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Review on CNT-based Electrode Materials for Electrochemical Sensing of Ascorbic Acid

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Abstract

Ascorbic acid plays a crucial role in the regulation of neurotransmitters and enzymes in the central nervous system. Maintaining an optimal level of ascorbic acid, which is between 0.6–2 mg/dL, is vital for preventing oxidative stress and associated health conditions, such as cancer, diabetes, and liver disease. Therefore, the detection of ascorbic acid is of the utmost importance. Electrochemical sensing has gained significant attention among the various detection methods, owing to its simplicity, speed, affordability, high selectivity, and real-time analysis capabilities. However, conventional electrodes have poor signal response, which has led to the development of modified electrodes with better signal response and selectivity. Carbon nanotubes (CNTs) and their composites have emerged as promising materials for the electrochemical detection of ascorbic acid. CNTs possess unique mechanical, electrical, and chemical properties that depend on their structure, and their large surface area and excellent electron transport properties make them ideal candidates for electrochemical sensing. Recently, various CNT composites with different materials and nanoparticles have been studied to enhance the electrochemical detection of ascorbic acid. Therefore, this review aims to highlight the significance of CNTs and their composites for improving the sensitivity and selectivity of ascorbic acid detection. Specifically, it focuses on the use of CNTs and their composites in electrochemical sensing to revolutionize the detection of ascorbic acid and contribute to the prevention of oxidative stress-related health conditions. The potential benefits of this technology make it a promising area for future research and development.

Keywords: Ascorbic acid, Carbon nanotube, Electrochemical detection, Nanocomposites

1. INTRODUCTION

Vitamin C, also known as ascorbic acid, is a water-soluble antioxidant. Its biochemically and physiologically active form has a γ-lactone structure, representing the L enantiomer of ascorbic acid [1,2]. Ascorbic acid facilitates collagen production, which is essential for the maintenance of skin, bones, cartilage, joint linings, teeth, gums, and blood vessels [3–5]. Additionally, it is involved in many biological processes, such as iron absorption, collagen synthesis, and immune response activation. It is crucial to monitor the level of ascorbic acid in the body because any abnormality can lead to cancer and various cardiovascular diseases [6,7].

Moreover, excessive intake of ascorbic acid can lead to various issues, such as diarrhea, nausea, vomiting, headache, insomnia, gastric irritation, altered taste perception, and renal impairment [8,9]. Various methods, such as gas chromatography [10], colorimetry [11], liquid chromatography [12], and capillary electrophoresis [13] have been studied for the detection of ascorbic acid. The main disadvantages of these methods include high cost, time-consuming sample preparation, and complex equipment [8]. The electrochemical method is simple, less time-consuming, affordable, has high selectivity, and allows real-time analysis. The use of bare electrodes results in poor response signals because of the sluggish electron transfer rate at the surface of the electrode [14,15]. Various materials, such as metal nanoparticles, metal oxides, polymers, clay, metal-organic frameworks, and carbon materials, have been actively studied to improve the signal response. Among these materials, carbon nanotubes (CNTs) have gained attention owing to their unique properties, such as high mechanical strength, chemical properties, field emission, and electron transport properties. Table 1 compares the properties and electrochemical performances of the various electrodes used for ascorbic acid sensing. Ascorbic acid is a critical biomolecule involved in numerous physiological processes, and its accurate detection and quantification are crucial

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in many fields, including environmental monitoring, food production, and pharmaceutical industries.

CNT- and composite-based materials have shown immense potential for electrochemical sensing because of their unique properties. They offer a wide range of benefits, making them ideal candidates for biomolecular sensing. A major advantage of CNT-based materials is their high surface-area-to-volume ratio, which enhances their electrocatalytic activity and sensitivity. Their high surface area facilitates highly sensitive detection of biomolecules, making them an excellent choice for medical diagnosis and environmental monitoring applications. Another benefit of CNT-based materials is their excellent conductivity, facilitating fast and efficient electron transfer during the sensing process. This feature enhances the accuracy and reliability of the measurement and enables real-time monitoring of biomolecule concentrations. CNT-based composites offer additional benefits, as they can be easily modified with functional groups that enhance their selectivity towards specific biomolecules, enabling the development of highly selective sensors that can accurately distinguish between different biomolecules.

Moreover, CNT-based materials exhibit excellent stability and reproducibility, which are essential properties for sensor applications in practical settings. Overall, CNTs and CNT composite-based materials offer a promising platform for developing highly sensitive, selective, and reliable electrochemical sensors for detecting a diverse array of biomolecules. With further research, these materials have the potential to drive innovation and exert substantial influence on various fields, including healthcare, food analysis, and environmental monitoring.[16–19]. This review describes various CNT-based composites that have been studied for their utilization in the electrochemical sensing of ascorbic acid.

Table 1. Various electrochemical sensing materials for ascorbic acid detection.

Material	Linear range (μM)	LOD (μM)	Sensitivity (μA mM^{-1} cm^{-2})	Ref
AgNP-Psi	20–600	0.83	1279	[51]
Hierarchical NiO/ ITO	25–800	1.127	760	[52]
CdO/SPCE	5–150	0.0535	420	[53]
Branch-trunk Ag	0.17–1925	0.06	35.512	[54]
RuO_2/Au	20–1000	11.6	342.8	[55]
Au-Cys-Bt/GCE	1–25000	0.87	30.0	[56]
$Cu(OH)_2$ nanorods/ SPE	2.5–10000	-	268	[57]
AuNP-SPCE	1.9–16.9	-	-	[58]
CL-TiN/GCE	50–1500	1.52	6.073	[59]
Nano RuOx/Ni	570–5700	-	296	[60]

2. CNT and Composites for Sensing

2.1 Metal-Organic Framework

A metal-organic framework (MOF) is a coordinating polymer that consists of inorganic units serving as connectors and an organic linker molecule. Inorganic units consist of metal ions/ clusters, whereas organic units comprise carboxylates, N-donor groups, and phosphonates [20,21]. These MOFs have high selectivity because they use π-π interactions, functional groups, open metal sites, and van der Waals interactions to react with analytes [22,23]. The porous nature of MOFs allows the analyte to accumulate within the MOF structure, which provides shape and size selection effects that enhance the sensitivity of electrochemical sensing [24,25]. MOFs are suitable candidates with fast response and high sensitivity for electrochemical sensor applications because of their unique properties, such as high specific surface areas, well-defined chemical structures, open metal active sites, well-defined periodic crystal structures, and tunable surface functionalities [26,27].

Yanping et al. [28] reported the synthesis of ZIF-65@ CNT through in-situ synthesis for the electrochemical detection of ascorbic acid. ZIF-65@ CNT was synthesized by growing ZIF-65 on the surface of carboxylated CNTs. The modified electrode was fabricated by drop-casting the sample onto a glassy carbon electrode. The prepared sample exhibited an increase in conductivity, and the resistance decreased by half, which can be attributed to the addition of CNTs. The prepared sample showed a limit of detection (LOD) of 1.03 μM and demonstrated high sensitivity towards ascorbic acid. They exhibited good selectivity and anti-interference properties in the presence of glucose, cysteine, and uric acid (Fig. 1).

Gayathri et al. [29] prepared a cobalt-bipyridine MOF on a multiwalled CNT by immobilization using a Nafion ionomer (MWCNTs@Co-bpy/Nf). Cobalt-bipyridine in the composite was used as a redox mediator. At the same time, Nafion supported the electrostatic interaction between Nafion and cobalt-bipyridine and the π-π interaction between the bipyridine ligand and the MWCNTs. MWCNTs were used to increase electrical conductivity and immobilize the MOF. The LOD and sensitivity towards ascorbic acid were calculated to be 23.25

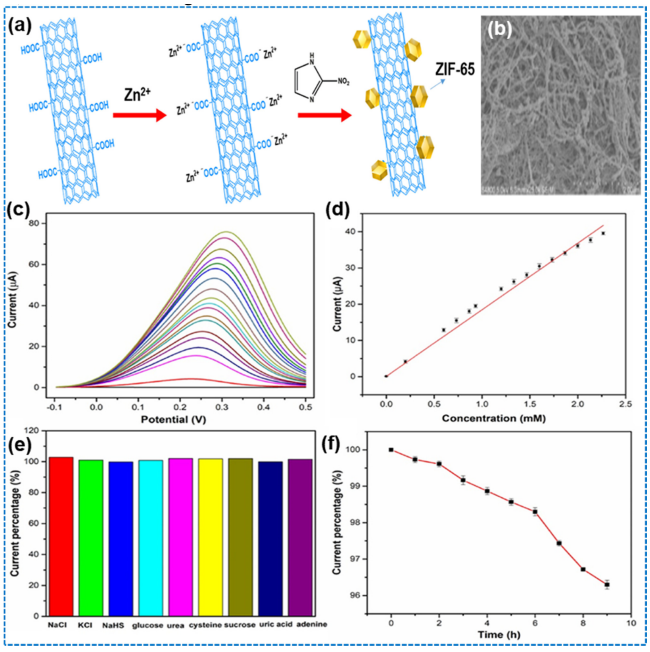

Fig. 1. (a) Schematic illustration of the designed electrochemical ascorbic acid sensor. (b) Scanning electron microscope (SEM) images of ZIF-65@ CNTs. (c) The differential pulse voltammetry (DPV) curves of ascorbic acid at ZIF65@ CNTs modified glassy carbon electrode (GCE), showing the presence of ascorbic acid at different concentrations ranging from 0.2 to 5.6 mM in phosphate buffer saline (PBS) (pH=7). (d) Calibration plot of peak current intensity vs. ascorbic acid concentration (0.2–2.267 mM). (e) DPV responses after adding interference species. (f) Time stability of DPV responses over 9 h. Reprinted with permission from Ref [28]. Copyrights (2020) Elsevier.

(±0.03) μA mM^{-1} cm^{-2} and 3.1 μM, respectively. The MWCNTs@Co-bpy/Nf sample showed excellent selectivity in the presence of various interferents and good recovery in real samples, including Limcee and Celin tablets, as well as beverages, such as Tropicana juices.

Wang et al. [30] reported the use of a manganese-based metal-organic frameworks @ MWCNT (Mn-BDC@MWCNT) nanocomposite for the electrochemical sensing of ascorbic acid, dopamine, and uric acid. A one-step solvothermal method was used to prepare the Mn-BDC@MWCNT composites. The presence of MWCNT in the composite led to the splitting of bulk Mn-BDC into thin layers, which increased its electronic conductivity and electrochemical performance. The prepared composite exhibited a porous slack structure, large specific surface area, high conductivity, and excellent electrochemical activity. It showed a lower LOD of 0.01 μM in the concentration range of 0.1–1150 μM. The Mn-BDC@MWCNT composite exhibited good stability, reproducibility, and selectivity. A real sample study showed that the prepared composite exhibited potential for practical detection of ascorbic acid, dopamine, and uric acid in urine samples.

2.2 Conducting Polymer

The conductive nature of the conducting polymer is due to the presence of charge carriers owing to the doping of their conjugated structure. Conducting polymers have been studied for various applications because of their unique properties, such as low cost, low weight, tunable electrochemical properties, and flexibility [31].

Xin Du et al. [32] reported the electrochemical detection of ascorbic acid using a carboxylated multi-walled CNT- poly (3,4-ethylene dioxythiophene) (CA-MWCNT-PEDOT) nanocomposite. A facile electrodeposition method was used to prepare nanocomposites. The prepared nanocomposites exhibited good electrochemical detection towards ascorbic acid. The electrochemical measurements were performed using a standard three-electrode system with Ag/AgCl, platinum wire, and glassy carbon electrodes as the reference, counter, and working electrodes, respectively. Electrodeposition was used to modify the glassy carbon electrodes. The tunneling electron microscope (TEM) image shows that the PEDOT was wrapped around the MWCNT. The electrochemical activity of the CA-MWCNT-PEDOT nanocomposite exhibited a high sensitivity and low detection limit of 1699.36 μA mM^{-1} cm^{-2} and 4.2 μM, respectively, in the concentration range of 100 μM to 20 mM. The nanocomposite exhibited good stability and reproducibility, with a relative standard deviation of 3.5%.

Chauhan et al. [33] prepared copper-nanoparticle-carboxylated MWCNT and polyaniline composites (CuNP/c-MWCNT/PANI) and studied their applications in the electrochemical sensing of ascorbic acid. The composite showed high electrochemical activity towards ascorbic acid with a LOD of 1.0 μM in the linear range of 5–600 μM. The response time was less than 2s and showed good reproducibility and stability. Serum, fruits, and vegetables were analyzed. The relative standard deviation for l-ascorbic acid in various fruit and vegetable juices ranged between 2.24 and 14.2% (Figs. 2 a–c).

Ying et al. [34] studied the electrochemical properties of mercaptosuccinic acid-polyaniline/multiwalled CNT (MSA-PANI/MWCNT)-modified electrodes. The working electrode was coated with MWCNT, and electrodeposition was used to deposit PANI on the MWCNT. In addition, MSA was tethered to PANI via a thiol-ene reaction. The prepared sample showed

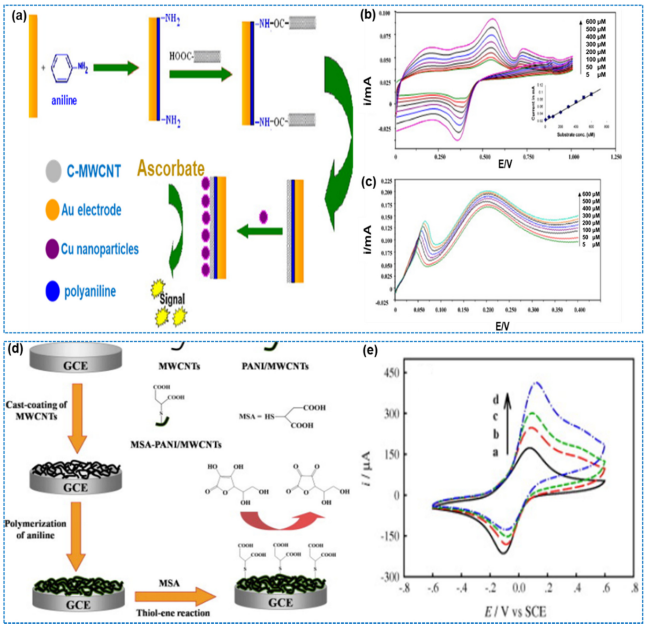

Fig. 2. (a) Steps involved in preparing Au electrode modified with CuNPs/c-MWCNT/PANI (b) Cyclic voltammograms of CuNP/c-MWCNT/PANI/Au electrode with ascorbic acid concentrations ranging from 5.0–600 μM in sodium phosphate buffer (concentration: 0.05 M, pH 7.5) at scan rate 20 mV s^{-1}. The inset shows a plot of ascorbic acid concentration vs. peak height in mA. (c) Linear sweep voltammetry of CuNPs/c-MWCNT/PANI/au electrode with ascorbic acid concentrations 5.0–600 μM in sodium phosphate buffer (concentration: 0.05 M, pH 7.5) at +0.4 V [33]. (d) Schematic illustration of the procedures for preparing the MSA–PANI/MWCNTs/GCE and biosensing principle, (e) Cyclic voltammograms of MSA–PANI/MWCNTs/GCE in 0.1 M PBS (pH 7.0) containing (a) 0, (b) 5, (c) 10 and (d) 20 mM of ascorbic acid. Scan rate: 50 mV s^{-1}. Reprinted with permission from Ref [36]. Copyrights (2017) Elsevier.

good electrochemical activity towards ascorbic acid owing to the high specific surface area of the MWCNT and anionic MSA tethered to the PANI backbones. MSA-PANI/MWCNT showed a high sensitivity and a low detection limit of 363 μA mM^{-1} cm^{-2} and 0.6 μM, respectively, in the linear range of 20 μM–29.6 mM at neutral pH. The prepared composite exhibits potential for utilization in various applications in the neutral aqueous solutions (Figs. 2 d and e).

2.3 Semiconductors

Metal oxide nanoparticles possess excellent photochemical and electrical properties owing to their size, stability, and high surface area. These metal oxides induce fast electron transfer between the transducer and analyte molecules [35].

Sangsefidi et al. [36] investigated the electrochemical sensing of CeO_2 and MWCNT on a pencil-graphite electrode. CeO_2 nanostructures have unique properties such as specific chemical reactivity, high thermal stability, the ability to store and transport oxygen, large oxygen storage capacity, and high refractive index [37–39]. A hydrothermal method was used to synthesize CeO_2 nanoparticles and modify the electrode with MWCNT to increase the sensitivity towards ascorbic acid. The x-ray diffraction (XRD) results showed that the prepared material had high purity, and the bandgap of the material was calculated to be 2.95 eV. A pencil-graphite electrode was used as the working electrode. The modified electrode showed a good electrochemical response towards ascorbic acid with a LOD of 8 nmol L^{-1}.

Karimi-Maleh et al. [40] prepared a ruthenium (II) complex–ZnO/CNT nanocomposite to investigate its electrochemical response towards ascorbic acid. The nanocomposites were prepared in three steps. The first step involved the chemical pretreatment of CNT, the second step involved dispersing CNT in distilled water, and the final step was the direct deposition of ZnO on the CNT. The electrochemical study was performed in a phosphate buffer (pH: 7) using a carbon paste electrode as the working electrode. The main advantage of this complex is that it is insoluble in aqueous media. The prepared nanocomposite showed LOD of 0.005, 0.5, and 1.0 μmolL^{-1} for different ascorbic acid concentration ranges of 0.008–251, 1.0–650, and 3.0–700 μmolL^{-1}. Perovskite consists of a general crystallographic structure, ABX_3, where A and B are cations, and X is the anion that binds A and B. These materials have been considered to have good chemical and electrochemical properties [41,42].

Atta et al. [43] studied the simultaneous electrochemical sensing of ascorbic acid and amlodipine using $NdFeO_3$/glycine/CNT. The developed nanocomposite modifiers exhibit high conductivity, enhanced surface area, surface fouling resistance, and stability. A carbon paste electrode, platinum wire and Ag/AgCl (4 molL^{-1} KCl saturated with AgCl) electrode were used as the working, counter, and reference electrodes, respectively. The detection limit, the limit of quantification, and sensitivity were calculated to be 5.32 μmolL^{-1}, 17.72 μmolL^{-1}, and 0.015 μA/μmolL^{-1}, respectively, in the concentration range of 500 to 2500 μmolL^{-1} (Fig. 3).

2.4 Doped CNTs

Doping MWCNT with heteroatoms has recently been studied

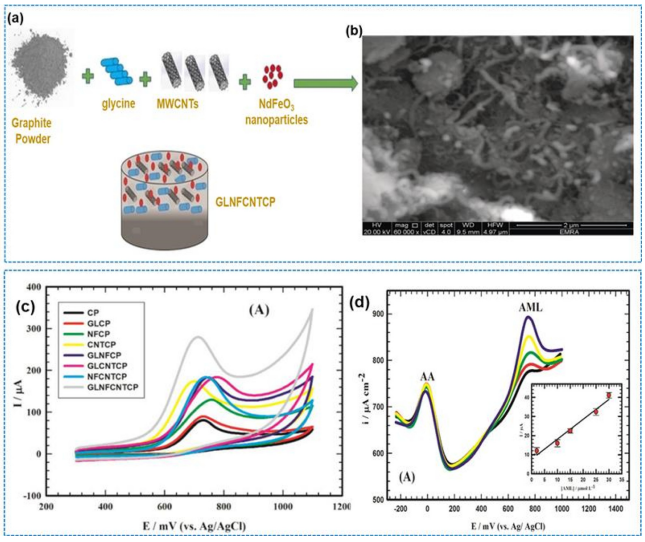

Fig. 3. (a) Structure of the GLNFCNTCP electrode. (b) SEM image of GLNFCNTCP. (c) Cyclic voltammograms of 1 $mmolL^{-1}$ of AML/0.1 $molL^{-1}$ PBS/pH 7.4 recorded at different working electrodes, including CP, GLCP, NFCP, CNTCP, GLNFCP, GLCNTCP, NFCNTCP, and GLNFCNTCP, at a scan rate 50 mVs^{-1}. (d) DPVs for AML in the concentration range of 2 $\mu molL^{-1}$ to 30 $\mu molL^{-1}$ in the presence of 2 $mmolL^{-1}$ of ascorbic acid/0.1 $molL^{-1}$ PBS/pH 7.4 at GLNFCNTCP-SDS. Inset: Calibration curve for AML in the linear dynamic range of 2 $\mu molL^{-1}$ to 30 $\mu molL^{-1}$ in the presence of 2 $mmolL^{-1}$ of ascorbic acid. Reprinted with permission from Ref [43]. Copyrights (2019) Wiley.

for applications in electrochemical sensing because it can tune the electrical and chemical properties of MWCNTs [44].

Naqvi et al. [45] studied the bimetallic doping of CNTs for the detection of ascorbic acid. Transition metals such as iron (Fe) and nickel (Ni) have good electrical and thermal conductivities, high surface-to-volume ratios, and d-band electrons that increase the electrochemical behavior. CNTs provide high conductivity and stability with a high surface area. A co-precipitation method was used to prepare Fe- and Ni-CNTs. SEM analysis of the prepared samples revealed an irregular morphology, and the particle size was calculated to be in the range of 80–100 nm. A three-electrode system was used for the electrochemical detection of ascorbic acid. The working, counter, and reference electrodes used for the study were glassy carbon, platinum wire, and Ag/AgCl, respectively. This study showed that the composite had a detection limit of 3.60 μM.

Tsierkezos et al. [46] studied the doping of boron into MWCNT. When boron is doped, it acts as an electron acceptor and improves the field-emission properties, which leads to an increase in the binding energies of the carboxyl groups. The boron-doped MWCNT were prepared using the chemical vapor method. The SEM image of the prepared film shows a straight bundle of CNT, which is shorter than that of pristine MWCNT. The diameters of the MWCNT in the prepared film is in the range of 100–150 nm. The SEM image also shows the formation of a Y-shaped structure due to defects in the nanostructure caused by the growth of MWCNT in the presence of boron. Three reference and counter electrodes were used for the electrochemical study: platinum plate and Ag/AgCl (saturated KCl) electrodes, respectively. For the working electrode, the prepared film was connected onto a platinum wire using a conducting silver coating. The electrochemical response of the boron-doped MWCNT towards ascorbic acid exhibited a detection limit of 1.21 μM. The interference uric acid and dopamine in the detection of ascorbic acid was studied. The results showed that the sensitivity of the MWCNTs increased when they were doped with boron.

2.5 Carbon-based Materials

Various carbon-based materials have recently been studied for their application in the electrochemical sensing of ascorbic acid because of their facile mass production and simple synthesis methods [31]. Graphene oxide has excellent properties, such as high surface area, chemical stability, and excellent thermal and electrical conductivity, owing to its honeycomb lattice structure [47].

Zhang et al. [48] studied the electrochemical performance of CNTs introduced into an rGO matrix. The formation of an rGO-CNT hybrid increased the electron transfer rate and porous structure, leading to an increase in the electrochemical sensing performance. Electrodeposition was used to synthesize the rGO-CNT hybrid-modified indium tin oxide (ITO) electrode to investigate the electrochemical detection of ascorbic acid, dopamine, and uric acid. ITO is a low-cost material suitable for mass production and practical applications, and it was used as the working electrode because of its unique physical and chemical properties [49]. The detection limit for the electrochemical sensing of ascorbic acid was calculated to be 5.31 μM in the estimated concentration range of 10–200 μM (fig. 4). An anti-interference study, conducted in the presence of NaCl, KCl, $NaNO_3$, $NaNO_2$, and glucose, showed no significant interference. The analysis of real human urine samples showed a 95.7% recovery rate.

Ramakrishna et al. [50] used graphene to fabricate nanocomposites of CNT doped with Pt. Carbon materials with metal or metal oxide nanoparticles exhibit good electrochemical

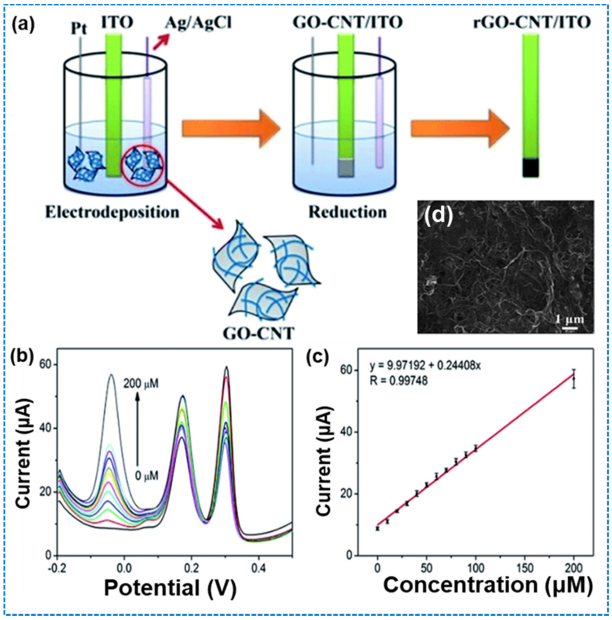

Fig. 4. (a) Schematic illustration of the fabrication and architecture of rGO-CNT/ITO, (b) Current intensity at different concentrations of ascorbic acid: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 200 μM. (c) Calibration plot of the concentration of ascorbic acid versus peak current, (d) SEM images of the obtained rGO-CNT hybrids [48]. Reprinted with permission from Ref [48]. Copyrights (2015) Royal Society of Chemistry.

activity because of their high number of active sites and high selectivity. Chemical vapor deposition was used to prepare the nanocomposites. The prepared nanocomposite was dispersed in ultrapure water, and about 20 μl of the composite solution was drop-casted on the polished glassy carbon electrode and dried at 70℃ overnight. The nanocomposite exhibited a good sensitivity of 0.186 μA μM^{-1} cm^{-2} in a concentration range of 200–900 μM. Vitamin C tablets, human serum, and urine were used to study the electrochemical performance of the prepared nanocomposite for real sample analysis, and the results showed recoveries in the range of 93–101%, indicating the potential of Pt–Gr–CNT as a platform for the simultaneous detection of biomolecules. A Table 2 presents the comparison of all CNT-based composites for ascorbic acid sensing.

3. CONCLUSIONS and OUTLOOK

In this review, CNT and their composite-based materials are discussed for application in the electrochemical analysis of ascorbic acid. The increased demand for portable sensors has prompted the investigation of electrochemical detection materials, with the selectivity of ascorbic acid in the presence of other biomolecules emerging as a primary concern. Although CNT have many advantages in the electrochemical sensing of ascorbic acid, future investigations should focus on (i) understanding the electrochemical interaction between CNT and ascorbic acid, (ii) improving the stability and reproducibility of the modified electrode, (iii) improving the selectivity and sensitivity of the modified electrode, and (iv) extending the application of the modified electrode for practical analysis. Owing to their unique properties, CNTs are perfect candidates for developing effective ascorbic acid sensors. With further research, it will be possible to develop CNT-based composites for electrochemical sensing with high selectivity, sensitivity, and practical applicability.

Table 2. Comparison table of various CNT-based materials for ascorbic acid detection.

Material	Linear range	LOD	Sensitivity	Ref
ZIF-65@ CNT	-	1.03 μM	-	[28]
MWCNTs@Co-bpy/Nf	-	23.25 (±0.03) μA mM^{-1}	3.1 μM	[29]
Mn-BDC@MWCNT	0.1-1150 μM	0.01 μM	-	[30]
CA-MWCNTs-PEDOT	100 μM to 20 mM	4.2 μM	1699.36 μA mM^{-1} cm^{-2}	[32]
CuNP/c-MWCNTs/PANI	5-600 μM	1.0 μM	-	[33]
MSA-PANI/MWCNT	20 μM–29.6 mM	0.6 μM	363 μA mM^{-1} cm^{-2}	[34]
CeO_2 and MWCNT	-	8 nmol L^{-1}	-	[36]
Ruthenium(II) Complex-ZnO/CNT	1.0–65 μmolL^{-1}	0.5, μmolL^{-1}	-	[40]
NdFeO3/glycine/CNT	500–2500 μmolL^{-1}	5.32 μmolL^{-1}	0.015 μA/μmolL^{-1}	[43]
(Fe, Ni)-CNTs	-	3.60 μM	-	[45]
boron-doped MWCNT	-	1.21 μM	-	[46]
rGO-CNT hybrid	10-200 μM	5.31 μM	-	[48]
Pt–Gr–CNT	200–900 μM	-	0.186 μA μM^{-1} cm^{-2}	[50]

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