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Mechanism of aqueous ultrasonic reaction: controlled synthesis, luminescence properties of amorphous cluster and nanocrystalline CdSe

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A novel sonochemical method was found to prepare amorphous CdSe cluster and hexagonal nanocrystalline CdSe in aqueous solution. An interfacial mechanism for the sonochemical formation of CdSe nanoparticles was confirmed. The exploration for luminescence properties of the as-prepared CdSe nanoparticles revealed its wide application in many fields.

Recently, great interest has been shown in ultrasonic synthesis technique.[1] Sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. The collapse of bubbles generates localized hot spots with transient temperatures of ~5000 K, pressures over 1800 kPa, and cooling rates in excess of 10^{10} K s^{-1}.[2,3] The energy provided is high enough to enable many chemical reactions to occur.

It has been suggested that three different regions[4] are formed during the aqueous sonochemical process: (a) the inner environment (gas phase) of the collapsing bubble, (b) the interfacial region, (c) the bulk solution. However, the site where the sonochemical reaction takes place, which interests many scientific explorers, is still unclear. Therefore, revealing the formation mechanism is important in many interdisciplinary areas.

Here, we report a controlled sonochemical synthetic method to obtain amorphous CdSe and wurtzite (hexagonal) CdSe nanoparticles. A possible interfacial mechanism for the sonochemical formation from amorphous CdSe clusters to nanocrystalline CdSe is proposed. The methods employed were as follows: the mixture of $Cd(NO_3)_2$ (0.005 mol), $NH_3\cdot H_2O$ (3 ml), Na_2SeO_3 (0.0025 mol), $N_2H_4\cdot H_2O$ (5 ml) were sonicated for 2 h. With an irradiation period of 6 s sonication 6 s pause, an orange precipitate (amorphous CdSe) was formed. With an irradiation period of 60 s sonication 12 s pause, a precipitate of crimson material (hexagonal CdSe) appeared. We also obtained a red intermediate by choosing an irradiation period of 10 s sonication 2 s pause. These insoluble materials were filtered and dried in air at room temperature.

The final products were characterized with a Bruker D8 advance X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å). In Fig. 1a two broad diffraction peaks showed the formation of amorphous matter, while, the reflections in Fig. 1c could be indexed to a pure hexagonal CdSe wurtzite structure with lattice constant a = 0.4299 nm, c = 0.701 nm. The broad peaks indicated that the particles were small in size. The average diameter of the as-prepared CdSe nanoparticles was estimated to be 5.38 nm by the Debye-Scherrer formula according to the XRD patterns. The peak locations in Fig. 1b were similar to those in Fig. 1a and Fig. 1c, which showed that the sample might be an intermediate product during the formation of hexagonal CdSe. All three samples were also characterized by Raman spectrum. The same characteristic vibration peak at 210 cm^{-1} for the formation of the Cd–Se bond was observed (Fig. 2), slightly shifted to ultraviolet owing to the nanosize effect.[5,6] It strongly demonstrated the formation of amorphous cluster and nanocrystalline CdSe.

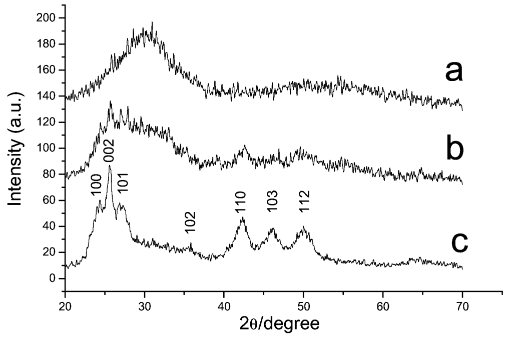

Fig. 1 Powder XRD patterns of the as-prepared (a) amorphous CdSe (b) intermediate phase of CdSe (c) hexagonal CdSe nanoparticles.

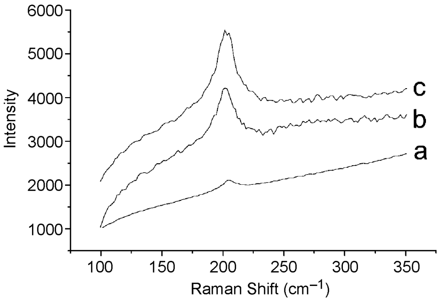

Fig. 2 Raman spectrum for the as-prepared (a) amorphous CdSe (b) intermediate phase of CdSe (c) hexagonal CdSe nanoparticles.

Transmission electron microscopy images (TEM) and electron diffraction patterns (ED) were taken with a H-800 transmission electron microscope. In Fig. 3a, agglomeration with many holes (25 nm) was observed. Electron microdiffraction showed only a diffuse ring characteristic of an

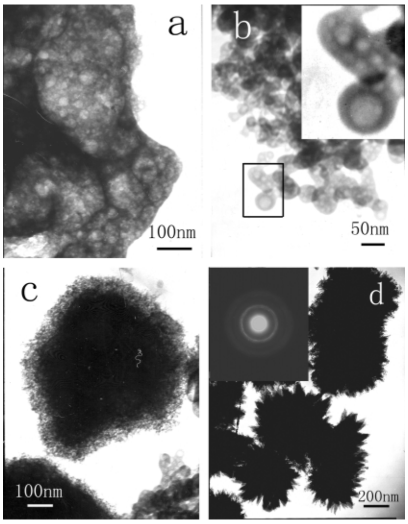

Fig. 3 TEM images of the as-prepared (a) amorphous CdSe, (b) (c) intermediate phase of CdSe and (d) hexagonal CdSe nanoparticles and ED pattern (inset) for hexagonal CdSe nanoparticles.

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amorphous material. In Fig. 3d, spherical particles with thorns were observed, and the average diameter of the thorn-like aggregate was about 500 nm. The ED measurements showed that the samples were well crystallized, and the diffraction rings were in accord with the corresponding reflection peaks (100, 002, 101,...) on the XRD patterns. To our surprise, the TEM image of the intermediate (Fig. 3b, c) showed two completely different morphologies. One was hollow sphere with diameter 20–50 nm, which was close to the size of the holes in amorphous CdSe. The other was spherical aggregate with diameter 600 nm, which was near to the size of the hexagonal CdSe aggregate. It further confirmed that the red precipitate was an intermediate of amorphous CdSe cluster and hexagonal CdSe nanocrystalline.

Based on the observed experimental results, an interfacial region could be proposed for the formation of CdSe in solution. Generally sonochemical reaction takes place in inner and interfacial regions. Volatile molecules penetrate the bubbles and react in the inner vaporous phase, while involatile molecules react in the interfacial region. In our reaction the reagents are far much less volatile than the solvent water, so they stay in the interfacial region to yield CdSe. The TEM images, agglomeration and spherical particles with many holes also powerfully support our supposition.

Although the size of bubbles is difficult to define due to many factors of the ultrasound system such as viscosity of the solvent, *etc*., it still offers a method to prepare mesoporous materials *via* ultrasound, which might have great use as catalysts, electrodes, and so on.[7,8]

The EDAX pattern for the as-prepared amorphous and hexagonal CdSe nanoparticles showed the presence of Cd and Se peaks. The average atomic ratio of Cd:Se neared 1 : 1, which was in good accord with the result of XRD study.

A possible chemical reaction route for the formation of CdSe nanocrystals can be summarized as follows:

$$3SeO_3^{2-} + 3N_2H_4 \rightarrow 3Se + 3N_2 + 3H_2O + 6OH^-$$

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O$$

$$2Se^{2-} + 2Cd(NH_3)_4^{2+} \rightarrow 2CdSe + 8NH_3$$

$$2SeO_3^{2-} + 3N_2H_4 + 2Cd(NH_3)_4^{2+} \rightarrow 2CdSe + 8NH_3 + 3N_2 + 6H_2O$$

It is noteworthy that the newly produced Se reduced from SeO_3^{2-} has high reactivity, and easily undergoes disproportion reaction in the alkaline solution to generate Se^{2-} and SeO_3^{2-}. The small Ksp (solubility product constant) of CdSe drives the whole reaction.

Ammonia liquor plays a critical role in the process. We use it to adjust the starting pH to 10 to prevent yielding Se, and to help the system to form a stable transparent solution before reacting by complexing with Cd^{2+} to avoid the formation of $CdSeO_3$ precipitate. It also help to prevent yielding $Cd(OH)_2$ in the product, making the CdSe nanocrystals purer.

Ultrasound irradiation provided the energy need for the reaction. When the experiments were carried out at room temperature without ultrasound irradiation, XRD measurements showed that the reaction did not occur at all, even after a sufficient length of time. The ultrasonic irradiation was fully responsible for the reaction.

Furthermore, we also studied the luminescence properties of the as-prepared CdSe.[9] Two luminescence peaks of amorphous CdSe were observed, the narrow exciton emission centered at 556 nm and the broad emission centered near 670 nm. The intermediate and hexagonal CdSe only showed a luminescence peak centered at 620 nm. The emission intensity was found to decrease while the amorphous CdSe transformed to hexagonal CdSe. The emission peak showed red shift through the transformation due to the arise of particle size, which was quite similar to the PL properies of ZnSe quantum dots.[10] Strong photo-luminescence enables CdSe nanocrystals to be widely used in many fields such as dense information storage, miniaturized sensors, efficient energy conversion, biological labels and light-harvesting.

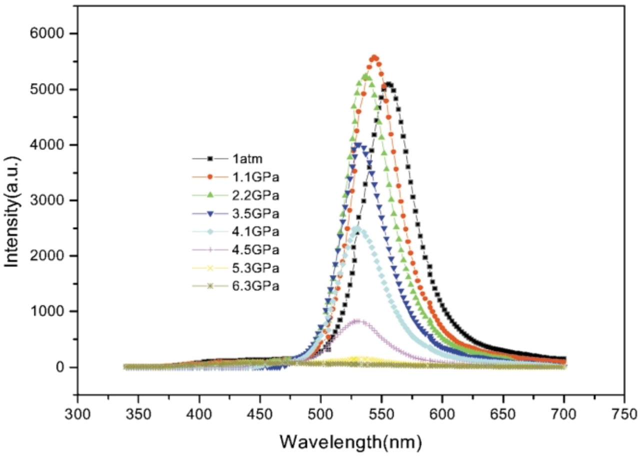

Fig. 4 High-pressure luminescenece spectrum for the as-prepared amorphous CdSe cluster.

The luminescence intensity of the as-prepared amorphous CdSe was 5 times as that of hexagonal CdSe, which encouraged us to make further study of the PL property of the amorphous CdSe. We conducted a High Pressure Luminescence study, and the results were shown in Fig. 4. With the increase of pressure (from 1 atm to 6.3 GPa), the emission peak showed blue shift (from 560 to 530 nm), and the peak intensity decreased (from 5000 to 100 a.u.). This can be well explained by solid–solid phase transition. Alivisatos and his co-workers found that the CdSe nanocrystals (43 Å in diameter) transformed from wurtzite to rock salt between 6.2 and 6.7 GPa in pressure.[11] The phase transition pressure is well above the bulk transition pressure of 2.8 GPa. Earlier work demonstrated that the elevation in transition pressure results from the cluster size. It is believed from the luminescence spectrum that solid–solid phase transition really occurs below 6.3 GPa (the highest pressure in our experiment) . It is noteworthy that the phase transition of nanocrystals is simpler (obeys simple unimolecular kinetics), because it contains very few defects in contrast to extended solids. Since transformation can be investigated *via* optical absorption, the as-prepared CdSe nanocrystals are expected to find great use in the study of transformation mechanisms.

In summary, a novel and simple method was found to obtain amorphous CdSe and hexagonal CdSe nanocrystals in aqueous solution. Through the study of XRD patterns and TEM images, the existence of an intermediate was confirmed, and the reaction was further demonstrated to occur within the interfacial region. A possible mechanism for the sonochemical formation of CdSe nanoparticles in aqueous solution was also proposed. The strong luminescence emission of the as-prepared CdSe nanoparticles reveals its wide potential application in many fields.

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