



A novel composite of graphene quantum dots and molecularly imprinted polymer for fluorescent detection of paranitrophenol



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ABSTRACT

A novel fluorescent sensor based on graphene quantum dots (GQDs) was synthesized for determination of paranitrophenol (4-NP) in water sample, where molecularly imprinted polymer (MIP) was incorporated in GQDs-based sensing system for the first time. A simple hydrothermal method was used to fabricate silica-coated GQDs. The final composite was developed by anchoring the MIP layer on the silica-coated GQDs using 3-aminopropyltriethoxysilane as functional monomer and tetraethoxysilane as crosslinker. The combination of GQDs and MIP endows the composite with stable fluorescent property and template selectivity. Due to resonance energy transfer from GQDs (donor) to 4-NP (acceptor), the fluorescence of the MIP-coated GQDs composite can be efficiently quenched when 4-NP molecules rebound to the binding sites. The composite was applied to the detection of the non-emissive 4-NP and exhibited a good linearity in range of 0.02–3.00 $\mu\text{g mL}^{-1}$ with the detection limit of 9.00 ng mL^{-1} ($S/N=3$). This work may open a new possibility for developing GQDs-based composite with selective recognition, and it is desirable for chemical sensing application.

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1. Introduction

As one of the severely toxic substituted phenols, paranitrophenol (4-NP) can cause headaches, drowsiness, nausea and cyanosis through acute inhalation or ingestion. So the use of 4-NP should be strictly controlled and supervised. The US Environmental Protection Agency (EPA) has provided the allowed limit of 4-NP in drinking water at 60 ng mL^{-1} (Wei et al., 2011). Various methods have been explored to detect 4-NP and applied in real samples, such as chromatographic techniques (Liu et al., 2007), electrochemical detection (Zhang et al., 2012c), chemiluminescence detection (Liu et al., 2010) and fluorescent monitoring (Catalin et al., 2001). Among them, the fluorescent method has several advantages such as a small amount of solvent consumption, time-saving measurement and simple sample pretreatment (Li et al., 2010a). The conventional fluorescent methods for detecting non-fluorescent 4-NP need inducers or derivatizations. Recently, some groups have been successfully explored new optical sensing system based on luminescent probe (such as ZnS:Mn²⁺ quantum dots), and provided a facial and label-free method for determining non-fluorescent analytes (Wang et al., 2009; Zhao et al., 2012).

Graphene quantum dots (GQDs), as recently emerging carbon-based materials, are graphene sheets smaller than 100 nm with a

unique sp² and sp³ hybrid structure (Dong et al., 2012; Jiang et al., 2013). They have attracted considerable attention on account of their special advantages, such as low toxicity, high fluorescent activity, robust chemical inertness, and excellent water solubility (Tetsuka et al., 2012). Due to these merits, GQDs have been proved to be potential candidates in photovoltaic devices, sensing and imaging fields (Ran et al., 2013).

Molecular imprinting is a well-known methodology to fabricate materials that function as synthetic receptors with predetermined binding sites (Lin et al., 2012). Molecularly imprinted polymers (MIPs) have notable features such as improved stability, effective cost, and rapid fabrication (Lian et al., 2012). Typically, MIPs are prepared via polymerization in the presence of template molecules followed by removal of the template. After templates are removed, the remaining cavities with complementary size, shape, and orientation of functionalities are left behind (Han et al., 2005; Lian et al., 2012). In recent years, surface molecular imprinting polymers attract more attention, due to the prominent advantages over traditional MIPs, such as enhanced mass transfer, rebinding percentage and high selectivity (Zeng et al., 2013; Zhou et al., 2010).

Silica materials have promising structural properties for imprinting matrix, as their rigid structures are highly suitable for the formation of a delicate recognition site (Jung et al., 2010). Imprinted silica films show fast kinetic binding for the template due to their nanosized thickness. In addition, silica coating is proven to be an ideal method to protect the fluorescent QDs (such as Mn-doped ZnS QDs) since the silica shell is chemically inert and

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optically transparent (Liu et al., 2010). Several groups have fabricated molecularly imprinted silica film on the surface of semiconductor quantum dots (such as Mn^{2+} doped ZnS QDs, CdSe QDs, CdTe QDs) (Wang et al., 2009; Zhang et al., 2012b). These optical sensors show special binding and selective recognition to the template molecules. Considering the known toxicological effect of heavy-metal-based QDs (such as CdTe, CdSe QDs) on humans and the environment, an eco-friendly fluorescent sensor based on MIP-coated GQDs was proposed for the first time in this paper.

Herein, a novel composite of MIP-coated GQDs was successfully fabricated and an eco-friendly fluorescent sensor was constructed to selectively detect 4-NP based on this composite. In the 4-NP sensing system, GQDs acted as fluorophores and imprinted silica film provided specific binding sites for analytes. The fluorescence of MIP-coated GQDs was greatly quenched when interacted with 4-NP. The results of experiments indicated that the MIP-coated GQDs composite combines the merits of imprinted silica materials and GQDs, showing fast kinetics, special binding sites, and improved fluorescence. The novel fluorescent sensor realized specific and selective detection of 4-NP from its interferences. Moreover, the MIP-coated GQDs sensor had a wider linear range and lower detection limit than some reported methods. The optical sensor was applied to the determination of 4-NP in real water samples with satisfactory results.

2. Experimental section

2.1. Reagents and materials

Graphite, sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), thionyl chloride (SOCl_2), 3-aminopropyltriethoxysilane (APTS), tetraethoxysilane (TEOS), 4-nitrophenol (4-NP), 2-nitrophenol (2-NP), hydroquinone and phenol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), triethylamine (TEA), benzene, N, N-dimethyl formamide (DMF), and dichloromethane (CH_2Cl_2) were obtained from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Other chemicals were obtained from SS Precision Chemical Co., Ltd. (Shanghai, China). All aqueous solutions were prepared with ultrapure water ($> 18 \text{ M}\Omega \text{ cm}$).

2.2. Instruments and measurements

Fourier transform infrared (FT-IR) spectroscopic measurements were performed on NEXUS670 Fourier transform infrared spectrometer (Nicolet, USA). Transmission electron microscopy (TEM) images were obtained using a Model JEM 2010 electron microscope (JEOL, Tokyo, Japan). The fluorescence measurements were carried out on a model F-7000 spectrophotometer (Hitachi, Japan). The UV–vis spectra were measured on a Varian Cary-100 spectrometer.

2.3. Synthesis of APTS-GO

APTS-GO was prepared according to the previous reports (Li et al., 2010b; Xiao et al., 2007). Briefly, 0.2 g GO was dispersed in 20.0 mL SOCl_2 and 4.0 mL benzene. The mixture was stirred for 24 h under 70°C at reflux. The obtained solid (GO-Cl) was washed with ultra-dried tetrahydrofuran (THF) three times and dried under vacuum at 50°C . In the next step, 0.1 g GO-Cl was dispersed in 20.0 mL DMF, then 0.25 mL APTS and 0.25 mL TEA were added into the flask. The mixture was heated to 120°C and stirred for 48 h. Afterwards, the mixture was centrifuged and the obtained product was washed with DMF and anhydrous ethanol for two times, respectively. The final product was dried under vacuum at 50°C over night.

2.4. Synthesis of silica-coated GQDs

The silica-coated GQDs were prepared by hydrothermal route according to Ref. (Pan et al., 2010) with some modification. 80.0 mg APTS-GO was dispersed in 36 mL distilled water in a poly(tetrafluoroethylene) (Teflon)-lined autoclave and heated at 200°C for 36 h. After cooling to room temperature, the resulting black suspension was filtered through a $0.22 \mu\text{m}$ microporous membrane. Finally, the colorless solution was collected and suspended steamed. The final volume of the solution was about 4 mL.

2.5. Synthesis of MIP- and NIP-coated GQDs

The imprinting polymer was fabricated on silica-coated GQDs via a typical sol–gel polymerization as previously reported with some modifications (Wang et al., 2009; Zhang et al., 2011b). 4-NP (20 mg), anhydrous ethanol (20 mL) and APTS (50 μL) were added to a 50 mL beaker and stirred for 30 min. Then, 4 mL silica-coated GQDs colloidal solution, 1.6 mL CH_3COOH (1 M), 200 μL TEOS was injected, and the mixture was kept stirring for another 15 h. The resultant MIP-coated GQDs were centrifuged and washed with anhydrous ethanol and distilled water for two times, respectively. After the templates were removed, the obtained MIP-coated GQDs were redispersed in 8 mL water under ultrasonication and kept refrigerated prior to use. The non-imprinted NIP-coated GQDs were prepared using the same method without adding any template molecules.

2.6. Measurements of fluorescent response to 4-nitrophenol

The fluorescent measurements were carried out with the excitation wavelength of 320 nm. The stock solution of MIP-coated GQDs was diluted 60 times, by mixing with Na_2CO_3 – NaHCO_3 buffer solution (pH 9). 600 μL above mixture was added to the cuvette, and then different amounts of 4-NP was injected. The final concentration of analyte can be known through simply calculation. The fluorescence intensity was measured immediately after fully mixing. The control experiments of NIP-coated GQDs were the same as that of MIP-coated GQDs.

2.7. Sample collection and pretreatment

The proposed procedure was applied to the determination of 4-NP in water samples collected from tap water and Yingtao river of East China Normal University. The real water samples were filtered through a $0.45 \mu\text{m}$ microporous membrane to eliminate particulate matters, and stored in precleaned glass bottles before analysis. 600 μL mixed solutions containing 540 μL water samples and 60 μL Na_2CO_3 – NaHCO_3 (1 M) buffer were added to the cuvette, then different quantities of 4-NP were added to the mixture solution and the resulting water solutions were used for fluorescent analysis. The content of the 4-NP was determined by the standard addition method.

3. Results and discussions

3.1. Preparation and characterization of composite

In order to improve the interaction between GQDs and molecularly imprinted silica matrix, GQDs have to be coated with a layer of silica before the sol–gel hydrolysis and condensation imprinted polymerization reaction (Mao et al., 2012). It means that the final composite was obtained by multi-steps. The major steps involved in the synthesis of MIP-coated GQDs are illustrated in Scheme 1. (i) Chemical modified GO with APTS (APTS-GO). APTS was used as a precursor of silica layer which formed in the

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