

Preparation and Effect of Lighting on Structures and Properties of GSH Capped ZnSe QDs

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Abstract L-glutathione (GSH) capped ZnSe quantum dots (QDs) were prepared by microwave-assisted aqueous synthesis. Then, the resulting QDs were illuminated under dark, ultraviolet light and incandescent light, respectively. Thereby effect of lighting on the structures and properties of QDs were studied systematically. It was revealed that particle size and element content of QDs took a sharp change after irradiation, while the crystal structure maintains nearly unaffected. Comparing to the ZnSe QDs under dark condition, counterparts irradiated by UV light possessed outstanding sphericity, size distribution and dispersion. And the content of sulfur (S) in ZnSe QDs irradiated by UV light was much higher relatively. The effect of lighting on vibration peaks of O–H was considerable. However, this effect was observed to be weak on other chemical bonds. The possible explanation ascribes to photo-chemical interactions can occur between S–H and O–H bonds on the surface of GSH ligand. The lighting induced GSH to occur photocatalytic oxidation on the surface of ZnSe QDs, which improved the optical properties of QDs. The effects of lighting rely on irradiation types, the sequence is UV light, incandescent light and dark from high to low.

Keywords ZnSe quantum dots · Lighting · Structures and properties · Mechanism

Introduction

Quantum dots (QDs) are semiconducting nanocrystals that are generally composed of group II–IV or III–V elements. These dots have unique physical, chemical, and optical properties due to size effect and quantum effect. QDs have narrow emission range, broad UV excitation range, and bright fluorescence, which render these dots a promising fluorescent probe and energy material [1, 2]. Therefore, in recent years, QDs have gained extensive attention [3–5].

However, QDs are somehow unstable under exposure to environment. Since physical and chemically reactions such as photocatalytic oxidation and peeling off of the ligands, splitting of protective shell, agglomeration of particles and digestion of core ion can occur under irradiation, which affects the structures and properties of QDs [6]. Photophysical properties of semiconductor QDs are primary determinants of their efficiency as fluorescence probes in biological systems [7]. In 2001, Aldana et al. [8] found that QDs modified by small hydrophilic sulfhydryl molecules were unstable in presence of light and oxygen. After undergoing three processes, namely, photocatalytic oxidation of thiol ligands on the surface of QDs, surface oxidation of QDs nanocrystals and subsiding and aggregating, finally QDs precipitated from the solution. Ma et al. [9] studied the confocal laser bleaching of QDs modified by sulfhydryl in euglena gracilis klebs 277 cell. They found that QDs were very stable when optical density was at $8 \times 10^{-5} \text{ W} \cdot \mu\text{m}^{-3}$. However, the light bleaching of QDs occurred in a few seconds when optical density increased to $6.4 \times 10^{-3} \text{ W} \cdot \mu\text{m}^{-2}$. This statement confirmed the photo instability of QDs as well. The prior advancements showed that

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lighting played a crucial role on the structure stability of QDs, and thereby affected the cytotoxicity of QDs. However, little attention was paid to concern the effect of lighting on structures and properties of QDs. In order to investigate the preparation and environmental chemical action of QDs, the studies of lighting effect on structures and properties of QDs and the mechanism behind would be of great significance.

In this study, GSH capped ZnSe QDs were prepared by microwave-assisted aqueous synthesis. And then, the ZnSe QDs samples were treated under dark, UV light and incandescent light conditions, respectively. We studied the influence of spectroscopic properties by UV–Vis absorption and fluorescence (FL) spectra. The structures and properties change of ZnSe QDs were verified by inductively coupled plasma-atomic emission spectrometry (ICP-AES), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Eventually, the mechanism behind the lighting effect on ZnSe QDs was explored.

Experimental Section

Materials

L-glutathione (GSH), zinc acetate ($\text{Zn}(\text{OAc})_2$), selenium powder (Se), potassium borohydride (KBH_4), sodium hydroxide (NaOH), isopropanol ($\text{C}_3\text{H}_8\text{O}$), Tris (hydroxymethyl) aminomethane, and other routine chemicals were purchased from Shenshi Chem. Ltd. All the chemicals used were of analytical grade and double distilled deionized water was used in all experiments.

Preparation of GSH Capped ZnSe QDs

In a typical procedure, the ZnSe precursor solution was prepared by adding freshly prepared KHSe solution to a Ar-saturated $\text{Zn}(\text{Ac})_2$ solution in the presence of L-Glutathione (GSH) as a stabilizer. The molar ratio of Zn:Se:GSH was set at 1: 0.1: 1.6. A 1 mL volume of ZnSe precursor solution was injected into the high pressure digestion tank with a volume of 100 mL. A series of high-quality ZnSe nanocrystals were prepared under microwave irradiation. After microwave irradiation, the reaction was terminated by allowing the reaction mixture to cool down to room temperature naturally. The obtained ZnSe@ZnS QDs sample was purified by centrifugation and decantation with the addition of isopropanol. Finally, these QDs were dissolved in Tris–HCl buffer solution and stored at 277 K.

Light Treatment of GSH Capped ZnSe QDs

To investigate the effect of lighting on structures and properties of QDs, the purified ZnSe QDs were assigned into three

groups, and then the three groups QDs were irradiated for 6 h under dark, UV light and incandescent light conditions, respectively. During the lighting experiments, the intensity of all lights nearly kept constant within the environmental irradiation range. The irradiated ZnSe QDs were freeze-dried into the powder samples and stored at dark.

Material Characterization

All absorption and fluorescence (FL) spectra of QD samples in aqueous solution were obtained at room temperature with a UV-1601PC (Shimadzu, Japan) UV–Vis spectrometer and a F-4500 (Hitachi, Japan) fluorophotometer with a cell of 1.0 cm path length, respectively. A 2 mL solution, containing appropriate concentration of QDs was poured into a cell. UV–visible spectra of all solutions were recorded in the range of 200–800 nm. The fluorescent intensity of the solution was recorded at excitation wavelength of 350 nm by using F-4500 fluorometer, and the slit widths used for excitation and emission were 5 nm, respectively.

The phase composition, morphology and microstructure of the QD samples were characterized using the following methods. The Zn, Se and S content were analyzed by Optima 4300DV Inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer). High resolution transmission electron microscopy (HRTEM) images were taken on a JEM-2010FER (WHR) transmission electron microscope with an X-ray energy dispersive spectroscopy (EDS) at an accelerating voltage of 20 kV. To prepare the HRTEM samples, a few droplet of dilute alcohol solution was dripped onto a carbon-coated copper grid, then dried at room temperature. X-ray powder diffraction (XRD) measurements were performed on a Bruker-AXS CD8 X-ray powder diffractometer with graphite monochromatized $\text{Cu K}\alpha$. A scanning rate of 0.05 deg/s was applied to record the pattern in the 2θ range of 10–70. The fourier transform infrared (FTIR) spectra were recorded on a NICOLET 5700 FTIR in the wave-number range of 4000–400 cm^{-1} . The spectra were collected at 2 cm^{-1} resolution with 128 scans by preparing KBr pellets with a 1:100 “sample-to-KBr” ratio.

Results and Discussion

Effect of Light Condition on Structure and Property of ZnSe QDs

UV–Vis Absorption and Fluorescence Spectra

The absorption and FL spectra of GSH capped ZnSe QDs under three different light irradiation conditions are shown in Fig. 1. As can be seen from Fig. 1, compared to dark, UV and Incandescent lights illumination make the UV-visible absorption and FL peak of QDs show few red shift slightly. But the

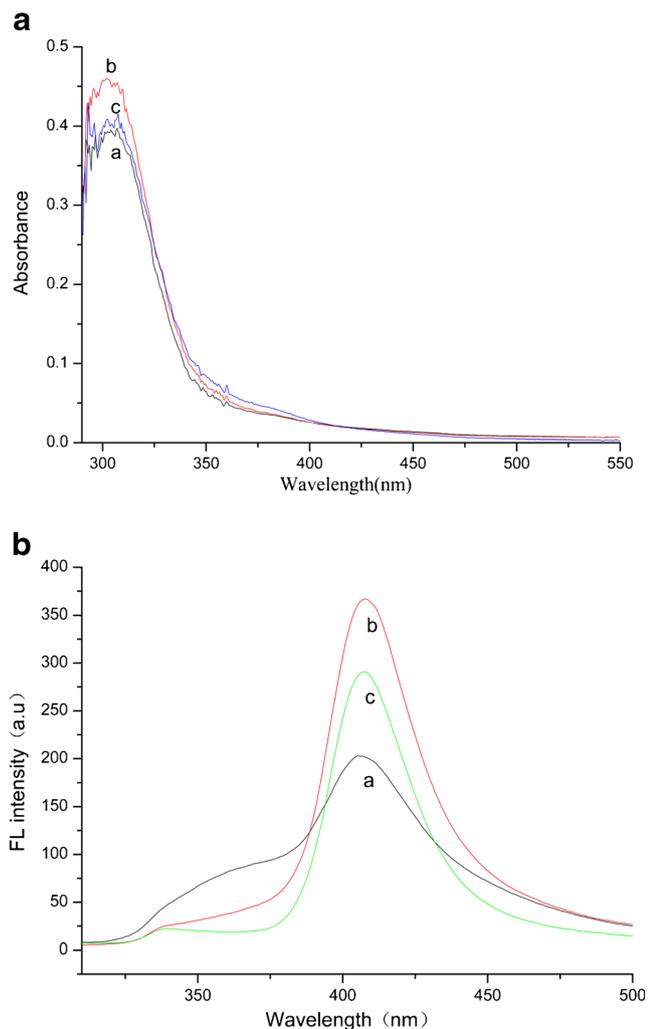


Fig. 1 **a** UV-Vis absorption spectra and **b** Fluorescence spectrum of ZnSe QDs under different light conditons (*a*: Dark; *b*: UV light; *c*: Incandescent light)

UV-visible absorption and FL peak intensity of QDs both increased dramatically, and the full width at half maximum (FWHM) of FL peak decreased in the following order (*a*→*c*→*b*). Among the three light conditions, the largest effect factor is the UV light, followed by Incandescent light and dark in sequence. This might be because the ZnSe QDs are not stable, and the passivation degree of ZnS shell on the surface of ZnSe core is not enough [10]. This can be confirmed by Table 1. From Table 1, we can see the molar ratio of S²⁻ and Zn²⁺ of ZnSe QDs increased under different light effect in this

order, *a*:14→*c*:15.1→*b*:16.8, which is in agreement with the change order of UV-visible absorption and FL peak.

The peak intensity increase of ZnSe QDs is due to the forming of ZnSe/ZnS core-shell structure. As described by the following equation (Eq. (1)), the thiol compounds GSH as a capping agent and stabilizer can release the S²⁻ under light radiation condition [11].



The S²⁻ reacted with excess Zn²⁺ in solution to make the ZnS. The ZnS wrapped on the surface of ZnSe to form ZnSe/ZnS core-shell QDs. The Zn²⁺ and S²⁻ have much larger combined strength than that of Zn²⁺ and Se²⁻. ZnS as a protective shell layer of ZnSe core can improve the fluorescence properties of ZnSe/ZnS QDs. On the other hand, although the vacancies of Se can lead to trap launcher, appropriate amounts of S²⁻ can adsorb onto the lattice surface of ZnSe QDs and fill the vacancies and inhibit the trap launcher [12]. So the ZnS shell formed on the surface of QDs and reduced the trap defects, which resulted in the increase of absorption and FL peak intensity of ZnSe QDs. Besides, the important phenomenon shown in Fig. 1, the appearance a secondary maximum in the fluorescence spectra. The possible explanation ascribes to the UV light with higher energy than Incandescent light. The much more electrons in QDs were excited by UV light, which resulted in the secondary maximum in the spectra.

ICP-AES Analysis

To reveal the correlation of structure, particle size and spectral performance of QDs, the chemical composition and structural of QDs were analyzed by using ICP-AES. The content and molar ratios of elements of ZnSe QDs treated by dark, UV light and incandescent light respectively are shown in Table 1. The S²⁻ content of ZnSe QDs irradiated by UV light and incandescent light are much higher than that of ZnSe QDs under dark condition. Furthermore, the S²⁻ content of ZnSe QDs irradiated by UV light were much more compared to that of ZnSe QDs irradiated by incandescent light. As a result, the effect of light conditions on structures and properties of ZnSe QDs are various with S²⁻ content, the sequence is UV light, incandescent light and dark from high to low.

Table 1 Content and molar ratios of elements of ZnSe QDs under different lights

Content of elements (mg/L)	Light types	S ²⁻	Se	Zn	Molar ratios of elements <i>n</i> _{S²⁻} : <i>n</i> _{Zn} : <i>n</i> _{Se}
a. Dark		77.76	0.67	11.20	14:1:0.049
b. UV light		86.22	0.60	10.46	16.8:1:0.047
c. Incandescent light		84.25	1.07	11.41	15.1:1:0.078

a. Dark; b. UV light; c. Incandescent light

XRD Pattern Analysis

To investigate the effect of light on the crystal structure and chemical properties of QDs, the QDs treated by different lights were analyzed using the XRD, as shown in Fig. 2. It is found that the ZnSe QDs treated with three kinds of lights appeared as sphalerite structure. The lighting only affected the XRD peaks intensity of ZnSe QDs, but not the position of peaks. Compared that of ZnSe QDs in dark, the XRD peaks intensity of ZnSe QDs increased after the UV light and incandescent lighting. The crystal grain size of QDs can be calculated according to Scherrer formula. So we know generally the more spikes strength, the larger size. As the superfluous Zn^{2+} in solution and S^{2-} generated by photolysis under light conditions interacted and formed ZnS shell, the size of the ZnSe QDs increased [13].

HRTEM Images Analysis

Figure 3 shows HRTEM images of the ZnSe QDs irradiated under different lights. Figure 3a is the TEM image of ZnSe QDs treated for 6 h under dark condition. It can be seen from the Figure, the dispersion of QDs were not very good, and the number of single round shape quantum dots were relatively small and particles generated agglomeration. The agglomeration might be caused by the high surface energy of ZnSe nanoparticles. Figure 3b is the TEM image of ZnSe QDs after UV irradiation 6 h. Compared with the ZnSe QDs in dark, the ZnSe QDs irradiated by UV light owned better sphericity and dispersion. The size distribution of ZnSe QDs were uniform, and the average particle size were about 2~3 nm.

Taken together, the types of lighting can affect the structures and properties of QDs. The UV light irradiation improved significantly the properties of ZnSe QDs. Based on the previous XRD results of this paper, we assure that the

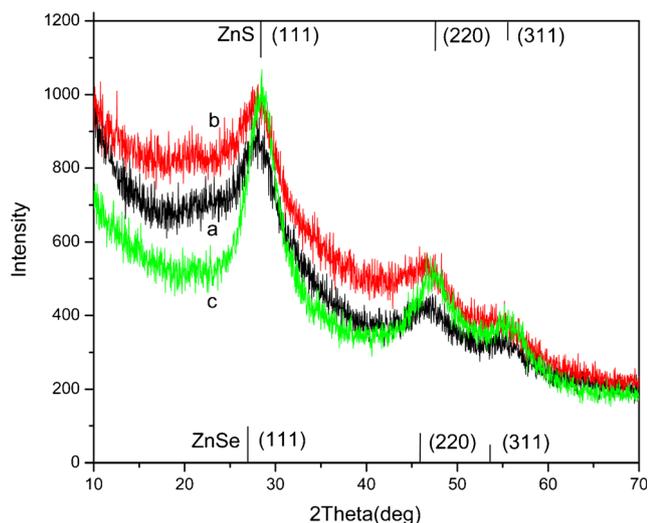


Fig. 2 XRD pattern of ZnSe QDs irradiated under different lights (*a*. Dark; *b*. UV light; *c*. Incandescent light)

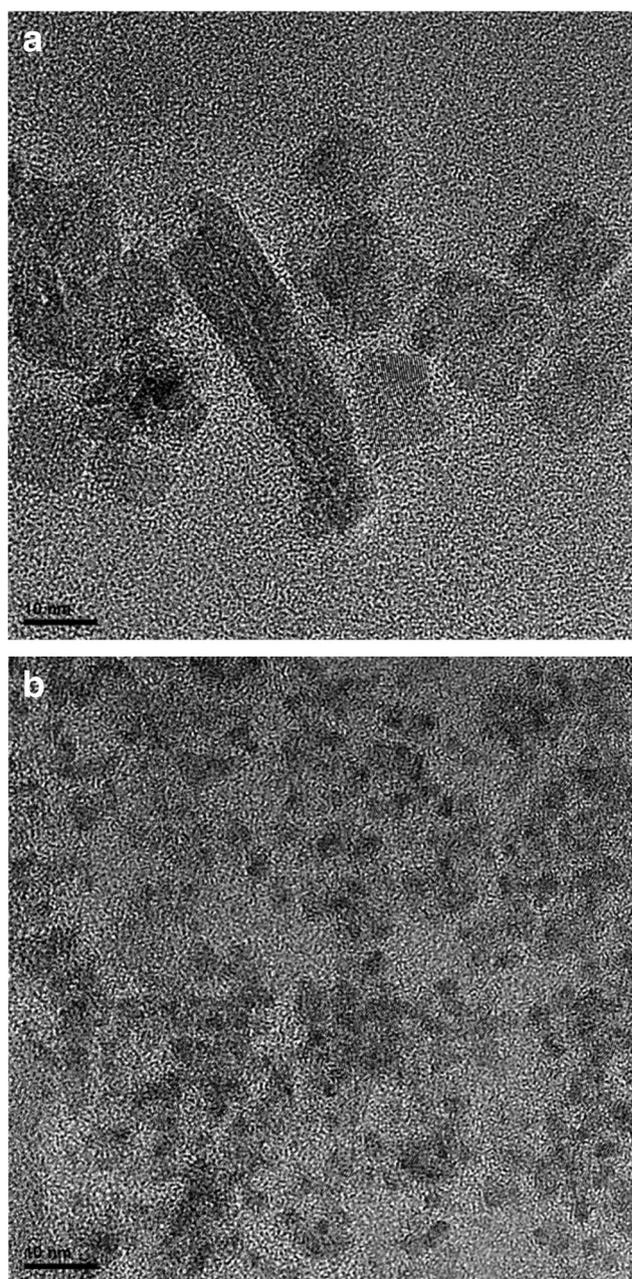
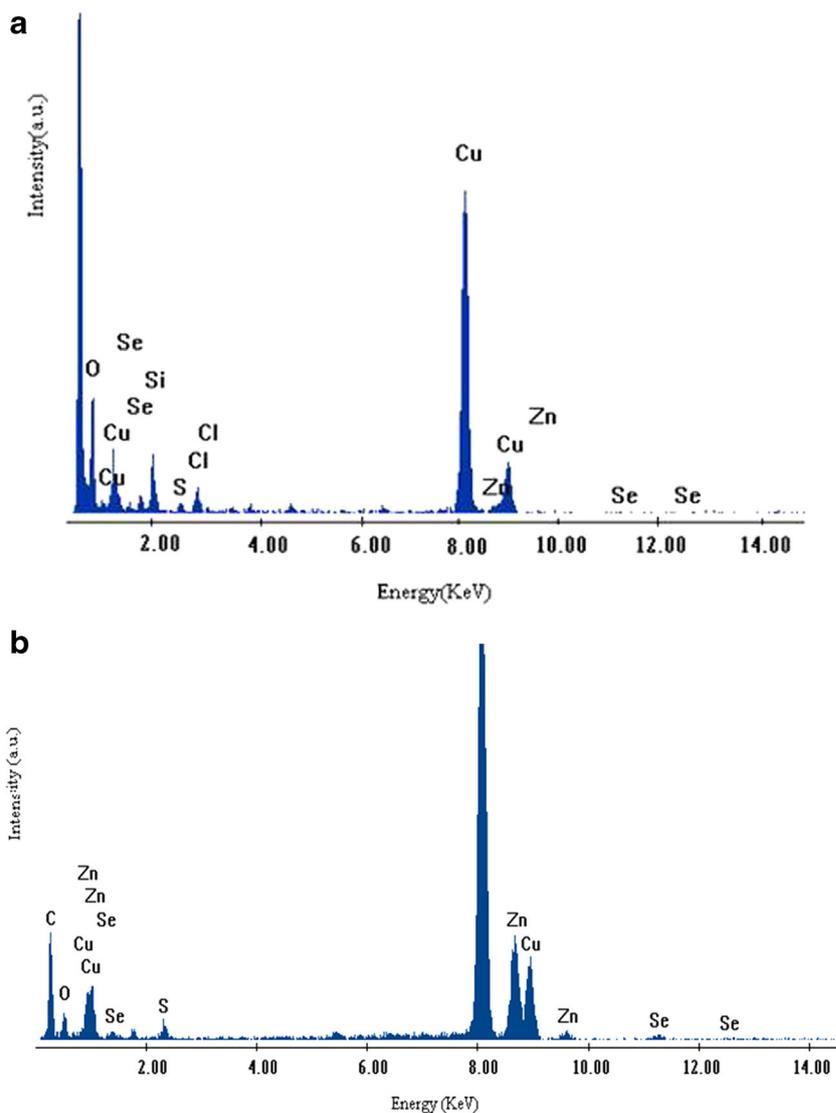


Fig. 3 HRTEM images of ZnSe/GSH QDs under **a** dark and **b** UV light

lighting resulted in the forming of ZnS shell on the surface of ZnSe QDs. ZnS band gap width is greater than that of ZnSe. ZnS, the important wide band-gap semiconductor material, favours the improving of optical properties of QDs [14].

Figure 4 shows the EDS spectra of ZnSe QDs under dark and UV light conditions. The atomic percent of S of ZnSe QDs under different lights are calculated, the results are shown in Table 2. Atomic percent of S under dark and UV light are 62.95, 84.57, respectively. Compared with the content of S of ZnSe QDs in dark, the content of S of ZnSe QDs irradiated by UV light is much more. The abundant S come from the photo degradation of GSH. This is consistent with the results

Fig. 4 EDS spectra of ZnSe QDs under **a** dark and **b** UV light



obtained by ICP-AES in this study, and is also another evidence of the ZnS coverage on ZnSe core.

FTIR Spectra Analysis

To investigate the changes of molecules structure and microscopic mechanism of surface ligand of ZnSe QDs under different lighting conditions, we compared the FTIR spectra of ZnSe QDs treated by three different lights. As shown in Fig. 5, the FTIR

Table 2 The atomic percentage of elements of ZnSe QDs under (A) dark and (B)UV light

Element types	Atomic percentage	
	A(dark)	B(UV light)
S ²⁻	62.95	84.57
Zn	33.00	13.31
Se	4.04	2.12
Total	100.00	100.00

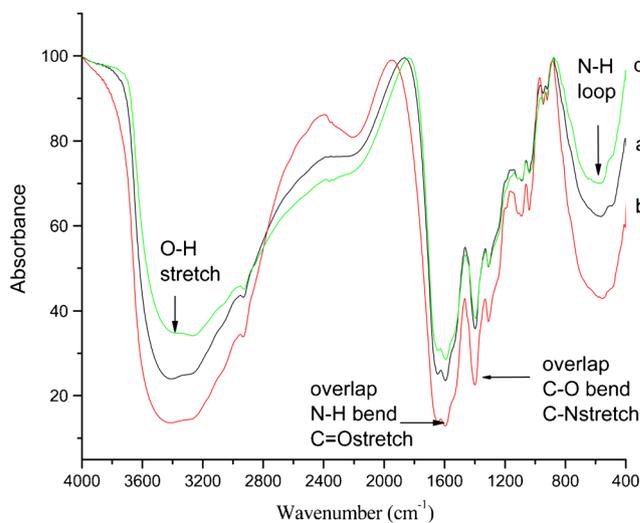
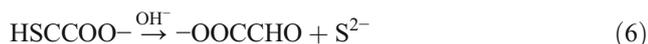
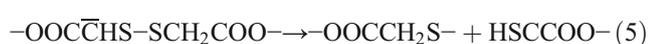
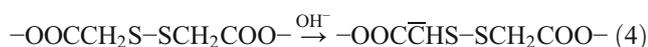
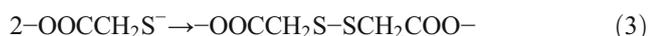
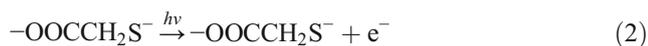


Fig. 5 FTIR spectra of ZnSe QDs under different lights

absorption peaks at 3400, 1600, 1400 and 560 cm^{-1} are assigned to O–H, C=O, C–O and C–N and N–H groups, respectively. The results show that the effect of lights on the peak of O–H stretching vibration is much bigger than that of other groups. There are still the –COOH and –NH₂ presence in the ZnSe QDs irradiated by three different lights. Compared with the feature absorption peak of O–H of ZnSe QDs in dark, that of O–H of ZnSe QDs irradiated by UV light lowered about 10 cm^{-1} . However, that of O–H of ZnSe QDs irradiated by Incandescent light raised about 35 cm^{-1} . This may be due to the light-induced the chemical combination between S–H group and O–H groups on the surface of ZnSe QDs, which resulted in the change of characteristic peak positions of QDs [15].

Effect Mechanism of Light on ZnSe QDs

The ZnS band gap (3.66 eV) is greater than that of ZnSe (2.67 eV). This wide band gap is very advantageous to improve the optical properties of materials. Due to the quantum size effect and dielectric confinement effect, the layer of ZnS coating on the ZnSe QDs will improve the fluorescence intensity and stability of QDs. However, the formation of ZnS shell on the surface of ZnSe QDs need the presence of S^{2-} and Zn^{2+} in reaction solution. Here ZnSe QDs are synthesized with the GSH as a coating agent. The GSH has a strong absorption in less than 300 nm wavelength range. The surface of QD nanoparticles are very sensitive to light. So the photocatalytic oxidation photolysis of GSH is apt to occur when the ZnSe QDs wrapped with GSH are exposed to UV light at 254 nm [8, 16]. According to the following equations (Eqs. (2)–(6)), the photolysis of GSH released the electron, thus generating sulfhydryl, and last producing S^{2-} under light and alkaline conditions.



It is believed that S^{2-} reacted with Zn^{2+} to form the ZnS shell layer on the surface of QDs. The ZnS shell provided a good passivation and improved the properties of QDs [17]. From the equations (Eqs. (2) and (6)), we can see that OH^- involved in photolysis process. The pH of solution played a key role to improve the properties of QDs during the lighting. The pH increases in favor of the formation of ZnS shell. The pH value 10.5 was the optimum value. This conclusion can be obtained from our another study [18]. Besides, the formation of ZnSe/GSH complex is also an important factor to improve

the properties and change the structures of QDs. Some other studies also suggested that different light conditions could affect the physical chemical characteristics of QDs [19–21]. All in all, photolysis, release of ions from QDs' solution and the formation of reactive oxygen species under light conditions are the main factors that affect the structures and properties of QDs. There are still much about light effect on the ZnSe QD structures and properties that aren't known and need to be further studied.

Conclusions

In the sum, we systematically studied the lighting effect on the structures and properties of GSH capped ZnSe QDs by UV–vis absorption, fluorescence, ICP–AES, XRD, HRTEM and FTIR techniques. It was demonstrated that lighting resulted in a slight increase of UV–vis absorption peak and fluorescence emission peak intensity of QDs, and the spectra accompanied with red shift of absorption band edge. The effect order of lighting on QDs was UV light, incandescent light and dark from strong to weak. This revealed lighting changed the diameter and surface structure of the QDs. Results from ICP–AES suggested lighting affected the content of S of QDs with influence order faying with spectra analysis. The XRD study indicated the sphalerite type structure of QDs was well maintained, but particles size was increased. Results from HRTEM suggested that the QDs in dark have big amount of agglomeration. However, counterparts irradiated by UV light possessed good size distributions and polydispersity, with mean diameter in 2–3 nm. Besides, EDS spectrum showed that atom percentage contents of S of QDs treated with dark and UV light was 62.95, 84.57, respectively, which basically matches the conclusion in ICP–AES. FTIR spectra proved that the –NH₂ and –COOH groups of QDs irradiated by lights still existed, but the absorption peak intensity and site of QDs changed to some extent. Lighting induced GSH on the QDs to occur photocatalytic oxidation, thus generating S^{2-} . So the interaction of S^{2-} with Zn^{2+} produced ZnS shell with broad-band gap, which improved the optical properties of QDs. In conclusion, UV light has more effect than candescent light and dark on the change of structures and properties of ZnSe QDs.

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