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“Signal on” electrochemiluminescence pentachlorophenol sensor based on luminol-MWCNTs@graphene oxide nanoribbons system

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ABSTRACT

A “signal on” electrochemiluminescence (ECL) sensor for pentachlorophenol (PCP) detection was constructed based on the amplified ECL of luminol at a multiwalled carbon nanotubes@graphene oxide nanoribbons (MWCNTs@GONRs) modified electrode. Due to the good electrocatalytic activity of MWCNTs@GONRs toward luminol system, the oxidation peak current of luminol at the MWCNTs@GONRs modified electrode was enhanced for ~6-fold than that of the bare electrode; and the ECL intensity of luminol was amplified for ~5.3-fold correspondingly. Furthermore, the amplified ECL signal of luminol was linear with the concentration of PCP in the range between 2 pg mL^{-1} and 10 ng mL^{-1} with a detection limit of 0.7 pg mL^{-1} ($S/N=3$). With the merits of good reproducibility, acceptable stability, wide linear range, low detection limit and simplicity, the proposed luminol ECL sensor showed great potential in the field of analytical applications.

1. Introduction

Graphene nanoribbons (GNRs), strips of graphene with a high length-to-width ratio and straight edges, have attracted much attention because of their unique geometry, mechanical robustness, and fundamental transport properties, as well as their potential application in nanodevices [1–3]. Especially, recently reports indicated that GNRs could accelerate the electron transfer on the electrode surface for amplifying the electrochemical signals due to their outstanding electric conductivity [4,5]. For example, used GNRs as electrode substrate materials to amplify the electrochemical signal and improve the sensitivity, Shi et al. reported an immunosensor with excellent analytical performance such as high sensitivity, convenient operability, stability and acceptable reproducibility [5]. However, in contrast to the single component GNRs, GNRs based nanocomposite combine the virtues of each component and exhibit integrated properties such as enhanced electrical conductivity and better excellent electrocatalytic activity, which is beneficial for the construction of electrochemical sensors with high sensitivity [6,7]. Most recently, a core–shell heterostructure of multiwalled carbon nanotubes@graphene oxide nanoribbons (MWCNTs@GONRs) was produced from longitudinal partially unzipping of MWCNTs and applied for electrochemical determination of polycyclic aromatic amines. The result showed that the oxidation peak currents of polycyclic aromatic amines at the MWCNTs@GONRs modified electrode are much higher than those at the MWCNTs and graphene modified electrodes due to the synergistic effects of MWCNTs and GONRs [8]. This result indicated that the MWCNTs@GONRs structure with good electrocatalytic activity showed grand potential in the fabrication of electrochemical sensing interface. However, studies on MWCNTs@GONRs based signal amplification has not been reported to our knowledge.

As a highly sensitive technique, electrochemiluminescence (ECL) has attracted considerable attention in various fields from bioassay to environment and food analysis [9,10]. Luminol or its derivatives, as one of the most commonly used ECL luminophores, were pointed out as efficient ECL systems to construct the ECL sensors by virtue of its low oxidation potential, inexpensive reagent consumption and the high emission yields [11–13]. However, the ECL intensity of luminol at the bare electrode was extremely weak, which might seriously hamper the analytical application of luminol ECL. In order to overcome this problem, various functionalized nanomaterials, especially carbonaceous based nanomaterials (such as carbon nanotube, graphene) have been employed to amplify the ECL signal of luminol for sensitive analytical application [14–16]. For instance, based on the electrocatalytic activity of Pd nanoparticles decorated MWCNTs on luminol ECL reaction, Haghighi’s group reported an ECL sensor for determination of dissolved O_2 and glucose with the merits of sensitivity, stability and selectivity [14]; by virtue of the excellent electron transfer ability and good solubility of carboxyl graphene,

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Li et al. fabricated a sensitive ECL immunosensor for α-fetoprotein based on the enhancement ECL intensity of luminol by carboxyl graphene [15]. All these results above indicated that as an effective technique, incorporating nanomaterials can be used for amplifying the ECL signals of luminol, which is of great significance for applying luminol ECL in electrochemical sensing.

Inspired by these above, MWCNTs@GONRs can be selected as an efficient catalyst in ECL sensors for amplifying the ECL signals of luminol system. In this work, the enhanced ECL behavior of luminol on a MWCNTs@GONRs modified electrode was developed. Further, a sensitive ECL sensor for pentachlorophenol determination was presented based on the strong and stable ECL signal.

2. Experimental

2.1. Reagents

PCP was purchased from J&K Scientific Ltd., MWCNTs ($\Phi \leq 10$ nm) were obtained from Shenzhen Nanotech Port Co., Ltd. A luminol (purchased from Sigma-Aldrich) stock solution (1 mM) was prepared by dissolving luminol in 0.1 M NaOH solution and stored in the refrigerator at 4 °C. 0.1 M phosphate buffer solution (PBS, pH9.0) was prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4, and adjusting the pH with 0.1 M NaOH. Other chemicals were of analytical grade and used without further purification, and all solutions were prepared with doubly distilled water.

2.2. Apparatus

Transmission electron microscopy (TEM) image was taken with a JEOL 2100 TEM (JEOL, Japan) operated at 200 kV, and the Raman spectra were obtained from RM 2000 microscopic confocal Raman spectrometer. The cyclic voltammograms (CVs) were performed with a CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China) and the ECL curves were recorded by a Model MPI-A ECL analyzer system (Xi'An Remax Electronic Science and Technology Co., Ltd., Xi'An, China). A conventional three-electrode system was used in all the electrochemical experiment where a glassy carbon electrode (GCE, 3 mm in diameter) as working electrode, a Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode, respectively. EIS was performed in a 0.1 M KCl solution containing 5 mM $Ru(NH_3)_6Cl_3$ with a frequency range from 0.1 Hz to 10 kHz at −0.2 V, and the amplitude of the applied sine wave potential in each case was 5 mV which was taken with a ZENNIUM electrochemical workstation (Zahner Instruments, Germany).

2.3. Preparation of MWCNTs@GONRs

MWCNTs@GONRs was prepared according to previous report with modifications [17]: 120 mg of MWCNTs was suspended in 40 mL of H_2SO_4/H_3PO_4 (9:1), and the mixture was allowed to stir 1 h before the addition of $KMnO_4$ (600 mg). The reaction mixture was heated at 65 °C for 2 h, and then was poured onto 400 mL of ice containing H_2O_2 (30%, 5 mL). The solution was filtered over a polytetrafluoroethylene membrane, and the remaining solid was washed with acidic water followed by ethanol.

2.4. Preparation of the modified electrode

Prior to modification, the GCE was first polished with sand paper followed by 1.0, 0.3, and 0.05 μm alumina slurry, respectively. After successive sonication in ethanol and double distilled water, the electrode was rinsed with double distilled water and allowed to dry at room temperature. Then the pretreated GCE was modified by dropping 6 μL of 0.5 mg mL^{-1} MWCNTs@GONRs/water solution and drying in room temperature to form the MWCNTs@GONRs modified electrode (denoted as MWCNTs@GONRs/GCE).

3. Results and discussion

3.1. Characterization of MWCNTs@GONRs

Fig. 1 shows the TEM images of the pristine MWCNTs and as-prepared MWCNTs@GONRs. For MWCNTs, the clear edge could be observed and its diameter is about 6–9 nm (Fig. 1A). For comparison, the edge of the MWCNTs@GONRs turns to be rough and unclear and the diameter increases to 16–23 nm (Fig. 1B), which indicate the edge of the MWCNTs@GONRs may be partially curled.

Fig. 2 displays the Raman spectra of MWCNTs and MWCNTs@GONRs. It is obvious that the G band of the MWCNTs@GONRs appeared to shift to a higher frequency (from 1582 cm^{-1} to 1594 cm^{-1}) and was broader than the G band of the pristine MWCNTs. And the intensity ratio of D band and G band (I_D/I_G) of MWCNTs@GONRs (0.95) is increased compared with that of MWCNTs (0.46), which is due to that the oxidation and intercalation of MWCNTs introduce the defects in them and thus caused the I_D/I_G increase [18–20]. All these results above strongly suggest the formation of MWCNTs@GONRs.

3.2. EIS analysis

EIS is an effective tool for studying the interface properties of surface-modified electrodes, and Fig. 3 displayed the impedance spectra of different electrodes in 0.1 M KCl with 5 mM $Ru(NH_3)_6Cl_3$. Obviously, the electron-transfer resistance at the MWCNTs@GONRs/

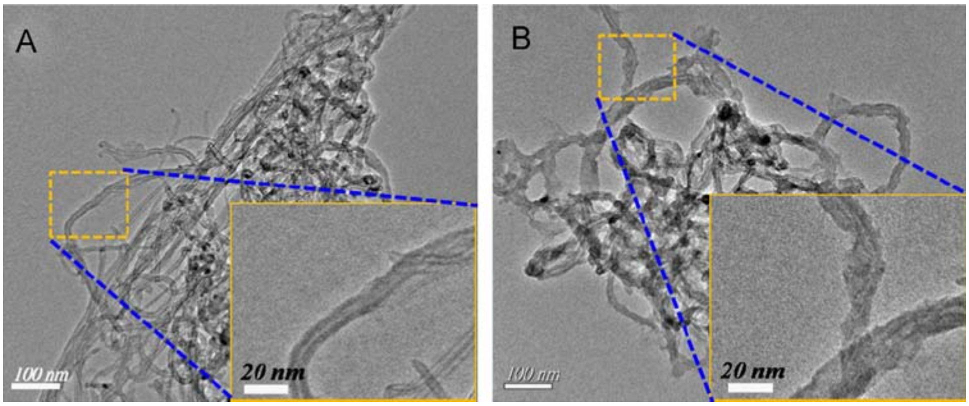

Fig. 1. TEM images of (A) pristine MWCNTs and (B) the as-prepared MWCNTs@GONRs.

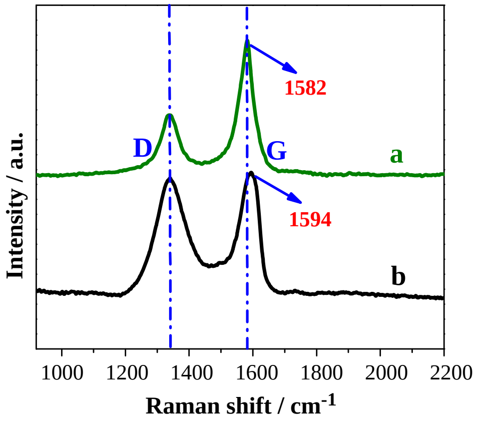

Fig. 2. Raman spectra of pristine MWCNTs (a) and the as-prepared MWCNTs@GONRs (b).

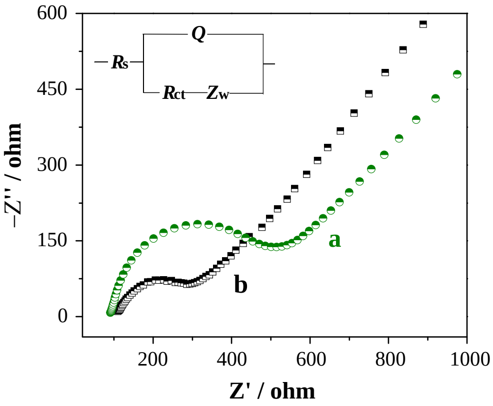

Fig. 3. EIS of bare GCE (a) and MWCNTs@GONRs/GCE (b) in 0.1 M KCl containing 5 mM $Ru(NH_3)_6Cl_3$ at −0.2 V vs. SCE; inset: the equivalent circuit for fitting the impedance data.

GCE is much smaller than that of bare GCE, suggesting that the MWCNTs@GONRs film could act as a good electron-transfer interface between the electrochemical probe and the electrode [21].

3.3. *Effect of luminol concentration on PCP detection*

In order to achieve the optimal performance for PCP determination, the effect of luminol concentration on the ECL behaviors of the luminol-MWCNTs@GONRs system were investigated in Fig. 4. It is obvious that the maximum enhancing effect of PCP on the change of ECL intensity was achieved when the luminol concentration was 10 μM. Therefore, 10 μM luminol was used in this experiment for PCP detection.

3.4. *Electrochemical and ECL behaviors of luminol at MWCNTs@GONRs/GCE*

The electrochemical behavior of luminol at different electrodes was investigated in 0.1 M PBS, as shown in Fig. 5A. Obviously, there was an oxidation peak appeared at both bare GCE (curve a) and MWCNTs@GONRs/GCE (curve b) at ~0.5 V, which was ascribed to the oxidation of luminol [22]. Moreover, it is obvious that the oxidation peak current obtained at MWCNTs@GONRs/GCE was enhanced ~6-fold than that of bare GCE, which manifests that the MWCNTs@GONRs modified on the electrode could facilitate the electrochemical oxide process of luminol [23].

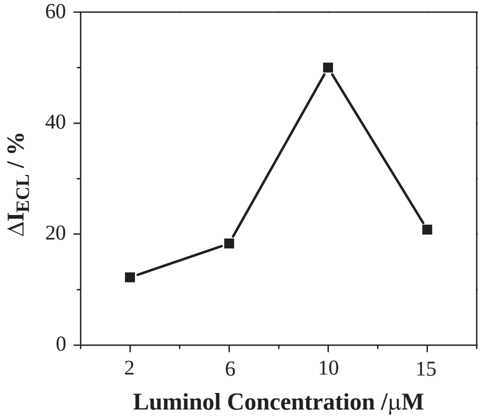

Fig. 4. Effect of luminol concentration on the change of ECL intensity with PCP.

Fig. 5B showed the corresponding ECL behaviors of luminol at the different electrodes. A relative low ECL signal at ~0.6 V was observed on bare electrode (curve a), which was attributed to the oxidation of luminol to luminol radical anion. And the ECL intensity of luminol on the MWCNTs@GONRs/GCE (curve b) was increased about ~5.3-fold as that of the bare electrode, which indicate that the modification of MWCNTs@GONRs on the electrode surface could enhance the ECL intensity of luminol effectively.

3.5. *Effect of PCP on the ECL signal of luminol*

The effect of PCP on the ECL intensity of this luminol-MWCNTs@GONRs system was also investigated. As shown in Fig. 6A, the addition of PCP resulted in a significant increase in the ECL intensity, indicating that this ECL system could be used for PCP monitoring effectively. Furthermore, the ECL stability of luminol on the MWCNTs@GONRs modified electrode was investigated in 0.1 M PBS (Fig. 6B). It is obvious that the ECL intensity was ca. 6500 a.u. and did not show obvious change when the ECL response was repeated under continuous cyclic scans for 13 cycles, indicating that the ECL intensity of this system was stable and beneficial for the fabrication of the ECL sensor.

3.6. *ECL detection of PCP*

Based on the enhancement of PCP on the ECL response of this luminol-MWCNTs@GONRs system, an effective way for ECL monitoring of PCP was proposed in Fig. 7. It was obvious that the ECL signals increased gradually with the increasing of PCP concentration (Fig. 7A), and the ECL intensity was linear dependent on the logarithm of PCP concentration in the range of 2 pg mL^{-1}–10 ng mL^{-1} with a detection limit of 0.7 pg mL^{-1} ($S/N=3$) (Fig. 7B), indicating that the proposed ECL sensor is remarkably reliable for sensitive determination of PCP.

3.7. *Reproducibility, stability and real sample analysis*

The intra-assay precision of the resulting ECL sensor is evaluated by assaying one modified electrode for three replicate determinations in 0.1 M PBS containing 10 μM luminol and 0.1 ng mL^{-1} PCP. Similarly, the inter-assay precision, or fabrication reproducibility, is estimated at three different electrodes. The RSD of intra-assay and inter-assay are found to be 5.9% and 8.7%, indicating an acceptable reproducibility. The long-term storage stability is a critical issue for practical application of the proposed ECL sensor. When stored at room temperature and measured at intervals over 3 days, no obvious decrease in the ECL response was observed in the first 6-day storage. After a 30-day storage period,

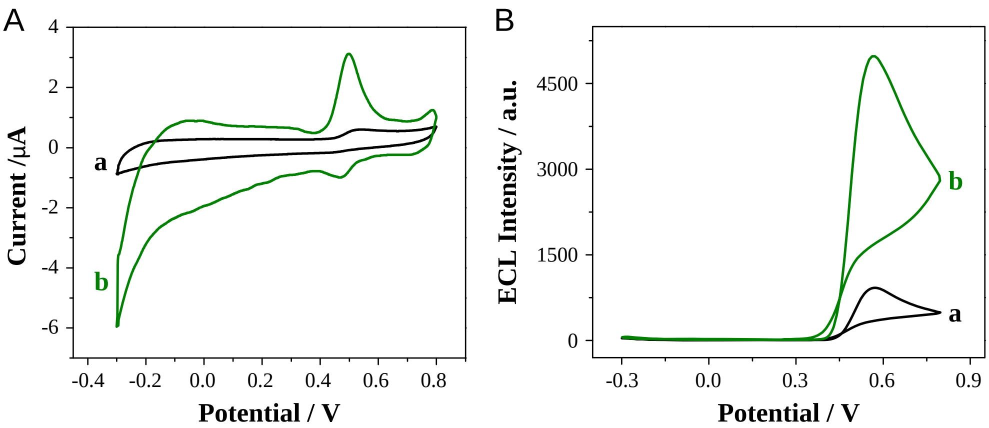

Fig. 5. (A) CV and (B) ECL-potential curves of bare GCE (a) and MWCNTs@GONRs/GCE (b) in 0.1 M PBS with 10 μM luminol.

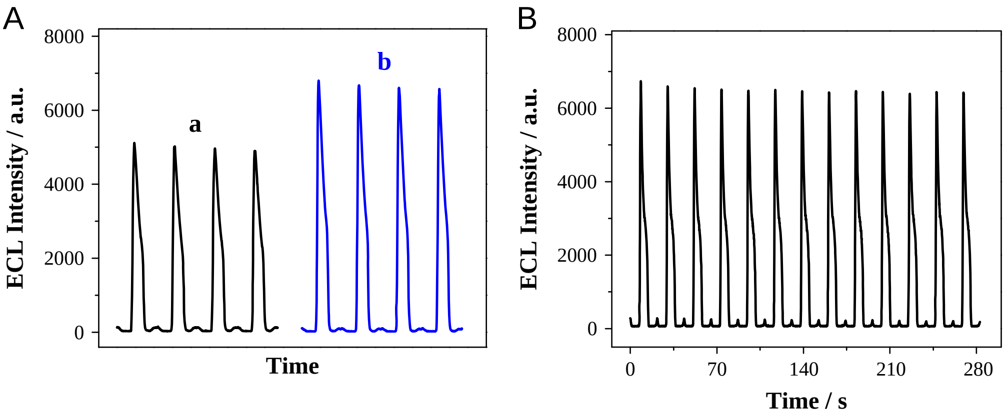

Fig. 6. (A) ECL behaviors of MWCNTs@GONRs/GCE (b) in 0.1 M PBS containing 10 μM luminol in the absence (a) and presence (b) of 1 ng mL^{-1} PCP; (B) ECL emission from the MWCNTs@GONRs/GCE in 0.1 M PBS containing 10 μM luminol under continuous cyclic scans from −0.3 V to 0.8 V for 13 cycles.

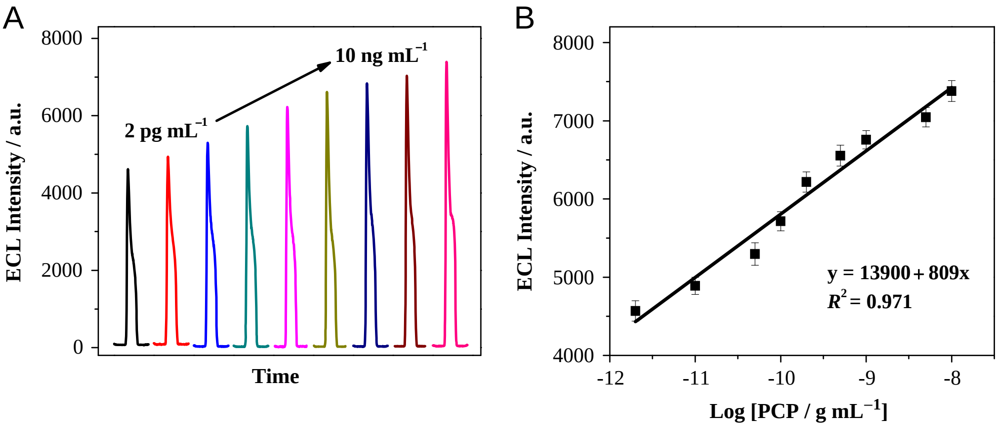

Fig. 7. (A) Effect of PCP concentration on the ECL behaviors of MWCNTs@GONRs/GCE in 0.1 M PBS with 10 μM luminol; (B) calibration curve for PCP detection. Error bars: ± S.D., $n=3$.

the sensor retained 84% of its initial response, indicating the acceptable stability of the sensor.

To demonstrate the practicality of the proposed ECL sensor, the recovery test was carried out by adding different amounts of PCP into tap and river water samples, and the results were presented in Table 1. As can be seen, the results were in good agreement with the given concentration of 0–50 pg mL^{-1} with average recoveries from 93.5% to 109% ($n=3$). These results indicated that this new method could be used for analysis of real samples.

4. Conclusions

In summary, a “signal on” ECL sensor for sensitive PCP detection was constructed based on MWCNTs@GONRs-catalyzed luminol ECL, which is a promising alternative approach to improve the sensitivity because of the good electrocatalytic activity of MWCNTs@GONRs toward luminol system. The ECL method based on MWCNTs@GONRs exhibited good performances for PCP determination including good reproducibility, acceptable stability, wide

Table 1
Recovery studies of PCP in tap and river water samples ($n=3$).

Sample	Taken (pg mL^{-1})	Found (pg mL^{-1})	Recovery (%)	RSD (%)
Tap water	0.00	Not detected	_	_
	10.0	10.9	109.0	4.6
	20.0	18.7	93.5	3.2
	50.0	47.6	95.2	4.9
River water	0.00	11.3	_	5.3
	10.0	23.6	105.8	4.7
	20.0	32.9	105.1	3.9
	50.0	63.6	103.7	5.4

linear range and low detection limit. Additionally, the proposed method was simple and uses relatively inexpensive reagents, which could provide a promising approach to develop efficient ECL sensor in ultra-trace environmental monitoring.

Acknowledgments

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