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REVIEW

Recent progress in nanocomposites based on conducting polymer: application as electrochemical sensors

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Abstract

Over the years, intensive research works have been devoted to conducting polymers due to their potential application in many fields such as fuel cell, sensors, and capacitors. To improve the properties of these compounds, several new approaches have been developed which consist in combining conducting polymers and nanoparticles. Then, this review intends to give a clear overview on nanocomposites based on conducting polymers, synthesis, characterization, and their application as electrochemical sensors. For this, the paper is divided into two parts: the first part will highlight the nanocomposites synthesized by combination of carbon nanomaterials (CNMs) and conducting polymers. The preparation of polymer/CNMs such as graphene and carbon nanotube modified electrode is presented coupled with relevant applications. The second part consists of a review of nanocomposites synthesized by combination of metal nanoparticles and conducting polymers.

Keywords Conducting polymers · Carbon nanomaterials · Metal nanoparticles · Nanocomposites

Abbreviations

1H NMR	1H nuclear magnetic resonance spectrometer
3D-RGO	Three-dimensional reduced graphene oxide
AA	Ascorbic acid
AFM	Atomic force microscope
AgNPs	Silver nanoparticles
AgNWs	Silver nanowires
AgαCRP	C-reactive protein
ANI	Aniline
ATP	Attapulgite
AuNPs	Gold nanoparticles
BET	Brunauer–Emmett–Teller
C-CNTs	Crosslinked carbon nanotubes
CNFs	Carbon nanofibers
CNMs	Carbon nanomaterials
CNs	Carbon nanospheres
CNTs	Carbon nanotubes
CPs	Conducting polymers
CPE	Carbon paste electrode
CRGO	Chemically reduced graphene oxide
CTAB	Cetyltrimethylammonium bromide
CuNPs	Copper nanoparticles
CuS	Copper sulfide
CV	Cyclic voltammetry
DA	Dopamine
DAN	Diaminonaphthalene
DMF	*N*,*N*-Dimethylformamide
DMFCs	Direct methanol fuel cells
DMSO	Dimethyl sulfoxide
EDOT	3,4-Ethylenedioxythiophene
EHDA	Electrohydrodynamic
EIS	Electrochemical impedance spectroscopy
f-MWCNTs	Functionalized MWCNT
FTIR	Fourier-transform infrared
GR	Graphene
GaN	Gallium nitride
GCE	Glassy carbon electrode

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GO	Graphene oxide
ITO	Indium tin oxide
LOD	Limit of detection
LOQ	Limit of quantification
MIP	Molecularly imprinted polymer
MIPM	Molecularly imprinted polymer membranes
MnO_2-NPs	Manganesedioxide nanoparticles
MNPs	Metal nanoparticles
MoS	Molybdenum disulfide nanosheets
MWCNT	Multi-walled carbon nanotubes
MWNTsg-PtBMA-*b*-PS	Multiwall carbon nanotube graft polystyrene-*block*-poly(*tert*-butyl methacrylate)
NiPs	Nickel ion particles
NPs	Nanoparticles
p-AHNSA	Poly4-amino-3-hydroxy-1-naphthalene sulfonic acid
PANI	Polyaniline
PdNPs	Palladium nanoparticles
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)–polystyrene sulfonic acid
PNPAg	Nanocomposite blend
Poly(DTCPA-*co*-BHTBT)	Poly((2,5-dithienyl-3,4-(1,8-naphthalene) cyclopentadienone)-*co*-4,7-bis(3-hexylthiophen-2-yl) benzo [c] [1,2,5] thiadiazole
PPy	Polypyrrole
PPyox	Overoxidized polypyrrole
PS	Polystyrene
PS-*b*-PtBMA	Polystyrene-block-poly(tert-butyl methacrylate)
PSS	Poly(sodium 4-styrenesulfonate)
PTh	Polythiophene
PtNPs	Platinum nanoparticles
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolydone
RGO	Reduced graphene oxide
RGO-g-PANI	Polyaniline grafted reduced graphene oxide
SDBS	Sodium dodecylbenzene sulfonate
SEBS	Poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene)
SEM	Scanning electron microscopy
SMZ	Herbicide simazine
SWCNT	Single-walled carbon nanotubes
SWV	Square wave voltammetry
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
XPS	X-ray photoelectron spectroscopy
YADH	Alcohol dehydrogenase

Introduction

Organic conducting polymers, born in 1977 with the pioneering work of MacDiarmid, have received great attention due to their potential application [1, 2]. Intensive research works have been devoted to preparation and characterization of conducting polymers such as polyaniline (PANI), polypyrrole (PPy), diaminonaphthalene (DAN), and their derivatives. Their application in batteries, sensors, capacitors, electronic devices, or electrochromic displays was very promising [3–5]. Carbon nanomaterials (CNMs) including fullerenes, single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), carbon nanofibers (CNFs), carbon nanospheres (CNs), graphene, and graphene oxide (GO) are novel materials of the twenty-first century [6] because of their large surface area, good environmental stability [7], exceptional electrical, thermal, chemical, and mechanical properties [8]. Due to these properties, CNMs had found a great interest in fields of composite materials and energy conversion [9], sensors [10], medicine [11], emission devices [12], and nanoscale electronic components [13].

Many efforts have been made to combine CNMs and polymers to produce functional nanocomposite materials with superior properties for fundamental and technological perspectives [10]. The conducting polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT) have been explored as matrices to incorporate a number of CNMs such as: fullerenes [14], single and multi-walled carbon nanotubes (CNTs) [15, 16], carbon nanofibers (CNFs) [17, 18], carbon nanospheres (CNs) [19, 20], graphene, and graphene oxide [21–23]. The incorporation of carbon nanomaterials in polymer matrices is a very attractive way to combine the mechanical and electrical properties [24]. These new nanocomposites open up new opportunities, ranging from sensors [25–27], electrochemical capacitor [28, 29], solar cells [30], transistors [31], to molecular electronic devices [22], etc. More recently, nanocomposite

based on CPs, and metal nanoparticles (MNPs) such as gold, platinum, palladium, and silver with different compositions and dimensions have been intensively investigated [32–36]. The incorporation of metal nanoparticles in polymers matrices would to a host nanocomposite with additional physical properties [37–39]. Several approaches have been described and employed to synthesize metal or metal oxide nanoparticle-conducting polymers nanocomposites [34, 38, 40]. Different approaches using electrochemical methods involving incorporation of metal nanoparticles during the electrosynthesis of the polymer, electrodeposition of metal nanoparticles on the preformed polymer electrodes, reduction of metal salts dissolved in a polymer matrix or incorporation of preformed nanoparticles during polymerization of monomers have been reported. Chemical preparation [41], sonochemical method [42], sol–gel technique [43], ultrasonic irradiation [44], and photochemical preparation [45] have also been used. Nanocomposites based on conducting polymers and nanoparticles (CNMs or MNPs) were the focus of increasing numbers of papers or reviews to understand fundamental aspects and the potential applications of these nanostructures [46]. According to the sciences direct web site, the number of paper devoted to nanocomposites based CP and NPs increased from 3427 in 2011 to 7444 in July 2017, as shown in Fig. 1, indicating the importance of nanomaterial composites.

The present review analyzes the recent progresses in the synthesis of nanocomposites based on conducting polymers and carbon nanomaterials and/or metal nanoparticles during the last years and their applications in the field of electrochemical sensors. It should be noted that only conducting polymers with conjugated-π-bond will be considered in this review.

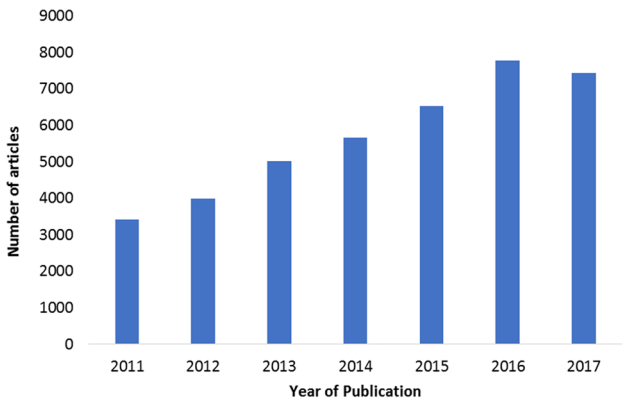

Fig. 1 Histogram representing the numbers of scientific articles published per year during the last 6 years (research performed on 10 July 2017 with "Science Direct", with CP and NPs)

Nanocomposites synthesized by combination of carbon nanomaterials and conducting polymers

Combination of conducting polymer matrix and carbon nanomaterials (CNMs) such as graphene, carbon nanofibers (CNFs), and carbon nanotubes (CNTs) to form polymer nanocomposites plays a very promising role due to their better structural and functional properties such as high aspect ratio, high mechanical strength, and high electrical properties [24, 47, 48]. In the last decade, large progress was made, resulting in the opening of new possibilities in the use of these properties for a variety of applications. The overall performances of CNMs/polymer nanocomposites are largely governed by the dispersion of CNM in the polymer matrix. Therefore, a homogeneous dispersion of CNM is an important issue in the preparation of CNM/polymer nanocomposites [17, 22, 49–51]. Up to date, a large number of reviews have been reported on composites of conducting polymers and CNMs for application in supercapacitors and chemical sensors [52–54]. Carbon nanotubes and graphene are considered as the most innovative CNMs who are attracting enormous interest for their use in sensors [52] and their potential application as energy storage materials [55]. The most commonly used conducting polymers are polyaniline (PANI), polypyrrole (PPy), and poly[3,4-ethylenedioxythiophene] (PEDOT) [56–58]. Several methods for synthesis of nanocomposites have been reported in the literature. CNM/polymer nanocomposites can be synthesized by electrochemical or chemical processing. Chemical method is the common processing that can be performed either by solution mixing or by in situ chemical polymerization. Solution mixing is the method in which CNMs and polymer are mixed with a suitable solvent, and then, the nanocomposites are formed after the evaporation of the solvent in a controlled condition. It was demonstrated that this method enables to drop-cast films with up to 60 wt% CNT content, although can result in reagglomeration of the CNTs during the casting/evaporation process [52]. In situ chemical polymerization achieved by oxidation of corresponding monomers using an oxidizing agent. The main advantage of this method is that it produces polymer grafted CNMs, mixed with free polymer chains. Moreover, due to the small size of monomeric molecules, the homogeneity of the resulting composite adducts is much higher than mixing CNTs and polymer chains in solution [59]. However, it cannot achieve the same level of homogeneity and integrity in its polymerized product as can be produced by electrochemical polymerization [56]. The electrochemical polymerization takes only some minutes instead of some hours in case of chemical polymerization. Polymers can be formed by

electrochemical deposition on electrodes modified with CNMs which leads to the better dispersion and interactions between CNMs and polymer. Better uniformity can be obtained by the electrochemically co-deposited composites from a solution containing monomers and dispersed CNMs leading to the most homogeneous network structure. Figure 2 shows the schematic illustration of the process of fabricating CNM/polymer nanocomposites with traditional chemical methods.

(a) Nanocomposites were prepared by in situ chemical polymerization involving monomer and carbon nanomaterials with different weight ratios after being sonicated to obtain homogenous mixture [60, 61].
(b) In mixing method, the commercial polymers were dissolved in suitable organic solvents, mixed and sonicated. Mangu et al. used *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) to dissolve PEDOT:PSS in the volume ratio of 3:1 and 2-propanol, ethylene glycol, DMSO, and DMF to dissolve PANI [62]. Then, carbon nanomaterials were added to this solution and sonicated. These nanocomposites obtained in solution form can be casted on suitable substrate or precipitated by filtration before being dried.

Electrochemical methods are investigated to prepare CNM/polymer nanocomposites and are summarized in Fig. 3. Two methods are generally used:

(a) The modified electrode was prepared by dropping of the well-dispersed carbon nanomaterials on the surface of the electrode substrate. Conducting polymers were electropolymerized using cyclic voltammetry in the presence of monomer dissolved in a solution generally in acidic medium [63, 64]. A typical example in Fig. 4 was obtained in our laboratory using this method and concern polymerization of 1,5-diaminonaphthalene with CNFs [65].
(b) Electrochemical co-deposition was performed in aqueous solution containing monomer and carbon nanomaterials, using potentiostatic, galvanostatic, or cyclic voltammetry (CV). The solution was stirred and ultrasonicated before polymerization. After electropolymerization, the modified electrode was washed thoroughly with water and dried at room temperature [66–68].

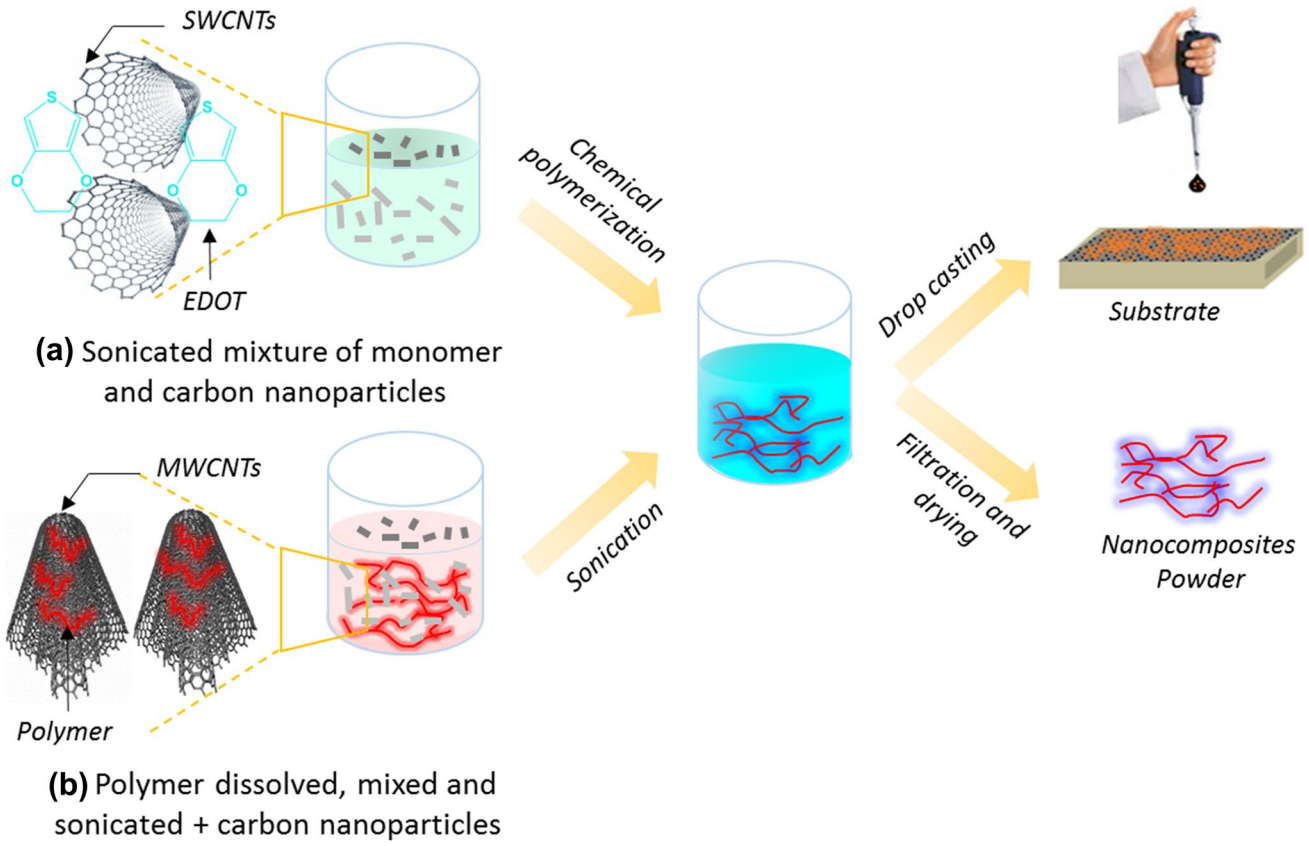

Fig. 2 Schematic illustration of chemical preparation method of CNMs/conducting polymer nanocomposites: **a** in-situ chemical polymerization of monomer and carbon nanoparticles, **b** sonication of commercial polymer solution and carbon nanoparticles

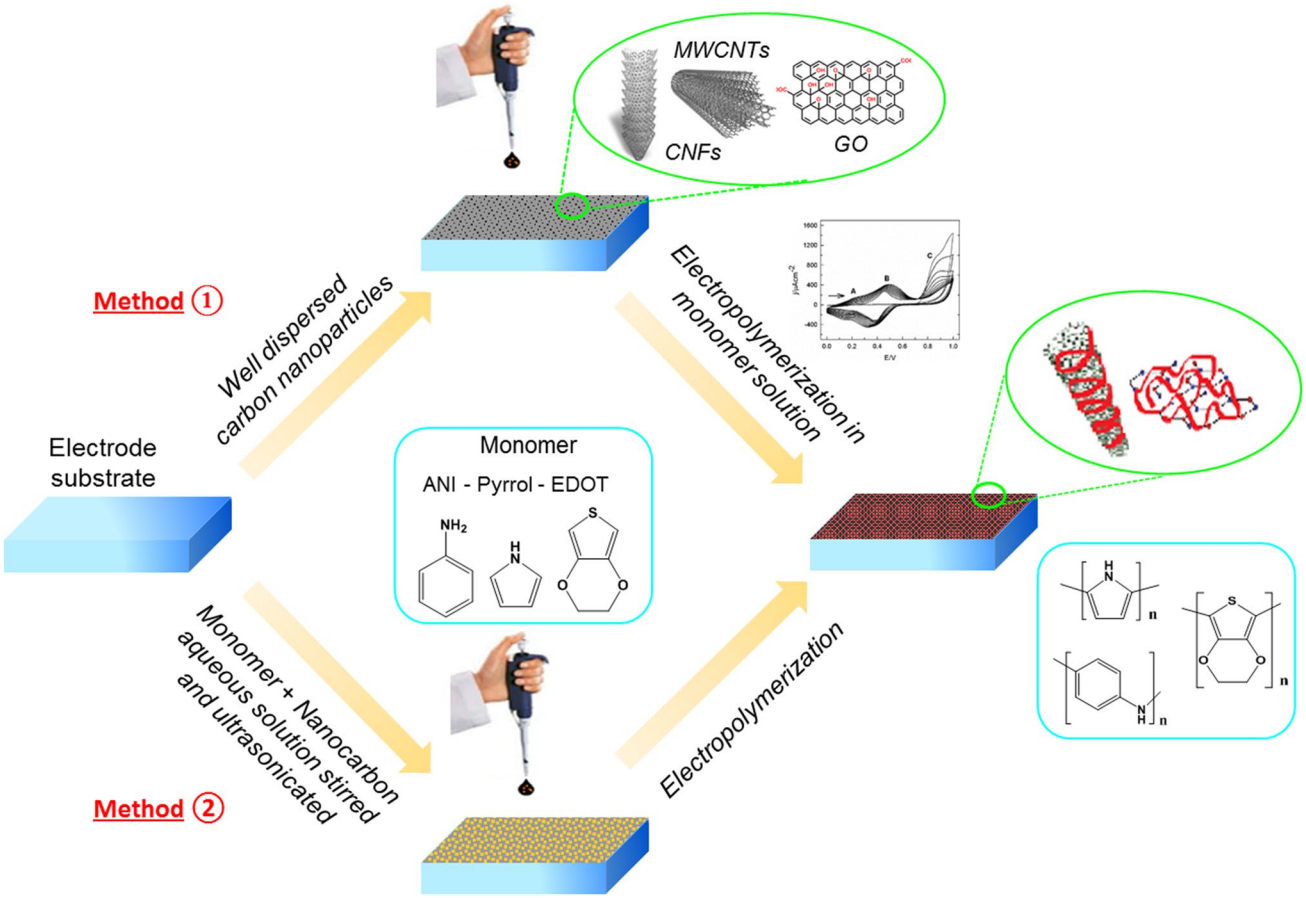

Fig. 3 Schematic illustration of electrochemical process of elaboration of CNMs/conducting polymer nanocomposites

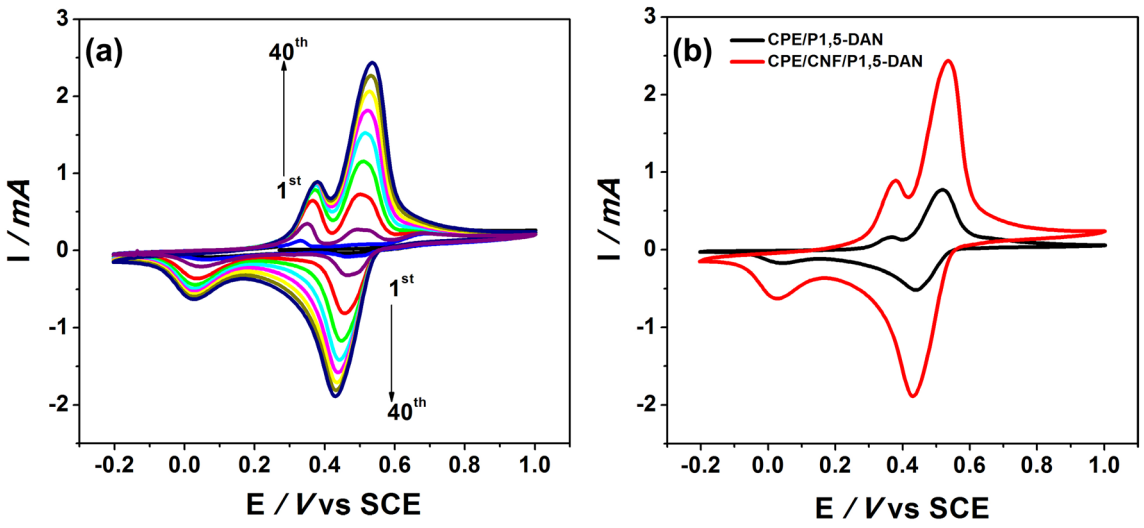

Fig. 4 **a** Cyclic voltammograms of electropolymerization of 1,5-DAN at the surface of CPE/CNF during 40 consecutive potential cycles between − 0.2 and 1.0 V in a 1.0 M HCl solution containing 5 mM 1,5-DAN, 50 mV s^{-1}, **b** compared voltammograms between CPE/poly(1,5-DAN) and CPE/CNF/poly(1,5-DAN) at the 40th cycle [65]

The properties of these nanocomposites are also related to the percentage of CNMs. The percentage of CNM plays an important role on the mechanical and electrical properties of nanocomposites and was studied by different authors. The influence of the percentage of CNT in CNT/PANI composite was investigated by Liu et al., increasing the mass ratio of CNT to aniline, the diameter of core–shell polymer decreased, and therefore, the composite conductivity decreased also. Less than 10% by weight, the composite CNT/PANI showed a gradually increasing conductivity [69]. Gui et al. developed three PANI/graphene oxide (GO) nanocomposite electrode materials from aniline (ANI) and GO by chemical polymerization with the mass ratio (ANI/GO) 1000:1, 100:1, and 10:1. The PANI/GO composite synthesized with the mass ratio (ANI/GO) 1000:1 possessed excellent capacitive behavior with a high specific capacitance due to the unique morphology of Mace-like PANI/GO composite [70]. It seems that the low percentage of carbon nanomaterials gives better results in them of conductivity and mechanical properties.

Nanocomposites based on carbon nanotubes

Since its discovery by Iijima in 1991, carbon nanotubes have revolutionized the field of polymer nanocomposites [71]. It was categorized as single-walled and multi-walled nanotubes. SWNTs are seamless cylinder graphite sheets. They have a diameter of 2 nm and a length of several micrometres, while MWNTs consist of multiple layers of graphene rolled in on themselves and separated from one another by 0.34 nm. Their diameter varied between 2 and 20 nm. A growing number of researchers worldwide have shown an interest in the combination of CNT with PANI. Recently, review articles have been published on the progress in the different synthesis methods of CNT/PANI nanocomposites. The identifications methods, the properties of the final product, and the progress towards technological applications have been investigated [72, 73]. CNT/PANI composites can be synthesized by electrochemical or chemical processing. CNT functionality is the key to improve dispersion of the nanotubes in the liquid (aniline, solvent) and consequently in the CNT/PANI composite. It also helps to direct formation of PANI chains at the surface of CNT instead of bulk PANI. Due to their easy synthesis, processability and possibility to combine the properties of CNT and the properties of PANI with synergic effects, CNT/PANI composites present great interest for various applications as chemical sensors, capacitors, fuel cells, and electronic devices. Recently, MWCNT-conducting polymer nanocomposites for gas-sensing applications were investigated. Mangu et al. demonstrated that the use of conducting polymers like polyaniline (PANI) and poly(3,4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT:PSS) enhances the gas-sensing capabilities. The MWCNT–PANI composite sensor synthesized was observed to show superior sensitivities and excellent reversibility to 100 ppm of NO_2 gas [62]. Later, Sharma et al. studied the thermal properties of the MWCNT-conducting polymer composite. They utilized MWCNT with PEDOT:PSS and PANI to develop high-temperature tolerant ammonia gas sensor. MWCNT–PEDOT:PSS composite was found to show better thermal stability than MWCNT–PANI composite. The MWCNT–PEDOT:PSS composite sensor was found to exhibit excellent response for trace level sensing (1–50 ppm) of ammonia gas than MWCNT–PANI composite [74]. Pure carbon nanotubes (CNTs) were also used to prepare PEDOT conducting polymer nanocomposite. Electrochemical polymerization of PEDOT/CNT nanocomposite was performed in EDOT aqueous solution containing only CNTs as the dopant. The solution was stirred and ultrasonicated for 10 min before polymerization at 1.2 V for 30 s. Due to the excellent stability of the PEDOT/CNT nanocomposite and its catalytic property towards dopamine (DA), a highly stable and sensitive DA sensor was developed that performs favorably in the presence of a high concentration of the common interferant ascorbic acid [66].

Polypyrrole is also an interesting conducting polymer who has the structural uniformity and high conductivity by strong π–π stacking between PPy conjugate backbone and graphitic sidewall of CNTs. To avoid all complicated multiple-step procedures to synthesize PPy/CNT-based nanocomposites, poly(sodium 4-styrenesulfonate) (PSS) polyelectrolyte has been added as supporting electrolytes as well as dopants to improve the solubility and dispersion of CNT. A one-step electrochemically polymerized method was used to fabricate the PPy/PSS-CNT composite electrodes. Thus, the aqueous solution for electrochemical polymerization consisted of pyrrole monomer, PSS, and long or short CNT. Comparing to the short CNT-incorporated PPy/PSS electrodes, long CNT-incorporated PPy/PSS electrodes show the relatively more superior capacitive behavior and cycle stability [75]. In other work, sodium dodecylbenzene sulfonate (SDBS) was used to disperse MWCNTs with ratio of 1:10 nanotubes to SDBS. MWCNTs, with different weight ratio (0.3, 0.5, 0.7, 0.9, and 1.1%) to the pyrrole monomer, were dispersed and sonicated in an SDBS solution. Then, PPy-MWCNTs' layer was synthesized by electrochemical polymerization of distillated pyrrole on MWCNT. PPy/MWCNT nanocomposite was used to improve the sensitivity and selectivity of sensors via interfacial interactions between MWCNTs and the conducting polymer. The nanocomposite layers were used to modify the gold layer to detect trace amounts of mercury (Hg), lead (Pb), and iron (Fe) ions using the surface plasmon resonance technique [76]. Nanocomposite of PPy and carboxylated MWCNT was synthesized by chemical polymerization for different MWCNT weight ratios. Six PPy-MWCNT nanocomposite samples

were prepared for different amounts of f-MWCNTs, and the weight ratio of functionalized MWCNT in PPy matrix varied from 0.25 to 8%. The PPy-MWCNT nanocomposite pellet sensors showed good sensitivity to NH_3 gas at room temperature. The most sensitive PPy-MWCNT nanocomposite sensor to NH_3 gas was obtained with 4 wt% MWCNT ratio [77]. Polyphenazines and poly(triphenylmethanes) as conducting polymers were also combined with CNT to develop electrochemical sensors and biosensors. Barsan et al. published recently a review on preparation and characterization of conducting polymer/CNT composites based on these phenazine polymers. The specific combination of phenazine/triphenylmethane polymers with CNT leads to an improved performance of the resulting sensing devices because of their complementary electrical, electrochemical and mechanical properties, and also due to synergistic effects. The main analytical applications as sensor were reported [78].

Nanocomposites based on graphene

Graphene oxide (GO) can be prepared in large scales from natural graphite. It was synthesized by a modified Hummers method as described in the previous studies [79]. It is a single sheet of graphite oxide-bearing oxygen functional groups on their basal planes. In recent years, GO has attracted great interest because of its superior mechanical, structural, and thermal properties and also its low cost compared to other conventional carbon nanomaterials like CNT. GO can be easily dispersed in aqueous solution and act as an excellent dopant for the chemical and electrochemical polymerization of conducting polymers due to the abundance of carboxyl groups that are negatively charged in aqueous solution. Kim et al. demonstrated that GO can play a role as a chemical oxidant for various CPs (polythiophene, polyaniline, and polypyrrole). In addition, diverse graphene/CP composites (graphene/polythiophene, graphene/polyaniline, and graphene/polypyrrole) can simply and rapidly be synthesized using the GO as both graphene precursor and chemical oxidant [80]. Poly[3,4-ethylenedioxythiophene] was largely studied to synthesize (GO/PEDOT) nanocomposites. Luo et al. have successfully synthesized GO/PEDOT nanocomposites by cyclic voltammetry using graphene oxide as dopant. The resulting nanocomposite is highly biocompatible with neuronal cells [68]. Due to their many negatively charged carboxyl groups, GO is an excellent dopant for the electropolymerization of conducting polymers. The formed film contains functional groups promoting any modification of the surface of the nanocomposite film. These groups reach carboxyl groups of GO partially exposed to the surface of the film PEDOT/GO. Normally, GO is an electrically insulating material, but its conductivity is recovered by restoring its network through its reduction to form what is called graphene or reduced graphene oxide. This reduction can be done thermally, electrochemically, or chemically using strong reducing agents such as hydrazine or sodium borohydride. GO is also an attractive platform for the production of functionalized graphene platelets with improved mechanical, thermal, and/or electronic properties [81–84]. Ambrosi and Pumera confirmed later that the electrochemical reduction is more interesting, because this process allows to control accurately the obtained chemical structures of graphene with reproducible density of the oxygen functionalities PEDOT/GO nanocomposite of reduced GO-doped conducting polymer PEDOT was prepared to improve electrochemical catalytic property of the resulting nanocomposite [85]. The same nanocomposite was electrodeposited on GCE and followed by electrochemical reduction. The obtained modified electrode was used as a sensitive sensor for DA detection without ascorbic and uric acids interference [86]. Seekaew et al. performed a gas sensor based on graphene–PEDOT:PSS composite film. Incorporating graphene in the polymer increased the specific adsorption surface area which has improved the NH_3 response [87]. The preparation and the thermoelectric proprieties of PEDOT composites containing PEDOT, reduced graphene oxide (RGO), and single-walled CNT (SWCNT) were also reported by Li et al. [88]. Nanocomposites based on PPy and GO exhibited enhancement in electrical conductivity. Bora et al. synthesized polypyrrole (PPy)/graphene oxide (GO) nanocomposites via liquid/liquid interfacial polymerization. The developed PPy/GO nanocomposite, comparing to pure polypyrrole, has shown improvement in electrical conductivity [89]. In another work, GO/PPy nanocomposites were performed by a one-step co-electrodeposition method. During the pyrrole electropolymerization, a negative charge of GO was incorporated into the polymer to balance the positive charge on the polymer. Moreover, the π–π interactions between GO and PPy play a considerably role in the formation of GO/PPy nanocomposites [67]. Overoxidized polypyrrole (PPyox) was used to synthesize PPyox/graphene nanocomposite due to their cation exchange and molecular sieve properties. The nanocomposite-modified GCE has been prepared and applied as dopamine sensors without the interference of ascorbic acid [64]. GO/PPy was also used to prepare molecularly imprinted polymer (MIP) for quercetin detection [63]. In the same way, the reduced form of graphene was combined with PPy for application as supercapacitors or sensors [90]. As example of sensor, Rong et al. have prepared GO/PPy by reducing GO to RGO and polymerization of PPy using potentiostatic mode. The resulted nanocomposites were applied for ammonia and Pb^{2+} detection [91]. In a comparative study, properties of PANI/G and PANI/MCWNT nanocomposites were investigated. It was proved that the charge transfer between the

PANI and carbon materials (MWCNTs and G) improved the electrical conductivity of PANI. The obtained composites have different morphologies and conductivities. It was elucidated that PANI/G composite has a plate form, while PANI/MCWNT composite is tubular [92]. An electrochemical biosensor based on PANI/RGO nanocomposite has been reported. The nanocomposite was synthesized by chemical oxidative polymerization method and was then used as the sensitive layer of a DNA adsorbent for detecting Hg^{2+}. The detection limit was 0.035 nM [93]. Nguyen et al. synthesized PANI grafted RGO composites via a two-step method. First, RGO was modified with 1,3-diaminopropane providing reactive NH_2 groups on surface witch can polymerize with aniline. The formed GO–NH_2 was then grafted with polymer chains by in situ chemical polymerisation. The RGO-g-PANI composites were used for the chemical detection of hydrogen peroxide in aqueous solutions [94]. The G/PANI-modified electrode allowed selective determination of the target metals in the presence of bismuth Bi(III). Graphene–polyaniline (G/PANI) nanocomposite was used to develop an electrochemical sensor for simultaneous detection of Zn(II), Cd(II), and Pb(II). To prevent nanoparticle aggregation during nanocomposites synthesis, they added polyvinylpyrrolidone (PVP) by a method called reverse dropping which creates a solution of well-dispersed particles [95]. Under optimal conditions, the detection limits were 1.0 μg L^{-1} for Zn(II) and 0.1 μg L^{-1} for both Cd(II) and Pb(II). Recently, electrospun graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fiber-modified screen-printed carbon electrode was investigated and optimized also to simultaneous determination of Pb^{2+} and Cd^{2+} in the presence of bismuth. The limits of detection were found to be 3.30 μg L^{-1} for Pb^{2+} and 4.43 μg L^{-1} for Cd^{2+} [96]. Poly(diaminonaphthalene) combined with RGO was synthesized in one step using cyclic voltammetry. The chelating capacity of poly(1,5 diaminonaphthalene) and the properties of RGO were used to elaborate a lead sensor [97].

Nanocomposites based on carbon black

Only one paper is devoted to carbon black. Mallya et al. used a nanocomposite of a novel thiophene-based conducting polymer and carbon black as a volatile organic compound sensor. The obtained sensors were tested for the determination of toluene, acetone, carbon tetrachloride, and cyclohexane and showed maximum response to toluene [98]. Since the low cost of carbon black more research must be conducted in this area.

In conclusion, the carbon nanomaterials and conducting polymer nanocomposites are very promising materials because of multifunctional and unique properties. Therefore, such nanocomposites have been reported in the literature as promising prototype materials for chemical sensors applications, as it is summarized in Table 1.

Nanocomposites synthesized by combination of metal nanoparticles and conducting polymers

Nanocomposites based on conducting polymers (CPs) and metal nanoparticles (MNPs) are a new class of nanomaterials that have received a considerable attention during the last decade [104]. These nanocomposites are formed by combining the unique properties of MNPs and CPs, in the aim to enhance the chemical and/or physical properties. The combination of these materials can give rise to a new nanostructure with novel properties and promising potential applications in various fields of nanoscience and nanotechnology. Recently, many efforts have been made to synthesize new nanocomposites of conducting polymers and metal nanoparticles with new properties and applications [105, 106].

In this part, we will give an overview about the most method used to synthesis different metal nanoparticles such as Au, Pt, Pd, Ag, Cu, and Bi. We will also discuss the main parameters affecting their structural, physical, and chemical properties. On the other hand, a special attention will be paid to the recent advances in the synthesis of nanocomposites based on metal nanoparticles and conducting polymers such as polythiophene (PTh), polypyrrole (PPy), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and their derivatives. We will also focus on their current catalytic and sensing applications.

Different strategies for the synthesis of metal nanoparticles

Metal nanoparticles could be prepared using two different approaches, which are bottom–up and top–down. In the first approach, the metal nanoparticles are fabricated by starting from metals atoms dissolved in aqueous or organics solution and then deposed under appropriate experimental conditions. In the second approach, the metal nanoparticles are prepared by subdivision of bulk metals usually using physical methods [107, 108]. Considering the above approaches, the methods of synthesis of metal nanoparticles could be classified to six mean methods, as shown in Fig. 5.

The chemical reduction is considered the common method reported in the literature for the synthesis of metal nanoparticles, which are formed by reducing metal salts in the presence of an appropriate reducing agent and a stabilizer usually a special ligand, polymer, or surfactant. The electrochemical methods are widely used in the synthesis of metal nanoparticles. The metal species is dissolved in

Table 1 Typical applications of CNMs/conducting polymer nanocomposites as sensor

Nanocomposite	Polymer	CNM	Application	LOD	Characterization	Refs.
PEDOT/GO	PEDOT	GO	Dopamine detection	39 nM	EIS–SEM	[86]
MWCNT–PEDOT:PSS MWCNT–PANI	PEDOT:PSS PANI	MWCNT	Ammonia gas sensor		FTIR–SEM–TEM	[74]
SEBS/MWCNT	SEBS	MWCNT	Temperature sensors		TGA, SEM	[99]
PPyox/graphene	PPyox	graphene	Detection of Dopamine	0.1 μM	SEM	[64]
MIP/GO	PPy	Graphene oxide	Quercetin determination	48 nmol L^{-1}		[63]
MWNTsg-PtBMA-*b*-PS	PS-*b*-PtBMA	MWNTs–COOH	$CHCl_3$ vapor sensor		FTIR, 1H NMR, TGA XRD, TEM, SEM	[100]
PEDOT/CNT	PEDOT	CNT	Dopamine detection	20 nM	SEM, CV	[66]
G/PANI	PANI	graphene	Zn(II) Cd(II) Pb(II)	1 μg L^{-1} 0.1 μg L^{-1} 0.1 μg L^{-1}	SEM, FTIR, CV	[95]
G/PANI/PS	PANI/PS	graphene	Simultaneous determination of Pb^{2+} and Cd^{2+}	3.30 μg L^{-1} (Pb^{2+}) 4.43 μg L^{-1} (Cd^{2+})	SEM, TEM, BET	[96]
3D-rGO@PANI	PANI	3D-RGO	Detection of Hg^{2+}	0.035 nM	XPS, SEM	[93]
Poly(DTCPA-*co*-BHTBT)–CB	poly (DTCPA-*co*-BHTBT)	carbon black	Volatile organic compounds (VOCs) sensor	15 ± 10 ppm	UV–vis, optical profilometer contact angle measurements AFM, FEG SEM	[98]
GO-PANI	PANI	GO	Carbaryl, carbofuran, methomyl	0.136 mg L^{-1} 0.145 mg L^{-1} 0.203 mg L^{-1}	CV, UV–Vis and FTIR spectrometry	[101]
PEDOT/GO	PEDOT	GO	Mercury (II)	2.78 nM	SEM, TEM	[102]
G/p-AHNSA	*p*-AHNSA	Graphene	Dopamine (DA) and 5-hydroxytryptamine (5-HT)	2 and 3 nM	CV, SWV, EIS, SEM	[103]

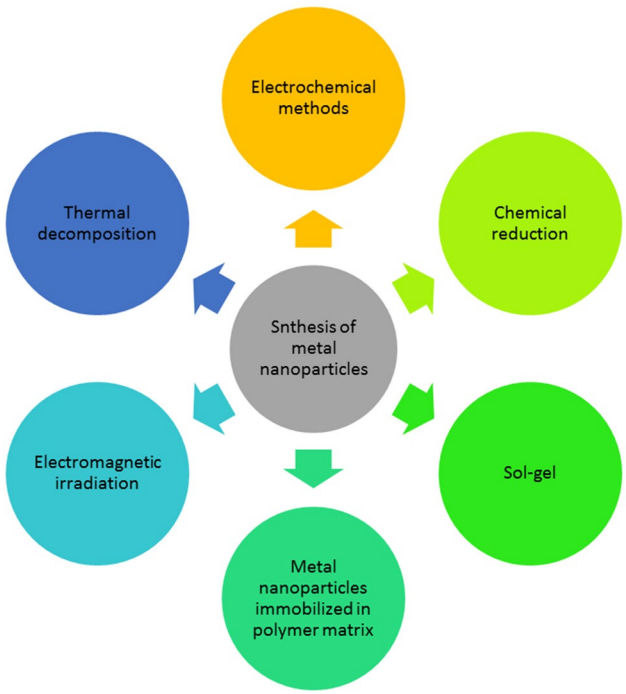

Fig. 5 Different methods used for the synthesis of metal nanoparticles

aqueous or organics solution, then followed by the reduction of metal ions on an appropriate support using cyclic voltammetric or a constant reduction potential.

- Metal nanoparticles immobilized in polymer matrix

  In general, there are three ways to obtaining metal nanoparticles within polymer matrix, including dispersion, deposition, and immersion. The dispersion method starts with mixing metal precursor with protective polymer and the metal ions are subsequently reduced in the solution. In deposition process, metal precursor which was mixed with protective polymer is deposited onto a substrate.
- Sol–gel

  Sol–gel methods are also considered as a very promising method for the synthesis of metals nanoparticles [109]. During their synthesis, the experimental conditions including pH, nature of solvent, and temperature strongly affects on properties of the synthesized metal nanoparticles.
- Electromagnetic irradiation

  The metal nanoparticles could also be prepared using electromagnetic irradiation methods including UV, microwave, ultrasonic, and laser irradiation [110, 111].
- Thermal decomposition

Another way for the synthesis of metal nanoparticles is heating volatile metal compounds in organic media or gas phase. The compounds degrade and liberate metal or the corresponding metal oxide in dispersed phase.

Nanocomposites based on conducting polymers and metal nanoparticles

There are four basic strategies for the preparation of the nanocomposites of conducting polymers and metal nanoparticles as mentioned in the review of Kondeatiev et al., the commonly used procedures for preparation of nanocomposite are:

Electrochemical method: the deposition of metal nanoparticles into the pre-synthesized polymer film, or during the electropolymerization process.

Chemical method: the nanocomposite can also be performed from colloid dispersions of polymers and metal nanoparticles, or in one-step synthesis from mixed solution containing monomer and metal ions. Conducting polymer–metal composites are obtained by oxidizing the conjugated monomer by transition metal cations, which induces the simultaneous formation of both the polymer matrix and the metal nanoparticles. Figure 6 summaries the most procedure used for preparation of these nanocomposite.

In addition, the electrochemical or chemical methods for synthesizing conducting polymer–metal nanocomposite are considered as well as the main factors affecting the structure and electrochemical properties of these composites [34]. The size of the synthesized nanocomposite was approximately ranging from 1 to 100 nm. The shape and size of the nanocomposite obviously depend on methods of deposition of metal nanoparticles and the shape of conducting polymers [40, 112]. The modification of some conducting polymers such as polythiophene (PTh), polypyrrole (PPy), and polyaniline (PANI) by serval metal nanoparticles was reported [113]. The obtained nanocomposites were used in

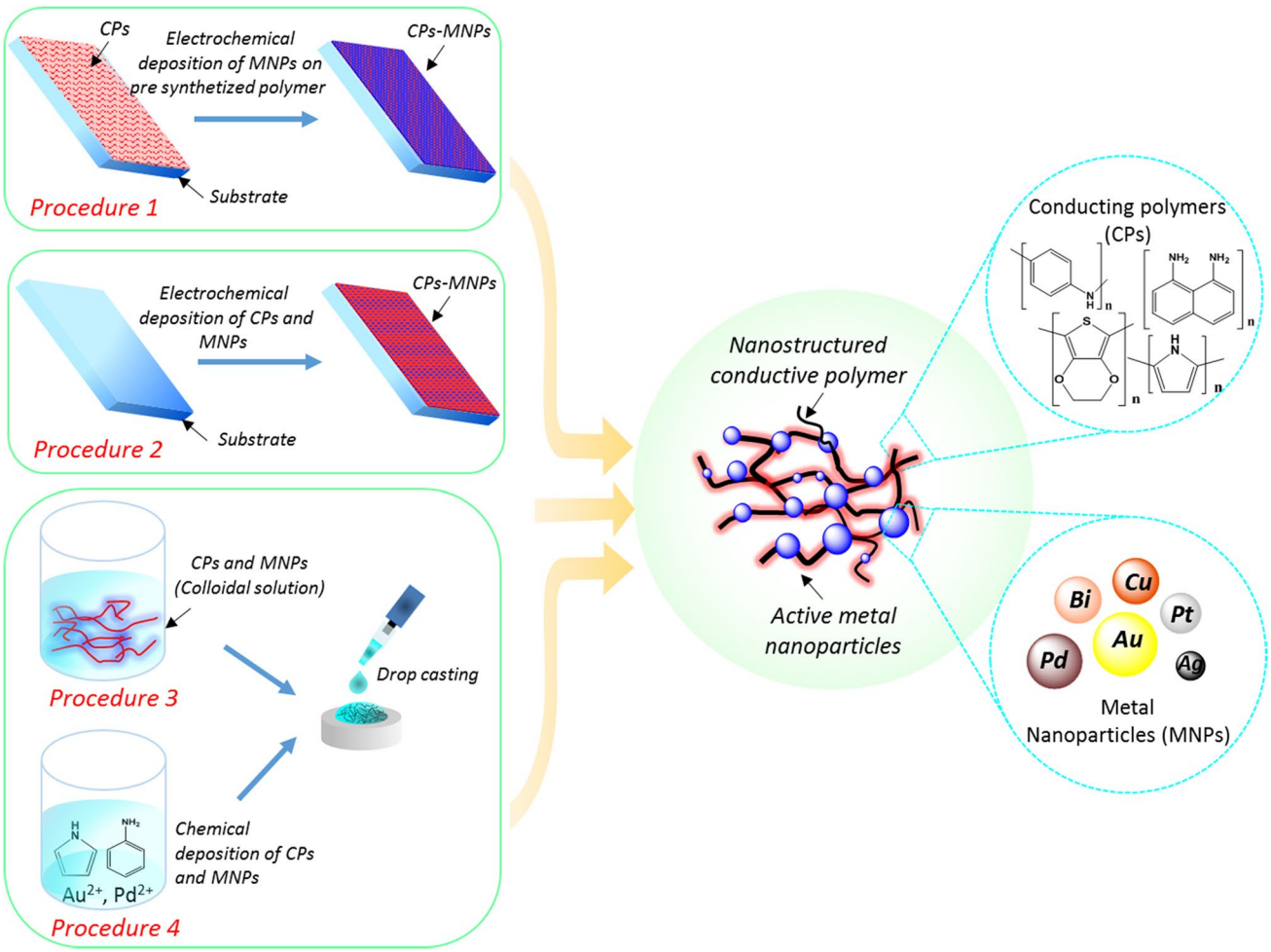

Fig. 6 Schematic illustration of the most procedure for the preparation of nanocomposites based on conducting polymer and metal nanoparticle CPs/MNPs

electrochemical sensors [114], energy technology, batteries, and fuel cells [115, 116].

Gold nanoparticles—polymer

Gold nanoparticles are widely used due to their very interesting properties and their catalytic power. The conducting polymers with gold nanoparticles as a nanostructured materials exhibit unique electrical, optical, and catalytic properties. These nanocomposites have been utilized for heavy metal, nitrite, ammonia gas, H_2O_2, dopamine, glucose, ascorbic acid, and uric acid detection. Different methods for preparation of nanocomposites AuNPs/CPs are used such as chemical, electrochemical, thermal evaporation, hydrothermal, and spin-coating method. At present, it has been found that the best way to synthesis polymer–metal nanocomposite is the deposition of metal nanoparticles into the polymer film. Metal nanocomposite is formed on the surface or in the bulk by drop casting or incorporation of pre-synthesized NPs during the electrochemical deposition of conducting polymer, as shown in Fig. 6. $HAuCl_4$ was used as a precursor for the preparation of AuNPs/polymer with a concentration from 3 to 10 mM. The size of the AuNPs is related to Au precursor concentration, polymer/AuNPs molar ratio, synthesis method, and synthesis time [117–122]. Huang et al. have developed a facile and well-controlled techniques to prepare water dispersible uniform AuNPs on PANI. Uniform gold nanoparticles with a size around of 2 nm were selectively reduced on polyaniline nanofibers, from aqueous solution of $HAuCl_4$. The strong interaction between protonated amine and $AuCl_4^-$ leads to an excellent electrocatalytical effect. The modified electrode exhibited a fast response time and high sensitivity for H_2O_2 sensing with a detection limit of 0.1 μM [117]. The same authors developed an electrochemical sensor for the oxidation of dopamine on molybdenum disulfide nanosheets–polyaniline (MoS–polyaniline) composites and gold nanoparticles (AuNPs)-modified glassy carbon electrode with a size of 13 nm. The graphene-like MoS–polyaniline composites were synthesized by hydrothermal method and a simple in situ polymerization procedure. The electrochemical sensor was applied to the dopamine detection in human urine sample [118]. Two approaches to incorporate the AuNPs with and without pre-functionalization into covalently assembled polythiophene films have been reported (NPs size 14.5 ± 4 nm). The adopted approaches involve alternate deposition of monomeric and polymeric species for creating multilayers. This method has been used to develop facile method for nanoparticles incorporation and to facilitate direct interaction between conducting polymers and nanoparticles. Both the approaches have merits and demerits on their own depending on the film requirements. However, the preparation of this nanocomposite takes a very long time (more than 6 days) [123]. In other work, the co-polymerization of polyvinylpyrrolidone and polyaniline was performed by cyclic voltammetry. The nanocomposite of gold nanoparticles with co-polymer was synthesized by electrodeposition methods on a glassy carbon electrode (GCE) in a homogeneous three-component solution consisting of aniline, PVP, and AuNPs. The modified electrode was used as glucose biosensor [124]. Recently, a nanocomposite of the self-assembly gold of nanoparticles with polystyrene-*b*-poly(4vinylpyridine) copolymer has been synthesized with a size of 27 nm for (bio) sensing applications [121]. Spherical gold nanoparticles, with a size of 3.5 nm, were used for preparation of glucose biosensors in the presence of conducting polymer and were successfully applied to beverages for the detection of glucose content in a linear range between 0.025 and 1.25 mM. The detection limit was 0.025 mM [125]. An approach to elaborate a novel nanocomposite in which gold nanoparticles in small size (4.2 nm) are dispersed on polypyrrole matrix has been developed by Zhang et al. [119]. The nanocomposite has showed great potential for detecting ammonia gas at room temperature. In addition, the bioimprinted ds-DNA and Au nanoparticles in the o-phenylenediamine were used to modified pencil graphite electrode as sensor for the determination of dopamine. This nanocomposite was prepared by electrochemical entrapment of ds-DNA and Au nanoparticles in the o-phenylenediamine. The nanocomposite was applied for the determination of dopamine in biological samples over the range of 20–7000 nM with a detection limit of 6 nM [122]. El-said et al. have synthesized poly(4-aminothiophenol) nanostructures layered on gold nanodots patterned indium tin oxide (ITO) electrode. The modified gold nanodots ITO electrode were fabricated by thermal evaporation of pure gold metal onto ITO surface through polystyrene monolayer. Then, a monolayer of 4-aminothiophenol was self-assembly immobilized onto the gold nanodots array/ITO electrode by electrochemical polymerization process. The size of AuNPs was 80 nm. The obtained electrode was used for detection of adenine and guanine in human serum sample [126]. The nanocomposite-based gold nanoparticles are usually decorated on molecularly imprinted polymer membranes (MIPM). In the work of Zhang et al., MIPM was used as biomimetic molecular recognition element involved in o-aminothiophenol functionalized Au nanoparticles (ATP-AuNPs) with a size of AuNPs 4.2 nm. The modified gold electrode was used for detection of herbicide simazine (SMZ) in several real samples. The linear dependency of peak current on SMZ concentrations was observed from 0.03 to 140 μM and detection limit was estimated to be 0.013 μM [120]. In a recent paper, an approach for synthesis of PEDOT/AuNPs composite was developed by Lin et al., consisting of electropolymerization of PEDOT from solution containing gold nanoparticles and EDOT monomer mixed in water solution. It was demonstrated that sensor is

highly stable, sensitive, and selective and it was used for the detection of nitrite in tap water [127]. Sadanandhan and Devaki have modified the glassy carbon electrode with PANI through electrochemical polymerization by cyclic voltammetry. Then, the gold nanoparticle AuNPs were deposited by chronoamperometry on the polymer. The performance of the sensor was then tested in blood samples for simultaneous sensing of dopamine, ascorbic acid, serotonin, and uric acid [128].

Platinum nanoparticles—polymer

The interesting properties of platinum at nanoscale dimension have gained research attention due to their potential application. The platinum nanoparticles are considered very effective as a matrix in detection of various kinds of biomolecules and macromolecules such as DNA, enzymes, other proteins, and antibodies. The same strategies used in the deposition of gold nanoparticles were used for the deposition of platinum leading to a nanoparticles with diameter ranging from 1 nm to some hundreds nm using $PtCl_3$ and H_2PtCl_6 as a precursor. The size and the distribution of platinum nanoparticles on the polyaniline and polypyrrole have been studied by varying the polymer matrix from nanofibers to nanotubes. The nanocomposites formed are very sensitive to the matrix morphologies. Small polymer nanostructure (nanofibers) provides a large number of heterogeneous nucleation sites for nucleating Pt nanoparticles, leading to better distribution and dispersion of the Pt nanoparticles (2 nM) [129]. Mishra et al. designed a new biosensor for the detection of human C-reactive protein (αCRP), by combining two types of advanced materials with complementary properties, polypyrrole film (PPy) and platinum nanoparticles (PtNPs). The long chain of PPy in the polymer composite acts as a space between the biomolecules and the transducer, wherein the Pt nanoparticles help in preserving the native protein conformation and reducing the steric hindrance for better probe orientation and accessibility of the biomolecules to the analyte. The obtained nanocomposite has demonstrated a large surface area and a high performance towards AgαCRP detection [130]. In the paper of Adeloju et al., the surface of the platinum electrode was first modified by thin film of platinum nanoparticles with a diameter of 30–40 nm priory the deposition polypyrrole film, providing large surface area for the deposition of ultrafine film polypyrrole. This strategy was employed to elaborate a biosensor for potentiometric detection of sulfite in wine and beer samples in the linear concentration range that extends from 0.75 to 65.50 μM of sulfite, with a detection limit of 12.4 nM, and a response time of 3–5 s [131]. Boomi and co-works reported the first chemical synthesis of the polyaniline-modified Pt–Pd nanoparticles. The obtained nanocomposites exhibited improved antibacterial activity when compared to pristine polyaniline and individual metal colloids. The Pt–Pd nanoparticles have spherical morphology and the particles' size was found around of 1–7 nm. The antibacterial properties depend strongly on the size of metal nanoparticles [132]. In addition, Zhai et al. fabricated an electrochemical biosensor for glucose with Pt nanoparticle/polyaniline hydrogel hetero structures. This biosensor was applied for glucose enzyme sensor with a wide linear calibration ranging from 0.01 to 8 mM and the detection limitation of 0.7 μM [133].

Silver nanoparticles—polymer

Hybrid nanocomposites based on conducting polymers (CPs) and silver nanoparticles (AgNPs) have recently become a tool in the preparation of new materials. The obtained nanomaterials exhibit a good level of electrical conductivity as well as tunable physical, chemical, and responsive properties. Several conducting polymers were used to produce these nanocomposites among them, polypyrrole (PPy), and polyaniline (PANI) [134].

In a detailed review, the strategies of fabrication of nanocomposite by combination of silver nanoparticles (AgNPs) and conducting polymers and their application have been reported. Various strategies for the synthesis of AgNPs were detailed such as, polyol process, solvothermal method, ultraviolet irradiation, photo-reduction technique, electrodeposition process, DNA template method, porous material template method, and wet chemical method. The role of various additives (inorganic anions, metal cations, and organic molecular species) on the aspect ratio of silver nanowires (AgNWs) has been reported. Moreover, different methods for the preparation of AgNWs/conducting polymers composite film are reviewed like spin coating, dip coatings and electro-hydrodynamic (EHDA), simple solution mixing techniques, and electrospinning [135]. Nia et al. reported a new nanocomposite sensors based on polypyrrole (PPy) decorated with silver nanoparticles (AgNPs) and its application as a non-enzymatic sensor for hydrogen peroxide (H_2O_2) detection. AgNPs–PPy was deposited on glassy carbon electrode by electrochemical method using cyclic voltammetry. The modified electrode revealed that PPy and AgNPs were uniformly formed and PPy was decorated with small particle size of AgNPs around of 25 nm [136]. In another application, Ghanbari has modified the glassy carbon electrode (GCE) with a pre-synthesized polypyrrole (PPy) nanofiber and then with AgNPs to form a nanocomposite of AgNPs/PPy/GCE. The modified electrode was used to determination of hydrazine with a detection limit of 2 μM [137]. It was reported in many studies that plants have potential to reduce metal ions both on their surface and in various organs and tissues. Alam et al. have used Ziziphus mauritiana fruit extract to synthesized sliver nanoparticle AgNPs. Then,

the enzyme of alcohol dehydrogenase (YADH) has been immobilized on chemical synthesized polyaniline-coated AgNPs [138]. This approach has been actively studied in recent years as an alternative, efficient, inexpensive, and environmentally safe method for producing nanoparticles with specific properties.

Zang et al. have reported the preparation of a new nanocomposite based on AgNPs–PPy-modified attapulgite (ATP) as a clay support by in situ UV-induced dispersion polymerization. AgNPs with a size around of 40 nm were obtained and the potential applications of obtained composite nanoparticles as an antibacterial agent was explored [139]. Recently, Bhadra et al. used polyaniline (PANI) and polyvinyl alcohol (PVA) with silver nanoparticles to synthesis the nanocomposite blend (PNPAg). Nanocomposites with lower Ag concentrations have highly aligned PNPAg nanofibers of diameter 50–80 nm and agglomerations compared to the higher concentrations of Ag and have good optical and electrical properties. Indeed, the room temperature electrical conductivity of the nanocomposites increased with Ag nanoparticles [140].

Palladium nanoparticles—polymer

Palladium nanoparticles (PdNPs) have been used in a variety of fields, especially as catalysts in organic reactions due to their superior chemical stability and catalytic activity [141]. Few works have been reported in the literature for developing the nanocomposites by the combination of palladium nanoparticles (PdNPs) and conducting polymers (CPs). Prodromidis et al. reported a simple electroless approach for the synthesis of PdNPs incorporated in polyaniline (PANI) via formation of a preorganized palladium polymer complex material followed by slow reduction. The PdNPs were uniformly dispersed in the polymer with a diameter size around 5–10 nm and a large electrochemically active surface area. The obtained nanocomposite was applied for electrooxidation of methanol and ethanol. The results suggest that this nanocomposite could be considered as an efficient anode in fuel cells [142]. In an excellent research work, Li et al. reported a facile strategy to produce a novel nanoparticulate polyacetylene-supported Pd(II) catalyst [NP–Pd(II)] for use in the aqueous Suzuki–Miyaura cross-coupling reaction, by simply treating an aqueous solution of $PdCl_4^{2-}$ with acetylene under ambient conditions. The nanocomposites reveal homogeneous distribution of the Pd(II) along the polyacetylene and the aggregation of the NP–Pd(II) with diameters of 2–3 nm that make this nanocomposite an ideal catalyst combining the advantages of both homogeneous and heterogeneous catalysts [143]. Sapurina et al. recently reported that polypyrrole nanotubes, prepared by chemical reaction in the presence of methyl orange, could be used as a conducting substrate for the deposition of noble-metal nanoparticles. The synthesized polypyrrole nanotubes were decorated with palladium, platinum, rhodium, or ruthenium nanoparticles by carbonization method. The catalytic activity of obtained composites was proved in the reduction of 4-nitrophenol to 4-aminophenol [144]. In addition, Hosseini et al. synthesized palladium nanoparticles/poly(3,4-ethylenedioxythiophene) nanofibers as a sensors for glucose and hydrogen peroxide detection by chronoamperometric method. This sensor shows a low detection limit of 1.6 μM for glucose and 0.05 μM for H_2O_2 in the range of 0.04–9 mM and 0.2–25 μM, respectively [145].

Other metal—polymer nanocomposites

Besides gold, platinum, palladium, etc, others metallic nanoparticles have been studied during the last decade such as copper, bismuth, and nickel. Copper nanoparticles (CuNPs) have fascinating properties such as the good thermal and electrical conductivity, nonlinear optical properties, and cost much less than the other metals. CuNPs are very well known for their potential application in cooling fluids for electronic systems, conductive inks, switches, or photochromic glasses in optical devices and nonlinear optical materials [146]. In addition, the CuNPs are widely used in electrochemistry as electrode materials. The effect of copper concentration and surfactants on the conductivity and stability of composite polymer-supported copper nanoparticles (CuNPs) were studied by Pham et al., and the nanoparticles with average diameter of 56 nm were synthesized by chemical reduction in the presence of cetyltrimethylammonium bromide (CTAB) and polyvinylpyrrolidone (PVP) as stabilizer. They have shown that these compounds prevent and protect the copper nanoparticles from the agglomeration and oxidation. The CuNPs were incorporated in PEDOT:PSS in aqueous solution to form conducting composite [147], who could be used for different applications. In situ chemical oxidation polymerization method was used to synthesis copper nanoparticles intercalated polyaniline nanocomposite. This nanocomposite was used to elaborate a sensor, which was applied for gas sensing towards different gases namely NH_3, CO, CO_2, NO, and CH_4 at room temperature. The sensor films exhibited a highly selective response for NH_3 with negligible response towards the other gases. Although the sensor have a drawback related to its sensitivity at high concentration, the saturation of the sensor was observed at concentration exceeding 50 ppm. The large surface area and charge transfer resulting of CuNPs intercalation in PANI matrix were the characteristics allowing the enhancement of the gas response [148]. The same method was used to synthesize nanocomposites of polypyrrole (PPy) containing copper sulfide (CuS). The nanocomposite was characterized by the means of FTIR, scanning electron microscope, and X-ray diffraction, differential scanning calorimetry, confirming the formation

of CuS/PPy nanocomposites with porous, granular, and globular surface morphology and crystallinity. Besides, the thermal stability and the conductivity were also studies, indicating a better thermal stability. The dielectric behavior increases the order ness and the packing. Despite dielectric loss arises due to the localized motion of the charge carriers. The conductivity of CuS/PPy nanocomposite increases with the increase in the concentration of CuS. The nanocomposites have a large scientific and technological interest and possible application like sensors [149]. Ternary NiO/CuO/PANI nanocomposites were synthesized by in situ growth of NiO/CuO nanoparticles via electrodeposition and electrochemical oxidation, in a PANI matrix prepared through electrodeposition. Due to the large surface area and good conductivity of NiO/CuO/PANI nanocomposite, a nonenzymatic sensor exhibited high electrocatalytic activity towards the oxidation of glucose. The modified electrode displayed higher sensitivity and a lower detection limit of 2.0 µM [150]. MnO_x nanoparticles have attracted large attention due to its abundance and relatively environmentally friendly nature [151]. To improve the capacitance property of PEDOT, Yang et al. used manganese dioxide nanoparticles MnO_2–NPs, to produce a high-performance electrochemical energy storage electrode. The PEDOT/MnO_2–NPs were prepared by simple thermal treatment and chemical vapor phase polymerization (VPP) methods. Despite the low conductivity and aggregation of MnO_2–NPs, the control of the loading and distribution of MnO_2–NPs in PEDOT matrix offer uniform dispersion of nanoparticles into porous PEDOT matrix, which enhance the performance of the composite electrode [39]. The conductive PEDOT:PSS matrix was also used by Ju et al., with tin selenide SnSe nanosheets to achieve high-performance polymer-based thermoelectric devices. The subsequent solvent treatment appears a promising strategy to create the nanocomposites [152]. Other nanocomposites based on Gallium nitride nanoparticles (GaN) and poly(3,4-ethylenedioxythiophene)-*co*-polypyrrole (GaN/PEDOT–PPY) were synthesized using supercritical ammonia method and by chemical oxidative polymerization method. The nanocomposite was used as an electrochemical catalyst for the oxidation of an antihelminthic drug mebendazole using differential pulse voltammetry [153]. Bismuth recognized with a low toxicity and widely used in electroanalytical as environmentally friendly electrode since the first publication of Wang et al., [154]. Bismuth nanoparticles were employed in synthesis of different nanocomposite materials for application in different area example power generation as thermoelectric material [155, 156] and electroanalysis as sensor. Polyaniline–bismuth oxide (PANI–Bi_2O_3) nanocomposite was used to fabricate a sensor for the detection of pramipexole in pharmaceutical formulation. The prepared electrode has lower charge transfer resistance leading to higher electrocatalytic activity. A highest concentration of PANI–Bi_2O_3 suspension causing thickness of the hybrid film and increasing concentration of surfactant leads to the increase of hydrophobicity of surfactant micelles that were decreased the performance of the sensor. The LOD and LOQ for the pramipexole detection are 1.10 and 3.35 µg/mL, respectively [157]. Salih et al. have modified carbon paste electrode (CPE) with poly(1,8-diaminonaphthalene) and bismuth film for detection of lead. The bi-poly1,8-DAN/CPE was prepared and characterized by cyclic voltammetry and electrochemical impedance spectroscopy. It was demonstrated that higher concentration could cause the reduction of active sites on the surface of electrode. The modified electrode was applied for the analysis of lead in water samples using square wave voltammetry in acidic medium [158]. Similarly, Elbasri et al. have fabricated the modified poly(1,8-Diaminonaphthalene) by nickel ions particles (NiPs) on carbon paste electrode (CPE) for electrocatalytic oxidation of methanol in alkaline medium for direct methanol fuel cells (DMFCs). The obtained composite was characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) [159]. Different metallic particles were used to develop a sensor for the electroanalysis of ascorbic acid (AA). Platinum electrode modified with polyterthiophene (P3T) and doped with metallic particles (Cu, Co, Ag, Au, and Pd) was fabricated by first the electropolymerization of the monomer and then the incubation of the modified electrode in metallic ions solution to form the composite materials. The good sensitivity was obtained with the P3T–Ag film towards the target molecule AA, due to the high electron conductivity and good stability of the silver nanoparticles. The limit of detection was found to be 5.1710^{-10} mol L^{-1} using square wave voltammetry (SWV) [160].

The incorporation of metal nanoparticles with conducting polymers has led to a significant increase in the performance of devices in terms of sensitivity, selectivity, multiplexed detection capability, capacitance, and portability. In general, nanomaterials have played a key role in chemistry, biology, physics, engineering, and medicine. Table 2 shows the characteristics and the applications as sensors and fuel cells based on various nanostructured conducting polymers and nanoparticles.

Challenges and trends

The preparation, electrical characterization, and applications of composite layers formed by dispersing carbon on metallic nanostructures in polymer have been described. Indeed, the attractive properties of carbon structures such as carbon paste, carbon nanotube, carbon nanofibers, and graphene make them suitable materials for polymerizations of a number of monomers. The combination of carbon materials with polymers improves the properties of these materials

Table 2 Nano-structured conducting polymer/nanoparticle-based sensors, biosensors, and other applications

Metal nanoparticles/conducting polymer	Application	Refs.
Au/polyaniline	Dopamine	[118]
Au/polyaniline	H_2O_2	[117]
Au/polyvinylpyrrolidone–polyaniline	Glucose	[124]
Pt/polypyrrole	C-reactive protein	[130]
Pt/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)	Solar cells	[161]
Ag/polypyrrole	Hydrazine	[137]
Ag/polypyrrole	H_2O_2	[136]
Pd/polyaniline	Fuel cells	[142]
Ni/poly(1,8-diaminonaphthalene)	Fuel cells	[159]
Au/poly(3,4ethylenedioxythiophene)	Cysteine	[162]
Au/poly(3,4-ethylenedioxythiophene)	Solar cells	[163]
Pd/poly(diphenylbutadiene)	Fuel cells	[164]

for different purposes (from electrochemical detection to fuel cell). From the work detailed in this review, it is clear also that the metallic nanoparticles such as gold, platinum, and silver combined with conducting polymers have much to offer in the different fields. However, to our best knowledge, no comparative study covering the electropolymerization of conducting polymer and carbon nanomaterial or metallic nanoparticles was reported. The fabrication of nanocomposites by chemical mode takes more time in all steps of preparation than electrochemical mode, either for nanoparticles synthesis or for polymerization. It could be take more than 48 h [165]. Furthermore, it was noted that the nanoparticles were generally synthesized by chemical ways which was more difficult compared to electrochemical one [166]. In addition to the use of many reagents, it requires a great deal of time and can spread out over long period [167]. In addition, all works mentioned that the modified electrode has good stability expressed by the responses of the electrodes found to be constant for the long term. The percentage of nanoparticles in the constitution of nanocomposites varies from one case to another. It was estimated to be between 0.1 and 20% [168–170]. We have seen that the combination of conducting polymers and carbon nanomaterials or nanoparticles has led to better properties of these components [46, 171–173]. Metallic nanoparticles offer unique advantages when used for electroanalysis: enhancement of mass transport, catalysis, and high-effective surface area. The carbon nanostructures have attracted significant research activity due to their great potential application. Therefore, the question is: what will be the behavior of the nanocomposites if we combine NPs/polymers/CNMs? The formation of multi-components nanocomposites was expected to improve their physical or chemical properties. Moreover, some advantageous properties were resulted by the fusion effects of these components including spectral, electronic, magnetic, optical properties, and specific surface area. Some interesting papers have been devoted to the strategies employed for the preparation of NPs/polymers/CNMs. As mentioned by recent papers, multi-component nanocomposites synthesized with the combination of CNMs/CPs and MNPs produce new materials with exciting properties such as catalysis, enhancement of mass transport, high-effective surface area, and conductivity. Moreover, various strategies for the preparation of nanocomposites have been reported [166, 174–179]. In the light of recent works, it remains a challenge to founding new approaches to synthesize new nanocomposite materials based on carbon nanoparticles or metallic nanoparticles. The idea is to improve the simplicity and efficiency of the new composite and extend the application of the composite materials in different fields with a low cost.

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