Sensors and Actuators B 259 (2018) 211–218

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Enhancing the quantum yield and Cu^{2+} sensing sensitivity of carbon dots based on the nano-space confinement effect of silica matrix

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ARTICLE INFO

Article history:
Received 17 August 2017
Received in revised form
29 November 2017
Accepted 11 December 2017
Available online 12 December 2017

Keywords:
Silica nanomatrix
Carbon dots
Fluorescence enhancement
Signal amplification
Cu^{2+} sensing

ABSTRACT

Although the analytical applications of the fluorescent carbon dots (CDs) were widely explored, the development of effective fluorescence signal amplification scheme based on the CDs was challengeable. In this work, we firstly found that, after CDs and polyethyleneimine (PEI) were together doped into silica nanoparticles via a reverse microemulsion route, the CDs inside as-prepared CDs/PEI/silica nanoparticles (CDs/PEI/SiO_2 NPs) presented the higher fluorescence quantum yield and stronger signal amplification ability than that of free-state CDs. Here, the possible fluorescence enhancing mechanism of CDs inside CDs/PEI/SiO_2 NPs was investigated by UV–vis absorption spectra, fluorescence spectra, IR spectra, transmission electron microscope and zeta potential technique and the possible mechanism was also proposed. In addition, the Cu^{2+} was selected as the model to investigate the signal amplification feature of the CDs/PEI/SiO_2 NPs. Our results showed that, encapsulation of CDs and PEI into silica NPs lead to a fluorescence enhancement of CDs, the fluorescence quantum yield of CDs increased from 13.7% to 38.6%. The as-prepared CDs/PEI/SiO_2 NPs exhibited 100-times sensitivity increasing for sensing Cu^{2+} compared with free-state CDs sensing scheme reported by the previous literature.

1. Introduction

In recent years, fluorescence signal amplification strategy, as one of the most promising directions to achieve the detection of the ultralow target species, has attracted tremendous attention [1–5]. For producing a novel signal amplification gain in response to ultralow analytes, different strategies such as the design and synthesis of excellent fluorophore molecular probes [6,7], sensing analytes by using conjugated polymers [5,8,9], incorporation of nanomaterials to increase loading of tags [1,10,11], etc. [12] have been reported.

Among these strategies, the silica nanomaterials-based fluorescence signal amplification platform [11,13–18] has been given much attention due to their advantages of easy synthesis and versatility. In this regard, the fluorescent dye-doped silica nanoparticles are of most popular since single silica nanoparticle could dope lots of dye molecules and present the great signal amplification ability [15,18]; however, the leaking effect of dye from silica particles and the limited photo-stability of dye molecules in silica matrix make these strategy challengeable in practical applications. Similarly, another paralleled widely applied fluorescence signal amplification scheme was developed by using dye-organized silica nanoparticles because they could sense the single target by the collective effect of the pre-organized fluorescence dyes [12,14]. However, the complicated chemical modification procedures for grafting dyes onto the surface or inside silica nanoparticles and the limited number of dye molecules for generating collective effect make this scheme challenged for highly sensitivity purpose. Thus, development of a new effective signal amplification scheme using silica nanoparticle is still desirable.

On the other hand, as new fluorescent nanomaterials, the carbon dots (CDs) have attracted tremendous attention in the past years due to their eminent properties such as chemical inertness, excellent photo-stability, tunable surface functionalities, good biocompatibility and low toxicity [19–21]. Based on these outstanding characteristics, the fluorescent CDs have been widely used in bioimaging [22–24], metal ions detection [25,26], catalysis [27] and photovoltaic devices [28,29] applications. However, up to now, to the best of our knowledge, no effective scheme was reported to explore the fluorescence signal amplification feature of CDs.

Herein, for the first time, we found that: after the PEI and CDs were together doped into silica nanoparticles via a reverse microemulsion route, the densely concentrated amine groups of PEI could greatly increase the fluorescence quantum yield of CDs

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https://doi.org/10.1016/j.snb.2017.12.061
0925-4005/

inside silica nanoparticles based on the nano-space confinement effect of rigid silica matrix and the supramolecular interaction of these amine groups of PEI with carboxyl groups of CDs. More importantly, compared to free-state CDs, based on the space confinement effect of silica matrix, the CDs inside as-prepared CDs/PEI/SiO_2 NPs presented the excellently fluorescence signal amplification ability to sense copper ions (Cu^{2+}). Our results showed that, compared to free-state CDs, except for about the 2.3 times quantum yield enhancing, the CDs/PEI/SiO_2 NPs presented a 100 times sensitivity increasing for sensing Cu^{2+}. In addition, compared to the dye pre-organized silica NPs signal amplification sensing scheme, the proposed scheme possessed the following advantages: firstly, the procedures for preparation of the CDs/PEI/SiO_2 NPs was very simple, they could be obtained by a one-pot method through a W/O microemulsion route; secondly, because the good photo-stability and the relatively large size of CDs, the CDs/PEI/SiO_2 NPs presented the excellent photo-stability and avoided the leaking effect of the fluorophores from silica NPs.

2. Experimental section

2.1. Chemicals and apparatus

Triton X-100 (TX-100), tetraethylorthosilicate (TEOS, 99.9%), polyethyleneimine with molecular weight 600 Da (PEI, 99.9%) was purchased from Sigma-Aldrich (United States); cyclohexane, acetone, ethanol and ammonium hydroxide (25–28 wt%) were obtained from Xian Chemical Reagent Factory; citric acid was obtained from Sinopharm Chemical Reagent Co., Ltd. (China); *n*-hexanol was purchased from Tianjin Chemical Reagent Factory; a stock solution of $Cu(NO_3)_2$ (0.01 M) was prepared, and then various concentrations were obtained by serial dilution of the stock solution; ultrapure water of which obtained from Milli-Q system (Millipore, 18.2 MΩ) was used in all experiments. All other reagents and solvents were of analytical grade and were used as received without further purification.

A multiposition magnetic stirrer (IKA, Germany) was used for preparation of nanoparticles. Nanoparticles were collected by a high-speed centrifuge (5804R, Eppendorf, Germany). A Tecnai G2 F20 transmission electron microscope (TEM, FEI in America) was used to characterize the morphology of nanoparticles. F-7000 fluorescence spectrophotometer (Hitachi, Japan) was used to measure fluorescence spectra of nanoparticles. UV–vis absorption spectra were characterized by an UV–vis spectrophotometer (U-3900, Hitachi).

2.2. The preparation of fluorescent PEI-passivated CDs

The PEI-passivated CDs were synthesized by a hydrothermal pyrolysis method according to the literature [26]. Briefly, 1.0 g of citric acid was dissolved in 10 mL of water and then was transferred into a teflon-lined stainless steel autoclave. Then, 5 mL of PEI solution (0.1 g mL^{-1}) was added under stirring, the mixture of PEI and citric acid was heated in an oven for 90 min (150 °C). The colorless mixture of PEI and citric acid turned into brown after being heated, suggesting the formation of CDs. Finally, the obtained CDs was purified by dialyzing against ultrapure water through dialysis membranes (Spectrumlabs, Rancho Dominguez, CA, USA) at 3000 Da cutoff for 48 h.

2.3. Synthesis of the CDs/PEI/SiO_2 NPs

CDs/PEI/SiO_2 NPs were synthesized by a one-pot method in room temperature through a reverse microemulsion route [30,31]. Briefly, 60 μL of as-prepared CDs solution and 50 μL of PEI (4–80 mg mL^{-1}) were added to the microemulsion solutions composed of TX-100 (1.77 mL), cyclohexane (7.50 mL), 1-hexanol (1.80 mL) and ultrapure water (300 μL). After the mixture was stirred for 1 h, 70 μL of TEOS and 50 μL of NH_4OH (25%–28%) were added. The ultimate mixture was stirred for 24 h to allow CDs/PEI/SiO_2 NPs formation. Then 6 mL of acetone was added to break the microemulsion and release the nanoparticles. The resultant particles were separated from the reaction mixture by centrifugation for 15 min (8000 rpm). The obtained CDs/PEI/SiO_2 NPs were washed two times with ethanol and three times with water.

3. Results and discussion

3.1. Characterization of the synthesized CDs

The TEM technique and the fluorescence spectra were used to characterize the synthesized CDs. The HRTEM results (as shown in Fig. 1) revealed that the sphere shape CDs were formed with sizes about 5 nm. Then, the fluorescence spectra of CDs at different excitation wavelengths were recorded. The results showed that, while the excitation wavelengths were red-shifted from 320 to 400 nm, the emission wavelengths of CDs changed from 464 to 485 nm gradually. The maximum excitation and emission wavelength of CDs was at about 360 nm and 475 nm, respectively (Fig. S1). This excitation-dependent fluorescence behavior was similar to that of

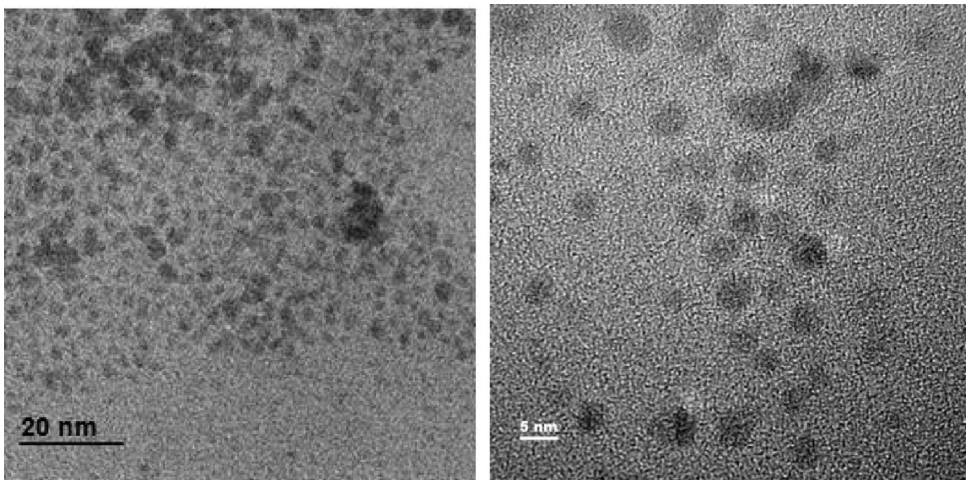

Fig. 1. HRTEM images of CDs.