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Correlation between the Photoluminescence and Oriented Attachment Growth Mechanism of CdS Quantum Dots

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Abstract: Water-soluble mercaptoacetic acid-coated 3.1 nm CdS quantum dots (QDs) with two concentrations were selected for studying the correlation between the photoluminescence and the crystal growth mechanism. By achieving the classic Ostwald ripening mechanism and oriented attachment (OA) growth mechanism, we have shown that the evolution of the emission spectra were obviously different. The change in both the surface and internal defects during OA crystal growth were responsible for the specific variation of the photoluminescence of CdS QDs. Strategies for obtaining QDs with different luminescent properties are suggested.

In recent years, luminescent quantum dots (QDs) such as those made from CdS, CdSe, and ZnS have triggered an increasing concern for their potential applications in biomarkers, light-emitting devices, and so on.[1] Researchers have already realized that the physical properties (e.g., the luminescence characteristics) are closely associated with the sizes,[1a] surface states,[2] and lattice defects of the QDs. Among these factors, the lattice defect is regarded as a crucial factor in determining the photoluminescence (PL) of QDs. However, universal knowledge about how to control the formation and disappearance of lattice defects is absent.

In fact, both the surface states and lattice defects are closely related to the crystal growth mechanisms. Recently, it was noticed that the nucleation and growth processes are related to the size and size distribution of the QDs,[3] and the luminescence mechanism of the QDs could be different during different synthetic periods.[4] However, most of the endeavors for improving the quantum yield of QDs are still based on the presumption that the classic Ostwald ripening (OR) growth mechanism is involved in the liquid-phase synthesis of nanocrystals, wherein nanocrystals are inclined to have relatively complete internal lattices, making the variation of the surface defects the main factor influencing the luminescent properties.[5] On the basis of this understanding, various studies have been focused on the passivation of surface dangling bonds via organic and inorganic coating. However, a recent investigation disclosed that a new growth mechanism named "oriented attachment" (OA), wherein two crystallographically oriented nanoparticles could combine directly to form a larger one, might be involved in or even dominate the synthetic process for nanomaterials.[6] When the OA mechanism is dominant, the nanocrystals may generally contain a large number of internal lattice defects.[6d] Since the OA and OR mechanisms could coexist during nanosynthesis,[6d] difficulties arise in the investigation of the relationship between the luminescence properties and the defect states. Obviously, in order to clearly understand the correlation between the luminescence properties and the QD formation process, synthetic conditions that facilitate only one of the growth mechanisms should be designed.

Normally, OR growth is independent of the concentration of the initial nanoparticles.[6b] It has been found that OR could be inhibited by the strong surface-capping situation on the nanoparticles.[6d] On the contrary, the growth rate of OA is closely related to the size and concentration of the initial nanoparticles. Generally, when the size of the initial nanoparticles is relatively small and the concentration is high, there is a high probability that two original particles could collide with each other to form a larger nanoparticle. Once OR growth is inactivated by surface-capping, the growth mechanism could be dominated by pure OA.[6b]

In this context, a surface-capped CdS QDs sample was selected as a precursor to coarsen at two selected concentrations (20 vs 0.1 mM). As shown in Figure 1, for the low-concentration CdS QDs (0.1 mM, $\sim 5.12 \times 10^{16}$ initial CdS QDs/L), fitting results revealed that the growth of CdS QDs mainly followed the OR mechanism (Figure 1a, solid line). For the high-concentration CdS QDs (20 mM, $\sim 1.03 \times 10^{19}$ initial CdS QDs/L), the growth of CdS QDs mainly followed the typical "1 + 1" OA growth kinetics (Figure 1d, solid line). As shown in the curve, the OA growth predominantly happened between two primary particles, so nanocrystals grew from the primary size of ~3.1 nm to a limiting size of ~3.9 nm (analytic details of the two growth mechanisms can be found on pp S2−S5 in the Supporting Information). Thus, achieving these two growth mechanisms individually allowed the relationship between the PL characteristics and the crystal growth to be analyzed as described below.

As shown in Figures 1b,c and 1e,f, under these two crystal growth modes, the evolution of the PL spectra was obviously different. As we know, the peaks at 470 and 550−600 nm could be attributed to the band-edge and defect-state PL of CdS QDs, respectively. It could be observed that the initial nanoparticles exhibited strong defect-induced luminescence, while no obvious band-edge luminescence was found. During the OR growth, the peak correlating to the defect states was rapidly quenched in the initial 30 min (Figure 1b, stage I). Afterward, the band-edge luminescence emerged and was quickly enhanced (Figure 1c, stage II). However, during the OA growth, the peak correlating to the defect states was rapidly enhanced in the initial 15 min and then decreased slightly during the period from 20 to 60 min (Figure 1e, stages I′ and II′). After 70 min, the luminescence of both the band edge and the defect states enhanced simultaneously (Figure 1f, stage III′).

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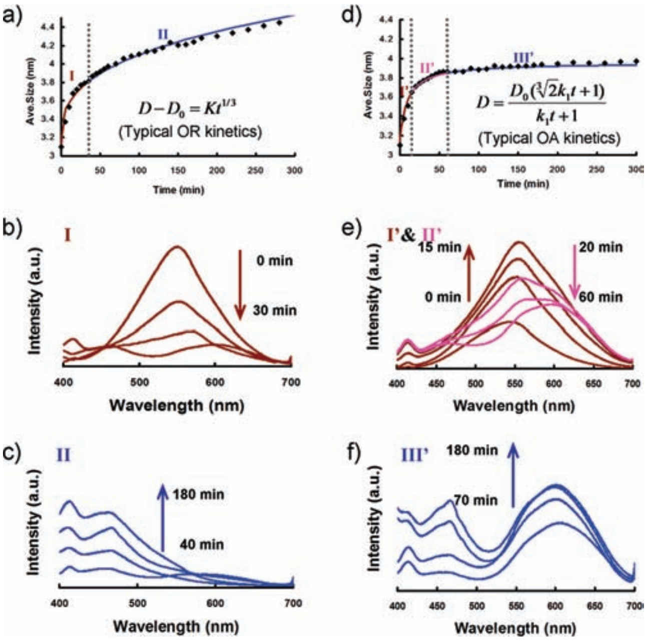

Figure 1. Evolution characteristics of the PL spectra of mercaptoacetic acid-coated 3.1 nm CdS QDs coarsened at 100 °C under two sets of conditions. (a) When the concentration of CdS QDs was 0.1 mM, the experimental growth data (square dots) were fit well by a typical OR kinetic equation (solid lines). (b, c) Evolution characteristics of the PL spectra coarsened in (b) stage I (0, 10, 24, 30 min) and (c) stage II (40, 70, 110, 160 min) of OR kinetics. (d) When the concentration of CdS QDs was 20 mM, the experimental growth data (square dots) were fit well by a typical OA kinetic equation (solid lines). The fitted results show the typical "1 + 1" mode, in which one-step coalescence between two primary particles occurs and the dominant reaction stops at secondary particles. (e, f) Evolution characteristics of PL spectra coarsened in (e) stage I′ (0, 5, 10, 15 min; brown curves) and stage II′ (20, 35, 60 min; pink curves) and (f) stage III′ (70, 110, 140, 180 min). The excitation wavelength for the PL spectra was 360 nm. The peak at 413 nm is the Raman scattering from water. The red shift of the defect emission from 550 to 600 nm during the initial period of both OR and OA growth could originate from the self-adjustment of the defect states (for more details, see p S7 in the Supporting Information).

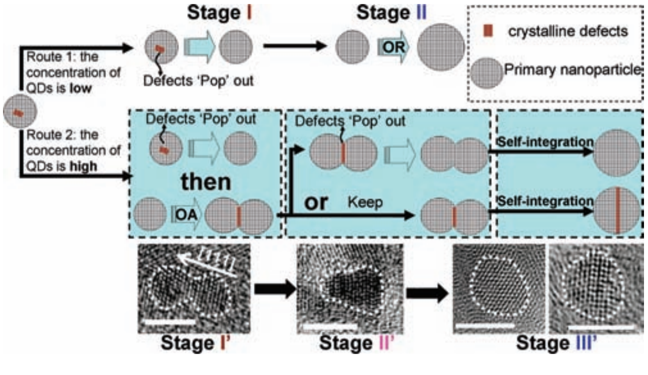

Figure 2. Evolution of the defect state and morphological state of nanoparticles during OA and OR growth. Route 1: nanoparticles grew via the OR mechanism. Route 2: nanoparticles grew via the "1 + 1" OA mechanism. Typical transmission electron microscopy (TEM) images were collected for the sample coarsened in the 20 mM CdS QDs solution for 10, 35, and 150 min, representing the nanoparticles in stages I′ (collision and oriented attachment), II′ (during self-integration), and III′ (after self-integration). The preferred crystallographic plane for OA growth is the sphalerite (111) plane. TEM scale bar: 5 nm.

The above phenomena can be illustrated well in Figure 2. The strong defect-induced luminescence of the initial nanoparticles could mainly be attributed to the internal lattice defects that arise from the fast deposition during the initial nucleation process.[7] At the beginning of the OR growth, these defects could be "popped" out of the nanocrystals (Figure 2, stage I), and thus, the PL of the defect state was quenched quickly. After 30 min, most of the internal defects from the nucleation process had disappeared. Thus, with the size increase, on one hand, the amount of surface defects decreased correspondingly; on the other hand, the crystallinity of the QDs increased. These two structural factors both helped to enhance the luminescence of the band edge and repress the luminescence of the defect states (Figure 2, stage II). During OA growth, in the initial 15 min (as illustrated in Figure 2, stage I′), two major competitive processes were ongoing: (i) elimination of the internal defects and (ii) formation of OA-induced defects. As we know, the combination of two primary particles into a secondary particle could create a high concentration of dislocations and defects between the two initial parts.[6] In this period, the formation rate of OA-induced defects could be much higher than the elimination rate of the internal defects, so the luminescence of the defect states tended to be enhanced. During the period from 20 to 60 min, when the primary particles were gradually consumed, the OA growth rate slowed. Accordingly, with the popping out of some of the OA-induced defects, the luminescence of the defect states was quenched slightly (Figure 2, stage II′). After 70 min, the self-integration of the nanostructures became dominant (Figure 2, stage III′). For some of the nanostructures, the internal defects could escaped over time, so high-crystallinity nanoparticles with enhanced band-edge luminescence could be achieved. However, once the internal defects were embedded too deep, the proportion of dislocations could be extended across the whole particle,[6d] so nanoparticles with enhanced defect-state luminescence were also produced. Here it is worth mentioning that we mainly considered the variation of the internal defects, since during our experimental design, the interference from aggregation, surface states, and environments were reduced as much as possible (for details, see p S7 in the Supporting Information).

Recently, low-cost aqueous synthesis of QDs has become increasingly important.[2a] Since aqueous synthesis is carried out at a relatively low temperature, where the defects cannot easily escape from the QDs, a suitable strategy should be well-designed for obtaining QDs with aimed luminescence properties. If we want to create QDs with strong defect-induced luminescence, we should induce the OA mechanism intentionally; moreover, the latter period of OA-based growth should be cut off in time to avoid the self-integration of the defect states and the enhancement of band-edge luminescence. On the contrary, if we want to obtain QDs with strong band-edge luminescence, the occurrence of OA-based growth should be avoided. Otherwise, the defects formed in the early stage of OA-based growth could be retained in the nanocrystals and produce strong defect-induced luminescence.

Actually, the factors that determine the appearance of the OA or OR growth mechanism are complicated and not simply determined by the initial concentration of QDs. In this work, it is very possible that in the high-concentration system, the density of the surfactant on CdS QDs was high. Thus, the OA process was more favored than another system (details can be found on p S6 in the Supporting Information).

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Supporting Information Available: Experimental details, analysis of the initial CdS QDs, determination of the growth kinetics, the reason that OA and OR growth mechanism happened, and the red shift of the defect emission. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The CdS QDs were capped and passivitated by mercaptoacetic acid, so the influence of the surface states on the PL spectra could be ignored (see p S7 in the Supporting Information).

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