Supramolecular Electrochemistry: Recent Trends and Perspectives

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1 General Overview

This chapter describes recent advances in the construction of functional self-assembled nanomaterials from molecular building blocks using supramolecular chemistry concepts and suitable self-assembly processes. Supramolecular self-assembly is the spontaneous arrangement of molecular components into well-defined nanostructures that can be stabilized by general interaction processes: (i) dynamic covalent (e.g. imine and disulfide bonding), (ii) reversible noncovalent interactions (e.g. electrostatic interactions, hydrogen bonds, hydrophobic, and hydrophilic interactions, and van der Waals interactions), and (iii) mutual associative approach [1].

The interaction of components at the molecular level allows the formation of self-assembled nanomaterials with diversified structures and functionalities. These nanoarchitectures can be achieved through molecular associative recognition, self-organization, and dynamic nature [2]. For this proposal, the use of molecular building blocks performs a crucial role in supramolecular self-assembly process due to their versatility and functionality.

Building blocks can also be oriented towards the development of robust architectures onto electrode, such as self-assembled monolayers (SAMs), layer-by-layer self-assembly, and electrochemical deposition. In this case, the electrochemical supramolecular approach can be utilized to investigate kinetic and thermodynamic study of electrochemical redox and electron transfer process from self-assembled organized structures as well as investigating the electron transport mechanism. We

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will describe how electrochemistry supramolecular can be utilized to control electrochemical conversion, affect the structure, and supramolecular systems properties. Special emphasis will be given to the electrochemistry mechanism of host–guest complexes, substrates modified, monolayer, and multilayer assemblies. Finally, we conclude with an outlook toward future developments of self-assembled nanomaterials for constructions of new (bio)sensor, energy storage, electronic, and electrochemical devices.

2 Versatile Building Blocks Used for Supramolecular Self-Assembly

Different individual components can be used for construction of supramolecular nanostructures, such as metallic nanoparticles (MNPs) [3], coordination compounds [4, 5], semiconductive oxides [6, 7], carbon-based materials [8], and biomaterials [9]. Figure 1 illustrates the shapes and structures of some building blocks discussed in this chapter. The following subsections have been organized in order to show the importance of the components in the context of supramolecular chemistry.

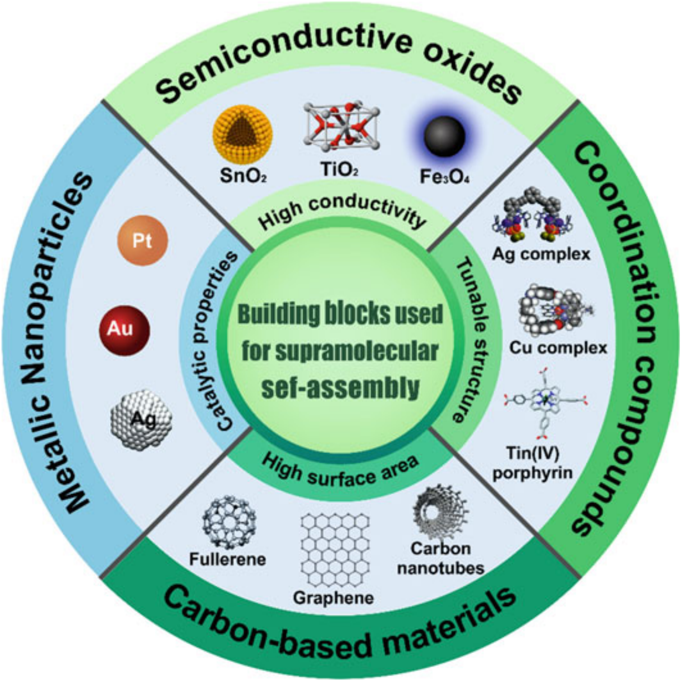

Fig. 1 Scheme of the versatile building blocks used in supramolecular chemistry. Adapted and reprinted with permission from Ref. [10, 11]. Copyright 2014 Royal Society of Chemistry

2.1 Metallic Nanoparticles

Metallic nanoparticles (MNPs) have received considerable attention of scientific community owing to their catalytic properties, antibacterial activity [12]; high surface-to-volume ratio and unique optical and electrical properties [13, 14]. The surface functionalization of MNPs enables the use of these as molecular building blocks for supramolecular chemistry.

Among the most used MNPs by literature we highlight the gold nanoparticles (Au NPs) due to their low toxicity, high chemical stability, and their unique and tunable plasmonic properties [13]. Zhang [3] used Au NPs as individual components to develop an improved glucose sensor. The high catalytic activity exhibited by Au NPs improved the charge transfer between the glucose and the GOX enzyme during the oxidation–reduction reaction resulting in a doubling of electrode sensitivity. The electrode containing the Au NPs showed high sensitivity (216.9 μA m mol L^{-1}) and low detection limit (1×10^{-6} mol L^{-1}), confirming that the electrode is a potential candidate for the non-invasive monitoring of glucose [3]. Golub et al. [15] used Pt NPs, CdS NPs, and Au NPs functionalized with an anticocaine aptamer subunit in the detection electrochemical, photoelectrochemical, and surface plasmon resonance (SPR) detection of the cocaine, respectively. The formation of the supramolecular complex obtained by the interaction between the Pt NPs-aptamer and the cocaine subunits allowed the detection of cocaine by the electro catalyzed reduction of H_2O_2. The photoelectrochemical detection of cocaine was achieved due to the photocurrents generated by the complex formed between the cocaine subunits and the CdS-NPs-aptamer, in the presence of amine triethanol as a hole-eliminator. The supramolecular Au-NPs-aptamer subunits-cocaine complex generated on the Au support allowed the SPR detection of cocaine through the reflectance changes when stimulated by the electronic coupling between the localized plasmon of the Au-NPs and the surface plasmon wave. All the developed aptasensors allowed an analysis of cocaine with a detection limit in the range of 10^{-6}–10^{-5} mol L^{-1} [15].

Lopes et al. [16] developed gold (Au NPs) and silver (Ag NPs) nanoparticles through a green route, using tannic acid (TA) as a reducing and stabilizing agent. The supramolecular interactions between Au NPs, Ag NPs and TA were responsible for the bathochromic shift (red-shifted) of the surface plasmonic resonance (SPR) bands of these nanoparticles [16].

2.2 Semiconductor Oxides

Metal oxide semiconductors represent a diverse and fascinating class of materials because of their high surface volume ratio, abundant active sites, and surface defects, which provide good detection limits, making them attractive for the development of materials with applications in various areas [17].

The magnetite nanoparticles (Fe_3O_4 NPs) have shown good biocompatibility, low toxicity, magnetic properties, easy to obtain, high surface area, and suitable functionalization, making them attractive for various chemical and bio related applications, such as enzyme interaction, drug delivery, wastewater treatment, and toxic analytes sensing [18, 19]. For example, Lima and collaborators [20] used Fe_3O_4 NPs, poly(allylamine hydrochloride) (PAH), poly(vinyl sulfonic acid) (PVS) and polypyrrole (Ppy) to develop layer-by-layer (LbL) films deposited onto gold substrate with three distinct supramolecular architectures: $(PAH/Ppy)_n$, $(Fe_3O_4\ NPs/PVS)_n$, and $(Fe_3O_4\ NPs/Ppy)_n$. The $(Fe_3O_4\ NPs/Ppy)_n$ film showed stronger electrostatic interaction, higher conductivity, as well as a more homogeneous substrate covering in comparison to the other developed films, demonstrating a synergistic effect between Fe_3O_4 NPs and ppy. The electrochemical and surface plasmon resonance analysis confirming that Fe_3O_4 NPs-Ppy film can be used as an electrochemical or optical non-enzymatic sensor for analytical detection [20].

Titanium oxide clusters—TOCs (also called polyoxotitanates or titanium–oxo clusters), belong to a class of molecular analogs of TiO_2 and titanate minerals, which have a well-defined structure and are passive in functionalization. TOCs have good chemical stability, photocatalytic properties, and redox activity, making them promising materials for developing hierarchical structures using bottom-up approaches [7]. Chen et al. [21] linked the TOCs-based tetrahedral clusters of Ti_4L_6 (L = embonate) with transition metal ions, such as Zn^{2+}, Co^{2+}, and Mn^{2+}. Ti_4L_6's tetrahedral geometry and its calixarene-like coordination active vertices facilitate the incorporation of coordination bond metal through π–π stacking interactions and other non-covalent interactions, which characterize it as an excellent building block. Metal–organic frameworks (MOFs) based on TOCs showed high water and heat resistance and excellent gas adsorption properties [21].

Zinc oxide is an n-type semiconductor, which has a wide band gap around 3.37 eV and high exciton binding energy ($\sim$60 meV). Due to its unique multifunctional physical and chemical properties, as well as its biological activity, it has called the attention of the scientific community a few years [22, 23]. Hassan and collaborators [24] developed a new nanomaterial from zinc oxide nanoparticles (ZnO NPs) microrecycled from spent Zn-C batteries, and 3D graphene hybrid aerogel. Graphene interacts weakly with ZnO NPs via van der Waals weak interaction, thus the electronic properties of graphene could be conserved in the hybrid material. The nanomaterial has elevated sensing properties with higher sensitivity, lower detection limit and fast response-recovery time, proving to be efficient for the detection of NO_2 due to the improvement in the conductivity of the nanomaterial and the porous structure of grapheme. It is interesting to point out that decorated ZnO NPs' gas detection mechanism follows the surface charge model [24].

2.3 Carbon-Based Materials

Carbon-based materials comprise an important class of materials used as molecular building blocks in supramolecular chemistry; this is mainly due to the wide variety of allotropes from 0 to 3D that provide numerous possibilities for constructing new supramolecular entities. They include graphene-based materials, fullerenes, carbon quantum dots, nano-onions, carbon nanotubes, nanocones called nanohorns, and nanodiamonds [25]. It is also important to emphasize that these materials mostly have low cost, good mechanical stability, flexibility, biocompatibility, in addition to being thermal and electrical conductors [26]. Figure 2 shows the structure of some carbon allotropes and their main properties.

Carbon dots are a newer class of carbon allotropes prepared by top-down and bottom-up approaches [8]. Due to excellent physico-chemical properties and biocompatibility, the carbon dots have aroused the scientific community's interest in recent years. It is noteworthy that with their ease of functionalization, they can be used as self-assembly building blocks [29]. Furthermore, carbon dots can be synthesized from abundant and non-toxic materials, such as biomass [30].

Sarkar et al. [29] developed carbon dots with different aliphatic/aromatic substitutions (cholesteryl, palmitoyl, naphthyl) with spacers, such as ethylenediamine, p-phenylenediamine, 2.2′-(ethylenedioxy) bis (ethylamine). Moreover, they demonstrated the formation of self-assemblies using amphiphiles exclusively based on carbon dots for the first time. Wang et al. [25] in turn, synthesized fluorescent carbon dots with [$GdCl_3Br$] with magneto-responsive properties (CQDGd) and used them

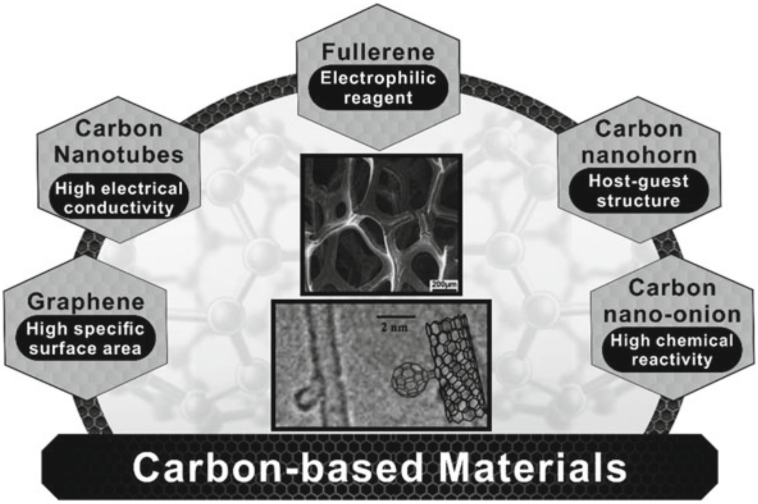

Fig. 2 Schematic representation of the main types Carbon-based materials. Adapted and reprinted with permission from Refs. [27, 28]. Copyright (2007 and 2012) American Chemical Society and Nature

as building blocks to form hybrid DNA nanospheres (ssDNA) using a simple self-assembly synthetic route. The phosphate and nitrogen bases of the dimple DNA strand served as self-assembly sites; thus, the CQDGd/ssDNA nanospheres were formed by interactions between Guanine and Cytosine through hydrogen bonds, hydrophobic interactions, and synergistic electrostatic forces [25].

Fullerenes are zero-dimensional (0D) carbon nanomaterials with hollow and perfectly spherical structures made up of five- and six-membered rings. There are several forms of fullerene, such as C_{60}, C_{70}, C_{76}, C_{82}, and C_{84}, with C_{60} being the most commonly studied [25, 31, 32]. These nanomaterials have a high affinity for electron transport [31] and have shown great potential in applications in areas, such as, energy and photocatalysis [32], solar cells, photodynamic therapy [33], biomedicine, among others. Shahzad et al. [34] used fullerene as a building block to develop a new heterogeneous photocatalyst for H_2 synthesis. Among the factors that contributed to the excellent performance of the photocatalyst, WO_3/fulereno@$Ni_3B/Ni(OH)_2$, the synergistic effect between the WO_3/fullerene nanocomposite and the cocatalyst, $Ni_3B/Ni(OH)_2$ stood out [34].

The combination of mechanical, thermal, optical, and electrical properties make graphene, a 2D (two-dimensional) material, the most widely investigated carbon-based material [26, 35]. Graphene has a unique crystal structure, having carbon atoms bonded in sp^2 hybridization, organized as a flat sheet of one atom thick [35]. One of their derived is graphene oxide which there is the presence of oxygenated groups, such as hydroxyls or carbonyls, in its structure. In recent years, graphene oxide, GO, has been used as a two-dimensional building block to form supramolecular hydrogels. Liu et al. [36] used graphene oxide to form hybrid supramolecular hydrogels with amino-functionalized silica nanoparticles (SiO_2–NH_2 NPs). Herein, SiO_2–NH_2 NPs interacted with GO nanosheets through hydrogen bonds between –NH_2 and –COOH in SiO_2–NH_2 and GO, respectively forming insoluble nano building blocks in a wide concentration range [36].

Another carbon allotrope that has received considerable attention from researchers in recent years is the carbon nanotube (CNT). CNTs can exhibit one, two, or more tubular graphite walls [31, 37]. The electronic properties and chirality of CNTs depend on how the graphene sheet is rolled during the tubular structure formation [37]. The strong interactions of van der Waals and π–π give CNTs a potent tendency to form aggregates, making their use difficult for some applications. However, their unique chemical, physical and electronic properties, excellent mechanical properties, and tunable surface functionality make CNTs promising in developing different materials, especially their electronic properties [38, 39]. In this sense, Ortiz et al. [39] proposed a new strategy for forming an innovative nanoarchitecture through the non-covalent functionalization of multi-walled nanotubes with ConcanavalinA (ConA), a protein, directly. ConA immobilization on multi-walled CNTs provided specific properties for supramolecular immobilization of glycoenzymes to construct bienzymatic glucose biosensors [39].

In the class of carbon allotropes, carbon dots have shown an upward trajectory for future applications due to luminescence properties, the possibility of green synthesis, and nanoscale dimensions. However, graphene-based materials represent the most studied carbon-based material, followed by carbon nanotubes until today [8].

2.4 Coordination Compounds

The directed synthesis of coordination compounds has attracted considerable attention in supramolecular chemistry and crystal engineering [4]. For instance, bis (benzimidazole) (Bbim) has been widely used in coordination chemistry, as it can join two or more metal centers, therefore, considered a ligand with variable denticity. Samoľová et al. [4] synthesized four new complexes with manganese (IV) and bis (benzimidazole) with different crystal structures in all complexes demonstrating that the Bbim ligand is a robust building block in the formation of supramolecular complexes [4]. Sun et al. [5] used polydiallyl malonylurea (PDAMU) as a building block to form complexes with silver ions (PDAMU-Ag). The PDAMU-Ag complex exhibited high antibacterial activity against Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*). Other results suggest that PDAMU can be used as a tool for constructing organometallic systems contributing to supramolecular chemistry and materials science [5].

The Prussian Blue (PB) and Prussian Blue Analog (PBA) complexes are important building blocks for the synthesis of different nanocomposites. These compounds have structural, thermal, and electrochemical properties which make them promising candidates for applications in different areas. PB and PBA present the general structural formula $M_{ax}{}^{+}[M_b(CN)_6]_y.\ nH_2O$, in which, for PB, $M_a = M_b = Fe$, and for PBA, M_a and M_b represent a transition element [40, 41]. It should be noted that PBA-based materials are low cost and easy to obtain [42]. Niu et al. [42] developed a Prussian blue analogue of nickel and cobalt and used it as a new high-efficiency non-enzymatic sensor for glucose detection. The developed Ni-Co PBA presented an excellent catalytic performance for the electro-oxidation of glucose when compared with pure Ni PBA and pure Co PBA. The analysis of the experimental data confirmed that the sensor based on Ni-Co PBA had a low detection limit (1.2 m mol L^{-1}), wide linear range (0.002–3.79 m mol L^{-1}), good selectivity and high sensitivity (149 μA mM^{-1} cm^{-2}) suggesting that this is a promising sensor for detecting glucose in real samples [42].

Rodrigues and collaborators [41] used the Prussian blue analogue of copper ($Cu_2[Fe(CN)_6]$) as components for the formation of the $CuO/Cu_2[Fe(CN)_6]$ nanocomposite and investigated its electrical properties in the presence of H_2O_2. The data obtained by cyclic voltammetry revealed a change in faradaic currents in the presence of peroxide; the nanocomposite showed two well-defined redox pairs (from Cu^{+}/Cu^{2+} and $CuFe^{2+}$ to $CuFe^{3+}$), on the other hand, the precursors, CuO and $Cu_2[Fe(CN)_6]$, showed only a slight intensified effect for oxidation [41].

Carvalho et al. [43] used the cobalt Prussian blue analogue, $Co_3[Co(CN)_6]_2$, to construct a magnetically separable nanocomposite through interaction with magnetic nanoparticles. The developed $Co_3[Co(CN)_6]_2/Fe_3O_4$ nanocomposite presented a nanocubic shape decorated with small magnetite spheres that interacted through dipole–dipole interactions. An increase in faradaic currents for the Co^{2+}/Co^{3+} pair present in the voltammograms of the hybrid nanomaterial compared to the isolated, $Co_3[Co(CN)_6]_2$ was observed. The magnetic properties of Fe_3O_4 NPs were preserved even after adsorption of cobalt Prussian blue analogue nanocubes. The nanocomposite also showed promising catalytic properties, demonstrating, therefore, that the approach used is effective to produce hybrid nanomaterials with a combination of magnetic and electrochemical properties [43].

Moraes and collaborators [44] developed a new hybrid material consisting of Prussian blue (PB) and cashew gum polysaccharide (CG), a biopolymer that has antibacterial, antitumor, healing, and gastric potential properties, in addition to being biocompatible, biodegradable, and non-toxic and determined its potential as an electrochemical sensor for the oxidation of drugs. The analysis of the data obtained by the electrochemical tests showed that the bionanocomposite formed, PBNPs@GC, has the capacity to oxidize some drugs, such as acetaminophen (ACT), metamizole (MTM), and methotrexate (MTX), indicating that this material shows promise for the development of sensors for clinical and pharmaceutical samples [44].

2.5 Others Classes of (Nano)materials

Another material class which is commonly used as a building block for supramolecular chemistry is polyphenols (tannins), which has several advantages for engineering biomaterials, as they are biodegradable, biocompatible, and abundant in nature. The properties of these biomaterials provide the possibility of use as antioxidant, drug delivery system, cell biohybrids, and for diagnosis [45]. The natural polyphenol, tannic acid (TA), and poly(2-n-propyl-2-oxazoline) (PnPropOx) were used by Mathivanan et al. [46] for the formation of TA/PnPropOx multilayer thin films joined by hydrogen bonding and hollow capsules manufactured by a sequential coating of TA and PnPropOx onto $CaCO_3$. The authors further investigated the interactive forces, stability, permeability, and film thickness. It was found that the multilayer thin films and capsules obtained were considered stable over a wide pH range (2–9) and that hydrogen bonds and hydrophobic interactions are responsible for improving the stability of the capsules [46].

Some biocompatible molecules, such as peptides, copolymers, phospholipids, and small synthetic molecules have evolved as building blocks with great potential for assembly into nanostructures with controllable size, shape, charge, and surface properties. These molecules can spontaneously assemble, forming ordered superstructures promising for applications in some areas, such as, energy, catalysis, optics, medicine, among others [9]. Long et al. [9] showed the recent advances in the development of trigonal building blocks in their work. Due to the unique structure of C_3 symmetry, molecules with trigonal geometry present advantages for their use in supramolecular self-assembly as their structure expands the variety of building blocks of supramolecular materials. Trigonal building blocks are generally small and easily obtainable molecules; in addition, they are more sensitive to stimuli than polymers, for example, which are structurally complex [9]. Trigonal molecules can be synthetic molecules [47, 48], nucleic acids [49], and peptides [50]. It should be noted that the peptides, being biodegradable and biocompatible, are attractive as building blocks for supramolecular biomaterials and can be used in different areas, such as biotechnology and biomedicine [50].

In addition to the carbon dots presented earlier, other quantum dot (QDs) materials have attracted the interest of the scientific community over the years mainly due to their tunable bandgaps and the possibility of functionalization, thus, making them efficient building blocks for many optoelectronic applications [51, 52]. Sol et al. [53] developed a Z-type composite photocatalyst based on TiO_2 nanorods decorated with of gC_3N_4 and Au quantum dots. The Z-type heterojunction formed at the r-TiO_2 and gC_3N_4 interface as well as the improved electron capture by the Au QDs were responsible for the improvement in the catalytic performance of the composite photocatalyst. Therefore, this work provides an efficient strategy to design high-performance photocatalysts using quantum dots and nanorods as building blocks [53].

Among the fields of supramolecular chemistry, "host–guest chemistry" performs a significant role in forming new supramolecular entities and has come to the scientific community's attention over the years. In host–guest chemistry, small molecules (guest) are reversibly encapsulated in the cavities of larger molecules (host) [54]. Cyclodextrins (CDs) [55], cucurbit[n]urils (CB[n]s) [56], calix[n]arenes (CA[n]) [54], and pillar[n]arenes (PA[n]) [54] are among the most used molecules as "host molecules". In 2019, Yao et al. [57] obtained a host–guest complex with β-cyclodextrin and methylene blue in a spray-coating based on hyaluronic acid. The obtained complex showed a good photodynamic antibacterial capacity and can be used to sterilize medical devices [57]. The tin(IV) porphyrin, viologen, and cucurbit[8]uril (CB[8]) complex developed by Shee et al. [56] can be utilized as a supramolecular sensor for the detection of aromatic compounds (hydroquinone, naphthalene). IN this work, the authors used a tin(IV)porphyrin functionalized with viologen "as a guest molecule" since the viologen units can be encapsulated within the CB cavity. In this case, the porphyrin served as a structural scaffold for the complexation host–guest [56].

Tang et al. [58] developed ferrocene-functionalized poly(ionic liquid) microgel nanoparticles (PIL-Fc NPs). The possibility of using PIL-Fc NPs as a building block for self-assembly was evaluated and confirmed by forming an inclusion complex between the obtained nanoparticles and the β-cyclodextrin dimer (β-CD). The supramolecular self-assembly was performed through the host–guest interaction of the ferrocene groups, present in the functionalized poly(ionic liquid) microgels, with the β-CD dimer [58].

3 Methods of Building Blocks Supramolecular Assembly onto Electrode Surfaces

The successful applications in the supramolecular electrochemistry are dependent on the deposition of the building blocks onto electrode surfaces. The supramolecular immobilization processes can improve molecular recognition, providing superior electrochemical stability and enhance electron transfer [59]. The supramolecular electrochemistry mechanism is guided by interactions that occur in the electrode interface [60]. Therefore, the supramolecular electrochemistry investigate the interactions at the molecular level between building blocks and electrode surface [60]. Furthermore, the reactivity of the interface constituted by site-specific supramolecular interaction/analyte are objects of study of supramolecular electrochemistry. Thus, the formed supramolecular structure onto electrode surface is influenced by the balance of all interactions that occur between the building blocks and the analyte (metals, ions, molecules, metabolites, proteins, hormones, nucleic acids, etc.) [60]. For example, hydrogen-bonding, electrostatic interactions and halogen-bonding (supramolecular anion receptors) can promote the anion recognition to improve their electrochemical sensing [61]. Moreover, supramolecular self-assembly of building blocks onto electrode surfaces exhibit high molecular recognition capability (via host–guest interaction, hydrogen-bonding and π–π interactions) that can be improve electrochemical performance of (bio)sensors [39, 62].

In the development these supramolecular structures, building blocks are immobilized onto electrode surfaces using various strategies [63–66]. Figure 3 presents a schematic representation of the main strategies used for supramolecular assembly of building blocks onto electrode surfaces.

These assembly methods are important because they have the capacity of form self-organized supramolecular architectures onto electrode surface. Table 1 presents the main advantages, disadvantages and suggested interaction in the electrochemical interface to form self-organized supramolecular structures onto electrodes surfaces. The self-assembled monolayes (SAMs), LbL self-assembly and electrochemical deposition methods are described with more detail in the following subsections.

3.1 Self-Assembled Monolayes (SAMs)

The SAMs method is one of the most used strategies for preparation of organic ultrathin films with controlled thickness and chemical functionalization. The self-assembly process is governed by chemical interaction of alkanethiols, dialkyl disulfides, alkylalkoxysilanes or sulfides with the surface of metallic or semiconductor electrodes (gold, copper, mercury, platinum, silver or silicon, indium tin oxide) [64, 67]. Various types of interactions can occur in the electrode interface include

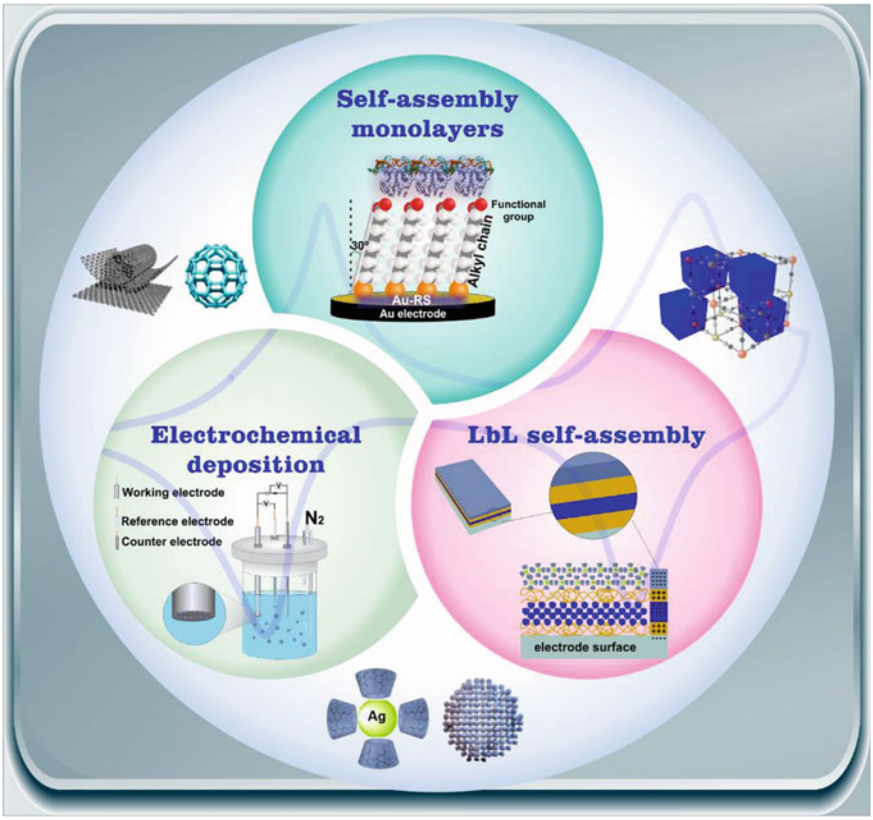

Fig. 3 Schematic representation of the main methods used to supramolecular assembly of building blocks onto electrode surfaces

chain-chain and non-bonded interactions (interchain van der Waals, steric, repulsive, and electrostatic forces), which ensure tight packing, stability and organization of the organic monolayer [64]. Moreover, SAMs nanoarchitectures form positive/negative/hydrophobic terminal chemical groups (–COOH, –OH, $-NH_2$, –CN, –SH, $-SO_3H$, –SiOH, CH_3) that can interact with others chemical species in the interface of the modified electrode [64, 67]. SAMs approach involve the formation of a (supra)molecular structures that exhibited unique physical and chemical properties on electronic devices such as organic film solar cells, organic thin film transistors, electrochemical sensors and biosensors [68, 69].

The SAMs approach improve aspects related the electronic functions of the organic film-based devices to as the dominant mechanism of charge transport and electrical output [68–70]. For example, the insertion of SAMs structures in the electrode/semiconductor interface of organic transistors can control/improve the charge injection and transport [68, 70]. Furthermore, the SAMs (supra)molecular films play

Table 1 The main advantages, disadvantages and suggested interaction in the electrochemical interface of the methods more employed to supramolecular assembly of building blocks onto electrode surfaces [63–66]

Method	Advantages	Disadvantages	Suggested interactions
Self-assembled monolayes (SAMs)	Ultrathin organic films of controlled thickness Flexibility in functionalising the end groups of SAM films Thermodynamically stable monolayers	Limited loading of materials Required specific compounds to the formation of the monolayers SAMs films are susceptible to shearing	Hydrogen bonding Van der Waals attraction Chemical interaction
LbL self-assembly	Method versatile of operation easy Versatility to choose of the building blocks Control of the multilayers films thickness and physicochemical properties	Presence of abundant residual polyelectrolyte from each deposition step Polymer adsorption behavior dependent of over a very narrow pH range Hydrogen bonding-based films showed low stability	Hydrogen bonding Electrostatic interactions charge-transfer interactions
Electrochemical deposition	Easy to implement and time-saving Reproducible control and uniformity over film thickness Ability to use diverse electrode of complex geometries	The modifier or monomer must be soluble in the electrolyte Current or voltage is required to film synthesis Removal film onto electrode surface is difficult	Hydrophobic interaction Ion-exchange π–π stacking interaction

an important role in the tuning of electronic, structural and morphological properties of the interface of molecular devices. Lin et al. (2020) examined the electric behavior of bulk-heterojunction (BHJ) organic photovoltaic (OPV) cells based in SAMs composed of [2-(9H-Carbazol-9-yl)ethyl]phosphonic acid (2PACz) [71]. Self-assembly molecules of 2PACz onto the indium tin oxide (ITO) surface were used as a hole-selective interlayer to enhance the power conversion efficiency and operational stability of ITO-2PACz. This behavior was because of the decrease contact-resistance, enhanced charge extraction in the ITO-2PACz/BHJ interface, high charge-carrier mobility before and after photoaging [71]. Very recently, it was reported a novel approach that involves interstitially mixed self-assembled monolayers (imSAMs) from a molecular diode of 2,2′-bipyridyl-terminated *n*-undecanethiol ($HSC_{11}BIPY$) and a nonrectifying diluent of *n*-octanethiol (HSC_8) onto gold substrates [72]. These methods consist in repeated surface exchange of molecules (ReSEM), resulting in filling of HSC_8 into interstices formed by bulky $HSC_{11}BIPY$, decreasing the defects within the monolayers [72]. Thus, the supramolecular packing structure of the SAMs enhanced electrical stability, functionalities and yields of working junctions.

Another important characteristic widely exploited of SAMs supramolecular architectures is the control and guidance of the terminal chemical groups that can specifically interact with analyte of interest [73–75]. The molecular interface based in the host–guest interaction was manufactured from cucurbit[7]uril (CB[7]) on mixed ferrocenylundecanethiolate/n-alkanethiolate SAMs onto gold electrode [73]. As a result, the supramolecular hosts assemblies at the nanometer scale demonstrated the capability of forming inclusion complexes (CB[7]@Fc) to probe the structural heterogeneity of ferrocenyl (Fc) SAMs [73]. Specific interactions were used by Li et al. (2019) to immobilize carboxyl-functionalized graphene (CFG) onto glassy carbon electrode (GCE) surface [74]. In this study, SAMs method was developed to promote the covalent interaction between ethylenediamine ($NHCH_2CH_2NH$) and CFG. The functionalized electrode (CFG-$NHCH_2CH_2NH$/CGE) SAMs-based was crucial to electrochemical detection of hydroxyl free radicals [74].

3.2 LbL Self-Assembled

Among the self-assembled building blocks-based methods, LbL self-assembled is one of most used strategies to make multilayer thin films with controlled thickness on a variety of electrode surfaces [76, 77]. The principle behind the of formation of multilayered films are based in various types of non-covalent and covalent interactions (e.g., electrostatic interactions, hydrogen bonding, charge-transfer interactions, coordination interactions, sol–gel processes, hydrophobic interactions, etc.) [78]. Consequently, LbL method is a highly versatile technique that exhibit different experimental approaches, such as dipping LbL assembly, spin-assisted LbL assembly and spray-assisted LbL assembly [79]. Among them, dipping LbL coating is the most used method to the produce functional supramolecular structures. The dipping LbL approach consists in alternating immersion of a charged conductive substrate into aqueous solutions of oppositely charged building blocks [76–79]. Then, rinsing the as-prepared films in appropriate solutions and drying under nitrogen atmosphere for the removal of weakly adsorbed species occurs as intermediate steps. In this assembly process, thickness and physicochemical properties of thin films can be controlled with precision through of adjustment of the experimental conditions including solution pH, ionic strength, addition of salt and polyelectrolyte charge density etc. [65, 76]. Based on this information, LbL method is one of the most easy and versatile strategies to supramolecular self-assembly of functional building blocks onto electrode surfaces. Therefore, the LbL self-assembly allows investigate and control supramolecular specific interactions that occurs in electrochemical interface constituted by building blocks and chemical species of interest. The self-assembly of building blocks in electrodes with desirable architectures and properties is of great importance for study the performance of electronic and electrochemical devices.

Regarding electrochemical sensors and biosensors, LbL method promote the improve in the electronic conductivity, and electroactive surface area, enabling an increase in sensitivity [80–83]. However, the most important aspect is the introduction and control of sensitive molecular recognition species in electrode surface that improve the selectivity capability in complex samples [81, 82]. For this purpose chemical groups can be anchored to interact specifically with target analytes through non-covalent and covalent interactions (e.g., host–guest interaction, electrostatic interactions, biospecific interactions, chiral recognition, "click chemistry" reaction, etc.) [78, 83]. A supramolecular electrochemical architecture with molecular recognition properties was prepared by LbL self-assembly of polyethylene imine-reduced graphene oxide (PEI-rGO) composites and cholesterol oxidase (ChOx) [81]. In this work, the electrostatic interaction between the positively charged PEI-rGO and negatively charged ChOx increase the electron transfer ability between the redox enzyme and the surface of glassy carbon electrode (GCE). This supramolecular interaction that occur at the electrochemical interface improve the electric conductivity and maintain the bioactivity of the ChOx [81]. Another example of supramolecular multilayers LbL strategy-based with biorecognition component (folic acid, FA) was demonstrated by Correia and colleagues [82]. The authors realized alternately deposition of positively charged polyallylamine hydrochloride (PAH) and negatively charged FA on indium tin oxide (ITO) electrodes. The multilayers structure increase electroactive surface area and improve sensitivity/selectivity to electrochemical detection of folate receptor alpha (FR-α) via binding affinity between FA and FR-α [82].

The LbL method allows study detailed electrochemical mechanisms and electrochemical reactions that occur on interface of electrodes used in energy conversion and storage devices [84]. Thus, the possibility of control the thickness and architecture of multilayed electrodes in nanoscale is crucial to understand the processes that involves competition between mass and charge transfer, modulation of interfacial dipole, and ion permeability [84]. Wang et al. (2021) developed LbL self-assembled nanostructured electrodes to investigate the electrochemical performance of lithium-ion batteries (LIBs) [85]. The electrostatic interaction and colloidal stability properties of building blocks (nanoparticles of lithium titanate, lithium iron phosphate, lithium manganese oxide, and carboxymethyl celulose) were useful for make LIBs based in the LbL self-assembly. The supramolecular interactions improved Li^+ intercalating phase and electron-conducting phase providing a high specific capacity during the charge/discharge cycles [85]. In another work, researchers explored the spray-assisted LbL assembly technique to make nanostructured electrodes and study their electrochemical behavior as flexible solid-state supercapacitor [86]. In this case, the method is based in alternating spray of graphene quantum dot-reduced graphene oxide (GQD-rGO) solution and an aqueous polyaniline (PANI) solution onto flexible conductive substrate of carbon fiber cloth (CFC) [86]. The spraying-based self-assembly process of GQD-rGO changed the CFC surface from hydrophobic to hydrophilic and enhanced the electrostatic interaction between PANI and CFC. The supramolecular strong interactions between GQD-rGO and PANI in the CFC electrode interface improved the cycling stability and specific capacitance [86].

3.3 Electrochemical Deposition

Compared with the approaches presente in Table 1, electrochemical deposition methods are most inexpensive with easy operational implement and time-saving, also showing reproducible and uniform film structrures onto various electrode geometries [59, 63, 66]. Because of these characteristics, the electrochemical deposition is extensively used to supramolecular self-assembly of building blocks on the conducting electrode surfaces. The electrochemical deposition has as principle the immersion of three electrodes (working, reference, and auxiliary) in suitable electrolyte solution where sufficient current or voltage is provided to reduce ionic metallic species and oxidize or reduce a monomer to polymerize it on the surface of the working electrode [59, 63, 66]. For this reason, the main approaches of electrochemical deposition are the electrodeposition of metal and metal-based (nano)materials and electropolymerization of polymeric species. The experimental and electrochemical parameters such as current densities/voltages, substrate surface, electrolyte pH, solution viscosity, and diffusion coefficient can be adjusted and play critical roles in the morphology thickness, uniformity and reactivity of the deposited film [59, 87]. Therefore, electrodeposition and electropolymerization are approaches of supramolecular electrochemistry to investigate the effects of electrodeposited films in the electrochemical behavior of (bio)sensors, corrosion protection, energy conversion and storage [88–96].

In the context of (bio)sensors, electrochemical deposition methods enhanced sensitivity and selectivity through of the supramolecular interactions of (bio)molecules with the electrochemical interface [88–90]. In this process, (supra)molecular recognition and (bio)recognition ability takes effect in the electrochemical behavior of (bio)sensors because of the host–guest interactions (inclusion complexes), hydrogen bonds, electrostatic interactions and halogen-bonding [88–92]. For example, cyclodextrins-based host–guest complexes confine the target analyte next of the electrode surface, providing a decrease or increase of the electric current of analytes' redox processes [89]. The electrodeposition was used as strategy of supramolecular electrochemical sensing by Uppachai and coworkers [91]. One of the first steps was electrodeposition of Au nanoparticles onto graphene oxide modified glassy carbon electrode (AuNPs/GO/GCE). To improve the detection of dopamine (DA), self-assembled mixed surfactants (TBABr/SDS) were added into electrolyte solution [91]. Thus, hydrophobic interaction and electrostatic attraction occur through C–H chain and charge terminal group of the TBABr/SDS with DA structure, respectively. These supramolecular interactions and synergistic effect of TBABr/SDS with AuNPs/GO provide an enhanced anodic peak current of DA [91]. Very recently, it was reported a novel approach based on preconcentration of the organic target analyte using the electropolymerization [92]. The poly-(para-aminophenol) film was electrochemically deposited in the glassy carbon electrode (GCE) surface. The specific interactions that occur in the CGE/OxPPAP electrode interface are important to elucidate the electrochemical mechanism in the detection the melamine (Mel). As a result, the covalent supramolecular interaction (Mel-aldehyde resins) between melamine and the aldehyde-rich CGE/OxPPAP surface increase sensitivity and selectivity to determine Mel in real milk samples [92].

Concerning others applications (anticorrosion, energy conversion and storage), electrochemical deposition approaches can influence in the supramolecular organization, electrochemical properties and performance of the building blocks on the electrode surfaces [93–96]. In this context, it was demonstrated the electrodeposition of graphene oxide (GO) from covalent interaction with electroactive monomer (carbazole, Cbz) [93]. The electrochemical step is governed by electropolymerization of Cbz that covalently bond to GO surface to electrodeposit the GO-Cbz structures onto indium tin oxide (ITO) surface. The supramolecular self-assembly of GO-Cbz films in the conductive regions of the electrode enabled excellent anticorrosion performance [93]. The electropolymerization of poly-1,4-bis(2-thienyl)benzene (PDTB) film was used to prepared a photocathode and investigate the processes of photoelectrochemical (PEC) hydrogen evolution [95]. Electrosynthesis resulted in the PDTB-base photocathodes with various microporous structures and regulated S oxidation states. This structural organization improve the light absorption capacity, and charge separation of the photocathodes. Thus, self-assembly of microporous structures by electropolymerization promoted narrow band gap and low charge transfer resistance that facilitated the transport of photogenerated electrons, resulting in the enhance hydrogen production potential [95].

4 Applications of Supramolecular Structures

Nanotechnology has attracted tremendous attention in the past years from several areas of knowledge, mainly due to the unique properties and prominent advantages of nanoscale materials and devices [97]. More recently, there has been an extensive use of nanotechnology to develop new functional systems used as sensors, biosensors, molecular recognition devices, energy storage, and much more, as it is schematic represented in Fig. 4 [98]. Electrochemistry plays an important hole on the application of nanoscale materials in different areas, ranging from catalysis and energy to (bio)sensors development, and beyond [99]. The synergism between nanomaterial properties (already mentioned earlier in this chapter) and electrochemical devices, makes them a powerful tool for several applications, especially owing to the high sensitivity, portability, low cost, simplicity of instrumentation, and versatility of such devices [100].

Electrochemical systems have been coupled with different types of nanomaterials like graphene and its derivatives, nanoparticles, etc., with an increasing range of possibilities [100]. In this context, the use of self-assembled building blocks as modifiers onto the surface of electrodes can be an interesting approach to improve the conductivity and other electrical and chemical properties of electrodes for a given

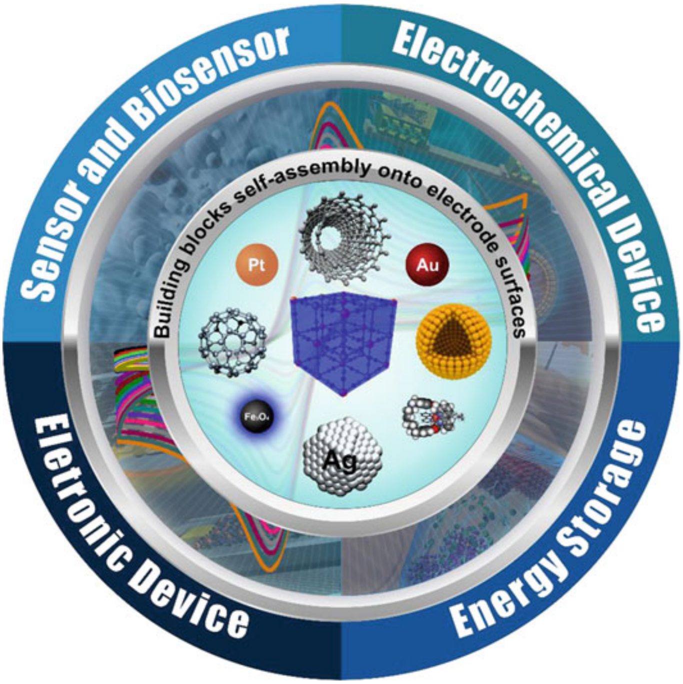

Fig. 4 Schematic illustration of the main applications of self-assembled building blocks onto electrode surfaces

application. Some interesting works involving supramolecular electrochemistry will be described as follows.

Roushani et al. (2020) described a nanoaptasensor to detect traces of an antibiotic commonly used in the treatment of bacterial infections called chloramphenicol (CAP). The device was constructed using graphene oxide functionalized with silver nanoparticles and (3-aminopropyl) triethoxysilane bounded to an aptamer (Apt/AgNPs/[NH_2-Si]-f-GO) modifying a glassy carbon electrode (GCE). 5×10^{-3} mol L^{-1} of $[Fe(CN)_6]^{3-}/^{4-}$ solution was employed as a redox probe in this approach. The high sensitivity and good linear concentration range of the nanoaptasensor is attributed to the presence of the AgNPs/[NH_2-Si]-f-GO layer. This layer has a large surface area on which more Apt can interact through covalent bonding, resulting in more active sites for the biorecognition event. The authors demonstrated an indirect mechanism for the detection of CAP in which the interaction between the electrode modifier and the analyte (that is, the biorecognition event) creates a physical barrier/restriction, hindering the redox reaction of the probe on the electrode surface, decreasing the peak current. The proposed device has several advantages, including low detection limit, sensitivity, adequate stability, and high selectivity, in addition to conjugation with biomolecules [101].

Gayda and collaborators (2021) reported the use of metallic nanoparticles of Palladium (Pd), obtained by green synthesis (gNPs) in the development of amperometric biosensors (ABSs), aiming to immobilize enzymes onto the surface of graphite electrodes (GEs). The authors claim that two bioelectrodes, AO-gPdNPs and laccase-gPdNPs, presented better amperometric responses when using the enzymes alcohol oxidase (AO) and laccase, respectively. The study also demonstrated that bioelectrodes modified with PdNPs had lower sensitivity to their substrates, wider linear ranges of detection and greater stability. These are desirable characteristics for enzymes that have a high sensitivity to their substrates, therefore, pointing out the promising potential of gPdNPs in the construction of enzymatic ABSs [102].

Recently, Avelino et al. (2021) described the achievement of a biosensor composed of polypyrrole (PPy) films and gold nanoparticles (AuNPs) used for specific detection of HPV genotypes. The biosensor was developed using flexible electrodes based on polyethylene terephthalate (PET) strips coated with indium tin oxide (ITO). The construction of the films took place in three stages: the first one was the electropolymerization of PPy, followed by the electrochemical deposition of AuNPs and the last one was the immobilization of cysteine (Cys) on the metallic surface by chemisorption. The authors claimed that the association of these functional materials allowed obtaining a platform with better electrochemical properties and high surface area, besides the excellent ability to identify minimal concentrations of specific types of HPV [103].

The same group reported a similar approach but focused on development of a genetic device for the assessment and monitoring of human infection by SARS-CoV-2 in the early, intermediate, and late stages of the disease. The nanostructured platform was built with polypyrrole (PPy) and gold nanoparticles (GNP) on miniaturized gold-doped indium tin oxide (ITO) electrodes, functionalized with oligonucleotide. The electrode was built through electrochemical polymerization, followed by an electrochemical deposition of GNPs, and finally, a chemisorption of Cys molecules in GNPs was performed. The biosensor exhibited high selectivity by not recognizing the biological target in samples from patients not infected with SARS-CoV-2. The proposed device obtained an estimated linear response range from 800 to 4000 μL^{-1} copies with a regression coefficient of 0.99 and a detection limit of 258.01 μL^{-1} copies, proving to be efficient in the diagnosis of SARS-CoV-2 [104].

Metallic semiconductor oxides, used as building blocks in electrodes, have gained prominence in the literature, due to the possibility of modifying amperometric, potentiometric and conductometric properties. Fatema and Oh (2021) reported the obtaining of graphene-based electrodes modified with mesoporous oxides of Zinc (Zr), Silicon (Si) and Indium (In) (ZrO_2–Ag–G–SiO_2 and In_2O_3–G–SiO_2), for detection of non-enzymatic glucose, ascorbic acid, and albumin in urine at physiological pH. The authors stated that the In_2O_3–G–SiO_2 electrode performed well over a wide range of urine electrolytes, and showed no activity against uric acid, suggesting a potential for biodetection of glucose in urine [105].

Hashemi et al. (2020) proposed the modification of graphene oxide (GO) with Ag and Iron Oxide (Ag–Fe_3O_4) hybrid metallic nanoparticles for real-time detection of ascorbic acid (AA) in plasma blood samples through electrochemical measurements.

The results showed that the modification of glassy carbon electrode (GCE) with such hybrid material significantly improved its sensitivity and selectivity. The authors further stated that the GCE modified with GO–Ag–Fe_3O_4 had detection limits and sensitivity of 74×10^{-9} mol L^{-1} and 1146.8 μA mM^{-1} cm^{-2}, respectively, within the concentration range of 0.2–60 μM. In addition, the modified electrode maintained 91.23% of its total performance after 15 days of detecting the AA oxidation peak, highlighting its stability/selectivity, and evidencing the notable application capability of the proposed platform [106].

Carbon-based materials such as carbon nanotubes (CNTs), graphene oxide (GO) with different shapes and sizes have been widely used for applications such as sensors, biosensors mainly due to their excellent electrical properties, as already stated earlier in this chapter [98]. Xia et al. (2022) obtained a biosensor (GOx/β-CD/MWCNTs/GCE) constructed from a graphite carbon electrode (GCE) modified with multiwalled carbon nanotubes (MWCNTs) functionalized with β-cyclodextrin and glucose oxidase (GOx), for the detection of glucose in honey. The study stated that the interaction of β-cyclodextrin (β-CD) with CNTs improved the dispersibility of the nanotubes in aqueous media, due to the internal hydrophobicity and external hydrophilicity of β-CD. The results obtained in this study revealed that the carbon nanotubes promoted the direct transfer of electrons from GOx, showing a linear response for glucose concentration in the range of 50 μM to 1.15 mM with a detection limit of 0.42 μM and a sensitivity of 32.28 μA mM^{-1} cm^{-2} [107].

It is important to highlight that the manipulation of matter at the nanoscale also enabled the construction of electrical devices used as capacitors and batteries for energy storage. Zamiri et al. (2021) synthesized a ternary nanocomposite consisting of three-dimensional graphene, silver nanoparticles and polyaniline (3DG-nAg-PANi) using an in-situ polymerization technique, for applications as asymmetric supercapacitor (ASC). The study showed that the incorporation of PANi with 3DG led to the rapid diffusion of Ag ions, significantly improving the conductivity of the nanocomposite, and increasing the peak area of the cyclic voltammogram. Therefore, the authors concluded that the synergistic combination of nanomaterials (3DG-nAg-PANi) improved the charge storage property of the electrodes, showing an increase of almost 2.5 times in capacitance when compared to 3DG/PANi composite, highlighting a potential use of such material for future energy storage devices [108].

Coordination compounds, such as Prussian Blue, has also been applied in development of electrochemical nanosystems (e.g., energy storage devices and (bio)sensors) for quite some time, with remarkable success reported in the literature over the last years [109]. As an example, Carvalho and Collaborators (2021) described recently the development of a carbon nanotube-based material (SWCNT-COOH) coupled with Prussian Blue nanoparticles (PBNPs) as an promising electrode modifier for the indirect detection of Ibuprofen (IBP) [110]. The electrode was built through the incorporation of PBNPs in the internal and external surface of the nanotube. Cyclic voltammetry (CV) data revealed that the presence of IBP decreases the electrochemical currents of the redox processes of PBNPs, featuring an inhibition effect that is proportional to the analyte concentration, suggesting an interaction between IBP and free Fe^{3+} sites in the complex structure. Thus, IBP could be detected indirectly at lower potential when compared to the direct IBP oxidation potential. This electrochemical behavior opens possibilities for future studies of IBP detection based on the inhibition effect of this analyte on the redox processes of PBNPs.

5 Conclusions

This chapter describes a brief electrochemistry supramolecular approach of smart self-assembled nanostructures constructed by appropriate choice of building blocks, synthetic route, and immobilization methods. The combined effect of lower-level components, that could only be observed at the nanoscale, point to another avenue to pursue within the constitutional dynamic chemistry. Special attention is given to choosing the electrochemical technique in order to provide information on energy and kinetics that is not available with spectroscopic and mass spectrometric techniques. Based on the studies summarized in this chapter, the nano-supramolecular assembled nanomaterials present the potential for various studies and applications including drug carriers, (bio)sensor, tumor diagnosis, electronic device, and energy storage.

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