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# Preparation of CdS Nanocrystals within Supramolecular Self-Assembled Nanoreactors and Their Phase Transfer Behavior

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A new strategy for the synthesis of CdS nanocrystals (NCs) within supramolecular self-assembly nanoreactors has been described. The self-assembly nanoreactors were readily constructed through the electrostatic interactions and ion pairs between palmitic acid and the terminal amine groups of hyperbranched polymer. In a chloroform/water two-phase system, aqueous Cd<sup>2+</sup> ions were spontaneously encapsulated into the cavities of self-assembly nanoreactors in chloroform. After reaction with S<sup>2-</sup> ions, the CdS NCs with high stability were obtained. By the addition of excess triethylamine, CdS NCs formed in the self-assembly nanoreactors were transferred from organic phase into aqueous phase. After dialysis and rotatory evaporation, aqueous CdS NCs could be redispersed into chloroform solution containing palmitic acid.

## 1. Introduction

Inorganic nanocrystals (NCs) exhibit unique size- and shape-dependent optical and electronic properties<sup>1–8</sup> and are of great interest in applications such as optoelectronics,<sup>9–11</sup> photovoltaic devices,<sup>12,13</sup> and biological labels.<sup>14,15</sup> In past decades, significant progress has been made in the synthesis, characterization, and shape control of NCs.<sup>1–21</sup> Usually, wet chemical routes including the nonaqueous TOPO/TOP technique and the use of low molecular weight thiols or polyphosphates as stabilizers in aqueous solution are widely used for the generation of nearly monodisperse and highly luminescent semiconductor NCs.

In recent years, an alternative approach that adopts block copolymers, dendrimers, hyperbranched polymers, and so forth as nanoreactors and stabilizers has been used to synthesize CdS

NCs.<sup>22–24</sup> Polymers first sequester Cd<sup>2+</sup> ions, and then, after reaction with S<sup>2-</sup>, they stabilize the resulting CdS NCs by preventing aggregation.<sup>23</sup> The NCs prepared within polymer templates integrate the characteristic properties of NCs and polymers together, so they easily form films and assemble on substrates. Such a strategy provides an opportunity for tuning the mechanical, optical, electronic, and magnetic properties of NCs.<sup>25</sup>

In this work, we present a general and facile route for the generation of CdS NCs using a supramolecular nanoreactor formed by the self-assembly of hyperbranched polymers and fatty acids. Different from NCs prepared by dendritic polymers only, the size distributions of NCs synthesized by supramolecular self-assembly can be better controlled. Furthermore, NCs produced by this method can be easily transferred between water and organic phases, which fertilizes their applications greatly. Although supramolecular micelles based on the self-assembly of dendritic polymers and long-chain or short-chain acid have been used to encapsulate water-soluble dyes or metal ions,<sup>26–28</sup> the synthesis and phase transfer of NCs based on this kind self-assembly has not yet been reported. On the other hand, we have noted that dendritic polymers such as polyethylenediamines (HPEIs) have been covalently modified with acyl chloride as well as by imine condensation into ketones and aldehydes to form core–shell

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structures.<sup>29</sup> Such amphiphilic structures have been used to encapsulate NCs<sup>30</sup> and dyes<sup>29</sup> or to synthesize NCs.<sup>31</sup> Compared to this method, the supramolecular self-assembly method described in this article possesses several advantages, such as occurrence without purification and easy phase-transfer.

## 2. Experimental Section

**2.1. Materials.** HPEI (degree of branching (DB) = 60%, average molecular weight ( $M_n$ ) = 10 000 g mol<sup>-1</sup>, polydispersity index (PDI) = 2.5) was purchased from Adrich. Hyperbranched poly(amidoamine) (HPAMAM) was synthesized from commercially available methyl acrylate (an AB monomer) and ethylenediamine (a C<sub>n</sub> monomer) by one-pot polymerization via the couple–monomer methodology.<sup>32</sup> The gel permeation chromatography (GPC) measurement showed that the number average molecular weight ( $M_n$ ) and the PDI after functionalization by benzoyl chloride were 8320 and 1.9, respectively. Cd(AC)<sub>2</sub> and CHCl<sub>3</sub> were purchased from Shanghai Reagent Company. Anhydrous Na<sub>2</sub>S was from Alfa Aesar. Ultrapure water (18.2 MΩ/cm) was used in all experiments.

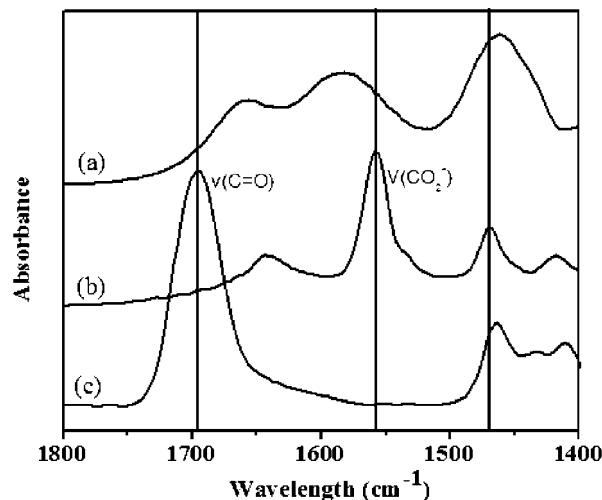
**2.2. Synthesis of CdS NCs in Supramolecular Self-Assembled Micelles.** In a typical synthesis, palmitic acid (PA) was added to amine-terminated HPEI chloroform solution in 1:1 molar ratio (PA/primary amine), thus supramolecular micelles were formed. Aqueous Cd(AC)<sub>2</sub> solution was added to this micelle chloroform solution. After vigorous stirring for 48 h, the upper aqueous layer was removed and then the substrate was deaerated with N<sub>2</sub> for 20 min, followed by injecting oxygen-free aqueous Na<sub>2</sub>S solution. The mixture was stirred for 1 h at room temperature. After standing for several hours, the optically clear CdS chloroform solution was separated.

**2.3. Phase Transfer of CdS NCs from Chloroform Phase into Aqueous Phase.** In a typical phase transfer, excess triethylamine was added to the chloroform solution of CdS NCs prepared within an HPEI/PA supramolecular nanoreactor in a vessel. After stirring for 1 h, isovolumetric ultrapure water was added. To initiate the phase transfer, the vessel was vigorously stirred. After several minutes, the transfer of NCs from organic phase to aqueous phase occurred, which could be easily detected by its color change.

**2.4. Measurements.** Infrared measurements were performed on a Bruker Equinox-55 FTIR spectrometer. Ultraviolet–visible (UV–vis) spectra were recorded on a Perkin-Elmer Lambda 20/2.0 UV/vis spectrometer. Transmission electron microscopy (TEM) and elemental characterization were done on a JEOL 2010 microscope with an energy-dispersive X-ray spectrometer (EDS) at an accelerating voltage of 200 kV. Dynamic light scattering (DLS) measurements were carried out at 25 °C by using Zetasizer Nano-S (Malvern Instruments, Ltd., Malvern, Worcestershire, U.K.).

## 3. Results and Discussion

When PA was added to amine-terminated HPEI chloroform solution in 1:1 molar ratio (PA/primary amine), supramolecular micelles formed. Figure 1 gives the Fourier transform infrared (FT-IR) spectra of HPEI, PA, and their complex. After complexation, the carboxyl band of PA at 1695 cm<sup>-1</sup> disappears, and an asymmetric carboxylate peak at 1558 cm<sup>-1</sup> appears. This indicates that electrostatic interactions between PA and HPEI exist.<sup>26</sup> Thus, a supramolecular micelle with a hydrophilic dendritic core and a hydrophobic alkyl shell has been prepared. DLS measurements (see Supporting Information, Figure S1) show that the hydrodynamic diameter of HPEI (3 mg/mL) is 5.1 nm, whereas the average size of the HPEI/PA complex (PA/primary amine = 1) is 6.8 nm, as reported previously.<sup>28</sup> These DLS



**Figure 1.** FT-IR spectra of (a) neat HPEI, (b) HPEI/PA complex (the molar ratio of primary amine groups to PA is 1) in chloroform solution, and (c) neat PA.

values also support that a supramolecular self-assembled micelle with a core–shell structure is formed.

HPEI/PA supramolecular micelles can bind the metal ions through their chelating nitrogens, thus they can be used as nanoreactors to synthesize metal or semiconducting NCs. Because of their reversibility as an electrostatic self-assembly, NCs prepared in such nanoreactors can be easily transferred between organic and aqueous phases upon breaking or rebuilding the self-assembly, as illustrated in Scheme 1. In a two-phase system, aqueous Cd<sup>2+</sup> ions were first transferred into the cavities of HPEI/PA micelles in chloroform, thus they were sequestered by these micelles. After reaction with S<sup>2-</sup> from aqueous phase, the HPEI/PA micelles stabilized the resulting CdS NCs by preventing aggregation. The present two-phase system for NCs possesses several advantages: (I) the load of Cd<sup>2+</sup> can reach a maximum extent, and excess Cd<sup>2+</sup> in the aqueous phase will not be transferred to the chloroform solution as a result of the complexing capacity of HPEI to Cd<sup>2+</sup>, thus the existence of free Cd<sup>2+</sup> in the chloroform solution can be prevented; and (II) redundant S<sup>2-</sup> will react with Cd<sup>2+</sup> sequestered by HPEI/PA micelles, and the excess S<sup>2-</sup> will only remain in the aqueous phase. The resulting CdS NCs solution exhibits light yellow color, and shows a long stability for months against aggregation.

In general, the electrostatic self-assembly driven by acid–base chemistry and ion pairing is reversible. As reported elsewhere, adding HCl or simple dilution with pure solvent will break this kind of self-assembly. Herein, with the addition of excess triethylamine to the chloroform solution of CdS NCs, the electrostatic interactions between triethylamine and PA compete with that of HPEI and PA. Thus, HPEI/PA supramolecular micelles are broken, and the hydrophobic PA molecules are dissolved into chloroform solution. Correspondingly, the surface of CdS NCs is changed from a hydrophobic PA layer to a hydrophilic HPEI layer. After adding ultrapure water to the chloroform solution and stirring vigorously, CdS NCs can be transferred into aqueous phase in the form of CdS–HPEI nanocomposites. The transfer of CdS NCs is evidenced by the light yellow color in aqueous phase, as shown in Figure 2. After dialysis and rotary evaporation, CdS NCs can be redispersed in chloroform solution containing PA in the form of CdS–HPEI/PA nanocomposites.

The hydrodynamic diameters of CdS nanocomposites were measured by means of DLS technique. Figure 3 shows that the

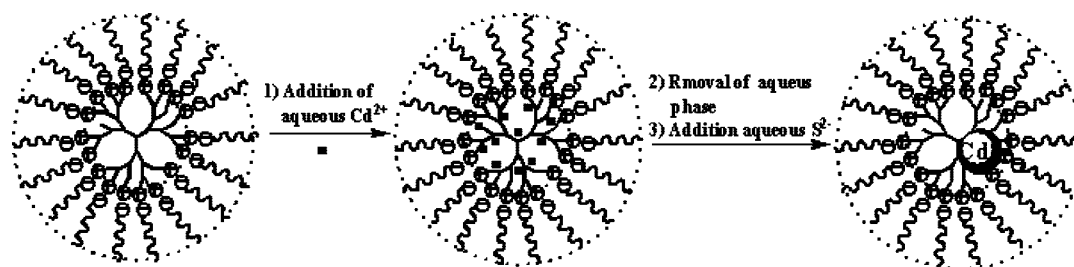
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**Scheme 1. Schematic Illustration of the Synthesis of CdS NCs within Self-Assembled Nanoreactors Prepared from Hyperbranched Polymer HPEI and Fatty Acid PA**



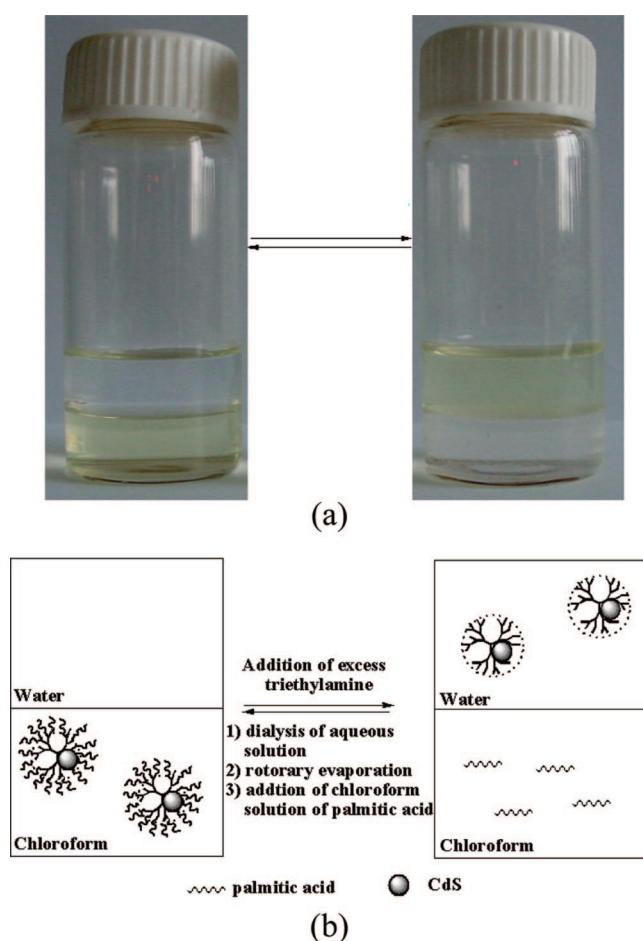
initial diameter of CdS nanocomposites prepared in chloroform phase (CdS–HPEI/PA) is 6.8 nm, while it decreases to 5.2 nm after phase transfer to aqueous phase. This can be tentatively attributed to the absence of PA on CdS NCs after phase transfer. DLS data also prove that the HPEI/PA supramolecular nanoreactors do not invert, but break after addition of triethylamine, as demonstrated in Figure 2b.

The size of CdS NCs can be estimated from the absorption peak using the Brus effective mass model.<sup>33</sup> The CdS NCs within self-assembled micelles exhibit an absorption plateau at 326 nm, as shown in Figure 4a. From the absorption plateau, the size of CdS NCs is estimated to be 2.5 nm. For CdS NCs transferred to aqueous phase, an absorption peak at 364 nm emerges (Figure 4b), and the Brus model predicts a NC diameter of 2.8 nm. In

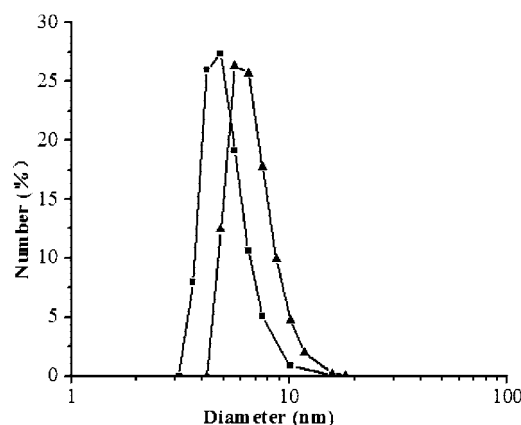
the phase transfer process, we can see that there is a slight increase for the size of CdS NCs. This can be tentatively attributed to the fact that CdS NCs stabilized by HPEI are less stable than those prepared in HPEI/PA and might grow.

TEM was employed to investigate the morphology of the as-prepared CdS NCs. Figure 5a shows a typical TEM image of CdS NCs obtained in the template of supramolecular micelles. The nanoparticles are monodisperse and isolated with a mean size about 3 nm. The corresponding EDS spectrum (see Supporting Information, Figure S2) gives the signals of Cd and S elements, confirming the existence of CdS NCs. After transferring into aqueous phase, the diameter makes little change compared with the initial NCs, as shows in Figure 5b.

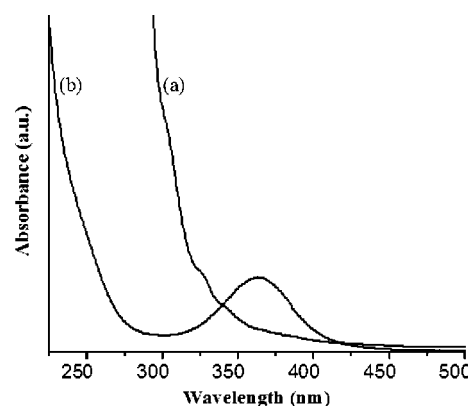
Figure 6 shows a comparison of FT-IR spectra between 4000  $\text{cm}^{-1}$  and 500  $\text{cm}^{-1}$  of HPEI, HPEI/PA, CdS NCs prepared within HPEI/PA, and CdS NCs transferred into aqueous phase in the form of CdS/HPEI nanocomposites. The broadband at 3383  $\text{cm}^{-1}$



**Figure 2.** (a) Phase transfer of CdS NCs prepared within HPEI/PA demonstrated by a photograph taken in daylight. Left: NCs prepared within self-assembled micelles of HPEI/PA. Right: NCs transferred into aqueous phase in the form of CdS/HPEI nanocomposites. (b) A schematic illustration of the transfer of CdS NCs between organic and aqueous phases.

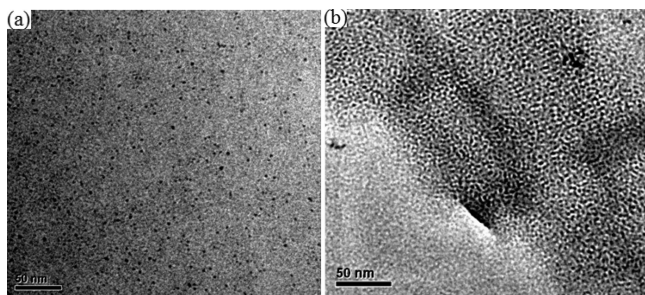


**Figure 3.** Size distribution of CdS nanocomposites before (triangles) and after (squares) phase transfer, measured by DLS.

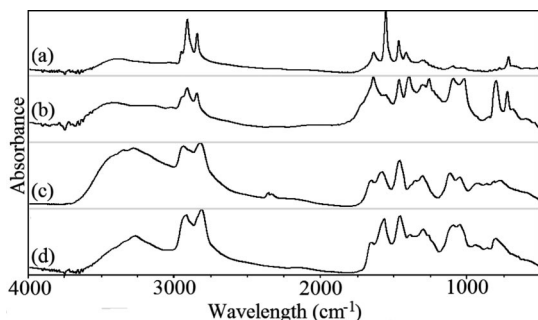


**Figure 4.** Absorption spectra of CdS NCs (a) before and (b) after phase transfer.





**Figure 5.** TEM images of CdS NCs (a) before and (b) after phase transfer. The scale bar is 50 nm.

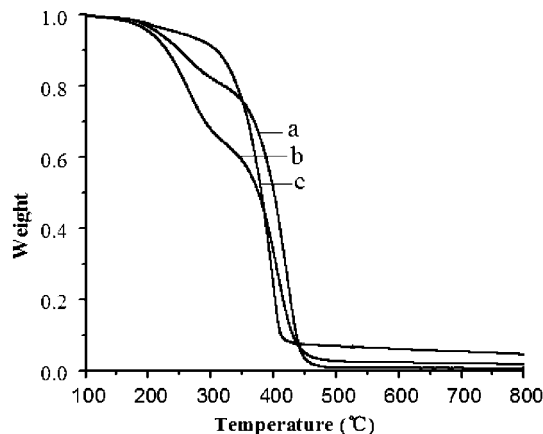


**Figure 6.** FT-IR spectra of (a) HPEI/PA, (b) CdS NCs prepared within HPEI/PA, (c) HPEI, and (d) CdS NCs transferred into aqueous phase in the form of CdS/HPEI nanocomposites.

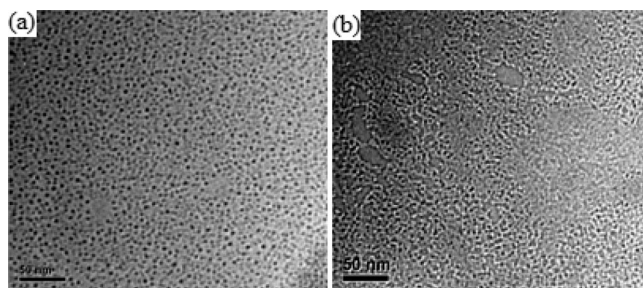
in Figure 6a is characteristic for the N–H stretching bond frequency of primary and secondary amine groups. The bands at 2916 and 2850  $\text{cm}^{-1}$  in Figure 6a correspond to asymmetric  $-\text{CH}_2-$  stretching vibration and symmetric  $-\text{CH}_2-$  stretching vibration, respectively. The scissoring vibration of primary amines in HPEI in Figure 6c appears at 1656  $\text{cm}^{-1}$ , while it shifts to 1643, 1642, and 1660 for samples a, b, and d in Figure 6, respectively. This may be due to the conformational change of HPEI after assembling along with PA or/and CdS NCs. A previous report on the synthesis of NCs with dendrimer templates also showed that the interaction between dendrimers and NCs led to the frequency changes in FT-IR.<sup>34</sup> From Figure 6d, we can also see that the  $-\text{CH}_3$  stretching vibration at 2956  $\text{cm}^{-1}$  disappears after CdS NCs are transferred into aqueous phase in the form of CdS/HPEI nanocomposites compared to Figure 6a,b. This suggests that HPEI/PA self-assembly breaks, and PA is no longer capped on CdS NCs along with HPEI.

The compositions of CdS NCs before and after phase transfer were measured by thermogravimetric analysis (TGA), as shown in Figure 7. At 800 °C, the weight losses of CdS NCs prepared within HPEI/PA and CdS NCs transferred in the aqueous phase in the form of CdS/HPEI nanocomposites are 98 wt% and 95 wt%, respectively. These values are lower than that of neat HPEI/PA (100 wt%), which can be attributed to the existence of CdS NCs. They also suggest that there is 2 wt% and 5 wt% CdS NCs in CdS nanocomposites before and after phase transfer, respectively.

HPEI is not only soluble in water but also can dissolve in chloroform, while hyperbranched polymer HPAMAM is only soluble in water. However, amine-terminated HPAMAM can dissolve in chloroform solution containing PA. Similar to the electrostatic self-assembly of HPEI/PA, the fatty acid molecules



**Figure 7.** TGA weight loss curves of (a) HPEI/PA, (b) CdS NCs prepared in HPEI/PA, and (c) CdS NCs transferred into aqueous phase in the form of CdS/HPEI nanocomposites. The heating rate was 20 °C/min.



**Figure 8.** TEM images of CdS NCs (a) prepared within self-assembled micelles HPAMAM/PA and (b) transferred in the aqueous phase in the form of CdS/HPAMAM nanocomposites. The scale bar is 50 nm.

of PA arrange around HPAMAM to form self-assembled micelles that have a hydrophilic dendritic core and a hydrophobic alkyl-chain shell. With the above-mentioned strategies, we also successfully realized the synthesis and phase transfer of CdS NCs within HPAMAM/PA self-assembled micelles. TEM images in Figure 8 reveal that uniform-sized NCs about 4.1 nm are obtained by using HPAMAM/PA self-assembled nanoreactors.

#### 4. Conclusion

In summary, we have demonstrated the synthesis of CdS NCs within supramolecular nanoreactors and their phase transfer behavior. The supramolecular self-assembly is driven by electrostatic interactions and ion pairs between PA and the terminal amine groups of hyperbranched polymers HPEI or HPAMAM. With this strategy, water-soluble hyperbranched polymers can be used to prepare NCs in the organic phase, and the phase transfer between organic phase and aqueous phase for NCs can be readily realized.

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**Supporting Information Available:** DLS data of HPEI and HPEI/PA and EDS spectrum of CdS NCs are provided in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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