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Green chemical approaches to ZnSe quantum dots: preparation, characterisation and formation mechanism

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ZnSe quantum dots (QDs) and flower-shaped nanocrystals (NCs) were successfully synthesised via a cheap, green and nontoxic route, using environmentally friendly N, N-dimethyl-oleoyl amide as the solvent of Se. The experimental results show that the as-prepared ZnSe QDs with a zinc-blende structure have a narrow size distribution and without resorting to any as-synthetic size-selective procedure. A systematic study of the ZnSe QDs formation process indicates the following properties: variation of some reaction parameters allows us to tune the particle sizes and plays a greater role in the determination of the monodisperse characterisation, for example, these parameters include the amount of ligand and precursors, the injection temperature of Se solution. These size tunabilities interpreted well by the growth kinetics. Another interesting result is that the ZnSe QDs aggregate to flower-shaped NCs, and the flower-shaped NCs also have size-dependence quantum effects as the prepared disperse ZnSe QDs.

Keywords: ZnSe; quantum dots; green chemistry; II–VI group semiconductors

1. Introduction

Synthesis of semiconductor quantum dots (QDs) or nanocrystals (NCs) by means of pyrolysis in hot surfactant mixtures has evolved over the past 10 years to produce a variety of high quality materials in colloidal solutions ranging from II–VI NCs, for example, CdS, CdSe, CdTe, HgTe, [1–6] ZnS, ZnSe and ZnTe, [7–9] to III–V, for example, InAs and InP, [6,10] and II–VI, for example, PbS and PbSe, [11,12] QDs. Semiconductor QDs are of great interest for both fundamental research and industrial applications, such as biomedical tag [13,14], lightemitting diodes [15,16], laser [17,18] and solar cells [19]. Most of the interest is focussed on CdSe QDs, because their optical spectra can be made to cover the whole visible range by simply tuning their particles size [20,21]. The highly toxic component cadmium, however, places CdSe QDs in a disadvantageous position or even in a doubtful future. Cadmium could be released from CdSe NCs. Any leakage of cadmium would be fatal to biological systems, and eventually cadmium containing products would

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cause environmental problems [22–24]. Therefore, attempts to develop noncadmium substitutes are currently the priority in this field. ZnSe, an important II–VI semiconductor, has attracted considerable attention for applications in photodetectors, and full-colour displays [25,26]. Additionally, ZnSe has significantly large exciton binding energy (21 meV) [27], which makes it an ideal candidate for efficient room-temperature exciton devices with improved temperature characteristics [28]. Several novel applications have been presented, which require size, shape and phase control of ZnSe nanostructured materials [29,30].

Recently, Pradhan and Peng [31] developed the synthesis of Mn-doped ZnSe QDs with a visible emitting window of 470–590 nm. This would ultimately eliminate the toxic components and make ZnSe NCs an ideal substitute of CdSe NCs. However, this synthetic approach and the previous ones involved the use of toxic and expensive starting material, such as trioctylphosphine (TOP) and tributylphosphine (TBP). For the environmental friendly aims, more and more researchers are integrating greener chemistry principles into their synthetic approaches for greener nanoproductions. A phosphine-free approach was introduced for the formation of high quality CdS QDs by using oleic acid (OA) and octadecene as the ligand and the noncoordinating solvent, respectively [32]. This approach is quite general and was employed for the synthesis of many other nanomaterials [33], including ZnSe [34]. In the case of ZnSe, phosphines were needed to dissolve Se powder and could not be eliminated. Recently, our group reported that Se could be dissolved in N, N-dimethyl-oleoyl amide (DMOA) at mild temperatures, where CdSe QDs were synthesised [35]. However, a greener route to ZnSe QDs still has challenges.

Here, we report on a cheaper, greener, phosphine-free route for preparation of ZnSe QDs with N, N-DMOA as a solvent to dissolve Se powder, which eliminates the need for air-sensitive, toxic and expensive chemical TOP, and uses natural surfactant OA to dissolve zinc acetate and form zinc oleate solution in the noncoordinating solvent. The possible mechanism of chemical reactions in our system leading to the ZnSe nanoparticle formation was proposed. Another interesting result is that the flower-shaped NCs which were formed by ZnSe QDs also show size-dependence quantum effects.

2. Experimental

2.1. Synthesis

ZnSe QDs were synthesised in a three-neck flask equipped with a condenser, magnetic stirrer, thermocouple and heating mantle. A fixed amount of zinc acetate (99.99%, $\text{Zn}(\text{CH}_3\text{COO})_2$) was added into OA (from the Sinopharm Chemical Reagent Co., Ltd, $\text{C}_{18}\text{H}_{34}\text{O}_2$) and 1-octadecene (ODE, 90%, from Acros, $\text{C}_{18}\text{H}_{36}$) in a 25 ml three-neck flask. The mixture was degassed at 120°C , then was heated to 290°C under Ar flow or air atmosphere in less than 5 min. Saturated Se stock solution in N, N-DMOA ($\text{C}_{22}\text{H}_{41}\text{NO}_2$) was obtained by dissolving Se powder (99.99%, 100 mesh) in DMOA. Then selenium solution was injected into the hot mixture. After the injection, the temperature was dropped to 270°C for the growth of ZnSe nanoparticles and continued for 2 min to get a light yellow solution. At different reaction time intervals, aliquots were taken from the flask; and then each aliquot was immediately cooled to room temperature to quench the reaction by mixing it with about 2 ml of cold toluene. The ZnSe QDs were precipitated by adding methanol into the toluene solution and were further separated and purified by repeated centrifugation and decantation. The purified nanoparticles redispersed in toluene

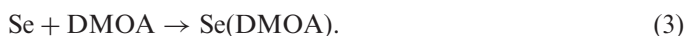
for UV-Vis, photoluminescence (PL), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) measurements without any size sorting. The flower-shaped ZnSe NCs were obtained via similar process, except that before the injection of Se solution, the mixture of zinc acetate and OA was elevated at 310°C and kept for growth.

2.2. Characterisation

All measurements were performed at room temperature. Absorption and PL spectra were measured by a Shimadzu UV-2550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. TEM and HRTEM images were recorded on a JEOL-2010 electron microscope at an accelerating voltage of 200 keV with an X-ray energy dispersed spectrometry (EDS). The crystal structure of as-synthesised product was analysed by XRD with Cu K α radiation on Rigaku D/Max- γ b diffractometer.

3. Results and discussion

The synthesis reaction (Scheme 1) can be described as follows:



Scheme 1. Possible chemical reactions involved in the formation of ZnSe NCs.

Equation (1) is the general reaction equation of the formation of ZnSe NCs in this experiment. Equation (2) is the process of forming Zn-complexes. Equation (3) is the process involving dissolution of Se powder in DMOA.

The size-dependent optical properties of ZnSe QDs can be monitored to determine their particle size and size distribution through the temporal evolution of absorption spectra. Figure 1(a)–(c) show the absorption spectra of ZnSe nanoparticles samples taken at different time intervals using different amounts of the ligand OA in the above synthesis. Zn ionic source was obtained from the mixture of 0.3 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$, 1 ml of OA and technological grade 1-ODE (the total was 3 ml). Saturated Se stock solution in N, N-DMOA ($\text{C}_{22}\text{H}_{41}\text{NO}_2$) was obtained by dissolving Se powder (0.2 mmol) in 5 ml DMOA. The samples of Figure 1(b) and (c) were the same condition as Figure 1(a) except that the amount of OA is 3 and 5 ml, respectively. It is obviously observed that the absorption spectra of Figure 1(a) is more in shape than in Figure 1(b) and (c), and the particle size of the samples of Figure 1(a)–(c) were increasing with increasing amount of OA according to the temporal evolution of absorption spectra. Figure 1(a) reveals that the small ZnSe QDs with an absorption peak at 379 nm would be formed in 10 s, and then developed to larger ZnSe QDs with an absorption peak at 388 nm in 30 s, then the absorption peak of the ZnSe QDs reached 399 nm in 150 s. Similar results were obtained when the amount of ligand OA is 3 ml, Figure 1(b) shows the first absorption peak of the ZnSe QDs is at 390 nm, the

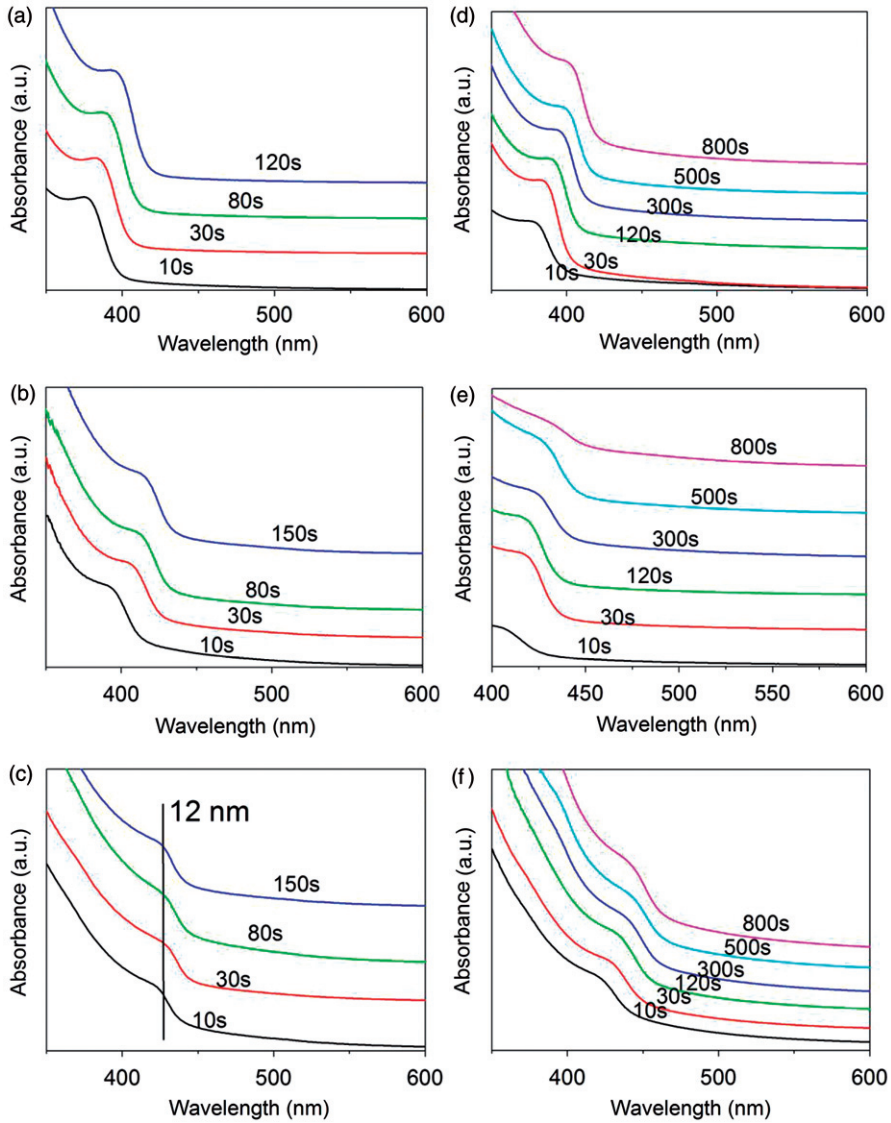


Figure 1. (a), (b) and (c) Temporal evolution of the UV-Vis absorption spectra of the as-prepared ZnSe QDs using 0.3 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.2 mmol of Se powder growth in ODE with the amount of 1, 3 and 5 ml OA, respectively. (d), (e) and (f) Temporal evolution of the UV-Vis absorption spectra of the as-prepared ZnSe nanoparticles with the amount of 1.5 ml OA, (d) using 0.4 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.2 mmol Se. (e) using 0.2 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.1 mmol Se and (f) using 0.1 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.05 mmol of Se.

absorption peak of ZnSe QDs reach 412 nm in 150 s. Due to the effects of capping ligand OA for passivating the particles surface, the capping ligand OA determines the rate of growth, and plays an important role in the number and size of nuclei formed after the injection [36]. A successful synthetic strategy for high-quality QDs should provide a wide

range of desired particle sizes. It is observed that increasing the amount of the ligand OA would result in relatively larger nanoparticles. Through the variation of ligand, size tuning ZnSe nanoparticles can be prepared effectively. Earlier, Yu and Peng reported that the NC growth rate would slow down and the size distribution would become significantly narrower when the ligand/precursor molar ratio decreased [32]. In their work, decreasing the molar ration was achieved through both reducing the amount of ligand and maintaining the amount of precursors, where they had tuned the size of CdS nanoparticles, similarly in our experiments, and we have obtained larger ZnSe nanoparticles through increasing the amount of the ligand OA. It is observed that the temporal ZnSe QDs grew to 12 nm, reaching the largest fixed particle size shown in Figure 1(c). In the synthesis, with the injection of Se solution into the three-neck flask, the reaction starts with an extremely fast nucleation process, followed by an early growth process. The two processes are so fast that the red-shifted absorption spectra could not be obtained. The similar phenomena have been observed by Dai et al., where the ZnSe nanoparticles grew to a fixed particle size at 10 nm because of the few amount of precursors [37]. Figure 1(d) and (f) shows the size dependence when altering the amount of precursors. Figure 1(d) is the temporal evolution of absorption spectra of the ZnSe QDs grown in a typical synthesis with 0.4 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.2 mmol of Se. It is observed that the ZnSe nanoparticles are relatively small with narrow size distribution, which can be demonstrated by their comparatively short absorption wavelengths and sharp absorption peaks (Figure 1d). The reactions in 0.2 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.1 mmol of Se powder, and 0.1 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.05 mmol of Se powder were carried out, which correspond to the absorption spectra of the Figure 1(e) and (f), respectively. The experimental results show that the absorption spectra of ZnSe QDs were broad absorption peaks and large particle sizes with a decreasing amount of precursors (Figure 1(d) and (f)). The experimental results also demonstrated that small particle sizes and desired size distribution could be obtained via altering both the amount of ligand and the precursors. These results indicate that there was a balance between nucleation and growth, which is necessary to the synthesis of QDs with narrow size distribution. The formation of monodisperse QDs requires a fast and short nucleation stage process. Too many or too few nuclei formed in the initial nucleation stage would break the balance between nucleation and growth. Moreover, the growth of QDs can be divided into two growth stages: focussing stage and defocussing stage. After the injection of Se solution into the zinc oleate solution, the size distribution is broad, when the particle sizes in solution are larger than the critical value, the smaller particles tend to grow faster than the larger ones; and then focussing of the size distribution occurs. With the depletion of monomers, the critical size becomes larger than the average size of particles; then large particles grow at the expense of small ones, and small ones disappear. This process is famous as a defocussing of size distribution (Ostwald ripening) [38]. As discussed above, to obtain the desired particle sizes and size distribution, such tunability can easily be gained via simply altering the amount of ligand or the amount of the precursors.

Figure 2(a) shows that temporal evolution of room-temperature PL spectra of ZnSe QDs obtained from the representative reaction performed in ODE with the amount of 1 ml OA. All PL spectra of samples are excited with a wavelength of 340 nm. The PL emission peak shifts from 391 nm to 450 nm without broadening emission bandwidth, which means the size of QDs become larger with reaction time increasing without obviously broadening of size distribution. Figure 2(b) illustrates the absorption and emission spectra of one

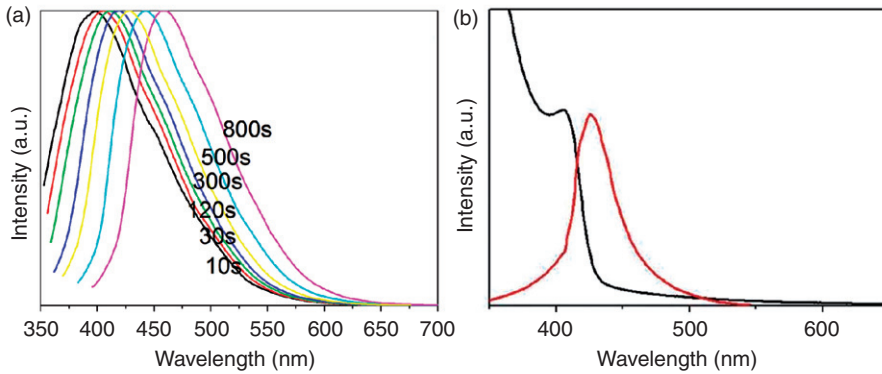


Figure 2. (a) Temporal evolution of room-temperature PL spectra of ZnSe nanoparticles obtained from the representative reaction performed in ODE with the amount of 1 ml OA. (b) Room-temperature UV-Vis absorption and PL spectra of a typical ZnSe nanoparticle sample synthesised in ODE with the amount of 3 ml OA.

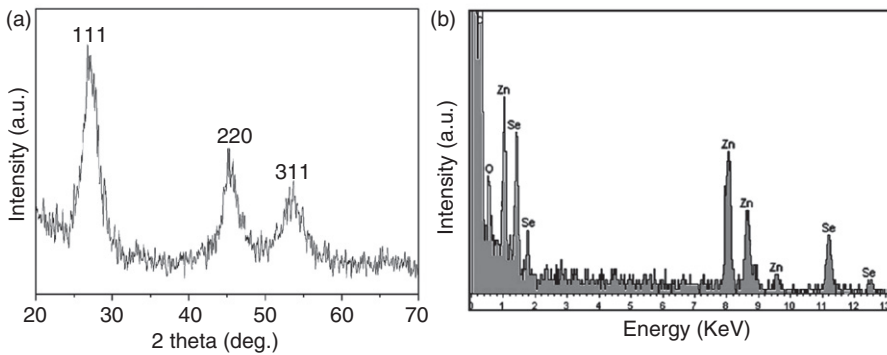


Figure 3. (a) XRD pattern of the as-prepared ZnSe nanoparticles. (b) EDS of the resulting ZnSe QDS.

typical QDs sample. The first absorption and emission peaks are at 403 nm and 416 nm, respectively, which show a 13 nm Stokes shift. The PL emission spectra is also a Gaussian shape, which clearly indicates a pure band-gap emission without any significant trap-state emission, and the full width at half-maximum (FWHM) is also observed to be narrow (about 32 nm), which suggests a regular surface of particles and a narrow size distribution. This sharp absorption and narrow emission peak indicate that the QDs are monodisperse, which will be further confirmed by TEM result of ZnSe nanoparticles discussed below.

Figure 3(a) shows the powder XRD patterns of the ZnSe QDs obtained by the present synthetic route. From the XRD pattern, three typical distinct features of zinc-blende structure can be distinguished: these diffraction features appearing at about 27.44° , 45.46° and 53.88° corresponding to the (111), (220) and (311) planes of the zinc-blende phase of ZnSe (JCPDS no 37-1463), respectively. The EDS measurements on the same sample indicate the presence of elemental Zn and Se, which confirmed the sample of ZnSe QDs.

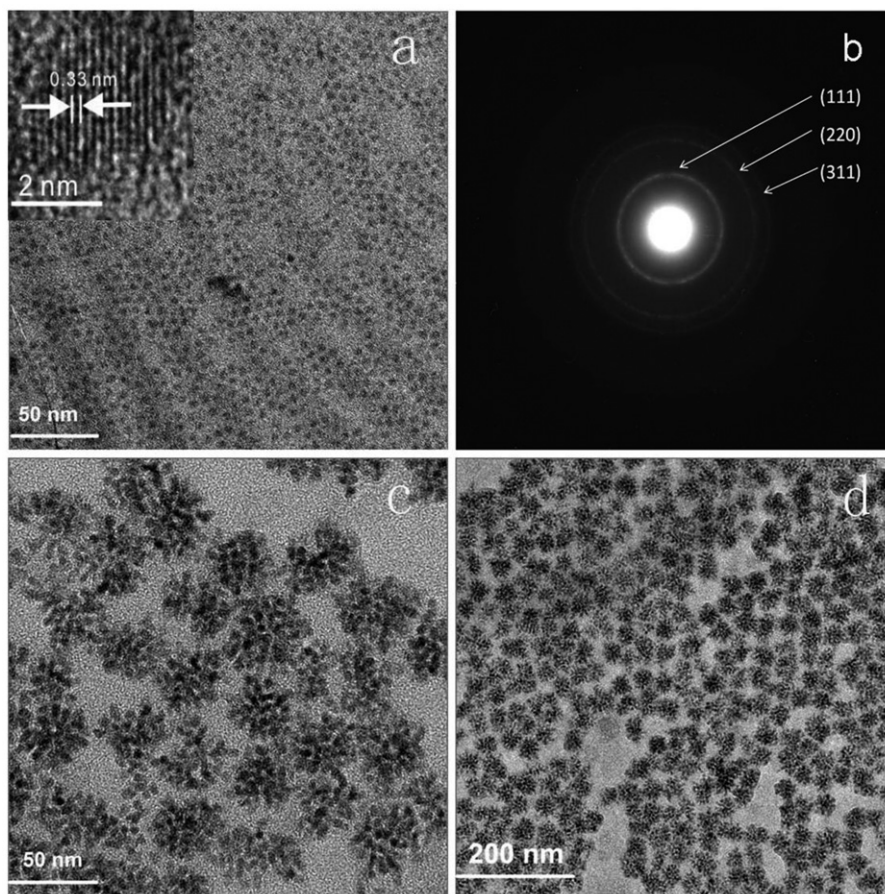


Figure 4. (a) and (b) TEM images and the SAED of the as-prepared ZnSe nanoparticles. (c) and (d) HRTEM and TEM images of the as-prepared ZnSe nanoflowers.

The atomic ratio of Zn and Se is 0.5507:0.4993 calculated from the EDS results, which is consistent with the assumption. Elemental C, O can also be distinguished due to OA capping ligand mainly.

Figure 4(a) shows TEM and HRTEM images of the as-prepared ZnSe nanoparticles. The average size of the ZnSe QDs is about 4 nm, which was obtained by injecting 0.2 mmol Se solution into 0.3 mmol $\text{Zn}(\text{CH}_3\text{COO})_2$ solution at 290°C. The HRTEM image showed an ensemble of ZnSe QDs assembled into a locally well-ordered closed-packed array. The HRTEM image reveals the higher crystallinity of the ZnSe QDs. It is observed that the ZnSe QDs were well crystallised, with interplanar distances of 0.33 nm, which was consistent with the (111) planes of cubic ZnSe. The selected area electron diffraction (SAED) pattern of ZnSe QDs shown in Figure 4(b) can also be indexed to the zinc-blende phase of ZnSe, corresponding to the XRD analysis results. Figure 4(c) and (d) show another phenomenon that the ZnSe QDs can aggregate to flower-shaped NCs, called nanoflower, which is similar to the previous reports [36]. Our ZnSe nanoflowers were

obtained by injecting the Se solution immediately after the Zn-complex solution reached 310°C, and was kept at 310°C for several minutes growth. The TEM images (Figure 4(c) and (d)) clearly show that the nanoflowers with a size of about 30 nm consisted of several aggregated 4 nm nanodots. Figure 5 shows the absorption and emission spectra of ZnSe nanoflowers. Similar to monodisperse ZnSe QDs, the sizes of flower-shaped NCs increase with the increasing reaction time, although the average sizes of the NCs are larger than the exciton radius.

Figure 6 is a schematic diagram of the formation process of the ZnSe nanoflowers. Previously, Peng et al. [39] also observed the formation of nanoflower, they have proposed a growth mechanism of the nanoflowers, in which the individual nanoparticle becomes unstable and aggregates into three-dimensional nanoflowers when the degree of ligand

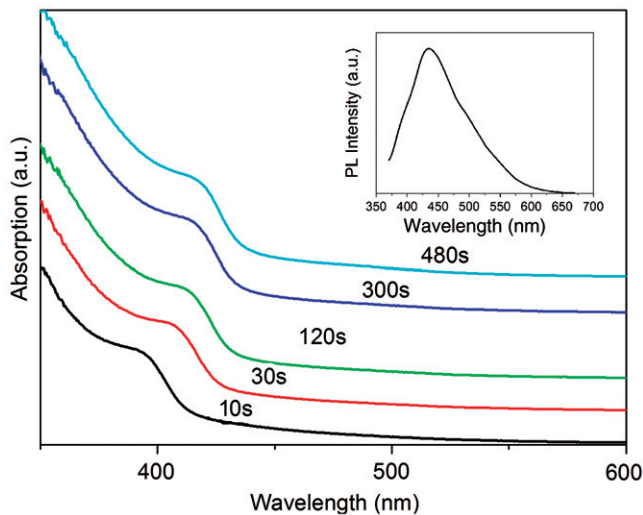


Figure 5. Temporal evolution of absorption spectra of the ZnSe nanoflowers grown in OA and ODE with 0.2 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.1 mmol Se at 310°C. Inset: PL spectra of a typical nanoflower sample.

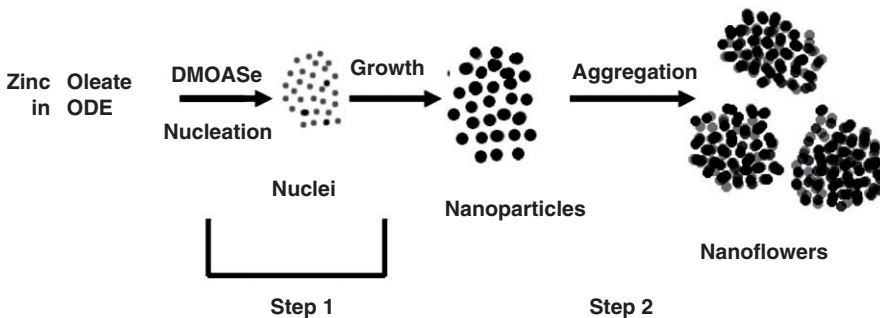


Figure 6. Schematic diagram of the formation process of the ZnSe nanoflowers.

protection is reduced to the limit ligand protection (LLP) domain. In our experiments, the nanoflowers were obtained by simply increasing the injection temperature of the Se solution, while the former was obtained via decreasing the ligand concentration. It has been suggested that the formation of nanoparticles underwent two dynamic processes [40,41], and a theoretical model was proposed by Libert et al. [42] for the controlled synthesis of CdS nanoparticles. According to the model, the first process is the nucleation and the nuclei growth to form the QDs. The sequential second process is the aggregation of the QDs to form the flower-shaped NCs. We thought that the ZnSe nanoflowers could be formed in a similar way, as shown in Figure 6. For the formation of the ZnSe QDs, nucleation takes place immediately after the injection and continues until the monomer concentration drops below a critical threshold value. For the aggregation process of the QDs to form the ZnSe nanoflowers, the surface free energy of the primary particles should be the driving force for the aggregation. In the synthesis of the monodisperse QDs reported in the literature [43], strong stabilising surfactant (such as TOPO) was always used to stabilise the formed QDs. If the stabilising ability of the ligand is weak in the synthesis system, the formed particles will detach from each other [39(a)]. In our synthesis of the ZnSe QDs, OA was used as the capping ligand, which has a strong capping ability. The ligand results in higher surface free energy of the ZnSe QDs, which provides the driving force for the aggregation of the QDs to form the ZnSe nanoflower. In fact, in the flower-shaped NCs, the ZnSe QDs contact with each other via van der Waals force of surfactant molecules, the individual QDs keep their own crystalline properties. This is why that the flower-shaped NCs also show size-dependence quantum effects as the synthesised disperse ZnSe QDs.

4. Conclusion

ZnSe QDs and flower-shaped NCs were successfully synthesised via a cheap, nontoxic and environmentally friendly route by using DMOA as the solvent of Se, which meets the principle of green chemistry. The experimental results show that the as-prepared ZnSe QDs with a zinc-blende structure have a narrow size distribution and without resorting to any as-synthetic size-selective procedure. The experimental results show that the particle size of nanoparticles can be easily tuned by simply altering the amount of ligand or the amount of precursors. Additionally, we provide both a new synthetic way to obtain ZnSe nanoflowers and a new growth mechanism to explain their formation. It is obtained through elevating the injection temperature to 310°C and keeping this temperature for growth. The ZnSe QDs contact with each other to form flower-shaped NCs via van der Waals force of surfactant molecules, the individual QDs still keep their own crystalline properties, and thus, the flower-shaped NCs also show size-dependence quantum effects as the synthesised disperse ZnSe QDs. The results present a new phosphine-free route, which could be used to synthesise other NCs.

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