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One-pot ultrafast preparation of silica quantum dots and their utilization for fabrication of luminescent mesoporous silica nanoparticles

Long Huang[a,1], Yurong Mu[a,1], Junyu Chen[a], Jianwen Tian[a], Qiang Huang[a], Hongye Huang[a], Fengjie Deng[a], Yuanqing Wen[a,*], Xiaoyong Zhang[a,*], Yen Wei[b,c,*]

[a] Department of Chemistry, Nanchang University, Nanchang 330031, China
[b] Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing 100084, China
[c] Department of Chemistry and Center for Nanotechnology, Chung-Yuan Christian University, Chung-Li 32023, Taiwan

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ABSTRACT

Silica quantum dots (SiQDs) and their luminescent composites have displayed great potential for biomedical applications owing to their chemical inert and low cost. In this work, we report a facile, cost-effective and ultrafast strategy to prepare a stable luminescent SiQDs using N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS) and salicylaldehyde as precursors for the first time. These luminescent SiQDs were further utilized for fabrication of luminescent mesoporous silica nanoparticles (MSNs) through direct encapsulation of SiQDs by MSNs. The novel synthetic and modified SiQDs uses commercial raw materials and the entire reaction can be completed within 30 s. The successful preparation of SiQDs and SiQDs@MSNs were characterized by various characterization equipments. The cell viability as well as cell uptake behavior of SiQDs@MSNs were also examined to evaluate their potential for biomedical applications. We demonstrated that these SiQDs@MSNs are low toxicity and of great potential for biological imaging. Based on the above results, we believe that these SiQDs@MSNs should be novel and promising candidates for biomedical applications owing to their intense fluorescence, biocompatibility and high specific surface areas.

1. Introduction

In recent years, the synthesis and applications of and luminescent nanomaterials and their composites have attracted the most research interest [1–15]. Among them, luminescent silica quantum dots (SiQDs) have been explored in many fields, such as biological imaging, optoelectronic devices, catalysis and drug delivery so on because of their unique optical properties, low toxicity, excellent surface tailorability, high natural abundance, low photobleaching properties, strong fluorescence and size dependent tunable emission [16–20]. The vast application prospect of SiQDs prompts their synthesis method becoming more updating and perfect [21–27]. For instance, Sato et al. synthesized nanometer-size SiQDs by reducing the original Si powders using etching solutions prepared by mixing with hydrofluoric acid (HF) and nitric acid [28]. The synthesized SiQDs demonstrated good control of emission wavelength, but involvement of high concentrations of HF. Erogbogbo and coworkers reported the preparation of water-dispersible and biocompatible SiQDs using phospholipid micelles [29]. Subsequently, He et al. presented a new microwave-assisted method for one-pot synthesis of water-dispersible SiQDs using silica nanowires (SiNWs) and glutaric acid as precursors without HF [30]. More recently, the doping of fluorescent carbon dots, organic dyes into silica nanoparticles has also been reported for the synthesis of luminescent nanoparticles recently [31–35]. The above methods described above have their respective merits. But all of them are facing the common problems: time-consuming, expensive. Meanwhile, for biological applications, surface modification of SiQDs is necessary, which is not only improving their hydrophilicity and biocompatibility, but also ameliorating the stability of SiQDs. In general, the modification methods of QDs mainly divide into three types: ligand exchange, grafting of polymers and silica shell capping. As compare with other methods, silica shell capping has many characteristics, such as its stability, biocompatibility, and versatile surface chemistry. Therefore, in this article SiQDs are encapsulated by mesoporous silica nanoparticles (MSNs) to improve stability, hydrophilicity and biocompatibility. Moreover, the MSNs possess large surface areas, which can be used for loading a large number of In conclusion, developing an efficient, fast and low-cost method to synthesize and modify high-quality SiQDs is important for the broad applications

* Corresponding authors.
E-mail addresses: m18600788382@163.com (Y. Wen), zhangxiaoyong@ncu.edu.cn (X. Zhang), weiyen@tsinghua.edu.cn (Y. Wei).
[1] These authors contributed equally to this work.

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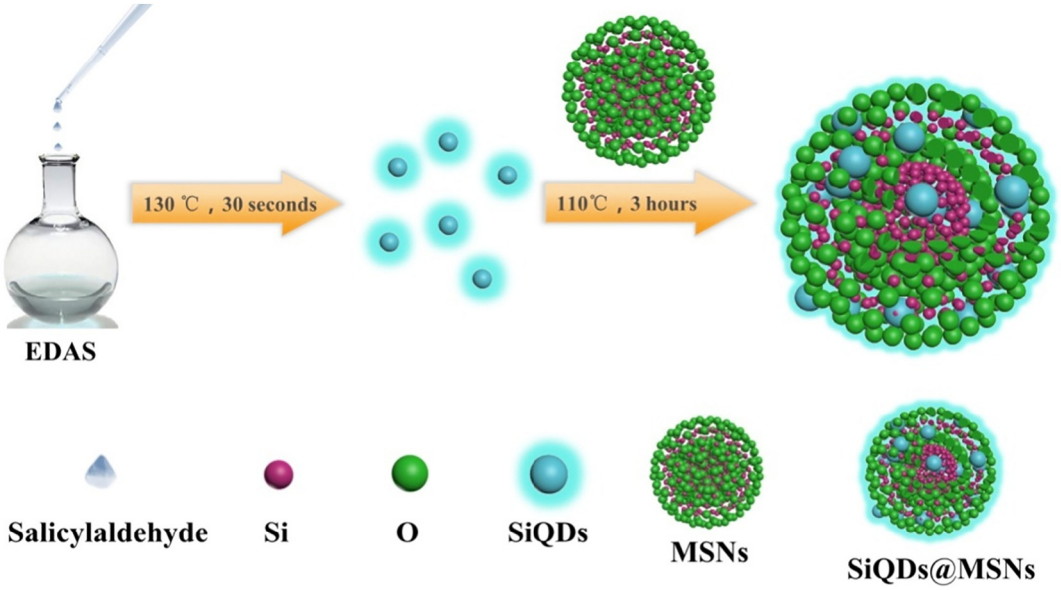

Scheme 1. The synthesis of SiQDs through the one-pot hydrothermal treatment and encapsulation of SiQDs into SiQDs@MSNs.

of SiQDs.

In this contribution, we report a facile, cost-effective and fast method to prepare a stable luminescent SiQDs. As illustrated in Scheme 1, N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS) was heated to 130 °C under nitrogen atmosphere, then salicylaldehyde was added rapidly and further reacted for 30 s. The resultant SiQDs with blue-green fluorescence can be obtained by dialysis of the crude products. The obtained SiQDs which took EDAS and salicylaldehyde as precursors are hydrophobic because their surfaces are covered with a large number of methoxyl groups. In order to improve the water solubility of SiQDs, these luminescent SiQDs are encapsulated by MSNs through condensing reaction between the methoxy groups of the SiQDs and hydroxyl groups of MSNs. SiQDs@MSNs that benefit from good biocompatibility, biological inertness and excellent hydrophilicity of MSNs exhibit low cytotoxicity and excellent hydrophilicity and biocompatibility. More importantly, their fluorescence stability in acid solutions is also greatly enhanced. With these excellent properties, the cell uptake behavior of SiQDs@MSNs was examined by Confocal Laser Scanning Microscope (CLSM) and results indicated that they can be effectively internalized by L929 cells. Moreover, the fast and efficient synthesis approach promises to be further explored to synthesize other quantum dots and the SiQDs modified by MSNs can even be used in other fields such as drug delivery, chemical sensor and so on.

2. Experimental procedures

2.1. Materials and instruments

N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS) (M_w: 222.36 Da, 95%) and salicylaldehyde (M_w: 122.12, 98%) were purchased from Aldrich. Cetyltrimethylammonium bromide (CTAB) (M_w: 364.45 Da, 99%) and tetraethyl ortho-orthosilicate (TEOS) (M_w: 208.33 Da, 99%) were supplied by Alfa Aesar. All of the reagents were of analytical grade and used as received without further purification. The microscopic morphology of the samples was observed by transmission electronic microscopy (TEM). The transmission electron microscope (TEM) micrographs were recorded on a Hitachi 7650B microscope operating at 120 kV. The TEM specimens were got by putting a drop of the sample ethanol suspension on a carbon-coated copper grid. Hydrodynamic size distribution of SiQDs and SiQDs@MSNs was determined by dynamic light scattering (DLS) based on a zeta Plus particle size analyzer (ZetaPlus, Brookhaven Instruments, Holtsville, NY). The characteristic functional group of the synthetic substances and materials were characterized by Fourier transform infrared (FT-IR) spectra. The FT-IR spectra were supplied from Nicolet 380 Fourier transform spectrometer by transmission mode ranging from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The fluorescence data including excitation and emission spectra were measured on fluorescence spectrophotometer (FSP, model: C11367-11) with a slit width of 10 nm, and the instrument of FSP were made in Hamamatsu (Japan).

2.2. Synthesis of SiQDs

10 mL of EDAS was put into a three-necked bottle which was full of nitrogen. The liquid was stirred and heated to 130 °C in the oil bath. And then 317 mg of salicylaldehyde was rapidly injected into the above liquid using a syringe. After 30 s, the reaction mixture was cooled to room temperature. Then the mixture was carefully poured into the dialysis bag (3500 Da). Subsequently, the sealed dialysis bag was placed in the sink with running water for 48 h. Finally, the final products (SiQDs) were obtained and then dried in a vacuum oven at 40 °C for 12 h.

2.3. Preparation of MSNs

In a round bottom flask, CTAB (100 mg, 0.274 mmol) and NaOH (30 mg, 0.75 mmol) were added to the ultrapure water (50 mL) and stirred violently at 80 °C for 0.5 h. Then the prepared 1 mL of TEOS was added dropwisely to above flask. After 4 h, the final mixture was separated by centrifugation at 8000 rpm for 3 min. The obtained white precipitate (impure MSNs) was washed by deionized water and ethanol for three times and dried at the vacuum drying oven at 40 °C for 24 h. In order to remove the residual template (CTAB), reflux and extraction were applied in the experiment. The impure MSNs which had been dried were dispersed in a methanolic solution of 6.00 mL of HCl (37.4%) in 100.00 mL of methanol and heated at 65 °C for 24 h. The resulting materials were separated and extensively washed with deionized water and methanol several times and dried in vacuum drying oven at 35 °C to yield pure MSNs.

2.4. Preparation of SiQDs@MSNs

The above pure MSNs (300 mg) was dispersed in 30 mL of toluene and stirred violently for 0.5 h. Moreover, 5 mL of SiQDs solution (30 mg