

Luminescent disordered nanostructures: synthesis and characterization of CdSe nano-agglomerates

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Abstract A disorderly nanostructured CdSe nano-agglomerates (NAs) with tunable emission are synthesized in aqueous solution. Although the CdSe NAs have diameters of about 20 nm that are larger than the Bohr radius of the crystal bulk, they show size-dependent emission similar to the CdSe nanocrystals. The CdSe NAs represent a collective energy state based on Anderson localization.

Keywords nano-agglomerates, CdSe, photoluminescence

1 Introduction

Semiconductor materials with various nanostructures and particle morphologies have attracted substantial interests for a long time due to their unique optical and electrical properties, which mainly caused by the quantum-confinement effects [1–7]. Their luminous properties, photo (electro)catalysis properties, and sensor properties are all can be rationally tuned by controlling their particle size, crystal orientation, and crystallinity. Among various semiconductors, CdSe nanomaterials, because their band gap can be adjusted in a wide range to cover the entire visible light range, have been paid more attention for their potential use in industrial and biomedical applications [6,7], which could be used in the engineering for one day. And therefore, numerous methods have been developed for CdSe nanomaterials to achieve effectively particle morphological controls [8,9], the assembly of uniform CdSe nanoparticles [9–11] and close-packed ensemble of CdSe nanocrystals [12–15]. Most of the researches focus on well-ordered CdSe crystals with perfect crystallinity, such

as nanocrystal, nanorod and nanowires [1–4,8,9], even the artificial atoms in colloidal crystal [9–11] and component in the close-packed ensemble [12–14]. In these works, the relationship between the size and physical properties were well established due to the intensive knowledge in the band structure analysis of well crystalized materials.

In another hand, non-crystalline nanomaterials with disordered crystal structures possess some unique properties comparing to highly crystalized nanomaterials, and there has been a great interest in the problem of electron localization in a disordered solid since Anderson published the famous paper in 1958 [15,16]. Along with the exciting development and extensive interest in nanomaterials and nanoelectronics in recent years, Anderson localization has been studied on numerically systems [17–19] and has some living examples, such as carbon nanotube [20], Ag nanocrystal [21] and porous silicon [22]. For the single amorphous nanoparticles, when the volume of the disordered solid go down to a regime which below the localization length, we have to ask first how the quantum size effect exercises its influence in a disordered nanosystem. CdSe maybe a good model material for studying the electron localization behavior in disordered solid because it allows us to characterize its band structure by using photoluminescence spectrum just in visible light range. However, CdSe nanomaterials with non-crystalline disordered structures have less been investigated to date.

Here we report a one-pot method to synthesize CdSe nano-agglomerates (NAs), which are assemblies of many CdSe nanoclusters as demonstrated by the transmission electron microscopy (TEM) characterization. Such NAs are prepared in aqueous phase, and most importantly, they have tunable emission spectra like the CdSe nanocrystals, although the size (about 20 nm) of the NAs is larger than the Bohr radius of the bulk crystal of CdSe. Moreover, we also obtained a CdSe NAs with enhanced photoluminescence (PL), which can be of great help in optical

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processing or information visualization systems and we believe that the characteristics of the NAs can be explained by Anderson localization and the NAs are the right system for studying electronic states in disordered nanostructures.

2 Experimental

2.1 Materials

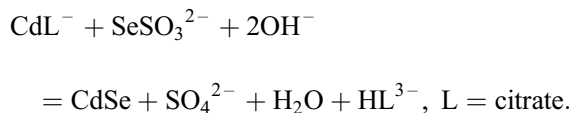
Cadmium chloride hemipentahydrate ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), sodium citrate tribasic dihydrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$), selenium powder (100 mesh, 99%), sodium sulfite (Na_2SO_3), and ethanol (anhydrous, $\geq 99.95\%$), 3,3',3''-phosphinidynetris(benzenesulfonic acid), trisodium salt (PTBT) were purchased from Sigma-Aldrich Corporation. All these chemicals were used without further purification. The water was deionized through a Nex Power 1000 water purification system (Human Corporation).

2.2 Synthesis of CdSe nano-agglomerates (NAs)

In a typical synthesis, 4 mL of 0.04 mol/L cadmium chloride (CdCl_2) aqueous solution was diluted to 50 mL in a three-necked flask, and 100 mg of trisodium citrate dehydrate was added into the CdCl_2 aqueous solution under stirring in an argon atmosphere. Na_2SeSO_3 aqueous solution was prepared by mixing Se powder and Na_2SO_3 under nitrogen atmosphere according to the following chemical reaction: $\text{Se} + \text{SO}_3^{2-} = \text{SeSO}_3^{2-}$.

After the temperature of the mixture solution of CdCl_2 and trisodium citrate was raised up to 100°C , 4 mL of fresh prepared 0.01 mol/L Na_2SeSO_3 aqueous solution was injected into the mixture. In our preparation, citrate was

used as stabilizer by a modified route from literatures [17,18]. The CdSe nanoclusters were synthesized according to the following chemical reaction:



The mixture was kept at 100°C under stirring for the growth of CdSe nanoclusters. The synthesized CdSe clusters are aggregated together to form CdSe NAs. After a certain time, the aggregation morphology of NAs can be further changed by adding excessive intermediate level ligand, 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt (PTBT), to the as-prepared solution of dispersive NAs and heating at 100°C for several hours.

2.3 Characterization

X-ray powder diffraction (XRD) patterns were recorded using a D/max 2500 V PC X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). TEM images were taken with a JEOL 2010 TEM operated at 200 kV. TEM samples were prepared by dropping suspensions on copper grids and dried at room temperature (25°C) for 24 h. The optical characterizations were performed at room temperature (25°C). UV–Vis absorption spectra were recorded on a Cary 500 UV/Vis/near-infrared (NIR) Varian spectrophotometer (USA). The photoluminescence excitation (PLE), PL spectra were recorded on a Perkin Elmer LS 55 Luminescence spectrometer. PL decay was performed using a PTI TimeMaster spectrometer. The X-ray photoelectron spectroscopy (XPS) were recorded on VG ESCALAB MK II X-ray photoelectron spectrometer.

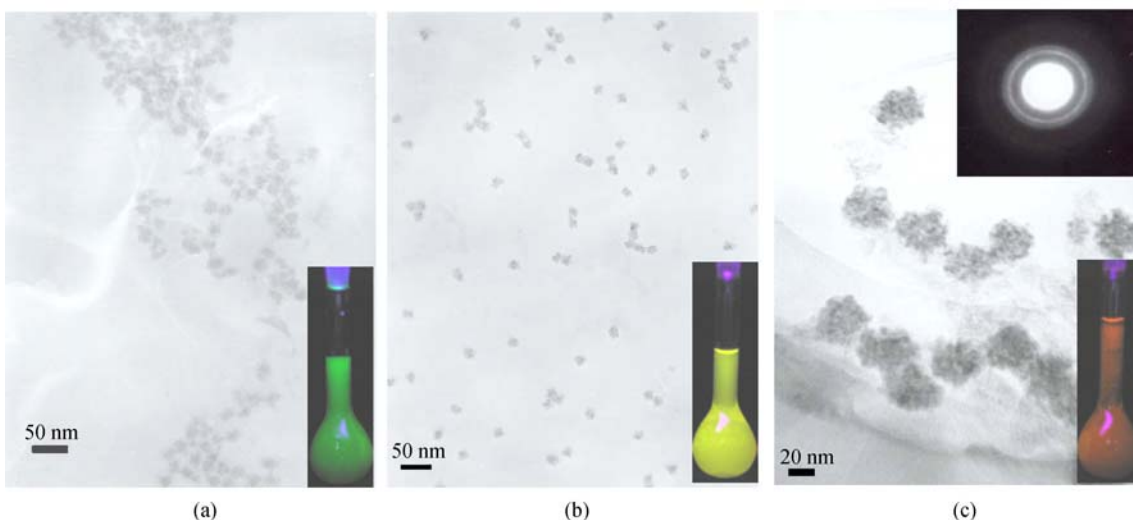


Fig. 1 Typical TEM images of as-prepared CdSe NAs (a, b, c) with ED pattern shown in the inset of (c), the size and corresponding PL of (a), (b), (c) is 17 nm (520 nm), 22 nm (581 nm), 25 nm (630 nm), respectively. The inset pictures also show size-dependent change of the PL color of colloidal solutions of CdSe NAs upon UV-excitation (365 nm)

3 Results and discussion

Three CdSe NAs samples with different size, 17, 22 and 25 nm, were synthesized in this work. A drop ($\sim 5 \mu\text{L}$) of each as-prepared CdSe NAs sample is placed on carbon coated copper grid for taking TEM. As shown in Figs. 1(a), 1(b) and 1(c), these NAs are all well dispersed, and each NA consists of many small nanoclusters with size less than 2 nm. The nanoclusters are disorderly packed, and there is no clearly boundary between the nanoclusters. The selected area electron diffraction (ED) pattern of NAs only shows one uniform distributed diffraction ring, indicating it is made of CdSe cluster with nearly amorphous crystal structure and random orientations. It is very interesting that although the size of the NAs are quite large, it is still relative to the PL spectrum peaks. The PL peaks of NAs materials with diameter of 17, 22 and 25 nm are located at 520 nm (green), 581 nm (yellow) and 630 nm (brown), respectively. When the size of the NAs increase, its PL peaks shows a clear red shift. This change trend is similar with that in CdSe nanocrystals as reported in numerous literatures. However, the size of the NAs are much larger than that of CdSe nanocrystals. A nanocrystal of CdSe with size larger than 15 nm only shows similar PL spectrum with bulk samples. Since the size of the clusters

in this work is less than 2 nm, it indicate that the shift of PL peaks are not simply caused by the size of the cluster, but related to the size of their aggregates, i.e. NAs.

Figure 2 shows the XPS and the wide-angle powder X-ray diffraction (WAXD) of the NAs. The XPS result reveals that the binding energy of Cd 3d_{5/2} is 405.7 eV and that of Se 3d is 54.4 eV, the ratio of Cd to Se is ~ 0.9 , which confirms that the composition of the NAs is CdSe. The NAs with different sizes show similar WAXD patterns and the reflections in the diffraction are very broad, and the particle size is calculated to be ~ 1.4 nm according to Scherrer equation based on the half-width of the diffraction peak, as Fig. 2 shows. The broad diffraction peaks arise from low sample crystallinity, which correspond to the TEM observations and can be explained by the lower reaction temperature relative to the preparation of CdSe nanocrystal by organic metal methods [8]. Based on the phenomenon we observed during synthesis and the TEM and XRD results, it is supposed that there are two steps in the formation of CdSe NAs: first CdSe nanoclusters are produced immediately when the two precursors are mixed indicated by the fast color change observed during the synthesis; second these freshly born citrate-protected clusters with strong surface energy subsequently coagulate to form NAs by reacting with each other, as illustrated in

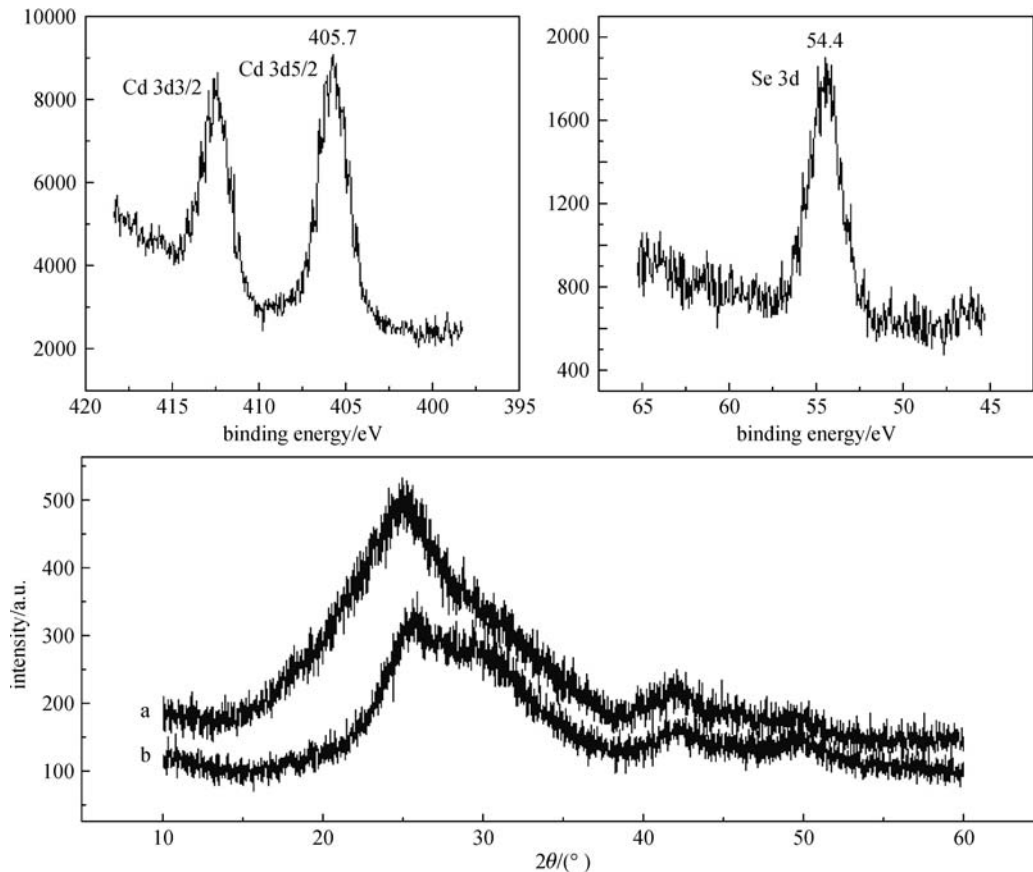


Fig. 2 XPS spectra (up) and the WAXD diffractograms (down) of CdSe NAs, which the PL emission peak is 596 nm (a) and 532 nm (b)

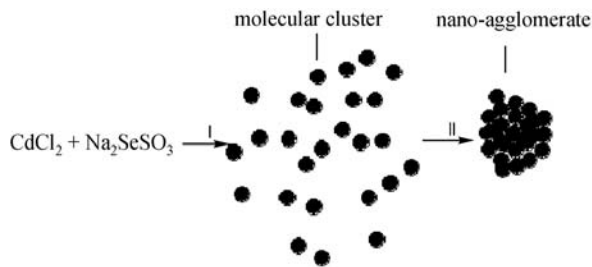


Fig. 3 Schematic model for the formation of CdSe NAs. I, pH = 10, 100°C; II, CdSe cluster coagulated to form NAs

Fig. 3. A longer reaction time at 100°C leads to a larger NAs, from 17 to 25 nm, but the sizes of the nanoclusters in these NAs are almost unchanged, always smaller than 2 nm.

The optical properties of CdSe NAs are quite different from those of the CdSe nanocrystals. Figure 4(a) showed the temporal evolution of absorption of CdSe NAs monitored during their growth in aqueous solution at

100°C. The growth dynamics of the NAs is monitored by taking samples from the reaction mixture at different instants of time. The longer reaction time is, the larger size agglomerates are formed. The increase of size of the NAs lead to a continuous red shift in their absorption spectrum. The edge of the absorption spectrum of NAs is found to exhibit a systematic modification. The modification of the absorption spectrum is attributed to the formation of collective electron states in the agglomerates. Similar structureless smooth band-edge absorption of close-packed CdSe nanoparticles have been observed earlier and considered as a possible precursor of the Anderson transition in a quantum dot ensemble [13–15]. Figures 4 (b) and 4(c) show the PLE and the PL spectra of three NAs samples with varied NAs sizes, 17 nm (green), 22 nm (yellow) and 25 nm (orange). The PL intensity of the NAs enhances about three times upon aging at room temperature for three days (Fig. 4(b)) and tends to be stable after seven days. In particular, two luminescence peaks are observed in the sample with lower emission wavelength, for example, the narrow exciton emission centered at

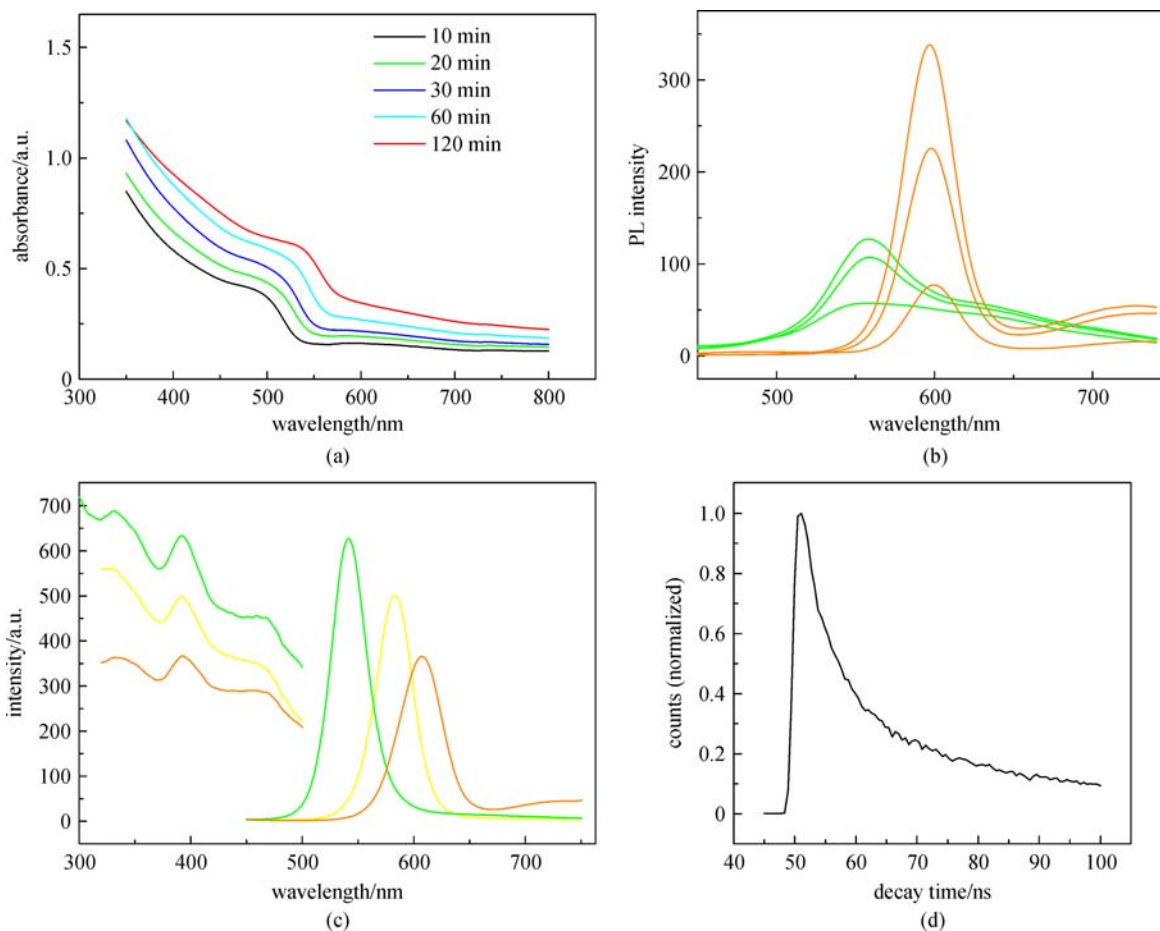


Fig. 4 (a) Temporal evolution of the absorption spectra of the CdSe NAs. (b) Enhancement of PL intensity upon aging at room temperature every 24 h (from the bottom up), $\lambda_{\text{ex}} = 390 \text{ nm}$. (c) Room temperature PL and PLE spectra of CdSe NAs (17 nm (green), 22 nm (yellow) and 25 nm (orange)). (D) For a CdSe NAs sample, ($\lambda_{\text{ex}} = 337 \text{ nm}$, $\lambda_{\text{em}} = 566 \text{ nm}$), the PL decayed with a lifetime of 8.4 ns. The PL decay is fitted exponentially. Here, ex, excitation spectrum; em, emission spectrum

558 nm and the broad emission centered near 625 nm corresponding to the trapped emission of CdSe nanocrystals that the relative intensity decreases upon aging. Comparing with the different PL emission peak of the NAs, the shapes of three PLE spectra are very similar and have three peaks at 348, 393, 460 nm, respectively (Fig. 4(c)), which indicate the electron transition induced by photo-excitation in the NAs is quite different from that of the CdSe nanocrystals. By changing the amounts of precursor or the reaction time, we can obtain emission color of the band-edge PL of the NAs shifting continuously from 630 nm (with a diameter of ~ 25 nm) to 520 nm (with a diameter of ~ 17 nm) as the sizes of the NAs decrease. The full width at half maximum (FWHM) of the PL spectra is about 40 nm for the crude solutions of CdSe NAs. Figure 4(d) shows that the PL decayed lifetime of CdSe NAs is about 8 ns.

It has been reported by Woggon et al. [14] that strong coupling results in a controllable steady growth of the delocalized electron state, which means a complete delocalization occurring and the strong intercluster coupling in the ensemble represents a collective energy state. In Ref. [14], the authors also declared “One can foresee new prospects in synthesis of mesoscopic structures whose electronic and optical properties are controlled by three-dimensional confinement of electrons within every nanocrystal and by collective phenomena due to spatial organization of nanocrystals.” The numerical estimates performed by Woggon et al. [14] are similar to the above results of CdSe NAs. In the close-packed ensemble, each cluster may act as an antenna, and the electron-hole pair created by photoexcitation of the single cluster is confined to the whole ensemble and delocalized over the whole agglomerates, larger scale delocalization means narrower band gap. Here the CdSe NAs have some special properties comparing with the close-packed ensemble: first, the crystallinity of NAs is low that has been confirmed by XRD and SAED patterns; second, the size of the NAs is controllable in nanoscale, which is necessary for the PL of the NAs. Based on these facts, it is thought that the CdSe NAs are more like the “mesoscopic structures” pointed out by Woggon et al. [14] that cited above.

In our opinion, the NAs may comprise a very interesting system for studying fundamentals of the electronic properties of disordered nanostructures. According to Anderson-Mott theory, it is believed that localized and non-localized electron states separated by the mobility edge in disordered solid are coexisted [19]. It is noteworthy that the energy state in the NAs is confined to a small region of space — the volume of the NAs, which has decreased to a regime of quantum size effects, the non-localized electron states disappear, and then there exists only wave function of localized states in the NAs, which is so-called Anderson localization [20]. In the situation of disordered materials, the rectification can be explained by the Anderson-Mott theory, which is illustrated in Fig. 5,

showing the comparison between the density of states in bulk and nanoscale disordered semiconductor and a hypothetical PL mechanism of disordered nanosystem. In the case of bulk disordered semiconductor, according to the Mott-CFO model [19], the localized states (the deep band tail) are separated from extended states by critical energies that called the mobility edges, and the difference between the energies of the mobility edges in the valence and conduction bands is called the “mobility gap” corresponding to the band gap in crystalline semiconductor. As size is reduced to a nanometer size regime, the density of electronic states change, i.e., the extended states vanished because of spatial limit and the energy levels of the localized states alter from continuous to discrete similar to the 0D nanocrystal. Under this condition, an electron transits from the occupied localized states to the unoccupied localized states by photoexcitation in the NA, thus an exciton (electron-hole pair) generates and is confined to and delocalized over the volume of the NA, and then the recombination of the electron and hole radiates a photon. The PL process is the same with the nanocrystals, and that is why the NAs have similar PL spectra with the nanocrystal. On the other hand, the number of the energy levels is more than that of the nanocrystal, so no discrete exciton absorption is observed in the absorption spectra and there are three peaks in the PLE spectra. Decreasing NA diameter increases the separation between the occupied localized states and the unoccupied localized states, which results in blue shift of the absorption edge and the PL peak.

Quantum confinement has been successfully used to explain the tunable band gap in semiconductor nanocrystal with controllable size, which is required in the regime below the Bohr radius (about 15.6 nm) [1,2,10]. When it comes to the nano-noncrystal, the confined regime must be rectified in respect that the CdSe NAs with bigger size (from diameter from 17 to 25 nm) also show tunable band gap similar to the CdSe nanocrystal, which are interpreted earlier in terms of strong intercluster coupling. In the situation of non-crystalline materials, the rectification can be explained by the Anderson-Mott theory [16], which is illustrated in Fig. 5, showing the comparison between the density of states in bulk and nanoscale non-crystalline semiconductor. In the case of bulk non-crystalline semiconductor, according to the Mott-CFO model [16], the localized states (the deep band tail) are separated from extended states by a critical energies that called the mobility edges, and the difference between the energies of the mobility edges in the valence and conduction bands is called the “mobility gap” corresponding to the band gap in crystalline semiconductor. As size is reduced to a nanometer size regime, quantum confinement effect arises by changes in the density of electronic states that the extended states vanished because of spatial limit and the energy levels of the localized states alter from continuous to discrete similar to the 0D nanocrystal. At this condition,

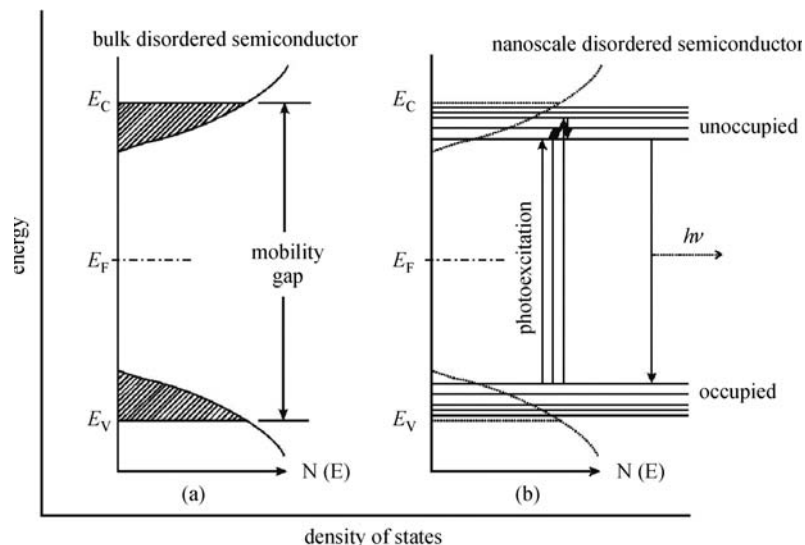


Fig. 5 (a) Mott-CFO model proposed for density of states in bulk disordered semiconductor, the localized states which are shown shaded are separated from the non-localized states by mobility edges in the conduction band (E_C) and the valance band (E_V). (b) In the case of nanoscale disordered semiconductor, the localized states become discrete because of quantum confinement; upon photo-excitation an electron transmit from the highest occupied localized state to the unoccupied localized states, and the recombination lead to a photon emission. E_F is the Fermi energy level

an electron transits from the occupied localized states to the unoccupied localized states by photoexcitation in the NA, thus an exciton (electron-hole pair) generates and is confined to and delocalized over the volume of the NA, and then the recombination of the electron and hole radiates a photon. The PL process is the same with the nanocrystals, which is the reason why the NAs have similar PL spectra with the nanocrystal. On the other hand, the number of the energy levels is more than that of the nanocrystal, so unlike the nanocrystal in the absorption spectra there is no discrete exciton absorption. Decreasing NA diameter increases the separation between the occupied localized states and the unoccupied localized states, which induces the blue shift in the absorption edge and PL peak. The optical properties of the NAs and the following NAs mass fit well to the above discussion.

The NAs mass with much larger size were further obtained by simply adding excessive intermediate level ligand, 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt (PTBT), to the as-prepared solution of dispersive NAs and heating at 100°C for several hours. The typical TEM images of the NAs and the NAs mass are shown in Fig. 6. The dispersive NAs aggregate together and fuse in a certain way, which looks like the porous silicon. The size of the mass is up to several micrometers, and the longer heating time the bigger and more compact mass formed. Unlike the dispersive NAs that consists of obvious small clusters, the NAs mass consists of sizable non-crystalline grains connecting by amorphous boundary, and it seems to be hollow for the boundary is darker than the grain. Although the NAs mass possess significant difference in morphology from the NAs, the selected area

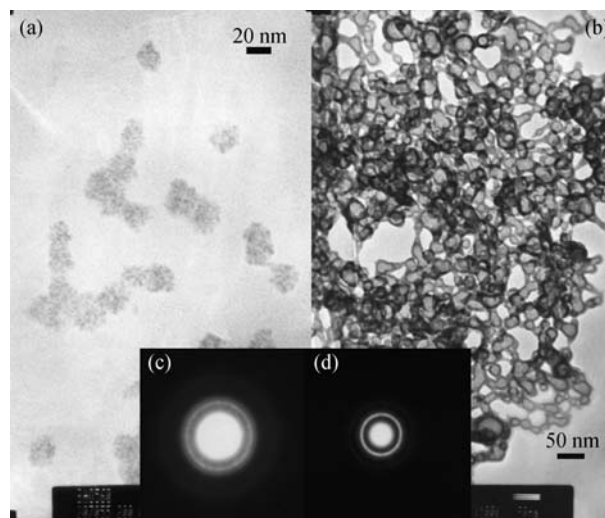


Fig. 6 Typical TEM images of the as-prepared dispersive NAs (a) and NAs mass (b), the ED patterns of them show notable difference ((c) is the dispersive NAs and (d) is the NAs mass)

ED pattern of the NAs mass shows still show a similar one uniform distributed diffraction ring, indicating it is still made of near amorphous CdSe crystal structure with random orientations

The UV-Vis spectra were recorded at different time to investigate the formation process of the NAs mass from NAs. It clearly demonstrated that by increasing the heating time, the edge of the absorption becomes indistinct due to the scattering of the mass of NAs, as shown in Fig. 7(a).

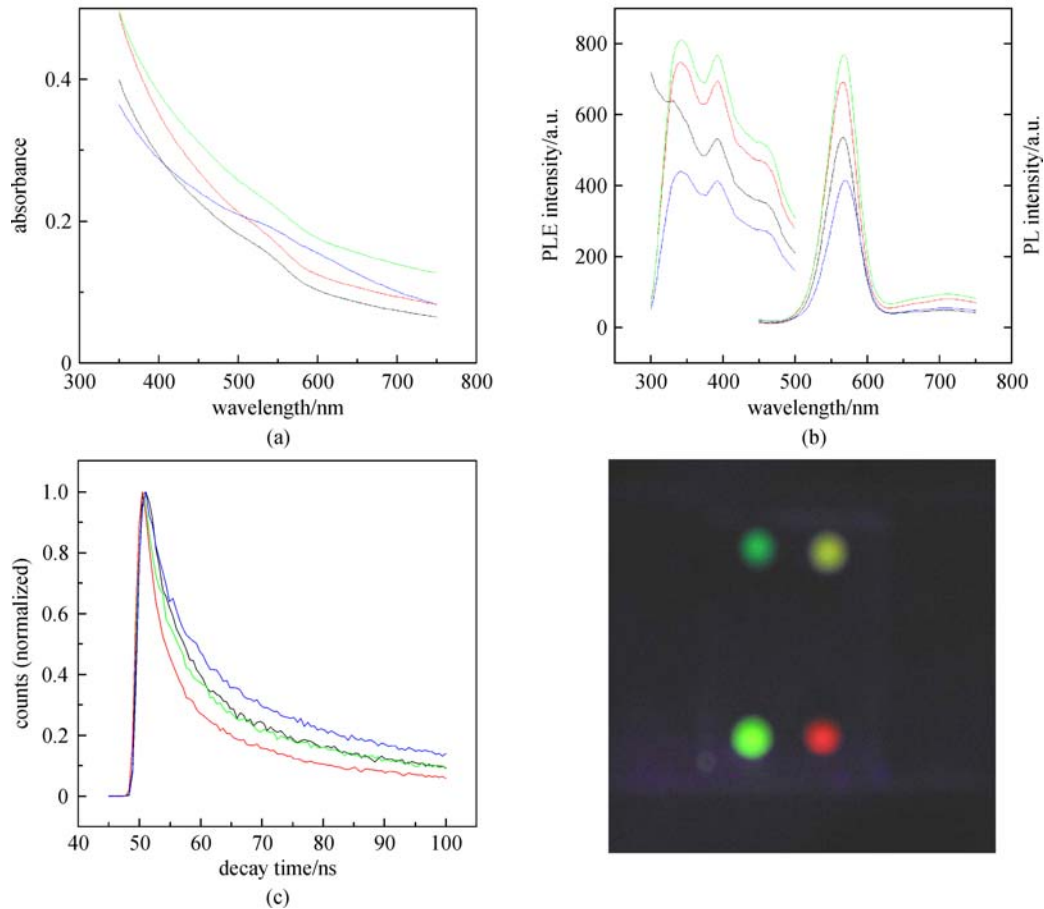


Fig. 7 Room temperature UV-Vis absorption spectra (a), PL and PLE spectra (b) and PL lifetime (c) of four samples, which are dispersive NAs (black line), added ligand PTBT and heated for 1 h (red line), 4 h (green line) and 26 h (blue line), respectively. All the samples are in aqueous solution, and the PL lifetimes are recorded at 566 nm ($\lambda_{\text{ex}} = 337$ nm). The last image is size-dependent change of the photoluminescence color of CdSe NAs mass deposited in the cavities on glass slide upon UV- excitation (365 nm)

While, very interestingly, we found that the formation of NAs mass from NAs and the increase of the size of the NAs mass by prolong the reaction time both do not change the position of the PL peak but only changes the PL intensity, which is contrary to the assembled nanocrystals [23]. In most previously reported materials, the aggregation and growth usually lead to a shift in PL peak position and a decrease in PL intensity. In our experiments, the PL intensity rises about 40% by heating for 4 h while depress by heating for 26 h (Fig. 7(b)). The mechanism of these changes is not clear by now. Meanwhile, the PLE spectra of the three samples of NAs mass have similar shape but show noticeable changes compare with the dispersive NAs: the peak at 343 and 392 nm remains unchangeable, while the PLE intensity at higher energy range decreases remarkably. Considering the different fine structure mentioned above, we think that the higher energy range is attributed to the small clusters containing in the dispersive NAs, which are not seen in the mass. The NAs mass show tolerable monochromaticity for the FWHM is about 40 nm.

For the dispersive NAs, the PL decayed with a lifetime

of 8.4 ns, while for the three samples of NAs mass, the PL decayed with lifetime of 6.1, 8.0, 10.5 ns, respectively. All the PL decays are fitted exponentially (Fig. 7(c)). The lifetime becomes longer with increased size.

As mentioned before, NAs with tunable emission were prepared by control the synthesis of the dispersive CdSe clusters. Figure 7(d) shows that upon UV-excitation these CdSe NAs mass emit strong fluorescence, which is deposited in cavities on glass slide. It is interesting that the NAs mass with disordered morphology and micrometers level size has controllable PL in the visible range of spectroscopy. In view of the structure observed by TEM and the synthesis process, we believe that the grains in the mass play the determined role because the PL results reveal that the band gap (the difference between the highest occupied and lowest unoccupied localized states) of the NAs does not alter in the formation process of NAs mass, which means that the Anderson localized states are reserved in the mass no matter what the disorder degree, composition or surface chemistry in the assemblies. Namely, the grains may behave as naturally formed quantum dots, upon photoexcitation an electron-hole pair

is created within the quantum confined grain, and the recombination leads to a photon emission.

4 Conclusion

In conclusion, monodisperse CdSe NAs with tunable emission were synthesized by a facile method in aqueous solution at a low temperature of 100°C without high pressure. The CdSe NAs are composed by the assembly of CdSe nanoclusters and possess disordered nanostructures. The optical and electronic properties of this nanomaterial are determined by the formation of collective electron states in the agglomerates based on Anderson localization. The CdSe NAs may have potential application in single electron transistor at room temperature because of the disordered random potential trap. According to the disordered Anderson Model, the disorder of random potential trap formed a collective trap that can restrict the transport of electron transfer in the NAs, thus the room temperature single-electron effects may be observed.

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