensing started decreasing when the scientific community realized the possible problematic related to the elimination of the ILs after their use from the environment (Bystrzanowska et al. 2019). More information concerning analytical application of ILs in sensing systems can be found in Yavir and coworkers' review (Yavir et al. 2019).

The use of other kinds of green nanomaterials used for building sensing and biosensing devices, like graphene, quantum dots, carbon dots, and metal and metal oxide nanoparticles, principally, may also be assessed. Table 11 reports optical devices and Table 12 electrochemical ones for multiple sensing applications.

With respect to the optical sensors described in Table 11, most of them are based on carbon or quantum dots, in some cases doped with lantanide metals to enhance the luminescence signal, and applied directly in buffer solutions. The variety of target analytes is much higher than in the previous case: nitrophenols, cations, anions, metals, amino acids, enzymes, guanine phosphorylated derivatives, and/or their nanocomposites. Some of them are considered as priority environmental pollutants and others have high applicability in biomedical or pharmaceutical fields. According to this classification, the type of samples measured are highly diverse, including cellular systems, such as MCF-7 and HeLa cells, soil samples, natural water samples, or serum samples. The limits of detection obtained for the analytes mentioned is quite low, most of them in the nanomolar range for more or less wide dynamic ranges.

On the other hand, Table 12 shows some examples of electrochemical sensing and (bio)sensing devices mainly based on carbon transducers modified with the aforementioned green nanomaterials. Their application is fundamentally focused on biomedical analysis, including some pharmaceuticals. That is why the real samples

Table 10 Sensors and biosensor systems based on different ionic liquids and most relevant figures of merits

Analyte (s)	Applied ILs	Composite components	Sample type	Reproducibility (RSD %)	LOD (μM)	Linear range (mM)	Sensitivity ($A \cdot M^{-1}\ cm^{-2}$)	References
H_2O_2	[C4C1Im][BF4]	HRP, TEOS	Water	3.1	1.1	0.02–0.26	7.2	Liu et al. (2005)
Glucose	[C4C1Im][BF4]	HRP, GOD, PTMSPA, Nafion®	Serum	3.6	10	0.05–7.0	0.0379	Chen et al. (2012)
Carbaryl, monocrotphos	[(NH2C3)C1Im][BF4]	GN, AchE,	Tomatojuice	–	5.3×10^{-9}; 4.6×10^{-8}	1.0×10^{-11}-1.0×10^{-5}; 1.0×10^{-10}-5.0×10^{-5}	–	Zheng et al. (2015)
Eserine, neostigmine	[C2C1Im][TCB]	TTF, TCNQ	Tapwater	6	2.6×10^{-7}; 0.3×10^{-3}	$(0.1–1000) \times 10^{-6}$; $(1–500) \times 10^{-6}$	–	Zamfir et al. (2013)
Caffeic acid	[C4C1Im][Br]; [C4C1Im][cl]	GN	Plasma	3.2; 1.4	18.0; 5.0	0.025–2.0; 0.025–2.0	1.657; 3.389	Valentini et al. (2015)
Cholesterol	[C8C1Im][TFA]	ChOx, Prussian blue	Water sample	–	4.4	0.01–0.4	–	Liu et al. (2013)
Dopamine	[C8C1Im][PF6]	MWCNTs	Human blood; serum	–	0.1	0.001–0.1	–	Zhao et al. (2005)
Glucose	[C8Pyrr][PF6]	MWCNTs	–	–	–	Up to 6	0.002	Kachoosangi et al. (2009)
Hb, HRP	[C4C1Im][BF4]	MWCNTs	–	6.8; 7.5	–	–	–	Tao et al. (2006)
Cholesterol	[C4C1IM][BF4]	Chi, ChOx, MWCNTs, au	Serum sample	1.9 (repeatability)	0.5	0.5–5.0	0.0002 A/M	Gopalan et al. (2009)

IL ionic liquid, *LOD* limit of detection, *Hb* hemoglobin, *HRP* horseradish peroxidase, *GOD* glucose oxidase, *[C4C1Im][BF4]* 1-butyl-3-methylimidazolium tetrafluoroborate, *[(NH2C3)C1Im][BF4]* 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate, *[C2C1Im][TCB]* 1-ethyl-3-methylimidazolium tetracyanoborate, *[C4C1Im][Br]* 1-butyl-3-methylimidazoliumbromide, *[C4C1Im][Cl]* 1-butyl-3-methylimidazoliumchloride, *[C8C1Im][TFA]* 1-butyl-3-methylimidazolium trifluoroacetate, *[C8C1Im][PF6]* 1-methyl-3-octylimidazolium hexafluorophosphate, *[C8Pyrr][PF6]* N-octylpyrrolidiniumhexafluorophosphate, *TEOS* tetra-ethyl-orthosilicate, *PTMSPA* poly[1-phenyl-2-(p-trimethylsilyl) phenylacetylene], *GN* graphene, *AChE* acetylcholinesterase, *TTF* tetrathiafulvalene, *TCNQ* tetracyanoquinodimethane, *ChOx* cholesterol oxidase, *MWCNTs* multi-walled carbon nanotubes, *Chi* chitosa

Table 11 Optical sensors and biosensor devices based on green nanomaterials and most relevant figures of merits

Analyte(s)	Green (nano)material	Sample type	LOD (nM)	Linear range (μM)	References
2-Nitrophenol, 4-nitrophenol	Carbon dots	–	1060; 500	0.001–1.0	Ren et al. (2018)
Fe(III)	Graphitic carbon quantum dots	–	2	0–1	Zhang et al. (2013b)
Phosphate	Eu-adjusted carbon dots	Artificial wetland water	51	0.4–15	Zhao et al. (2011)
Thallium	Mn-doped ZnSeQDs&carbondots	Serum, water, soil	≈ 4.9	≈ 24–490	Lu et al. (2018)
Fe(III), pyrophosphate	Carbon dots	–	60; 300	0.2–100; 1–100	Chen and Tseng (2017)
Lysine	Carbon dots	Inside cellular systems	94	0.5–260	Song et al. (2017)
Thioredoxin reductase	Carbon dots	MCF-7 and HeLa cells	20	–	Sidhu et al. (2018)
Guanosine 3′-diphosphate-5′-diphosphate (ppGpp)	Tb(III)-modified carbon dots	–	50	0.5–15	Chen and Jiang (2018)
Ascorbic acid	Graphene QDs	HeLa cells	270	0–800	Feng et al. (2017)
Fe(III)	Carbon dots	Lake water	–	0.01–46	Qu et al. (2013b)
2,4,6-Trinitrophenol	Carbon dots/ Fe_3O_4NPs-MIPs	Tap/lake water	0.5	0–100	Wang et al. (2019a)

LOD limit of detection, *QDs* quantum dots, *Fe_3O_4NPs* Fe_3O_4 nanoparticles, *MIPs* molecularly imprinted polymers

where the determination has been accomplished correspond to human samples (i.e., serum, blood, and urine). Only in two cases food and environmental samples are measured. As observed in the previous devices reported, limits of detection are at nanomolar level; besides, reproducibility is excellent (lower than 5–7%) and, when applicable, sensitivity is also quite good. Other examples can be seen in Table 12, but exclusively referred to real environmental, biomedical, and food industrial uses. Excellent figures of merits are reported in all cases.

Hence, most of these (bio)sensing devices can be or are susceptible of being produced and/or used directly in industry. As discussed in the previous paragraphs and tables, the performance of these analytical systems are more than adequate for fulfilling the industry requirements whatever the purpose they are used for: detection and/or determination, quality, and waste control, in different kinds of industrial companies, such as food, environmental, biopharmaceutical, and biomedical industries (Siontorou 2019).

Table 12 Electrochemical sensors and biosensor devices based on green nanomaterials and most relevant figures of merits

Analyte(s)	Green (nano) material	Composite components	Sample type	Reproducibility (RSD %)	LOD (μM)	Linear range (mM)	Sensitivity ($A{\cdot}M^{-1}\ cm^{-2}$)	References
p-nitrophenol	MnO NPs	BCA/AuE	–	–	15.65	0.2–0.55	0.16	Kumar et al. (2017)
Hydrogen peroxide	rGO/FeNPs	GCE	–	–	0.056	1×10^{-4}–2.15	0.2085	Amanulla et al. (2017)
Glucose	rGO-PtNPs-GOx	GCE	–	–	1.21	2–10	0.0275	Akkaya et al. (2018)
Glucose, *Escherichia coli*	fPtNCF-GN paper		–	–	0.08 ± 0.02; ≈4 $CFU{\cdot}mL^{-1}$	0–0.5; 4–10^5 $CFU{\cdot}mL^{-1}$	3.59 ± 0.68 A·M; 16.1 Ω·log $CFU^{-1}{\cdot}mL^{-1}$	Burrs et al. (2016)
Uric acid, tyrosine	MIP/rGO	GCE	Human serum and urine samples	4.68	0.0032; 0.046	1×10^{-5}- 0.1;1×10^{-4}-0.4	–	Zheng et al. (2018)
Hydrogen peroxide	rGO-Nafion/AuNPs	GCE	–	0.47	2	0.02–23	0.575	Lv et al. (2016)
Glucose	Electro-chemically rGO/DexP	SPE	Human serum	6.7	20	0.05–100	–	Li et al. (2018)
Cathecol	PEDOT-rGO-Fe_2O_3-PPO	GCE	Green tea	3.2	0.007	4×10^{-5}–6.2×10^{-3}	0.0108 $A{\cdot}M^{-1}$	Sethuraman et al. (2016)
Nitromethane	Hb-CS/rGO-CS	GCE	Fresh water samples	3.7	1.5	5×10^{-3}–1.46	–	Wen et al. (2016)
Chloramphenicol	TiN–rGO	GCE	–	4.39	0.02	5×10^{-5}–0.1	–	Kong et al. (2016)
Glucose	GelMA:NiPs-RGO	GCE	Human blood serum	2.1	0.005	1.5×10^{-4}-10	0.056 $A{\cdot}M^{-1}$	Darvishi et al. (2018)

(continued)

Table 12 (continued)

Analyte(s)	Green (nano) material	Composite components	Sample type	Reproducibility (RSD %)	LOD (μM)	Linear range (mM)	Sensitivity ($A{\cdot}M^{-1}\ cm^{-2}$)	References
CEA, PSA	Anti-CEA/EDC/NHS/PdAuPt/COOH-rGO/au; anti-PSA/EDC/NHS/PdAuPt/COOH-rGO/au	Immunosensor platform	Human serum	5.6	8; 2 $pg{\cdot}ml^{-1}$	12–8.5 × 10^4; 3–6 × 10^4 pg mL^{-1}	212.1; 258.7 $A{\cdot}L{\cdot}g^{-1}$	Barman et al. (2018)
Glycerol	CuONPs/Pe-MWCNTs	GCE	Biodiesel	10	5.8 × 10^{-6} $g{\cdot}L^{-1}$	9 × 10^{-6}–1 × 10^{-3} $g{\cdot}L^{-1}$	5.5 ± 0.3 × 10^{-5} $A{\cdot}L{\cdot}g^{-1}$	Arévalo et al. (2017)
Triglycerides	CNP-L/CuONPs/MWCNTs/Pe	GCE	Human serum	5.9	3.2 × 10^{-3}-3.6 × 10^{-3} $g{\cdot}L^{-1}$	0.001–0.53 $g{\cdot}L^{-1}$	1.64 × 10^{-6} $A{\cdot}L{\cdot}g^{-1}$	Di Tocco et al. (2018)
Organophosphorous pesticides: Paraoxon and carbaryl	MWCNT–$(PEI/DNA)_2$/OPH/AChE	GCE	Apples (agricultural industry)	–	0.5–10	0.5 × 10^{-3}–0.04;0.01–0.08	0.021–0.00941 $A{\cdot}M^{-1}$	Zhang et al. (2015)
Organophosphorous pesticide: Dimethoate	CNTs/ZrO_2/PB/NfGMP-AChE	SPCE	Cabbage (Agricultural industry)	5.2	5.6 × 10^{-4} $ng{\cdot}mL^{-1}$	1.0 × 10^{-3}-10 $ng{\cdot}mL^{-1}$	–	Gan et al. (2010)
Choline (in food industry)	Glass/ZnONR/COD-HRP/PHA	Optical platform (chemiluminiscence)	Milk	4.1 ± 0.5	0.5	0.006–2	–	Pal et al. (2014)
Xanthine (in food industry)	XOD/ZnO-NP/CHIT/c-MWCNT/PANI	PtE	Fish meat	5.30	0.1	1 × 10^{-4}–0.1	–	Devi et al. (2012)

PSA	Ti/Pt sputtered (microfluidic channel)	Slide glass by photolithographic system	Human plasma	–	100 fg·mL^{-1}	10–1 × 10^{5} fg·mL^{-1}	5.3 MΩ·dec imalpoint^{-1}	Shin et al. (2016)

CEA carcinoembryonic antigen, *PSA* prostate specific antigen, *NPs* nanoparticles, *rGO* reduced graphene oxide, *GOx* glucose oxidase, *fPtNCF* fractal Pt nano cauliflower, *GN* Graphene, *MIP* molecularly imprinted polymer, *DexP,* phenoxyl-dextran, *PEDOT* poly(3,4-ethylenedioxythiophene), *PPO* polyphenol oxidase, *Hb* hemoglobin, *CS* chitosan, *TiN* titanium nitride, *GelMA* gelatin methacryloyl hybrid hydrogel, *EDC/NHS* 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide, *Pe* Pectin, *MWCNT* multi-walled carbon nanotubes, *CNP-L* lipase-modified magnetic nanoparticles, *BCA* butyl carbitol acetate, *AuE* gold electrode, *GCE* glassy carbon electrode, *SPE* screen-printed electrode, *PSA* prostate specific antigen, *PEI* polyethyleneimine, *OPH* organo phosphate hydrolase, *AChE* acetylcholine esterase, *CNTs* carbon nanotubes, *PB* Prussian blue, *Nf GMP* Nafion gold magnetic nanoparticles (Fe_3O_4/Au), *ZnONR* ZnO nanorods, *COD* choline oxidase, *HRP* horseradish peroxidase, *PHA* phosphonohexadecanoicacid, *XOD* xanthine oxidase, *CHIT* chitosan, *PANI* polyaniline, *c-MWCNT* carboxylated-MWCNT, *GCE* glassy carbon electrode, *SPCE* screen-printed carbon electrode, *PtE* platinum electrode, *LOD* limit of detection

5 Industrial Application of (Bio)Sensing Devices

As mentioned in Sect. 4, analytical sensing constitutes high interest in the chemical industry, attracting great attention nowadays. Thus, the employment of robust analytical systems with suitable performance in the in situ analytical detection/determination or quality control is being implemented in industry. In this section, some applications of (bio)sensing devices able to be used at industrial scale are reported.

Several recent reports concerning the application of sensing devices in several fields of interest such as food, clinical, and medicines at industrial scale are highlighted. A recent review is focused on the application of biosensors for whole-cell bacterial detection. The interest of portable stand-alone biosensors in the rapid detection and diagnosis of critical illnesses (meningitis, food-borne pathogens, sexually transmitted diseases, anthrax detection) is reported. Furthermore, the review discusses recent progress in the use of the biosensors without the need for sample processing compared with current methods of bacterial detection. A particular focus on electrochemical biosensors is made (Ahmed et al. 2014). Another review encompasses recent developments in the technological innovations concerning the detection of food allergens. Hypersensitivity towards this kind of allergens is increasing worldwide. Therefore, improving the methodology for food allergens detection will permit the identification of individual immune triggers, the prediction of the response severity, and the monitoring of allergen tolerance over time. Neethirajan and coworkers reported several biosensors as innovative analytical devices for enzymes, antibodies, aptamers, and single-stranded DNA detection. Optical, electromechanical, and electrochemical biosensors employed in the detection of food allergens are also reviewed (Neethirajan et al. 2018b).

A review about nanogenerators for self-powered gas sensing discusses their ability as technological and economical driver for global industries. Nanogenerators are applied as self-powered environmental sensors and the paper summarized 24 references of nanogenerators-based self-powered gas sensors (Wen et al. 2017).

Another paper reported the virtual sensing technology, known as soft-sensors in the area of chemical engineering. This technology is a key to estimate successfully product quality when online analyzers are not available. The applications are broad and extendable to fields such as petrochemical, steel, and pharmaceutical industries (Kano and Fujiwara 2013).

Therefore, with some effort made by all the societal sectors: public in general, academia and industries, and always thinking on as much global as possible sustainability, some of these (bio)sensing devices might reach the widespread usefulness and success of the currently most extended biosensor, the glucometer, which in many cases is also complemented with the determination of other related analytes, such as cholesterol and lactic acid, among others (Calabria et al. 2017; Pilas et al. 2017; Cunha-Silva and Arcos-Martinez 2018; Kotanen et al. 2018). In this way, not only would biomedical point-of-care diagnoses be possible, but also environmental, pharmaceutical, and food ones.

6 Conclusions

As it has been highlighted throughout this chapter, Chemical Industry, with the aim of Academia and increasingly with the growing support of Society, is currently looking for and reaching, in many cases, sustainability thanks to Green Chemistry. This multidimensional philosophy can offer many different alternatives and tools to redirect the modern industry to a more ecological and efficient manufacturing and production. The concept of "reducing" (costs, energy, wastes, and materials, among others), sustainable and green education, and government policies are considered important milestones to bring this matter to a successful conclusion.

Particularly, green synthesis is part of the foundations of Green Chemistry, since the search for the perfect synthesis with all its implications (safe, atom economy, high yield, etc.) is of vital importance to achieve sustainable industrial production. Moreover, efficient synthetic routes can be extended to different areas, especially to Analytical Chemistry, where the use of sensors and biosensors can represent a green choice with respect to conventional methodologies, as widely reported in literature during the last decade. Their many advantages among which stand out rapidity, analytical performance, on line and in situ measurements and cost-effectiveness, make them of great relevancy for being used in many kinds of industries as for analyte detection/determination as for quality control. That is why it is essential to know the different possibilities regarding the green synthesis of materials and nanomaterials that can be used for building sensors and biosensors.

In this chapter, a summary of the most relevant green materials synthesis or biosynthesis routes is provided. Special attention has been paid to ultrasound and microwave technologies. During the past few decades, both has been widely recognized as ecological and clean, as well as cost and time effective, having been demonstrated that their use fulfills most of the 12 Principles of Green (Analytical) Chemistry and is quite sustainable for synthesis purposes of both organic and inorganic materials. Moreover, the use of biological compounds to synthesize complex molecules or nanostructures, preferably by a one-pot method, is also emphasized. The focus is put on the employment of plant extracts, biopolymers, and microorganisms, such as algae, bacteria, and fungi. The possibility of combining microwave or ultrasound technologies and any of them with some biosynthetic route is also discussed through the most recent and representative achievements reported in literature within the field of green synthesis of (nano)materials. It is also necessary to mention that the most important and current trends in green (nano)materials production affects to graphene, carbon and graphene quantum dots, multi-walled carbon nanotubes, metal and metal oxide nanoparticles and polymers. A very wide set of examples concerning green synthesized materials is reported in Sect. 3, most of them already applied or with high potential applicability in industry. Furthermore, the possibility of replacing actual and more expensive metal, glassy carbon or ITO-based materials to new ceramic electrode materials, mainly for electrochemical devices, is also explored. The versatility and greenness of their scheme of synthesis and their excellent analytical performance makes them a strong alternative to

typical and conventional electrode materials. It has been demonstrated as well that the applicability of the mentioned green (nano)materials for analytical (bio)sensing is widely extended even at industrial level. An extensive set of optical or electrochemical devices employed for that purpose are described on depth according to their most relevant quality analytical parameters: limit of detection, sensitivity, linear range, and reproducibility. As reported, the kind of analytes that can be determined with (bio)sensing devices includes the fields of food, environment and medicine and healthcare.

Despite all, the path of industry towards sustainability has just begun and there is still too much work to do in order to completely erase the prejudices and the fear to chemistry, in general; in other words to banish chemophobia. However, one thing is absolutely clear: our life without chemistry or chemicals would be unthinkable, since life itself is chemistry.

Acknowledgments J.J. García-Guzmán thanks University of Cadiz for his post-doc contract (Plan Propio 2018/2019-UCA). D. López-Iglesias greatly acknowledge financial support of ESF funds (Sistema de Garantía Juvenil depending on Ministerio de Empleo y Seguridad Social and Junta de Andalucía, Spain) for his contract (E-11-20180043137). Authors thank Institute of Research on Electron Microscopy and Materials (IMEYMAT) for their economic support as well.

References

Abdi V, Sourinejad I, Yousefzadi M, Ghasemi Z (2018) Mangrove-mediated synthesis of silver nanoparticles using native *Avicennia marina* plant extract from southern Iran. Chem Eng Commun 205:1069–1076. https://doi.org/10.1080/00986445.2018.1431624

Abdullah AH, Ismail Z, Zainal Abidin AS, Yusoh K (2019) Green sonochemical synthesis of few-layer graphene in instant coffee. Mater Chem Phys 222:11–19. https://doi.org/10.1016/j.matchemphys.2018.09.085

Abo Elsoud MM, El Kady EM (2019) Current trends in fungal biosynthesis of chitin and chitosan. Bull Natl Res Cent 43:59. https://doi.org/10.1186/s42269-019-0105-y

Agarwal H, Nakara A, Shanmugam VK (2019) Anti-inflammatory mechanism of various metal and metal oxide nanoparticles synthesized using plant extracts: a review. Biomed Pharmacother 109:2561–2572. https://doi.org/10.1016/j.biopha.2018.11.116

Ahmad N, Sharma S, Alam MK et al (2010) Rapid synthesis of silver nanoparticles using dried medicinal plant of basil. Colloids Surf B Biointerfaces 81:81–86. https://doi.org/10.1016/j.colsurfb.2010.06.029

Ahmad NH, Mustafa S, Man YBC (2015) Microbial polysaccharides and their modification approaches: a review. Int J Food Prop 18:332–347. https://doi.org/10.1080/10942912.2012.693561

Ahmad A, Wei Y, Syed F et al (2017) The effects of bacteria-nanoparticles interface on the antibacterial activity of green synthesized silver nanoparticles. Microb Pathog. https://doi.org/10.1016/j.micpath.2016.11.030

Ahmed A, Rushworth JV, Hirst NA, Millner PA (2014) Biosensors for whole-cell bacterial detection. Clin Microbiol Rev 27:631–646. https://doi.org/10.1128/CMR.00120-13

Ahmed HB, Zahran MK, Emam HE (2016) Heatless synthesis of well dispersible Au nanoparticles using pectin biopolymer. Int J Biol Macromol 91:208–219. https://doi.org/10.1016/j.ijbiomac.2016.05.060

Akkaya B, Çakiroğlu B, Özacar M (2018) Tannic acid-reduced graphene oxide deposited with Pt nanoparticles for switchable bioelectronics and biosensors based on direct electrochemistry. ACS Sustain Chem Eng 6:3805–3814. https://doi.org/10.1021/acssuschemeng.7b04164

Alam AM, Park BY, Ghouri ZK et al (2015) Synthesis of carbon quantum dots from cabbage with down- and up-conversion photoluminescence properties: excellent imaging agent for biomedical applications. Green Chem 17:3791–3797. https://doi.org/10.1039/c5gc00686d

Algarra M, González-Calabuig A, Radotić K et al (2018) Enhanced electrochemical response of carbon quantum dot modified electrodes. Talanta 178:679–685. https://doi.org/10.1016/j.talanta.2017.09.082

Algul O, Kaessler A, Apcin Y et al (2008) Comparative studies on conventional and microwave synthesis of some benzimidazole, benzothiazole and indole derivatives and testing on inhibition of hyaluronidase. Molecules 13:736–748. https://doi.org/10.3390/molecules13040736

Ali Mohsin ME, Elias M, Arsad A et al (2016) Ultrasonic irradiation: a novel approach for conductive polymer. J Eng Appl Sci 11:2557–2560. https://doi.org/10.3923/jeasci.2016.2557.2560

Altemimi A, Lakhssassi N, Baharlouei A et al (2017) Phytochemicals: extraction, isolation, and identification of bioactive compounds from plant extracts. Plan Theory 6:42. https://doi.org/10.3390/plants6040042

Amanulla B, Palanisamy S, Chen SM et al (2017) A non-enzymatic amperometric hydrogen peroxide sensor based on iron nanoparticles decorated reduced graphene oxide nanocomposite. J Colloid Interface Sci 487:370–377. https://doi.org/10.1016/j.jcis.2016.10.050

Amine A, Arduini F, Moscone D, Palleschi G (2016) Recent advances in biosensors based on enzyme inhibition. Biosens Bioelectron 76:180–194. https://doi.org/10.1016/j.bios.2015.07.010

Anastas P, Eghbali N (2010) Green chemistry: principles and practice. Chem Soc Rev 39:301–312. https://doi.org/10.1039/b918763b

Anastas PT, Warner JC (1998) Green chemistry: theory and practice. Oxford University Press, New York

Anderson LA, Islam MA, Prather KLJ (2018) Synthetic biology strategies for improving microbial synthesis of "green" biopolymers. J Biol Chem 293:5053–5061. https://doi.org/10.1074/jbc.TM117.000368

Ando T, Kimura T (1990) Reactivity and selectivity in organic sonochemical reactions involving inorganic solids. Ultrasonics 28:326–332. https://doi.org/10.1016/0041-624X(90)90040-U

Apetrei RM, Carac G, Bahrim G et al (2018) Modification of *Aspergillus niger* by conducting polymer, polypyrrole, and the evaluation of electrochemical properties of modified cells. Bioelectrochemistry 121:46–55. https://doi.org/10.1016/j.bioelechem.2018.01.001

Araga R, Sharma CS (2017) One step direct synthesis of multiwalled carbon nanotubes from coconut shell derived charcoal. Mater Lett 188:205–207. https://doi.org/10.1016/j.matlet.2016.11.014

Arduini F, Cinti S, Caratelli V et al (2019) Origami multiple paper-based electrochemical biosensors for pesticide detection. Biosens Bioelectron 126:346–354. https://doi.org/10.1016/j.bios.2018.10.014

Arévalo FJ, Osuna-Sánchez Y, Sandoval-Cortés J et al (2017) Development of an electrochemical sensor for the determination of glycerol based on glassy carbon electrodes modified with a copper oxide nanoparticles/multiwalled carbon nanotubes/pectin composite. Sensors Actuators B Chem 244:949–957. https://doi.org/10.1016/j.snb.2017.01.093

Armenta S, Garrigues S, de la Guardia M (2008) Green analytical chemistry. TrAC Trends Anal Chem 27:497–511. https://doi.org/10.1016/j.trac.2008.05.003

Attar A, Cubillana-Aguilera L, Naranjo-Rodriguez I et al (2015) Amperometric inhibition biosensors based on horseradish peroxidase and gold sononanoparticles immobilized onto different electrodes for cyanide measurements. Bioelectrochemistry 101:84–91. https://doi.org/10.1016/j.bioelechem.2014.08.003

Azizi Samir MAS, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules 6:612–626. https://doi.org/10.1021/bm0493685

Azizi S, Shahri MM, Rahman HS et al (2017) Green synthesis palladium nanoparticles mediated by white tea (*Camellia sinensis*) extract with antioxidant, antibacterial, and antiproliferative activities toward the human leukemia (MOLT-4) cell line. Int J Nanomedicine 12:8841–8853. https://doi.org/10.2147/IJN.S149371

Backes C, Higgins TM, Kelly A et al (2017) Guidelines for exfoliation, characterization and processing of layered materials produced by liquid exfoliation. Chem Mater 29:243–255. https://doi.org/10.1021/acs.chemmater.6b03335

Bahadir EB, Sezgintürk MK (2015) Applications of commercial biosensors in clinical, food, environmental, and biothreat/biowarfare analyses. Anal Biochem 478:107–120. https://doi.org/10.1016/j.ab.2015.03.011

Baig RBN, Varma RS (2012) Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis. Chem Soc Rev 41:1559–1584. https://doi.org/10.1039/c1cs15204a

Balachandran YL, Panarin AY, Khodasevich IA et al (2015) Environmentally friendly preparation of gold and silver nanoparticles for Sers applications using biopolymer pectin. J Appl Spectrosc 81:962–968. https://doi.org/10.1007/s10812-015-0036-9

Banerjee B (2017) Recent developments on ultrasound assisted catalyst-free organic synthesis. Ultrason Sonochem 35:1–14. https://doi.org/10.1016/j.ultsonch.2016.09.023

Bang JH, Suslick KS (2010) Applications of ultrasound to the synthesis of nanostructured materials. Adv Mater 22:1039–1059. https://doi.org/10.1002/adma.200904093

Bankura KP, Maity D, Mollick MMR et al (2012) Synthesis, characterization and antimicrobial activity of dextran stabilized silver nanoparticles in aqueous medium. Carbohydr Polym 89:1159–1165. https://doi.org/10.1016/j.carbpol.2012.03.089

Bao SJ, Lei C, Xu MW et al (2013) Environmentally-friendly biomimicking synthesis of TiO_2 nanomaterials using saccharides to tailor morphology, crystal phase and photocatalytic activity. CrystEngComm 15:4694–4699. https://doi.org/10.1039/c3ce40310f

Baranwal A, Mahato K, Srivastava A et al (2016) Phytofabricated metallic nanoparticles and their clinical applications. RSC Adv 6:105996–106010. https://doi.org/10.1039/c6ra23411a

Bari R, Tamas G, Irin F et al (2014) Direct exfoliation of graphene in ionic liquids with aromatic groups. Colloids Surf A Physicochem Eng Asp 463:63–69. https://doi.org/10.1016/j.colsurfa.2014.09.024

Barman SC, Hossain MF, Yoon H, Park JY (2018) Trimetallic Pd@Au@Pt nanocomposites platform on -COOH terminated reduced graphene oxide for highly sensitive CEA and PSA biomarkers detection. Biosens Bioelectron 100:16–22. https://doi.org/10.1016/j.bios.2017.08.045

Baro M, Nayak P, Baby TT, Ramaprabhu S (2013) Green approach for the large-scale synthesis of metal/metal oxide nanoparticle decorated multiwalled carbon nanotubes. J Mater Chem A 1:482–486. https://doi.org/10.1039/c2ta00483f

Bayrami A, Alioghli S, Rahim S, Habibi-yangjeh A (2019) A facile ultrasonic-aided biosynthesis of ZnO nanoparticles using *Vaccinium arctostaphylos* L. leaf extract and its antidiabetic, antibacterial, and oxidative activity evaluation. Ultrason Sonochem 55:57–66. doi: https://doi.org/10.1016/j.ultsonch.2019.03.010

Begum S, Ahmaruzzaman M (2018) Green synthesis of SnO_2 quantum dots using *Parkia speciosa* Hassk pods extract for the evaluation of anti-oxidant and photocatalytic properties. J Photochem Photobiol B Biol 184:44–53. https://doi.org/10.1016/j.jphotobiol.2018.04.041

Behravan M, Hossein Panahi A, Naghizadeh A et al (2019) Facile green synthesis of silver nanoparticles using *Berberis vulgaris* leaf and root aqueous extract and its antibacterial activity. Int J Biol Macromol 124:148–154. https://doi.org/10.1016/j.ijbiomac.2018.11.101

Bellido-Milla D, Cubillana-Aguilera LM, El Kaoutit M et al (2013) Recent advances in graphite powder-based electrodes. Anal Bioanal Chem 405:3525–3539. https://doi.org/10.1007/s00216-013-6816-2

Belontz SL, Corcoran PL, Davis H et al (2019) Embracing an interdisciplinary approach to plastics pollution awareness and action. Ambio 48:855–866. https://doi.org/10.1007/s13280-018-1126-8

Benakashani F, Allafchian AR, Jalali SAH (2016) Biosynthesis of silver nanoparticles using *Capparis spinosa* L. leaf extract and their antibacterial activity. Karbala Int J Mod Sci 2:251–258. https://doi.org/10.1016/j.kijoms.2016.08.004

Bergmann M, Tekman M, Gutow L (2017) Marine liter. Sea change for plastin pollution. Nature 544:297. https://doi.org/10.1038/544297b

Bernardo-Boongaling VR, Serrano N, García-Guzmán J et al (2019) Screen-printed electrodes modified with green-synthesized gold nanoparticles for the electrochemical determination of aminothiols. J Electroanal Chem 847:113184. https://doi.org/10.1016/j.jelechem.2019.05.066

Bhardwaj D, Singh A, Singh R (2019) Eco-compatible sonochemical synthesis of 8-aryl-7,8-dihydro-[1,3]-dioxolo[4,5-g]quinolin-6(5H)-ones using green TiO_2. Heliyon 5:e01256. https://doi.org/10.1016/j.heliyon.2019.e01256

Bilal M, Iqbal HMN (2019) Naturally-derived biopolymers: potential platforms for enzyme immobilization. Int J Biol Macromol 130:462–482. https://doi.org/10.1016/j.ijbiomac.2019.02.152

Blanco E, Esquivias L, Litrán R et al (1999) Sonogels and derived materials. Appl Organomet Chem 13:399–418. https://doi.org/10.1002/(SICI)1099-0739(199905)13:5<399::AID-AOC825>3.0.CO;2-A

Boomi P, Ganesan RM, Poorani G et al (2019) Biological synergy of greener gold nanoparticles by using *Coleus aromaticus* leaf extract. Mater Sci Eng C 99:202–210. https://doi.org/10.1016/j.msec.2019.01.105

Boury B, Plumejeau S (2015) Metal oxides and polysaccharides: an efficient hybrid association for materials chemistry. Green Chem 17:72–88. https://doi.org/10.1039/c4gc00957f

Božanić DK, Djoković V, Blanuša J et al (2007) Preparation and properties of nano-sized Ag and Ag_2S particles in biopolymer matrix. Eur Phys J E 22:51–59. https://doi.org/10.1140/epje/e2007-00008-y

Bracamonte MV, Lacconi GI, Urreta SE, Foa Torres LEF (2014) On the nature of defects in liquid-phase exfoliated graphene. J Phys Chem C 118:15455–15459. https://doi.org/10.1021/jp501930a

Büntgen U, Krusic PJ, Piermattei A et al (2019) Limited capacity of tree growth to mitigate the global greenhouse effect under predicted warming. Nat Commun 10:2171. https://doi.org/10.1038/s41467-019-10174-4

Burrs SL, Bhargava M, Sidhu R et al (2016) A paper based graphene-nanocauliflower hybrid composite for point of care biosensing. Biosens Bioelectron 85:479–487. https://doi.org/10.1016/j.bios.2016.05.037

Bystrzanowska M, Pena-Pereira F, Marcinkowski Ł, Tobiszewski M (2019) How green are ionic liquids?—A multicriteria decision analysis approach. Ecotoxicol Environ Saf 174:455–458. https://doi.org/10.1016/j.ecoenv.2019.03.014

Calabria D, Caliceti C, Zangheri M et al (2017) Smartphone–based enzymatic biosensor for oral fluid L-lactate detection in one minute using confined multilayer paper reflectometry. Biosens Bioelectron 94:124–130. https://doi.org/10.1016/j.bios.2017.02.053

Calvo-Flores F, Isac-Garcia J, Dobado JA (2018) Emerging pollutants: origin, structure and properties, 1st edn. Wiley-VCH, Weinheim

Cayuela A, Soriano ML, Carrillo-Carrión C, Valcárcel M (2016) Semiconductor and carbon-based fluorescent nanodots: the need for consistency. Chem Commun 52:1311–1326. https://doi.org/10.1039/c5cc07754k

Chalupa R, Nesměrák K (2018) Analytical chemistry as a tool for suppressing chemophobia: an introduction to the 5E-principle. Monatsh Chem 149:1527–1534. https://doi.org/10.1007/s00706-018-2224-9

Chandran SP, Chaudhary M, Pasricha R et al (2006) Synthesis of gold nanotriangles and silver nanoparticles using Aloe vera plant extract. Biotechnol Prog 22:577–583. https://doi.org/10.1021/bp0501423

Chang WT, Chao YH, Li CW et al (2019) Graphene oxide synthesis using microwave-assisted vs. modified Hummer's methods: efficient fillers for improved ionic conductivity and suppressed methanol permeability in alkaline methanol fuel cell electrolytes. J Power Sources 414:86–95. https://doi.org/10.1016/j.jpowsour.2018.12.020

Chankaew C, Tapala W, Grudpan K, Rujiwatra A (2019) Microwave synthesis of ZnO nanoparticles using longan seeds biowaste and their efficiencies in photocatalytic decolorization of organic dyes. Environ Sci Pollut Res. 26:17548–17554. https://doi.org/10.1007/s11356-019-05099-w

Charde MS, Shukla A, Bukhariya V, Chakole RD (2012) A review on: a significance of microwave assist technique in green chemistry. Int J Phytopharm 2:39–50. https://doi.org/10.7439/ijpp.v2i2.441

Chatel G (2016) Sonochemistry: new opportunities for green chemistry. World Scientific Publishing Europe Ltd, London

Chatel G (2018) How sonochemistry contributes to green chemistry? Ultrason Sonochem 40:117–122. https://doi.org/10.1016/j.ultsonch.2017.03.029

Chen GQ, Jiang XR (2018) Engineering microorganisms for improving polyhydroxyalkanoate biosynthesis. Curr Opin Biotechnol 53:20–25. https://doi.org/10.1016/j.copbio.2017.10.008

Chen TH, Tseng WL (2017) Self-assembly of monodisperse carbon dots into high-brightness nanoaggregates for cellular uptake imaging and iron(III) sensing. Anal Chem 89:11348–11356. https://doi.org/10.1021/acs.analchem.7b02193

Chen X, Zhu J, Tian R, Yao C (2012) Bienzymatic glucose biosensor based on three dimensional macroporous ionic liquid doped sol-gel organic-inorganic composite. Sensors Actuators B Chem 163:272–280. https://doi.org/10.1016/j.snb.2012.01.053

Chen K, Dong Noh Y, Li K et al (2013) Microwave-hydrothermal crystallization of polymorphic MnO_2 for electrochemical energy storage. J Phys Chem C 117:10770–10779. https://doi.org/10.1021/jp4018025

Chen GX, Zhou JW, Liu YL et al (2016) Biosynthesis and regulation of wheat amylose and amylopectin from proteomic and phosphoproteomic characterization of granule-binding proteins. Sci Rep 6:33111. https://doi.org/10.1038/srep33111

Chen BB, Liu ML, Zhan L et al (2018) Terbium(III) modified fluorescent carbon dots for highly selective and sensitive ratiometry of stringent. Anal Chem 90:4003–4009. https://doi.org/10.1021/acs.analchem.7b05149

Cherry KE, Sampson L, Galea S et al (2018) Spirituality, humor, and resilience after natural and technological disasters. J Nurs Scholarsh 50:492–501. https://doi.org/10.1111/jnu.12400

Cho HU, Park JM (2018) Biodiesel production by various oleaginous microorganisms from organic wastes. Bioresour Technol 256:502–508. https://doi.org/10.1016/j.biortech.2018.02.010

Christian P, Von Der Kammer F, Baalousha M, Hofmann T (2008) Nanoparticles: structure, properties, preparation and behaviour in environmental media. Ecotoxicology 17:326–343. https://doi.org/10.1007/s10646-008-0213-1

Chua CK, Pumera M (2014) Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. Chem Soc Rev 43:291–312. https://doi.org/10.1039/c3cs60303b

Chunfa D, Xianglin Z, Hao C, Chuanliang C (2016) Sodium alginate mediated route for the synthesis of monodisperse silver nanoparticles using glucose as reducing agents. Rare Met Mater Eng 45:261–266. https://doi.org/10.1016/s1875-5372(16)30051-0

Cifric S, Nuhic J, Osmanovic D, Kisija E (2020) Review of electrochemical biosensors for hormone detection. In: Badnjevic A, Škrbić R, GurbetaPokvić L (eds) CMBEBIH 2019, IFMBE proceedings, vol 73. Springer, Cham, pp 173–177

Clark JH (2005) Green chemistry and environmentally friendly technologies. In: Afonso CAM, Crespo JG (eds) Green separation processes: fundamentals and applications. Wiley-VCH Verlag GmbH & Co. KGaA, Wienheim, pp 3–18

Cordero-Rando MM, Hidalgo-Hidalgo de Cisneros JL, Blanco E, Naranjo-Rodriguez I (2002) The sonogel-carbon electrode as a sol-gel graphite-based electrode. Anal Chem 74:2423–2427. https://doi.org/10.1021/ac010782u

Cosbey A (2013) Green industrial policy and the world trading system. SSRN Electron J 17:12. https://doi.org/10.2139/ssrn.2344558

Cravotto G, Boffa L (2014) Combined ultrasound-microwave irradiation for the preparation of nanomaterials. Standford Publishing, Redwood City

Cravotto G, Cintas P (2006) Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications. Chem Soc Rev 35:180–196. https://doi.org/10.1039/b503848k

Cravotto G, Rinaldi L, Carnaroglio D (2015) Efficient catalysis by combining microwaves with other enabling technologies. In: Horikoshi S, Serpone N (eds) Microwaves in catalysis. pp 155–170. Wiley-VCH, Weinheim

Cubillana-Aguilera LM, Palacios-Santander JM, Naranjo-Rodriguez I, Hidalgo-Hidalgo-De-Cisneros JL (2006) Study of the influence of the graphite powder particle size on the structure of the sonogel-carbon materials. J Sol-Gel Sci Technol 40:55–64. https://doi.org/10.1007/s10971-006-9151-7

Cubillana-Aguilera LM, Palacios-Santander JM, Estevez-Hernandez OL et al (2010) 1-Furoylthiourea-sonogel-carbon electrodes: structural and electrochemical characterization. Talanta 82:129–136. https://doi.org/10.1016/j.talanta.2010.04.005

Cubillana-Aguilera LM, Franco-Romano M, Gil MLA et al (2011) New, fast and green procedure for the synthesis of gold nanoparticles based on sonocatalysis. Ultrason Sonochem 18:789–794. https://doi.org/10.1016/j.ultsonch.2010.10.009

Cunha-Silva H, Arcos-Martinez MJ (2018) Dual range lactate oxidase-based screen printed amperometric biosensor for analysis of lactate in diversified samples. Talanta 188:779–787. https://doi.org/10.1016/j.talanta.2018.06.054

Da Silveira Pinto LS, De Souza MVN (2017) Sonochemistry as a general procedure for the synthesis of coumarins, including multigram synthesis. Synthesis 49:2677–2682. https://doi.org/10.1055/s-0036-1590201

Dahoumane SA, Mechouet M, Wijesekera K et al (2017) Algae-mediated biosynthesis of inorganic nanomaterials as a promising route in nanobiotechnology—a review. Green Chem 19:552. https://doi.org/10.1039/c6gc02346k

Dandan H, Quinfu L, Hongfei C, Kuo L (2017) Graphene synthesis via chemical reduction of graphene oxide using lemon extract. J Nanosci Nanotechnol 17:6518–6523

Darvishi M, Mohseni-Asgerani G, Seyed-Yazdi J (2017) Simple microwave irradiation procedure for the synthesis of CuO/graphene hybrid composite with significant photocatalytic enhancement. Surf Interfaces 7:69–73. https://doi.org/10.1016/j.surfin.2017.02.007

Darvishi S, Souissi M, Kharaziha M et al (2018) Gelatin methacryloyl hydrogel for glucose biosensing using Ni nanoparticles-reduced graphene oxide: an experimental and modeling study. Electrochim Acta 261:275–283. https://doi.org/10.1016/j.electacta.2017.12.126

Das R, Bandyopadhyay R, Pramanik P (2018) Carbon quantum dots from natural resource: a review. Mater Today Chem 8:96–109. https://doi.org/10.1016/j.mtchem.2018.03.003

De la Guardia M, Garrigues S (eds) (2012) Handbook of green analytical chemistry, 1st edn. Wiley, Chichester

De Salas F, Pardo I, Salavagione HJ et al (2016) Advanced synthesis of conductive polyaniline using laccase as biocatalyst. PLoS One 11:e0164958. https://doi.org/10.1371/journal.pone.0164958

De Silva KKH, Huang HH, Joshi RK, Yoshimura M (2017) Chemical reduction of graphene oxide using green reductants. Carbon N Y 119:190–199. https://doi.org/10.1016/j.carbon.2017.04.025

De Silva KKH, Huang H, Yoshimura M (2018) Progress of reduction of graphene oxide by ascorbic acid. Appl Surf Sci 447:338–346. https://doi.org/10.1016/j.apsusc.2018.03.243

De Xie J, Lai GW, Huq MM (2007) Hydrothermal route to graphene quantum dots: effects of precursor and temperature. Diam Relat Mater 79:112–118. https://doi.org/10.1016/j.diamond.2017.08.014

Debalina B, Reddy RB, Vinu R (2017) Production of carbon nanostructures in biochar, bio-oil and gases from bagasse via microwave assisted pyrolysis using Fe and co as susceptors. J Anal Appl Pyrolysis 124:310–318. https://doi.org/10.1016/j.jaap.2017.01.018

Devi R, Yadav S, Pundir CS (2012) Amperometric determination of xanthine in fish meat by zinc oxide nanoparticle/chitosan/multiwalled carbon nanotube/polyaniline composite film bound xanthine oxidase. Analyst 137:754–759. https://doi.org/10.1039/c1an15838d

Dhanani T, Shah S, Gajbhiye NA, Kumar S (2017) Effect of extraction methods on yield, phytochemical constituents and antioxidant activity of *Withania somnifera*. Arab J Chem 10:S1193–S1199. https://doi.org/10.1016/j.arabjc.2013.02.015

Dhyani V, Bhaskar T (2018) A comprehensive review on the pyrolysis of lignocellulosic biomass. Renew Energy 129:695–716. https://doi.org/10.1016/j.renene.2017.04.035

Di Tocco A, Robledo SN, Osuna Y et al (2018) Development of an electrochemical biosensor for the determination of triglycerides in serum samples based on a lipase/magnetite-chitosan/copper oxide nanoparticles/multiwalled carbon nanotubes/pectin composite. Talanta 190:30–37. https://doi.org/10.1016/j.talanta.2018.07.028

Dickens MJ, Luche JL (1991) Further evidence for the effect of ultrasonic waves on electron transfer processes—the case of the Kornblum-Russell reaction. Tetrahedron Lett 32:4709–4712. https://doi.org/10.1016/S0040-4039(00)92288-3

Ding JH, Zhao HR, Bin YH (2018) A water-based green approach to large-scale production of aqueous compatible graphene nanoplatelets. Sci Rep 8:5567–5572. https://doi.org/10.1038/s41598-018-23859-5

Dinh NX, Van Quy N, Huy TQ, Le A-T (2015) Decoration of silver nanoparticles on multiwalled carbon nanotubes: antibacterial mechanism and ultrastructural analysis. J Nanomater. https://doi.org/10.1155/2015/814379

Dong LL, Ding YC, Huo WT et al (2019) A green and facile synthesis for rGO/Ag nanocomposites using one-step chemical co-reduction route at ambient temperature and combined first principles theoretical analyze. Ultrason Sonochem 53:152–163. https://doi.org/10.1016/j.ultsonch.2019.01.002

Du W, Jiang X, Zhu L (2013) From graphite to graphene: direct liquid-phase exfoliation of graphite to produce single- and few-layered pristine graphene. J Mater Chem A 1:10592–10606. https://doi.org/10.1039/c3ta12212c

Du F, Zhu L, Dai L (2017) Carbon nanotube-based electrochemical biosensors. Biosens Nanomater Nanodev 3:59. https://doi.org/10.1201/b16234

Durge R, Kshirsagar RV, Tambe P (2014) Effect of sonication energy on the yield of graphene nanosheets by liquid-phase exfoliation of graphite. Procedia Eng 97:1457–1465. https://doi.org/10.1016/j.proeng.2014.12.429

El Bouhouti H, Naranjo-Rodríguez I, Hidalgo-Hidalgo de Cisneros JL et al (2009) Electrochemical behaviour of epinephrine and uric acid at a sonogel-carbon l-cysteine modified electrode. Talanta 79:22–26. https://doi.org/10.1016/j.talanta.2009.02.057

El-Naggar ME, Shaheen TI, Fouda MMG, Hebeish AA (2016) Eco-friendly microwave-assisted green and rapid synthesis of well-stabilized gold and core-shell silver-gold nanoparticles. Carbohydr Polym 136:1128–1136. https://doi.org/10.1016/j.carbpol.2015.10.003

Elsupikhe RF, Shameli K, Ahmad MB et al (2015) Green sonochemical synthesis of silver nanoparticles at varying concentrations of κ-carrageenan. Nanoscale Res Lett 10:302–309. https://doi.org/10.1186/s11671-015-0916-1

ENDS (2003) REACH caught up in EU's competitiveness agenda

ENDS (2004) Retailers voice support for REACH chemicals reform

Eriksen M, Lebreton LCM, Carson HS et al (2014) Plastic pollution in the World's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS One 9:e111913. https://doi.org/10.1371/journal.pone.0111913

Eshghi M, Vaghari H, Najian Y, Najian MJ (2018) Microwave-assisted green synthesis of silver nanoparticles using *Juglans regia* leaf extract and evaluation of their physico-chemical and antibacterial properties. Antibiotics 7:68. https://doi.org/10.3390/antibiotics7030068

European Comission (2001). White paper: "Strategy for a future chemicals policy". COM 88. Available at https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52001DC0088&from=EN

Fang L, Yuan W, Wang B, Xiong Y (2016) Growth of graphene on Cu foils by microwave plasma chemical vapor deposition: the effect of in-situ hydrogen plasma post-treatment. Appl Surf Sci 383:28–32. https://doi.org/10.1016/j.apsusc.2016.04.148

Fathy NA (2017) Carbon nanotubes synthesis using carbonization of pretreated rice straw through chemical vapor deposition of camphor. RSC Adv 7:28535–28541. https://doi.org/10.1039/c7ra04882c

Feng H, Li Y, Lin S et al (2014) Nano Cu-catalyzed efficient and selective reduction of nitroarenes under combined microwave and ultrasound irradiation. Sustain Chem Process 2:14. https://doi.org/10.1186/2043-7129-2-14

Feng LL, Wu YX, Zhang DL et al (2017) Near infrared graphene quantum dots-based two-photon nanoprobe for direct bioimaging of endogenous ascorbic acid in living cells. Anal Chem 89:4077–4084. https://doi.org/10.1021/acs.analchem.6b04943

Feng J, Pang B, Chen Y et al (2018) Investigation on tunable optical properties and structures of graphene quantum dots doped with sulfur-containing groups. ECS J Solid State Sci Technol 7:M180–M185. https://doi.org/10.1149/2.0171811jss

Fortineau A-D (2004) Chemistry perfumes in your daily life. J Chem Educ 81:45–50. https://doi.org/10.1021/ed081p45

Francis S, Joseph S, Koshy EP, B. M (2018) Microwave assisted green synthesis of silver nanoparticles using leaf extract of elephantopus scaber and its environmental and biological applications. Artif Cells Nanomed Biotechnol 46:795–804. doi: https://doi.org/10.1080/21691401.2017.1345921

Franco-Romano M, Cubillana-Aguilera L, Gil-Montero M, Palacios-Santander JM, Naranjo-Rodríguez I, Hidalgo-Hidalgo-de-Cisneros J (2013) Method for producing materials by means of sonogel technology catalysed by plant extracts and material produced thereby, p 13. Patent number WO2015018951. University of Cadiz (Spain)

Franco-Romano M, Gil MLA, Palacios-Santander JM et al (2014) Sonosynthesis of gold nanoparticles from a geranium leaf extract. Ultrason Sonochem 21:1570–1577. https://doi.org/10.1016/j.ultsonch.2014.01.017

Fresco-Cala B, Soriano ML, Sciortino A et al (2018) One-pot synthesis of graphene quantum dots and simultaneous nanostructured self-assembly via a novel microwave-assisted method: impact on triazine removal and efficiency monitoring. RSC Adv 8:29939–29946. https://doi.org/10.1039/c8ra04286a

Fujita N (2014) Starch biosynthesis in rice endosperm. AGri-Biosci Monogr 4:1–18. https://doi.org/10.5047/agbm.2014.00401.0001

Gaba M, Dhingra N (2011) Microwave chemistry: general features and applications. Indian J Pharm Educ Res 45:175–183

Gabriel C, Gabriel S, Grant EH et al (1998) Dielectric parameters relevant to microwave dielectric heating. Chem Soc Rev 27:213. https://doi.org/10.1039/a827213z

Gahlawat G, Choudhury AR (2019) A review on the biosynthesis of metal and metal salt nanoparticles by microbes. RSC Adv 9:12944–12967. https://doi.org/10.1039/c8ra10483b

Gaikwad S, Han S (2019) A microwave method for the rapid crystallization of UTSA-16 with improved performance for CO_2 capture. Chem Eng J 371:813–820. https://doi.org/10.1016/j.cej.2019.04.112

Gałuszka A, Migaszewski Z, Namieśnik J (2013) The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. TrAC Trends Anal Chem 50:78–84. https://doi.org/10.1016/j.trac.2013.04.010

Gan N, Yang X, Xie D et al (2010) A disposable organophosphorus pesticides enzyme biosensor based on magnetic composite nano-particles modified screen printed carbon electrode. Sensors 10:625–638. https://doi.org/10.3390/s100100625

Garadkar KM, Ghule LA, Sapnar KB, Dhole SD (2013) A facile synthesis of $ZnWO_4$ nanoparticles by microwave assisted technique and its application in photocatalysis. Mater Res Bull 48:1105–1109. https://doi.org/10.1016/j.materresbull.2012.12.002

García-Guzmán JJ, López-Iglesias D, Cubillana-Aguilera L et al (2018) Assessment of the polyphenol indices and antioxidant capacity for beers and wines using a tyrosinase-based biosensor prepared by sinusoidal current method. Sensors (Basel) 19:66. https://doi.org/10.3390/s19010066

García-Guzmán J, López-Iglesias D, Marin M et al (2019) Electrochemical biosensors for antioxidants. In: Inamuddin D, Khan R, Mohammad A, Asiri A (eds) Advanced biosensors for health care applications, 1st edn. Elsevier, Amsterdam, pp 105–146

Gautam V, Singh KP, Yadav VL (2018) Polyaniline/MWCNTs/starch modified carbon paste electrode for non-enzymatic detection of cholesterol: application to real sample (cow milk). Anal Bioanal Chem 410:2173–2181. https://doi.org/10.1007/s00216-018-0880-6

Gavrilescu M, Demnerová K, Aamand J et al (2015) Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. New Biotechnol 32:147–156. https://doi.org/10.1016/j.nbt.2014.01.001

German N, Ramanaviciene A, Ramanavicius A (2019) Formation of polyaniline and polypyrrole nanocomposites with embedded glucose oxidase and gold nanoparticles. Polymers (Basel) 9:806. https://doi.org/10.3390/polym11020377

Ghule LA, Shirke BS, Sapnar KB et al (2011) Preparation of zinc oxide nanorods by microwave assisted technique using ethylene glycol as a stabilizing agent. J Mater Sci Mater Electron 22:1120–1123. https://doi.org/10.1007/s10854-010-0270-0

Gizdavic-Nikolaidis MR, Stanisavljev DR, Easteal AJ, Zujovic ZD (2010) A rapid and facile synthesis of nanofibrillar polyaniline using microwave radiation. Macromol Rapid Commun 31:657–661. https://doi.org/10.1002/marc.200900800

Godoy AP, Ecorchard P, Beneš H et al (2019) Ultrasound exfoliation of graphite in biphasic liquid systems containing ionic liquids: a study on the conditions for obtaining large few-layers graphene. Ultrason Sonochem 55:279–288. https://doi.org/10.1016/j.ultsonch.2019.01.016

Golinska P, Rathod D, Wypij M et al (2017) Mycoendophytes as efficient synthesizers of bionanoparticles: nanoantimicrobials, mechanism, and cytotoxicity. Crit Rev Biotechnol 37:765–778. https://doi.org/10.1080/07388551.2016.1235011

González-Álvarez RJ, Naranjo-Rodríguez I, Hernández-Artiga MP et al (2016) Experimental design applied to optimisation of silica nanoparticles size obtained by sonosynthesis. J Sol-Gel Sci Technol 80:378–388. https://doi.org/10.1007/s10971-016-4129-6

Gopalan AI, Lee KP, Ragupathy D (2009) Development of a stable cholesterol biosensor based on multi-walled carbon nanotubes-gold nanoparticles composite covered with a layer of chitosan-room-temperature ionic liquid network. Biosens Bioelectron 24:2211–2217. https://doi.org/10.1016/j.bios.2008.11.034

Gribble GW (2013) Food chemistry and chemophobia. Food Secur 5:177–187. https://doi.org/10.1007/s12571-013-0251-2

Grunwald P (2012) Metabolic pathway engineering. Biocatalysis 3:830–856. https://doi.org/10.1142/9781848162310_0013

Gu H, Chen X, Chen F et al (2018) Ultrasound-assisted biosynthesis of CuO-NPs using brown alga *Cystoseira trinodis*: characterization, photocatalytic AOP, DPPH scavenging and antibacterial investigations. Ultrason Sonochem 41:109–119. https://doi.org/10.1016/j.ultsonch.2017.09.006

Gudikandula K, Vadapally P, Singara Charya MA (2017) Biogenic synthesis of silver nanoparticles from white rot fungi: their characterization and antibacterial studies. OpenNano 2:64–78. https://doi.org/10.1016/j.onano.2017.07.002

Guex LG, Sacchi B, Peuvot KF et al (2017) Experimental review: chemical reduction of graphene oxide (GO) to reduced graphene oxide (rGO) by aqueous chemistry. Nanoscale 9:9562–9571. https://doi.org/10.1039/c7nr02943h

Guibal E, Vincent T, Navarro R (2014) Metal ion biosorption on chitosan for the synthesis of advanced materials. J Mater Sci 49:5505–5518. https://doi.org/10.1007/s10853-014-8301-5

Hafeez HY, Lakhera SK, Ashokkumar M, Neppolian B (2019) Ultrasound assisted synthesis of reduced graphene oxide (rGO) supported $InVO_4$-TiO_2 nanocomposite for efficient hydrogen production. Ultrason Sonochem 53:1–10. https://doi.org/10.1016/j.ultsonch.2018.12.009

Hai X, Mao QX, Wang WJ et al (2015) An acid-free microwave approach to prepare highly luminescent boron-doped graphene quantum dots for cell imaging. J Mater Chem B 3:9109–9114. https://doi.org/10.1039/c5tb01954k

Hassan HMA, Abdelsayed V, Khder AERS et al (2009) Microwave synthesis of graphene sheets supporting metal nanocrystals in aqueous and organic media. J Mater Chem 19:3832–3837. https://doi.org/10.1039/b906253j

Hassanien R, Husein DZ, Al-Hakkani MF (2018) Biosynthesis of copper nanoparticles using aqueous Tilia extract: antimicrobial and anticancer activities. Heliyon 4:e01077. https://doi.org/10.1016/j.heliyon.2018.e01077

Hay ID, Rehman ZU, Moradali MF et al (2013) Microbial alginate production, modification and its applications. Microb Biotechnol 6:637–650. https://doi.org/10.1111/1751-7915.12076

He M, Zhang J, Wang H et al (2018) Material and optical properties of fluorescent carbon quantum dots fabricated from lemon juice via hydrothermal reaction. Nanoscale Res Lett 13:175. https://doi.org/10.1186/s11671-018-2581-7

Henam SD, Ahmad F, Shah MA et al (2019) Microwave synthesis of nanoparticles and their antifungal activities. Spectrochim Acta A Mol Biomol Spectrosc 213:337–341. https://doi.org/10.1016/j.saa.2019.01.071

Hernandez Y, Nicolosi V, Lotya M et al (2008) High-yield production of graphene by liquid-phase exfoliation of graphite. Nat Nanotechnol 3:563–568. https://doi.org/10.1038/nnano.2008.215

Hernández N, Williams RC, Cochran EW (2014) The battle for the "green" polymer. Different approaches for biopolymer synthesis: bioadvantaged vs. bioreplacement. Org Biomol Chem 12:2834–2849. https://doi.org/10.1039/c3ob42339e

Hidalgo-Hidalgo de Cisneros J, Cordero-Rando M, Naranjo Rodríguez I, et al (2003) Materiales compuestos sonogel-carbono y sonogel-carbono modificados, un procedimiento para su preparación y su aplicación a la fabricación de electrodos y sensores amperométricos, p 7. Patent number ES2195715. University of Cadiz (Spain)

Hidalgo-Hidalgo-de-Cisneros JL, Cordero-Rando M., Naranjo Rodríguez I, et al. (2001) Materiales compuestos sonogel-carbono y sonogel-carbono modificados, un procedimiento para su preparación y su aplicación a la fabricación de electrodos y sensores amperométricos

Hou X, Li Y, Zhao C (2016) Microwave-assisted synthesis of nitrogen-doped multi-layer graphene quantum dots with oxygen-rich functional groups. Aust J Chem 69:357–360. https://doi.org/10.1071/CH15431

Hou D, Liu Q, Wang X et al (2018) Facile synthesis of graphene via reduction of graphene oxide by artemisinin in ethanol. J Mater 4:256–265. https://doi.org/10.1016/j.jmat.2018.01.002

Hu H, Zhao Z, Zhou Q et al (2012a) The role of microwave absorption on formation of graphene from graphite oxide. Carbon N Y 50:3267–3273. https://doi.org/10.1016/j.carbon.2011.12.005

Hu Y, Zou Y, Wu H, Shi D (2012b) A facile and efficient ultrasound-assisted synthesis of novel dispiroheterocycles through 1,3-dipolar cycloaddition reactions. Ultrason Sonochem 19:264–269. https://doi.org/10.1016/j.ultsonch.2011.07.006

Huang H, Liang C, Sha H et al (2019) Microwave assisted hydrothermal way towards highly crystalized N-doped carbon quantum dots and their oxygen reduction performance. Chem Res Chinese Univ 35:171–178. https://doi.org/10.1007/s40242-019-8343-y

Husin MR, Arsad A, Hassan A, Hassan O (2014) Influence of different ultrasonic wave on polymerization of polyaniline nanofiber. Appl Mech Mater 618:50–54. https://doi.org/10.4028/www.scientific.net/amm.618.50

Iskandar F, Hikmah U, Stavila E, Aimon AH (2017) Microwave-assisted reduction method under nitrogen atmosphere for synthesis and electrical conductivity improvement of reduced graphene oxide (rGO). RSC Adv 7:52391–52397. https://doi.org/10.1039/c7ra10013b

Ismail Z, Kassim NFA, Abdullah AH et al (2017) Black tea assisted exfoliation using a kitchen mixer allowing one-step production of graphene. Mater Res Express 4:1–11. https://doi.org/10.1088/2053-1591/aa7ae2

Izaoumen N, Cubillana-Aguilera LM, Naranjo-Rodríguez I et al (2009) β-Sonogel-carbon electrodes: a new alternative for the electrochemical determination of catecholamines. Talanta 78:370–376. https://doi.org/10.1016/j.talanta.2008.11.027

Jacob MV, Rawat RS, Ouyang B et al (2015) Catalyst-free plasma enhanced growth of graphene from sustainable sources. Nano Lett 15:5702–5708. https://doi.org/10.1021/acs.nanolett.5b01363

Jahan I, Erci F, Isildak I (2019) Microwave-assisted green synthesis of non-cytotoxic silver nanoparticles using the aqueous extract of Rosa santana (rose) petals and their antimicrobial activity. Anal Lett 52:1860–1873. https://doi.org/10.1080/00032719.2019.1572179

Jain S, Mehata MS (2017) Medicinal plant leaf extract and pure flavonoid mediated green synthesis of silver nanoparticles and their enhanced antibacterial property. Sci Rep 7:1–13. https://doi.org/10.1038/s41598-017-15724-8

Jana M, Saha S, Khanra P et al (2014) Bio-reduction of graphene oxide using drained water from soaked mung beans (*Phaseolus aureus* L.) and its application as energy storage electrode material. Mater Sci Eng B Solid-State Mater Adv Technol 186:33–40. https://doi.org/10.1016/j.mseb.2014.03.004

Janus Ł, Piątkowski M, Radwan-Pragłowska J et al (2019) Chitosan-based carbon quantum dots for biomedical applications: synthesis and characterization. Nano 9:274. https://doi.org/10.3390/nano9020274

Jiang L, Yu X, Qi X et al (2013) Multigene engineering of starch biosynthesis in maize endosperm increases the total starch content and the proportion of amylose. Transgenic Res 22:1133–1142. https://doi.org/10.1007/s11248-013-9717-4

Kachoosangi RT, Musameh MM, Abu-Yousef I et al (2009) Carbon nanotube-ionic liquid composite sensors and biosensors. Anal Chem 81:435–442. https://doi.org/10.1021/ac801853r

Kajihara K (2013) Recent advances in sol-gel synthesis of monolithic silica and silica-based glasses. J Asian Ceramic Soc 1:121–133. https://doi.org/10.1016/j.jascer.2013.04.002

Kalaiselvi A, Roopan SM, Madhumitha G et al (2015) Synthesis and characterization of palladium nanoparticles using *Catharanthus roseus* leaf extract and its application in the photocatalytic degradation. Spectrochim Acta Part A Mol Biomol Spectrosc 135:116–119. https://doi.org/10.1016/j.saa.2014.07.010

Kalaivani R, Maruthupandy M, Muneeswaran T et al (2018) Synthesis of chitosan mediated silver nanoparticles (Ag NPs) for potential antimicrobial applications. Front Lab Med 2:30–35. https://doi.org/10.1016/j.flm.2018.04.002

Kandasamy G (2019) Recent advancements in doped/Co-doped carbon quantum dots for multipotential applications. C 5:24

Kano M, Fujiwara K (2013) Virtual sensing technology in process industries: trends and challenges revealed by recent industrial applications. J Chem Eng Japan 46:1–17. https://doi.org/10.1252/jcej.12we167

Kauffman GB (1991) Chemophobia. Chem Br 27:512–516

Kaur M, Kaur M, Sharma VK (2018) Nitrogen-doped graphene and graphene quantum dots: a review onsynthesis and applications in energy, sensors and environment. Adv Colloid Interf Sci 259:44–64. https://doi.org/10.1016/j.cis.2018.07.001

Kenry K, Liu B (2018) Recent advances in biodegradable conducting polymers and their biomedical applications. Biomacromolecules 19:1783–1803. https://doi.org/10.1021/acs.biomac.8b00275

Khan U, O'Neill A, Porwal H et al (2012) Size selection of dispersed, exfoliated graphene flakes by controlled centrifugation. Carbon N Y 50:470–475. https://doi.org/10.1016/j.carbon.2011.09.001

Kharisov BI, Kharissova OV, Ortiz Méndez U, De La Fuente IG (2016) Decoration of carbon nanotubes with metal nanoparticles: recent trends. Synth React Inorg Met Nano-Metal Chem 46:55–76. https://doi.org/10.1080/15533174.2014.900635

Khomand E, Afsharpour M (2019) Green synthesis of nanostructured SiCs by using natural biopolymers (guar, tragacanth, Arabic, and xanthan gums) for oxidative desulfurization of model fuel. Int J Environ Sci Technol 16:2359–2372. https://doi.org/10.1007/s13762-018-1678-y

Kim Y-R, Bong S, Kang Y-J et al (2010) Electrochemical detection of dopamine in the presence of ascorbic acid using graphene modified electrodes. Biosens Bioelectron 25:2366–2369. https://doi.org/10.1016/j.talanta.2012.05.013

Kimling MC, Caruso RA (2012) Sol-gel synthesis of hierarchically porous TiO_2 beads using calcium alginate beads as sacrificial templates. J Mater Chem 22:4073–4082. https://doi.org/10.1039/c2jm15720a

Koel M, Kaljurand M (2019) Green analytical chemistry, 2nd edn. Royal Society of Chemistry, London

Kogawa AC, Salgado HRN (2015) Comparative study over methods developed for quantification of darunavir in tablets by environmental friendly infrared and capillary electrophoretic techniques. J Int Res Med Pharm Sci 2:99–105

Kong FY, Chen TT, Wang JY et al (2016) UV-assisted synthesis of tetrapods-like titanium nitride-reduced graphene oxide nanohybrids for electrochemical determination of chloramphenicol. Sensors Actuators B Chem 225:298–304. https://doi.org/10.1016/j.snb.2015.11.041

Kotanen CR, Karunwi O, Alam F et al (2018) Fabrication and in vitro performance of a dual responsive lactate and glucose biosensor. Electrochim Acta 267:71–79. https://doi.org/10.1016/j.electacta.2018.02.042

Kumar C (ed) (2007) Nanomaterials for biosensors, 1st edn. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Kumar RR, Prasad S (2011) Metabolic engineering of bacteria. Indian J Microbiol 51:403–409. https://doi.org/10.1007/s12088-011-0172-8

Kumar R, Tiwari RS, Srivastava ON (2011) Scalable synthesis of aligned carbon nanotubes bundles using green natural precursor: neem oil. Nanoscale Res Lett 6:92. https://doi.org/10.1186/1556-276X-6-92

Kumar V, Singh K, Panwar S, Mehta SK (2017) Green synthesis of manganese oxide nanoparticles for the electrochemical sensing of p-nitrophenol. Int Nano Lett 7:123–131. doi: https://doi.org/10.1007/s40089-017-0205-3

Kumar A, Kostikov Y, Orberger B et al (2018) Natural laterite as a catalyst source for the growth of carbon nanotubes and nanospheres. ACS Appl Nano Mater 1:6046–6054. https://doi.org/10.1021/acsanm.8b01117

Kumar I, Mondal M, Meyappan V, Sakthivel N (2019) Green one-pot synthesis of gold nanoparticles using *Sansevieria roxburghiana* leaf extract for the catalytic degradation of toxic organic pollutants. Mater Res Bull 117:18–27. https://doi.org/10.1016/j.materresbull.2019.04.029

Kuttippurath J, Kumar P, Nair PJ, Pandey PC (2018) Emergence of ozone recovery evidenced by reduction in the occurrence of Antarctic ozone loss saturation. Clim Atmos Sci 1:42. https://doi.org/10.1038/s41612-018-0052-6

Lahcen AA, García-Guzmán JJ, Palacios-Santander JM et al (2019) Fast route for the synthesis of decorated nanostructured magnetic molecularly imprinted polymers using an ultrasound probe. Ultrason Sonochem 53:226–236. https://doi.org/10.1016/j.ultsonch.2019.01.008

Lancaster M (2002) Principles of sustainable and green chemistry. In: Clark JH, Macquarrie D (eds) Handbook of green chemistry and technology. Blackwell Science Ltd, London, pp 10–27

Lavin-Lopez MP, Paton-Carrero A, Sanchez-Silva L et al (2017) Influence of the reduction strategy in the synthesis of reduced graphene oxide. Adv Powder Technol 28:3195–3203. https://doi.org/10.1016/j.apt.2017.09.032

Lee SY, Krishnamurthy S, Cho CW, Yun YS (2016) Biosynthesis of gold nanoparticles using *Ocimum sanctum* extracts by solvents with different polarity. ACS Sustain Chem Eng 4:2651–2659. https://doi.org/10.1021/acssuschemeng.6b00161

Leicht A, Heiss J, Wong JB (2018) Issues and trends in education for sustainable development. UNESCO Publishing, Paris

Leong T, Ashokkumar M, Sandra K (2011) The fundamentals of power ultrasound—a review. Acoust Aust. 39:54–63

Li YL, Kinloch IA, Shaffer MSP et al (2004) Synthesis of single-walled carbon nanotubes by a fluidized-bed method. Chem Phys Lett 384:98–102. https://doi.org/10.1016/j.cplett.2003.11.070

Li X, Cai W, An J et al (2009) Large-area synthesis of high-quality and uniform graphene films on copper foils. Science 324:1312–1314. https://doi.org/10.1126/science.1171245

Li M, Liu D, Wei D et al (2016) Controllable synthesis of graphene by plasma-enhanced chemical vapor deposition and its related applications. Adv Sci 3:1600003. https://doi.org/10.1002/advs.201600003

Li B, Yu A, Lai G (2018) Self-assembly of phenoxyl-dextran on electrochemically reduced graphene oxide for nonenzymatic biosensing of glucose. Carbon N Y 127:202–208. https://doi.org/10.1016/j.carbon.2017.10.096

Li S, Li G, Chen Q, Wang F (2019) Facile green synthesis of degraded-PVA coated TiO_2 nanoparticles with enhanced photocatalytic activity under visible light. J Phys Chem Solids 129:92–98. https://doi.org/10.1016/j.jpcs.2019.01.002

Liang T, Qian J, Yuan Y, Liu C (2013) Synthesis of mesoporous hydroxyapatite nanoparticles using a template-free sonochemistry-assisted microwave method. J Mater Sci 48:5334–5341. https://doi.org/10.1007/s10853-013-7328-3

Lidström P, Tierney J, Wathey B, Westman J (2001) Microwave-assisted green organic synthesis. Tetrahedron 57:9225–9283. https://doi.org/10.1039/9781782623632-00001

Liu P, Wang R (2019) Public attitudes toward technological hazards after a technological disaster. Disaster Prev Manag 28:216–227. https://doi.org/10.1108/dpm-08-2018-0244

Liu Y, Wang M, Li J et al (2005) Highly active horseradish peroxidase immobilized in 1-butyl-3-methylimidazolium tetrafluoroborate room-temperature ionic liquid based sol-gel host materials. Chem Commun:1778–1780. https://doi.org/10.1039/b417680d

Liu YQ, Zhang M, Wang FX, Pan GB (2012) Facile microwave-assisted synthesis of uniform single-crystal copper nanowires with excellent electrical conductivity. RSC Adv 2:11235–11237. https://doi.org/10.1039/c2ra21578k

Liu X, Nan Z, Qiu Y et al (2013) Hydrophobic ionic liquid immoblizing cholesterol oxidase on the electrodeposited Prussian blue on glassy carbon electrode for detection of cholesterol. Electrochim Acta 90:203–209. https://doi.org/10.1016/j.electacta.2012.11.119

Lodeiro C, Capelo-Martínez J-L (2009) Beyond analytical chemistry. In: Capelo-Martínez J-L (ed) Ultrasound in chemistry: analytical applications. Weinheim, Wiley-VCH Verlag GmbH, pp 129–149

López-Iglesias D, García-Romero M, Cubillana-Aguilera LM, et al (2016) Materiales compuestos sonogel-carbono-polímeros conductores y sus variantes: procedimiento de fabricación y su aplicación en la constitución de (bio) sensores electroquímicos, p 41. Patent number ES2670985. University of Cadiz (Spain)

López-Iglesias D, García-Guzmán JJ, Bellido-Milla D et al (2018) The Sonogel-carbon-PEDOT material: an innovative bulk material for sensor devices. J Electrochem Soc 165:B906–B915. https://doi.org/10.1149/2.1021816jes

Lu X, Zhang J, Xie YN et al (2018) Ratiometric phosphorescent probe for thallium in serum, water, and soil samples based on long-lived, spectrally resolved, Mn-doped ZnSe quantum dots and carbon dots. Anal Chem 90:2939–2945. https://doi.org/10.1021/acs.analchem.7b05365

Luo D, Zhang G, Liu J, Sun X (2011) Evaluation criteria for reduced graphene oxide. J Phys Chem C 115:11327–11335. https://doi.org/10.1021/jp110001y

Luo W, Gaumet JJ, Magri P et al (2019) Fast, green microwave-assisted synthesis of single crystalline Sb 2 Se 3 nanowires towards promising lithium storage. J Energy Chem 30:27–33. https://doi.org/10.1016/j.jechem.2018.03.013

Lv Y, Wang F, Zhu H et al (2016) Electrochemically reduced graphene oxide-Nafion/Au nanoparticle modified electrode for hydrogen peroxide sensing. Nanomater Nanotechnol 6:30. https://doi.org/10.5772/63519

Macdonald GJ (2019) Keeping up with bioprocess changes. Genet Eng Biotechnol News 39:37–38, 40. https://doi.org/10.1089/gen.39.03.10

Mahamuni NN, Gogate PR, Pandit AB (2006) Ultrasound-accelerated green and selective oxidation of sulfides to sulfoxides. Ind Eng Chem Res 45:8829–8836. https://doi.org/10.1021/ie061006l

Mahata S, Sahu A, Shukla P et al (2018) The novel and efficient reduction of graphene oxide using *Ocimum sanctum* L. leaf extract as an alternative renewable bio-resource. New J Chem 42:19945–19952. https://doi.org/10.1039/c8nj04086a

Majer E, Llorente B, Rodríguez-Concepción M, Daròs JA (2017) Rewiring carotenoid biosynthesis in plants using a viral vector. Sci Rep 7:41645. https://doi.org/10.1038/srep41645

Majetich G, Hicks R (1995) Application of microwave-accelerated organic synthesis. Radiat Phys Chem 45:567–579. https://doi.org/10.1016/0969-806X(94)00071-Q
Majidian P, Tabatabaei M, Zeinolabedini M et al (2018) Metabolic engineering of microorganisms for biofuel production. Renew Sust Energ Rev 82:3863–3885. https://doi.org/10.1016/j.rser.2017.10.085
Makarov VV, Love AJ, Sinitsyna OV et al (2014) "Green" nanotechnologies: synthesis of metal nanoparticles using plants. Acta Nat 6:35–44
Maleki S, Mærk M, Hrudikova R et al (2017) New insights into *Pseudomonas fluorescens* alginate biosynthesis relevant for the establishment of an efficient production process for microbial alginates. New Biotechnol 37:2–8. https://doi.org/10.1016/j.nbt.2016.08.005
Malinova I, Qasim HM, Brust H, Fettke J (2018) Parameters of starch granule genesis in chloroplasts of *Arabidopsis thaliana*. Front Plant Sci 9:761. https://doi.org/10.3389/fpls.2018.00761
Manjamadha VP, Muthukumar K (2016) Ultrasound assisted green synthesis of silver nanoparticles using weed plant. Bioprocess Biosyst Eng 39:401–411. https://doi.org/10.1007/s00449-015-1523-3
Manley JB, Anastas PT, Cue BW (2008) Frontiers in green chemistry: meeting the grand challenges for sustainability in R&D and manufacturing. J Clean Prod 16:743–750. https://doi.org/10.1016/j.jclepro.2007.02.025
Mao S, Lu G, Chen J (2014) Nanocarbon-based gas sensors: progress and challenges. J Mater Chem A 2:5573–5579. https://doi.org/10.1039/c3ta13823b
de Marco BA, Rechelo BS, Tótoli EG et al (2019) Evolution of green chemistry and its multidimensional impacts: a review. Saudi Pharm J 27:1–8. https://doi.org/10.1016/j.jsps.2018.07.011
Martina K, Tagliapietra S, Barge A, Cravotto G (2016) Combined microwaves/ultrasound, a hybrid technology. Top Curr Chem 374:1–27. https://doi.org/10.1007/s41061-016-0082-7
Martinez-Guerra E, Gude VG (2014) Synergistic effect of simultaneous microwave and ultrasound irradiations on transesterification of waste vegetable oil. Fuel 137:100–108. https://doi.org/10.1016/j.fuel.2014.07.087
McCaslin CA, Petrusca DN, Poirier C et al (2015) Impact of alginate-producing *Pseudomonas aeruginosa* on alveolar macrophage apoptotic cell clearance. J Cyst Fibros 14:70–77. https://doi.org/10.1016/j.jcf.2014.06.009
McKenzie TG, Karimi F, Ashokkumar M, Qiao GG (2019) Ultrasound and sonochemistry for radical polymerization: sound synthesis. Chem Eur J 25:5372–5388. https://doi.org/10.1002/chem.201803771
Mckinnon D (1981) Chemophobia. Chem Eng News 59:5
Mehrotra P (2016) Biosensors and their applications—a review. J Oral Biol Craniofacial Res 6:153–159. https://doi.org/10.1016/j.jobcr.2015.12.002
Mendoza-Cachú D, López-Miranda JL, Mercado-Zúñiga C, Rosas G (2018) Functionalization of MWCNTs with Ag-AuNPs by a green method and their catalytic properties. Diam Relat Mater 84:26–31. https://doi.org/10.1016/j.diamond.2018.03.004
Merkoçi A (ed) (2009) Biosensing using nanomaterials. Wiley, New York
Mhanna A, Chupin L, Brachais CH et al (2018) Efficient microwave-assisted synthesis of glycerol monodecanoate. Eur J Lipid Sci Technol 120:1–8. https://doi.org/10.1002/ejlt.201700133
Mittal AK, Chisti Y, Banerjee UC (2013) Synthesis of metallic nanoparticles using plant extracts. Biotechnol Adv 31:346–356. https://doi.org/10.1016/j.biotechadv.2013.01.003
Mizukoshi Y, Oshima R, Maeda Y, Nagata Y (1999) Preparation of platinum nanoparticles by sonochemical reduction of the Pt(II) ion. Langmuir 15:2733–2737. https://doi.org/10.1021/la9812121
Moghimi-Rad J, Isfahani TD, Hadi I et al (2011) Shape-controlled synthesis of silver particles by surfactant self-assembly under ultrasound radiation. Appl Nanosci 1:27–35. https://doi.org/10.1007/s13204-011-0004-5
Mordini A, Faigl F (2008) New methodologies and techniques for a sustainable organic chemistry. Intech Open, Siena
Morgon PA (ed) (2015) Sustainable development for the healthcare industry: reprogramming the healthcare value chain, 1st edn. Springer International Publishing, Cham

Murugaboopathi G, Parthasarathy V, Chellaram C et al (2013) Applications of biosensors in food industry. Biosci Biotechnol Res Asia 10:711–714. https://doi.org/10.13005/bbra/1185

Mustafa F, Andreescu S (2018) Chemical and biological sensors for food-quality monitoring and smart packaging. Foods 7:168. https://doi.org/10.3390/foods7100168

Muthukrishnan AM (2015) Green synthesis of copper-chitosan nanoparticles and study of its antibacterial activity. J Nanomed Nanotechnol 6:251–255. https://doi.org/10.4172/2157-7439.1000251

Muthuvel A, Adavallan K, Balamurugan K, Krishnakumar N (2014) Biosynthesis of gold nanoparticles using *Solanum nigrum* leaf extract and screening their free radical scavenging and antibacterial properties. Biomed Prev Nutr 4:325–332. https://doi.org/10.1016/j.bionut.2014.03.004

Nair RV, Thomas RT, Sankar V et al (2017) Rapid, acid-free synthesis of high-quality graphene quantum dots for aggregation induced sensing of metal ions and bioimaging. ACS Omega 2:8051–8061. https://doi.org/10.1021/acsomega.7b01262

Narayan R, Kim SO (2015) Surfactant mediated liquid phase exfoliation of graphene. Nano Converg 2:1–19. https://doi.org/10.1186/s40580-015-0050-x

Nasef MM, Zakeri M, Asadi J et al (2016) Environmentally benign and highly regioselective ring opening of epoxides accelerated by ultrasound irradiation. Green Chem Lett Rev 9:76–84. https://doi.org/10.1080/17518253.2015.1137975

Nasrollahzadeh M, Momeni SS, Sajadi SM (2017) Green synthesis of copper nanoparticles using *Plantago asiatica* leaf extract and their application for the cyanation of aldehydes using K4Fe(CN)6. J Colloid Interface Sci 506:471–477. https://doi.org/10.1016/j.jcis.2017.07.072

Naveen MH, Gurudatt NG, Shim Y-B (2017) Applications of conducting polymer composites to electrochemical sensors: a review. Appl Mater Today 9:419–433. https://doi.org/10.1016/j.apmt.2017.09.001

Nayak J, Devi C, Vidyapeeth L (2016) Microwave assisted synthesis: a green chemistry approach. Int Res J Pharm Appl Sci 3:278–285

Neethirajan S, Ragavan V, Weng X, Chand R (2018a) Biosensors for sustainable food engineering: challenges and perspectives. Biosensors 8:23. https://doi.org/10.3390/bios8010023

Neethirajan S, Weng X, Tah A et al (2018b) Nano-biosensor platforms for detecting food allergens—new trends. Sens Bio-Sensing Res 18:13–30. https://doi.org/10.1016/j.sbsr.2018.02.005

Nemamcha A, Rehspringer JL, Khatmi D (2006) Synthesis of palladium nanoparticles by sonochemical reduction of palladium(II) nitrate in aqueous solution. J Phys Chem B 110:383–387. https://doi.org/10.1021/jp0535801

Nguyen DN, Yoon H (2016) Recent advances in nanostructured conducting polymers: from synthesis to practical applications. Polymers (Basel) 8:118. https://doi.org/10.3390/polym8040118

Nguyen HY, Le XH, Dao NT et al (2019) Microwave-assisted synthesis of graphene quantum dots and nitrogen-doped graphene quantum dots: Raman characterization and their optical properties. Adv Nat Sci Nanosci Nanotechnol 10:025005. https://doi.org/10.1088/2043-6254/ab1b73

Nizamuddin S, Baloch HA, Siddiqui MTH et al (2018) An overview of microwave hydrothermal carbonization and microwave pyrolysis of biomass. Rev Environ Sci Biotechnol 17:813–837. https://doi.org/10.1007/s11157-018-9476-z

Nomanbhay S, Salman B, Hussain R, Ong MY (2017) Microwave pyrolysis of lignocellulosic biomass—a contribution to power Africa. Energy Sustain Soc 7:23. https://doi.org/10.1186/s13705-017-0126-z

Obaidullah M, Bahadur NM, Furusawa T et al (2019) Microwave assisted rapid synthesis of Fe_2O_3@SiO_2 core-shell nanocomposite for the persistence of magnetic property at high temperature. Colloids Surf A Physicochem Eng Asp 572:138–146. https://doi.org/10.1016/j.colsurfa.2019.03.062

Okitsu K, Mizukoshi Y, Yamamoto TA et al (2007) Sonochemical synthesis of gold nanoparticles on chitosan. Mater Lett 61:3429–3431. https://doi.org/10.1016/j.matlet.2006.11.090

Okitsu K, Sharyo K, Nishimura R (2009) One-pot synthesis of gold nanorods by ultrasonic irradiation: the effect of pH on the shape of the gold nanorods and nanoparticles. Langmuir 25:7786–7790. https://doi.org/10.1021/la9017739

Oliveira JR, Kotzebue LRV, Ribeiro FWM et al (2017) Microwave-assisted solvent-free synthesis of novel benzoxazines: a faster and environmentally friendly route to the development of bio-based thermosetting resins. J Polym Sci Part A Polym Chem 55:3534–3544. https://doi.org/10.1002/pola.28755

Omoriyekomwan JE, Tahmasebi A, Zhang J, Yu J (2019) Mechanistic study on direct synthesis of carbon nanotubes from cellulose by means of microwave pyrolysis. Energy Convers Manag 192:88–99. https://doi.org/10.1016/j.enconman.2019.04.042

Ovais M, Khalil AT, Ayaz M et al (2018) Biosynthesis of metal nanoparticles via microbial enzymes: a mechanistic approach. Int J Mol Sci 19:4100. https://doi.org/10.3390/ijms19124100

Padalkar S, Capadona JR, Rowan SJ et al (2010) Natural biopolymers: novel templates for the synthesis of nanostructures. Langmuir 26:8497–8502. https://doi.org/10.1021/la904439p

Pal S, Sharma MK, Danielsson B et al (2014) A miniaturized nanobiosensor for choline analysis. Biosens Bioelectron 54:558–564. https://doi.org/10.1016/j.bios.2013.11.057

Palacios-Santander JM, Cabeza-Saucedo J, García-Romero M, et al (2017) Materiales compuestos Sonogel-Nanotubos de Carbono y Sonogel-Nanocarbono: procedimiento de fabricación y su aplicación para la construcción de electrodos y (bio)sensores electroquímicos, p 38

Palma-Goyes RE, Vazquez-Arenas J, Romero-Ibarra IC, Ostos C (2018) Microwave-assisted solvothermal one-pot synthesis of RuO_2 nanoparticles: first insights of its activity towards oxygen and chlorine evolution reactions. ChemistrySelect 3:12937–12945. https://doi.org/10.1002/slct.201802695

Pandey K, Jain A, Meena AK et al (2013) Camphor based carbon nano tubes: a recent advancement in green chemistry. Bull Environ Pharmacol Life Sci 3:3–6

Pang J, Bachmatiuk A, Ibrahim I et al (2016) CVD growth of 1D and 2D sp2carbon nanomaterials. J Mater Sci 51:640–667. https://doi.org/10.1007/s10853-015-9440-z

Park JE, Atobe M, Fuchigami T (2006) Synthesis of multiple shapes of gold nanoparticles with controlled sizes in aqueous solution using ultrasound. Ultrason Sonochem 13:237–241. https://doi.org/10.1016/j.ultsonch.2005.04.003

Park SY, Thongsai N, Chae A et al (2017) Microwave-assisted synthesis of luminescent and biocompatible lysine-based carbon quantum dots. J Ind Eng Chem 47:329–335. https://doi.org/10.1016/j.jiec.2016.12.002

Patil SB, Annese VF, Cumming DRS (2019) Commercial aspects of biosensors for diagnostics and environmental monitoring. In: Deep A, Kumar S (eds) Advances in nanosensors for biological and environmental analysis, 1st edn. Elsevier, Amsterdam, pp 133–142

Pawełczyk A, Sowa-kasprzak K, Olender D (2018) Microwave (MW), ultrasound (US) and combined synergic MW-US strategies for rapid functionalization of pharmaceutical use phenols. Molecules 23:2360. https://doi.org/10.3390/molecules23092360

Pei S, Cheng HM (2012) The reduction of graphene oxide. Carbon N Y 50:3210–3228. https://doi.org/10.1016/j.carbon.2011.11.010

Pekdemir S, Onses MS, Hancer M (2017) Low temperature growth of graphene using inductively-coupled plasma chemical vapor deposition. Surf Coat Technol 309:814–819. https://doi.org/10.1016/j.surfcoat.2016.10.081

Peng W, Li H, Liu Y, Song S (2016) Comparison of Pb(II) adsorption onto graphene oxide prepared from natural graphites: diagramming the Pb(II) adsorption sites. Appl Surf Sci 364:620–627. https://doi.org/10.1016/j.apsusc.2015.12.208

Perin G, Araujo DR, Nobre PC et al (2018) Ultrasound-promoted synthesis of 2-organoselanylnaphthalenes using Oxone® in aqueous medium as an oxidizing agent. PeerJ 6:e4706. https://doi.org/10.7717/peerj.4706

Pilas J, Yazici Y, Selmer T et al (2017) Optimization of an amperometric biosensor array for simultaneous measurement of ethanol, formate, D- and L-lactate. Electrochim Acta 251:256–262. https://doi.org/10.1016/j.electacta.2017.07.119

Pirtarighat S, Ghannadnia M, Baghshahi S (2019) Biosynthesis of silver nanoparticles using *Ocimum basilicum* cultured under controlled conditions for bactericidal application. Mater Sci Eng C 98:250–255. https://doi.org/10.1016/j.msec.2018.12.090

Płotka-Wasylka J, Namieśnik J (eds) (2019) Green analytical chemistry: past, present and perspectives, 1st edn. Springer Nature Singapore, Singapore

Płotka-Wasylka J, Kurowska-Susdorf A, Sajid M et al (2018) Green chemistry in higher education: state of the art, challenges, and future trends. ChemSusChem 11:2845–2858. https://doi.org/10.1002/cssc.201801109

Plumejeau S, Alauzun JG, Boury B (2015) Hybrid metal oxide@biopolymer materials precursors of metal oxides and metal oxide-carbon composites. J Ceram Soc Japan 123:695–708. https://doi.org/10.2109/jcersj2.123.695

Preiss LC, Landfester K, Muñoz-Espí R (2014) Biopolymer colloids for controlling and templating inorganic synthesis. Beilstein J Nanotechnol 5:2129–2138. https://doi.org/10.3762/bjnano.5.222

Qiu B, Li Z, Wang X et al (2017) Exploration on the microwave-assisted synthesis and formation mechanism of polyaniline nanostructures synthesized in different hydrochloric acid concentrations. J Polym Sci Part A Polym Chem 55:3357–3369. https://doi.org/10.1002/pola.28707

Qu D, Zheng M, Du P et al (2013a) Highly luminescent S, N co-doped graphene quantum dots with broad visible absorption bands for visible light photocatalysts. Nanoscale 5:12272–12277. https://doi.org/10.1039/c3nr04402e

Qu S, Chen H, Zheng X et al (2013b) Ratiometric fluorescent nanosensor based on water soluble carbon nanodots with multiple sensing capacities. Nanoscale 5:5514–5518. https://doi.org/10.1039/c3nr00619k

Rahman G, Najaf Z, Mehmood A et al (2019) An overview of the recent Progress in the synthesis and applications of carbon nanotubes. C 5:3. https://doi.org/10.3390/c5010003

Rai M, Ingle A, Gupta I et al (2013) Potential role of biological systems in formation of nanoparticles: mechanism of synthesis and biomedical applications. Curr Nanosci 9:576–587. https://doi.org/10.2174/15734137113099990092

Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A (2009) Graphene: the new two-dimensional nanomaterial. Angew Chem Int Ed 48:7752–7777. https://doi.org/10.1002/anie.200901678

Rasaee I, Ghannadnia M, Baghshahi S (2018) Biosynthesis of silver nanoparticles using leaf extract of *Satureja hortensis* treated with NaCl and its antibacterial properties. Microporous Mesoporous Mater 264:240–247. https://doi.org/10.1016/j.micromeso.2018.01.032

Rasheed T, Bilal M, Iqbal HMN, Li C (2017) Green biosynthesis of silver nanoparticles using leaves extract of *Artemisia vulgaris* and their potential biomedical applications. Colloids Surf B Biointerfaces 158:408–415. https://doi.org/10.1016/j.colsurfb.2017.07.020

Rashid HU, Yu K, Umar MN et al (2015) Catalyst role in chemical vapor deposition (CVD) process: a review. Rev Adv Mater Sci 40:235–248

Ravichandran S, Karthikeyan E (2011) Microwave synthesis - a potential tool for green chemistry. Int J ChemTech Res 3:466–470

Reddy B, Bandi R, Alle M et al (2018) Microwave assisted rapid green synthesis of gold nanoparticles using *Annona squamosa* L. peel extract for the efficient catalytic reduction of organic pollutants. J Mol Struct 1167:305–315. https://doi.org/10.1016/j.molstruc.2018.05.004

Ren G, Tang M, Chai F, Wu H (2018) One-pot synthesis of highly fluorescent carbon dots from spinach and multipurpose applications. Eur J Inorg Chem 2018:153–158. https://doi.org/10.1002/ejic.201701080

Roh HK, Lee GW, Chung KY, Kim KB (2019) Revisiting $NaTi_2(PO_4)_3$/nanocarbon composites prepared using nanocarbons with different dimensions for high-rate sodium-ion batteries: the surface properties of nanocarbons. J Alloys Compd 787:728–737. https://doi.org/10.1016/j.jallcom.2019.02.167

Ropeik D (2015) On the roots of, and solutions to, the persistent battle between "chemonoia" and rationalist denialism of the subjective nature of human cognition. Hum Exp Toxicol 34:1272–1278. https://doi.org/10.1177/0960327115603592

Rossini EL, Milani MI, Pezza HR (2019) Green synthesis of fluorescent carbon dots for determination of glucose in biofluids using a paper platform. Talanta 201:503–510. https://doi.org/10.1016/j.talanta.2019.04.045

Roy S (2016) Chemistry in our daily life: preliminary information. Int J Home Sci 2:361–366
Rudd JA, Gowenlock CE, Gomez V et al (2019) Solvent-free microwave-assisted synthesis of tenorite nanoparticle-decorated multi-walled carbon nanotubes. J Mater Sci Technol 35:1121–1127. https://doi.org/10.1016/j.jmst.2019.01.002
Ruíz-Baltazar Á d J, Reyes-López SY, Mondragón-Sánchez M d L et al (2018) Biosynthesis of Ag nanoparticles using *Cynara cardunculus* leaf extract: evaluation of their antibacterial and electrochemical activity. Results Phys 11:1142–1149. https://doi.org/10.1016/j.rinp.2018.11.032
Sacco M, Charnay C, De Angelis F et al (2015) Microwave-ultrasound simultaneous irradiation: a hybrid technology applied to ring closing metathesis. RSC Adv 5:16878–16885. https://doi.org/10.1039/c4ra14938f
Saeed S, Hashmi AS, Ikram-ul-Haq et al (2016) Bioconversion of agricultural by-products to alginate by Azotobacter vinelandii and physico-chemical optimization for hyper-production. J Anim Plant Sci 26:1516–1521
Sahoo S, Hatui G, Bhattacharya P et al (2013) One pot synthesis of graphene by exfoliation of graphite in ODCB. Graphene 2:42–48. https://doi.org/10.4236/graphene.2013.21006
Salifairus MJ, Abd Hamid SB, Soga T et al (2016) Structural and optical properties of graphene from green carbon source via thermal chemical vapor deposition. J Mater Res 31:1947–1956. https://doi.org/10.1557/jmr.2016.200
Sangeetha G, Rajeshwari S, Venckatesh R (2011) Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: structure and optical properties. Mater Res Bull 46:2560–2566. https://doi.org/10.1016/j.materresbull.2011.07.046
Schmid J, Sieber V, Rehm B (2015) Bacterial exopolysaccharides: biosynthesis pathways and engineering strategies. Front Microbiol 6:496. https://doi.org/10.3389/fmicb.2015.00496
Schmitz H, Johnson O, Altenburg T (2015) Rent management—the heart of green industrial policy. New Polit Econ 20:812–831. https://doi.org/10.1080/13563467.2015.1079170
Sekhon BS (2010) Microwave-assisted pharmaceutical synthesis: an overview. Int J PharmTech Res 2:827–833
Setaro A (2017) Advanced carbon nanotubes functionalization. J Phys Condens Matter 29:423003
Sethuraman V, Muthuraja P, Anandha Raj J, Manisankar P (2016) A highly sensitive electrochemical biosensor for catechol using conducting polymer reduced graphene oxide–metal oxide enzyme modified electrode. Biosens Bioelectron 84:112–119. https://doi.org/10.1016/j.bios.2015.12.074
Shafiei-Irannejad V, Soleymani J, Azizi S et al (2019) Advanced nanomaterials towards biosensing of insulin: analytical approaches. TrAC Trends Anal Chem 116:1–12. https://doi.org/10.1016/j.trac.2019.04.020
Shah M, Fawcett D, Sharma S, et al (2015) Green synthesis of metallic nanoparticles via biological entities. Materials 8:7278–7308. https://doi.org/10.3390/ma8115377
Shahvelayati AS, Sabbaghan M, Banihashem S (2017) Sonochemically assisted synthesis of N-substituted pyrroles catalyzed by ZnO nanoparticles under solvent-free conditions. Monatsh Chem 148:1123–1129. https://doi.org/10.1007/s00706-016-1904-6
Shamaila S, Sajjad AKL, Ryma N u A et al (2016) Advancements in nanoparticle fabrication by hazard free eco-friendly green routes. Appl Mater Today 5:150–199. https://doi.org/10.1016/j.apmt.2016.09.009
Shen T, Wang Q, Guo Z et al (2018) Hydrothermal synthesis of carbon quantum dots using different precursors and their combination with TiO_2 for enhanced photocatalytic activity. Ceram Int 44:11828–11834. https://doi.org/10.1016/j.ceramint.2018.03.271
Shi K, Yan J, Lester E, Wu T (2014) Catalyst-free synthesis of multiwalled carbon nanotubes via microwave-induced processing of biomass. Ind Eng Chem Res 53:15012–15019. https://doi.org/10.1021/ie503076n
Shin KS, Ji JH, Hwang KS et al (2016) Sensitivity enhancement of bead-based electrochemical impedance spectroscopy (BEIS) biosensor by electric field-focusing in microwells. Biosens Bioelectron 85:16–24. https://doi.org/10.1016/j.bios.2016.04.086

Shirke BS, Korake PV, Hankare PP et al (2011) Synthesis and characterization of pure anatase TiO_2 nanoparticles. J Mater Sci Mater Electron 22:821–824. https://doi.org/10.1007/s10854-010-0218-4

Shukla AK, Iravani S (eds) (2019) Green synthesis, characterization and applications of nanoparticles. Elsevier, Amsterdam

Sidhu JS, Singh A, Garg N et al (2018) Carbon dots as analytical tools for sensing of thioredoxin reductase and screening of cancer cells. Analyst 143:1853–1861. https://doi.org/10.1039/c7an02040f

Singh AK, Talat M, Singh DP, Srivastava ON (2010) Biosynthesis of gold and silver nanoparticles by natural precursor clove and their functionalization with amine group. J Nanopart Res 12:1667–1675. https://doi.org/10.1007/s11051-009-9835-3

Siontorou CG (2019) University-industry relationships for the development and commercialization of biosensors. In: Thouand G (ed) Handbook of cell biosensors. Springer Nature, Cham, pp 1–16

Skellam E (2019) Strategies for engineering natural product biosynthesis in fungi. Trends Biotechnol 37:416–427. https://doi.org/10.1016/j.tibtech.2018.09.003

Smitha SL, Philip D, Gopchandran KG (2009) Green synthesis of gold nanoparticles using *Cinnamomum zeylanicum* leaf broth. Spectrochim Acta Part A Mol Biomol Spectrosc 74:735–739. https://doi.org/10.1016/j.saa.2009.08.007

Son M, Ham MH (2017) Low-temperature synthesis of graphene by chemical vapor deposition and its applications. FlatChem 5:40–49. https://doi.org/10.1016/j.flatc.2017.07.002

Song J, Han B (2015) Green chemistry: a tool for the sustainable development of the chemical industry. Natl Sci Rev 2:255–258. https://doi.org/10.1093/nsr/nwu076

Song JY, Jang HK, Kim BS (2009) Biological synthesis of gold nanoparticles using *Magnolia kobus* and *Diopyros kaki* leaf extracts. Process Biochem 44:1133–1138. https://doi.org/10.1016/j.procbio.2009.06.005

Song W, Duan W, Liu Y et al (2017) Ratiometric detection of intracellular lysine and pH with one-pot synthesized dual emissive carbon dots. Anal Chem 89:13626–13633. https://doi.org/10.1021/acs.analchem.7b04211

Stankovich S, Dikin DA, Piner RD et al (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon N Y 45:1558–1565. https://doi.org/10.1016/j.carbon.2007.02.034

Stephens GL, Kahn BH, Richardson M (2016) The super greenhouse effect in a changing climate. J Clim 29:5469–5482. https://doi.org/10.1175/JCLI-D-15-0234.1

Strauss CR (2002) Applications of microwaves for environmentally benign organic chemistry. In: Clark JH, Macquarrie D (eds) Handbook of green chemistry and technology. Blackwell Science Ltd, London, pp 397–415

Sukumaran SS, Tripathi S, Resmi AN et al (2019) Influence of surfactants on the electronic properties of liquid-phase exfoliated graphene. Mater Sci Eng B Solid-State Mater Adv Technol 240:62–68. https://doi.org/10.1016/j.mseb.2019.01.003

Sun H, Wu L, Wei W, Qu X (2013) Recent advances in graphene quantum dots for sensing. Mater Today 16:433–442. https://doi.org/10.1016/j.mattod.2013.10.020

Sundaresan P, Karthik R, Chen SM et al (2019) Ultrasonication-assisted synthesis of sphere-like strontium cerate nanoparticles (SrCeO3 NPs) for the selective electrochemical detection of calcium channel antagonists nifedipine. Ultrason Sonochem 53:44–54. https://doi.org/10.1016/j.ultsonch.2018.12.013

Suresh D, Nethravathi PC, Udayabhanu, et al. (2015) Green synthesis of multifunctional zinc oxide (ZnO) nanoparticles using *Cassia fistula* plant extract and their photodegradative, antioxidant and antibacterial activities. Mater Sci Semicond Process 31:446–454. doi: https://doi.org/10.1016/j.mssp.2014.12.023

Sweeney JB, Bethel PA, Gill DM et al (2019) Synthesis of a protected keto-lysidine analogue via improved preparation of arabino-isocytosine nucleosides. Org Lett 21:2004–2007. https://doi.org/10.1021/acs.orglett.9b00086

Tao W, Pan D, Liu Q, Yao S, Nie Z, Han B (2006) Optical and Bioelectrochemical Characterization of Water-Miscible Ionic Liquids Based Composites of Multiwalled Carbon Nanotubes. Electroanalysis 18(17):1681–1688

Tappiban P, Smith DR, Triwitayakorn K, Bao J (2019) Recent understanding of starch biosynthesis in cassava for quality improvement: a review. Trends Food Sci Technol 83:167–180. https://doi.org/10.1016/j.tifs.2018.11.019

Tetlow IJ, Emes MJ (2017) Starch biosynthesis in the developing endosperms of grasses and cereals. Agronomy 7:81. https://doi.org/10.3390/agronomy7040081

Thakur S, Karak N (2012) Green reduction of graphene oxide by aqueous phytoextracts. Carbon N Y 50:5331–5339. https://doi.org/10.1016/j.carbon.2012.07.023

Thakur MS, Ragavan KV (2013) Biosensors in food processing. J Food Sci Technol 50:625–641. https://doi.org/10.1007/s13197-012-0783-z

Thitisaksakul M, Jiménez RC, Arias MC, Beckles DM (2012) Effects of environmental factors on cereal starch biosynthesis and composition. J Cereal Sci 56:67–80. https://doi.org/10.1016/j.jcs.2012.04.002

Tian R, Zhong S, Wu J et al (2016) Facile hydrothermal method to prepare graphene quantum dots from graphene oxide with different photoluminescences. RSC Adv 6:40422–40426. https://doi.org/10.1039/c6ra00780e

Timothy J, Cintas P (2002) Sonochemistry. In: Clark JH, Macquarrie D (eds) Handbook of green chemistry and technology. Blackwell Science Ltd, London, pp 372–396

Tiwari BK (2015) Ultrasound: a clean, green extraction technology. TrAC Trends Anal Chem 71:100–109. https://doi.org/10.1016/j.trac.2015.04.013

Torabfam M, Jafarizadeh-Malmiri H (2018) Microwave-enhanced silver nanoparticle synthesis using chitosan biopolymer: optimization of the process conditions and evaluation of their characteristics. Green Process Synth 7:530–537. https://doi.org/10.1515/gps-2017-0139

Torres-Palma RA, Serna-Galvis EA (2018) Sonolysis. In: Advanced oxidation processes for wastewater treatment: emerging green chemical technology. Elsevier Inc., Medellín, pp 177–213

Tran TS, Park SJ, Yoo SS et al (2016) High shear-induced exfoliation of graphite into high quality graphene by Taylor-Couette flow. RSC Adv 6:12003–12008. https://doi.org/10.1039/c5ra22273g

Trenberth KE, Dai A, Van der Schrier G et al (2014) Golbal warming and changes in drought. Nat Clim Chang 4:17–22

Tripathi N, Pavelyev V, Islam SS (2017) Synthesis of carbon nanotubes using green plant extract as catalyst: unconventional concept and its realization. Appl Nanosci 7:557–566. https://doi.org/10.1007/s13204-017-0598-3

Trost BM (1991) The atom economy—a search for synthetic efficiency. Science 254:1471–1477. https://doi.org/10.1126/science.1962206

Trost BM (1995) Atom economy—a challenge for organic synthesis: homogeneous catalysis leads the way. Angew Chem Int Ed Engl 34:259–281. https://doi.org/10.1002/anie.199502591

U.S. Environmental Protection Agency (1992) Environmental Education and The National Environmental Education Act of 1990. https://www.epa.gov.tw/public/Attachment/78716464493.pdf. Accessed 3 Jul 2019

Uchida H, Aryal HR, Adhikari S, Umeno M (2016) Low temperature plasma CVD grown graphene by microwave surface-wave plasma CVD using camphor precursor. J Phys Sci Appl 6:34–38. https://doi.org/10.17265/2159-5348/2016.02.005

Ukkund SJ, Darshanram KZ et al (2019) Microwave assisted green synthesis and characterization of silver nanoparticles from *Hibiscus* leaf extract and investigation of their antimicrobial activities. AIP Conf Proc:2080. https://doi.org/10.1063/1.5092885

UNIDO (2011) Green industry initiative for sustainable industrial development. Vienna. (Avaliable at: https://www.unido.org/our-focus/cross-cutting-services/green-industry/green-industry-initiative)

Uysal Unalan I, Wan C, Trabattoni S et al (2015) Polysaccharide-assisted rapid exfoliation of graphite platelets into high quality water-dispersible graphene sheets. RSC Adv 5:26482–26490. https://doi.org/10.1039/c4ra16947f

Vágó A, Szakacs G, Sáfrán G et al (2016) One-step green synthesis of gold nanoparticles by mesophilic filamentous fungi. Chem Phys Lett 645:1–4. https://doi.org/10.1016/j.cplett.2015.12.019

Valentini F, Roscioli D, Carbone M et al (2015) Graphene and ionic liquids new gel paste electrodes for caffeic acid quantification. Sensors Actuators B Chem 212:248–255. https://doi.org/10.1016/j.snb.2015.02.033

Vásquez-Ponce F, Higuera-Llantén S, Pavlov MS et al (2017) Alginate overproduction and biofilm formation by psychrotolerant *Pseudomonas mandelii* depend on temperature in Antarctic marine sediments. Electron J Biotechnol 28:27–34. https://doi.org/10.1016/j.ejbt.2017.05.001

Vijaya Kumar P, Mary Jelastin Kala S, Prakash KS (2019) Green synthesis of gold nanoparticles using Croton Caudatus Geisel leaf extract and their biological studies. Mater Lett 236:19–22. https://doi.org/10.1016/j.matlet.2018.10.025

Vogiazi V, De La Cruz A, Mishra S et al (2019) A comprehensive review: development of electrochemical biosensors for detection of cyanotoxins in freshwater. ACS Sensors 4:1151–1173. https://doi.org/10.1021/acssensors.9b00376

Vu THT, Tran TTT, Le HNT et al (2015) A new green approach for the reduction of graphene oxide nanosheets using caffeine. Bull Mater Sci 38:667–671

Wang J, Fang BS, Chou KY et al (2014) A two-stage enzymatic synthesis of conductive poly(3,4-ethylenedioxythiophene). Enzym Microb Technol 54:45–50. https://doi.org/10.1016/j.enzmictec.2013.10.002

Wang J, Guleria S, Koffas MAG, Yan Y (2016) Microbial production of value-added nutraceuticals. Curr Opin Biotechnol 37:97–104. https://doi.org/10.1016/j.copbio.2015.11.003

Wang C, Gao X, Chen Z et al (2017) Preparation, characterization and application of polysaccharide-based metallic nanoparticles: a review. Polymers (Basel) 9:689–722. https://doi.org/10.3390/polym9120689

Wang M, Fu Q, Zhang K et al (2019a) A magnetic and carbon dot based molecularly imprinted composite for fluorometric detection of 2,4,6-trinitrophenol. Microchim Acta 186:86. https://doi.org/10.1007/s00604-018-3200-0

Wang Y, Zhang H, Lu X et al (2019b) Advances in 2-phenylethanol production from engineered microorganisms. Biotechnol Adv 37:403–409. https://doi.org/10.1016/j.biotechadv.2019.02.005

Wathey B, Tierney J, Lidström P, Westman J (2002) The impact of microwave-assisted organic chemistry on drug discovery. Drug Discov Today 7:373–380. https://doi.org/10.1016/S1359-6446(02)02178-5

Wei C, Li CJ (2002) Grignard type reaction via C-H bond activation in water. Green Chem 4:39–41. https://doi.org/10.1039/b110102c

Wei D, Qian W (2008) Facile synthesis of Ag and Au nanoparticles utilizing chitosan as a mediator agent. Colloids Surf B Biointerfaces 62:136–142. https://doi.org/10.1016/j.colsurfb.2007.09.030

Wei C, Li Z, Li CJ (2004) The development of A3-coupling (aldehyde-alkyne-amine) and AA3-coupling (asymmetric aldehyde-alkyne-amine). Synlett 9:1472–1483. https://doi.org/10.1055/s-2004-829531

Weizhong Q, Fei W, Zhanwen W et al (2003) Production of carbon nanotubes in a packed bed and a fluidized bed. AICHE J 49:619–625. https://doi.org/10.1002/aic.690490308

Wen C, Zhao N, Zhang DW et al (2014) Efficient reduction and exfoliation of graphite oxide by sequential chemical reduction and microwave irradiation. Synth Met 194:71–76. https://doi.org/10.1016/j.synthmet.2014.04.023

Wen Y, Wen W, Zhang X, Wang S (2016) Highly sensitive amperometric biosensor based on electrochemically-reduced graphene oxide-chitosan/hemoglobin nanocomposite for nitromethane determination. Biosens Bioelectron 79:894–900. https://doi.org/10.1016/j.bios.2016.01.028

Wen Z, Shen Q, Sun X (2017) Nanogenerators for self-powered gas sensing. Nano-Micro Lett 9:45. https://doi.org/10.1007/s40820-017-0146-4

Wróblewska-Krepsztul J, Rydzkowski T, Michalska-Pożoga I, Thakur VK (2019) Biopolymers for biomedical and pharmaceutical applications: recent advances and overview of alginate electrospinning. Nano 9:404. https://doi.org/10.3390/nano9030404

Wu Z, Ondruschka B, Cravotto G et al (2008) Oxidation of primary aromatic amines under irradiation with ultrasound and/or microwaves. Synth Commun 38:2619–2624

Wu Z, Cherkasov N, Cravotto G et al (2015) Ultrasound- and microwave-assisted preparation of lead-free palladium catalysts: effects on the kinetics of diphenylacetylene semi-hydrogenation. ChemCatChem 7:952–959. https://doi.org/10.1002/cctc.201402999

Xie LY, Li YJ, Qu J et al (2017) A base-free, ultrasound accelerated one-pot synthesis of 2-sulfonylquinolines in water. Green Chem 19:5642–5646. https://doi.org/10.1039/c7gc02304a

Xie X, Zhou Y, Huang K (2019) Advances in microwave-assisted production of reduced graphene oxide. Front Chem 7:355. https://doi.org/10.3389/fchem.2019.00355

Xu H, Zeiger BW, Suslick KS (2013) Sonochemical synthesis of nanomaterials. Chem Soc Rev 42:2555–2567. https://doi.org/10.1039/c2cs35282f

Xu M, Peng W, Cai J et al (2015) Ultrasound-assisted synthesis and characterization of ultrathin copper nanowhiskers. Mater Lett 161:164–167. https://doi.org/10.1016/j.matlet.2015.08.092

Xu Y, Cao H, Xue Y et al (2018) Liquid-phase exfoliation of Graphene: An overview on exfoliation media, techniques, and challenges. Nano 8:942–974. https://doi.org/10.3390/nano8110942

Xu Y, Du C, Steinkruger JD et al (2019) Microwave-assisted synthesis of AuNPs/CdS composite nanorods for enhanced photocatalytic hydrogen evolution. J Mater Sci 54:6930–6942. https://doi.org/10.1007/s10853-018-03294-7

Yadi M, Mostafavi E, Saleh B et al (2018) Current developments in green synthesis of metallic nanoparticles using plant extracts: a review. Artif Cells Nanomed Biotechnol 46:S336–S343. https://doi.org/10.1080/21691401.2018.1492931

Yakout SM, Mostafa AA (2015) A novel green synthesis of silver nanoparticles using soluble starch and its antibacterial activity. Int J Clin Exp Med 8:3538–3544

Yang JM, Ji SJ, Gu DG et al (2005) Ultrasound-irradiated Michael addition of amines to ferrocenylenones under solvent-free and catalyst-free conditions at room temperature. J Organomet Chem 690:2989–2995. https://doi.org/10.1016/j.jorganchem.2005.03.030

Yang P, Zhu Z, Chen M et al (2018) Microwave-assisted synthesis of xylan-derived carbon quantum dots for tetracycline sensing. Opt Mater (Amst) 85:329–336. https://doi.org/10.1016/j.optmat.2018.06.034

Yavir K, Marcinkowski Ł, Marcinkowska R et al (2019) Analytical applications and physicochemical properties of ionic liquid-based hybrid materials: a review. Anal Chim Acta 1054:1–16. https://doi.org/10.1016/j.aca.2018.10.061

Yaws CL (2009) Thermophysical properties of chemicals and hydrocarbons, 1st edn. Elsevier Science, New York

Yin R, Shen P, Lu Z (2019) A green approach for the reduction of graphene oxide by the ultraviolet/sulfite process. J Colloid Interface Sci 550:110–116. https://doi.org/10.1016/j.jcis.2019.04.073

Yoo IH, Kalanur SS, Seo H (2019) Deposition of Pd nanoparticles on MWCNTs: green approach and application to hydrogen sensing. J Alloys Compd 788:936–943. https://doi.org/10.1016/j.jallcom.2019.02.298

You Y, Mayyas M, Xu S et al (2017) Growth of NiO nanorods, SiC nanowires and monolayer graphene: via a CVD method. Green Chem 19:5599–5607. https://doi.org/10.1039/c7gc02523h

Yu T, Wang H, Guo C et al (2018) A rapid microwave synthesis of green-emissive carbon dots with solid-state fluorescence and pH-sensitive properties. R Soc Open Sci 5:180245. https://doi.org/10.1098/rsos.180245

Zahran MK, Ahmed HB, El-Rafie MH (2014) Facile size-regulated synthesis of silver nanoparticles using pectin. Carbohydr Polym 111:971–978. https://doi.org/10.1016/j.carbpol.2014.05.028

Zamfir LG, Rotariu L, Bala C (2013) Acetylcholinesterase biosensor for carbamate drugs based on tetrathiafulvalene-tetracyanoquinodimethane/ionic liquid conductive gels. Biosens Bioelectron 46:61–67. https://doi.org/10.1016/j.bios.2013.02.018

Zarzuela R, Luna MJ, Gil MLA et al (2018) Analytical determination of the reducing and stabilization agents present in different *Zostera noltii* extracts used for the biosynthesis of gold nanoparticles. J Photochem Photobiol B Biol 179:32–38. https://doi.org/10.1016/j.jphotobiol.2017.12.025

Zhang Y, Suslick KS (2015) Synthesis of poly(3,4-ethylenedioxythiophene) microspheres by ultrasonic spray polymerization (USPo). Chem Mater 27:7559–7563. https://doi.org/10.1021/acs.chemmater.5b03423

Zhang J, Du J, Han B et al (2006) Sonochemical formation of single-crystalline gold nanobelts. Angew Chem Int Ed 45:1116–1119. https://doi.org/10.1002/anie.200503762

Zhang Y, Zhang L, Zhou C (2013a) Review of chemical vapor deposition of graphene and related applications. Acc Chem Res 40:2329–2339. https://doi.org/10.1021/ar300203n

Zhang YL, Wang L, Zhang HC et al (2013b) Graphitic carbon quantum dots as a fluorescent sensing platform for highly efficient detection of Fe^{3+} ions. RSC Adv 3:3733–3738. https://doi.org/10.1039/c3ra23410j

Zhang Y, Arugula MA, Wales M et al (2015) A novel layer-by-layer assembled multi-enzyme/CNT biosensor for discriminative detection between organophosphorus and non-organophosphrus pesticides. Biosens Bioelectron 67:287–295. https://doi.org/10.1016/j.bios.2014.08.036

Zhang C, Cui Y, Song L et al (2016) Microwave assisted one-pot synthesis of graphene quantum dots as highly sensitive fluorescent probes for detection of iron ions and pH value. Talanta 150:54–60. https://doi.org/10.1016/j.talanta.2015.12.015

Zhang J, Wang H, Xiao Y et al (2017) A simple approach for synthesizing of fluorescent carbon quantum dots from tofu wastewater. Nanoscale Res Lett 12:611. https://doi.org/10.1186/s11671-017-2369-1

Zhang HJ, Liu LZ, Zhang XR et al (2019) Microwave-assisted solvothermal synthesis of shape-controlled $CoFe_2O_4$ nanoparticles for acetone sensor. J Alloys Compd 788:1103–1112. https://doi.org/10.1016/j.jallcom.2019.03.009

Zhao Y, He J (2019) Novel template-assisted microwave conversion of graphene oxide to graphene patterns: a reduction transfer mechanism. Carbon N Y 148:159–163. https://doi.org/10.1016/j.carbon.2019.03.081

Zhao Y, Gao Y, Zhan D et al (2005) Selective detection of dopamine in the presence of ascorbic acid and uric acid by a carbon nanotubes-ionic liquid gel modified electrode. Talanta 66:51–57. https://doi.org/10.1016/j.talanta.2004.09.019

Zhao HX, Liu LQ, De Liu Z et al (2011) Highly selective detection of phosphate in very complicated matrixes with an off-on fluorescent probe of europium-adjusted carbon dots. Chem Commun 47:2604–2606. https://doi.org/10.1039/c0cc04399k

Zhao Y, Huang Z, Chang W et al (2017) Microwave-assisted solvothermal synthesis of hierarchical TiO_2 microspheres for efficient electro-field-assisted-photocatalytic removal of tributyltin in tannery wastewater. Chemosphere 179:75–83. https://doi.org/10.1016/j.chemosphere.2017.03.084

Zheng Y, Liu Z, Jing Y et al (2015) An acetylcholinesterase biosensor based on ionic liquid functionalized graphene-gelatin-modified electrode for sensitive detection of pesticides. Sensors Actuators B Chem 210:389–397. https://doi.org/10.1016/j.snb.2015.01.003

Zheng W, Zhao M, Liu W et al (2018) Electrochemical sensor based on molecularly imprinted polymer/reduced graphene oxide composite for simultaneous determination of uric acid and tyrosine. J Electroanal Chem 813:75–82. https://doi.org/10.1016/j.jelechem.2018.02.022

Zhong X, Fei G, Xia H (2010) Synthesis and characterization of poly(3,4-ethylenedioxythiophene) nanoparticles obtained through ultrasonic irradiation. J Appl Polym Sci 118:2146–2152. https://doi.org/10.1002/app.32531

Zhou W, Zhang F, Liu S et al (2014) Microwave-assisted hydrothermal synthesis of graphene-wrapped CuO hybrids for lithium ion batteries. RSC Adv 4:51362–51365. https://doi.org/10.1039/c4ra09144b

Zhou Q, Zhou M, Li Q et al (2019) Facile biosynthesis and grown mechanism of gold nanoparticles in *Pueraria lobata* extract. Colloids Surf A Physicochem Eng Asp 567:69–75. https://doi.org/10.1016/j.colsurfa.2019.01.039

Zhu J, Jia J, Kwong FL et al (2012) Synthesis of multiwalled carbon nanotubes from bamboo charcoal and the roles of minerals on their growth. Biomass Bioenergy 36:12–19. https://doi.org/10.1016/j.biombioe.2011.08.023

Zhu L-F, Yao Z-C, Ahmad Z et al (2018a) Synthesis and evaluation of herbal chitosan from ganoderma lucidum spore powder for biomedical applications. Sci Rep 8:14608. https://doi.org/10.1038/s41598-018-33088-5

Zhu Y, Ji H, Cheng HM, Ruoff RS (2018b) Mass production and industrial applications of graphene materials. Natl Sci Rev 5:90–101. https://doi.org/10.1093/nsr/nwx055

Zlotski S, Uglov V (2017) Facile sol-gel synthesis of metaloxide nanoparticles in a cellulose paper template. J Nanomed Nanotechnol S8:002. https://doi.org/10.4172/2157-7439.S8-002