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Facile synthesis of sulfur-doped graphene quantum dots as fluorescent sensing probes for Ag^+ ions detection

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ABSTRACT

Sulfur-doped graphene quantum dots (S-GQDs) with bright blue emission have been prepared by a facile one-pot hydrothermal treatment. A specific compound, 1,3,6-trinitropyrene, which has a mother nucleus structure similar with graphene, was chosen as the carbon source and 3-mercaptopropionic acid (MPA) was employed for S-doping and carboxyl groups modification. The synthesized S-GQDs were characterized by atomic force microscopy (AFM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and fluoscence (FL) spectrum. Results indicated that S-GQDs possessed single layer graphene structure with mean size of about 2.5 nm and presented an excitation-independent photoluminescence behavior with maximum excitation/emission wavelength at 360/450 nm, respectively. The sulfur-doping of GODs drastically improved their electronic and chemical properties, which afforded the S-GQDs a sensitive response to Ag^+ ions. Furthermore, the S-GQDs were successfully explored as a sensing probe for Ag^+ detection with high sensitivity and selectivity. A wide linear range of 0.1-130.0 μM with a low detection limit of 30 nM was obtained. The facile preparation method and the high performace of the as-prepared S-GQDs present promising potential for their applications in sensing, biological imaging and catalysis.

1. Introduction

Recently, photosensitive nanomaterials have been attractive in bioimaging[1,2]· optoelectronicdevice [3], catalysis [4], matrix for deposition of surface-clean metal nanoparticles [5,6], sensing detection [7–9], and and etc. As novel type of zero-dimensional (0D) luminescent nanomaterials and new member of the graphene family, graphene quantum dots (GQDs) have ignited tremendous research interests. Owing to the pronounced quantum confinement and edge effects, carbon-based GQDs present extraordinary optical and electrical characteristics which are not obtainable in other kinds of QDs. For example, compared with traditional semiconductor QDs (e.g. CdS, CdSe, CdTe) that are expensive and contain cytotoxic heavy metal constituents, GQDs show many advantages including low toxicity, excellent solubility, stable luminescence, high biocompatibility and tunable band gap [10–12]. Therefore, the development of facile method for easy and controllable synthesis of functional GQDs is now at the center of research efforts. Until now, two major methods inculding top-down and bottom-up strategies have been developed to prepare GQDs. The top-down methods mainly focus on the cutting of graphene sheets into GQDs using concentrated acid oxidation [13], UV-Fenton oxidation [14], electrochemical oxidation [15], microwave auxiliary oxidation [16], etc. However, the top-down method might be limited by low product yield and harsh conditions because of the large usage of strong acid or oxidant. On the contrary, the bottom-up approaches apply small organic precursor molecules to construct GQDs structure through catalytic or thermal treatment processes [11,17]. Environmentally friendly production of GQDs with large scale, homogeneous size and morphology can be achieved.

As recently demonstrated, heteroatom doping (oxygen, boron, nitrogen, phosphor, sulfur, etc.) can change various properties of GQDs including electronic structure, band gap, chemical reactivity, and optical properties [18,19]. In contrast to B, N or P doping, doping of sulfur (S) into the framework of GQDs might be relatively difficult because the formation of C—S bond is hard to achieve. The reasons lie in two aspects. On the one hand, S atom is larger than C atom and the C—S bond length (1.78 Å) is 25% longer than that of the C—C bond. On the other hand, the difference of electronegativity between S (2.58) and C (2.55) is very close and negligible polarization (or charge transfer) exists in the C—S bond [19]. Consequently, only few studies covered sulfur-doped carbon dots (S-CDs) or GQDs (S-GQDs) had been reported until now. In term of S-CDs, Xu

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et al. synthesized S-CDs using hydrothermal method starting from sodium citrate and sodium thiosulfate, that was used as probes toward Fe^{3+} detection [20]. Hu et al. prepared S-CDs by treating waste frying oil with concentrated sulfuric acid, that was suitable for cell imaging [21]. Kwon et al. perpared S-CDs with a strong long-wavelength absorption band using bis(2-ethylhexyl) sulfosuccinate sodium salt, glucose and thioglycolic acid [22]. Chandra et al. prepared S-CDs from thiomalic acid and concentrated sulfuric acid. After adjoin with gold nanoparticles and DNA, potential applications in bioanalysis were evaluated [23]. For S-doped GQDs, Li et al. prepared S-GQDs by electrolysis of graphite in sodium *p*-toluenesulfonate medium, that was also used as probes for Fe^{3+} detection [24]. Li et al. prepared S-GQDs by a hydrothermal method using fructose and sulphuric acid as source materials [25]. Though S-GQDs have now rarely been reported, the S-doping in GQDs might greatly extend the arsenal of GQDs and their potential applications. Furthermore, studies on S-doped graphene have proven that the mismatch of the outermost orbitals of S and C will induce a non-uniform spin density distribution, which might consequently endow S-GQDs with surface reactivity or catalytic properties [19]. Therefore, the development of smart bottom-up methodology for preparing novel S-GQDs with high crystal quality is highly desired. Moreover, the investigation on the properties and potential applications of S-GQDs is also necessary.

In this paper, one-pot synthesis of S-GQDs was developed via a simple hydrothermal method. A specific compound, 1,3,6-trinitropyrene, that has a mother nucleus structure similar to that of graphene and three strong electrophilic sites, was chosen as the carbon source. 3-mercaptopropionic acid (MPA) with —SH and —COOH was employed as the sulfur source for both S-doping and carboxyl groups modification. The as-prepared S-GQDs exhibited blue emission, single layer graphene structure, uniform size, and excitation-independent photoluminescence behavior. As known, Ag^+ has been widely applied in industry of electronics, photography, mirrors, and pharmacy [26–28]. However, long term exposure of Ag^+ in water might be toxic to animals and human beings. N-doped GQDs (N-GQDs) and amine-terminated GQDs have been reported as FL probe for the detection of Ag^+ ion. For instance, Tabaraki et al. prepared N-doped GQDs from glucose and ammonia, that exhibited as sensing probes for Ag^+ ions determination with linear range of 0.2–40 μM and the limit of detection of 168 nM, respectively [29]. Suryawanshi et al. firstly synthesized GQDs by treating bio-waste (dead leaves) with acid mixture of concentrated H_2SO_4 and HNO_3 (3:1 ratio). Afterwards, GQDs was further modified to produce amine-terminated GQDs by ammonia solution using hydrothermal treatment. Those amine-terminated GQDs were applied for detection of Ag^+ ion with detection limit of 0.033 $g\,L^{-1}$ to 0.1 $g\,L^{-1}$ [30]. Owing to the drastical improvement of the surface chemical reactivities, the application of our S-GQDs for sensitive detection of Ag^+ ions were described and discussed in detail.

2. Experimental section

2.1. Materials and reagents

Pyrene, 3-mercaptopropionic acid, NaOH, NaH_2PO_4, Na_2HPO_4 and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were obtained from Aladdin Chemistry Co. Ltd. (China). Aqueous solutions of K^+, Na^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} were prepared from their chloride salts. Aqueous solutions of Ag^+, Cd^{2+}, Pb^{2+} were prepared from their nitrate salts. All chemicals were of analytical grade and used as received. All aqueous solutions were prepared with ultrapure water (18.2 MΩ cm, Milli-Q, Millipore).

2.2. Instrumentations

UV-vis absorption spectum was obtained on a UV–vis 2650 spectrophotometer (Shimadzu Corporation, Japan). Fluorescence spectrum was recorded on an RF-5301PC spectrofluorometer (Shimadzu Corporation, Japan). Transmission electron microscopic (TEM) photograph was taken on a JEM-2100 transmission electron microscope at operating voltage of 200 kV (JEOL Ltd., Japan) to investigate the microstructures and size distribution. Height profiles of S-GQDs were acquired by atomic force microscopy (AFM) images (MF*P*-3D AFM microscope, Asylum research). Elemental analysis of the S-GQDs was performed by X-ray photoelectron spectroscopy (XPS) with a PHI5300 electron spectrometer using 250 W, 14KV, Mg Kα radiation (PE Ltd., USA). Inductively coupled plasma-mass spectrometry (ICP-MS) was used to give the standard concentration of Ag^+ ions (NexIoN 300D, PE Ltd., USA).

2.3. One-step preparation of S-GQDs

Using pyrene as the initial substrate, 1,3,6-trinitropyrene was synthesized according to the literature [31]. Then S-GQDs were prepared by one-pot hydrothermal process using 1,3,6-trinitropyrene as the carbon source and 3-mercaptopropionic acid (MPA) as the sulfur source. Briefly, 0.1 M MPA and 20 mg/mL 1,3,6-trinitropyrene were firstly mixed by ultrasonic for 1 h. Then the resulting suspension was placed into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 200 °C for 10 h. After cooling down to room temperature, the cloudy solution containing water-soluble GQDs was filtered through a 0.22 mm microporous membrane to remove insoluble carbon product. Then, un-reacted small molecules were removed by dialyzing in a dialysis bag (retained molecular weight of 1000 Da) against ultrapure water for 24 h. The obtained sample was further dialyzed in a dialysis bag (retained molecular weight: 3500 Da) against ultrapure water for 24 h to remove impurities with large size. After dialysis, a pale-yellow aqueous suspension of the S-GQDs was obtained and freeze dried.

2.4. Measurement of quantum yield (QY)

QY was calculated according to the following equation:

$$Y_{\mu} = Y_S \times \frac{F_u A_S}{F_S A_{\mu}}$$

where Y_{μ} and Y_s are the quantum yield of the S-QGDs and the standard substance, F_u and F_s respectively stand for the integral fluorescence intensity of the test S-QGDs and the diluted standard solution and A_{μ} and A_s are the maximum absorbance value of S-QGDs and the diluted standard solution, respectively.

2.5. Fluorescent detection of Ag^+ using S-GQDs

The detection of Ag^+ was carried out in HEPES buffer solution (2.0 mM, pH 7.0)[32]. In a typical run, S-GQDs solution (0.01 mg/mL) was dispersed in the buffer and then mixed with different amount of Ag^+. After the resulting solution was shaken well and incubated for 10 min at room temperature, the fluorescence emission spectra (excited at 360 nm) were recorded. The detection measurements were performed in triplicate. The relative fluorescence intensity $(F_0 - F)/F_0$ versus Ag^+ concentration were used for calibration. Here, F_0 and F are the fluorescence intensities of S-GQDs in the absence and presence of different concentration of Ag^+, respectively.

Analysis of real sample using the as-prepared S-GQDs was also performed using environmental sample matrix. Water of Jinsha Lake (Hangzhou, China) was collected and concentrated 50 times (Sample 1). Sample 2 and 3 were obtained by adding Ag^+ into sam-