Electrochemical sensors based on functionalized carbon nanotubes modified with platinum nanoparticles for the detection of sulfide ions in aqueous media

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MS received 8 January 2019; revised 12 January 2019; accepted 14 January 2019; published online 13 February 2019

Abstract. Vertically aligned carbon nanotube (CNT) arrays were synthesized by thermal chemical vapor deposition (CVD) on stainless steel substrates coated by cobalt nanoparticles as catalyst. Morphological and elemental analyses conducted by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) revealed that bamboo-like CNTs were blocked by Co nanoparticles at the tips. The fabricated nanotubes underwent functionalization by electrochemical oxidation in sulfuric acid, and the subsequent structural studies, as well as Fourier transform infrared (FTIR) spectroscopy confirmed that the tips of functionalized CNTs were opened while oxygenated functional groups were generated at the sidewalls and tube endings. In order to enhance the catalytic performance of the functionalized CNT-based electrodes, platinum nanoparticles were deposited on nanotubes by the potentiostatic and pulse potential electrodeposition processes, and the optimum operating parameters in both techniques were determined. The catalytic activities of these two electrodes towards methanol oxidation were determined by cyclic voltammetry (CV) testing, and a superior electrocatalytic activity and poisoning tolerance were detected for the electrode prepared by pulse deposition. The sensing performance of the pulse plated Pt/CNT electrode for the electrochemical detection and oxidation of dissolved sulfide ions was investigated. A sensitivity of $0.632 \mu\text{A } \mu\text{M}^{-1}\text{cm}^{-2}$ and a detection limit of $0.26 \mu\text{M}$ were obtained, indicating the enhanced capabilities of the developed sensor as a promising candidate for various industrial and environmental applications.

Keywords. Functionalized carbon nanotubes; platinum nanoparticles; electrodeposition; methanol oxidation; sulfide sensor.

1. Introduction

The unique electrical, thermal, chemical, and mechanical properties of carbon nanotubes (CNTs) have made them intriguing candidates for the development of new electronic devices, chemical/electrochemical sensors and biosensors, transistors, hydrogen storage cells, supercapacitors, and lithium-ion batteries.^{1–5} CNT-based electrodes are extremely promising for low concentration sensing applications due to their large surface area, high electrical conductivity, high strength, and exceptional electrocatalytic activity that account for the extraordinary capabilities of CNTs as high-performance electrochemical sensors.⁶ Chemical vapor deposition (CVD) methods, including microwave plasma enhanced

and thermal CVD, are the most extensively used processes for the synthesis of vertically aligned carbon nanotubes since they enable the production of larger quantities of more electrochemically reactive CNTs under easily controllable conditions and at lower costs as compared to other production techniques such as arc discharge and laser ablation.⁷ The synthesis of CNTs by the thermal CVD method involves the decomposition of gaseous carbon precursors at elevated temperatures on the surface of nanosized transition metal catalysts such as nickel, iron, or cobalt.⁸ Despite the high efficiency of the thermal CVD process, the formation of byproducts and impurities such as metal encapsulated nanoparticles at the tips of CNTs is an inevitable drawback that can be extremely detrimental to physicochemical properties of the fabricated nanotubes.⁹ To tackle this issue, the electrochemical oxidation

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technique can be employed to open the closed tips of CNTs and simultaneously produce oxygen-containing functional groups at tube endings and defects along the sidewalls. This approach can significantly alter the electronic and structural properties of nanotubes, expedite the electron transfer kinetics at their surfaces, and make them selective to target analytes, thereby enhancing the performance of CNTs as electrochemical sensors.¹⁰ Moreover, the modification of functionalized CNTs with nanosized noble metals such as gold, platinum, or palladium can further improve the reactivity of nanotubes towards the electrochemical oxidation of organic compounds such as methanol, and will substantially boost their sensitivity for the detection of a wide range of biomolecules including hydrogen sulfide, DNA, and glucose.¹¹ Among various materials reported in the literature, Pt nanoparticles have attracted considerable research attention owing to their remarkable electrocatalytic activity.¹² Although different methods such as sputtering and electrophoretic deposition have been applied for the synthesis of Pt-modified CNTs, the electrodeposition technique has been proven to offer distinct advantages over alternative approaches due to providing an appropriate control over the size and density of the deposited Pt nanoparticles.^{13–15} However, this technique still has problems related to the non-uniform distribution, agglomeration, and detachment of Pt nanoparticles. Hence, the optimization of the electrodeposition conditions is a matter of great concern in order to facilitate the homogenous dispersion of Pt nanoparticles on the large surface area of CNTs and effectively develop an electrocatalytic sensing platform.¹⁶ Nevertheless, no research has so far compared the impacts of the potentiostatic and pulse potential electrodeposition of Pt nanoparticles on the morphological structure and electrocatalytic activity of Pt-modified CNTs. The idea of using CNT-based sensors for the detection and electrochemical oxidation of sulfide ions has been the subject of much interest.¹⁷ Aqueous hydrogen sulfide solutions play an important role within biogeochemical processes and wastewater treatment technology; however, the uncontrolled release of high concentrations of sulfide can considerably threaten the surrounding ecosystems and endanger human health.¹⁸ Although few researchers have examined the electrochemical detection of dissolved sulfide by CNT-based sensors,¹⁹ the influence of the modification of CNTs by Pt nanoparticles on the sensing properties of Pt-modified CNTs for the detection of sulfide ions in aqueous media has been unexplored. In this work, vertically aligned CNT-based electrodes modified with nanosized Pt particles were fabricated for the detection and oxidation of sulfide ions in aqueous media. The objective of this paper was to examine the operating

parameters for the electrodeposition of platinum in order to synthesize Pt/CNT electrodes with the optimal electrocatalytic performance and morphological structure. Furthermore, this study aimed to explore the sensitivity of the optimized Pt-modified CNTs towards sulfide ions in aqueous media.

2. Experimental

Type 304 stainless steel substrate was etched in a 9 M sulfuric acid solution (H_2SO_4 98%, Merck) for 10 min so that the protective chromium oxide layer was removed and the surface of the substrate was activated. Afterwards, a thin cobalt layer was electrodeposited as an active catalyst on the substrate from a bath containing double distilled water, 0.25 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 M H_3BO_3 , and 1 M Na_2SO_4 . All reagents were analytical grade from Merck. The bath temperature was maintained at 25 °C and the pH was adjusted to a value of 3.8 ± 0.2 . Electrodeposition of cobalt was conducted using a Metrohm Autolab 302 N system in a conventional three-electrode cell consisting of 0.5 cm $\times$ 0.5 cm etched stainless steel and 2 cm $\times$ 1 cm platinum plates as working and counter electrodes, respectively, and the potential was recorded with respect to the saturated calomel electrode (SCE). Linear sweep voltammetry (LSV) test was carried out to estimate the potential suited for the deposition of Co nanoparticles, and the potentiostatic technique was applied to deposit the cobalt layer. Synthesis of carbon nanotubes (CNTs) was performed by thermal chemical vapor deposition (CVD) technique, based on the pyrolysis of ethylenediamine. The applied reactor consisted of a tube furnace (Carbolite, STF 15/75 model) and a quartz tube (inner diameter 6 mm, length 110 cm). Initially, the tube furnace was heated to 750 °C and subsequently, the cobalt-coated substrates were placed in the preheated furnace and sintered for 4 min under a flow of N_2 gas. Afterwards, N_2 was bubbled through the ethylenediamine container and ethylenediamine was introduced into the furnace at a flow rate of 400 cm³ min⁻¹. Finally, after a reaction time of 30 min, the reactor was naturally cooled to room temperature under N_2 protection, and CNTs were fabricated. A TESCAN VEGA II scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer was utilized to examine the morphology and elemental composition of the synthesized pristine CNTs. Since the CNTs produced by thermal CVD on the cobalt-coated substrates contained metallic particles which blocked the ends of nanotubes, the electrochemical oxidation technique was employed to modify the closed tips of nanotubes and simultaneously functionalize them. All the electrochemical processes were performed in a three-electrode cell including the CNT-coated specimen as working electrode, a platinum foil as a counter electrode, and an SCE as a reference. The electrochemical oxidation was carried out in a 0.2 M H_2SO_4 solution by cycling the potential 10 times between -1 and 0.1 V vs. SCE at 50 mV s⁻¹,

Table 1. Operating parameters for the electrodeposition of Pt nanoparticles on functionalized CNTs by different techniques

Deposition technique	Electrode	Deposition potential (V vs. SCE)	Deposition time (s)	Number of cycles
Potentiostatic	Pt ₁ /CNT	− 0.5	100	
	Pt ₂ /CNT	− 0.6	100	
	Pt ₃ /CNT	− 0.8	100	
	Pt ₄ /CNT	− 0.6	50	
Pulse Potential	Pt ₅ /CNT	E _{on} = − 0.6, E _{off} = − 0.35	T _{on} = 10, T _{off} = 100	10
	Pt ₆ /CNT	E _{on} = − 0.6, E _{off} = − 0.35	T _{on} = 50, T _{off} = 10	10
	Pt ₇ /CNT	E _{on} = − 0.6, E _{off} = − 0.35	T _{on} = 100, T _{off} = 10	10

and the surface morphology of the oxidized CNT- based electrode was monitored by SEM. Fourier transform infrared (FTIR) spectroscopy was used to ensure the formation of functional groups on the surface of CNTs after oxidation. The FTIR spectrum was recorded on a Shimadzu IRAffinity-1 spectrophotometer, controlled by a PC running IR solution software that accompanied the equipment. Approximately 1 mgr of oxidized CNTs was picked up from the surface of the electrode and was well mixed into 400 mgr potassium bromide, and the obtained powder was pressurized to convert to a thin and transparent pellet. Finally, transmittance spectrum of infrared beams was collected in the range 400–4000 cm^{−1} and the functional groups were identified. To further enhance the catalytic property of the functionalized CNT electrode, potentiostatic and pulse potential deposition techniques were utilized to modify the functionalized CNTs with platinum nanoparticles. The aqueous electrolyte (pH 0.6) was composed of 1 mM H₂PtCl₆·6H₂O (~40% Pt, Merck) and 0.5 M H₂SO₄ (98%, Merck), with a functionalized CNT working electrode, a platinum wire counter electrode, and an SCE. The electroplating bath was purged with N₂ at room temperature for 10 min prior to the deposition of platinum and the operating parameters are summarized in Table 1. Pt nanoparticles were also deposited on unfunctionalized (pristine) CNT electrode for comparison. The surface morphologies of Pt-modified CNTs were studied by SEM, and the optimal operating parameters were determined.

The electrocatalytic activities of the optimal electrodes prepared by the potentiostatic and pulse potential deposition techniques towards methanol oxidation were investigated. Prior to the methanol oxidation analyses, the selected electrodes were activated by cyclic voltammetry (CV) in an N₂ saturated 0.5 M H₂SO₄ aqueous solution and surface contaminations were eliminated. In this regard, a cyclic potential range of − 0.2 to 1.0 V vs. SCE at a scan rate of 50 mV s^{−1} was selected to avoid probable alteration of Pt structure that might take place outside this potential range. Afterwards, the electrochemical oxidation of methanol on the surfaces of optimal Pt/CNT electrodes was examined in a mixed solution containing 0.5 M H₂SO₄ and 1.0 M methanol, and the voltammetric curves were recorded between − 0.2 and 1.0 V vs. SCE at a sweep rate of 50 mV s^{−1}. The sensing properties of the fabricated electrodes were assessed as electrochemical sensors towards the detection of sulfide ions. Electrochemical experiments were carried out via an EG&G PAR

potentiostat model 273A, with a conventional three-electrode system, including the pulse plated Pt/CNT electrode as the working electrode, a platinum wire (1 mm diameter) as the counter electrode, and an SCE as a reference. The electrolyte contained different concentrations of sodium sulfide nonahydrate (Sigma-Aldrich, UK), 3.5% NaCl (Merck, Germany), and distilled water, with an adjusted pH of 6.8 at 25 °C. Differential pulse voltammetry (DPV) and CV measurements were recorded from − 1 to 1 V under different conditions of sulfide ion concentrations (0–4 Mm) and scan rates (40–100 mV s^{−1}) to determine the electrochemical sensitivity of the electrode and identify the mechanism of the oxidation of sulfide ions. A comparison of the Differential Pulse Voltammetry (DPV) and CV techniques was performed, and the most efficient technique for obtaining the highest sensitivity towards sulfide ions was determined. The electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the oxidation behavior of the designed sensor towards different sulfide ion concentrations. The testing equipment was an Autolab PGSTAT 302 N system, and a conventional three-electrode cell including the pulse plated Pt/CNT specimen as the working electrode, an SCE as a reference, and a platinum plate as the counter electrode was employed. The EIS tests were conducted at a frequency range of 100 kHz to 0.05 Hz at a potential of 0.25 V with an AC excitation amplitude of 10 mV. Amperometric current-time response curves were also recorded to study the detective performance of the sensor while a magnetic stirrer provided the convective transport during the amperometric measurements. A transmission electron microscope (TEM, EM-10C Model) was used to explore the unzipping of the pulse plated Pt/CNT electrode after the sulfide oxidation process.

3. Results and Discussion

3.1 Electrodeposition of catalyst nanoparticles and morphological study of CNTs

In order to determine the optimal potential for the deposition of cobalt on the stainless steel substrate prior to the growth of CNTs, the LSV curve was plotted in the range of 0 to − 1.7 V at a scan rate of 50 mV s^{−1}. As depicted in Figure 1, there is a cathodic peak at − 1.1 V, corresponding to cobalt deposition. At more negative

Figure 1. Linear sweep voltammetry curve for the electrodeposition of cobalt on stainless steel substrate prior to the growth of CNTs at a scan rate of 50 mV s^{-1} .

potential values, the current density increases rapidly and the evolution of hydrogen hinders the metal deposition. Hence, the potential of -1.1 V was selected as the optimum deposition potential and it was applied for 5 s to deposit a thin cobalt film on the substrate.

Pristine CNTs were synthesized on the cobalt layer, and the structure and morphological features of the obtained nanotubes were analyzed by SEM. According to Figure 2a, the uniform diameter of CNTs varies in the range of $150\text{--}200 \text{ nm}$, and as the sintered cobalt layer is dense enough for catalyzing the growth of nanotubes, high-density CNTs are produced. The local bending of the CNTs tips can be observed and virtually all of the tubes are closed at both ends. Figure 2b indicates that due to the high density of cobalt nanoparticles and the Van der Waals forces between the tubes, CNT arrays are vertically aligned and keep a relatively homogeneous distribution. This figure reveals the bamboo-like structure of nanotubes, and this type of structure is typically generated when nitrogen-containing chemicals such as ethylenediamine are used as the precursor for the fabrication of CNTs by the CVD process.²⁰ Additionally, the presence of nitrogen gas provides a favorable condition for the formation of bamboo-like CNTs. The role of nitrogen is to keep the surface of the thin cobalt layer active and clean during the pretreatment of catalyst nanoparticles and perhaps at the initial stage of the CNTs growth. Moreover, nitrogen enhances the bulk diffusion of carbon into the catalyst nanoparticles, leading to the formation of bamboo-shaped nanotubes.²¹ Figure 2c displays the top view SEM image of nanotubes with close ends at high magnification. To gain a detailed insight into the chemical properties of CNTs, point A on the tip of a nanotube in Figure 2c was characterized by EDX analysis. The chemical composition of point A represents that the tip of the examined CNT is chiefly

composed of carbon, showing that the growth of the tube occurs from its closed-end tip. The existence of cobalt at the end of the CNT indicates that a tip-growth mechanism occurs where the catalyst nanoparticles are detached from the surface during the CNT growth. It should be noted that during the initial stage of the nanotubes nucleation, the precursor is decomposed and carbon atoms diffuse into the catalyst particles, leading to the formation of a carbon cap around cobalt particles. In the growth process, the caps created on the carbon-coated particles lift off and further carbon atoms constantly join the edges of the caps, developing tubes which grow away from the particles. These tubes contain small amounts of cobalt particles that are separated from the surface and move towards the tips of CNTs.⁹

3.2 Electrochemical functionalization of CNTs

The electrochemical oxidation technique was employed to open the closed tips of pristine CNTs and simultaneously functionalize them so that the electrochemical performance of nanotubes could be enhanced. Figure 3 demonstrates the CV curves of the CNT-based electrode recorded in a $0.2 \text{ M H}_2\text{SO}_4$ solution by cycling the potential from -1 to 0.1 V at 50 mV s^{-1} . In order to accurately detect the changing behavior of nanotubes in different cycles, the CVs were plotted in the 1st, 5th, and 10th cycles. The first scan of the potential does not exhibit a well-defined oxidation peak, while after the 5th and 10th scans wide oxidation peaks are observed between -0.4 V (i.e., open circuit potential) and 0.1 V , indicative of the electrochemical oxidation of the CNTs. It has been reported that CNT purification by oxidation in the sulfuric acid solution yields the formation of oxygenated functional groups (predominantly carboxylic acid) at the sidewalls and tube endings.²² As depicted in Figure 3, the peaks shift toward more negative potentials and higher current densities in successive cycles. This can be attributed to the formation of functional groups during the prior cycle which significantly enhances the electrochemical reactivity of nanotubes, leading to the acceleration and intensification of oxidation in the proceeding cycle.

Figures 4a and 4b illustrate the morphological characteristics of CNT arrays after the 1st and 10th cycles of electrochemical oxidation in $0.2 \text{ M H}_2\text{SO}_4$, respectively. It is evident that the electrochemical oxidation cuts CNTs in smaller segments substantially decreases the diameter of nanotubes, and removes metal catalysts resulting in open-ended CNTs. Moreover, the electrochemical purification usually increases the concentration of sidewall defects and improves the

Figure 2. SEM images of (a) Low magnification top view; (b) high magnification side view; (c) high magnification top view of vertically aligned pristine CNT arrays. EDX elemental analysis was performed on a nanotube tip.

surface reactivity; therefore, it is favorable for the functionalization of un-capped CNTs.¹⁰

In order to investigate the influence of electrochemical oxidation on the formation of functional groups on the surface of CNTs, nanotubes were characterized by FTIR. Figure 5 shows the transmittance infrared spectrum of the CNT electrode after 10 oxidation cycles in a 0.2 M H₂SO₄ solution. The wide peak at 3427 cm⁻¹ and other smaller peaks at 2910 cm⁻¹ and 2360 cm⁻¹ refer to the O–H stretch of the hydroxyl group. Besides, two peaks appear at 1270 and 1170 cm⁻¹ which are assigned to C–O bonding, while the peaks at 1630 and 1400 cm⁻¹ can be associated to the C=O and C–C stretching of the CNTs, respectively.²³ The FTIR spectrum obviously

confirms that the main functional group produced on the surface of CNTs is the carboxyl group (COOH) consisting of a carbonyl group (C=O) with a hydroxyl group (O–H) attached to the same carbon atom. The COOH groups are formed due to the slight oxidation of the surface of nanotubes during the electrochemical process and are successfully attached to the surface of CNTs. It is worth mentioning that functional groups produced on the walls of CNTs along with defects introduced by the oxidation of tubes significantly improve the electrochemical performance of the CNT electrode by altering its electrical structure, increasing its wettability, and expediting the electron transfer kinetics at the surface of the electrode.²⁴

3.3 Electrodeposition of Pt nanoparticles on functionalized CNTs

In order to enhance the catalytic performance of the functionalized CNT electrode as an electrochemical sensor, Pt catalyst nanoparticles were deposited on CNTs by the potentiostatic and pulse potential electrodeposition techniques, and a comparative analysis of these two methods was conducted.

3.3a Potentiostatic electrodeposition: Initially, to investigate the influence of surface functionalization of CNTs on the electrodeposition of platinum, Pt nanoparticles were deposited on pristine and functionalized (10

Figure 3. Electrochemical oxidation of the CNTs in 0.2 M H_2SO_4 by potential cycling between -1 and 0.1 V vs. SCE at 50 mV s^{-1} . For more clarity, only the 1st, 5th, and 10th CV curves are displayed.

cycles oxidized) CNTs by the potentiostatic technique. The selected potential and time for the deposition of Pt nanoparticles were -0.6 V and 100 s, respectively (Pt_2/CNT electrode in Table 1). The surface morphologies of $\text{Pt}_2/\text{pristine CNT}$ and $\text{Pt}_2/\text{functionalized CNT}$ electrodes are demonstrated in Figure 6. During the electrochemical deposition of platinum on CNTs, nanotubes act as deposition platforms and enable the electrical attachment of Pt nanoparticles without reacting with the metal salt solution.²⁵ However, as depicted in Figure 6a for the pristine CNT electrode, the neutral surface of CNTs does not support the attachment of metallic particles. In this case, only the surface defects, rather than the entire surface of CNTs, serve as active nucleation sites and yield a non-uniform distribution of Pt nanoparticles. As the deposition proceeds, previously deposited

Figure 5. FTIR spectrum for functionalized CNTs after 10 oxidation cycles in 0.2 M H_2SO_4 .

Figure 4. Top-view SEM images of functionalized CNT arrays after the (a) 1st and (b) 10th cycles of electrochemical oxidation in 0.2 M H_2SO_4 . The corresponding insets are at the higher magnifications.

Figure 6. SEM images of **a** Pt₂/pristine CNTs and **b** Pt₂/functionalized CNTs.

particles also get involved as nucleation sites and therefore, some agglomerated particles are separately formed on the surface of nanotubes. However, according to Figure 6b, Pt nanoparticles uniformly deposit on the walls of functionalized CNTs, and a homogeneous distribution of Pt nanoparticles is obtained. This uniform morphology can be attributed to the oxygen-containing functional groups which are generated on nanotubes during the electrochemical oxidation process.²⁶ These functional groups act as ligands with a strong affinity for metal ions and assist the attachment of Pt nanoparticles on the external surfaces of CNTs. In other words, carboxylic groups which are available on the outer walls of functionalized CNTs are beneficial to obtain a uniform distribution of Pt nanoparticles by providing more nucleation centers which facilitate the deposition and stabilization of platinum.

In order to examine the influence of various deposition potentials on the surface morphology of Pt-modified CNTs and to study the size and distribution of Pt nanoparticles, the deposition of Pt on functionalized CNTs was carried out at -0.5 , -0.6 , and -0.8 V for 100 s. Figure 7 displays the SEM images of Pt₁/CNT, Pt₂/CNT, and Pt₃/CNT electrodes at two different magnifications. According to Figure 7a, it can be observed that Pt₁ nanoparticles are not distributed uniformly, and highly agglomerated particles are created on the surface of CNTs. At the reduction potential of -0.5 V, the driving force for nucleation is inadequate to overcome the activation energy; therefore, particles growth predominates over nucleation, and a smaller number of larger platinum particles is obtained. Moreover, at a low

deposition potential, there are relatively few nucleation sites available on the surface of CNTs and thus, Pt₁ ions nucleate on the preceding Pt₁ clusters rather than on the new sites of CNTs, thereby inducing the agglomeration of flower-like platinum clusters in some regions. Figure 7b depicts the SEM image at a higher magnification, and as the crystal growth tends to be the dominant mechanism during the crystallization of platinum, the size of Pt₁ nanoparticles varies between approximately 100 and 150 nm. Figures 7c and 7d depict SEM images of Pt₂/CNT electrode, and it is evident that at a more negative potential the nucleation and deposition of Pt₂ nanoparticles mainly occur on the sidewalls of CNTs. As the driving force for the nucleation of Pt₂ nanoparticles increases at the deposition potential of -0.6 V, the number of nucleation sites uniformly increases on the entire surface of nanotubes and consequently, the deposition of a large number of small platinum particles is facilitated. In this case, the size of the deposited Pt₂ nanoparticles are smaller than that of Pt₁ nanoparticles, and it is measured to be about 70 nm. Figures 7e and 7f show the morphological structure of CNTs after the deposition of Pt₃ nanoparticles, and it can be observed that under the deposition potential of -0.8 V, the structure of CNTs are slightly disordered and randomly oriented Pt₃ particles are noticeable on the surface of nanotubes. It has been confirmed that if platinum is electrodeposited under highly negative potentials, the evolution of hydrogen in the acidic electrodeposition bath will reduce the cathode efficiency and disturb the deposition.²⁷ Thus, the intensive evolution of hydrogen gas around the cathode at the deposition potential of -0.8 V accounts for

Figure 7. SEM images of functionalized CNTs after the potentiostatic deposition of Pt nanoparticles for 100 s; (a), (b) Pt₁/CNT ($E = -0.5$ V); (c), (d) Pt₂/CNT ($E = -0.6$ V); (e), (f) Pt₃/CNT ($E = -0.8$ V).

Figure 8. (a) Low magnification and (b) high magnification SEM images of Pt₄/CNT electrode ($E = -0.6$ V, $t = 50$ s).

the disordered CNTs and Pt₃ nanoparticles. It should be noted that the crystallization of nanoparticles starts with the nucleation of Pt₃ crystals on the active sites of CNTs followed by crystals growth. However, the excessive growth of particles does not occur as the hydrogen evolution reaction subsequently takes place and interrupts the further growth of particles, promoting the formation of particles with the average size of 30 nm.

Based on the above analysis, Pt₂/CNT electrode exhibits the optimal structure and thus, the deposition potential of -0.6 V was selected to study the influence of altering the deposition time on the morphology of platinum nanoparticles. Figure 8 represents the SEM images of Pt₄/CNT electrode for which platinum nanoparticles were deposited under the reduction potential of -0.6 V for 50 s. Comparing Figures 7c with 8a, it can be observed that over a prolonged deposition time, Pt₂ nanoparticles grow cylindrically on the peripheral surface of CNTs, whereas during a shorter deposition time, the deposition of Pt₄ nanoparticles mainly occurs at CNTs tips and this triggers the agglomeration of nanotubes tips in some regions. Furthermore, a comparison of Figures 7d with 8b reveals that for a given deposition potential, if the deposition time is shortened from 100 to 50 s, the size of Pt nanoparticles does not vary and is about 70 nm. In other words, the extended deposition time of 100 s does not assist the growth of nanoparticles, though it provides more opportunity for hydrogen ions to absorb and discharge on the electrode. Consequently, further growth of Pt nanoparticles is hindered due to the interference of hydrogen gas evolution with platinum deposition.

3.3b Pulse potential electrodeposition: As mentioned above, the optimized sample prepared by the potentiostatic technique was selected as Pt₂/CNT electrode for which platinum nanoparticles were deposited under -0.6 V for 100 s. However, in order to improve the catalytic behavior of the obtained CNTs, a more uniform distribution of Pt nanoparticles with a smaller size is needed to be obtained. For this purpose, the deposition of Pt nanoparticles was carried out by the pulse electrodeposition technique which involved a swift alternating of the potential between a cathodic value and the open circuit potential (OCP) at which no net current flowed through the external circuit. According to Table 1, the cathodic potential of -0.6 V was selected as E_{on} and it was applied for three constant durations of $T_{on} = 10, 50,$ and 100 s, while E_{off} was OCP (i.e., -0.35 V) which was applied for two durations of $T_{off} = 10$ and 100 s in 10 consecutive cycles. The influence of various cathodic pulse durations (T_{on}) and current-off times (T_{off}) on the surface morphology of Pt-modified CNTs is illustrated in Figure 9. According to Figures 9a and 9b, Pt₅ nanoparticles that are deposited on functionalized CNTs after 10 cycles of $E_{on} = -0.6$ V, $T_{on} = 10$ s, $E_{off} = -0.35$ V, and $T_{off} = 100$ s are not distributed uniformly. Actually, Pt₅ nanoparticles deposit on the active sites of the electrode during the first short cathodic pulse and since metal ions do not have enough time to deposit, a few embryos are nucleated. In the subsequent cathodic pulses, since the reduction of platinum ions on the surface of CNTs requires high nucleation energy, Pt₅ nanoparticles tend to deposit on the previously generated nuclei, resulting in the formation of a

Figure 9. SEM images of functionalized CNTs after the pulse deposition of Pt nanoparticles prepared under the condition of $E_{\text{on}} = -0.6$ V and $E_{\text{off}} = -0.35$ V; (a), (b) Pt_5/CNT ($T_{\text{on}} = 10$ s, $T_{\text{off}} = 100$ s); (c), (d) Pt_6/CNT ($T_{\text{on}} = 50$ s, $T_{\text{off}} = 10$ s); (e), (f) Pt_7/CNT ($T_{\text{on}} = 100$ s, $T_{\text{off}} = 10$ s).

non-uniform and inhomogeneous structure. On the other hand, due to a prolonged current-off time, platinum nanoparticles find sufficient opportunity to grow, and particles with the average size of 150 nm are obtained. Additionally, because of the longer pulse pause, hydrogen evolution accompanying the growth of Pt₅ particles may disturb CNTs orientation and induce structural inhomogeneity. As can be seen from Figures 9c and 9d, when T_{on} is increased to 50 s and T_{off} is decreased to 10 s, Pt₆ nanoparticles mainly concentrate on the tips of CNTs as spherical clusters but they are also evenly distributed at the sidewalls of nanotubes with an average size of 50 nm. Nanotube tips are generally believed to be more reactive than the sidewalls due to their stronger electrical field; thus, the adsorption affinity of CNTs tips for the attraction of the platinum ions is more intense than that of the sidewalls.²⁸ As a result, during the cathodic cycles which are applied for the relatively short duration of 50 s, Pt₆ nanoparticles principally tend to deposit on the CNTs tips and they have less chance to form a thick layer on the sidewalls. To overcome this issue, the surface coverage can be tuned with the deposition time in cathodic pulses. Figures 9e and 9f demonstrate that under the same deposition condition, as T_{on} is increased to 100 s, Pt₇ nanoparticles are mainly dispersed at the sidewalls rather than the tips of CNTs, and walls are uniformly covered with a dense network of metal nanoparticles. In this case, the deposition of particles on the external wall of nanotubes fills the spaces between CNTs, promoting the formation of a more compact structure. Comparing Figures 9d and 9f indicates that the particle size is almost unchanged at about 50 nm due to the short off-current pulses ($T_{off} = 10$ s) which do not facilitate the excessive growth of Pt₇ nanoparticles. A comparison of Figures 7c and 7d with 9e and 9f reveals that the particle size and surface coverage can be controlled by the electrodeposition technique, and the Pt₇/CNT electrode prepared by pulse potential deposition exhibit a highly uniform and compact structure of more refined platinum nanoparticles on the walls of CNTs as compared to the Pt₂/CNT electrode prepared by the potentiostatic technique.

3.4 Electrocatalytic performance of Pt-modified CNTs

In order to investigate the influence of the electrodeposition technique upon the electrocatalytic activity of Pt-modified CNTs, Pt₂/CNT and Pt₇/CNT electrodes were chosen as the optimal samples and the methanol oxidation efficiencies of these two electrodes were compared. To remove surface contaminations prior to methanol oxidation analyses, CV experiments were conducted in a 0.5 M H₂SO₄ solution with potentials

Figure 10. Cyclic voltammograms of Pt₂/CNT and Pt₇/CNT electrodes in N₂ saturated (a) 0.5 M H₂SO₄ and (b) 0.5 M H₂SO₄ + 1 M CH₃OH aqueous solutions, at a scan rate of 50 mV s⁻¹.

ranging from -0.2 to 1 V at a sweep rate of 50 mV s^{-1} . Figure 10a depicts that the cyclic voltammograms of Pt₂/CNT and Pt₇/CNT electrodes are similar to that of a polycrystalline Pt electrode.²⁹ In the forward scan, two hydrogen desorption peaks and a double-layer region are present, followed by an oxidation peak that is ascribed to the formation of PtO *via* the following reactions;

The PtO layer is reduced during the reverse scan, and two hydrogen adsorption peaks are observed after the double-layer region. All the potential regions are nearly identical for Pt₂/CNT and Pt₇/CNT electrodes; however, the current intensities at hydrogen adsorption/desorption and Pt oxidation/reduction peaks are higher for the sample prepared by pulse deposition. The higher current values at hydrogen desorption peaks for the sample prepared by pulse deposition indicates expedited desorption of hydrogen from the surface of the Pt₇/CNT electrode that can have a beneficial impact

on the catalytic activity of the electrode. Moreover, the higher current intensity of platinum oxidation peak suggests that a high quantity of Pt-O and Pt-OH species are produced on the surface of the Pt₇/CNT electrode which can subsequently contribute to the oxidation of the adsorbed intermediates during methanol oxidation.³⁰ The superior electrochemical activity of the pulse plated electrode is owing to the uniform distribution of refined platinum nanoparticles on the sidewalls of CNTs in the Pt₇/CNT electrode. Accordingly, the higher surface coverage of CNTs by Pt₇ nanoparticles provides a larger active surface and boosts the catalytic property of this electrode.

According to Figure 10b, the methanol oxidation efficiencies of the electrodes are evaluated by CV analysis in an N₂ saturated 0.5 M H₂SO₄ + 1 M CH₃OH solution in the potential range of −0.2 to 1 V at a rate of 50 mV s^{−1}. While similar behavior has been observed for methanol oxidation on pure platinum electrodes in acidic solutions, the peak potentials obtained for Pt₇/CNT and Pt₂/CNT electrodes are less positive than that reported for pure Pt electrodes.³¹ This is due to the presence of functional groups such as carbonyl and hydroxyl on the surface of functionalized CNTs which serve as active oxygen sites and facilitate the oxidation of methanol and enhance the electrocatalytic activity of the electrodes. The oxidation of methanol on Pt is carried out through the following reactions;

Accordingly, the overall equation can be considered as follows;

Based on Figure 10b, the impacts of deposition techniques on the electroactivity of the prepared electrodes for methanol oxidation can be easily identified by examining the onset potentials, peak current densities of methanol oxidation, and the ratios of forward to reverse peak current densities. The onset potential is related to the breaking of C–H bonds in methanol molecules that are absorbed on Pt nanoparticles, and this parameter is 0.28 V and 0.17 V for Pt₂/CNT and Pt₇/CNT electrodes, respectively. These values indicate that the morphological structure of the electrode prepared by pulse deposition reduces the initial required energy and promotes methanol oxidation. As the potential is swept toward more positive values in the forward scan, the adsorption of methanol molecules on the Pt nanoparticles leads to the formation of Pt(CO)_{ads} (Eq. (3)),

and simultaneously, the oxidation of water occurs and Pt(OH)_{ads} is generated (Eq. (4)). The adsorption and oxidation reactions culminate in peaks at 0.71 and 0.63 V for Pt₂/CNT and Pt₇/CNT electrodes, respectively, and in parallel, Pt nanoparticles which are poisoned by CO can be regenerated via the reaction of adsorbed CO with OH to yield CO₂ (Eq. (5)). By sweeping the voltage to more anodic values, the oxidation of methanol is accompanied by the formation of more by-products which have a blocking/poisoning effect and decrease the current density. The lower value of the potential at the oxidation peak in the forward scan for the Pt₇/CNT electrode in comparison to that of the Pt₂/CNT electrode is indicative of the reduced required potential for methanol oxidation on the electrode prepared by pulse deposition. Moreover, the current value at this peak is higher for the Pt₇/CNT electrode in comparison to the Pt₂/CNT electrode. SEM observations in Figures 7c, 7d and 9e, 9f can be used to justify the superior electrocatalytic performance of the pulse plated electrode over the sample prepared by the potentiostatic technique. As compared to the Pt₂/CNT electrode, the Pt₇/CNT electrode possesses a highly compact structure with more refined and uniformly distributed platinum nanoparticles which provide a higher density of exposed active sites for trapping methanol molecules, leading to the enhanced electrocatalytic performance of the specimen prepared by pulse deposition.

In the reverse sweep, the oxidation peaks signify the desorption of CO generated through methanol oxidation during the forward scan, and the desorbed CO is thereupon converted to CO₂. It should be noted that while Pt nanoparticles are considered as effective catalysts for methanol oxidation, they tend to be self-poisoned by reaction intermediates such as CO which are formed during dehydrogenation of the methanol. The electrode efficiency on methanol oxidation can be evaluated with regard to the tolerance of Pt nanoparticles towards poisoning by carbon monoxide in terms of a ratio of the forward to reverse peak current densities. According to Figure 10b, this ratio is estimated to be 1.15 and 1.73 for Pt₂/CNT and Pt₇/CNT electrodes, respectively, representing the superior poisoning tolerance of the Pt₇/CNT electrode. The enhanced tolerance of the pulse plated electrode to CO poisoning is attributed to the compact coverage of CNTs with well-dispersed Pt₇ nanoparticles that can effectively inhibit the adsorption of CO during the anodic sweep and subsequently decrease CO poisoning in the reverse sweep. This attribute, along with the slightly lower onset and oxidation peak potentials and significantly higher current density in the forward scan for the Pt₇/CNT electrode confirm the superior electrocatalytic activity and lower self-poisoning of the

Figure 11. Cyclic voltammetric response of the Pt₇/CNT electrode to increasing (a) concentrations of sulfide from 0 to 4 mM (pH = 6.8) at a scan rate of 50 mV s⁻¹ (the dashed curve belongs to the non-modified CNT electrode at a concentration of 4 mM); (b) scan rates from 40 to 100 mV s⁻¹ at a sulfide concentration of 4 mM.

electrode prepared by pulse deposition as compared to the specimen fabricated by the potentiostatic technique.

3.5 The performance of pulse plated Pt/CNT electrodes as electrochemical sensors

Based on the above analysis, the Pt₇/CNT electrode which was fabricated by the pulse potential deposition of Pt nanoparticles on 10 cycles functionalized CNTs exhibited the optimized morphological and electrochemical properties. To further verify the crucial role of platinum nanoparticles in the electrochemical behavior of the CNTs, sensing properties of the Pt₇/CNT electrode for the electrochemical detection and oxidation of sulfide ions was examined. Figure 11a displays the cyclic voltammetric response of the Pt₇/CNT electrode to increasing concentrations of sulfide ions from 0 to 4 mM (pH = 6.8) over the potential range of -1 to 1 V at a scan rate of 50 mV s⁻¹. The CV curve of the functionalized but non-modified CNT electrode was also plotted in a solution containing 4 mM sulfide for comparison (dashed line). The anodic currents

measured in the absence of sulfide ions are negligibly small compared to those measured in its presence, indicating that the anodic currents are definitely due to the oxidation of sulfide ions. As the concentration of sulfide is increased to 4 mM, an oxidative current emerges at about -0.7 V and it continues to rise until it reaches an oxidation peak at 0.25 V, after which a steady response is obtained. It should be emphasized that hydrogen sulfide is generally considered as a weak acid and in an aqueous solution; it tends to become deprotonated to form the mono-protonated hydrogen sulfide anion;

The mechanism of the action of Pt nanoparticles on the sensing properties of Pt-modified CNTs for the detection of sulfide ions in aqueous media is dependent upon pH. In alkaline solutions, HS⁻ is the predominant species, and sulfide oxidation on platinum results in the formation of elemental sulfur bonded onto the catalyst nanoparticles, according to the following reactions:³³

However, in acidic solutions, the presence of H₂S dominates, and the oxidation of sulfide to sulfate is favored, through to the following reactions:¹⁷

It has been demonstrated that at pH 6.8 and 25 °C, about 30 and 70 vol.% of the sulfide will be present as HS⁻ and H₂S, respectively.³² Thus, H₂S is the predominant species in the acidic solution employed in this research, and the oxidation peaks in Figure 11a can be ascribed to the adsorption and oxidation of H₂S on Pt₇ nanoparticles through Eq. (10) and Eq. (11). No reduction peak is detected in the reverse scan, confirming that the electrochemically generated oxidation products do not undergo a reduction in the potential range studied. Analysis of the dashed CV curve reveals that at a sulfate concentration of 4 mM, the functionalized but non-modified CNT electrode exhibits a decreased oxidation current values compared to those of the Pt₇/CNT electrode, with an oxidation peak at 0.48 V. It can be concluded that the catalytic properties of platinum nanoparticles deposited on the sidewalls of CNTs account for the slight shift of the oxidation peak to less positive potentials and higher current densities, leading to an enhanced capability for the electrochemical detection of sulfide. The inset in Figure 11a illustrates that for the Pt₇/CNT electrode, peak current values vary linearly over the sulfide concentration range with a sensitivity of 0.632 μA μM⁻¹ cm⁻²

Figure 12. Differential pulse voltammograms obtained at the Pt₇/CNT electrode for the oxidation of different concentrations of sulfide from 0 to 4 mM (pH = 6.8) at a scan rate of 50 mV s⁻¹ (step potential: 0.01 V, modulation amplitude: 0.01 V, modulation time: 0.05 s, interval time: 1 s).

that is substantially higher than that measured for the non-modified CNTs electrode (0.081 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$, results not shown here).

Further assessment of the sulfide oxidation process was carried out by investigating the influence of different scan rates (40, 60, 80 and 100 mV s⁻¹) on the CV curves of the Pt₇/CNT electrode at a sulfide concentration of 4 mM. Figure 11b demonstrates that the oxidation peaks shift to more positive potentials and higher current densities as the scan rate is increased. Such behavior is typical of a diffusion-controlled oxidation process in which at higher scan rates, sulfide concentration gradient increases in the solution and sulfide anions have to diffuse from the bulk electrolyte to become oxidized on the sidewalls of CNTs and deposited Pt nanoparticles. As depicted in the insets in Figure 11b, the linearity of E_p vs. $\log v$ as well as i_p vs. $v^{1/2}$ plots further confirms that the oxidation of sulfide anions involves an irreversible electron transfer process that is under diffusion control.

In order to investigate which voltammetric technique is more sensitive for the detection of sulfide ions on the pulse plated electrode, DPV was employed over the concentration range of 0–4 mM. Operating conditions for DPV studies were stepped potential of 5 mV, modulation amplitude of 25 mV, modulation time of 0.05 s, and interval time of 1 s. Figure 12 shows differential pulse voltammograms for sulfide oxidation on the Pt₇/CNT electrode at a scan rate of 50 mV s⁻¹, along with corresponding calibration graphs of the oxidation current versus sulfide concentration. Based on the corresponding linear regression equation, the sensitivity value estimated by DPV is 0.509 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ that is relatively lower than the 0.632 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ value obtained by CV. Thus, the CV method appears to be more efficient for achieving the highest sensitivity on the developed sensor.

Figure 13. Nyquist plots for the Pt₇/CNT electrode recorded in electrolytes containing different concentrations of sulfide between 0 and 4 mM. Frequency range: 100 kHz–0.05 Hz, potential: 0.25 V, AC amplitude: 10 mV.

The EIS technique was used to further investigate the oxidation performance of the designed sensor. Figure 13 represents the Nyquist plots of the Pt₇/CNT electrode in electrolytes containing different concentrations of sulfide between 0 and 4 mM, recorded at a frequency range of 100 kHz to 0.05 Hz at a potential of 0.25 V with an AC excitation amplitude of 10 mV. The Nyquist diagrams exhibit a capacitive loop at higher frequencies associated with the double layer capacity, followed by a straight line at lower frequencies, which is the typical feature of a diffusion-controlled process.³⁴ It is also evident that with an increase in the sulfide contraction, the charge-transfer resistance (R_{ct}) at the electrode/solution interface increases while the values of the electrochemical double layer capacitance and diffusional impedance decrease. This trend can be attributed to the formation of sulfide oxidation products such as sulfate species that cause fouling effect at the electrode surface. The charge-transfer resistance which equals the semicircle diameter controls the electron-transfer kinetics of the oxidation of sulfide to sulfate at the electrode interface. The sensing performance of the Pt₇/CNT electrode was evaluated *via* monitoring the changes in R_{ct} upon the analysis of different concentrations of sulfide ions. The inset in Figure 13 displays the calibration plot of the charge transfer resistance values obtained for the Pt₇/CNT sensor as a function of sulfide concentration. The sensor response varies linearly ($R^2 = 0.999$) with the concentration, and the detection limit is estimated as 0.29 μM at a signal-to-noise ratio of 3.

In order to determine the lower limit of detection, which is the lowest concentration of sulfide that can be detected by the sensor, the current-time response of the Pt₇/CNT electrode was plotted at the oxidation potential of 0.25 V. According to Figure 14, the measurements were performed with the successive addition of 10 μM

sulfide after each 60 seconds. The Pt₇/CNT sensor responds quickly to these continuous sulfide additions, producing steady-state signals during repeated 60 seconds. The response time (i.e., the time required to reach 95% of the maximum steady-state current) is estimated to be within 5 s, indicating the facile electron transfer process through the designed sensor. The inset in Figure 14 displays the calibration graph of the response current as a function of sulfide concentration, that is used for the calculation of the detection limit. It is evident that the Pt₇/CNT electrode exhibits two separate linear sections in the concentration ranges of 0–40 μM and 40–100 μM for which the regression equations are i ($\mu\text{A cm}^{-2}$) = $-5.2995 + 3.0971 C$ (μM) ($R^2 = 0.989$) and i ($\mu\text{A cm}^{-2}$) = $-317.9 + 10.868 C$ (μM) ($R^2 = 0.997$), respectively. The detection limit of

Figure 14. The amperometric response of the Pt₇/CNT electrode to successive addition of sulfide at an applied potential of 0.25 V vs. SCE.

the Pt₇/CNT sensor is estimated to be 0.26 μM at a signal-to-noise ratio of 3. The amperometric results confirm the EIS measurements; however, since the limit of detection observed by the amperometric measurements is more precise, the lower detection limit of the designed sensor is considered as 0.26 μM . These data not only indicate the effectiveness of the designed electrode for the detection of low concentrations of sulfide in the range of 40–100 μM but also confirm the capability of this electrode as a sensitively amperometric sensor to detect much lower concentrations of sulfide in the range of 0–40 μM . With regard to the values of sensitivity and detection limits reported for different types of carbon nanotubes,¹⁷ the enhanced sensitivity of the Pt₇/CNT electrode towards changes in sulfide concentrations along with a low limit of detection reveals that the fabricated sensor can be reliably applied to monitor sulfide at trace levels for various industrial and environmental applications.

A comparison of the analytical performance of the Pt₇/CNT electrode with other reported sulfide sensors is represented in Table 2. The analytical parameters of our designed sensor are comparable or superior to the results reported for the electroanalytical determination of sulfide at the surface of different modified electrodes.

Despite all promising features, CNT-based electrodes might undergo electric field-induced morphology changes that lead to the oxidative unzipping of carbon nanotubes to graphene nanoribbons, thereby impacting the performance and long term stability of the electrodes.⁴² To investigate the unzipping of the pulse plated Pt₇/CNT sensor, the morphology of nanotubes

Table 2. Comparison of different electrochemical sensors for the determination of aqueous sulfide

Electrode	Sensitivity ($\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$)	Detection limit (μM)	Response time (s)	References
Nickel powder-modified carbon composite electrode (Ni-CCE)	0.008	1.19	2	[35]
Glassy carbon electrode (GCE)	0.057	0.1	10	[36]
Vanadium pentoxide film-modified glassy carbon electrode (V_2O_5 -GCE)	0.089	1.9	8	[37]
Copper complex and multiwall carbon nanotubes-modified glassy carbon electrode (Cu(II)/MWCNTs/GCE)	0.034	1.2	1	[38]
Reduced graphene sheets-modified glassy carbon electrode (RGS- GCE)	0.014	4.2	10	[39]
Hematoxylin-modified pencil graphite electrode (HMT-PGE)	0.022	0.4	20	[40]
Hematoxylin multi-walled carbon nanotubes-modified carbon paste electrode (HM-MWCNTs-CPE)	0.1026	0.2	3	[41]
Pulse plated Pt-modified carbon nanotube electrode (Pt/CNT)	0.632	0.26	5	This work

Figure 15. (a) SEM and (b) TEM images of the Pt₇/CNT sensor after the oxidation of 4 mM dissolved sulfide ions at the potential of 0.25 V vs. SCE for 24 h.

was studied after the oxidation of 4 mM dissolved sulfide ions at the potential of 0.25 V for 24 h. The SEM and TEM images in Figures 15a and 15b depict that Pt-modified CNTs are stable and Pt nanoparticles are uniformly distributed at the CNTs surface. Moreover, no complete or partial exfoliation or unzipping of nanotubes can be observed after the electrochemical process, and the integrity of Pt-modified CNTs does not change after the sulfide oxidation. In other words, the applied potential of 0.25 V in the presence of 4 mM sulfide ions does not generate sufficient electric field on the electrode/electrolyte interface and cannot trigger the transformation of CNTs to longitudinally unzipped graphene nanoribbons. This is justifiable because according to other researchers, even in the case of highly concentrated acid solutions, the onset potential for the unzipping of carbon nanotubes is much higher than the oxidation potential applied in the current study.^{43,44}

4. Conclusions

The thermal CVD process was utilized to synthesize vertically aligned carbon nanotubes (CNTs) on stainless steel substrates. To catalyze the growth of nanotubes, a thin layer of cobalt catalyst nanoparticles was electrodeposited on the substrates under the optimum deposition potential of -1.1 V vs. SCE, leading to the formation of bamboo-shaped CNTs with close ends. Functionalization and purification of CNTs by

10 cycles of electrochemical oxidation in sulfuric acid solution opened the tips of nanotubes while generating oxygen-containing functional groups, mainly carboxyl, at the sidewalls and tube endings. Surface modification of nanotubes was carried out by the electrodeposition of Pt nanoparticles on CNT-based electrodes, and the optimum operating parameters were determined as $E = -0.6$ V, $t = 100$ s and $E_{\text{on}} = -0.6$ V, $T_{\text{on}} = 100$ s, $E_{\text{off}} = -0.35$ V, $T_{\text{off}} = 10$ s in the potentiostatic and pulse potential deposition techniques, respectively. The functionalized CNT-based electrode modified by pulse deposited Pt nanoparticles exhibited a superior catalytic performance towards methanol oxidation reaction accompanied by an improved tolerance to CO poisoning as compared to the electrode modified by the potentiostatically deposited particles. This was ascribed to the extremely uniform distribution of more refined platinum nanoparticles that provided a higher density of exposed active sites for trapping methanol molecules on the surface of the electrode fabricated by pulse deposition. The pulse plated Pt/CNT electrode could effectively detect dissolved sulfide with a sensitivity of $0.632 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ and a detection limit of $0.26 \mu\text{M}$, and the oxidation of sulfide anions on the designed sensor involved the formation of sulfate species, rather than elemental sulfur, through an irreversible diffusion-controlled process. These data suggest the remarkable capabilities of the fabricated sensor as a promising candidate for numerous applications in water and wastewater treatment technologies.

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