

Short Communication

Polyaniline/MWCNT Nanocomposite as Sensor for Electroanalytical Determination of Phenol in Oil Field Wastewater

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The determination of phenol content in oilfield wastewater is very important in environmental control. In this paper, we present an in situ polyaniline-carbon nanotube (PANI/CNT) nanocomposite for the surface modification of a glassy carbon electrode. The modified sensor has a very sensitive electrochemical response to phenol and can linearly detect the phenol of 10 μM to 0.5 mM with a very low detection limit. Our proposed sensor has also been successfully used for phenol detection of actual samples of oilfield wastewater.

Keywords: Polyaniline; Carbon nanotubes; Electrochemical sensor, Phenol, Oilfield wastewater

1. INTRODUCTION

As one of the important energy sources, oil and natural gas account for a large proportion of the world's energy composition. With the increasing consumption and demand for oil and gas, the exploitation of oil and gas has also started to rise dramatically. Due to the increase of oil exploration and development activities, the pollutants generated also have increased, causing increasingly serious pollution to the environment [1–12]. How to effectively control the environmental pollution caused by exploitation has become an important issue facing all countries in the world. Oilfield wastewater is a complex mix of emulsified crude oil and hydrogen sulfide, as well as soluble salts, heavy metals, solid particles, and other natural impurities [13–22]. It also contains chemical additives, oxygen removers, lubricants, fungicides, scale inhibitors, and acids that are injected into the formation.

Oilfield wastewater contains a large amount of petroleum hydrocarbons and other toxic pollutants, which has great potential harm to the environment and human health. Quantitative detection of the types and contents of pollutants plays an important role in water quality treatment and evaluation. Phenol and its derivatives are important organic pollutants in oilfield wastewater. Due to their high toxicity, the concentration of these substances has been strictly controlled in environmental protection. Currently, phenol determination methods include spectrophotometry, liquid chromatography and an electrochemical method. Compared with the first two methods, the electrochemical method has the advantages of good stability, high sensitivity, cheap equipment, low price, high degree of automation and easy miniaturization, and it is a good choice for the detection of phenol in field wastewater.

However, common commercial electrodes have limited sensitivity and selectivity for the direct detection of phenol. Therefore, the surface modification of commercial electrodes has become a common method to improve the performance of electrodes. Nanocomposite materials began in the late 1980s. Due to the variety of nanocomposite materials and the unique properties of nanophase composite particles, they are praised as "the most promising materials in the 21st century". Nanocomposites are composed of two or more solid phases in at least one dimension at a nanoscale size. These solids may be amorphous, semi-crystalline, or crystalline and may be inorganic, organic, or both. Because the nanoscale particles have a high specific surface area, the addition of these particles to the polymer can greatly increase the performance of the polymer in mechanics due to its thermal, magnetic and optical properties.

Carbon nanotubes (CNTs), discovered by Iijima in 1991, are the most characteristic one-dimensional nanomaterials, with a length of microns and a diameter of nanometres, an extremely high aspect ratio and super mechanical properties [17,23–29]. CNTs have many applications, such as nanoelectronic devices, catalyst carriers, electrode materials, hydrogen storage materials and composite materials. Because of their unique properties, scientists are calling CNTs the "super fibre" of the future [30–34]. CNTs play many roles in composite materials because of their many excellent properties. Their super mechanical properties can greatly improve the strength and toughness of composites. Their unique conductive and photoelectrical properties can improve the conductivity of polymer materials and prepare new photopolymer composites [35–40]. Their unique structure can be used to prepare one-dimensional nanocomposites filled with metals or metal oxides. Research on CNT composites has become a very important field. In recent years, polymer/CNTs have become an important research direction in the field of nanocomposites. Theoretical calculation shows that CNTs have a higher mechanical property than other whisker materials, with high axial strength and stiffness. The hollow, seamless, and tubular structure of CNTs gives them low density and good structural stability, which makes them attractive in the field of composites. With the wide application of polymer materials in industry and daily life, the composites of CNTs and polymer materials has added engineering value.

In this work, polyaniline (PANI) was synthesized in situ by acidified CNTs. First, the surface modification and acidification of CNTs was carried out to disperse them in the reaction system. Second, hydrochloric acid and aniline were added to the reaction system. Then, ammonium persulfate was used as an oxidant to disperse CNTs, by ultrasonic wave, in an aniline/hydrochloric acid solution system. Aniline was adsorbed on the surface of CNTs for the in situ polymerization. The prepared PANI/CNTs

were used for surface modification of a glassy carbon electrode (GCE). The modified GCE was then used for electroanalytical determination of phenol in oilfield wastewater.

2. EXPERIMENTAL

All chemicals were analytical grade.

Acidification of CNTs: A certain amount of CNTs was placed into a three-necked bottle at different concentration ratios, and approximately 30 mL concentrated sulfuric acid (H_2SO_4) and 10 mL concentrated nitric acid (HNO_3) were added. Then, the three-necked bottle was placed into an ultrasonic wave for 30 min. The purpose of this step was to preliminarily disperse the CNTs and make the hard agglomerations between the molecules open up and become soft agglomerations. The above ultrasonic CNTs were heated and stirred at 50 °C. They were rapidly cooled to room temperature under ice water to prevent a re-oxidation reaction. Centrifugation was then used for water washing until it was neutral. Then, they were taken out and put on a dish to dry for 24 h.

Purification of aniline: Aniline has high reactivity at room temperature and is easily oxidized. A certain amount of crude aniline was taken from a measuring cylinder and put into a 500 mL three-necked bottle with some zeolite. Vacuum distillation was carried out by heating with air. A colourless, transparent, viscous liquid was obtained as purified aniline.

Preparation of polyaniline/CNT composites: A certain amount of CNTs was weighed and placed into a three-necked flask in different proportions. A measuring cylinder was used to measure 4 mL of aniline solution after its distillation. The CNTs were fully immersed in aniline, and then, 50 mL of 1 M HCl solution was added; the suspension was stirred with a glass rod to make it evenly mixed and then dispersed by ultrasound for 1 h of sonication. After sonification, the suspension was mixed with ice water, and stirred at a speed of 400 r/min. After being stirred and cooled in an ice bath for 20 min, ammonium persulfate solution, dissolved with 1 M HCl, was added to a drip funnel. The reaction was kept for 5 h. In the reaction process, the colour of the solution was light green, blue-green, green, and finally dark green. The products obtained after the reaction were filtered and washed with hydrochloric acid, acetone and distilled water; washed until the filtrate was colourless; and then dried in vacuum for 24 h at 60 °C.

Electrode modification and electrochemical measurement: The prepared polyaniline/CNTs were then dispersed into water to produce a concentration of 0.5 mg/mL. Then, a certain amount of the dispersion was dropped on the GCE surface and dried naturally. The modified electrode was denoted as PANI/CNTs/GCE. All electrochemical determination was conducted with a CHI760E working station. A Pt wire and Ag/AgCl (3 M KCl) were used as the counter electrode and reference electrode, respectively.

3. RESULTS AND DISCUSSION

The prepared PANI/CNTs/GCE needed activation treatment. To study the electrochemical behaviour of the electrode and electrochemical detection of phenol, cyclic voltammetry was used to

sweep the electrode surface of the prepared PANI/CNTs/GCE several times in an electrolyte of 0.1 M PBS to reach a stable state. PANI/CNTs/GCE could reach a stable state by sweeping the electrode surface 20 times in a PBS of pH=7.4.

Electrochemical impedance spectroscopy (Nyquist plots) is an effective method to describe the resistance of electron transfer at electrode interfaces. It can be divided into a high-frequency region and a low-frequency region. The radius of the arc in the high-frequency region represents the resistance of electron transfer, and the linear section in the low-frequency region represents the resistance of material diffusion. As shown in Figure 1, the electrochemical impedance spectrum of the bare GCE has the largest arc in the high-frequency region, indicating that the electrode surface has a high electron transfer resistance. The electrochemical impedance spectrum of CNTs/GCE is almost a straight line in the whole frequency range and has a very low electron transfer resistance, indicating that the acidized CNTs still have a high conductivity. A thinner layer was better to reduce the contact resistances among the PANI/CNT composite strips and between the PANI-CNT strips and current collector surface [41]. The radius of the high frequency arc of PANI/CNTs/GCE is between the two, indicating that PANI exists on the surface of the electrode. Compared with the CNT-modified electrode, the interface electron transfer resistance of PANI/CNTs/GCE increases but is still lower than that of the bare GCE. The good porous structure of the CNT network is favourable for the diffusion of electrolyte ions [42]. On the other hand, this type of structure could be very useful in paving the way for the PANI/CNT network to attach to it, in turn, inhibiting agglomeration of the PANI/CNT composite and enhancing the active area for ion exchange from PANI [19,43–51].

The cyclic voltammetry curve of PANI/CNTs/GCE in a phosphate buffer solution with a 0.1 M PBS (pH=7.4) are shown in Figure 1B. The cyclic voltammetry curve showed no detectable redox peak, indicating that PANI/CNT was a non-electroactive substance.

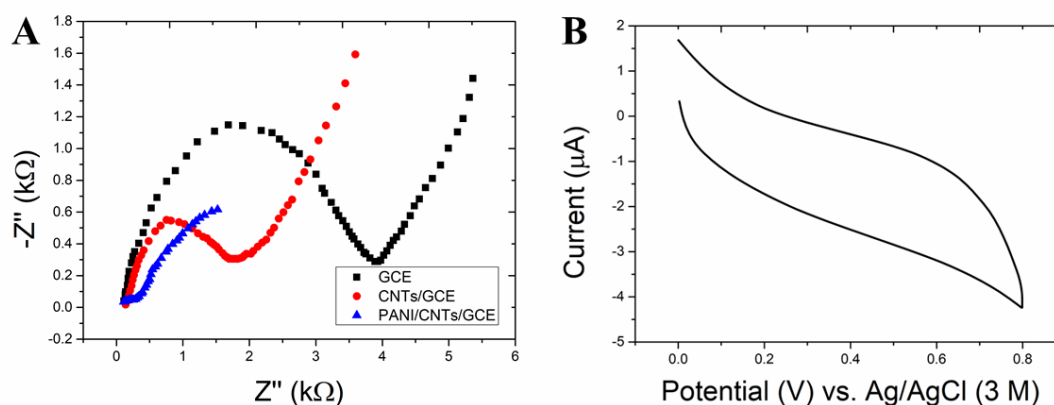


Figure 1. (A) Electrochemical impedance diagram of GCE, CNTs/GCE, PANI/CNTs/GCE. (B) CV profile of PANI/CNTs/GCE in a 0.1 M PBS with pH=7.4.

To compare the electrochemical behaviour of differently modified electrodes with the same concentration of phenol, the CV diagram of GCE, CNTs/GCE, PANI/CNTs/GCE, in a solution containing 0.1 mM of phenol, is shown in Figure 2. The bare GCE showed an oxidation peak at 0.52 V,

with a weak current response. No reduction peak was observed in the potential regression process, indicating that the process was irreversible. The oxidation peak current on CNTs/GCE was higher than that of the bare GCE, which indicated that CNTs had a catalytic effect on phenol. However, due to the small peroxide potential of oxygen evolution, the oxidation peak of phenol overlapped with the oxygen evolution process, and the oxidation peak of phenol could not be identified. In addition, the phenol oxidation peak of PANI/CNTs/GCE was an order of magnitude higher than that of GCE and CNTs/GCE. Therefore, a modified PANI/CNTs-composite GCE comprehensively utilized the effect and conductivity of PANI and CNTs and showed a better catalytic effect on phenol. The rapid response property and ultra-high sensitivity of the present sensor should be attributed to the porous structure of PANI/CNTs [52]. Moreover, this result was expected since the number of edge atoms that serve as reactive sites for electron transfer are extremely augmented in the case of CNTs [53].

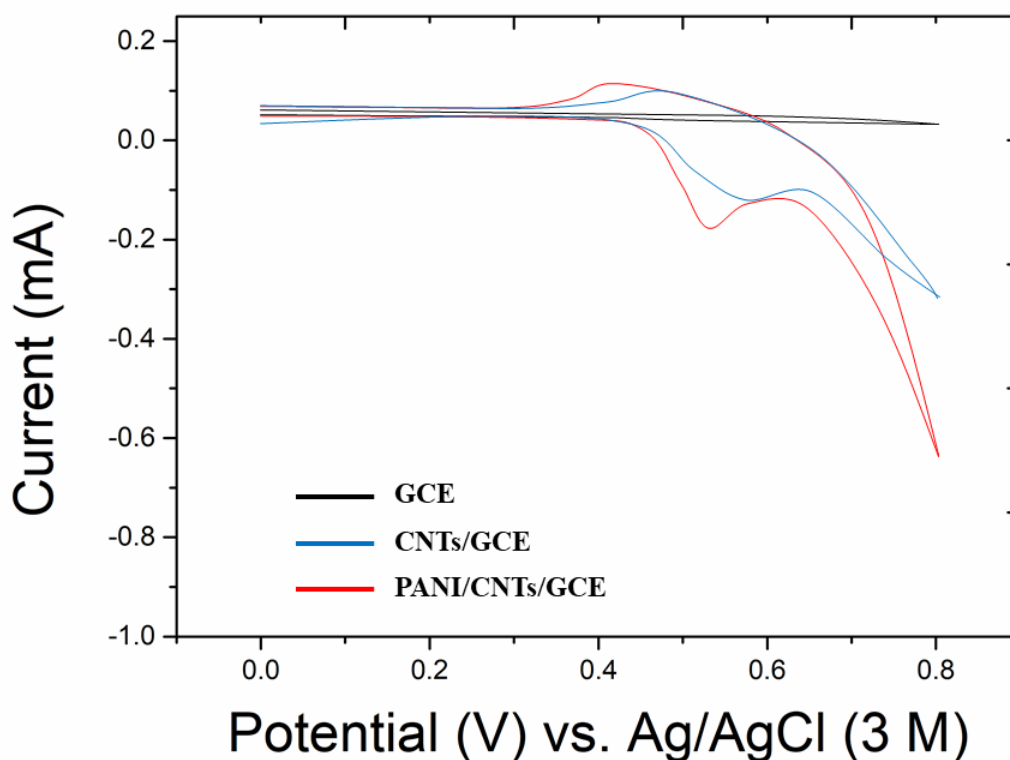


Figure 2. Cyclic voltammety curves of the differently modified electrodes towards 0.1 mM phenol.

The chronocurrent method is an effective method to study the relationship between response current and time under a certain potential. To apply the PANI/CNTs/GCE for phenol detection in oilfield wastewater, the standard curve of the electrochemical response current and phenol concentration is essential. This work adopts chronoamperometry to record and produce two current-time curves under the best possible conditions for different concentrations of phenol with the modified electrodes and then through data fitting, converting them into an electricity-concentration curve. Thus, the response current and phenol concentration standard curves are obtained.

To maximize the value of the phenol response, the chronocurrent method was used to study the response value of a certain amount of phenol under different potentials. The oxidation potential candidates of PANI/CNTs/GCE were selected as 0.4 V, 0.5 V, 0.55 V and 0.6 V. A constant potential in the electrolyte was set under the three-electrode system to record the measured timing current curve. When the timing current curve reached a stable state, 30 μM of 0.03 mM phenol solution was continuously added. The obtained I-T curve is shown in Figure 3. It can be seen from this figure that the current response value to phenol reached a maximum at 0.5 V. Therefore, 0.5 V is selected as the determination potential.

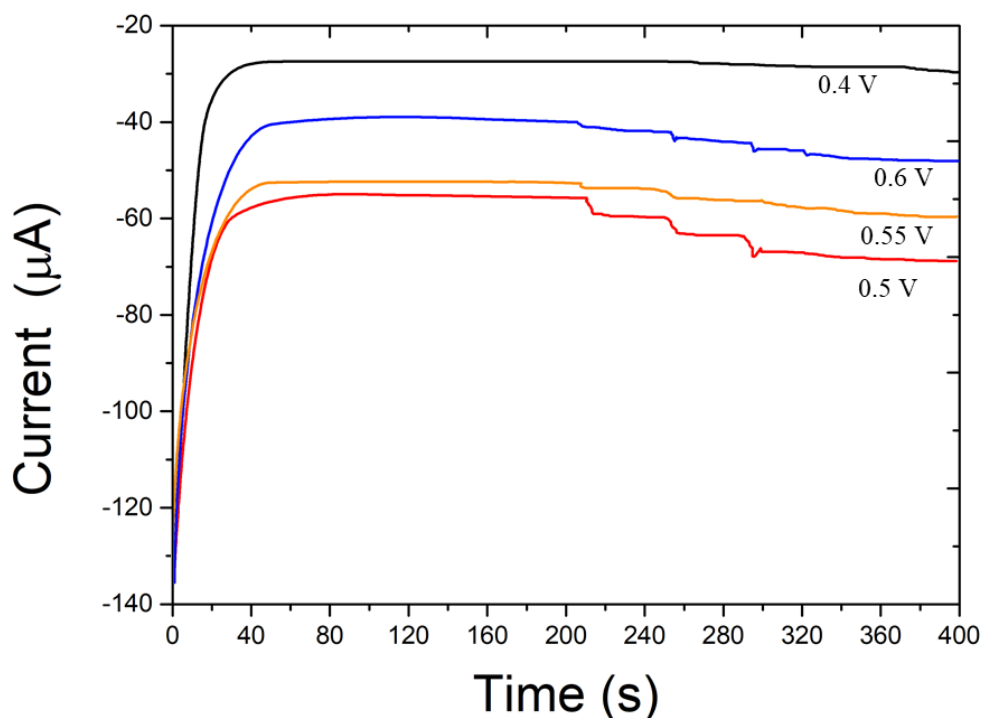


Figure 3. I-T curves of PANI/CNTs/GCE when adding 0.03 mM phenol at different potentials

Table 1. Comparison of phenol determination by different methods of reported electrochemical sensors.

Electrode	Method	Detection range	Limit of detection	Reference
Zn-Al-NO ₃ layered double hydroxide film	CV	7 μM to 180 μM	2.6 μM	[54]
B-clay-enzyme sensor	CV	0.004 μM to 18 μM	4 nM	[55]
Cholinesterase-modified electrode	CV	0.35 μM to 1.7 μM	26 nM	[56]

The analytical performance of the PANI/CNTs/GCE towards different concentrations of phenol is shown in Figure 4A. As shown in the figure, the current response increased immediately when the introduction of phenol solution reached a stable state within 3 s. The relationship of current responses and phenol concentrations can be found in Figure 4B. A linear relationship between current responses and phenol concentrations from 10 μM to 0.5 mM was observed. A limit of detection can be calculated to be at 3.4 μM based on the signal to noise ratio of 3. Table 1 shows the analytical methods and analytical properties of several phenol biosensors found in the literature. As observed, it is obvious that the proposed method showed a wider linear range and a lower detection limit.

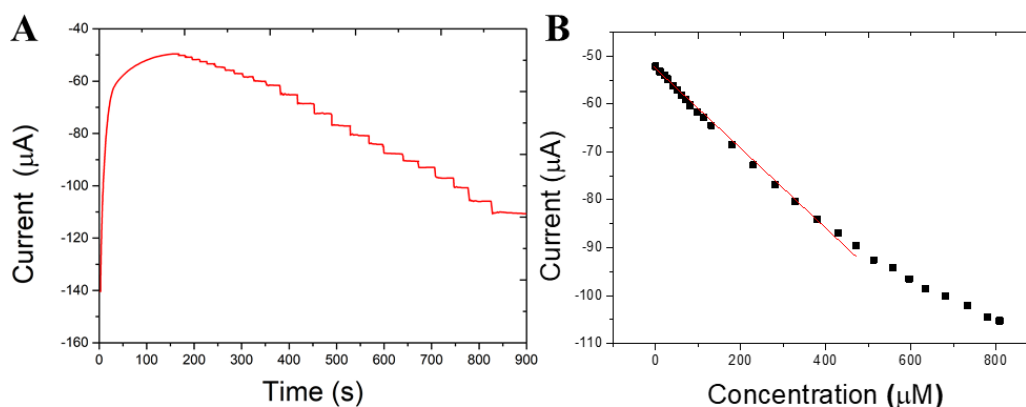


Figure 4. (A) I-T curves of PANI/CNTs/GCE when adding different amount of phenol at 0.5 V. (B) Plot of concentration of phenol vs. current response.

To test and verify the accuracy and feasibility of the method, ten individually prepared PANI/CNTs/GCEs were used to carry out repetitive detection experiments on the 0.1 mM phenol solution (Figure 5). The oxidation peak current value was observed, and the relative standard deviation was calculated to be 4.6%, indicating that the electrode had good repeatability for phenol detection. The results confirmed that PANI/CNTs are effective sensors for detecting phenol.

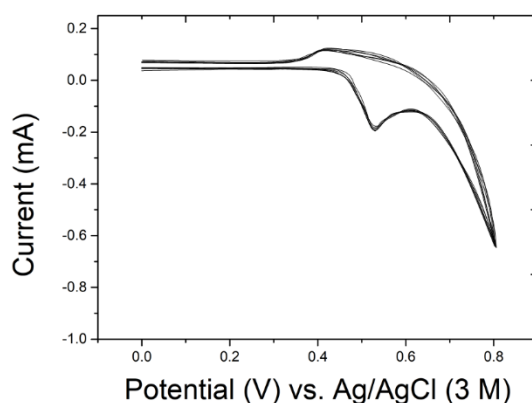


Figure 5. Cyclic voltammety curves of ten PANI/CNTs/GCE towards 0.1 mM phenol.

In the presence of bisphenol, hydroquinone, catechol, resorcinol, p-chlorophenol, K^+ , Cu^{2+} , Ca^+ , Fe^{3+} , Pb^{2+} , Mg^{2+} , Al^{3+} , Br^- , NO_3^- , and SO_4^{2-} at concentrations 100 times higher than phenol, the results showed that the presence of these substances did not interfere with the detection of phenol. Table 2 shows the detailed results.

To verify the applicability of the method, the sensor was used with real samples. Oilfield wastewater was filtered prior to analysis, and 5 mL of the wastewater sample was diluted 5 times with PBS buffer solution. Then, 20 μ L of phenol was added to the diluted samples, and PANI/CNTs/GCE was used to determine the 3 samples in parallel 5 times. According to the test results in Table 3, the average content of phenol detected in oilfield wastewater samples was 16.22 μ M, and the average recovery rate was 99.57%. For determination of volatile phenols, 4-aminoantipyrine extraction spectrophotometry is the accepted standard method. Table 4 shows the results of the same samples measured by the standard method. The comparison shows that the PANI/CNTs/GCE in Table 1 has a higher accuracy in the measurement of phenol.

Table 2. Interference study result using PANI/CNTs/GCE.

Interference species	Current change (%)	Interference species	Current change (%)
Bisphenol	3.1	Hydroquinone	2.7
Catechol	1.9	Resorcinol	2.2
p-chlorophenol	2.2	K^+	0.3
Cu^{2+}	2.3	Ca^+	0.6
Fe^{3+}	3.2	Pb^{2+}	1.1
Mg^{2+}	1.9	Al^{3+}	1.2
Br^-	4.0	NO_3^-	0.5
SO_4^{2-}	0.7		

Table 3. Oilfield wastewater sample analysis using PANI/CNTs/GCE.

Sample	Detection (μ M)	Added (μ M)	Found (μ M)	Recovery (%)
1	14.55	20.00	34.13	98.78
2	16.23	20.00	35.89	99.06
3	17.88	20.00	38.21	100.87

Table 4. Oilfield wastewater sample analysis using 4-aminoantipyrine extraction spectrophotometry method.

Sample	Detection (μ M)	Added (μ M)	Found (μ M)	Recovery (%)
1	13.45	10.00	26.88	114.63
2	18.66	10.00	28.90	100.84
3	19.33	10.00	28.43	96.93

4. CONCLUSION

In this paper, an electrochemical sensor based on a modified PANI/MWCNT composite electrode was prepared, and electrochemical detection of phenol was conducted under a three-electrode system. PANI/MWCNTs have excellent electrocatalytic and electrical properties, which can catalyse the oxidation of phenol. Under the best conditions, the proposed sensor could linearly detect phenol from 10 μM to 0.5 mM, and the detection limit can reach 3.4 μM .

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