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Carbon Nanotube-Conducting Polymer Composites as Electrode Material in Electroanalytical Applications

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Additional information is available at the end of the chapter

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Abstract

This chapter gives a brief overview of the preparation, characterization, and analytical applications for combinations of polymers and carbon nanotubes (CNTs) that have been prepared in different ways, which are used as an electrode material. For this purpose, multiwalled or single-walled CNTs are composed of different types of conductive polymers. The preparation of CNT-conducting polymer composite electrodes was explained by their deposition order. Chemical and morphological surface characterizations of composite electrodes were presented by scanning electron microscopy, transmission electron microscopy, atomic force microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. In addition, CNT-based polymer composite electrode usage in sensor applications for trace organic/inorganic compounds and energy applications is discussed in the last part of this chapter.

Keywords: Carbon nanotubes, conducting polymers, composite electrodes, metal nanoparticles scanning, electron microscopy

1. Introduction

Recently, considerable attention focused on nanometer-sized structures, which show great catalytic activity due to their high surface area to volume ratio and their effective properties such as magnetic, optical, electronic, and catalytic activity. Carbon nanotubes (CNTs) are one of the most attracted materials in this field. The historical roots of CNTs started in the 1960s

when Roger Bacon produced graphene sheets rolled into scrolls, which were supported by microscopic and diffraction results. CNTs were actually discovered by Sumio Iijima in 1991, who published CNTs as “helical microtubules of graphitic carbon,” and these soon are known as multiwalled CNTs (MWCNTs). Two years later, Iijima published another type of 1.37-nm-diameter single graphene cylinder, which today are known as single-walled CNT (SWCNTs). Whereas MWCNTs consisted of more than one rolled graphene that is telescoped, SWCNTs only formed from a single graphene sheet. The wrapping of the graphene sheet to form cylindrical nanotubes can occur with different angles. CNTs are sorted by this angle values as zigzag, chiral, and armchair, which affect their property that resulted in the metallic (armchair) or semiconducting (zigzag) CNTs [1].

CNTs have excellent thermal and electrical conductivity and large surface area compared to the other carbon-based materials. Moreover, CNTs formed with sp^2 bonded carbons that are stronger than sp and sp^3 bonds that provide the improved properties, such as flexibility and tensile strength [2, 3]. CNTs are insoluble in water due to their nonpolar nature, although they can be covalently or noncovalently functionalized, which make them preferable to incorporate with different compounds to obtain multifunctional materials as electrode modifiers [4, 5]. The special properties of CNTs, such as easy functionalization ability, high surface area, and unique thermal, mechanical, and electrical properties, make them an appealing component for composite materials, which resulted in the attraction of great interest on CNT-based composites [6, 7].

A composite material is a mixture of different components, which is homogeneous when seen in macroscopic scale and heterogeneous in microscopic scale and shows better physical and chemical properties than those of the individual components used alone. In the case of using CNTs as a conductive component, conducting polymers (CP) attracted great interest among all other secondary components due to their high conductivity to weight ratio and special optical and mechanical properties, which were first reported in 1994 by Ajayan et al. [8, 9]. CNT-polymer composites not only have taken all the advantages of the individual components, such as mechanical and optical properties, electrocatalytic activity, electrical conductivity, and charge density, but also have improved them by a synergistic effect. For this reason, these composite materials can achieve an efficient electrocatalysis [10, 11]. CNTs and polymers can be bound to each other covalently or noncovalently. Conjugated polymers or free electron pair containing heteroatoms in organic polymers can interact with CNTs via van der Waals, π -stacking, or hydrophobic forces, which correspond to noncovalent bonding. Another way is called covalent chemical bonding or grafting that puts together CNTs and polymers with strong chemical bonds by “grafting to” or “grafting from” approaches [12].

CNT-CP composites found a wide range of application field, such as biomedical applications [13], orthopedic implants [14], treatment of periodontal diseases in dentistry [15], and detector for volatile organic compounds [16]. In addition, due to their easily functionalized characteristic and improved electrical and mechanical properties, CNT-CPs have attracted great attention as electrode material for sensing and energy applications [17–20].

2. Preparation of CNT-CP composite electrodes

2.1. Synthesis, purification, and dispersion of CNTs

CNTs can be produced mainly by three different methods: laser ablation, electric arc discharge, and chemical vapor deposition (CVD). CVD provides the synthesis of aligned SWCNTs or MWCNTs with more controllable diameters and lengths. The purification protocol of CNT is an important issue that changes the catalytic activity of CNTs, such as heating the CNTs at temperature under decomposition, chemical treatments with concentrated HNO_3 reflux with H_2SO_4 or HCl , or hydrogen peroxide (H_2O_2) reflux. Dispersing nanotubes at the individual nanotube level is critical for the improved performance of CNTs in most applications, which mainly are sorted as water-soluble dispersions of CNTs with adsorbed surfactants, such as sodium dodecyl sulfate (SDS), dodecyl-benzene sodium sulfonate, and cetyltrimethylammonium bromide, and dispersions of CNTs in organic solvents, such as dimethyl formamide, dimethyl acetamide, tetrahydrofuran, and dimethyl pyrrolidone [21, 22].

2.2. Preparation pathways of CNT-CP composite electrodes

Different procedures for immobilizing the CNT-CP composites onto electrode (E) surface have been described as follows: (i) electropolymerization of monomers after CNT modification on bare electrode surface (CP/CNT/E), (ii) CNT modification after monomer electropolymerization on bare electrode surface (CNT/CP/E), and (iii) CP and CNT can be modified together on bare electrode surface (CNT-CP/E). These CNT-CP preparation pathways are shown with a diagram in (Figure 1). The activity and synergistic effect of the prepared CNT-CP composite electrodes towards organic or inorganic compounds can be changed by a preparation pathway that also affects the thickness of the polymer on bare electrode or CNT surface, polymer growth, and surface porosity of the resulting composite. In most of the studies, CNT-CP composites were prepared by following the first pathway [23].

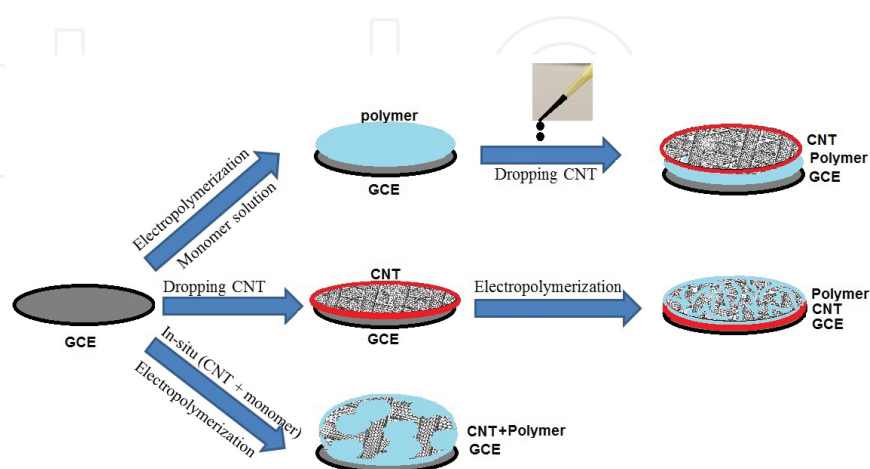


Figure 1. Schematic illustration for preparation pathways of CNT-CP composite electrodes.

2.2.1. CP/CNT/E

The first step for the preparation of CP/CNT-modified electrode is to modify CNTs on bare electrode surfaces, which can be achieved by mainly two ways: dropping the appropriate volume of CNT dispersion on the bulk electrode surface and remains until dispersant evaporation or using the CNT paste electrode that was prepared by mixing CNT and mineral oil. The second step involves the electrochemical deposition of CPs on CNT-modified electrodes, which can be achieved by following the one of the two routes: electropolymerization of CP on CNT/E by applying repetitive potential cycles with cyclic voltammetry (CV) or by applying constant potential with certain time.

Pyrrrole (Py), which is one of the most commonly used CPs, was electropolymerized on CNT/E surface mostly by CV [24–26]. Polypyrrole (PPy) was formed on single-stranded DNA (ssDNA)/MWCNT paste electrode in the range 0 to +0.75 V versus saturated calomel electrode (SCE) with 50 mV s⁻¹ for six cycles in 0.1 M PBS (pH 7.0) containing 0.05 M Py and 2.0×10⁻⁵ M 32-mer probe oligonucleotide for the electrochemical detection of DNA hybridization [27]. In another study, electrodeposition of PPy film on CNT/glassy carbon electrode (GCE) was carried out from an aqueous solution containing 0.02 M tiron and 0.01 M Py by potential cycling between 0.0 and +0.8 V (vs. Ag/AgCl) at a scan rate of 50 mV s⁻¹ for a total of five scans [28].

Poly(aniline) (PANI) and poly(flavin adenine dinucleotide) (FAD)-modified CNT composite electrodes were prepared by CV, which was performed using the mixture of 50 mM aniline and 1 mM FAD in pH 2.28 aqueous solution that was polymerized with consecutive cycles over a suitable potential region from -0.35 to 1.0 V at 50 mV s⁻¹ [29]. In other study, the electropolymerization of thiophene and derivatives was carried out using different techniques, such as CV and chronoamperometry. The electropolymerization via CV was carried out with varied potential cycles between 0 and -1.7 V versus Ag/AgCl at 50 mV s⁻¹ in sodium perchlorate, acetonitrile, or H₂SO₄ [30–33]. The polymerization with chronoamperometric technique was achieved with the deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) at 1.1 V for 90 s by immersing the β-cyclodextrin (β-CD)-SWCNT/GCE in aqueous solution containing 0.01 M EDOT and 0.02 M LiClO₄ [34].

2.2.2. CNT/CP/E

The first step for the preparation of CNT/CP/E is the electropolymerization of CP on bulk electrode surface using CV [35] and chronoamperometry [36, 37]. PEDOT/GCE was obtained individually by one-step electropolymerization of 10 mM monomer on GCE surface in 50 mM LiClO₄ by applying a constant potential of 1.1 versus SCE with 90 s deposition time, which was followed by the modification of CNTs on PEDOT/GCE surface by the drop-dry technique [38].

2.2.3. CNT-CP/E

The codeposition of CNT and CP has several advantages, such as using fewer amounts of chemicals and obtaining more uniform surfaces. The homogeneous existence of both components in composite films provides high catalytic activity and sensitivity [39]. CNT-CP/E is

generally prepared by the immersion of bulk electrode into the supporting electrolyte containing both CNT and monomer, which is attached to the electrode surface by CV [40–45] or chronoamperometry [46]. CNT-CP electrodes that contain PPy as CP were prepared by applying eight potential cycles from -0.2 to 0.8 V at 0.1 V s^{-1} scan rate in 0.1 M PPy + 0.2 mg/mL SWCNTs + 0.1 M SDS solution [47]. In another study, CNT-CP composite electrode was prepared by chronoamperometry, which used PEDOT as CP. PEDOT-SWCNT composite on the platinum (Pt) disk electrode surface was prepared by immersion of Pt disk electrode in 0.05 M phosphate buffer solution (pH 6.5) containing 0.02 M EDOT, 1 mg mL^{-1} SWCNT, 0.02 M sodium *N*-lauroylsarcosinate, and 0.02 M $LiClO_4$ followed by the constant potential polymerization at 1.1 V versus SCE for 60 s [48].

3. Characterization of CNT-CP composite electrodes

The developments in composite materials have increased demand for characterization techniques to improve the function and quality of structures. The characterization of CNT-CP composite properties is important in many research fields of material science, including heterogeneous catalysis, semiconductor thin-film technology, corrosion resistance, and studies of the behavior and functions of biological membranes. For this purpose, CNT-CP composite electrodes are characterized by electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

EIS is generally used to improve the understanding of multistep reactions, such as diffusion impedance, charge transfer, double-layer capacitance, and solution resistance. The charge transfer resistance (R_{ct}) value was obtained from a semicircle diameter of Nyquist plot at high frequencies that were related to dielectric and insulating characteristics of the electrode/electrolyte interface [49]. In Nyquist diagrams, a straight line with a slope of approximately 45° was related to a mass transport process via electroactive compound diffusion [50].

SWCNTs are a well-defined system in terms of electronic properties compared to the MWCNTs that Zhang et al. composed—poly(styrene sulfonic acid) sodium salt (PSS) with SWCNT on GCE surface to form the CNT-CP composite electrode. They showed the EIS results of bare GCE, SWCNT-modified GCE, and PSS film-modified GCE SWCNT/PSS-modified GCE in the presence of 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 0.1 M KCl to compare the activity of the surfaces. The EIS of GCE- and SWCNT-modified electrode has close R_{ct} values of 121 and 253 Ω , respectively, which are shown as a line that corresponds to the diffusion-controlled electrode process. The negative PSS film and the probe ion $[Fe(CN)_6]^{3-/4-}$ result in a larger repulsion effect, where PSS/GCE shows a much higher interfacial R_{ct} (7.21×10^3 Ω), whereas a lower R_{ct} (4.13×10^3 Ω) value was obtained in the case of PSS film-modified GCE. This behavior is attributed to the higher conductivity and larger surface area of SWCNTs in PSS film that facilitates the electron transfer [51].

XPS, also known as electron spectroscopy for chemical analysis, is generally used to identify the chemistry of solid surfaces. The sample is irradiated with monoenergetic X-rays causing

photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. The energy of photoelectrons is characteristic of the target material, and the measurement of the energy spectrum (number of count vs. kinetic/binding energy) provides valuable information about the top 2 to 20 atomic layers depending on the material studied. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of all elements, except helium and hydrogen, in the periodic table are determined. Karim et al. synthesized and characterized the SWCNT-poly(thiophene) (PTh) composites. XPS analysis enlightened the chemical composition of SWCNT-PTh. Although there is no s2s or s2p spectrum observed in the case of SWCNTs, the s2p core level is formed in the spectrum by the addition of PTh to nanotubes. The s2p core-level spectrum of PTh and SWCNT-PTh can be divided into at least two spin-orbit-split doublet (s2p3/2 and s2p1/2) peaks at approximately 163.6 and 163.7 eV, which were related to the sulfur atoms [52].

SEM is a useful technique to obtain information about the surface morphology of electrode surface. TEM is also used for the same purpose, which has the ability to show the more detailed image about surface in atomic size with narrow focusing areas. Both techniques use electron beams for getting information about the material surface but collect different electrons for imaging.

Lin et al. studied MWCNT and PEDOT to form CNT-CP composite electrodes, which also contain FAD. They identified the surface morphologies of PEDOT, PEDOT-FAD/MWCNT, and MWCNT/PEDOT-FAD-modified indium tin oxide (ITO) electrodes with SEM, where the last two correspond to the electrode modification with MWCNT before and after the electrocodeposition of PEDOT and FAD. SEM images obviously represent the importance of modifier order, which are exactly different from each other. These modified electrodes show a globular shape, except for MWCNT/PEDOT-FAD, and this can be attributed to the coverage of all MWCNT surface by polymer film. The location of the MWCNTs after the electrocodeposition of PEDOT and FAD is more compact in the composite electrode [31].

Au nanoparticle-modified bromocresol purple (BCP) monomers were combined with CNTs on GCE surface, which was prepared by Kocak et al. [17] for the investigation of the electrochemical behavior of hydrazine oxidation. The evaluation of surface morphology of polymer-CNT composite electrodes was carried out with the SEM technique. **(Figure 2a)** proves that the uniform surface was obtained after modified GCE surface with acid-treated CNT. The web-like appearance of poly(BCP) film that was linked on the walls of the CNTs was smooth and homogeneous **(Figure 2b)**

The morphological characteristics of the copolymers of PANI and PPy, which are poly(aniline-co-pyrrole) [poly(An-co-Py)], copper chloride (CuCl₂)-doped poly(An-co-Py) [poly(An-co-Py)Cu], and CuCl₂-doped poly(An-co-Py)/MWCNTs [poly(An-co-Py)Cu CNT] nanocomposites, were investigated by TEM analysis by Dhibar et al. The image of poly(An-co-Py) Cu composite represents the uniformly dispersed PANI and PPy on the electrode surface. In the case of poly(An-co-Py)Cu CNT nanocomposite, the surface of MWCNTs was uniformly coated with CuCl₂-doped poly(An-co-Py). This uniform coating is attributed by the

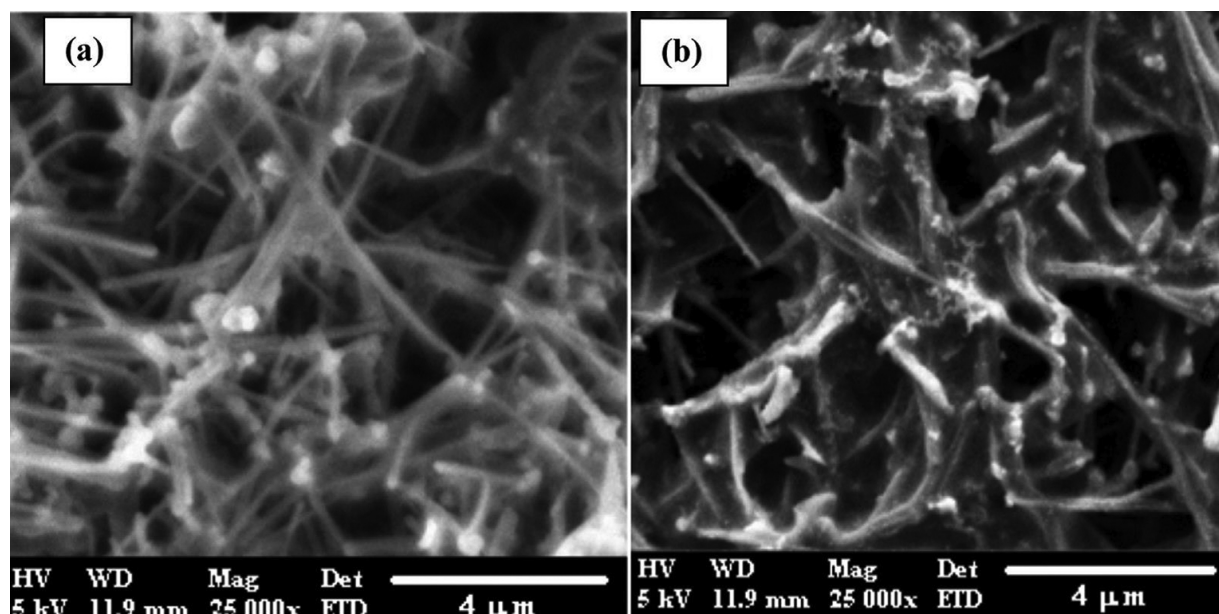


Figure 2. SEM images of (a) CNT/GCE, (b) poly(BCP)/CNT/GCE. Adapted by permission of author [17].

researchers to not only the π - π electron interaction with MWCNTs and polymers but also hydrogen bonding interaction between the amino group of aniline and carboxyl groups of the MWCNTs [53].

AFM is a probe microscopic technique that has the ability to produce atomic-scale images of the surface. Interatomic forces between the tip and the sample are measured, wherein the conductivity of the material is not important [54]. Umasankar et al. used the AFM technique to investigate the surface morphology of CNT-CP composite electrodes, which were prepared by the composition of MWCNTs, Nafion (NF), and poly(malachite green) (PMG) on GCE, gold, and ITO electrodes by the potentiodynamic method. The NF-PMG film shows smaller beads of NF and PMG deposited on the electrode surface. However, there were no bead formations if only NF was coated over the electrode; instead, a porous NF film was formed. MWCNT-NF-PMG had higher thickness than the other two films. These AFM results reveal the coexistence of MWCNT-NF and PMG in the composite film [55].

4. Electroanalytical applications of CNT-CP composite electrodes

This section gives an overview about the applications of CNT-CP composite electrodes in sensing applications. The electroanalysis of organic and inorganic molecules in real samples is an important area. Therefore, the preparation of an efficient composite electrode surface is a challenging issue for sensing applications, as a lot of studies focus on the development of new active materials. One of these enhanced materials is the CNT-CP composite, which is used for various electroanalytical applications. These analytical applications are summarized in **Table 1**.

Analyte	Electrode	Preparation pathway	Polymerization media; technique	Linear range (μM)	LOD (μM)	References
DA	DNA/PAMAM /MWCNT-Chit /Au	CP/CNT/E	—	0.2–10.0, 10.0–100.0	0.03	[46]
	PSS/SWCNT	CP/CNT/E	—	0.016–600.0	0.008	[51]
	ssDNA/SWCNT /PABA	CP/CNT/E	0.05 M 3-aminophenylboronic acid monomer, 0.04 M KF, 0.5 M H_2SO_4 ; CV	0.001–0.01	0.0006	[58]
	PPy/SWCNT /DM/GCE	CP/CNT/E	0.02 M tiron and 0.01 M Py; CV	0.02–100.0	0.003	[25]
	PGA-SWCNT	CP/CNT/E	PBS (pH 7.2) containing 5 mM glutamic acid; CV	3.3–26.6	0.38	[59]
	PEDOT-FAD /MWCNT	CP/CNT/E, CNT/CP/E	H_2SO_4 (pH 1.5) containing 0.01 M EDOT monomer or 0.01 M EDOT+0.1 mM FAD; CV	6.0–75.0	6.0	[31]
	NF/SWCNT/ P3MT/GCE	CNT/CP/E	0.1 M 3MT and 0.1 M NaClO_4 dissolved in acetonitrile; CV and the potentiostatic mode	0.02–0.10, 0.10–1.00, 1.00–6.00	0.005	[35]
	NF/SWCNT/ PMT/GCE	CNT/CP/E	0.1 M MT and 0.1 M tetrabutylammonium perchlorate dissolved in acetonitrile; the potentiostatic mode	1.5–20.0, 20.0–120.0	—	[37]
EP	PBCB-MWCNTs-DHP	CP/CNT/E	0.1 M phosphate buffer (pH 7.4) containing 0.1 M NaNO_3 ; CV	0.05–10.0	0.01	[39]
	PMG/MWCNT /GCE	CP/CNT/E	10 mM PMG containing 0.5 M NaNO_3 and 0.025 M NaH_2PO_4 - Na_2HPO_4 (pH 6.0); CV	0.1–100	0.0820	[60]
	SWCNTs-PMB	CP/CNT/E	1.0 mM MB in PBS;	150.0–3750.0	96.0	[61]

Analyte	Electrode	Preparation pathway	Polymerization media; technique	Linear range (μM)	LOD (μM)	References
5-HT	P(EDOP-SWCNTs)/GCE	CP/CNT/E	CV 1.0 mM EDOP, 1.0 mg SWCNTs, and 0.05 M TBAP/MeCN	0.1–10.0	0.005	[41]
L-Trp	PGA/CNTPE	CP/CNT/E	0.1 M PBS (pH 7.0) containing 0.05 M glutamic acid; CV	0.05–100.0	0.01	[68]
CAT	f-SWCNT/PEDOTM/GCE	CNT/CP/E	10 mM monomers on GCE surface in 50 mM LiClO ₄ with a constant potential	0.039–40.84	0.013	[38]
Catechol	MWCNT-NF-PMG	CP/CNT/E	5 mM PMG present in pH 1.5 M H ₂ SO ₄ aqueous solution; CV	360.0–4350.0	29.3	[55]
L-dopa	PPy-CNT-GCE	CP/CNT/E	Aqueous solution containing 0.02 M tiron and 0.01 M Py; CV	1.0–100.0	0.10	[28]
NADH	PMG-CNT	CP/CNT/E	0.4 mM MG in 0.01 M borate buffer (pH 9.1) with 0.1 M NaNO ₃ ; CV	NR	NR	[66]
Lysine	LOx/AuNP/c-MWCNT/PANI/Au, LOx/AuNP/c-MWCNT/DAB/Au	CNT/CP/E	Aniline in 1.0 M HCl and DAB (0.05 M) in PBS (pH 7.4); CV	5.0–600.0, 20.0–600.0	5.0, 600.0	[67]
Glucose	PNb-SWCNT	CP/CNT/E	PBS (pH 8.5) containing Nb; CV	100.0–8.5×10 ³	0.05	[63]
	GOx/poly(2,6-DAP)/MWCNT/GC	CP/CNT/E	0.1 M HCl and 4 mM 2,6-DAP; CV	0.42–8.0×10 ³	0.13	[62]
	GOx-PoPD/AuNP-ATP-	CP/CNT/E	5 mM oPD and 2 mg mL ⁻¹ GOx in acetate	50.0–8.85×10 ³	15.0	[64]

Analyte	Electrode	Preparation pathway	Polymerization media; technique	Linear range (μM)	LOD (μM)	References
	cMWCNT		buffer (pH 5.4); CV			
	PPy/CNT/GOD	CP/CNT/E	0.5 M Py in PBS (pH 7); CV	500.0–5.0 \times 10 ⁴	500.0	[43]
	Au/POAP/CNT/GOD	CP/CNT/E	5.0 mM o-AP+13 mg/mL CNT+50 U/mL GOD in acetate buffer (pH 5.0)	10.0–10.0 \times 10 ³	10.0	[65]

ATP, 4-aminothiophenol; Chit, chitosan; DM, dodecylamine monolayer; LOx, lysine oxidase; NR, not reported; PABA, poly(aniline boronic acid); PAMAM, poly(amidoamine).

Table 1. Applications of CNT-CP composite electrodes

Dopamine (DA) plays an important role as a neurotransmitter in the renal, hormonal, cardiovascular, and central nervous systems, as determined in different samples by voltammetry with different kinds of CP consisting of CNT composite electrodes. MWCNT-chitosan/poly(amidoamine)/DNA nanocomposite-modified gold electrode, which was fabricated by layer-by-layer modification, was used for DA and uric acid (UA) under the coexistence of ascorbic acid (AA) [46]. The biosensor-based polymer-CNT showed strong catalytic activity toward the oxidation of DA and UA. The originally overlapped signals of UA, DA, and AA oxidation at the bare electrode was also separated into three well-defined peaks with this biosensor. The detection limits of DA and UA were found to be 0.03 and 0.07 mM, respectively. Zhang et al. [51] reported the preparation of PSS-SWCNT-modified glassy electrode composite electrode and use for detecting DA in the presence of AA. In this study, PSS can provide a good microenvironment for DA due to the negative charges of polymeric surface. The results show that the oxidation peak current is proportional to the concentration of DA in the range of 1.6×10^{-8} to 6.0×10^{-4} M. The detection limit ($S/N=3$) was calculated as 8.0×10^{-9} M. These values indicated that the PSS/SWCNT film-modified GCE exhibits remarkable selectivity to determine DA in the presence of AA. Another CNT-CP composite electrode, which was used for DA and UA determination, is poly(acrylic acid)-(PAA) MWCNT/GCE [56]. PAA-MWCNT composite was prepared by mixing MWCNT powder with PAA aqueous solution under sonication. There is no interference of excess AA due to AA that demonstrates no voltammetric peak at PAA-MWCNT/GCE. PAA-MWCNT/GCE can catalyze the electro-oxidation of UA, which makes it possible to detect the lower level of UA. The lowest detection limits ($S/N=3$) were 20 nM DA and 110 nM UA. The higher sensitivity and selectivity should be originating from the combination of MWCNT and polymer film. The DA determination in the presence of excess AA was also determined by another CNT-CP electrode, which is Prussian blue nanoparticles supported on poly(*m*-aminobenzene sulfonic acid)-SWCNT-modified edged plane pyrolytic graphite electrode (EPPGE) [57]. The detection limit was calculated as 2.8 nM

for DA. The modified electrode was found to be electrochemically stable and reusable and can be used for drug analysis.

DA can be also electrochemically detected with a thin layer of *in situ* polymerized poly(aniline boronic acid) (PABA)/CNT composite and a thin layer of the highly permselective NF film [58]. The NF film was used for the elimination of the AA interference by a charge-discriminating membrane to preferentially accumulate the positively charged DA and reject the negatively charged ascorbate at the electrode surfaces in physiological pH. The detection limit (1.5 nM) is slightly higher than that without NF (0.6 nM). The CNT-CP composite increased the effective electrode surface area; therefore, the density of boronic acid groups in polymeric backbone is available for DA binding. Another CNT-CP composite electrode, which was used for DA determination, was prepared by layer-by-layer modification with dodecylamine monolayer, CNT, and tiron-doped PPy [25]. The modified electrode was sensitive to DA in the presence of excess AA. A linear response was obtained between the oxidation peak current and DA concentration in the range of 2.0×10^{-8} to 1.0×10^{-4} M with a detection limit of 3.0 nM (S/N=3). The useful lifetime of composite electrode can be estimated as 40 days. All of these values indicated that the new electrode was used for the determination of DA in real samples. The analysis of DA in the presence of AA and UA was also carried out with alternative CNT-CP composite electrode, which is polyglutamic acid (PGA) patterned CNT electrodes [59]. PGA selectively detected DA in the presence of AA and UA due to the negative charges on both AA (pKa=4.1) and UA (pKa=5.75) and positive charges on DA (pKa=8.89) at physiological pH (7.2). Hence, the negative charges on the carboxylate groups on the PGA-SWCNT film surface interact with positive charge DA. DA detection was linear in the range of 3.3 to 26.6 μ M ($R^2=0.994$) and the limit of detection (LOD) was found as 0.38 μ M. PGA-SWCNT composite electrodes are used for detecting DA in real sample. Lin et al. also studied AA, DA, and UA determination with MWCNT/PEDOT-FAD hybrid composite [31]. The electrocatalytic properties of AA, DA, and UA were improved with MWCNT/PEDOT-FAD hybrid composite compared to PEDOT, PEDOT-FAD, MWCNT/PEDOT, and PEDOT-FAD/MWCNT due to the good recognition of AA, DA, and UA based on the obvious redox peaks and current responses. With this composite electrode, the detection limit of AA, DA, and UA could be estimated as 4.0×10^{-4} , 6.0×10^{-6} , and 2.0×10^{-6} M, respectively. The proposed hybrid composite was also used for H₂O₂ determination. It will be useful in the development of multifunctional biosensors.

In addition, poly(3-methylthiophene) (P3MT)-modified GCE with NF/SWCNT film was also developed for the determination of DA in the presence of excess AA and UA [35]. The experimental results implied that the enhancement of the DA current response with composite electrode was caused by combining the advantages of P3MT, CNTs with NF. The detection limit was estimated 5.0 nM (S/N=3). Furthermore, the interferences of AA and UA were effectively reduced. This CNT-CP composite electrode could be applied to the determination of DA contents in DA hydrochloride injection and human serum. Another combination of CNT and CP for the sensitive and selective determination of DA is NF, SWCNTs, and P3MT film-modified GCE [37]. The modified electrode displays higher electrocatalytic activity towards AA, DA, and UA because of the combining unique properties of SWCNT (high specific surface area and electrocatalytic and adsorptive properties) with the cation selectivity of NF. The

combination of CP and CNTs improves the sensitivity and selectivity of bare electrode towards DA determination. Among the studies given in Table 1, the lowest detection limit was found as 0.6 nM with 3-aminophenylboronic acid, and SWCNT includes ssDNA composite electrode. The cause of the high sensitivity is explained that boronic acid groups are accessible for DA binding and increasing of the effective electrode surface area due to DNA-wrapped SWCNTs.

Another biologically important compound, epinephrine (EP), which exists in the tissues and body fluids in the form of cations that control the function of the nervous system, was also determined with CNT-CP composite electrodes. One of them is poly(brilliant cresyl blue) and dihexadecyl phosphate dispersed MWCNT GCE (PBCB-MWCNTs-DHP/GCE), which was prepared by an *in situ* electropolymerization method [39]. The authors emphasized that the improved response of EP with PBCB-MWCNTs-DHP/GCE could be caused from the hydrogen bonding and p-p interactions between EP and PBCB. The experimental results indicate that the current response displays a good linear relationship with the concentration of EP in the range of 5.0×10^{-8} to 1.0×10^{-5} M with a detection limit of 1.0×10^{-8} M. Another study described the preparation of GCE modified with MWCNTs and PMG film (PMG/MWCNT/GCE) to develop a sensor for simultaneous determination of AA, EP, and UA [60]. The obtained catalytic peak current was linearly dependent on the AA, EP, and UA concentrations in the ranges of 0.4 to 100.0, 0.1 to 100.0, and 0.3 to 90.0 mM, respectively. The detection limits for AA, EP, and UA were 0.23, 0.0820, and 0.12 mM, respectively. The sensor was applied to the determination of AA, EP, and UA in real samples. In addition, conductive CNT-CP composite containing MWCNT and poly(methylene blue) (PMB) was synthesized on GCE, gold, and ITO electrodes by potentiostatic methods for EP, AA, and DA [61]. The detection limits using semiderivative square wave voltammetry in the presence of 10 mM AA are 96 mM EP and 8.53 mM DA (S/N=3). Although the sensitive determination of EP was carried out with all CP-CNT composite electrode, the best sensitivity (0.01 μ M) and linearity (0.05–10.0 μ M) were obtained at PBCB-modified MWCNT composite electrode.

The voltammetric determination of catechol and catechin (CAT), which are known as antioxidants, was also determined using CNT-CP composite electrodes. PMG-coated MWCNT composite electrodes [55] were used for biochemical compounds catechol and quinol. The electrocatalysis studies indicated that well-separated voltammetric peaks of catechol and quinol were obtained with a peak separation of 147 mV. The sensitivity values for catechol and quinol were calculated as 0.4 and 3.2 mA mM⁻¹ cm⁻², respectively. Another composite electrode used for CAT determination was proposed as SWCNT/poly(hydroxymethylated-3,4-ethylenedioxythiophene) (PEDOTM) composite electrodes [38]. The CNT-CP composite electrode has a wide linear response for CAT in the concentration range between 0.039 and 40.84 μ M, with a low detection limit of 0.013 μ M. Also, the modified electrode showed a good reproducibility and long-term stability as well as high selectivity. The sensor was applied analysis of CAT in commercial green tea.

Glucose determination is important for clinical diagnostics, bioscience research, and food chemistry [62]. For this reason, the CNT combined with CP modified enzymatic or nonenzymatic electrodes are used for the detection of glucose. One of these electrodes that have been used for glucose determination is SWCNTs functionalized with poly(Nile blue A) composite

electrode (PNb-SWCNT) fabricated by electrochemically cycling the potential of the SWCNT/GCE in Nb solution [63]. The response of the composite electrode showed a linear dependence on the concentration of glucose in the range of 0.01 to 8.5 mM with correlation coefficient of 0.997 and the detection could be estimated as 5.0 mM (S/N=3). Kamyabi et al. described another CNT-CP composite electrode, which is covalently immobilized glucose oxidase on a poly(2,6-diaminopyridine)/CNT electrode [GOx/poly(2,6-DAP)/MWCNT/glassy electrode] [62]. The reason of the markable improvement of glucose current response was explained as the synergistic effect of the high active surface area of both CP and CNT. The sensor showed two linear responses to glucose in the concentration ranging from 0.42 μM to 8.0 mM with a correlation coefficient. The composite electrode was applied to glucose determination in the biological samples. Gold nanoparticle (AuNP) functionalized MWCNT-poly(*o*-phenylenediamine) (PoPD) composite film electrode [64] was also synthesized for glucose determination. The biosensor presented a linear range from 0.05 to 8.85 mM with a sensitivity of 27.93 mA $\text{mM}^{-1} \text{cm}^{-2}$ and a detection limit of 0.015 mM for the detection of glucose. The modified electrode was applied to the determination of glucose in human blood serum samples. Another study for glucose determination is the use of CNT-PPy composite film electrode [43]. The biosensor exhibits excellent response performance to glucose with a linear range from 0.5 to 50 mM. Additionally, the biosensor displays rapid response, high sensitivity, and long-term stability. One of the CNT-CP composite electrodes for glucose determination is glucose oxidase immobilized poly(*o*-aminophenol)/CNT/Au electrode (Au/POAP/CNT/GOD), which is electrochemically polymerized at a gold electrode surface [65]. The biosensor has a lower detection limit (0.01 mM) than Au/POAP/GOD due to the high surface area and excellent electrical conductivity.

A comparison of detection limits showing the best result for sensitive determination glucose was obtained by the use of PNb-SWCNT composite electrode (LOD=0.05 μM) and the best linearity between the analytical signal and glucose concentration found by the use of GOx/poly(2,6-DAP)/MWCNTs composite electrode (0.42–8.0 $\times 10^3$ μM).

p-Acetamidophenol is an antipyretic and analgesic drug compound that has extensive applications in pharmaceutical industries. It is important to keep the drug concentration in therapeutic range in that an accurate and sensitive determination for this compound is necessary. Potentiostatic methods have been used for the synthesis of highly active, conductive biocomposite film (MWCNT-PANIFAD) on gold and screen-printed carbon electrodes. The composite electrode contains MWCNTs and PANI-FAD copolymer (PANIFAD) that are used for the *p*-acetamidophenol determination successfully [29]. Levodopa (L-dopa) is a biologically important compound that increases the DA level of the brain, which helps the treatment of Parkinson's disease. An excessive level of L-dopa in plasma causes nausea and vomiting in that the detection and its concentration determination is a necessary feature in pharmaceutical and clinical procedures, which are achieved successfully by the CNT-CP electrode prepared by the modification of GCE with MWCNT and PPy doped with tiron [28]. Nicotinamide adenine dinucleotide (NADH) is a coenzyme found in all living organisms and is involved in many important enzymatic reactions. SWCNT/PNb nanocomposite electrode and poly(methylene green)-CNT (PMG-CNT)-modified electrode were used to determine the NADH in a

fast, easy, and accurate way [63, 66]. Another application field of CNT-CP are vitamins that they applied successfully to find the vitamin content of commercial juices. PEDOT methanol/ascorbate oxidase/NF-SWCNTs (PEDOTM/AO/NF-SWCNT) were used for this purpose [36].

Amino acids are also biologically essential compounds, and their level in the human system is associated with some diseases. For instance, lysine, an essential amino acid, causes intellectual disability or behavioral problems when its concentration exceeds the therapeutic range. The most straightforward, rapid, and cost-effective way is the use of electrochemical sensing techniques as alternative among all other techniques. Many composite electrodes were prepared using AuNPs and carboxylated MWCNTs (c-MWCNT) decorated on (i) PANI and (ii) poly(1,2-diaminobenzene) (DAB) electrodes for the electrochemical detection of lysine [67]. Tryptophan (L-Trp) is another essential amino acid that is also added to food products and pharmaceutical formulations. The detection of L-Trp quantity in the brain is too important due to its toxic effect. Liu et al. suggested the electrode surface that is prepared with conductive PGA film and highly active CNTs, which determined L-Trp with high selectivity, good stability, and reproducibility [68].

Paracetamol (acetaminophen; *N*-acetyl-*p*-aminophenol) is a long established and one of the most popular and commonly used analgesic and antipyretic drugs that reduce fever and relieve cough, cold, and muscular aches, migraine headache, backache, and toothache pains [69]. Therefore, the selective and sensitive determination of paracetamol is an important research field in pharmaceutical chemistry. Barsan et al. have studied paracetamol determination with redox polymer PMG and functionalized CNTs (fCNTs). They used two configurations (both CNT/CP/E and CP/CNT/E) for electrode preparation. In the first type of electrode configuration, MG was electropolymerized on a graphite composite electrode and then combined with fCNT (fCNT/PMG/CE). The second type of composite electrode configuration was prepared by electropolymerization of MG on the fCNT covered graphite composite surface (PMG/fCNT/CE) to evaluate the performance of both surfaces on the voltammetric behavior of paracetamol. The best analytical performance for paracetamol determination was obtained at PMG/fCNT/CE using amperometric technique. To identify the electrical conductivity of the composite electrode surfaces, electrochemical impedance studies were also performed and the EIS results show that electrodes containing both PMG and fCNT were superior to those with only one component for application as sensors [70]. In another study, MWCNT-poly(thionine) (PTH) nanostructures were formed on carbon film electrodes (CFE), the polymer film being formed beneath or on top of MWCNT, to give two different sensor architectures, PTH/MWCNT/CFE or MWCNT/PTH/CFE. CV experiments and EIS results represented the faster diffusion, and easier electron transfer was observed at PTH/MWCNT/CFE for sensing acetaminophen [71]. On the contrary, the voltammetric behavior of paracetamol was also studied with molecularly imprinted polymer film of *o*-phenylenediamine, which was combined with carboxyl functionalized MWCNTs onto a GCE surface. In this study, paracetamol was determined successfully in the range of 2.0×10^{-7} to 4.0×10^{-5} mol L⁻¹, with a detection limit of 5.0×10^{-8} mol L⁻¹ by the help of CNT-CP composite. The recovery value of sensor ranging from 94 to 105% proves the possible application of paracetamol in real samples [72].

L-AA (vitamin C) is an essential antioxidant for human beings, with many physiological and biochemical functions. AA has been widely applied in large quantities to food products, drinks, animal feed, pharmaceutical formulations, and cosmetics due to its valuable properties, such as pH regulating and antioxidant. An abnormal AA concentration in human body fluids is associated with various diseases [73]. Therefore, a highly sensitive, accurate, and selective determination of methods for AA is needed due to its biological importance in pharmaceutical, clinical, and food industry samples. In recent years, many research groups have developed new types of electrochemical sensors and methods for AA detection. In one of the studies, CNT-CP composites were prepared with a polyimide (PI)/aminofunctionalized MWCNT composite material for the determination of AA [74].

Sphingolipids are long-chain aliphatic amines, with C18 and small amounts of C16 to C19 dihydroxy bases are their naturally most common components. Sphingolipids have crucial roles in membrane and cell regulation as second messengers for growth; therefore, the development of the accurate quantification method of different sphingoid bases is demanded. Carballo et al. achieved the detection of long-chain aliphatic amines using the CNT-CP composite electrode. Poly(Ni-protoporphyrin) film (pNiPP) containing MWCNT was used to cover a GCE to obtain an active surface for sphingolipid detection. The hybrid material (pNiPP/MWCNT) successfully combines the permselectivity of pNiPP with the high conductivity of MWCNT [75]. DNA sensors have attracted great interest because of their application importance in medical genome research, diagnosis, and forensic science. Li et al. offered flexible MWCNT/polydimethylsiloxane (PDMS)-based electrodes that were fabricated and used for electrochemical DNA sensors. They achieved a successful determination by differential pulse voltammetry with a detection limit of 1.3×10^2 pM with good DNA sequence differentiation ability [76]. In another study, AuNP/SWCNT/PANI composite-modified disposable pencil graphite electrode (AuNP/SWCNT/PANI/PGE) prepared by CNT-CP/E pathway was used for DNA detection. PGE was immersed in a solution containing monomer (0.1 M aniline) and SWCNTs (2 mg mL^{-1}) in 0.1 M HClO_4 and the constant potential of 0.8 V was applied for the modification of both CP and CNT on the electrode surface. The electrode provided a simple, easy, time-effective, fast, and cheap detection scheme for DNA [77].

Xanthine (2,6-dihydroxypurine) is a purine base present in human body tissues and fluids and in other organisms. Many stimulants are derived from xanthine, including caffeine and theobromine. The determination of xanthine in blood sample and tissue is crucial for the diagnosis of gout, hyperuricemia, xanthinuria, and renal failure. In addition, in the food industry, elevated levels of hypoxanthine and xanthine are important biomarkers as a sign of meat spoilage. Dervisevic et al. offered a composite CNT-CP surface for enzyme immobilization of xanthine oxidase, which was developed by incorporating MWCNT in poly(glycidyl methacrylate) and vinylferrocene (GMA-co-VFc) copolymer film. The proposed p(GMA-co-VFc)/MWCNT coated electrodes have improved analytical performance for xanthine determination in terms of good sensitivity, selectivity, low response time (4 s), wide linear range, and low detection limit of 0.12 mM. This xanthine biosensor gave reliable results in measuring xanthine concentration in the fish meat [78].

UA (2,6,8-trihydroxypurine) is the primary end-product of purine metabolism, and its concentration must be kept at a certain level in the body. The excessive level of UA in the urine and serum resulted in diseases, such as Lesch-Nyhan, gout, hyperuricemia, cardiovascular, and kidney-related diseases. Therefore, the detection of UA is of great importance in many areas, including physiological investigations and disease diagnosis. The electrochemical accurate, selective, and sensitive determination of UA has led to the development of active electrode surfaces. For this aim, Erden et al. proposed a new UA biosensor that was constructed based on ferrocene containing polymer poly(vinylferrocene) (PVF), c-MWCNTs, and gelatin (GEL)-modified GCE. The c-MWCNT/GEL/PVF composite was characterized by SEM, CV, and EIS to express the modification of both CNT and CP contents on the surface and its activity towards UA oxidation. The proposed CNT-CP composite electrode showed high selectivity and sensitivity accompanied by the low detection limit of 2.3×10^{-8} M to UA [79]. Serotonin (5-hydroxytryptamine, 5-HT) is a neurotransmitter playing an important role in the emotion system, where low levels of 5-HT are related to several disorders, such as anxiety, depression, and migraine. Therefore, it seems necessary to develop the catalytic surface to determine the 5-HT level accurately. According to this aim, Cesarino et al. prepared composite electrode surface by the CNT-CP/E pathway. The Pt electrode was immersed in 25.0 mL of 0.2 mol L⁻¹ NaCl solution containing 443 μ L Py and 5.0 mg MWCNT and sonicated for 10 min with 70% amplitude. MWCNTs, PPy was successfully modified on the Pt electrode surface where 5-HT was determined selectively with an LOD value of 0.15 μ mol L⁻¹ [80]. In addition, 5-HT determination was also carried out with poly(3,4-ethylenedioxyppyrrrole)-SWCNT [P(EDOP-SWCNT)] composite electrodes [41]. P(EDOP-SWCNT)-coated GCE improved oxidation peak currents and lowered the oxidation overpotential due to a stereoporous interfacial layer CNT-CP composite electrode. Hence, the sensor demonstrated high sensitivity and selectivity for 5-HT and showed excellent stability and reproducibility. The linear response was in the range of 1.0×10^{-7} to 1.0×10^{-5} M, with a correlation coefficient of 0.998 on the anodic current. The lower detection limit was calculated as 5.0 nM. On the contrary, environmental protection is a critical concern, as polymer-CNT composites are used for the determination of pollutants, such as pesticides and phenolic compounds. Phenolic compounds are present in many wastewater streams of the oil, paint, polymer, and pharmaceutical industries, which should be determined successfully for environmental protection. With the help of CNT-CP composite electrode, which is prepared by the combination of MWCNT-PPy-horseradish peroxidase, 18 phenol derivatives were determined by amperometric technique with high sensitivity [42]. 4-Nitrophenol, another phenolic compound, was reported as a potential carcinogen and mutagen determined with GCE modified with poly(diphenylamine)/MWCNTs- β -CD (PDPA/MWCNT- β -CD) film electrode in ppb level [81]. 2-Aminophenol (2-AP) and 4-aminophenol (4-AP) are toxic industrial wastes that cause serious hazards on biological systems, so their accurate determination is important. With the help of improved characteristics of CNT-CP composite electrodes, which are prepared by electropolymerization of β -CD and L-arginine (L-Arg) on the surface of CNTs@graphene nanoribbons (CNTs@GNRs) core-shell heterostructure, 2-AP and 4-AP were determined simultaneously in nanomolar level [82]. The crucial role of highly toxic phenolic compounds such as catechol and quinol in industrial applications causes their coexistence as environmental pollutants. PMG-coated MWCNT film electrode is

used for the determination of catechol and quinol with ease of fabrication and sufficient stability [55]. Pesticides are another environmental concern, which reach a destination other than their target species, including air, water, bottom sediments, and food. MWCNT/P3MT composite electrode was used for the sensitive determination of various kinds of pesticides, including herbicide (isoproturon), insecticides (voltage, cypermethrin, deltamethrin, and fenvalerate), and an acaricide (dicofol) [32]. In another study, organophosphorus pesticides that known as cholinesterase inhibitors were determined by biosensors that are prepared by the combination of acetylcholinesterase (AChE) enzyme, a CP; poly(4-[2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl]benzenamine) [poly(SNS-NH₂)]; and fCNTs. The proposed biosensor offered a fast response time (6 s), a wide linear range (0.05 and 8.00 mM), and a low detection limit (0.09 mM), which is successfully used for the real sample analysis in fortified tap water samples [83].

Hydrazine is a water-soluble volatile colorless liquid that is used in various chemical industries, although it is a harmful substance for the environment. It causes serious damage to the lungs, kidneys, and the central nervous system if it is absorbed by the human system [84]. Thus, the development of an effective surface for the sensitive determination of hydrazine is required. 4,5-Dihydro-1,3-thiazol-2-ylsulfanyl-1,2-benzenediol containing sulfur and nitrogen groups was electrochemically polymerized on an MWCNT/GCE; this resulted to CNT-CP composite that has wide linear range with an LOD of 0.6 mM for hydrazine determination [85]. Persulfate is a stable and powerful oxidant that is used for the degradation of organic contaminants in groundwater and wastewater. Although persulfate has a wide range of applications, there are only several methods for its determination. One of them is the electrochemical technique that is studied with the composite electrode prepared by the combination of electropolymerized silicomolybdate (SiMO) and PEDOT on MWCNT/GCE. The SiMO-PEDOT/MWCNT electrode can effectively analyze S₂O₈²⁻ due to its low overpotential, high stability, fast response, low cost, and high sensitivity with a 10⁻⁶ M detection limit [86]. Nitrite is a versatile chemical compound used in a wide range of applications from dye manufacture to food preservation. The potential for nitrite to be metabolized to carcinogenic *N*-nitrosamine in the stomach and the conversion of hemoglobin to methemoglobin that interferes with the oxygen transport system and its widespread presence in food products and beverages have necessitated its monitoring [87]. For this purpose, composite electrode consisting of 5-amino-1,3,4-thiadiazole-2-thiol electrochemically deposited on acid functionalized MWCNTs was used for nitrite determination in nanomolar level with amperometry [88]. In another study, poly(vinylferrocenium)/MWCNT composite-modified disposable PGE (PVF⁺/MWCNT/PGE) was prepared by electropolymerization of PVF in the presence of MWCNTs with one-step electropolymerization. The prepared composite CNT-CP electrode was successfully applied to a commercial mineral water sample for nitrite determination [89].

5. Conclusion

This chapter summarized the preparation, characterization, and analytical applications of CNT-CP composite materials in electrochemistry. CNT-CP composite electrodes are prepared

in three different ways, which are polymer attachment after CNT modification, CNT modification after polymerization, and CP and CNT modified together on electrode surface. The activity and synergistic effect of the prepared CNT-CP composite electrodes towards organic or inorganic compounds changed with the preparation pathway, which also affects the thickness of the polymer on bare electrode or CNT surface. CNT-CP composite electrodes were characterized by SEM, TEM, AFM, and EIS techniques to understand the morphology and prove the existence of modifiers on the prepared surfaces. Although the surface morphology of CNT-CP composite electrode surface is lightened with SEM, the more detailed image about surface in atomic size with narrow focusing areas is obtained with TEM. Another characterization tool is EIS, which is generally used to improve the understanding of multistep reactions such as diffusion impedance, charge transfer, double-layer capacitance, and solution resistance. The observing of atomic-scale images of the surface is achieved using AFM. The existing remarkable features of CNTs, such as large accessible surface area, high mechanical strength, and low electrical resistance, improved the activity of CPs, which, based on CNT-CP composite electrodes, make as great candidate for a wide range of electroanalytical and fuel cell applications.

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