Journal of Colloid and Interface Science 437 (2015) 28–34

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Carbon dots functionalized by organosilane with double-sided anchoring for nanomolar Hg^{2+} detection

Wentai Wang [a,b,c], Tak Kim [a,b], Zifeng Yan [c], Guangshan Zhu [a], Ivan Cole [d], Nam-Trung Nguyen [a], Qin Li [a,b,*]

[a] Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane, QLD 4111, Australia
[b] Environmental Engineering, Griffith University, Brisbane, QLD 4111, Australia
[c] State Key Laboratory of Heavy Oil Processing Key Laboratory of CNPC, China University of Petroleum, Qingdao, China
[d] CSIRO Materials Science and Engineering, Victoria, Australia

ARTICLE INFO

Article history:
Received 13 July 2014
Accepted 7 September 2014
Available online 16 September 2014

Keywords:
Carbon dots
Fluorescent nanoparticles
Hg^{2+} detection
Water quality

ABSTRACT

Surface functional groups on carbon dots (CDs) play a critical role in defining their photoluminescence properties and functionalities. A new kind of organosilane-functionalized CDs (OS-CDs) were formed by a low temperature (150 °C) solvothermal synthesis of citric acid in N-(β-aminoethyl)-γ-aminopropylmethyl-dimethoxysilane (AEAPMS). Uniquely, the as-synthesized OS-CDs have dual long chain functional groups with both —NH_2 and —$Si(OCH_3)_3$ as terminal moieties. Double sided anchoring of AEAPMS on CDs occurs, facilitated by the water produced (and confined at the interface between CDs and solvent) when citric acid condenses into the carbon core. The resultant OS-CDs are multi-solvent dispersible, and more significantly, they exhibit excellent selectivity and sensitivity to Hg^{2+} with a linear detection range of 0–50 nM and detection limit of 1.35 nM. The sensitivity and selectivity to Hg^{2+} is preserved in highly complex fluids with a detection limit of 1.7 nM in spiked 1 M NaCl solution and a detection limit of 50 nM in municipal wastewater effluent. The results show that the OS-CDs synthesised by the solvothermal method in AEAPMS may be used as an effective Hg^{2+} sensor in practical situations.

1. Introduction

Despite being one of the most toxic heavy metal ions, mercury (Hg^{2+}) ion is widespread and widely used in industry, and causes serious environmental and health concerns [1–4]. With stringent regulations on Hg^{2+} contamination in drinking water in place (e.g. the maximum contamination limit for Hg^{2+} is 2 ppb in the USA [5], 1 ppb in Australia and the European Union [6,7]), detection and remediation of Hg^{2+} in water has always been a field of high importance. The increased necessity and practice in wastewater recycling in recent years has further increased the urgency of developing facile and accurate Hg^{2+} detection methods. Many analytical methods for Hg^{2+} detection have been developed including surface-enhanced Raman scattering (SERS) technique [8], surface plasmon resonances [9], inductively coupled plasma mass spectrometry [10], fluorescence chemosensors [11] and electrochemical methods [12], etc. Most of the Hg^{2+} fluorescence probes are metal-based, such as gold and silver nanoparticles and nanowires [13–15]. Organic molecules and semiconductor quantum dots were also applied as fluorescence probes for Hg^{2+} detection [15,16]. However, the above fluorescence probes possess some disadvantages, which greatly limit their practical applications, such as high cost, toxicity of the probe materials, poor stability and complex synthesis procedures. Therefore, new Hg^{2+} fluorescent probes that can overcome the above limitations are highly desirable.

Carbon dots (CDs) are a class of carbon-based nanoparticles that comprise discrete carbogenic nanoparticles with sizes below 10 nm. CDs have emerged as versatile fluorescent nanoparticles possessing unique features such as high quantum yields [17], nontoxicity, nonblinking, high photostability and vast accessibility [18–20], with strong potential to be applied in bio-imaging, sensing and optoelectronic devices [19,21–24]. CDs can be synthesized through a number of methods including laser ablation [25], electrochemical exfoliation [26], carrier-supported aqueous route [19], combustion route [27], hot injection [28], hydrothermal [29] and microwave treatment [30] etc. These methods generally result in hydrophilic CDs with abundant —COOH and —OH groups on surface, which are amenable for further functionalization.

Owing to the rich surface functional groups, CDs have been demonstrated as an effective fluorescence probe for the detection of copper ions [31], ferric ions [32], silver ions [33], as well as mercury ions [34] in water. The presence of the cation analyte quenches the CD fluorescence with the fluorescence intensity being proportional to the concentration of analytes, most likely

* Corresponding author at: Queensland Micro- and Nanotechnology Centre, Griffith University Nathan Campus, Brisbane, Australia. Fax: +61 7 555 28226.
E-mail address: qin.li@griffith.edu.au (Q. Li).

http://dx.doi.org/10.1016/j.jcis.2014.09.013
0021-9797/

due to the effect of electron transfer. In terms of Hg^{2+} sensing, CDs potentially offer advantages such as high sensitivity, economic and green synthesis routes, convenient detection procedures amongst others [35].

However, there is still much room for improvements in order to bring CDs closer to practical applications, such as simpler and more efficient synthesis methods, tunable emission bands, enhanced quantum yield (QY), heightened sensitivity, specificity and durability in complex fluids, such as wastewater effluent. Wastewater effluent contains large amount of organic matters, bacteria and viruses; it has high fluorescence background and is prone to interact or contaminate nanoparticle surfaces, representing a challenging sample type for fluorescence probes.

Herein, we report a new kind highly photoluminescent (PL) organosilane functionalized CDs (OS-CDs) for Hg^{2+} detection, which were synthesized by a low temperature solvothermal treatment of citric acid in coordination solvent, N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane (AEAPMS), in an enclosed system. In addition to high QY and excellent stability, the resultant OS-CDs show multi-solvent dispersibility, being dispersable in water and most of the common organic solvents. Importantly, the as-prepared OS-CDs is an effective fluorescence probe with superior selectivity and sensitivity to Hg^{2+} with a detection limit of 1.35 nM (0.27 ppb) and a linear range of 0–50 nM. Furthermore, the OS-CDs' sensing ability to Hg^{2+} in real municipal wastewater and water of high salinity is preserved, still achieving nanomolar sensitivity. This work may broaden the potential of OS-CDs in practical use for Hg^{2+} detection.

2. Material and methods

2.1. Materials

Citric acid anhydrous was purchased from Sigma–Aldrich. N-(β-aminoethyl-γ-aminopropylmethyldimethoxysila (AEAPMS) was purchased from Beijing Shenda Fine Chemical Co., Ltd. Sodium hydroxide, sodium chloride, potassium chloride, calcium chloride, magnesium sulfate, zinc sulfate heptahydrate, cadmium chloride hydrate, chromium trichloride and sodium hypochlorite were purchased from Chem-Supply. Hydrochloride acid, silver nitrate, mercury (II) chloride and cobaltous oxalate dehydrate, and solvents including dimethylsulfoxide (DMSO), methanol, dimethyl formamide (DMF), acetone, ethanol, tetrahydrofuran (THF), toluene and hexane were all purchased from Alfa Aesar. All chemicals and reagents were used as received without any further purification.

2.2. Synthesis of organosilane-functionalized CDs

The typical procedure of solvothermal synthesis of OS-CDs is as follows: 0.5 g citric acid anhydrous was added into 10 ml AEAPMS with continuous stirring. The mixture was then transferred into an autoclave with a PTFE inner vessel and placed in oven at 150 °C for 4 h. Brownish liquid was obtained after the reaction process. The product was dispersed in Milli-Q water or other appropriate solvents, followed by purifying three times with an Al_2O_3 filled chromatographic column for removing the residue reactants. The collected fraction was further filtered by a 0.22 μm syringe filter to remove the large particles. Finally, the solution was centrifuged for 30 min at 12,000 rpm for further purification, and the supernatant was collected as the product.

2.3. Characterization

The hydrodynamic particle size and zeta potential were measured by dynamic light scattering (DLS) on a Malvern Instrument Zetasizer Nano-ZS. Atomic force microscopy (AFM, Dimension 3000) analysis was carried out with tapping mode on a platinum coated mica substrate. FT-IR spectra were collected on a Perkin-Elmer Spectrum 100 with a resolution of 4 cm^{-1} in transmission mode. A baseline correction was applied after the measurement. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Kratos Axis Ultra photoelectron spectrometer which uses Al Kα (1253.6 eV) X-rays. The UV–vis absorption and fluorescence emission were measured by a Jasco V670 UV–VIS spectrometer and a Thermal Scientific Lumina fluorescence spectrometer, respectively. The concentration of CDs was determined by a gravimetric method (details in Supporting Information).

2.4. Multi-solvent dispersibility test

100 μL of OS-CDs was dropped into 5 ml of various solvents, such as DMSO, methanol, DMF, acetone, ethanol, THF, toluene and hexane, as well as Milli-Q water, respectively, and mixed uniformly. The samples were kept at the room temperature for 2 weeks.

To observe the transfer of CDs from toluene to water, 100 μL of OS-CDs was first dispersed into 5 ml toluene, and then 5 ml of Milli-Q water was slowly added into above solution. An interface was clearly observed between water and toluene. The vial was placed under a 365 nm UV lamp to observe the movement of OS-CDs between the organic and water phases.

2.5. Procedures for Hg^{2+} sensing

Detection of Hg^{2+} in pure water was performed at room temperature. OS-CDs solution with a given concentration was prepared before measurement. 2 ml of OS-CDs solution was transferred into a quartz cuvette followed by addition of calculated amount of Hg^{2+} solution. After mixing uniformly and incubating for 30 min, the PL emission spectra were collected.

Detection of Hg^{2+} in municipal wastewater effluent was tested in wastewater effluent which was collected from Redland Wastewater Treatment Plant, Brisbane, Australia, and has gone through secondary treatment. The wastewater sample was filtered with a 0.22 μm syringe filter firstly to remove large particles. A given concentration of OS-CDs in wastewater was then prepared. 2 ml of above OS-CDs in wastewater solution was transferred to a quartz cuvette for PL measurement. Hg^{2+} solution was then added into the vial step-wisely to increase the concentration from 1 nM. Each time after adding Hg^{2+} solution, a 30 min time interval was given to allow a good diffusion-driven mixing in the vial, before the PL measurement.

3. Results and discussion

3.1. Synthesis and physiochemical characterization of OS-CDs

The analysis of the OS-CDs morphology by transmission electron microscopy was challenging because the AEAPMS passivated OS-CDs tend to draw moisture from the air and turn into a gel-type material, similar to previous reports [28]. The AFM images of the OS-CDs in Fig. 1A provide the two-dimensional (2D) and 3D morphology. The size monodispersity of OS-CDs by counting the height of 150 particles was shown in Fig. 1B, indicating the size of OS-CDs is mainly distributed in the range of 1–2.5 nm. The DLS data (Fig. 1C) also shows a narrow size distribution in the range of 0.5–2 nm. The smaller size derived by DLS can be attributed to the better dispersion of CDs in water, whilst agglomeration may have occurred during the drying process of AFM sample preparation.