



Fabrication of valine-functionalized graphene quantum dots and its use as a novel optical probe for sensitive and selective detection of Hg^{2+}



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ABSTRACT

The functionalization of graphene quantum dots has become a powerful method to modulate its chemical, electronic and optical properties for various applications. In the study, we reported a facile synthesis of valine-functionalized graphene quantum dots (Val-GQDs) and its use as a novel fluorescent probe for optical detection of Hg^{2+} . Herein, Val-GQDs was synthesized by the thermal pyrolysis of citric acid and valine. The resulting Val-GQDs has an average size of 3 nm and the edge of graphene sheets contains the rich of hydrophilic groups, leading to a high water-solubility. Compared to the GQDs prepared by thermal pyrolysis of citric acid, Val-GQDs exhibits a stronger fluorescence (>10-fold) and better photostability (>4-fold). Interestingly, the existence of valine moieties in the Val-GQDs results in a more sensitive fluorescent response to Hg^{2+} . The fluorescent signal will linearly decrease with the increase of Hg^{2+} concentration in the range from 0.8 nM to 1 μM with the correlation coefficient of 0.992. The detection limit is 0.4 nM ($S/N = 3$), which the sensitivity is >14-fold that of GQDs. The analytical method provides the prominent advantage of sensitivity, selectivity and stability. It has been successfully applied in the optical detection of Hg^{2+} in real water samples. The study also provides a promising approach for the design and synthesis of functionalized GQDs to meet the needs of further applications in sensing and catalysis.

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1. Introduction

Because of high toxicity and severe threat to ecological system and human health, heavy metal contamination has become increasingly serious along with the industrial development, and attracted much attention throughout the world [1]. The investigation has demonstrated that mercury, one of the most toxic heavy metals, has recognized accumulative and persistent characters, which can accumulate in vital organs and tissues of animal and human body through the skin, gastrointestinal or respiratory [2–4]. Long-term exposure to mercury, even at a very low concentration, will have an adverse effects on human health and environment. The accumulated mercury in the human body over time ultimately causes digestive, kidney and especially neurological diseases [5,6]. In addition, the most common forms of water soluble mercury can exist stable in water [7]. All these potential threats make mercury contamination become a global environmental problem [8]. To protect environment and human health, the United States Environment Protection Agency proposed the upper limit of Hg^{2+} in drinking water at

10 nM [9]. There is a great need to develop reliable analytical method for rapid detection of Hg^{2+} with high sensitivity.

Many analytical technologies have been well developed for the detection of trace Hg^{2+} , including atomic absorption/emission spectrometry (AAS/AES) [10,11], inductively coupled plasma mass spectrometry (ICP-MS) [12], surface enhanced Raman scattering (SERS) [13], flow injection technique (FIA) [14] and electrochemical method [15]. These methods offer the advantages of high accuracy, but they usually require high costs, large amounts of samples, sophisticated instruments and complicated sample preparation processes, which largely limit their practical applications [16]. In the recent years, the fluorescent sensor for Hg^{2+} detection was given a special attention on the account of its low-cost, fast response, high selectivity and sensitivity [17]. The performance of fluorescent material play key roles in the fabrication of fluorescent sensors. It not only determines the stability of the sensors to a certain extent, but also seriously affects the sensitivity and selectivity of the analytical methods. Hence, choosing an appropriate fluorescent reagent is the most important work for the specific fluorescent assay. Organic fluorophores, semiconductor quantum dots [18], and metal nanoclusters [19–21] are typical fluorescent materials for Hg^{2+} sensors. However, the present fluorescent sensors based on the above fluorescent materials are difficult to be widely applied to routine analysis due to their intrinsic limitations. Often, organic fluorophore suffers from relatively low photo-stability and weak fluorescence, seriously affecting their sensitivity and

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accuracy for the optical detection. Semiconductor quantum dots contain heavy metals as essential elements, which bring up dangers to the organisms and environment. Although metal nanoclusters such as gold, silver and copper nanoclusters can replace noxious semiconductor quantum dots due to their comparable fluorescence intensity and good biocompatibility, they still lack of sufficient yield and optical properties. There is a great need to develop high-performance fluorescent materials for fluorescent sensing. More recently, graphene quantum dots (GQDs) as new emerging fluorescent materials has drawn a great deal of research interest owing to its fantastic characteristic compared with conventional semiconductor quantum dots, including low cytotoxicity, robust chemical inertness, low photo-bleaching, and excellent biocompatibility [22,23]. The investigations have demonstrated that GQDs has a great prospect in applications of bio-imaging [23], catalysis and photocatalysis [24,25], and energy conversion and storage [26], particularly as attractive alternatives of sensing material for various fluorescent assay [27]. To date, many fluorescent sensors based on GQDs for Hg^{2+} detection have been developed. However, present GQDs-based fluorescent sensors suffer from no ideal photo-stability and sensitivity for detection of trace Hg^{2+} [28]. These deficiencies greatly limit their applications in sensing. Many ways have been successfully attempted to enhance the fluorescent performance of GQDs. Among these, the chemical functionalization of GQDs is the most effective mean for modifying their chemical, electronic and optical properties [28]. It can also introduce some specific chemical moieties, which would improve the fluorescent efficiency and selectivity of GQDs for the detection of metal ions [29,30]. The preparation of functionalized graphene quantum dots usually requires two steps, namely, the formation of graphene quantum dots and the subsequent functionalization. As chemically active groups in the GQDs lack of enough stability and are easy to fall off from the graphene sheets in the functionalization process. This makes the final product contains less functional groups or structures, thus leading to a slow reaction rate and low sensitivity for their applications in the detection of Hg^{2+} or other metal ions.

In the study, we reported a facile synthesis of valine-functionalized graphene quantum dots (termed as Val-GQDs). The Val-GQDs was prepared by pyrolysis of citric acid and valine, in which the formation of graphene quantum dots and its functionalization is completed in one step with high yield. The resulted Val-GQDs offers a stronger fluorescence, better photo-stability, and more sensitive and selective fluorescent response to Hg^{2+} compared to the GQDs obtained by pyrolysis of citric acid. The optical sensor based on the Val-GQDs has been successfully applied in ultrasensitive detection of Hg^{2+} in real water samples.

2. Materials and methods

2.1. Materials and reagents

Citric acid monohydrate, L-valine, sodium hydroxide (NaOH), and mercuric sulfate were purchased from Shanghai Chemical Company (Shanghai, China). All other chemicals were analytical grade without further purification. Britton-Robinson buffer solution (BR buffer, $\text{H}_3\text{PO}_4\text{-HAc-H}_3\text{BO}_3$, 0.04 M) was prepared in the laboratory and its pH value was adjusted using 0.2 M NaOH solution. Ultrapure water (18.2 M Ω cm) purified from Milli-Q purification system was used throughout the experiment.

2.2. Apparatus

UV-visible spectra were recorded on a TU-1901 spectrometer with a DH-2000 deuterium and tungsten halogen light source in absorbance mode (Beijing Purkinje General Instrument Co., Ltd., China). Fluorescence spectra were recorded by a Cary Eclipse fluorescence spectrophotometer (Varian, America). Transmission electron microscope (TEM) image was obtained by a JEOL 2010 FEG microscope at 200 KeV. Atomic force microscopic (AFM) image was obtained on a Multimode 8 force microscope (Bruker, Germany). X-ray photoelectron spectroscopy

(XPS) measurement was carried out on a PHI 5700 ESCA spectrometer using Al HR radiation ($h\nu = 1486.6$ eV). Infrared spectrum (IR) was recorded on a Nicolet FT-IR 6700 spectrometer.

2.3. Synthesis of valine-functionalized graphene quantum dots

In a typical synthesis, 0.5 g of citric acid was dissolved in 1 ml of ultrapure water, then 0.25 g of valine was added into the above solution under sonication. The mixture was then heated at 200 °C for 2.5 h with a heating rate of 10 °C min^{-1} . After cooling down to room temperature, the collected solid product was dissolved in 1 M NaOH solution, and its acidity was slowly adjusted to pH 7. Finally, the solution was dialyzed in ultrapure water through a dialysis membrane for 48 h to remove unreacted reagents. The solid product was obtained by freeze drying and stored at 4 °C for further use. The procedure was also used for preparation of other Val-GQDs samples with different valine amounts. For comparison, a control sample (termed as GQDs) was also prepared using the same procedure unless no addition of valine.

2.4. Method for studying photo-stability

The photo-stability experiment of Val-GQDs and GQDs samples was carried in a 20 ml vial filled with different GQDs under a xenon lamp irradiation (300 W). At given time intervals, 1 ml of the solution was collected and then its fluorescence spectrum was measured on a fluorescence spectrophotometer.

2.5. Quantum yield measurement

The quantum yield (Φ) of Val-GQDs was calculated by comparing the integrated fluorescence intensities and absorbance values (<0.05) of the GQDs samples with the reference quinine sulfate [31]. The absorbance for quinine sulfate and Val-GQDs were measured in a TU-1901 spectrometer. The fluorescence spectra of the samples were recorded under the same testing conditions. Then the integrated fluorescence intensity from fluorescence spectrum was calculated. At last the quantum yield of Val-GQDs (in water) was calculated according to the following equation:

$$\Phi = \Phi_r \frac{m\eta^2}{m_r\eta_r^2} \quad (1)$$

where Φ is the quantum yield of Val-GQDs, Φ_r is the quantum yield of quinine sulfate, m is the slope obtained from the linearizing plot of integrated

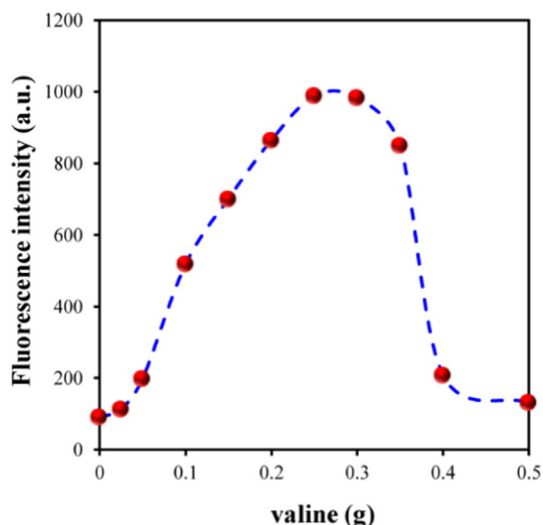


Fig. 1. Effect of valine amount on fluorescence intensity.

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