

Microwave-assisted One-pot Synthesis of Yellow Cu: ZnSe/ZnS Quantum Dots Using Selenium Dioxide Containing Copper Impurity

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Abstract

Cu:ZnSe/ZnS core/shell quantum dots exhibiting yellow fluorescent emission were synthesized in aqueous phase via a one-pot microwave irradiation approach, where glutathione (GSH) as stabilizer and selenium dioxide (SeO₂) containing Cu as selenium source, respectively. The QDs obtained at the optimal conditions without any post-treatment present high crystallinity, which was confirmed by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The core/shell structure was confirmed by X-ray photoelectron spectra (XPS) and Powder X-ray diffraction (XRD). The binding of GSH on the surface of QDs through thiol ligands was proved by the characterization of Fourier Transform Infrared Spectroscopy (FTIR), suggesting the biocompatibility of the obtained QDs.

Keywords: Cu:ZnSe/ZnS QDs; Microwave Irradiation; Selenium Dioxide

1 INTRODUCTION

Recently, semiconductor quantum dots (QDs) have aroused tremendous research interests in the fields of physics, chemistry, biology and engineering. Because of quantum confinement effect, QDs have shown some unique physical and chemical properties when their size is close to or smaller than the dimension of exciton within corresponding bulk materials [1–3]. Regarding the inherent toxicity of cadmium-based QDs such as CdSe, CdTe and CdS that may hinder the safe use in biological systems [4–6], it is of great significance to develop a kind of less toxic labeling material which does not contain any Class A element (Cd, Pb, and Hg). ZnSe QDs come into being in such a case. Generally, the bulk emission of ZnSe QDs is located in the UV-blue spectral region (less than 500 nm), metal impurities such as Cu, Mn are often added as dopant into the crystalline ZnSe QDs (d-dots) in order to modulate the emission of ZnSe QDs into the visible range. In 2001, Norris et al. developed an organometallic method for the synthesis of Mn-doped ZnSe (Mn:ZnSe) QDs and confirmed that the Mn impurities were embedded inside the nanocrystals [7]. In 2005, Peng et al. introduced the nucleation-doping strategy in the preparation of Mn:ZnSe QDs using high-temperature organometallic synthesis[8]. However, these procedures are environmentally unfriendly, and the as-prepared QDs cannot directly used for biological system. In recent year, direct synthesis of doped quantum dots (d-dots) in aqueous solution was more appealing though the procedure was much more difficult due to the employment of different solvents, precursors, reaction conditions and reaction mechanisms [9]. In 2009, Zhang et al. showed the first case of aqueous synthesis of internally doped Cu:ZnSe QDs[10]. Unfortunately, the as-prepared QDs presented poor chemical stability. Later, Xu et al. reported the improved method for the synthesis of Cu:ZnSe/ZnS QDs with excellent stability through two-step reactions in which the core/shell structure and the internal- doped impurities provided dual protection for the doped Cu impurities[11]. Dong et al. also investigated a two-step method to synthesize water-soluble ZnSe:Mn/ZnS core/shell d-dots[12]. To the best of our knowledge, no report has been published on the aqueous one-pot synthesis of Cu:ZnSe/ZnS core/shell QDs with selenium dioxide containing Cu as Se source.

Herein, we developed a green and rapid route for the synthesis of low-toxic Cu:ZnSe/ZnS core/shell QDs using

microwave irradiation and SeO₂ containing Cu impurities as Se source and Cu source, respectively.

2 MATERIAL AND METHODS

2.1 Chemicals and Device

Zinc acetate (Zn(Ac)₂•2H₂O, 99.0+%), L-glutathione (GSH, 98+%) and reagent grade isopropanol were all obtained from Sigma-Aldrich and used as received without any further purification, while selenium dioxide (containing 0.017% Cu impurities, 98%) and other routine chemicals were purchased from Shenshi Chem. Ltd. All the operations were carried out in aqueous solution and ultrapure water (18.2 MΩcm⁻¹) was used throughout. The synthesis of Cu:ZnSe/ZnS core/shell QDs was performed on a microwave digestion/extraction system (Milestone, Italy) with some exclusive inner vessels.

2.2 Synthesis of Aqueous Cu: ZnSe/ZnS Core/shell QDs

Typically, 166 mg (0.9 mmol) Zn(Ac)₂•2H₂O and 369 mg (1.2 mmol) glutathione (GSH) were dissolved in 200 ml ultrapure water and stirred for 10 min without bubbling with inert gases. Then the solution was adjusted to pH 10.4 using NaOH solution before 5.6 mg (0.05 mmol) selenium dioxide was introduced. After stirring for another 10 min, the resulting solution was transferred to the microwave exclusive vessel and placed inside the digestion furnace to irradiate at 98 °C for 60 min (700 W). After the reaction, the irradiated solution was cooled down to room temperature naturally and the as-prepared QDs were used directly for FL scanning without any post-treatments. The as-prepared QDs could be purified by precipitation and centrifugation using isopropanol as precipitator and the solid sample used for the characterization of XRD, XPS and FTIR could be obtained through lyophilization.

2.3 Characterization of Cu:ZnSe/ZnS Core/Shell QDs

UV-vis absorption spectra were performed on a UV-1601 (Shimadzu, Japan) UV-vis spectrophotometer, and FL spectra were conducted on an F-4600 (Hitachi, Japan) fluorophotometer, respectively. X ray fluorescence spectroscopy (XRF) was obtained on a S4 Pioneer spectrometer (Bruker AXS). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were acquired on a JEM 2100 high-resolution transmission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was obtained on a XSAM-800 apparatus (Kratos, England) using Mg-Kα source at 1253.6 eV. Powder X-ray diffraction (XRD) was carried out on a MiniFlex AXS CD8 X-ray powder diffractometer (Bruker, Germany) with graphite monochromatized Cu Kα radiation (λ=1.54178 Å). Fourier Transform Infrared Spectroscopy (FTIR) was performed with an iS50 FT-IR spectrometer (Thermo Fisher Nicole, US) through potassium bromide tableting.

3 RESULTS AND DISCUSSION

3.1 Synthesis of Cu:ZnSe/ZnS Core/shell QDs

Generally, the synthesis of Cu:ZnSe/ZnS core/shell QDs was realized through a two-step route. Firstly, Cu:ZnSe QDs were prepared in aqueous solution by heating a mixture containing Zn²⁺, Cu²⁺, thiol stabilizer and some active Se source (NaHSe or H₂Se). Then, protective ZnS shells for solving the intrinsic instability outside core QDs were formed by injecting the as-prepared Cu:ZnSe QDs into the mixture of Zn²⁺, thiol stabilizer and some kind of S source such as thioacetamide (TAA) at low temperatures[11]. Based on the work of Ma et al. on the synthesis of ZnSe/ZnS core/shell QDs[13], we reported the first work of one-pot aqueous synthesis of Cu:ZnSe/ZnS QDs using a kind of Se source containing Cu via a microwave irradiation.

In our previous experiment design, we tried to prepare ZnSe /ZnS core/shell QDs using SeO₂ as Se source according to the Ma's method [13]. While in fact, only yellow fluorescence was obtained, totally different from that of ZnSe /ZnS QDs with strong blue fluorescence emission. So SeO₂ were used to analyze the element contents by XRF and the result was shown in Table 1.

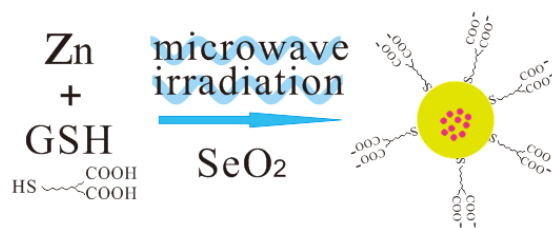


FIG. 1 SCHEMATIC ILLUSTRATION OF SYNTHESIS OF WATER-SOLUBLE Cu:ZnSe /ZnS CORE/SHELL QDs.

TABLE 1 THE ELEMENT CONTENTS OF SeO₂ CHARACTERIZED BY XRF.

Element	O	Mg	Al	Si	Cu	Se
Content (%)	29.1	1.07	0.300	0.028	0.017	69.4

Obviously, except the main element Se and O in the sample of SeO₂, there are some impurities such as Mg, Al Si and Cu. Though the content of Cu was very low, it would probably cause the change of the fluorescence emission of the obtained QDs. To further verify our conjecture, high-purity SeO₂ without Cu from another manufacture was used in the reaction and no yellow fluorescence emission was observed (data not shown). So the Cu impurity in SeO₂ was the key factor for the optical properties of the obtained QDs. That is, using SeO₂ containing Cu in the synthesis of ZnSe/ZnS QDs, we got Cu:ZnSe /ZnS core/shell QDs. This unexpected finding provided a new design route for the synthesis of metal-doped QDs.

3.2. Optical Properties and Structural Characterization

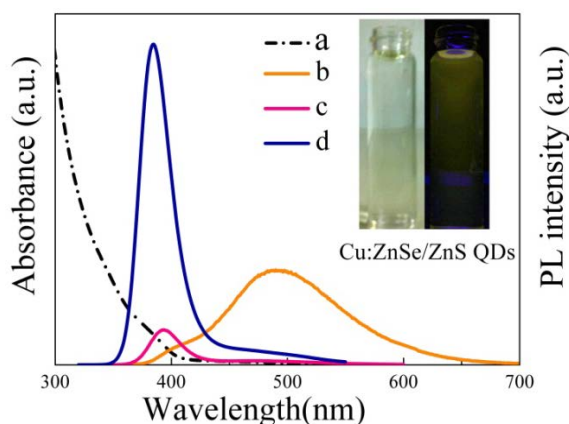


FIG. 2 UV-VIS ABSORPTION (A), FLUORESCENCE SPECTRA OF Cu:ZnSe/ZnS QDs (B), ZnSe/ZnS QDs (C, D) SYNTHESIZED WITH NaHSe AND Na₂SeSO₃ AS SE SOURCE, RESPECTIVELY. INSET SHOWS THE DIGITAL PICTURES OF Cu:ZnSe/ZnS QDs UNDER ROOM LIGHT (LEFT) AND 365 NM UV (RIGHT) RADIATION.

The GSH/Zn/Se molar ratio, microwave irradiation temperature, time and pH value of the precursor solution are the crucial factors for the PL properties of the as-prepared Cu:ZnSe/ZnS QDs. Fig. 2 displayed the representative UV-vis absorption and fluorescence spectra of Cu:ZnSe/ZnS QDs obtained under the optimal experimental conditions. Obviously, both the absorption spectra and fluorescence spectra present the characteristic structure of semiconductor nanocrystals. Moreover, the fluorescence spectra displayed broad full-width at halfmaximum (FWHM) since the emission of Cu:ZnSe/ZnS QDs mainly comes from the level of Cu impurities, which agreed well with the previous report [11]. For comparison, the fluorescence spectra of ZnSe/ZnS QDs synthesized with NaHSe and Na₂SeSO₃ as Se source, respectively, were also shown in Fig.2. One can clearly see that, both the fluorescence spectra of ZnSe/ZnS QDs obtained with NaHSe and Na₂SeSO₃ as Se source presented band edge emission in the near-ultraviolet region with a very narrow FWHM though there were differences in their fluorescence strength, which completely different from that of Cu:ZnSe/ZnS QDs. The yellow fluorescence of the as-prepared Cu:ZnSe/ZnS QDs under irradiation with a 365 nm ultraviolet light was also shown in the digital picture, which corresponded well with the fluorescence spectra.

The crystal structure of the obtained Cu:ZnSe/ZnS QDs were displayed by the XRD pattern as presented in Fig. 3. It can be noted that the broad peaks are typical for semiconductor nanoparticles. Three strong diffraction peaks located

at 28.6°, 48.4° and 57.1°, respectively, were much closer to the (111), (220) and (311) planes of cubic ZnS structure (JCPDS No. 05-0566) rather than that of cubic ZnSe (JCPDS No. 37-1463), indicating the presence of ZnSe/ZnS core/shell structure. The crystalline sizes of the Cu:ZnSe/ZnS QDs can be obtained by Scherrer's equation[14] with the (111) peak and the calculated average size was 4.2 nm, which agreed well with the result from the TEM and HRTEM observation.

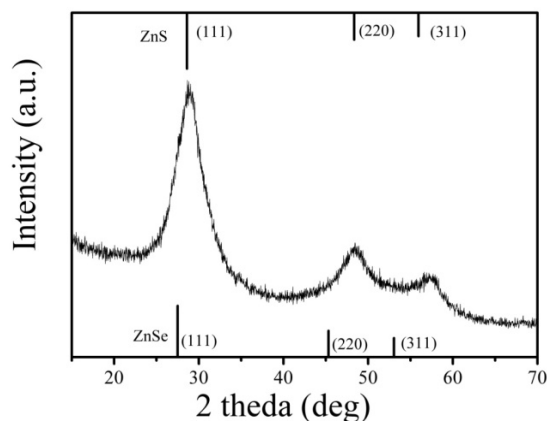


FIG. 3. XRD PATTERNS OF Cu:ZnSe/ZnS QD. STANDARD DIFFRACTION LINES OF CUBIC ZnSe AND CUBIC ZnS ARE ALSO SHOWN FOR COMPARISON.

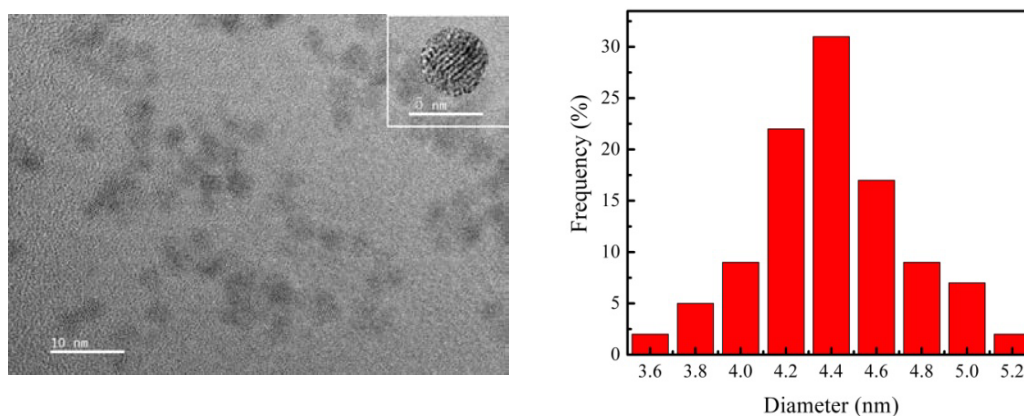


FIG. 4 TEM, HRTEM IMAGES AND THE PARTICLE SIZE DISTRIBUTIONS OF THE OBTAINED Cu:ZnSe/ZnS QDs. SCALE BARS ARE 10 NM (TEM) AND 5 NM (HRTEM), RESPECTIVELY.

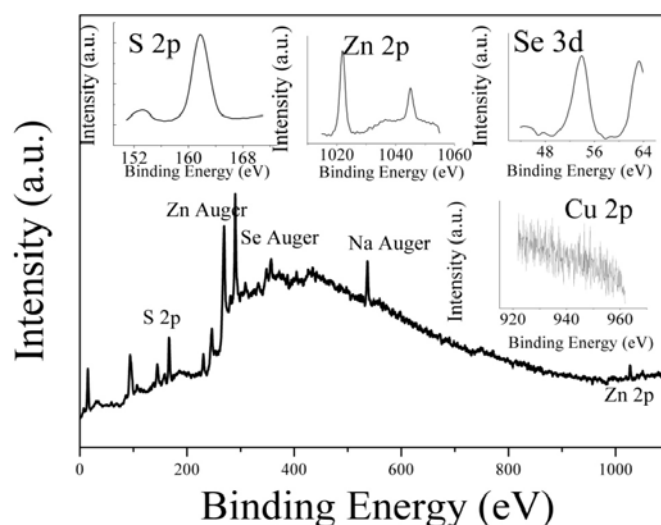


FIG. 5 SURVEY X-RAY PHOTOELECTRON SPECTRA (XPS) OF Cu:ZnSe/ZnS CORE/SHELL QDs. THE INSETS SHOW THE DETAILS OF THE S 2p, Se 3d, Zn 2p AND Cu 2p SPECTRA, RESPECTIVELY.

The TEM, HRTEM images and the corresponding particle size distribution of the obtained Cu:ZnSe/ZnS QDs were shown in Fig.4. One can clearly observe that the obtained Cu:ZnSe/ZnS QDs displayed nearly spherical shape. The diameters of the nanoparticles were measured to be 4.4 ± 0.8 nm via counting each individual size for 200 particles in the TEM images. The obvious lattice planes that extend straight across the nanoparticles from the HRTEM images suggest the high degree of crystallinity of the obtained Cu:ZnSe/ZnS QDs.

As an efficient technique to identify the surface compositions and structures of semiconductor QDs, X-ray photoelectron spectroscopy (XPS) were used to analyze the obtained Cu:ZnSe/ZnS QDs and the results were displayed in Fig. 5. The Survey XPS of Cu:ZnSe/ZnS core/shell QDs showed the characteristic Zn 2p peak at 1022.3 eV, S 2p peak at 161.8 eV, and Se 3d peak at 54.1 eV, respectively, suggesting the presence of these elements. It is worth noting that, no obvious peaks of Cu were observed in the obtained QDs, which could due to the very low content of Cu in the sample. Additionally, only one peak of S at 161.8 eV was observed, which is attributed to S₂– in the ZnS shell, not the peak at 161.1 which is assigned to Zn-GSH on the QDs surface [15-17]. This agreed well with that of 161.7 eV for the reported hydrothermal synthesized Cu:ZnSe/ZnS QDs[11]. The XPS result provided another evidence of the core/shell structure of the obtained Cu:ZnSe/ZnS QDs. With the protective shells, the internally doped ZnSe QDs can improve their fluorescence stability in different surroundings [18,19].

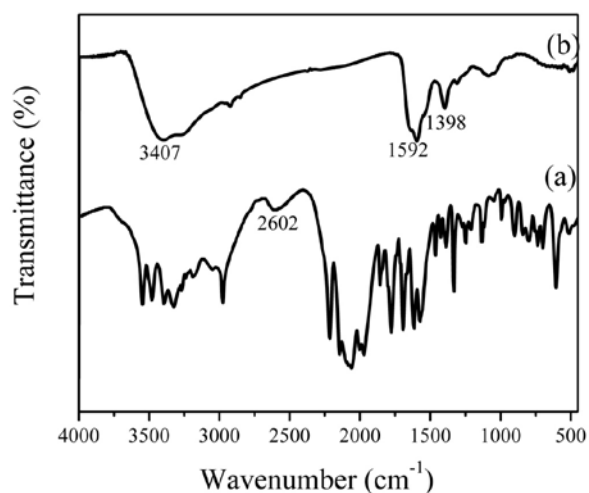


FIG. 6 FT-IR SPECTRA OF PURE GSH (A) AND Cu:ZnSe/ZnS CORE/SHELL QDs (B), RESPECTIVELY.

In order to investigate the chemical composition of the ligands capping on the surface of the Cu:ZnSe/ZnS core/shell QDs, a further characterization of Fourier Transform Infrared Spectroscopy (FTIR) of pure GSH and Cu:ZnSe/ZnS QDs was performed and the results were displayed in Fig. 6. One can clearly see that, the obvious change was the characteristic S–H stretching vibration at 2602 cm⁻¹ in the spectroscopy of GSH disappeared in that of Cu:ZnSe/ZnS QDs, suggesting that GSH binds on the surface of QDs through S-H groups[20]. The other characteristic peaks such as O–H vibration, N–H vibration, C=O vibration, C–O vibration and C–N vibration presented with small shifts not only in the spectroscopy of GSH but also in that of Cu:ZnSe/ZnS QDs, implying both carboxyl and amino functional groups exist on the surface of the obtained QDs. All these data proved the successful binding of GSH on the surface of the obtained QDs. GSH is found mainly in the cell cytosol and other aqueous phases of the living system. So GSH is considered as one of the most common biocompatible thiol ligands, which makes the obtained QDs highly biocompatible when used as biological probes.

4 CONCLUSIONS

In conclusion, we described a simple one-step route to prepare high-quality Cu:ZnSe/ZnS core/shell QDs via microwave irradiation. Our data demonstrated that the key factor influenced the fluorescence properties was the Cu impurity in the Se source SeO₂. The results of XRD and XPS illustrated that the obtained QDs possess a core-shell structure, that is Cu:ZnSe/ZnS QDs, rather than Cu:ZnSe QDs. The images of TEM and HRTEM suggest the high degree of crystallinity and the binding of GSH endowed this nanomaterial with high biocompatibility, which can be expected to have wide applications for fluorescent probes in biolabelling and imaging.

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