Green Synthesis of Hierarchically Structured Metal and Metal Oxide Nanomaterials

Malobi Seth, Hasmat Khan, Susanta Bera, Atanu Naskar, and Sunirmal Jana

Abstract

Scientific and technological innovations are rapidly occurring in today's world. These innovations include development of numerous functional nanomaterials among which hierarchically structured nanomaterials (HSNs) are most important owing to their enormous applications in different fields like biomedical, wastewater management, energy storage, sensing, and so on. Alternative to conventional synthesis methods which can cause harmful effects to human health and environment, several green chemical, physical and biological methods are known for producing different metal and metal oxide-based HSNs. It is to be noted that adoption of these methods is increasing as these methods are environmentally sustainable. Green chemical and physical methods involve use of environmentally benign solvents and reagents. In some cases, these are also energy efficient. Additionally, several biological materials including microorganisms, plants, biomolecules are known to be well accepted as befitting reactants/templates for synthesizing several HSNs. However, these methods further need an in-depth mechanistic realization toward large-scale production for practical applications. This chapter is mainly focused upon an understanding of green chemistry-based methodologies for the synthesis of metal and metal oxide HSNs and their potential applications. Finally, the present challenges and future prospect of the methodologies toward making biocompatible and environmentally sustainable HSNs with useful functional properties for advanced applications are discussed briefly.

Keywords

Green synthesis • Green chemical, physical and biological methods • Green reagents and templates with green techniques • Metal and metal oxide nanomaterials • Hierarchical nanostructures

1 Introduction

Scientific and technological innovations are rapidly occurring in today's world. More than often, the advancements in research for these innovations are occurring at a cost of multifold enhancement of environmental pollution. Human civilization's immense scientific prowess is causing the worst of natural calamities of this century, making difficult the coexistence of humans and our Mother Nature. After years of exploitation, the scientific community has been alarmed since last two decades and concentrating on minimizing the harmful environmental impact of science toward reducing the consumption of non-renewable resources and approaching new paradigms for prevention of environmental pollution (Gao et al. 2012). On this aspect, green chemistry or sustainable chemistry came into limelight. The subject basically concentrates on designing appropriate synthetic methods toward minimizing the use of harmful chemicals/reactants or eliminating the generation of hazardous side products. The green synthesis of nanomaterials is primarily based upon twelve principles that mainly include the synthesis and use of non-toxic chemicals, utilization of renewable feedstock, designing of energy efficiency and degradable waste products (Kreuder et al. 2017). The important of this green synthesis is to use environmentally benign solvents and reagents; non-toxic reducing and capping agents that can in-turn minimize the generation of toxic derivatives/products. Several nanomaterials can be synthesized by adopting green synthesis methods (Gahlawat and Roy Choudhury 2019; Hulkoti and Taranath 2014). Among

M. Seth · H. Khan · S. Bera · A. Naskar · S. Jana (✉)
Specialty Glass Division, CSIR-Central Glass and Ceramic Research Institute, 196 Raja S. C. Mullick Road, Jadavpur, Kolkata, 700032, West Bengal, India
e-mail: sjana@cgcri.res.in

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these nanomaterials, metal and metal oxide-based nanomaterials with hierarchical structures have attracted significant attention for both the aspects of fundamental and technological research (Gahlawat and Roy Choudhury 2019; Yuliarto et al. 2019). In this regard, researchers have already adopted green chemical, physical, and biological methods for synthesizing various metal and metal oxide nanomaterials. Green chemical methods involve the use of environmentally benign solvents and reagents. The physical methods include microwave and light-assisted synthesis, thermal deposition, electrochemical anodization, and so on. In some cases, these methods are found to be energy efficient as well as environmentally sustainable. Biological methods involve the use of biologically active materials that function as reagents and templates. These have advantages of being cost effective, eco-friendly, and biocompatible. Also, these are widely abundant in nature. In this purpose, microorganisms like bacteria, fungi, algae, yeast, and also plant or plant-derived materials are being used. It is noteworthy that in the green synthesis method, the active chemicals/phytochemicals from microorganisms and plants have been used as reducing, structure directing, and capping agents (Hulkoti and Taranath 2014; Mohammadinejad et al. 2016; Ebrahiminezhad et al. 2018). In addition, the use of biotemplates such as cellulose, collagen, eggshell membranes, and butterfly wings as natural templates has also been found in the synthesis of metal and metal oxide nanomaterials (Zan and Wu 2016).

Nowadays, hierarchically structured nanomaterials (HSNs) including metal and metal oxide-based nanomaterials are very interesting in fundamental science and also these are highly useful for potential applications (Trogadas et al. 2016). In this case, upon tactful designing of the reaction conditions in the aforesaid green synthesis methods with appropriate green reagents and templates, metal and metal oxide-based HSNs can be synthesized effectively. It is known that the term *hierarchy* comes from Greek words *hieros* (sacred) and *archein* (rule) that refers to an institutional framework where each and every unit are ranked according to their importance. Also, the structural hierarchy has reined in Mother Nature in umpteen variations of living beings and biological materials from macroscopic to microscopic scales. Moreover, the hierarchy of natural materials arises from a complex reciprocity between surface structure, morphology, and physical as well as chemical properties of the biologically active components. Importantly, synthesized hierarchically structured nanomaterials means higher dimension of a micro- or nanostructures consisting of numerous assemblies of low dimensional nanobuilding blocks arranged in a particularly organized manner with less agglomerated configuration (Lee 2009). The nanobuilding blocks that comprise a hierarchical structure may be the array of nanoparticles creating different shapes including but not limited to 1D nanowires, nanotubes and nanobelts, 2D nanosheets and nanocubes, 3D nanoflowers, superstructures and hollow structures or may be the array of well-aligned meso- and microporous hierarchical structures. Hierarchical metal and metal oxide nanostructures exhibit special properties like large surface area with high surface-to-volume ratio. Sometimes, hierarchical porosity endows high antimicrobial activity, effective photon-harvesting, and efficient charge transfer abilities (Yuliarto et al. 2019; Yang et al. 2017). Such advanced functional properties/special characteristics make them advantageous for wide range of applications including biomedical, photocatalysis, environmental remediation, sensors, optoelectronics, photoelectrochemical energy conversion and storage (Bera et al. 2016a,b,c,2017; Khan et al. 2020; Seth et al. 2020).

In this chapter, we critically discuss the *state-of-the-art* research on the green synthesis of metal and metal oxide-based HSNs, their growth mechanisms and applications in various fields. Further, the present challenges and future prospect of green synthesized hierarchically structured nanomaterials have been briefly discussed.

2 Advantages of Green Synthesis Methods

Typical bottom-up synthesis processes with toxic solvents and hazardous chemical compounds as surfactants/complexing/stabilizing/capping agents that are very tough to decompose and most of them are non-recyclable (Yuliarto et al. 2019) are generally used for obtaining metal and metal oxides. Moreover, the chemical waste produced as side derivatives/products obtained at the end of the synthesis can have detrimental effects on environment, biodiversity, and human health. These harmful wastes are present as (a) toxic gases that lead to air pollution, (b) liquids which cause water pollution, and (c) solids that are disposed on soil increase ground water pollution. Hence, various attempts are found to be taken to mitigate the pollution by minimizing the use of hazardous chemicals by utilizing the synthesis methods of green chemistry. It is worthy to note that the methods, solvents, and chemicals/raw materials used for the synthesis of metal and metal oxide nanomaterials *via* these pathways have to be ecologically sound, energy efficient, recyclable and non-toxic to human health and wildlife as well. Another advantage of these methods is that the microorganisms and plant/plant-derived extracts that are used for the synthesis can mostly be used for multiple purposes in such a way that the active biochemicals present in the extracts can function simultaneously as reducing agents, capping agents, and stabilizing agents as per the need of a particular material synthesis (Hulkoti and Taranath 2014; Mohammadinejad et al. 2016). In this way, the atom economy which is one of the vital principles of green chemistry is also being maintained. Sometimes, the hydrocarbons in the extracts can also act as biofuels for making the final products. These are also cost effective, biodegradable, and largely abundant in nature. Also, the reaction conditions and methods of green chemistry can strategically be used for metal and metal oxide HSNs synthesis. Moreover, the phase structure and morphology as well as the size of the nanomaterials can be controlled by tuning reaction temperature, time, concentration of extracts, and solvents toward the generation of hierarchically structured nanomaterials (Yang et al. 2017). It is also seen that in the biotemplate-mediated synthesis, the creation of hierarchical nanomaterials is particularly efficient as the nanostructures are replicated from the natural micro/nanoscale hierarchical structures of naturally occurring templates. After deposition, the biotemplate is to be burnt off at higher temperatures *via* a suitable calcination/heat treatment process that lead to create hierarchical network and/or arrays of meso- and macroporous structure.

3 Green Synthesis Methods for Hierarchically Structured Metal and Metal Oxide Nanomaterials

Various methods are known today for the green synthesis of HSNs *via* the formation of nanoparticles (NPs). These methods involve the use of energy efficient techniques, non-toxic green solvents and reagents as well as the use of plant extracts or microbes (bacteria, fungi, yeast, and algae) or biotemplates (Khandel et al. 2018). It is now distinct and significant that the green synthesis is the most convenient approach for the synthesis of the nanomaterials toward restoring sustainable environment. It is an authentic and unique way not only because of its non-toxicity to gradually deteriorating environment at present but also, it can produce contamination free nanoparticles with distinct hierarchical morphologies. On the basis of different synthesis methods used for the preparation of metal and metal oxide HSNs, these can mainly be categorized into biological, physical, and chemical methods (discussed details in the next subsections).

3.1 Biological Methods

Application of various kinds of microorganisms (bacteria, fungi, yeast, algae, etc.), plant and plant-derived substances in the synthesis of HSNs have been discussed in this section. These biological components/species are used as reactant and/or templates.

3.1.1 Using Microorganism

Microorganisms as Reactant

Microorganisms (such as bacteria, fungi, and algae) are appropriate candidates for the synthesis of nanomaterials because of their unique ability to reduce metal ions toward the formation with high growth rates (Gahlawat and Roy Choudhury 2019). It is observed that some microbes with a certain defense mechanism are evolved to fight off the toxicity excreted by heavy metals because microbes endure harsh and toxic environment consistently. The defense mechanisms which include intracellular sequestration, efflux pumps, change in metal ion concentration and extracellular precipitation help the bacteria to survive the generated stresses. It is noteworthy that the aforementioned processes are to be utilized for metal and metal oxide-based HSNs synthesis for various applications (to be discussed later).

During synthesis of a specific nanometal, He et al. (2008) observed that the bacteria *Rhodopseudomonas capsulate* extracellularly reduced chloroaurate ions to AuNPs. The proteins in the enzymes secreted by bacteria can reduce the gold ions forming AuNPs which is further capped by the protein molecules developing Au nanowires. Moreover, *Rhizopusoryzae* fungi-mediated *in vitro* synthesis of nanoflower-like stable AuNPs is also reported. In this case, the cell wall of proteins played dominant role in the reduction of gold ions and formation of AuNPs (Kitching et al. 2016). In another example, the nanosheets of TiO_2 architectures had been synthesized by using three kinds of bacteria, namely *Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli* (Zhang et al. 2019a). The phospholipids leaking from bacteria are found to be covering the generated TiO_2 nanoparticles creating steric barrier leading to the formation of nanosheets. Instead of bacteria, yeast mold broth powder has also been used for the synthesis of carbon-doped ZnO with a silver heterostructure at the interfaces (Shen et al. 2015). It is noticed that *Saccharomyces cerevisiae* present in yeast extract can promote secondary ZnO aggregation, amino acids, or other functional groups in the extract that suppressed the growth along the c-axis toward the formation of various ZnO superstructures. Furthermore, dextrose in the broth powder can condense and form an amorphous film of carbon on the ZnO particle surface with hierarchical morphology and helps to introduce silver nanoparticles (Fig. 1). Different metals and metal oxide nanomaterials with their hierarchical morphologies synthesized by using microorganisms as reactant are displayed in Table 1.

Microorganism as Template

Microbial superstructures (like bacteria, fungi, yeast, and algae) are generally used as biotemplate (Table 2) to direct deposition, assembly, and patterning of metal and metal

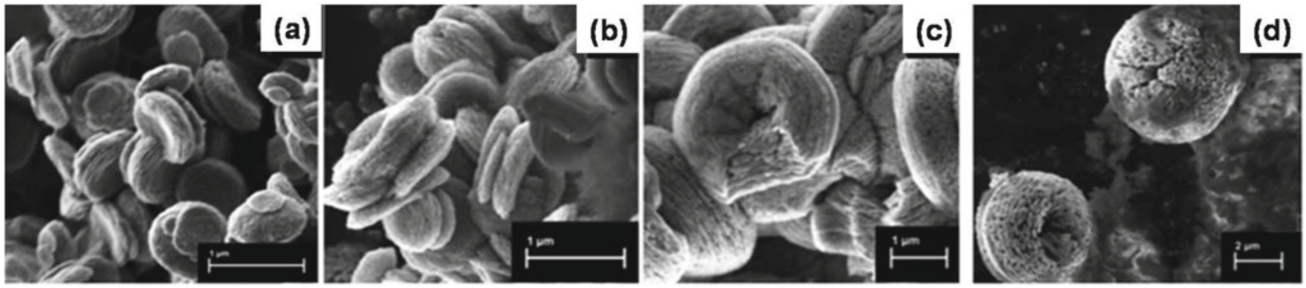

Fig. 1 SEM images of ZnO with hierarchical morphologies synthesized with Zn^{2+}concentration of 12.5 mM (**a**), 25 mM (**b**), 50 mM (**c**), and 100 mM (**d**). Copyrights reserved to the American Chemical Society (Shen et al. 2015)

Table 1 Characteristics of metal/metal oxide HSNs synthesized using microorganisms as reactants

Reactant	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Bacteria					
Rhodopseudomonas capsulata	Au	Nanowires	Diameter, 50–60 nm	Microelectronics, opt oelectronics, nanoscale electronic devices	He et al. (2008)
Staphylococcus aureus, Bacillus subtilis, Escherichia coli	TiO_2	Nanosheets assembled hierarchical architecture	–	Photocatalytic and electrocatalytic applications	Zhang et al. (2019a)
Bacillus subtilis	ZnO	Microsphere assembled by hair-like nanostructure	Diameter, 10–15 nm	Photocatalytic dye degradation	Dhandapani et al. (2020)
Klebsiella pneumoniae, Escherichia coli and Pseudomonas jessinii	AgCl coated with AgNPs	Cubes, flowers	–	–	Müller et al. (2016)
Yeast					
Yeast mold broth	C, Ag modified ZnO	Nanoplatelets, twin-nanodisks, thick microdonuts, microapples wrapped by graphene-like sheets, microspheres, microhamburgers	Nanoplates, 30–50 nm	Photocatalytic activity	Shen et al. (2015)
Fungi					
Rhizopusoryzae	AuNPs	Nanoflowers	24–62 nm	Biomedical applications	Kitching et al. (2016)

oxide-based HSNs by microbes-templating method (Zhou et al. 2007). This method provides a sustainable, economical, and convenient strategy compared to traditional template-directed method. The abundant functional groups like carboxylic, phosphate, amine, etc., are present in microbial cell wall along with enzymes to bind metal ions *via* coordination or electrostatic attraction onto the cell. The steps for surface activation or functionalization are found to be reduced in this method. There are several mechanisms developed by these species to overcome the toxic effects of heavy metals (Hulkoti and Taranath 2014). It is observed that when the cell walls are used as biotemplate, the replica of metal and metal oxide nanostructures is formed. A suitable example is *Spirulina* that had been used as biotemplate for the fabrication of nanosheets assembly of AgNPs (Sun et al. 2019). The intracellular highly ordered texture of *Spirulina* typically contains bioactive components such as nucleoid, layered thylakoid, polyhedral carboxysome, and so on. They can act as supporting base of nanosheets that formed under the spatially repression of the cellular structure. On the other hand, hollow porous ZnO microspheres (Zhou et al. 2007) and hierarchical ZnO nanostructures (Hussein et al. 2009) had been synthesized by using the biotemplates, *Streptococcus thermophiles* and *Bacillus cereus*, respectively. For the growth of hierarchical ZnO nanostructures, *Bacillus cereus* had been used to

Table 2 Characteristics of metal/metal oxide HSNs synthesized using microorganisms as template

Species	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Bacteria					
Staphylococcus aureus, Bacillus subtilis, and Escherichia coli	TiO_2	Nanosheets assembled hierarchical architecture	–	Photocatalytic and electrocatalytic applications	Zhang et al. (2019a)
Streptococcus thermophilus	ZnO	Hollow porous microspheres	Particle size, 20–40 nm; pore size, 2.5–11 nm	–	Zhou et al. (2007)
Bacillus cereus	ZnO	Raspberry (composed of nodules)- and plate-like structures	Nodules, 20–30 nm; plate thickness, ~25 nm	–	Hussein et al. (2009)
Staphylococcus aureus	TiO_2	Hierarchically porous	Macro and mesopores	Photocatalytic oxidation and reduction	He et al. (2014)
Micrococcus lylae	Co_3O_4	Porous, flower-like microspheres	2–10 nm	Electrochemical application	Shim et al. (2013)
Yeast					
Yeast	TiO_2	Hierarchical mesoporous	Pore size, 3–15 nm	Biosensor, fuel cell, and metal–air battery fields	Cui et al. (2009)
Yeast	TiO_2	Lamella	50 nm	Photodegradation of dye	Bao et al. (2012)
Yeast	In_2O_3	Hollow microspheres	~20 nm	Photocatalytic dye degradation	Pan et al. (2018)
Yeast	NiO/C	Hollow microspheres	50 nm	Anode for Li-ion batteries	Tian et al. (2018)
Fungi					
Cladosporium cladosporioides	NiO	Nanostructured microtubules	–	Energy storage applications	Atalay et al. (2016)
Algae					
Spirulina	AgNPs	Nanosheets	Nanogaps, ~4 nm	Antibacterial and surface enhanced Raman scattering (SERS) properties	Sun et al. (2019)
Nannochloropsis oculata	MnO/C	Hierarchically porous	10–100 nm	Catalysis, gas sensing, and energy storage	Xia et al. (2013)
Foraminiferal shells	Co, Ag, Cu, Pt, Au	3D hierarchical structures	–	Filter for water purification, electrocatalysts for ethanol oxidation	Diab et al. (2019)

control intracellularly Zn^{2+}deposition and nucleation/growth of ZnO on or within *B. cereus* cell. This step had been followed by calcination at 500 °C to form raspberry- and plate-like structures, depending upon the organelles where zinc species nucleate and act as template. On the other hand, LPD-modified hierarchically porous TiO_2 nanostructures had been synthesized using *Staphylococcus aureus* as biotemplate (He et al. 2014) (Fig. 2).

3.1.2 Using Plant

In green nanotechnology, plant-mediated synthesis is popularizing among the researchers due to their cost-effectiveness, biodegradability, biocompatibility, and recyclability. Every part of a plant including flower, leaf, fruit, pollen, grain, stem, seed, bark, bran, and peel can be used as green reagents or templates for the biosynthesis of nanomaterials (Ebrahiminezhad et al. 2018). These extracts consist of various biologically active compounds (phyto-chemicals) such as proteins, amino acids, vitamins, polysaccharides, polyphenols, alkaloids, quinones, organic acids, flavonoids, terpenoids, catechins, and co-enzymes (Mohammadinejad et al. 2016). These compounds can act as reducing agents/capping agents for metal and metal oxide HSNs synthesis. Moreover, the HSNs can be produced by exploiting natural morphology of plant as biotemplate.

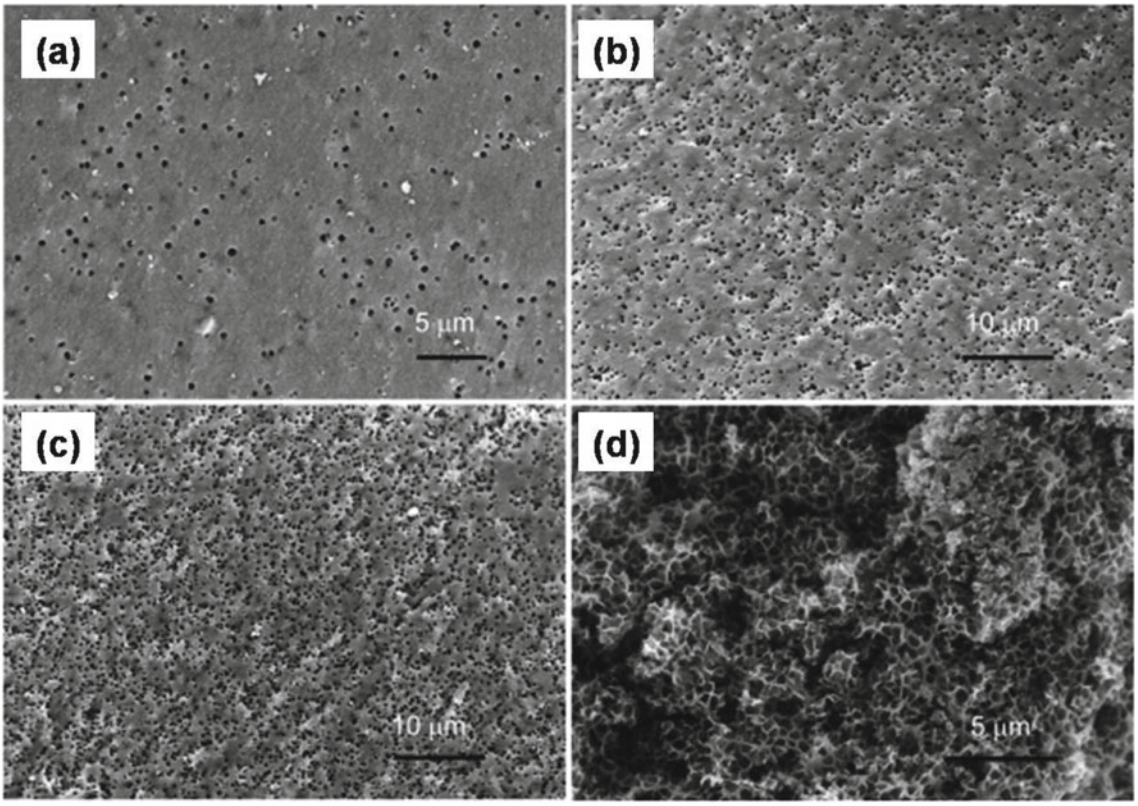

Fig. 2 SEM images of hierarchically porous TiO_2 using **a** 1, **b** 4, **c** 12 and **d** 48 × 10^{11} *S. aureus* as template. Copyrights reserved to the American Chemical Society (He et al. 2014)

Plant as Reactant

Extracellular plant-mediated synthesis of metal and metal oxide nanomaterials/HSNs simply involves the use of plant extract as reactant (Table 3). It is to be noted that the preparation and mixing of extract into aqueous solution of metal ions is to be performed in well-controlled condition. As for example, dendritic silver nanostructure constructed from AgNPs (Fig. 3) had been synthesized by using white grape pomace extract (Carbone et al. 2019). Also, an interesting dendritic nanostructure of Pd was formed in a coffee ring-like fashion while banana peel is used as a reducing agent (Bankar et al. 2010). The functional groups present in the cellulose, pectin, and hemicelluloses—the main constituents in banana peel—–are said to be acting as reducing agents. Polyphenols present in the extract had been identified as reducing and capping agents for the synthesis of the different hierarchical nanostructures. In another study, black grape skin extract had been used for the ZnO superstructures/HSNs synthesis (Udayabhanu et al. 2017). Interestingly, with increasing the concentration of the extract, different structures (Mysore pak to canine teeth to hollow pyramid to ornament gem) were formed. The authors also reported the grape extract with polyphenols, flavanoids, tannins, and phytolexins not only can perform as strong reducing or capping agent for Zn^{2+}but also can function as fuel for the combustion of zinc nitrate at 500 °C toward the formation of ZnO superstructures/HSNs. On the other hand, amino acids and sugar in aloe extract had been used as capping agents for encapsulation of Ti^{4+}ions, forming nanorods/nanoflowers of TiO_2. It had been seen that the morphology of the nanomaterial is dependent upon the concentration of aloe extract (Li et al. 2020). It is interesting to note that after adopting hydrothermal process, these morphologies changed into 3D tripyramidal structure.

Plant as Template

The idea of using plant as biotemplate (Table 4) is to introduce naturally occurring well-ordered and hierarchical structures in artificially designed nanomaterials to enhance their properties and functions by virtue of the generated structures (Zan and Wu 2016). Plant-derived biotemplates are very popular because of their availability in large quantity, renewability, and cost-effectiveness. On this aspect, wood is an excellent choice as biotemplate owing to the presence of several species with hierarchically porous macroscopic structures (Liu et al. 2009). In one relevant example, Zn^{2+}ions adsorbed onto the cell walls of wood through capillary adsorption during infiltration of precursor

Table 3 Characteristics of metal/metal oxide HSNs synthesized using plants as reagents

Reagents	Nanomaterial	Morphology/shape	Dimension	Property/application	References
White grape pomace	Ag	Hierarchical dendritic structure	33 ± 6 nm	Electrochemical and antifungal properties	Carbone et al. (2019)
Banana peel	Pd	Coffee ring	50 nm	–	Bankar et al. (2010)
Black grape skin	ZnO	Superstructures	20 nm	Photocatalytic dye degradation, antibacterial, electrochemical sensing of hydrazine	Udayabhanu et al. (2017)
Aloe	TiO_2	3D tripyramidal nanostrcutures, nanorods, nanoflowers	~10 nm	Photocatalytic degradation of antibiotic materials	Li et al. (2020)
Cynodondactylon and *Cyperusrotundus* grass extracts	CuO	Rice spikelet like nanostrcutures, 1D, nanorods, 2D nanoprisms, 3D nanoparticles	16 nm	Antibacterial	Suresh et al. (2020)
Lemon juice, peel	MnO_2	Nanorods	Diameter, ~17 nm	Electrode for LiB	Hashem et al. (2018)
Pepper	Fe_3O_4–Pd	Dendritic Pd, spherical Fe_3O_4	Dendrites diameter, <100 nm; Fe_3O_4 nanoparticles, ~50 nm	Superparamagnetic and photocatalytic properties	Khaghani et al. (2017)
Watermelon rind	ZnO	Nanorods interconnected with small flower formation	Length, 100–200 nm; width, 80–130 nm	Photocatalytic and optoelectronic applications	Singh et al. (2017)
Azadirachta indica	ZnO	Plates, bullets, flower, prismatic tip, closed pine cone	Hexagonal NPs, 10–30 nm	Photocatalytic dye degradation, antibacterial and antioxidant properties	Madan et al. (2015)
Sapindus mukorossi fruit	CuO	Nanowires	~10 nm	Electrochemical sensing of dopamine	Sundar et al. (2018)
Rape pollen grains	SnO_2	Hierarchically porous interconnected network	SnO_2 membrane thickness, ~10 nm; mesopore, 5–20 nm	Gas sensing	Song et al. (2012)

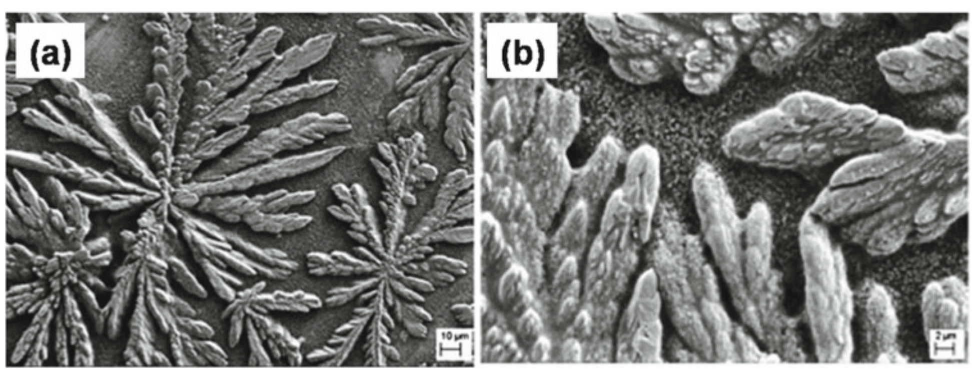

Fig. 3 SEM images **(a, b)** of dendritic Ag from grape pomace. Copyrights reserved to the Elsevier (Carbone et al. 2019)

solution and deposited onto the cell walls homogeneously. After calcination, the wood template burnt off and hierarchically porous ZnO formed by preserving the original template of wood. It is also noted that different nanostructures and nanoflowers of ZnO can be generated using palm olein as biotemplate depending upon the concentration of the template (Ramimoghadam et al. 2013a, b). In this case, initially the self-assembly of palm olein was found to occur followed by the arrangement of zinc acetate over the self-assembly of olein forming a stable inorganic-organic hybrid. In the final step, i.e., after template removal through calcination, the ZnO nanostructures were distinctly formed.

Table 4 Characteristics of metal/metal oxide HSNs synthesized using plants as templates

Template	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Wood	ZnO	Hierarchically porous	Pore size, 25–52 nm	Gas sensing	Liu et al. (2009)
Rice	ZnO	Flower-like, star like structure	40–100 nm	–	Ramimoghadam et al. (2013a)
Palm olein	ZnO	Flowers assembled by nanoplates	~50 nm	–	Ramimoghadam et al. (2013b)
Regenerated cellulose membrane	TiO_2	Nanorods	Length, 45 nm; diameter, 10 nm	Photocatalytic dye degradation	Mohamed et al. (2016)
Green leaves	TiO_2	Porous morph-structures	Layer thickness, ~15 nm; pore size, ~2–10 nm	Photocatalytic dye degradation	Li et al. (2009)
Sunflower Pollen	ZrO_2	Spinous core–shell microspheres	Nanoparticles, ~50–80 nm	Hydrogen storage	Yang et al. (2011)
Collagen fiber	TiO_2–CeO_2	Nanofiber bundles	50–100 nm	Lithium storage	Wei et al. (2019)
Collagen fiber	Ce_x/TiO_2	Mesoporous nanofiber bundles	Thickness, 20–50 nm; pore size, 2–10 nm	Photocatalytic dye degradation	Xiao et al. (2013)
Peltophorum pterocarpum pollen grain	SnO_2	Porous motif	16–25 nm	Potential gas sensing	Fazil et al. (2015)
Basil leave extract	Co_3O_4/C	Porous nanorods assembled by nanospheres, nanocapsules	Nanospheres diameters, 5–15 nm; nanocapsules, 10–20 nm length	Catalysed hydrogen generation	Abu-Zied and Alamry (2019)
Nanocellulose/alginate	CeO_2	3D porous interconnected nanostructures	Pore size, 2–3 nm	–	Moyer et al. (2019)
Cotton	SnO_2	Porous microtubules	Pore size, 23–47 nm	Gas sensing	Ma et al. (2019)
Apple pectin	ZnO	Hollow double-caged peanut built from nanorods	Nanorods, ~100 nm	Photocatalytic dye degradation	Wang et al. (2012)
China rose petal	CeO_2	Porous nanosheets	Thickness, ~7 nm; pores size 2–4 nm	Potential catalyst	Qian et al. (2011)
Grapefruit exocarp	SnO_2	Hierarchically porous	Pore size, 2–10 nm	Formaldehyde gas sensing	Zhang et al. (2016)
Gingko leaves	Co_3O_4	Hierarchically porous structure	Nanoparticles, 30–100; pores, 10–200 nm	Electrochemical biosensing	Han et al. (2015)
Mung bean sprout	$BaCrO_4$	Dendritic superstructures	50–150 µm long side branches	Electronic light device	Yan et al. (2006)
Onion inner coat	$SrCrO_4$	Dumbbell assembled by nanorods	Nanorods width 30–50 nm	–	Chen et al. (2008)
Starch	Bi_2O_3	Nanorods	50 nm	Catalyst for oxidative aromatization	Farzaneh et al. (2017)

In another example, the regenerated cellulose membrane had been used as template for the synthesis of TiO_2 nanorods (Mohamed et al. 2016). This study suggested that the hydrophilic membrane promoted the interaction of hydroxyl groups and Ti^{4+} ions by electrostatic attraction toward the development of TiO_2 nanoparticles that finally made nanorods. It has also been reported that morph-TiO_2 can be synthesized by replication of the structural features of hierarchical and porous template-green leaves (Li et al. 2009).

3.1.3 Using Other Green Templates

As discussed in the previous subsections, a significant attention has been paid upon the synthesis of HSNs using biomaterials as templates. However, the research is not only limited toward synthesizing metal and metal oxide HSNs by using microorganisms or plant and plant-derived parts, rather using different living organisms and their parts with unique microstructures (Table 5). In this respect, Zhang et al. (2018) reported the fabrication of Ag butterfly wing scale arrays using butterfly wing as template. It is well known that butterfly wings have very unique and ordered 3D spatial microstructures that are responsible for brilliant blue coloration and iridescence of their wings (Zhang et al. 2006). In the analysis of chemical composition of wings, the presence of proteins, amino acids are found as major functional groups. These groups can absorb or interact with Zn^{2+} and accelerate to crystallize as ZnO nanoparticles. Upon further calcination and simultaneous pyrolysis of the scales, the formation of ZnO hierarchical structures was observed (Zhang et al. 2006). It is also seen that bioreplication of two types of butterfly wings can led to produce quasi-honeycomb-like, hollow concavities and cross-ribbing structures of TiO_2 deposited over fluorine-doped glass substrate (Zhang et al. 2009).

Eggshell membrane (ESM) is another fascinating material used as a biotemplate for controlling of nucleation, assembling and patterning of unique morphologies of metal and metal oxide HSNs (Zan and Wu 2016). Glycoprotein, a component of shell membrane is made up of $–NH_2$, –OH, –COOH groups that act as structure directing as well as capping agents for the synthesis of metal and metal oxide nanoparticles/HSNs. In aqueous solution of metal oxide precursors, the inorganic material cross-linked and polymerized toward the formation of inorganic/biotemplate complexes which are mesoscopically ordered due to the self-assembling nature of glycoprotein. The organics of ESM biotemplate can be removed through high-temperature calcination, leaving the network-like porous morphology of metal oxide intact (Mallampati and Valiyaveetti 2013). Biomorphic ZnO interwoven microfibers (Dong et al. 2007a), hierarchical mesoporous Mn_3O_4 (Mallampati and Valiyaveetti 2012), and a series of 3D micro/nanocomposite porous structured metal oxides such as CeO_2, Co_3O_4, CuO,

Table 5 Characteristics of metal/metal oxide HSNs synthesized using green templates

Template	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Butterfly wings bioscaffold	AgNPs/graphene	Butterfly wing scale arrays	50–150 nm	Trace chemical detection	Zhang et al. (2018)
Butterfly wings	ZnO	Replica	15 nm	–	Zhang et al. (2006)
Butterfly wings	TiO_2	Quasi-honeycomb-like structure, two-dimensional array shallow concavities structure	50–100 nm	Potential application on dye-sensitized solar cell	Zhang et al. (2009)
Eggshell membrane	CeO_2, Co_3O_4, CuO, NiO and ZnO	Interwoven microporous tubular structures	Nanocrystallites, 20–50 nm	Extraction of nanoparticles from water	Mallampati and Valiyaveetti (2013)
Eggshell membrane	ZnO	Porous interwoven nanofibers	Nanofiber diameter, 200 nm; pore size, ~1 nm	Highly efficient photocatalysts, optical devices	Dong et al. (2007a)
Eggshell membrane	Mn_3O_4	Porous fibrous network	Crystallite size, ~20 nm	Dye adsorption	Mallampati and Valiyaveetti (2012)
Eggshell membrane	SnO_2	Interwoven hollow tubular structure	Tube wall thickness, ~80 nm	–	Dong et al. (2006)
Eggshell membrane	ZnO, Co_3O_4, PdO	Hierarchically porous interwoven nanofibrous structure	Pore size, 20–30 nm for ZnO; 30 nm for Co_3O_4; 80 nm for PdO	–	Dong et al. (2007b)
Eggshell membrane	Co_3O_4	3D hierarchically porous interconnected nanofibers	~50 nm	Non-enzymatic electrochemical detection of glucose	Fan et al. (2016)
Glutamine	ZnO	Nanorods	–	Photocatalytic dye degradation	Alkaim et al. (2016)
Albumen	ZnO	Brush-like morphology assembled by nanorods	90 nm	–	Nouroozi and Farzaneh (2011)

NiO, and ZnO (Dong et al. 2007b) can be produced *via* a hierarchical organization of nanocrystals using ESM as biotemplate.

3.2 Physical and Chemical Methods

3.2.1 Green Techniques

Microwave-assisted process is a convenient approach for heating. It is known as eco-friendly or green technique as in this method, the microwave energy directly interacts with the reaction system as opposed to the traditional heating technique (Lei et al. 2014). This method has several advantages like fast and steady volumetric heating and substantial reduction in synthesis time, causes to develop porous and hierarchically structured metal and metal oxide nanomaterials. As an example, the advantage of microwave-assisted synthesis over conventional hydrothermal heating can be explained by virtue of the growth mechanism of hierarchical CuO@reduced graphene oxide (rGO) (Yin et al. 2019). It is seen that microwave irradiation can promote a heteronuclear nucleation mechanism of monodispersed CuO NPs anchored evenly over rGO nanosheets compared to large particles of CuO randomly distributed on rGO nanosheets under hydrothermal condition. Thermal decomposition of $Zn(NO_3)_2$ at different temperatures led to generate different ZnO superstructures/HSNs like hexagonal pyramids and tulip, bud, apple, dahlia, sunflower, and wheat grains within 500 °C (Udayabhanu et al. 2016). Other than the microwave-assisted synthesis, organic free electrodeposition (Xia et al. 2018; Ji et al. 2019), anodization (Momeni et al. 2016), and light-assisted methods (Das et al. 2017; Hu et al. 2016) had also been reported as efficient green methods for the synthesis of metal oxide HSNs (Table 6).

3.2.2 Green Reagents

Different amino acids (Kang et al. 2013; Gao et al. 2008), metal powders (Zhang et al. 2011), biopolymers (Wang et al. 2016; Zong et al. 2016), salts (Chen et al. 2018) are generally used as green reagents (Table 7) for the green synthesis of different nanomaterials. In this regard, Kang et al. (2013) reported the green synthesis of nanosheets assembled hierarchical silver microspheres in a surfactant/template-free route using different amino acids as structure directing agent and ascorbic acid as reducing agent. Interestingly, amino acids with simple structures (e.g., alanine, glycine) and more complicated structures (e.g., glycine, glutamine, asparagine) would generate different microstructures. Ye et al. (2015) reported the evolution of Pt–Au dendrimer-like HSNs supported on polydopamine-functionalized graphene. In this

Table 6 Characteristics of metal/metal oxide HSNs synthesized using alternate green techniques

Technique	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Microwave	$NiCo_2O_4$	Flower-shaped microsphere consisting of petal-like nanosheets	Nanopetals thickness, ~15 nm; width, 0.1 µm	High performance supercapacitor	Lei et al. (2014)
Microwave	CuO@rGO	Hierarchical nanostructure	4–12 nm	H_2S-sensing	Yin et al. (2019)
Thermal decomposition of precursor	ZnO	Superstructures-hexagonal pyramid, flower, bud, fruit-grain-like structures	–	Photocatalysis of dye, photoluminescence, and electrochemical biosensing	Udayabhanu et al. (2016)
Electrodeposition	Fe_3O_4 @Fe^o	Dendritic	Nanoparticles, 50 nm	Phenol oxidation	Xia et al. (2018)
Organic free electrodeposition	Ag/Cu_2O	Nanopyramids, nanoflakes, nanoplates	Nanopyramids, ~ 311 nm height	SERS applications	Ji et al. (2019)
Electrochemical anodization	CuO	Nanoneedles consist of a bundle of irregular polygonal wires	70–90 nm	Photocatalytic dye degradation	Momeni et al. (2016)
Light assisted method	MnO_2	Nanoflowers assembled by thin intersected nanosheets	Nanosheets thickness, ~4 nm	Photocatalytic degradation of dye	Das et al. (2017)
Light assisted	MnO_2	Desert rose-like 3D hierarchical nanostructures composed of curly and interlaced nanosheets	Nanosheets, ~50 nm	Proposed supercapacitor	Hu et al. (2016)
Microwave	CuO	Hollow cocoon	Thickness, 50 nm	Applications in biosensor, optical	Deng et al. (2011)

(continued)

Table 7 Characteristics of metal/metal oxide HSNs synthesized using alternate green reagents

Reagent	Nanomaterial	Morphology/shape	Dimension	Property/application	References
Polyethylene glycol (PEG)	Au–CuO	Flower-like structure composed of nanosheets	Nanosheets thickness, ∼ 30 nm; nanoparticles, ∼1.8–12 nm	Catalytic reduction of p-nitrophenol	Gao et al. (2012)
Alanine, glycine, glutamine, asparagine	Ag	Hierarchical Ag microsphere assembles by nanosheets	Microspheres, 2–3 µm, 3–4 µm diameter; nanosheets, 50–150 nm thickness	Sensitive chemical detection and monitoring plasmon-driven reactions	Kang et al. (2013)
Tyrosine	CuO	Hierarchical hollow micro/nanostructure assembled by nanosheets	Nanosheets, 250 nm diameter	Electrode materials for lithium-ion batteries	Gao et al. (2008)
Mg powder	Ag	Dendrites, dendritic flowers and rods	Branches diameter, 40 nm	Potential application in fuel cells, SERS detection	Zhang et al. (2011)
Green reagents	Co_3O_4/C	Hierarchically nanoporous	3–30 nm; pores, 2–4 nm	Supercapacitor	Wang et al. (2016)
Food grade sodium alginate	δ-MnO_2	Nanosheets inter tangled porous flowers	43 nm; micropore, 1–2 nm	Supercapacitor	Zong et al. (2016)
Surfactant, template free	SnO_2	Dahlia-flower like structure	Nanosheets thickness, 10–15 nm; nanoparticles, 20–50 nm	Photocatalytic dye degradation	Chen et al. (2018)
Ascorbic acid	Pt–Au	Dendrimer	26 nm	4-nitrophenol reduction	Ye et al. (2015)
Surfactant free	ZnO	Porous nanoflakes assembled nanostructures	5–40 nm	Solid catalyst	Sinhamahapatra et al. (2012)
D-(+)-glucose powder	Cu_2O–CuO	Hydrangea microspheres assembled by nanosheets	Microspheres diameter, 3–5 µm; nanosheets, 80 nm thickness	–	Yang et al. (2013)
PEG	Au NPs	Hierarchically mesoporous sponge	∼12 nm	Potential applications in chemical and biological analysis	Lee et al. (2016)
Green reagents	Ag/WO_{3-x}	Nanowires, nanowires bundles, 3D chestnut-like nanostructures	800 nm nanotips	SERS sensing	Huang et al. (2017)
Green template and precursor	Mn_3O_4, MnO_2	Hierarchical mesoporous microcuboids assembled by nanosheets	Nanosheets thickness, ∼70 nm	Anode materials for lithium-ion batteries	Hu et al. (2018)

process, initially, the reduction and self-polymerization of dopamine results in polydopamine-functionalized graphene. Afterward, the amine and catechol groups preferentially attached with $PtCl^{2-}$ and $AuCl^-$ by electronic conjugation which finally reduced by ascorbic acid to form the nanocomposite. It is also known that surfactant free synthesis (Chen et al. 2018; Sinhamahapatra et al. 2012) of metal oxide-based HSNs is efficient in regard of atom economized approach of green chemistry.

3.2.3 Green Solvents

A very promising category of green solvents is deep eutectic solvents (DES) because these are cost effective, eco-friendly, non-toxic and convenient for large-scale production compared to traditional ionic liquids (Wang et al. 2018). These green solvents (Table 8) are capable of producing different hierarchical TiO_2 structures (microrods and quasi-crassulapeforata, quasi-peanuts and hierarchical microspheres). Apart from these solvents, glycerol is a widely

Table 8 Characteristics of metal/metal oxide HSNs synthesized using green solvents

Solvent	Nanomaterial	Morphology/shape	Dimension	Property/application	References
DES (deep eutectic solvents)	TiO_2	Microspheres, quasi-microspheres, microrods and quasi-crassulapeforata-like structure constructed by nanodisks	–	Photocatalytic water splitting	Wang et al. (2018)
Green solvent, template free	ZnO	Wool ball structure assembled by nanoflakes	Thickness, 20–25 nm	Photocatalytic dye degradation	Singh et al. (2016)
Template/surfactant free	$ZnFe_2O_4$	Shuttle-shaped mesoporous microrods assembled by 1D nanofiber subunits	Nanofibers, 100–200 nm	Anode for LIBs	Hou et al. (2015)
Green solvent	CuO–ZnO	Flower	ZnO flower, ∼554 nm; CuO nanoparticles, ∼50–90 nm	Anticorrosion properties of thin film	Beshkar et al. (2017)
Water solvent	Co_3O_4	Nanoflakes assembled nanostructure	Thickness, 2–3 nm	H_2O_2 sensing	Su et al. (2015)
Green solvent	WO_3	Nanowires emerged from the edges of stacked nanoplates	Nanowire diameter, <20 nm	Photochemical water splitting	Nayak et al. (2017)
Green solvent	$CoMn_2O_4$	Porous micro/nanostructures	20–100 nm	Anode for LIB	Li et al. (2017)

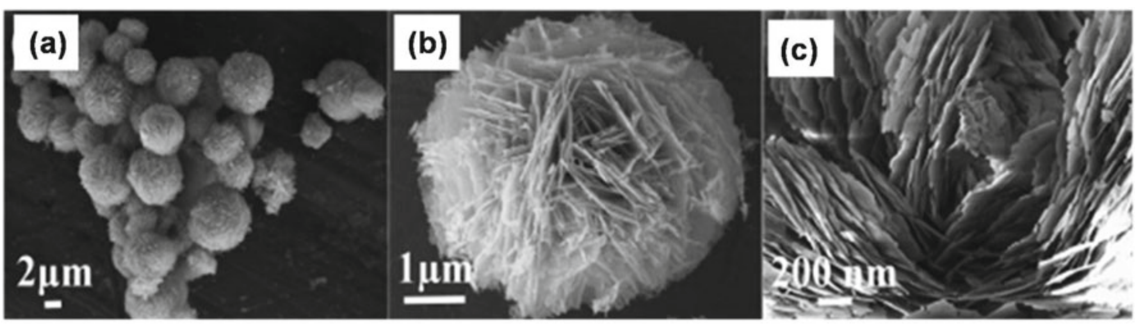

Fig. 4 FESEM images of hierarchical self-assembled 3D ZnO superstructures at different magnifications. Copyrights reserved to the American Chemical Society (Singh et al. 2016)

used green solvent. Hierarchical 3D wool ball-like ZnO superstructures (Fig. 4) had been synthesized using urea (additive)-glycerol/water/ethanol assisted hydrothermal method. Glycerol had been used as chelating agent to Zn^{2+} as well as capping agent for regulating the morphology while the presence of different dosages of urea controls the morphology from urchin-like to wool ball-like structure of ZnO (Singh et al. 2016). On the other hand, hierarchical shuttle-shaped mesoporous $ZnFe_2O_4$ microrods assembled by 1D nanorods had been synthesized using the combination of green solvents, i.e., glycerol and water (Hou et al. 2015). In this process, the viscosity of glycerol was more than water. This influenced the diffusion rate of ions in glycerol slower than water that led to higher aggregation rate of the nanorods; eventually fused together to form the shuttle-shaped structures. Similarly, flower-like CuO/ZnO hybrid hierarchical nanostructures had been fabricated on copper substrate in which ethylene glycol was used as reducing agent as well as solvent (Beshkar et al. 2017).

4 Growth Mechanism of Metal and Metal Oxide HSNs

On the basis of the above reported literature as described in the previous sections/subsections of different green synthesis methods/techniques used for the fabrication of metal and metal oxide HSNs, one can classify the methods into

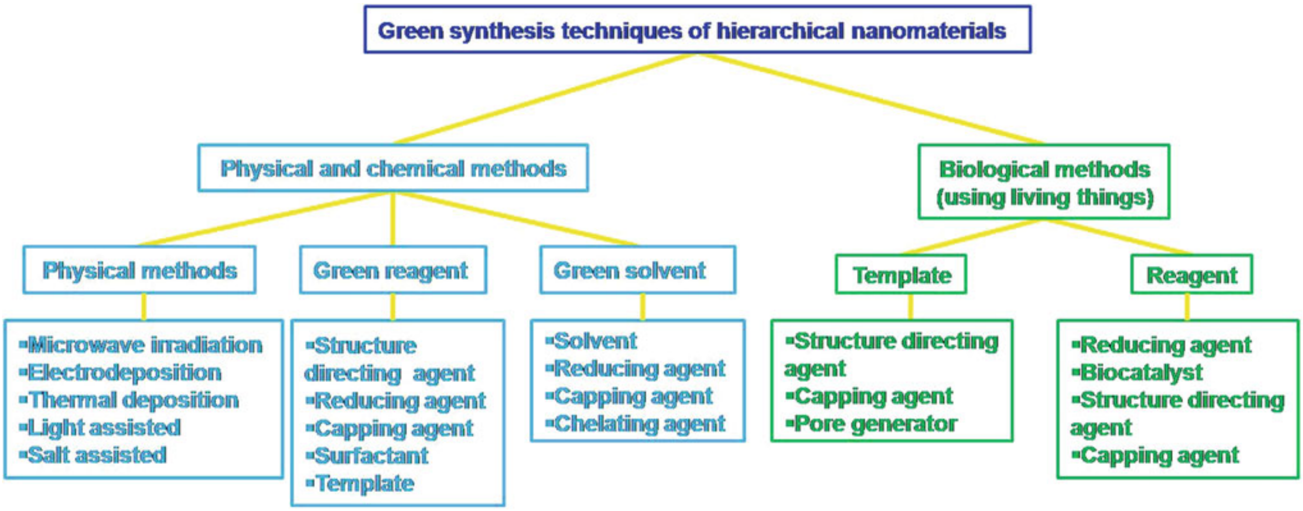

Fig. 5 Different green methods for the synthesis of metal and metal oxide HSNs

(a) physical, (b) chemical, and (c) biological methods (Fig. 5). For understanding the growth mechanism of the nanomaterials, it is essential to enter into the insights of the different methods, i.e., green physical, green chemical and green biological methods. In the literature, there are large numbers of reports available that has already been discussed in this chapter and the explanation on probable mechanistic aspects related to growth of nanoparticles toward the formation of hierarchically structured nanomaterials is also discussed. However, no generalized growth mechanism is yet found. This section describes the mechanistic pathways of formation of metal/metal oxide HSNs synthesized by physical, chemical, and biological methods with submethods also.

4.1 Biological Method

In recent years, the biogenic synthesis process also known as biological synthesis method toward producing metal/metal oxide nanomaterials has attracted substantial attention (Hulkoti and Taranath 2014). In this process, the nanomaterials can be synthesized using microorganisms and plant extracts. The biosynthesis can actually provide nanoparticles with ordered and controlled morphology (shape, size) and physiochemical properties as compared to some chemical and physical methods (Khandel et al. 2018; He et al. 2008). In this respect, there are previous reports on biocompatible and eco-friendly synthesis process based on microorganism (Hulkoti and Taranath 2014). The synthesized products can be used for pharmacological applications. However, one major disadvantage is that the mass production of the nanomaterials using microorganisms is often more expensive because of existing some of the critical handling protocols. On the other hand, the main advantage of plant-based synthesis approaches over conventional methods is being environmentally benign, low-cost, and scalable. In these processes, the use of high temperature, pressure, and toxic chemicals are not necessary. In brief, the microorganism and plant can be used in two ways for the synthesis of nanomaterials—(a) as reagent and (b) as template. In the next subsection, we will further discuss how they can function as reagents and templates.

4.1.1 Biomolecules as Reagents

It is important to mention that a common mechanism for the synthesis of nanoparticles employing microbes, for example, bacteria, fungi, algae, and yeast or biomolecules as reagents has yet not been conceived distinctly. One of the reasons is that the reaction mechanism of a biological reagent with a specific reactant like metal ions leading the formation of nanomaterials does not match with the other. In this respect, the formation of nanomaterials by microbes is known as an outcome of their defense mechanism toward the metal ions. Most of the reported works referred to enzymes, proteins. and lipids as the main biologically active materials that act as reducing, capping, and structure directing agents during the nanomaterials synthesis (Hulkoti and Taranath 2014; Mohammadinejad et al. 2016; Carbone et al. 2019). This is mostly due to of the defense mechanism of the microbes toward reduction of metal ions (He et al. 2008) and their aggregation with catalyzing the reaction medium (Dhandapani et al. 2020). The cell wall of the microorganisms also plays a crucial role in intracellular synthesis of nanoparticles/HSNs. In this process, an electrostatic interaction occurs between the positive charge of metal ions with the negative charge of the cell wall. The proteins that composes the cell wall enzymes reduce metal ions, resulting

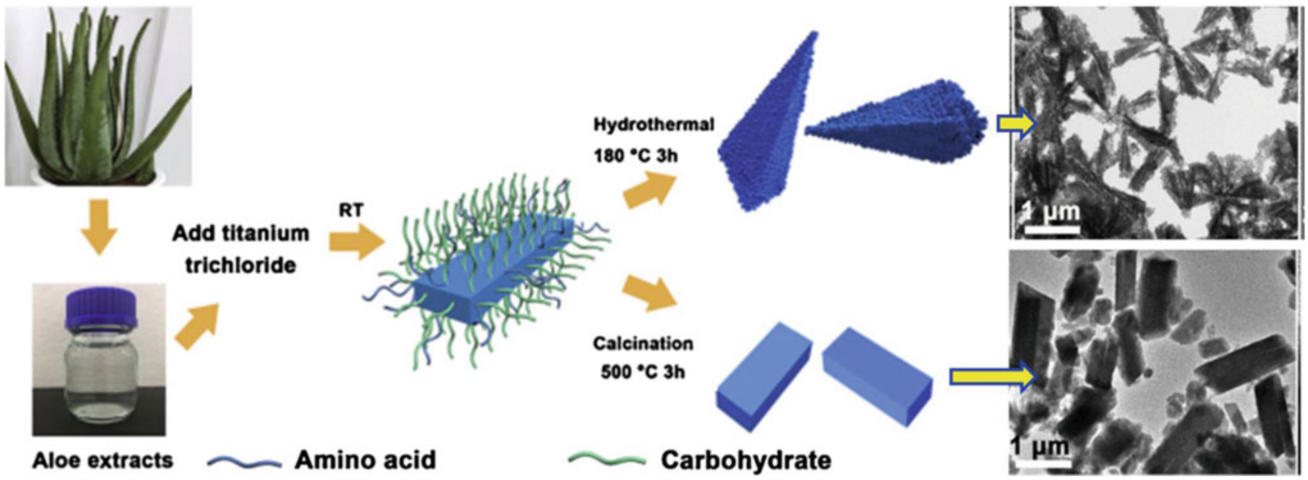

Fig. 6 Scheme for fabrication of tripyramidal and rod-like TiO_2. Copyrights reserved to the Elsevier (Li et al. 2020)

the formation of nanoparticles/nanomaterials with hierarchical structures (Kitching et al. 2016).

Similarly, plants have ability to precisely producing a variety of highly ordered hierarchical nanostructures. It is seen that various water soluble plant metabolites such as polyphenols, flavanoids, tannins, phytolexins, terpenoids, proteins, flavonoids, alkanoids, limonoids, amino acids, cellulose, saponin, pectin and hemicelluloses can act as reducing, capping and complexing agents for the synthesis of metal and metal oxide HSNs (Fig. 6) (Carbone et al. 2019; Bankar et al. 2010; Udayabhanu et al. 2017; Li et al. 2020; Suresh et al. 2020; Khaghani et al. 2017; Singh et al. 2017; Madan et al. 2015; Sundar et al. 2018).

4.1.2 Biomolecules as Templates

In our nature, different microorganisms are present in diverse morphologies such as spheres, rods, spirals, icosahedrons, and so on (Hulkoti and Taranath 2014; Khandel et al. 2018). Sometimes, these are varying size in length starting from nano to mesoscopic scales providing the base for metal ions that can act as low-cost and eco-friendly templates in potential applications of micro- and nanofabrication *via* green synthesis especially for hollow micro/nanoporous metal and metal oxide nanomaterials. So far, bacteria, fungi, yeast and algae have been employed successfully as biotemplates for the synthesis of controllable structures of various nanomaterials. A major advantage of this process is the specific morphology of a microbe. This offers a uniform and tunable biotemplate as base of the metal ions. Functional groups like OH–, CHO–, COO–, etc. present in the microbial cell wall bind the metal ions by electrostatic force of attraction whereas the cell wall acts as nucleation site of the metal ions. These avoid the need of additional surface modifying or templating agent for further ripening, self-assembly, and the growth of metal and/or metal oxide toward the formation of hierarchical nanostructures. After calcination, the decomposition of an organic microbial template as well as escape of CO_2 and H_2O occurs. Thus, one can make hierarchically porous nanostructures and in some cases, it results in the formation of hollow microstructures due to complete decomposition of the template. A brief mechanism of the synthesis of hierarchically ordered mesoporous TiO_2 using yeast (Cui et al. 2009) as biotemplate is displayed in Fig. 7.

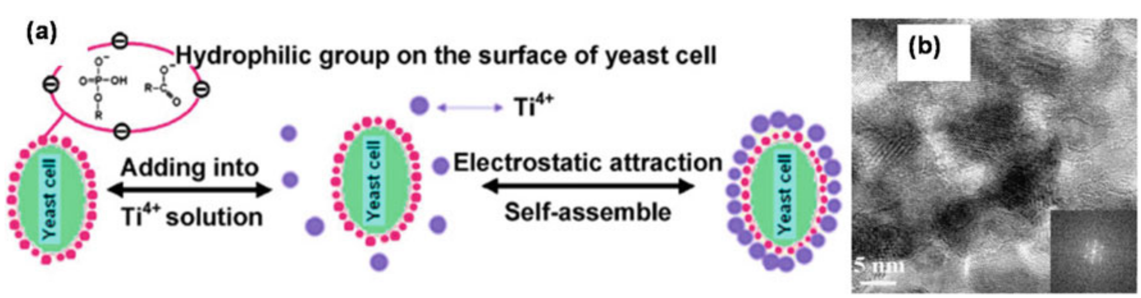

Fig. 7 **a** Illustration of ordered hierarchical mesoporous TiO_2 preparation process and **b** the corresponding HRTEM image of nano TiO_2. Copyrights reserved to the Elsevier (Cui et al. 2009)

Nature has already performed a fine job in creating humongous hierarchy in the structures of the living beings and creatures such as insects, plants and plant-derived products. Particularly, at the micro- and nanometer scales, these naturally abundant structures show such degree of elegance that it overshadows current man-made bioinspired structures as synthesized in conventional manners (Mohammadinejad et al. 2016; Ebrahiminezhad et al. 2018; Zan and Wu 2016). In general, the process consists of two dominant stages—(a) the assembly of the precursor and (b) template removal (Zan and Wu 2016). At first, a biotemplate is dipped into a precursor metal solution, which then diffuses and permeates into the template. In the next, the precursor metal ions self-assemble onto specific sites of the template *via* a molecular recognition process, deposit homogenously over the template by electrostatic attraction between metal ions and the functional groups (carboxylic, hydroxyl, amine, etc.) present in the cell wall template and form a stable organic–inorganic composite/hybrid/complex (Ramimoghadam et al. 2013a; Han et al. 2015; Mallampati and Valiyaveetti 2012). In the following steps, further growth of the precursor through the template occurs in which the template acts as the structure directing agent and the functional groups act as capping agents. When the growth of the nanomaterial extends up to its thickness capacity, the growth is ceased due to lack of space. Afterward, as the template is removed by calcination, porous metal/metal oxide nanomaterials are formed with magnificent hierarchy of the replicated specific template. Wood (Liu et al. 2009) (Fig. 8), pollen (Yang et al. 2011; Fazil et al. 2015), nanofibers (Wei et al. 2019; Xiao et al. 2013; Moyer et al. 2019), leaf (Li et al. 2009; Abu-Zied and Alamry 2019; Han et al. 2015), cotton (Mohamed et al. 2016; Ma et al. 2019), flower petals (Qian et al. 2011), fruit exocarps, inner coats and sprouts (Yan et al. 2006; Chen et al. 2008), rice and starch (Ramimoghadam et al. 2013a; Farzaneh et al. 2017) are some of the plant-derived biotemplates that had been used for the green synthesis for variety of nanomaterials. On the other hand, butterfly wings (Zhang et al. 2018,2006,2009) and eggshell membranes (Mallampati and Valiyaveetti 2013; Dong et al. 2007a,b; Fan et al. 2016), albumen (Nouroozi and Farzaneh 2011), and glutamine (Nouroozi and Farzaneh 2011) are the examples of widely used insect/animal-derived biotemplates.

4.2 Physical and Chemical Methods

The physical methods/techniques that are used in green synthesis of hierarchically structured nanomaterials involve requirement of less energy than the conventional methods. These can also reduce the use of harmful solvents, surfactants, and templates. Moreover, these are environment friendly and often cost effective. Microwave-assisted synthesis method is one of the most energy and time efficient methods that has been used widely for the synthesis of hierarchical nanomaterials (Lei et al. 2014; Tompsett et al. 2006). As the microwave energy increases, the heating rate of the medium and time of the overall reaction are reduced *vis-á-vis* a lower consumption of overall energy is possible. Microwave synthesis allows more uniform heating of the reaction mixture that leads to form homogeneous distribution of nanocrystals. This is expected to be one of the very crucial parameters toward the formation of hierarchical nanostructures.

Thermal decomposition and electrochemical deposition are another green approaches for the synthesis of ultra-pure nanostructured materials without using any fuel or leaving off toxic side products to the environment. As for example, 3D hierarchical nanopyramids and nanosheets array of Ag/Cu_2O and CuO nanoneedles had been fabricated using electrochemical deposition method (Ji et al. 2019; Momeni et al. 2016). In this respect, a reported study suggested that by controlling the reaction time and temperature, diverse superstructures of ZnO can be obtained (Udayabhanu et al. 2016).

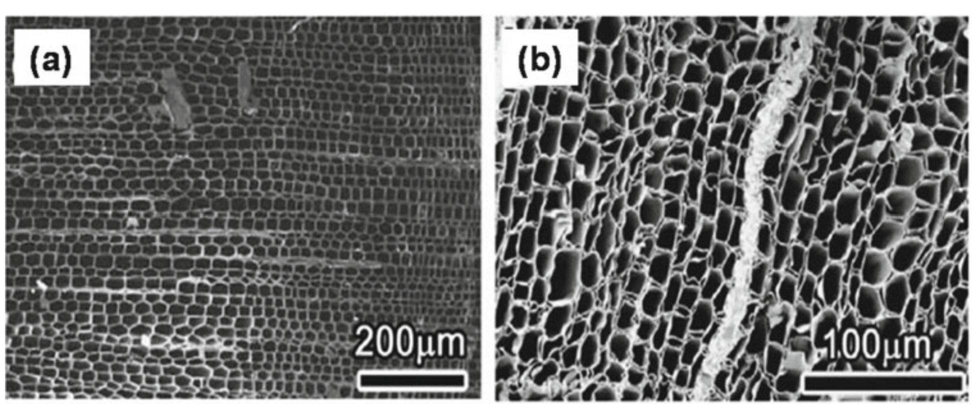

Fig. 8 FESEM images of **a** carbonized wood and **b** prepared ZnO using wood. Copyrights reserved to the Elsevier (Liu et al. 2009)

Using the precursor materials that undergo visible light-assisted decomposition is a unique and eco-friendly method for the synthesis of hierarchical nanostructures of especially metal oxides (Das et al. 2017; Hu et al. 2016). In this method, high temperature, heat or reducing agents are not required and only the presence of light is required for accelerating the reaction toward formation of nanostructures. For example, in a green and sustainable pathway, the sunlight-assisted decomposition phenomenon of $KMnO_4$ gives rise to hierarchical flower-like MnO_2.

Environmentally benign reagents such as amino acid (Gao et al. 2008), metal (Zhang et al. 2011), glucose (Yang et al. 2013), polyethylene glycol (Gao et al. 2012; Lee et al. 2016), and dopamine (Ye et al. 2015) have been used in the green synthesis of HSNs. In this case, the reagents can perform multifunctions such as reducing agents, structure directing agents, and capping agents in a surfactant and template-free synthesis. Thus, atom economy that is one of the principles of green synthesis can also be maintained properly. Although the exact functional mechanism is very difficult to investigate, the organic functional groups like carboxylic and amines groups present in the green regents are known to be responsible for their multifunctionalities. It is noteworthy that biopolymer alginate has generally been used as cross-linker for manganese ions to form hierarchically structured nanoporous metal oxide hybrids (Wang et al. 2016) (Fig. 9) whereas the reducing agent, surfactant and structure directing agents are to be found responsible for creating flower-like nanopetal assembly of δ-MnO_2 (Zong et al. 2016).

Some of the reported studies show that no additional foreign reagents and reducing agents have been used but complex (Sinhamahapatra et al. 2012) and metal oxide framework (Hu et al. 2018) can act as reducing and structure directing/evolving agents for the synthesis of hierarchical metal and metal oxide nanomaterials. Sinhamahapatra et al. (2012) reported the synthesis of hierarchically structured porous ZnO, where the assembled bundles of woolen threads like hydrozincite, $Zn_5(CO_3)_2(OH)_6$ architectures had initially been synthesized and used as the precursor. Upon calcination, the evolution of CO_2 and H_2O took place with the formation of porous nanostructures of ZnO retaining original morphology of hydrozincite (Fig. 10).

Sustainable solvents and additives are other important materials used for the green synthesis of metal and metal oxide HSNs. Water, ethanol, glycerol, ethylene glycol, and urea are some of environmentally benign solvents and additives that are used widely. These solvents function as reducing agents (Beshkar et al. 2017), chelating/capping agents (Singh et al. 2016), and structure directing agents (Singh et al. 2016; Hou et al. 2015; Nayak et al. 2017) in the synthesis process. The combination of hydrogen-bond acceptors (glycine, betaine, or acetylcholine chloride) and donors (urea, oxalic acid, ethylene glycol, or glycerinum) had been used strategically for controlling the morphology of TiO_2 nanostructures where these materials played the role of solvent, template, and inhibitor (Wang et al. 2018).

5 Applications of Hierarchically Structured Metal and Metal Oxide Nanomaterials

In this section, different potential applications of green synthesized metal and metal oxide nanostructures have been discussed. These applications basically rely upon the properties of metal and metal oxides such as morphology and porosity developed during the process of synthesis.

5.1 Biomedical Application

Nanomaterials produced by green synthesis methods have a wide range of applications in biomedical and pharmacological fields for antibacterial, antifungal, and antioxidant applications (Yuliarto et al. 2019). Due to small particle size and high surface area of the nanomaterials, they can easily attach to microbial membranes in a closer proximity

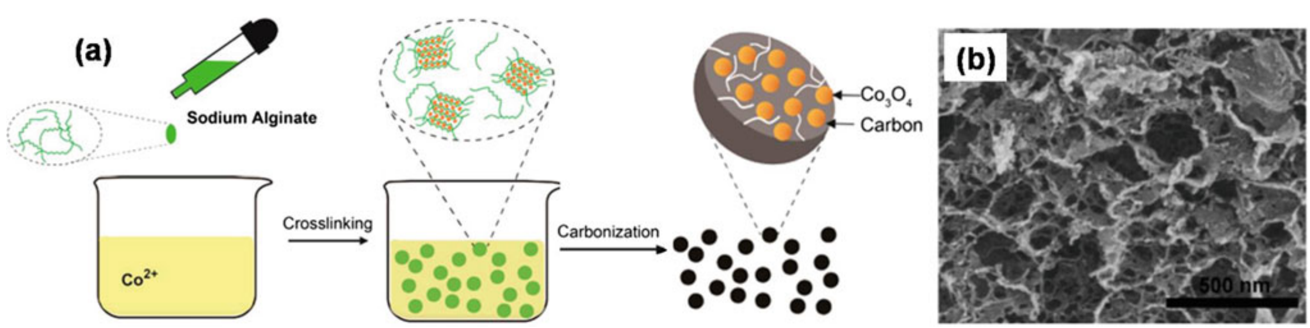

Fig. 9 **a** Schematic of the synthesis process and **b** SEM image of nanoporous Co_3O_4/C hybrids. Copyrights reserved to the American Chemical Society (Wang et al. 2016)

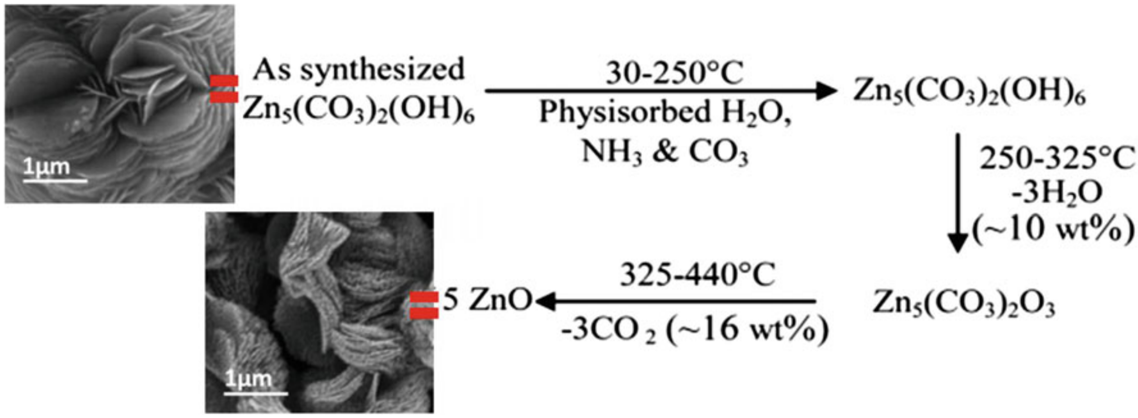

Fig. 10 Schematic for the synthesis of ZnO replications from hydrozincite. Copyrights reserved to the Royal Society of Chemistry (Sinhamahapatra et al. 2012)

compared to their bulk counterparts (Seth et al. 2020). Although, the mechanism of antimicrobial activity has not been understood clearly, the physical damage of the cell wall caused by the nanoparticles had been reported to be responsible for cell death of microbes. Release of metal ions from nanostructures is also said to be playing an important role for the antimicrobial activity. In this respect, *Spirulina* templated Ag nanosheets showed excellent bactericidal activity against *S. aureus*. Additionally, the slow release of Ag^+ ions reduces the chance of adverse impact of ionic silver to our environment (Sun et al. 2019). Moreover, a study revealed that the Ag^+ possess good adaptability. Thus, it can be used in applications such as food safety. Fungicidal activity of dendritic Ag nanoparticles against plant pathogen *F. Graminearum* can practically be used in crop plant protection (Carbone et al. 2019). It has been reported that nanoflowers-shaped Au nanoparticles are hemocompatible and can be used as suitable bioconjugates in therapeutic and biomedical fields (Kitching et al. 2016). It is important to note that the accessibility of Ag^+ ions in the hierarchical dendritic architecture had been reported to be the limiting factor for its fungicidal activity. In another example, ZnO superstructures showed antibacterial activity against both gram positive and negative bacteria (Udayabhanu et al. 2017; Madan et al. 2015). Also, hierarchical CuO nanostructures showed antibacterial activity against gram positive and gram negative bacterial strains (Suresh et al. 2020). The probable factor for killing the bacteria is attributed to generation of reactive oxygen species (superoxide and hydroxide radicals) formed by CuO nanostructures and the affinity of amine as well as carboxylic acid groups present on the cell wall of bacteria may result the formation of Cu^{2+} ions. Moreover, CuO nanoparticles can easily enter into comparatively bigger pores of bacteria causing malfunction in cell enzyme resulting cell death. They also have the potential antioxidant properties, attributed to their small crystal size and hierarchical bullet shaped morphology.

5.2 Environmental Remediation

5.2.1 Wastewater Treatment

To color the final products, various dyes are substantially used in textile, paper, plastic, cosmetic, leather, drug and food processing industries. These dyes are eventually released into water bodies and soil that can severely affect the environment, hamper the ecosystem of water body and cause serious health hazards to human beings (Fang et al. 2019). A considerable amount of research had already been performed for the fabrication of metal/metal oxide nanomaterials as efficient photocatalysts for degradation of the organic dyes under UV/visible light irradiation (Bera et al. 2016c). In the photocatalysis process, toxic organic pollutants photo-degrade into non-toxic by-products through mineralization, without further waste production. In this respect, semiconductor absorbs photon with energy equal or more than the band gap of the semiconductor can generate electrons and holes in the semiconductor system. If the recombination rate of charge carriers is slow, the species will travel to the surface, where the free electrons reduce oxygen and forms peroxides/superoxides and holes that oxidize water and forms OH· (Udayabhanu et al. 2017). These highly reactive and unstable species finally lead to photo-degrade organic dyes. It is also known that biosynthesized nanomaterials exhibit an excellent photocatalytic performance due to high surface-to-volume ratio and the existence of higher number of active sites compared to polycrystalline materials (Fang et al. 2019). Other important factors that affect the photocatalysis performance are crystallinity, porosity, particle size, morphology, particle size distribution and band gap of a photocatalyst.

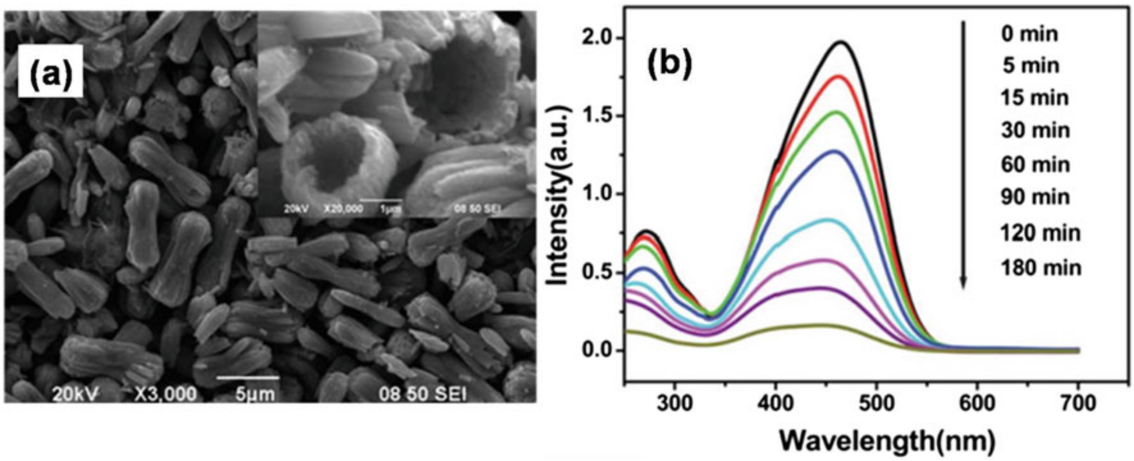

Fig. 11 FESEM image (**a**) and photocatalytic study, (**b**) hollow peanut-like ZnO powder. Copyrights reserved to the Royal Society of Chemistry (Wang et al. 2012).

TiO_2 and ZnO are some of the well-known photocatalysts mostly used in water pollution alleviation *via* photocatalysis as they are cost effective, non-toxic, chemically, and mechanically stable and they can easily form hierarchically structured nanomaterials. In an example, hollow double-caged peanut-like ZnO microstructures had been reported for the photocatalytic degradation of methyl orange under UV irradiation (Wang et al. 2012) (Fig. 11). After 180 min of irradiation, the characteristic peak of the dye was found to be eliminated by ZnO. The large surface area of nanorods assembled peanut structure and commodious interspaces of ZnO microstructure are highly effective for the diffusion and mass transportation of dye molecules and hydroxyl radicals for photocatalytic degradation of dye. In this respect, Li et al. (2009) reported an improvement in photocatalytic activity of leaf templated hierarchical porous morph-TiO_2 than non-templated TiO_2, indicating the contribution of porous and layered nanostructure of morph-TiO_2 toward the catalytic activity.

Adsorption is also an efficient method of dye removal from wastewater. Nanofibrous network of Mn_3O_4 had been used for absorbing a wide range of organic dyes by electrostatic attraction between the surface of Mn_3O_4 and organic compounds in aqueous solution (Mallampati and Valiyaveetti 2012).

5.2.2 Energy Storage

Transition metal oxide-based nanomaterials have been widely used as potential electrode materials (PEMs) for pseudocapacitors (Zhang et al. 2019b), Li-ion batteries (Hashem et al. 2018; Wei et al. 2019; Gao et al. 2008; Hou et al. 2015; Hu et al. 2018; Li et al. 2017), and supercapacitors (Wang et al. 2016; Zong et al. 2016; Sinhamahapatra et al. 2012). On this aspect, flower-like nanostructured $NiCo_2O_4$ that composed of ultrathin nanopetals (thickness ~15 nm) having large specific surface combined with narrow pore size distribution can be considered as one of the significant examples of PEMs (Lei et al. 2014). It is seen that the flower-superstructure composed of mesoporous nanopetals with high surface area is responsible for exhibiting high capacitance and stability of $NiCo_2O_4$, as the nanopetals can provide a large number of electroactive sites for Faraday reaction. Consequently, the microflower can act as an *ion-buffering reservoir* and expedites a quicker permeation process of electrolyte into nanopetal matrix. Zhang *et al.* reported (Zhang et al. 2019b) the synthesis of hierarchical porous MnO@biocarbon (BC) nanocomposite using molted salt assisted method. The highly porous HSN can be used as supercapacitor electrode materials for electrochemical energy storage as well as lithium-ion battery anodes.

5.2.3 Sensing

Gas sensing is analyzed by detection of the variation of conductance of a sensing material that occurs because of the surface reactions between the target gas molecules and the sensing particles (Lee 2009). Obviously, for gas sensing, the surface area with higher hierarchical porosity is required so that the porous network with excellent interconnectivity and mass transportability can supply plentiful connective multiscale channels toward the transportation of gas molecules to directly sensing by metal oxide nanoparticles (Song et al. 2012). In addition, the temperature is a crucial factor affecting the sensitivity of gas sensing performance of metal oxide nanomaterials.

It is also noticed that pollen coats of rape pollen grains have been used to synthesize highly connective hierarchical porous network structure of SnO_2 (Song et al. 2012). Interconnected mesoporous network further can be extended to macro- to nanoscale pores. This makes SnO_2 an excellent candidate for selective sensing of C_2H_5OH, CH_3COCH_3 and

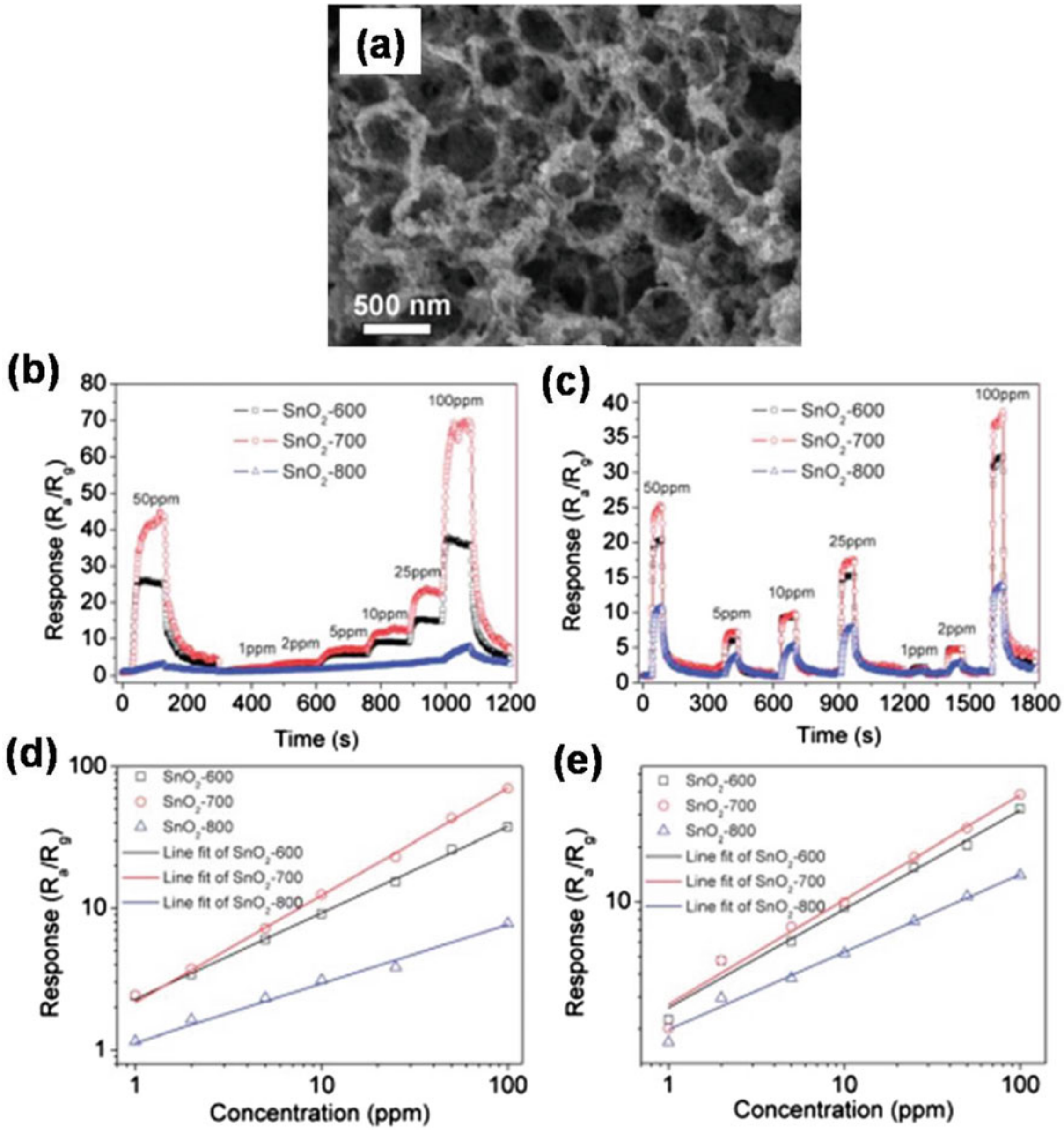

Fig. 12 **a** FESEM image of SnO_2, sintered at 700°C; **b**, **c** real-time response curves and **d**, **e** response dependens on gas concentrations of the sinters; **b**, **d** to C_2H_5OH at 210 °C; **c**, **e** to CH_3COCH_3 at 290 °C. Copyrights reserved to the Royal Society of Chemistry (Song et al. 2012).

Cl_2 (Fig. 12). In another example, wood template-mediated synthesis of hierarchically porous ZnO showed exceptional selective gas sensing for H_2S (Liu et al. 2009). In this case, the hierarchically porous ZnO with higher porosity and surface area provided more surface adsorption positions and reacting areas for oxygen and test gases that helped the target gases to transfer more quickly leading to increase gas response, in comparison to lower gas sensitivity of non-template based ZnO.

Green synthesized 3D chestnut-like structures of Ag decorated WO_{3-x} are found to be used as clean, stable, and recyclable SERS substrate which is able to identify and provide the fingerprint structural information on various analytes even at low concentration (Huang et al. 2017). The material also has exceptional self-cleaning ability.

6 Present Challenges and Future Prospect

Nowadays, hierarchically structured metal and metal oxide nanomaterials have been widely studied for their special surface structures and remarkable applications in various fields including but not limited to pharmaceutical, biomedical, electronics and environmental remediation. These nanomaterials are particularly in demand because of their characteristic features like large surface area with exceptional surface morphology with high porosity. Biological mode has become an important part of nanotechnology where bioagents are used as reagents and templates for the synthesis of hierarchical nanomaterials. However, certain limitations are there in these nanomaterials for their practical production and relevant applications. These must need to be resolved by the scientific community. Firstly, one of the major limitations lies in the lack of complete and in-depth understanding of mechanism of biofabrication of the nanoparticles/nanomaterials. There are several reports available in literature where reasonable hypotheses had been proposed to explain the experimental results and biologically active molecules responsible for biomineralization of metal ions using bioextracts/templates. However, a detailed analysis of the biochemical mechanism is further needed for the development of green HSNs with desired and controlled structure, size, morphology, dispersity, and related properties (Gahlawat and Roy Choudhury 2019; Deng et al. 2011) toward their real applications. Secondly, large-scale production of nanomaterials synthesized by adopting green synthesis methods is mostly obstructed by inability to fully control the structure, size, and morphology of hierarchical nanomaterials along with other concerns toward polydispersity and low yield. The synthesis of nanomaterials at ambient temperature by using natural reagents as reducing/capping/structure directing agents without any toxic additives may make the process for large-scale production in cost-effective and environmental friendly. Also, the large-scale production of monodispersed nanomaterials with narrow size distribution and high yield can be achieved by optimizing the diverse synthesis parameters such as solution pH, temperature and time of reaction, concentration ratio of biomolecules and metal precursors. Interestingly, instead of bacteria, fungi can be used for the production of humongous concentration of nanoparticles as fungi is able to discharge larger amounts of proteins which lead to higher productivity of nanomaterials. In addition, an exploration of microbial diversity of novel, sustainable microorganisms with varying shape may be used as reagent/template for the synthesis of hierarchical nanomaterials. Often, the nanomaterials cannot be effectively separated or regenerated after participating in catalytic/adsorption reactions, hence effective techniques must be established for this purpose. Finally, the synthesis of HSNs using microorganisms is a slow-going process that may take up to several hours or even few days. Green chemical and physical methods as discussed in this chapter can be established as less time-consuming method because they need less time to complete and produce materials with controlled shape and size and higher yield of products. These methods are also easy to handle in comparison to microorganisms which have a high risk of contamination. Another important issue is the biocompatibility and bioavailability of the produced nanomaterials and their environmental sustainability. In this regards, more extensive research and clinical trial are required to study the cytotoxicity and genotoxicity of the synthesized nanomaterials for their practical use in biomedical, pharmaceutical and agricultural fields as well as wastewater purification.

Without causing any further harm to our environment, the green synthesis methods that evolved from the greatness of nanotechnology toward production of large-scale hierarchically structured nanomaterials has a bright future for application in various sectors like health, water, food, and energy. A collaborative research is indeed necessary for understanding the detailed mechanistic aspects, exploration of new biological agents and finding out innovation by cost-effective biological, physical, and chemical green synthesis methods.

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