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Facile synthesis of carbon quantum dot/silver nanocomposite and its application for colorimetric detection of methimazole

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ABSTRACT

Here we present a very simple and fast method for preparation of carbon quantum dot/silver (CQD/Ag) nanocomposites at room temperature. Glucose-derived CQDs were prepared by a facile microwave-assisted method and used as both reducing and stabilizing agents for synthesis of CQD/Ag nanocomposites. We found that a unique interaction between as-prepared nanocomposites and antithyroid drug methimazole occurs in the solution, which results in a sharp color change from yellow to red. At the same time, the intensity of surface plasmon resonance peak of CQD/Ag nanocomposites at 400 nm decreases and a new peak appears at higher wavelengths. This finding formed a basis for developing a new colorimetric detection method for methimazole. The calibration curve for this drug was linear in the concentration range of 2.0–40 $\mu g\,L^{-1}$ with a detection limit of 1.0 $\mu g\,L^{-1}$. The method was applied to the determination of methimazole in urine samples with satisfactory results.

1. Introduction

Silver nanoparticles (AgNPs) have attracted great interest due to their unique and tunable optical properties originating from local surface plasmon resonance (LSPR). Spherical AgNPs in 10-nm size range have a strong LSPR absorption band with a maximum around 390 nm [1]. The position of this peak depends on the size and shape of NPs and their local dielectric environment. As the NP size increases, the LSPR peak is red-shifted due to the electromagnetic retardation in larger particles [2,3]. Such LSPR-based optical phenomena have served as a platform for developing several interesting sensors and biosensors [4–7]. At the same time, various materials have been used as reducing agents and stabilizers for preparation of AgNPs. Among them, carbon-based nanomaterials are very interesting and have attracted tremendous attention in the past few years [8–13].

Carbon quantum dots (CQDs) are carbon nanoparticles with sizes below 10 nm which exhibit interesting physicochemical properties such as size- and wavelength-dependent photoluminescence, resistance to photobleaching and ease of bioconjugation. These outstanding characteristics of CQDs make them promising in various fields [14–23]. Recently CQDs have been used as reducing agents for synthesis of metal nanoparticles for sensing applications. For example, Wang et al. [8] exploited carbon dots for preparation of Ag@Carbon dot composites and determined glucose during the synthesis process. Shen et al. [10] also applied CQDs as reducing agents for the growth of AgNPs and developed an optical probe for assay of biothiols using the prepared NPs. Chen and coworkers [24] reported a new approach for in situ growth of AgNPs on the surface of graphene quantum dots (GQDs) and exploited them for colorimetric detection of H_2O_2 and glucose. Moreover, Shi et al. [25] used nitrogen doped GQDs (N-GQDs) as a reducing agent and stabilizer for the formation of N-GQDs/AgNPs hybrid and developed a colorimetric method for discrimination of dihydroxybenzene isomers. Despite various advantages of these methods, the synthesis procedures in most of them need high temperature and/or long reaction time.

Methimazole is one of the major drugs for treatment of hyperthyreosis. It is a thioamide that inhibits thyroid hormone synthesis by blocking peroxidase-catalyzed reactions and iodination of the

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tyrosine residues of thyroglobulin [26]. It has been reported that methimazole may also cause dose-related side effects including cutaneous reactions, arthralgia, gastrointestinal upset and agranulocytosis [27]. Therefore, determination of methimazole in biological fluids is important and various analytical methods including chromatography [28,29], electrochemistry [30–32], spectrophotometry [33,34], fluorescence [35,36] and chemiluminescence [37,38] have been reported for this purpose.

Herein, we report on a facile synthesis of CQD/Ag nanocomposites using glucose-derived CQDs as both reducing and stabilizing agents. These nanocomposites showed a unique color change from yellow to red in response to trace amounts of methimazole. Based on this phenomenon, we have established a novel colorimetric method for the determination of methimazole in urine samples.

2. Experimental

2.1. Apparatus

UV–vis absorption spectra were recorded by a Cary-100 Spectrophotometer (Varian; www.varianinc.com) using 1.0-cm standard quartz cells. Fluorescence spectra were recorded by RF-540 spectrofluorimeter (Shimadzu, Japan). The Fourier transform infrared (FTIR) spectra were recorded on a FT-IR spectrophotometer (Tensor 27, Bruker). X-ray powder diffraction (XRD) pattern was measured by a Siemens D 500 instrument (Germany). The size and shape of CQDs were characterized by transmission electron microscopy (TEM, EM 900, Zeiss, Germany). High-resolution transmission electron microscopy (HRTEM) measurements were carried out using a JEOL 2010 UHR microscope operating at 200 keV. Images were collected using a Gatan Orius SC200 CCD camera. Samples were prepared by depositing a 4 μL drop of CQD/Ag suspension on commercial carbon TEM grids. XPS spectra were recorded by a Kratos Axis Ultra DLD spectrometer with a monochromatic Al Kα X-ray and a multichannel detector. Raman spectra were recorded using a micro-Raman spectrometer (Renishaw in Via Reflex), using a Nd: YAG laser with a wavelength of 532 nm equipped with a CCD detector at room temperature.

2.2. Reagents

All reagents were of analytical-reagent grade. Doubly distilled deionized water (obtained from Ghazi Serum Co. Tabriz, Iran) was used throughout the experiment. Glucose, Silver nitrate ($AgNO_3$) and NH_3 were all purchased from Merck (Darmstadt, Germany). Pure methimazole was kindly provided by Loghman Company (Tehran, Iran).

2.3. Synthesis of CQDs

CQDs were synthesized from glucose by a microwave-assisted method [39]. Briefly, 6.0 mL of 11% aqueous solution of glucose was put into a glass bottle with a cover and heated in a conventional microwave oven at 720 W for 10 min. During this process the color of the residue changes to yellow which implies the formation of CQDs. The volume of obtained CQDs was adjusted to 6.0 mL with deionized water and purified by dialysis against deionized water for 5 h (the cutoff of the dialysis membrane was equivalent to MW = 2000 Da).

2.4. Preparation of CQD/Ag nanocomposites

CQD/Ag nanocomposites were prepared by chemical reduction of $AgNO_3$ with CQDs at room temperature. 3.0 mL of the prepared CQD solution, 1.0 mL of 0.01 M $AgNO_3$ and 0.5 mL of 0.0625 M NH_3 were added into a 50-mL volumetric flask and diluted to the mark with deionized water. The reaction mixture was incubated at room temperature for 10 min. The obtained yellow solution of CQD/Ag nanocomposites was stable for more than one month in the refrigerator at 4° C (Fig. S1, Electronic Supplementary Materials, ESM).

2.5. General procedure for determination of methimazole

Typically, 2.5 mL of CQD/Ag nanocomposites and 200 μL of 0.12 M Britton–Robinson buffer solution (pH 4.0) were added into a 5.0-mL volumetric flask. Then, an appropriate amount of methimazole standard or sample solution was added and final volume of the mixture was adjusted to 5.0 mL with deionized water. After incubation for 15 min at room temperature, the absorbance was measured at 400 nm.

2.6. Sample preparation

Drug-free human urine samples were obtained from volunteers and spiked by adding suitable concentrations of standard methimazole. No special pretreatment was necessary for samples. 50 μL of each sample was taken for analysis according to the general procedure.

3. Results and discussion

3.1. Characterization of CQDs

In this work, a simple microwave-assisted method was used for synthesis of CQDs from glucose as a carbon source [39,40]. During the microwave heating, glucose is pyrolyzed and then converted to CQDs. TEM image of the CQDs, shown in Fig. 1a, indicates that the prepared CQDs are fairly uniform and their sizes are below 10 nm. UV–vis absorption spectrum of CQDs (Fig. 2a) exhibits two distinct absorption peaks at 226 and 281 nm, which are attributed to the π–π^* transition of C=C and the n–π^* transition of C=O, respectively [14]. The fluorescence spectra of CQDs are shown in Fig. S2 (ESM). As can be seen, the prepared CQDs exhibit an excitation-dependent fluorescence and maximum emission (~455 nm) is obtained with an excitation wavelength of 400 nm.

3.2. Characterization of CQD/Ag nanocomposites

We used the synthesized CQDs as reducing and stabilizing agents for preparation of stable CQD/Ag nanocomposites. According to the FT-IR spectrum (Fig. S3, ESM), there are some functional groups on the surface of CQDs such as hydroxyl, which possess reducing activity. Therefore, CQDs can serve as the electron donors in the reaction with electron-withdrawing agents. Moreover, FT-IR spectrum confirms the presence of carboxyl groups on the surface of CQDs which have a strong affinity for Ag^+ ions. So these ions are probably adsorbed on the surface of CQDs via carboxyl groups. Hence, CQDs can act as stabilizing agents to prevent the aggregation of the produced nanocomposites [8,10,12,25]. In order to confirm the formation of CQD/Ag nanocomposites, XRD pattern, EDS, XPS and Raman spectra of the as-prepared nanocomposites were recorded. According to EDS spectrum (Fig. S4, ESM), the carbon and Ag content of CQD/Ag nanocomposites is about 60.0 and 1.0 A%, respectively. The XPS spectrum shows C1s, Ag 3d and O1s peaks at 284, 367 and 531 eV, respectively (Fig. 3a). As demonstrated by high-resolution XPS of C1s (Fig. 3Ac), the as-prepared nanocomposites contain C—O, C=C and C=O groups. Additionally, the XPS peaks which appeared at 371 eV and 365 eV can be attributed to the binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$, respectively (Fig. 3b). These results confirm that AgNPs are decorated on the surface of CQDs. The carbon and Ag content of nanocomposite according to XPS was found to be 57 and 0.26 At%. The XRD pattern of nanocomposites