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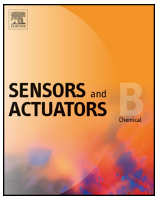

Highly fluorescent nitrogen and sulfur co-doped graphene quantum dots for an inner filter effect-based cyanide sensor

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ABSTRACT

In this work, nitrogen and sulfur co-doped graphene quantum dots (N,S-GQDs), exhibiting bright blue fluorescence with an excellent quantum yield of 67%, were facilely prepared by one-pot pyrolysis of citric acid (carbon source) and cysteine (N and S sources). Compared to conventional GQDs, the doping of nitrogen/sulfur had significantly altered and uniformed the surface state, and the as-obtained N,S-GQDs displayed an excitation-independent emission behavior, where the fluorescence decay curve was nearly a single exponential. On the basis of the well-known inner filter effect of silver nanoparticles (AgNPs) and cyanide (CN^-)-induced etching of AgNPs, the fluorescence of N,S-GQDs could be quenched by AgNPs, and the nonfluorescence state of the as-prepared N,S-GQD-AgNP ensemble would be switched on in the presence of CN^-. Meanwhile, the addition of N,S-GQDs has almost ignorable effect on the absorption spectrum of the AgNP solution, however, the subsequent introduction of CN^- would significantly decrease the absorbance value owing to the aforementioned etching behavior of CN^-. Therefore, a N,S-GQD-based fluorescent and AgNP-related colorimetric dual-mode analytical system for efficacious determination of CN^- has been rationally designed and successfully developed for the first time. Furthermore, the detection limits were found to be 0.52 μM and 0.78 μM for fluorescent and colorimetric sensors individually under the optimal experiment conditions. The proposed N,S-GQD-AgNP-based assay can be successfully utilized to the quantitative determination of CN^- in spiked tap water samples.

1. Introduction

Graphene quantum dots (GQDs), the graphene sheets with lateral dimensions less than 100 nm [1], have fuelled intensive research interest recently owing to their outstanding optical properties, low toxicity, high stability, good biocompatibility and robust organic inertness derived from the quantum confinement and edge effects [2–4].Therefore, recent advances have been made in the development of effective strategies to prepare GQDs. Generally, the approaches for synthesizing GQDs can be classified into two main groups: top-down [5–7] and bottom-up methods [8,9]. The top-down methods, which primarily refer to cutting of larger graphene sheets into nanosized ones by using physical or chemical approaches, are usually not very satisfactory due to complex process, severe conditions, expensive starting materials and low product yield [10,11]. Alternatively, bottom-up approaches have been devised to achieve fluorescent GQDs. Especially intriguing, doping GQDs with heteroatoms (such as N, B, Si and S) is easier in bottom-up routes by carefully selecting the diversified precursors, which would effectively tune the intrinsic properties of GQDs, including optical characteristics, surface and local chemical features[12–16]. N,S-CDs with high fluorescence quantum yield (FLQY) have been synthesized through hydrothermal treatment [17], but complex and time-consuming pretreatment processes were involved. A simple microwave-assisted method was also developed to prepare graphitic-like N,S-CDs with blue fluorescence [18]. It owns a less-than-ideal FLQY and extra urea was indispensable in the route. Therefore, efficient ways to get N,S-GQDs with both improved FLQY and simple process are still highly desired, and pyrolysis treatment [19] might be a good option. Additionally, cysteine, one of the simplest and most common N,S-containing biological molecules, would be an ideal candidate for doping GQDs with N and S atoms.

The excellent fluorescence properties of GQDs that are similar to those of semiconductor QDs make them promising in chemosensing and biosensing. Conventionally, target analytes sensing by

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GQDs was always based on energy and/or charge transfer from GQD architectures to the targets, which is often marked by fluorescence quenching of the GQDs [20–23]. However, the "turn off" sensing principle usually suffers from relatively low sensitivity and is susceptible to external factors, leading to false positives. In contrast, the "turn on" fluorescence sensors help to facilitate detection results more reliable and have been extensively developed, recently. Thereinto, incorporating GQDs into the design of fluorescence resonance energy transfer (FRET) or inner-filter effects (IFE) systems to establish elaborated "turn on" sensors is one of the thought-provoking topics [24,25].

Cyanide (CN^-) is known as a highly toxic and dangerous anion which affects the ability of cells to utilize oxygen [26]. Hence, there is considerable interest in finding readily available, simple-to-use and inexpensive methods to detect CN^-. By taking advantages of the capability of CN^- to etch noble metal nanoparticles (such as AuNPs and AgNPs) [27], simple colorimetric sensors for CN^- have been already reported. Furthermore, it has reported that based on IFE of AuNPs or AgNPs, fluorescence chemosensors with improved sensitivity and selectivity could be easily achieved by using organic fluorophore as fluorometric reporter [28]. On one hands, previously reported CN^- sensors were mainly focused on the single optical readout. To make the experimental results more credible and versatile, method with multiple outputs to complement each other is needed. On the other hands, GQDs are more promising fluorophores in fabrication of IFE-based sensors due to their superior optical properties [29], and no GQDs participant sensor for CN^- has been reported.

Herein, we prepared the N,S-GQDs with high FLQY by a simple one-pot pyrolysis method, using citric acid (CA) and cysteine as starting materials. The use of cysteine in synthetic process could uniform the surface states and increase the FLQY of GQDs efficiently through doping GQDs with heteroatoms. Subsequently, the AgNP-quenched fluorescence of GQDs and the quenching theory as well as the dual-mode sensor construction for CN^- therewith were studied comprehensively. Compared with the existing organic fluorophore-based CN^- detection strategies [28,30], intriguing features of this sensing system were that the unique fluorescence properties of GQDs and the dual-readout modes can ensure a more convincing and ideal signal output. The special interaction between CN^- and AgNPs rendered this IFE-based sensor facile, economic as well as highly selective.

2. Experimental

2.1. Chemicals and materials

Citric acid was purchased from Sigma-Aldrich (St. Louis, MO, USA). L-Cysteine and L-Alanine were obtained from Shanghai Sangon Biotech. Co., Ltd. (China). Sodium sulfide (Na_2S) was procured from Chengdu Cracia Chemical Technology Co., Ltd. (China). NaF, NaCl, $NaClO_4$, NaBr, $NaBrO_3$, NaI, $NaNO_2$, $NaNO_3$, Na_2SO_4, Na_2SO_3, NaSCN, Na_3PO_4, Na_2CO_3, NaAc and EDTA were bought from Beijing Chemical Reagent Co. (China). All of these reagents were analytical grade and used as received. The water used throughout the experiments was ultrapure water purified by a Milli-Q water system (resistivity 18.25 MΩ cm, Millipore, USA).

2.2. Instruments

Transmission electron microscopy (TEM) images of GQDs and AgNPs were obtained using a Tecnai G2 F20 (FEI) transmission electron microscope operated at 200 kV. Atomic force microscopic (AFM) image was performed on a NanoScope Multimode AFM (Veeco, USA) using the tapping mode AFM. X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB MK II spectrometer (VG Scientific) with Al Kα radiation as the X-ray source. X-ray powder diffraction (XRD) study was carried out using Bruker D8 Advance (Bruker AXS, Germany) with a graphite monochromator using Cu Kα radiation. Fourier transform infrared (FTIR) data were acquired with a VERTEX 70 Fourier transform infrared spectrometer (Bruker). UV–vis absorption spectra were recorded by Cary 50 UV–vis spectrophotometer (Varian). Fluorescence measurements were carried out using a F-4600 fluorescence spectrophotometer (Hitachi). The time-resolved fluorescence decay was performed on an Edinburgh FLSP-920 spectrofluorometer (Edinburgh, UK) with a 375 nm LED as the excitation source.

2.3. Synthesis of N,S-GQDs

N,S-GQDs were prepared by pyrolysis of CA and L-Cysteine at 240 °C. Briefly, 1.0 g CA was initially mixed with 0.30 g L-Cysteine. Then the mixture was put into a 5 mL beaker and heated to 240 °C using a heating mantle. About 2 min later, the mixture was liquated. Subsequently, the color of the liquid was changed from colorless to pale yellow and finally orange in 10 min. Then, the liquid was dissolved into Milli-Q ultrapure water. The resultant orange N,S-GQD solution was stored in the dark at room temperature.

As a control, undoped-GQDs were synthesized by using CA as the carbon source, and N-GQDs were synthesized by using CA as the carbon source and L-Alanine as the nitrogen source, respectively.

2.4. Synthesis of AgNPs

AgNPs were synthesized by using ascorbic acid as reductant and citrate as stabilizer [31]. All glasswares used in the preparation were soaked in aqua regia ($HCl:HNO_3 = 3:1$) and rinsed thoroughly with ultrapure water before use. Typically, an 8.0 mL aqueous solution containing ascorbic acid (0.6 mM) and trisodium citrate (3.0 mM) was adjusted to pH 10.0 by 0.1 M NaOH solution. Then 0.08 mL of 100 mM $AgNO_3$ was added under a stirring speed of 900 rpm in a 30 °C water bath. The reaction solution was observed to change from colorless to yellow, and 15 min later, no further change in color took place, indicating the reaction was complete. The obtained AgNPs were aged at 100 °C for 2 h to become more spherical-like in shape. The resultant AgNP solution was cooled to room temperature and stored in the dark at 4 °C.

2.5. The sensing procedure

A freshly prepared mixture solution containing 10 μL of 41.7 μg/mL N,S-GQDs and 100 μL of AgNPs in NaOH-$NaHCO_3$ buffer (10 mM, pH 10.0) was used for CN^- detection, into which KCN with different concentrations were added. The mixture solution was equilibrated for 5 min at ambient temperature, and then used for spectral measurements. Each sample was repeated three times.

3. Results and discussion

3.1. Structural characterization of N,S-GQDs

As previously reported, after the moderate pyrolysis procedure, citric acid can be partially carbonized to form GQDs containing abundant small sp^2 clusters that isolated within the whole graphite structure [19]. In this work, to tune the optical characteristics, surface state and local chemical features, L-Cysteine was introduced to dope GQDs with N and S atoms by a simple one-pot pyrolysis treatment (Scheme S1, Electronic Supplementary information (ESI)).