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Stable, small, and water-soluble Cu-doped ZnS quantum dots prepared via femtosecond laser ablation

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ABSTRACT

Cu-doped ZnS (ZnS:Cu) quantum dots were prepared in de-ionized water by femtosecond laser ablation of a bulk ZnS:Cu target. The obtained quantum dots exhibit good colloidal stability and water solubility, showing narrow and symmetric Cu-related emission, which is analogous to the well-known blue emission from bulk ZnS:Cu. The mean size of the quantum dots varies from 2.1 to 4.0 nm by changing the laser fluence, resulting in a redshift of the emission peak from 375 to 400 nm. The experimental results demonstrate that femtosecond laser ablation is an effective method for preparing doped quantum dots.

1. Introduction

Semiconductor nanocrystals or quantum dots, with the continuous tunability of their optical and electronic properties have been widely explored as biomedical labeling reagents since 1998 [1–7]. Doped semiconductor quantum dots, specifically ones not containing heavy metal ions, have the potential to become a class of mainstream emissive materials [6,7]. Besides their low toxicity, the doped emitters can also overcome a couple of intrinsic disadvantages of undoped ones, such as strong self-quenching caused by small ensemble Stokes shift [8] and the sensitivity to thermal, chemical, and photochemical disturbances [5]. Therefore, considerable efforts have been made to prepare high-quality doped quantum dots [6–12]. Generally, small, water-soluble doped quantum dots with relatively narrow size distribution are fabricated by a chemical method [5–7]. However, this method is usually complicated and inevitably introduces toxic byproducts. Therefore, developing a facile route of directly preparing high-quality doped quantum dots is necessary and challenging.

Laser-induced ablation of a solid target is known as an alternative physical method for nanofabrication. This method allows easy control of the quantum dots size and contamination byproducts, because the nanofabrication can be carried out in a controllable, contamination-free environment [13–16]. Therefore, laser-induced ablation has been widely developed to fabricate metal nanoparticles and semiconductor quantum dots in a gas/vacuum [13,17–19] as well as in a liquid medium [14–16,20–22]. Nevertheless, up to now, there is almost no report on preparing doped quantum dots via laser ablation.

In this Letter, we report the fabrication of water-soluble Cu-doped ZnS quantum dots in de-ionized water via femtosecond laser ablation. Herein, small and relatively homogeneous ZnS:Cu quantum dots with variable mean size are prepared by adjusting the laser fluence. The as-prepared samples show exceptional colloidal stability at least for one year. In addition, we also study their optical characteristics. The results indicate that the obtained quantum dots have widely potential applications in fluorescence biomedical labels.

2. Experimental

2.1. Sample preparation

The apparatus and parameters used for the laser ablation were similar to those used previously to prepare CdS quantum dots [16]. The typical experiment was carried out with a Ti/sapphire laser, which provides 100 fs at full width at half maximum pulses (wavelength of 800 nm, maximum energy of 1 mJ/pulse, repetition rate of 1 kHz). The laser beam was focused onto the target using a 5-cm focal length quartz lens to give pulse fluences between 2.0 and 2.9 J/cm^2. The corresponding samples were named as samples A, B, C, D, and E in turn as shown in Fig. 3. The spot radius of the laser beam on the target surface was adjusted to 50 μm. The laser irradiated vertically to a ZnS:Cu crystal plate that was fixed as the ablation target on the bottom of a cuvette filled with 3 ml of de-ionized water. The cuvette was placed on a three-dimensional optical adjusting rack, which repetitively moved horizontally at a constant speed of 0.1 mm/s. The height of the water layer above the target surface was about 6 mm. The ablations were performed during 60 min for sample C in order to obtain enough particles for XRD and XPS experiments and 5 min for all other samples.

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2.2. Measurements

X-ray diffraction (XRD) data were collected on a Rigaku D/max-rA X-ray diffractometer using a Cu target radiation source. The X-ray photoelectron spectra (XPS) were taken on a VG ESCALAB MK II electron energy spectrometer using Mg KR (1253.6 eV) as the X-ray excitation source. Absorption spectra were recorded on a UV-3101PC UV–vis–NIR scanning spectrophotometer (Shimadzu). Emission spectra of ZnS quantum dots were recorded on a Hitachi F-4500 spectrophotometer equipped with a 150 W Xe-arc lamp. Photoluminescence (PL) spectrum of target material was excited by the 365 nm line of a 150 W Hg lamp and the PL signal was detected by a CCD detector (spec-10, 400B/LN) in conjunction with a SpectraPro 2300i monochromator. Fluorescent dynamics was measured on an FL920-Fluorescence Lifetime spectrometer (Edinburgh Instruments) with MCP-PMT, in which the excitation source was an NF900 nanosecond flash lamp with 1 ns pulse duration. The particle size, distribution, and crystallinity were inspected with a transmission electron microscope (TEM, JEM-2010) and transmission electron diffraction (TED) techniques. All measurements were taken at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of ZnS:Cu quantum dots for sample C. The diffraction peaks observed at 28.6°, 47.5° and 56.4° can be index as cubic zinc blende phase (1 1 1), (2 2 0) and (3 1 1) diffraction peaks according to JCPDS No. 05-0566. No other diffraction peak is found, indicating the obtained sample is pure ZnS:Cu quantum dots. The peaks are broader than that of the ZnS bulk pattern, indicating the formation of nanocrystals. The crystallite size is estimated to be about 3 nm using the line widths of these diffraction peaks based on the Debye–Scherer formula.

The purity and composition of the nanoparticles were further examined by XPS as shown in Fig. 2. The binding energies (BE) are 161.3 eV for S_{2p}, 1022.8 and 1046.1 eV for $Zn_{2p}^{3/2}$ and $Zn_{2p}^{1/2}$, respectively, as shown in the insets of Fig. 2. These results are consistent with the BE values reported by Prathap et al. [23]. The Cu^{2+} XPS peak is nearly absent probably due to its very low concentration. The peaks of C_{1s} and O_{1s} might come from H_2O, O_2 and CO_2 adsorbed on the surface of the ZnS:Cu nanostructures in air. The survey spectra indicate that the product is pretty pure and no other by-products are found.

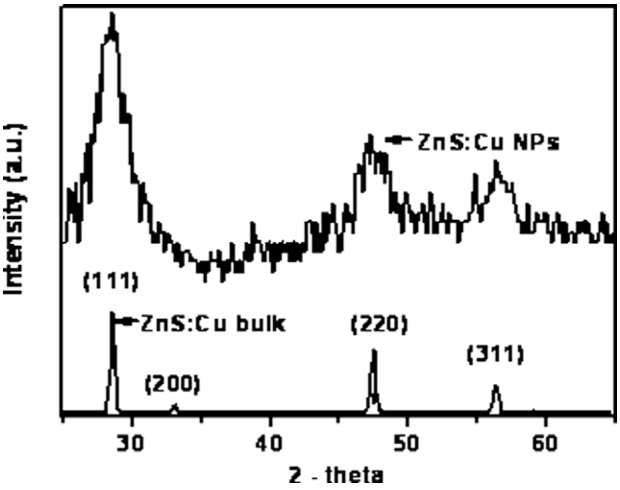

Fig. 1. X-ray diffraction patterns of ZnS:Cu bulk material and ZnS:Cu quantum dots ablated at 2.5 J/cm^2 (sample C).

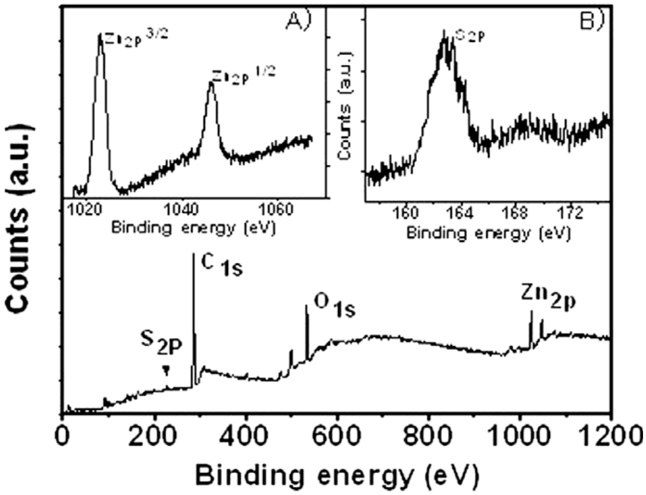

Fig. 2. Survey XPS spectrum for ZnS nanoparticles. Insets A and B correspond to Zn_{2p} and S_{2p} core spectra, respectively. The Zn 2*p* core is spin-orbit split into $2p^{3/2}$ and $2p^{1/2}$.

Fig. 3 shows UV–vis absorption spectra and TEM images of as-prepared ZnS:Cu quantum dots at different laser fluence. As seen in Fig. 3, the obtained ZnS:Cu quantum dots ablated at a laser fluence of 2.9 J/cm^2 (Sample E) exhibit a well-resolved $1S_e$–$1S_h$ excitonic transition of ZnS [24] at about 306 nm. The absorption shoulder is considerably blueshifted due to a quantum confinement effect compared to the absorption onset of bulk ZnS (337 nm). With decreasing the laser fluence from 2.9 to 2.0 J/cm^2, the excitonic absorption shoulder is shifted gradually to 278 nm from about 306 nm, suggesting that the quantum dots with a smaller size are produced at lower laser fluence. The result agrees well with our previous report and has been substantially explained by laser-matter interaction mechanics [16]. The TEM pictures and corresponding size distribution (where sizes of about 150 quantum dots are manually measured according to TEM images) of quantum dots in Fig. 3 show that they are homogeneous in size and the single-peak Gaussian extrapolation is adequate for all the three samples. The mean sizes determine to be about 4.0, 2.9, and 2.1 nm, respectively, for samples E, C, and A, which agree well with the theory of tight-binding scheme [25]. The transmission electron diffraction (TED) results further reveal that ZnS:Cu quantum dots with the cubic zinc blende structure and the particles are aggregates of smaller crystallites (see insets in Fig. 3).

From the TEM pictures, we can see all three samples are homogeneous in size. To some extent, the size distribution is greatly associated with the laser parameters such as pulse duration, repetition rates, and focal spot size, which directly affect the ablation mechanism. When the femtosecond radiation acts on the target, the electrons localized on the target surface will be ionized due to nonlinear electrodynamical process, resulting in the formation of hot electron plasma, localized electronic and vibrational excitations [26]. Then energy will transfer by radiative and non-radiative relaxation in plasma and phonon system. At last, the after-heating process will play an important role when the repetition rate is higher than the critical value [26]. In our case, because the repetition rate of 1 kHz is lower than the critical value [26] for ZnS:Cu at focal spot radius of 50 μm, the after-heating process can play a small and insignificant role. Thus the high-temperature effects such as melting, evaporation are absent and non-thermal processes can be expected to dominate at all stages. Therefore, the formation of nanoparticles is only related to the atoms and nanoscale clusters which ejected from the expansion of hot electric plasma [27] at first stage. The absence of the after-heating process can counteract