Manipulating the growth of aqueous semiconductor nanocrystals through amine-promoted kinetic process†

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In the conventional procedure of the preparation of aqueous semiconductor nanocrystals (NCs), the growth of NCs was mainly through the thermodynamics-favored Ostwald ripening process. It required additional energy to promote NC growth, such as reflux, hydrothermal method, microwave irradiation, and sonochemical synthesis. Energy-promoted growth usually led to the decomposition of mercapto-ligands and therewith decreased the quality of NCs. Consequently, in this study, the growth of aqueous semiconductor NCs was designed through an amine-promoted kinetic process, which efficiently shortened the growth duration and avoided the decomposition of ligands, thus providing a universal method for preparing various aqueous binary and ternary NCs.

Owing to the size-dependent optical properties, semiconductor nanocrystals (NCs) are envisaged as both important models of condensed matter physics and promising materials for photoelectric applications.1,2 Consequently, great efforts are devoted to synthesizing NCs through various physical and chemical protocols, among which the colloid chemical route is one of the most successful methods, characterized by the capability to tune the sizes, shapes, and surface chemistries of NCs.3–6 The colloid chemical method is also flexible for synthesizing NCs either in high boiling point organic solvents (organometallic synthesis and its derivative methods) or in aqueous media (aqueous synthesis),3,6 thus widely extending the applications of NCs from hybrid solar cell to biocompatible labeling.7–9 Both organometallic and aqueous synthesis have their own advantages and disadvantages, respectively, because of the differences in raw materials, growth media, and especially growth conditions.10 In this context, although aqueous synthesis is seemingly closer to the “green chemistry” concept, the quality of preformed NCs is usually worse than that of organometallic synthetic ones. Namely, aqueous synthetic NCs inherently possess a broader emission width, lower quantum yield (QY), and larger Stokes shift.10–12 Although many auxiliary technologies have been attempted to improve the quality of aqueous synthetic NCs,12–24 the origin of these disadvantages is as yet unrevealed, which limits the technical progress of aqueous synthesis.

Basically, the size-dependent bandgap emission of NCs is originated from the electron-hole (exciton) recombination.3 The reduction of NC size widens the gap between valence band and conduction band, thus increasing the energy of excitons when going from bulk crystals to NCs, and then to smaller NCs. However, the exciton recombination is also influenced by the lattice vibration (optical phonon) of NCs, because a photoinduced electron and/or hole may couple with the lattice vibration.25 Note that the strength of exciton–phonon coupling (EPC) is determined by the anomaly of the atomic array in NCs; namely, a large anomaly enhances EPC. In comparison to bulk crystals, the atomic array of NCs is more disordered. It enhances the EPC strength, thus greatly influencing the luminescence position, efficiency, and lifetimes of NCs.26 Therefore, EPC is helpful for understanding the temperature-, composition-, and structure-dependent spectral shift of semiconductor NCs. The synthesis methods of NCs may significantly influence EPC strength by affecting the spatial array of atoms. In comparison to organometallic synthesis, mercapto-compounds are used as capping ligands in aqueous synthesis.10 For the energy-promoted growth of aqueous NCs through the thermodynamics-favored Ostwald ripening (OR) process (such as conventional reflux, hydrothermal method, microwave irradiation, and sonochemical synthesis), the decomposition of mercapto-ligands usually occurs and therewith embeds sulfur into NCs.10–15 Thus, the anomaly of atomic array increases as well as the enhancement of EPC strength. In this scenario, the spectra of aqueous synthetic NCs should be inherently different from organometallic synthetic ones without avoiding the decomposition of mercapto-ligands.

Recently, a kinetics-favored agglomeration growth was observed at the initial stage of NC growth in aqueous media.27–30 Dependent on the species of ligands, pH, and concentration, NCs may grow through the adhesion and coalescence of small clusters and/or NCs. At this stage, NCs grow rapidly even at room temperature.27,28 Because the kinetics-favored growth requires no energy, the decomposition of mercapto-ligands in conventional thermodynamics-promoted growth might be avoided by extremely prolonging the duration of kinetic growth. Consequently, in this study, the growth of aqueous semiconductor NCs is deliberately designed through an amine-promoted kinetic process. The embedment of sulfur into NCs from the decomposition of mercapto-ligands becomes avoidable, thus providing a new method to further improve the quality of aqueous synthetic NCs.

† Electronic supplementary information (ESI) available: Temporal size evolution, XPS characterization, XRD peak position, average size and size distribution, and zeta potentials of CdTe NCs in the presence of simple amines, stepwise formation constants for Cd2+ with MPA, NH3, and N2H4, and amine-promoted growth for other aqueous binary and ternary NCs. See DOI: 10.1039/b919655b
As shown in Fig. 2, the addition of $N_2H_4$ also facilitated the observed growth of NCs at the initial stage. Namely, kinetics-favored stage. However, the strong interaction between Cd and amine-containing mercapto-ligands in turn decreased the colloidal stability of preformed NCs, making NCs separate from solution during storage. Consequently, in this study, we attempted to use various water-soluble simple amines to promote CdTe NC growth rather than mercapto-ligands. Fig. 1 indicated the temporal evolution of the UV-vis absorption and photoluminescence (PL) spectra of 3-mercaptopropionic acid (MPA)-stabilized CdTe NCs at 100 °C simultaneously in the presence of different concentration of ammonia (NH$_3$) or hydrazine (N$_2$H$_4$). Meaningfully, the addition of NH$_3$ or N$_2$H$_4$ significantly accelerated NC growth. According to growth rate, the amine-promoted growth of NCs could be divided into two stages. The mean size rapidly increased during the first 2–4 h reflux, whereas the growth rate clearly slowed in the following growth (Fig. 1b and d, and Fig. S1†). At the first stage, characterized by the fast growth of NCs, NC growth was through kinetics-favored agglomeration, whereas at the second stage the growth was through thermodynamics-favored OR. Fig. 1b and d clearly indicated that the fast growth of NCs in the presence of NH$_3$ or N$_2$H$_4$ mainly occurred at the first stage; namely, kinetics-favored stage. For example, a dramatically rapid growth of NCs was observed in the presence of 1.75 mol L$^{-1}$ N$_2$H$_4$. With only 2 h reflux, the UV-vis absorption peak shifted to 646 nm, and the calculated diameter of NCs was 4.3 nm (Fig. 1d and Fig. S1†). This meant the addition of amines to a NC collective could facilitate the growth of NCs through kinetics-favored progress. Besides, a smaller Stokes shift was observed for the NCs prepared by amine-promoted growth in comparison to those in the absence of amines (Table 1). This implied that embedding S into the bulk of CdTe NCs was partially avoided by amine-promoted growth rather than a thermodynamics-favored stage. High-resolution TEM (HRTEM) images presented that CdTe NC growth was kinetics-favored process. Moreover, X-ray powder diffraction (XRD) investigation presented that the lattice parameters of CdTe NCs prepared by N$_2$H$_4$-promoted growth fitted well to the zinc blende structure of the bulk CdTe crystal (Fig. 2d and Table S2). Only a small shift of XRD peak positions towards cubic CdS crystal was observed. It was different from the CdTe NCs prepared by conventional reflux or any other energy-promoted method. These results clearly proved that N$_2$H$_4$-promoted NC growth avoided embedding S into the NC bulk, which was consistent with the XPS analysis (Table S1†).

Transmission electron microscopy (TEM) images indicated that the CdTe NCs by N$_2$H$_4$-promoted growth were in the form of quasi-spherical particles, but their size distribution was broader than those prepared by conventional reflux (Fig. 3 and Table S3†). It revealed that NC growth was through random kinetic adhesion and coalescence of small clusters and monomers. High-resolution TEM (HRTEM) images presented that CdTe NCs possessed cubic structure without twinning planes and stacking faults (inset of Fig. 3), indicating amine-promoted growth might eliminate the embedded of S into NC bulk.

The mechanism of amine-promoted growth was understandable according to the colloidal stability theory. In this scenario, aqueous NCs were essentially stabilized by their...
surface charges; the overlapping of electric double-layer generated interparticle electrostatic repulsion. Entire NCs possessed an inorganic core, ligand layer, adsorbed layer, and diffuse layer from inside to outside (Scheme 1). The inorganic core and the ligand layer respectively represented NC photoelectric functionality and the assembly behavior. The adsorbed layer corresponded to the contact adsorbed ions: namely, the assumed boundary of solid NCs and the liquid environment. For a growing NC, moreover, the diffusion of monomers from the solution to NC surface should traverse the diffuse layer.29 This property must be considered in the process of NC growth, because the electrostatic interaction significantly governed the total interactions between NCs and their monomers.29 The effect of electrostatics on the growth of aqueous NCs has been systematically revealed.29,30 Namely, the growth rate depended on the equilibrium of various interparticle interactions. The experimental variables that lowered electrostatic repulsion facilitated the growth of NCs. A fast growth would be achieved through lowering the charges of monomers. For MPA-stabilized CdTe system, Cd monomers were in the form of Cd(MPA), Cd(MPA)$_2$/C$_0$, Cd(MPA)$_3$/C$_0^4$, and Cd(MPA)$_m$/C$_0^{2(m−1)}$.22 Because the molar ratio of Cd/MPA was 1 : 2.4, Cd monomers were mainly in the form of Cd(MPA)$_2$/C$_0$. Besides, among these monomers, the neutral monomer of Cd(MPA) was easier to migrate through diffuse layer than the charged ones due to the weak electrostatic repulsion between Cd(MPA) and NCs.29 With the addition of NH$_3$ or N$_2$H$_4$, moreover, they could compete with MPA by coordinating with Cd, thus forming Cd(MPA)$_m$/(NH$_3$)$_{(2(m−2))}/C_0$, or Cd(MPA)$_m$/(N$_2$H$_4$)$_{(2(m−2))}/C_0$ (Scheme 1). It greatly lowered the charges of Cd monomers,

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<th>Reflux duration/min</th>
<th>Stokes shift/nm</th>
<th>0.175 mol L$^{-1}$ NH$_3$</th>
<th>0.175 mol L$^{-1}$ N$_2$H$_4$</th>
<th>0.875 mol L$^{-1}$ N$_2$H$_4$</th>
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Fig. 2 N$_2$H$_4$-promoted CdTe NC growth at room temperature. Temporal evolution of the UV-vis absorption and PL emission spectra (a), and UV-vis peak (b) of MPA-stabilized CdTe NCs. (c) Fluorescence photographs of NC solutions with different emission colors. (d) XRD pattern of NCs with different emission colors. The concentration of Cd$^{2+}$ was 0.5 mmol L$^{-1}$, whereas the molar ratio of Cd/MPA/Te was 1 : 2.4 : 0.2. The concentration of N$_2$H$_4$ in (a), (c) and (d) was 12 mol L$^{-1}$.

Fig. 3 TEM and HRTEM (inset) images of CdTe NCs. NCs were prepared through the storage of precursors in the presence of 12 mol L$^{-1}$ N$_2$H$_4$ at room temperature for 5 min (a), 2 h (b), 24 h (c), and 129 h (d). The corresponding UV-vis absorption and PL spectra, fluorescence photographs, and XRD pattern were indicated in Fig. 2a, c and d.
than their decomposition. The concentration of NH$_3$ or N$_2$H$_4$ must be increased fixing N$_2$H$_4$ concentration but decreasing NC concentration (Fig. S3). This result also supported that the increase of the weak coordination interaction between N$_2$H$_4$ and Cd monomers became easier to adhere and fuse with NCs, promoting the growth of NCs. In this context, the coordination between Cd and MPA was much stronger than that with NH$_3$ or N$_2$H$_4$ (Table S5†). Consequently, in order to increase the growth rate of CdTe NCs, the concentration of NH$_3$ or N$_2$H$_4$ must be increased (Fig. 1b and d). Besides, a fast growth was also observed by fixing N$_2$H$_4$ concentration but decreasing NC concentration (Fig. S3†). This result also supported that the increase of the coordination between Cd and N$_2$H$_4$ lowered the charges of Cd monomers and therewith facilitated the growth of NCs. Furthermore, the addition of N$_2$H$_4$ presented a faster growth than that of NH$_3$ (Fig. 1). It was attributed to the relatively weak coordination interaction between N$_2$H$_4$ and Cd (Table S5†), which mainly facilitated the growth of NCs rather than their decomposition.$^{19,28}$ Amine-promoted growth was also available for CdTe NCs stabilized by other mercapto-ligands, especially for 1-thioglycerol (TG) (Fig. S4†). Because TG-stabilized CdTe NCs grew very slowly through conventional reflux at 100 °C,$^{10}$ amine-promoted growth provided an efficient method for obtaining TG-stabilized NCs with orange and red emission. Meaningfully, the PLQY of the as-prepared NCs reached to 10%, the highest for TG-stabilized CdTe NCs ever reported.$^{10}$ Moreover, through the addition of NH$_3$ or N$_2$H$_4$, the growth of other aqueous NCs was also facilitated, for instance ZnS, CdS, Zn$_x$Cd$_{1-x}$S, and CdSe$_y$Te$_{1-x}$ (Fig. S5†), indicating the current strategy could be generalized to the preparation of various binary and ternary semiconductor NCs in water.

In conclusion, we report a general and facile method to direct the growth of aqueous semiconductor NCs through kinetics-favored process; the addition of NH$_3$ or N$_2$H$_4$ into growing NCs weakened the electrostatic repulsion between Cd monomers and NCs, greatly facilitating the agglomeration growth of NCs. In comparison to the conventional thermodynamics-favored growth, the decomposition of mercapto-ligands is avoidable and therewith prevents the embedment of S into NCs. As a result, the strength of EPC was reduced, characterized by the small Stokes shift. Because this attempt provided a new strategy for tuning the growth process of aqueous NCs simultaneously without lowering their PLQY, our efforts are currently devoted to revealing the detailed mechanism of amine-promoted growth as well as to synthesizing various aqueous NCs through this method.

**Experimental method**

Aqueous solutions of the precursors of CdTe NCs were obtained by adding freshly prepared solutions of NaHTe to N$_2$-saturated CdCl$_2$ solutions at pH 9.0 in the presence of mercapto-ligands.$^{15,28}$ The concentration of the precursors was 0.02 mol L$^{-1}$ with reference to the concentration of Cd$^{2+}$, whereas the molar ratio of Cd$^{2+}$/ligand/HTe was 1:2.4:0.2. Subsequently, the proper amount of ammonia or hydrazine hydrate was mixed with the precursors, and was diluted to the desired concentrations using deionized water. The precursors were not purified prior to the addition of ammonia or hydrazine hydrate. The resulting mixture was either refluxed at 100 °C or stored at room temperature to maintain the growth of CdTe NCs. As NCs reached the desired size, NH$_3$ and N$_2$H$_4$ were removed by precipitating NC solution using 2-propanol and centrifugation. The collected precipitates of NCs were re-dispersible in water. Following a similar procedure, except using Na$_2$S or NaHSe and NaHTe, and Zn(NO$_3$)$_2$, CdCl$_2$, or Zn(NO$_3$)$_2$ and CdCl$_2$, ZnS, CdS, Zn$_x$Cd$_{1-x}$S, and CdSe$_y$Te$_{1-x}$ precursors and corresponding NCs were prepared.

UV-visible absorption spectra were obtained using a Shimadzu 3100 UV-vis spectrophotometer. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. The excitation wavelength was 400 nm. All optical measurements were performed at room temperature under ambient conditions. The PLQYs of NCs were estimated at room temperature using quinine in aqueous 0.5 mol L$^{-1}$ H$_2$SO$_4$ as PL reference.$^{6}$ Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. HRTEM imaging was implemented by a JEM-2100F electron microscope at an acceleration voltage of 200 kV with a CCD camera. HRTEM imaging was implemented by a JEM-2100F electron microscope at an acceleration voltage of 200 kV with a CCD camera. X-ray powder diffraction (XRD) investigation was carried out using Siemens D5005 diffractometer. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg K$_\alpha$ excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. Zeta potential measurements were performed using a Zetasizer.
NanoZS (Malvern Instruments). Each sample was measured ten times, and the average data were presented.

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