



## Selective detection of picric acid using functionalized reduced graphene oxide sensor device



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### ABSTRACT

A reduced graphene oxide sensor device was fabricated through self-assembling graphene oxide onto an interdigitated gold microelectrode followed by electrochemically reducing. After modification with 1-pyrenebutyl-amino- $\beta$ -cyclodextrin, the sensor exhibits high sensitivity and selectivity to picric acid. The sensor response ( $\Delta I$ ) increases linearly with concentration in the range of 5  $\mu\text{M}$  to 215  $\mu\text{M}$ . The sensitivity and detection limit of this method were estimated to be 0.00613  $\mu\text{A} \mu\text{M}^{-1}$  and 0.54  $\mu\text{M}$ , respectively. The improved performance can be attributed to the unique structure of  $\beta$ -cyclodextrin (hydrophobic internal cavity and hydrophilic external surface), which endows its great tendency to integrate with hydrophobic  $-\text{NO}_2$  groups of picric acid. Picric acid extracted from real water by ether can be determined effectively with this method, which demonstrates that the present method is sensitive and suitable for the determination of picric acid in drinking water sources.

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### 1. Introduction

Phenol is one of the most common organic water pollutants, because it is toxic even at low concentrations for human and animals [1–3]. Picric acid, one of the various phenols, will do massive damages to human eyes, skin and respiratory systems [4]. The detection of picric acid is of great importance because a large amount of industries such as organic synthesis and drugs analysis all inevitably involve picric acid [5], which imposes severe risks on human health and the environment. As a consequence, many efforts have been devoted to the development of efficient technologies for the determination of picric acid in the environment.

In the past decades, various approaches have been explored to quantify the picric acid effluents, such as fluorimetry chemical technologies [6], chemical methods [7], capillary electrophoresis [8] and spectrophotometry [9]. For example, Venkatramiah et al., have successfully developed a fluorescent chemosensor based on fluoranthene for the detection of picric acid, in which static fluorescence quenching is the dominant process by intercalative

$\pi$ – $\pi$  interactions between fluoranthene and nitroaromatics [6]. Junqueira et al., have reported an electrochemical method for quantitative analysis of picric acid explosive based on its electrochemical reduction at copper surfaces [7]. Parham et al., have reported a spectrophotometric method for removal, preconcentration and determination of trace amounts of picric acid in water samples [9]. However, most of these methods require a complicated sample pre-treatment process, long analysis time, expensive instruments and some of them may also bring secondary pollutants, which limited their applications in the determination of picric acid in real samples. Hence, it is still essential to further explore a new analytical technique with simple operation.

It is widely recognized that graphene, a two dimensional monolayer sheet of  $\text{sp}^2$  hybridized carbon [10], is a novel and highly promising carbon material due to its unique nanostructure and extraordinary properties [11–13], such as good mechanical flexibility [14], large surface area [15] and excellent electrical conductivity [16], etc. People have investigated these properties [17] and fabricated various microelectrical devices, such as field-effect transistors [18–21], ultrasensitive sensors [22–26], and electromechanical resonators [27]. In addition, cyclodextrins (CDs) are famous for forming an inclusion complex with multiple guest molecules due to their special molecular structure-hydrophobic internal cavity and hydrophilic external surface [28,29]. The novel structure endows them with great tendency to combine with

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hydrophobic groups  $-\text{NO}_2$  of picric acid. Therefore, a graphene sensor modified with  $\beta$ -cyclodextrin could be an effective method for detection of picric acid.

In this paper, we report a novel method for the determination of picric acid using a reduced graphene oxide (rGO) sensor modified with 1-pyrenebutyl-amino- $\beta$ -cyclodextrin (PyCD). The PyCD-rGO sensor can be fabricated through four steps involving the synthesis of graphene oxide (GO), the self-assembly of GO, the electrochemical reduction of graphene oxide (rGO) and modification with PyCD. Both the rGO sensor and PyCD-rGO sensor exhibit good sensitivity and recovery to picric acid. As expected, the PyCD-rGO sensor exhibits higher response and wider linear range to picric acid than rGO sensor.

## 2. Experimental details

### 2.1. Synthesis and characterization of graphene oxide

All the chemicals are of analytical grade and used as received without further purification. The graphene oxide was synthesized from graphite flakes using a modified Hummers method involving the steps of graphite oxidation, exfoliation [30]. Typically, 180 mL of concentrated  $\text{H}_2\text{SO}_4$  and 20 mL of concentrated  $\text{H}_3\text{PO}_4$  were slowly added to a mixture of 1.0 g of graphite and 6.0 g of  $\text{KMnO}_4$  with continuous stirring and cooling. Then the mixture was heated to  $50^\circ\text{C}$  and stirred for 12 h. The reaction was cooled to room temperature and poured onto 400 mL ice with 3 mL 30%  $\text{H}_2\text{O}_2$ . The obtained product was collected by centrifugation, washed repeatedly with deionized water, 30% HCl and ethanol and vacuum-dried overnight at room temperature. Finally, 5 mg of as-synthesized GO nanosheets were dispersed in deionized water (20 mL) by ultrasonic treatment for 12 h to form a homogeneous dispersion. The sensor devices were characterized by scanning electron microscopy (SEM, Hitachi S-4800, operated at 5.0 kV) and atomic force microscopy (AFM, SPA-300HV & SPI3800N, Seiko). The Raman spectra of GO and rGO were obtained at room temperature with an Olympus BX41 Micro-Raman spectrometer in back-scattering geometry with the laser excitation of 532 nm at a power level of 1.7 mW.

### 2.2. Synthesis of PyCD

Mono-6-deoxy-6-amino- $\beta$ -cyclodextrin ( $\beta$ -CD- $\text{NH}_2$ , 98.5%) was purchased from Shandong Binzhou Zhiyuan Bio-Technology Co., Ltd.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.75–2.95 (t, 2H,  $\text{NH}_2$ ), 3.00–3.15 (m, 28H, H4, H5, H6), 3.40–3.70 (m, 13H, OH-6, H3), 3.70–4.00 (d, 7H, H2), 5.03 (m, 21H, OH-2,3, H1) ppm. IR (KBr)  $\nu$ : 3414.16, 2934.35, 1642.35, 1411.47, 1152.77, 1133.19, 949.72, 700.79, 582.22  $\text{cm}^{-1}$ ; HRMS (EI) Calcd. For  $\text{C}_{42}\text{H}_{71}\text{O}_{34}\text{N}$ : 1133.3934, found 1134.4175  $[\text{M} + \text{H}]^+$ .

Preparation of 1-pyrenebutyl-amino- $\beta$ -cyclodextrin [31]: 1-pyrenebutyric acid (0.06 g, 0.2 mmol), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC-HCl, 0.0383 g, 0.2 mmol), 4-methylmorpholine *N*-oxide (NMM, 0.0404 g, 0.4 mmol) and 6-chloro-1-hydroxibenzotriazol (CHBT, 0.0339 g, 0.2 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 10 mL) in the presence of a small amount of molecular sieves under an atmosphere of  $\text{N}_2$ . A DMF solution (5 mL) of  $\beta$ -CD- $\text{NH}_2$  (0.2 g, 0.18 mmol) was then added dropwise. The mixture was stirred for one day in an ice bath and then for another day at room temperature, before being left to stand for 5 h until no more precipitate deposited. The precipitate was removed by filtration, and the filtrate was poured into acetone (50 mL). The precipitate formed in acetone was collected by filtration. The crude product was dissolved in deionized water (10 mL) and

kept at room temperature for one day. The precipitate which formed was collected by filtration and washed with acetone and deionized water to give a pale yellow solid (0.17 g, 68%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 1.07–3.0 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.30–3.64 (m, CD-H2-6), 4.50 (s, 2H,  $\text{CH}_2\text{CO}$ ), 4.51–4.70 (m, 6H, CD-OH6), 4.84–4.90 (m, 7H, CD-H1), 5.71–5.77 (m, 14H, CD-OH2), 7.74–8.41 (m, 9H, pyrene-H) ppm; IR (KBr)  $\nu$ : 3391.60, 2929.85, 1651.38, 1545.34, 1420.25, 154.27, 1139.20, 950.47, 852.71, 763.79, 710.57, 577.46  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}$ : 267, 325 nm (pyrene-); HRMS (EI) Calcd. for  $\text{C}_{62}\text{H}_{86}\text{O}_{35}\text{N}_2$ : 1418.5088, found 1419.9923  $[\text{M} + \text{H}]^+$ , 1442.4538  $[\text{M} + \text{Na}]^+$ .

### 2.3. Fabrication of rGO sensor

The interdigitated gold microelectrode (gold 20 nm, titanium 10 nm) with 20- $\mu\text{m}$  gaps was fabricated using electron beam lithography on a Si wafer with a 1- $\mu\text{m}$  coating of  $\text{SiO}_2$ . The electrode was sonicated for 0.5 h and then rinsed thoroughly with deionized water several times. In a typical procedure, 0.2  $\mu\text{L}$  of GO dispersion was pipetted onto the surface of the interdigitated electrode. After about 5 h, the homogeneous dispersion would diffuse to form a GO film which connected the channel of the electrode, followed by drying in air for 4 h. After that two gold wires were welded on the soldered dots by silver paste and dried at  $120^\circ\text{C}$  for 6 h. Ultimately, the GO sensor with two gold wires as a working electrode was immersed into 20 mM  $\text{KH}_2\text{PO}_4$  solution and a cathodic potential of  $-0.7\text{V}$  was applied to the GO sensor by using potentiostat for about 10 min [32]. In this way, the rGO sensor was successfully prepared after the GO film was reduced to rGO film. PyCD decoration of rGO sensor: Before assembling PyCD molecules on the rGO surface, the device was washed with DMF twice. Then 0.1 g of PyCD was dissolved in 5 mL DMF. Subsequently, the device was dipped into PyCD solution for 12 h and then washed with deionized water several times. Fig. 1 illustrates the fabrication process of rGO sensor. The reduction of GO and all electrical measurements were performed on an electrochemical workstation (BAS Epsilon).

## 3. Results and discussion

### 3.1. Structure and morphology of the sensor

Structure of the sensor device and morphology of the GO film were characterized by SEM. Fig. 2a and b show the SEM images of the sensor device. It clearly shows that the uniformly formed interdigitated electrodes were separated by a 20  $\mu\text{m}$  gap. GO film deposited on the interdigitated electrodes was verified by SEM, as shown in Fig. 2c and d. Compared with Fig. 2a and c demonstrates that continuous and uniform GO film is deposited on the gap between the interdigitated electrodes. The GO film deposited on sensor device displays the characteristic wrinkle morphology, as observed in the SEM image (Fig. 2d), which further verifies the high dispersibility of the GO. Furthermore, it should be noted here that the polar surface functional groups made GO highly dispersible in aqueous medium. Therefore, GO dispersion can form an even and uniform film on the interdigitated electrodes. AFM analysis was employed to characterize the thickness of the GO film deposited on the sensor device. Fig. 3 shows the AFM image and the height profile of GO film. A continuous and uniform GO film was observed. The thickness of the prepared GO film was 1.0–3.6 nm, corresponding to 1–3 layers of GO film. The average thickness of GO sheets was about 1.0 nm, which was in good agreement with previous reports [33]. The surface root-mean-square roughness ( $R_q$ ) of the GO film was analyzed. The  $R_q$  value of the GO film was 2.75 nm, which were comparable to those of GO films prepared by Wang et al. [34]. Fig. 4 shows the typical Raman spectra of GO and rGO on the sensor

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