A New Two-Phase Route to Cadmium Sulfide Quantum Dots Using Amphiphilic Hyperbranched Polymers as Unimolecular Nanoreactors

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ABSTRACT: A new two-phase route was developed to prepare monodisperse cadmium sulfide (CdS) quantum dots (QDs) with a narrow size distribution. In a two-phase system, chloroform and water were used as separate solvents for palmitoyl chloride functionalized hyperbranched polyamidoamine (HPAMAM-PC) and cadmium acetate/sodium sulfide, respectively. The amphiphilic HPAMAM-PC, with a hydrophilic dendritic core and hydrophobic arms, formed stable unimolecular micelles in chloroform and was used to encapsulate aqueous Cd^{2+} ions. After the reaction with S^{2-} ions from the aqueous phase, monodisperse and uniform-sized CdS QDs stabilized by HPAMAM-PC unimolecular micelles were obtained. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 991–997, 2011

Key words: branched; micelles; nanocomposites

INTRODUCTION

Semiconductor quantum dots (QDs) show unique size- and shape-dependent optical and electronic properties[1,2] and are currently applied extensively to applications in light-emitting devices,[3–6] nonlinear optical devices,[7] solar cells,[8] and biolabeling.[9,10] At present, various methods have been developed for the synthesis of high-quality QDs, such as the nonaqueous trioctyl phosphine oxide/trioctyl phosphine (TOPO/TOP) technique[11–13] and the aqueous route with different thiols[14–17] or polymers[18–22] as stabilizers. However, to realize the real applications of these fluorescent QDs, the stabilization of these inherently instable particles with inorganic or organic materials as matrices is a prerequisite. Several feasible approaches have been proposed. Among them, the incorporation of as-prepared QDs into polymer matrices or the *in situ* preparation of QDs within polymers has attracted more attention. Compared with the postprocessing of QDs by polymers, a one-pot procedure to synthesize QDs within polymeric matrices would be more convenient, albeit the quantum yield (QY) and the broad emission spectrum of QDs prepared in this way should be improved further.

Herein, we present a facile two-phase route for the preparation of cadmium sulfide (CdS) QDs with amphiphilic hyperbranched polymers as unimolecular nanoreactors and stabilizers. In contrast to linear block copolymers, amphiphilic hyperbranched polymers, as one important subclass of dendritic polymers, have internal cavities and plenty of functional groups.

Additional Supporting Information may be found in the online version of this article.

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Importantly, amphiphilic hyperbranched polymers with a core–shell structure can form stable unimolecular micelles in solvents, which can be distinguished from the strong physical aggregation of linear block copolymers.[23,24] Therefore, amphiphilic hyperbranched polymers might be ideal matrices for the preparation of QDs. Compared with the method of preparing CdS QDs within neat dendritic polymers, the method using amphiphilic hyperbranched polymers as unimolecular nanoreactors possesses several advantages, including occurrence without purification and better control of the size and size distribution of QDs. It also shows advantages illustrated later: (1) the ratio of Cd^{2+} ions to amphiphilic palmitoyl chloride functionalized hyperbranched polyamidoamine (HPAMAM-PC) is no longer a concern because the excess Cd^{2+} ions would not be transferred to the interiors of HPAMAM-PC; (2) redundant S^{2-} cannot react with Cd^{2+} sequestered by HPAMAM-PC micelles, and excess S^{2-} will only remain in the aqueous phase; and (3) the maximum load of HPAMAM-PC to CdS QDs can be easily achieved.

EXPERIMENTAL

Materials

Ethylenediamine (EDA), triethylamine, $CHCl_3$, and $Cd(CH_3COO)_2{\cdot}2H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anhydrous Na_2S was purchased from Alfa Aesar (Lancaster, Pennsylvania, USA). Methylacrylate (MA) was purified under reduced pressure before use. Ultrapure water (18.2 MΩ/cm) was used in all of the experiments.

Synthesis of hyperbranched polyamidoamine (HPAMAM)

HPAMAM was synthesized from commercially available MA (an AB monomer) and EDA (a Cn monomer; 1 : 1 molar ratio) by a one-pot polymerization via couple–monomer methodology. Typically, 19.82 g (0.33 mol) EDA and 5 mL of methanol were put into a flask placed in a cryohydrate bath, and then, 28.41 g (0.33 mol) of MA mixed with 25 mL of methanol was added dropwise to the flask under stirring. The system was allowed to react at room temperature for 48 h. Then, the flask was fixed onto a rotary evaporator to remove the methanol *in vacuo*. After the reaction proceeded for 1 h at 60°C, 2 h at 100°C, 2 h at 120°C, and 2 h at 140°C in the rotary evaporator *in vacuo*, a slightly yellow dope was obtained.[25]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, δ): 1.80–2.30 (NH_2, NH), 2.30–2.50 ($COCH_2$), 2.50–3.0 [$COCH_2CH_2NH$, $NH(CH_2)_2NH$, $NH(CH_2)_2NH_2$], 3.20–3.50 (NCH_2), 3.50–4.0 (CH_3O).

End-capping of HPAMAM with palmityl chloride

Chloroform (12 mL) and triethylamine (6.05 mL) were added to 2.4814 g of HPAMAM in a flask placed in a cryohydrate bath. Then, 6.62 mL of palmityl chloride dissolved in 12 mL of a chloroform solution was slowly added. The mixture was stirred at room temperature for 24 h and was then washed with water several times. The chloroform phase was dried with anhydrous magnesium sulfate and then filtered. Subsequently, the filtrate was concentrated and then drop-added to methanol. After the precipitate was dried *in vacuo* at 50°C for 24 h, the end-capped polymer (HPAMAM-PC) was obtained (weight-average molecular weight = 1.1×10^4, polydispersity index = 2.7).[26]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, δ): 0.83–0.91 (3H, CH_3), 1.25 (24H, CH_2), 1.60 (2H, CH_2), 1.80–2.30 (NH_2, NH), 2.3–2.97 ($NCOCH_2$, NCH_2), 3.19–3.82 (NCH_2, OCH_3).

Synthesis of CdS QDs within unimolecular HPAMAM-PC

Typically, 5 mL of an aqueous $Cd(CH_3COO)_2$ solution (6 m*M*) was added to 40 mL of a chloroform solution of the amphiphilic HPAMAM-PC (2.5 mg/mL) in a conical flask. After vigorous stirring for 48 h and standing for several hours, the upper layer of the aqueous solution was removed, and then, the flask was deaerated with N_2 for 20 min; this was followed by the dropwise addition of 2 mL of an aqueous solution of oxygen-free Na_2S (7.5 m*M*). The mixture was stirred for 3 h at room temperature. After it stood for several hours, the optically clear CdS chloroform solution was separated.

Measurements

^{1}H-NMR measurements were carried out on a Varian Mercuryplus 400 NMR spectrometer (Pala Alto, California, USA) with $CDCl_3$ as a solvent. The content of Cd was measured by an Iris Advangtage 1000 inductively coupled plasma emission spectrograph (Waltham, Massachusetts, USA). Dynamic light scattering (DLS) measurements were performed in a chloroform solution at 25°C with a Zetasizer Nano S (Malvern Instruments, Ltd., Malvern, Worcestershire, United Kingdom). The ultraviolet–visible (UV–vis) spectrum was recorded on a PerkinElmer Lambda 20/2.0 UV–vis spectrometer (Waltham, Massachusetts, USA). Emission spectra were collected with a Varian Cary Eclipse fluorescence spectrometer (Pala Alto, California, USA). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL 2010 microscope (Tokyo, Japan) with energy-dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 200 kV. We

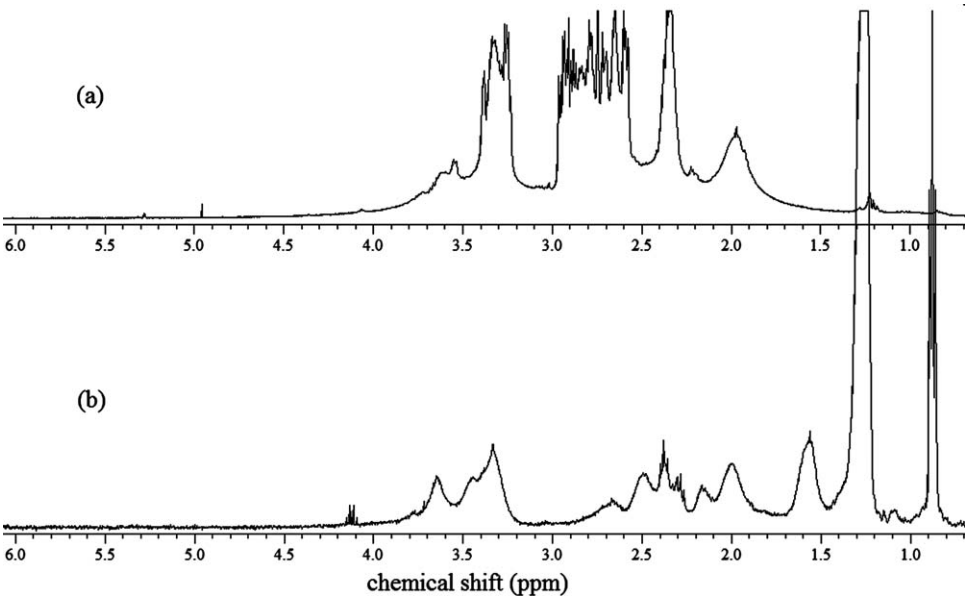


Figure 1 ^{1}H-NMR spectra of (a) amine-terminated polyamidoamine (HPAMAM) and (b) HPAMAM-PC (400 MHz in $CDCl_3$ at 298 K).

prepared grids by dropping a $CHCl_3$ solution of the QDs onto carbon-coated copper grids. The infrared measurements were performed on a Bruker Equinox-55 Fourier transform infrared (FTIR) spectrometer (Karlsruhe, Germany). Thermogravimetric analysis (TGA) was performed under nitrogen on a TGA Q5000IR thermal analyzer (New Castle, Delaware, USA).

RESULTS AND DISCUSSION

NMR characterization of the unimolecular HPAMAM-PC

^{1}H-NMR (Fig. 1) spectra were used to characterize the structure of the amphiphilic HPAMAM-PC. For HPAMAM, peaks corresponding to the double bond of MA were not found, whereas the hydrogen signal of methoxyl groups was observed at about $\delta = 3.5$–4.0 ppm, as shown in Figure 1(a). For HPAMAM-PC, shown in Figure 1(b), the peaks at $\delta = 1.25$ and 0.86 ppm corresponded to methylene ($-CH_2-$) and methyl ($-CH_3$) in palmitoyl. The peaks at $\delta = 1.8$–2.3 ppm were assigned to the amino group in the molecular chain. The ^{1}H-NMR results show that around 50% of the amino groups were end-capped.

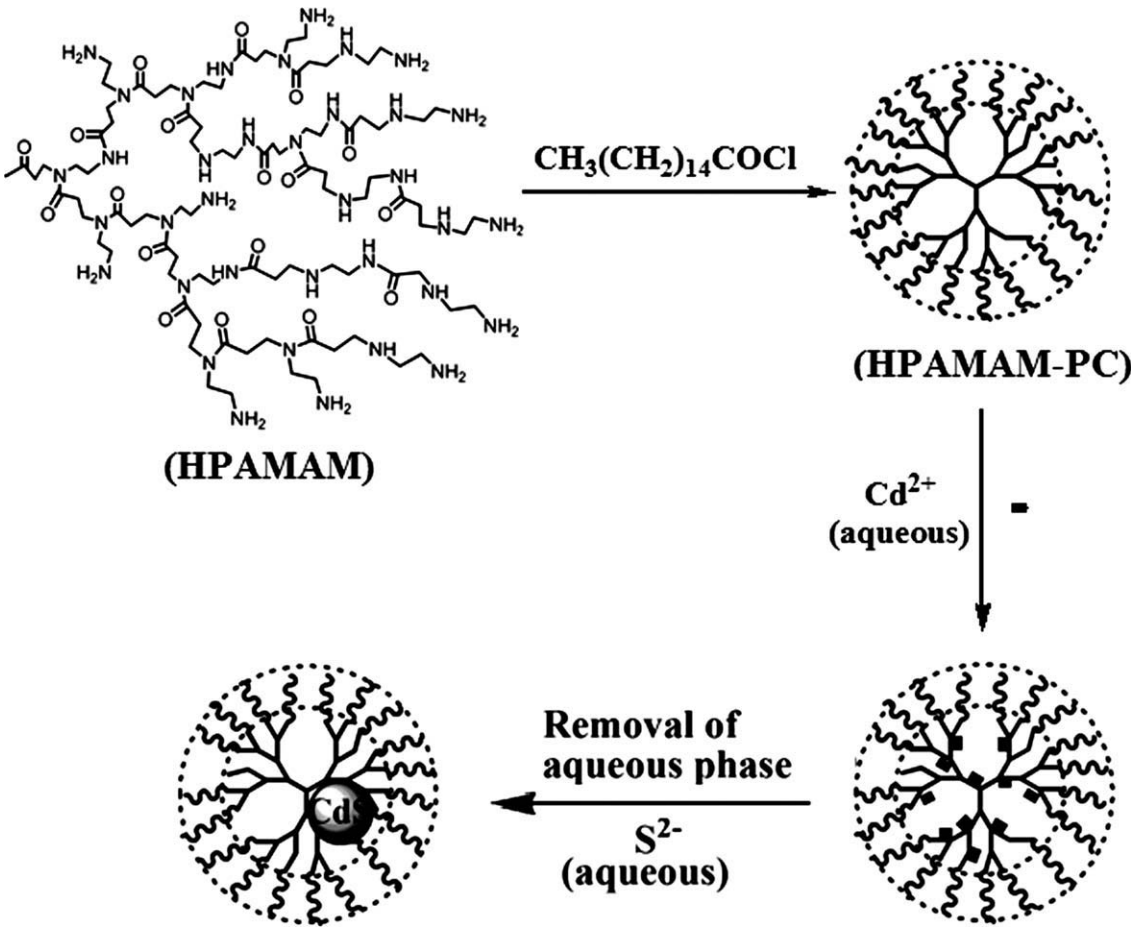
Preparation of CdS QDs within the unimolecular HPAMAM-PC

The preparation of CdS QDs was conducted as follows: aqueous Cd^{2+} ions were first encapsulated in the cavities of HPAMAM-PC in a chloroform solution under vigorous stirring. After the removal of the aqueous phase and reaction with S^{2-} from the aqueous phase, CdS QDs stabilized by HPAMAM-PC resulted. Scheme 1 depicts the proposed mechanism for the preparation of CdS QDs with HPAMAM-PC unimolecular micelles as stabilizers and nanoreactors.

Key role of HPAMAM-PC

In the chloroform solution, the HPAMAM-PC unimolecular micelles consisted of a hydrophilic hyperbranched core surrounded by a hydrophobic shell. The core of the micelles acted as a microreservoir and stabilizer for the incorporation of hydrophilic guests, whereas the hydrophobic shell provided solubility in chloroform and prevented intermolecular aggregation. Moreover, the HPAMAM-PC polymers contained primary, secondary, and tertiary amines that could bind Cd^{2+} ions. Thus, Cd^{2+} ions could be transferred from the aqueous phase into the chloroform phase containing HPAMAM-PC. Here, the core–shell structure and numerous amines of HPAMAM-PC played an important role in the phase transfer of Cd^{2+} ions. The maximum ratio between HPAMAM-PC and the amount of entrapped Cd^{2+} was also investigated, as shown in Figure S1 (see the Supporting Information).

For the single-phase synthesis of CdS QDs within polymers, the molar ratio of Cd^{2+}/polymers needs to be regulated because the free Cd^{2+} will lead to the occurrence of bulk CdS particles. However, for the two-phase system in this study, the amount of Cd^{2+} no longer needed to be considered because the loading capability of HPAMAM-PC to Cd^{2+} ions was fixed and redundant Cd^{2+} ions were not extracted into the interiors of HPAMAM-PC in chloroform. Thus, excessive aqueous Cd^{2+} solution could be added. The quantity of Cd^{2+} in HPAMAM-PC was determined by inductively coupled plasma measurements, and CdS



Scheme 1 Schematic illustration of the preparation of CdS QDs using HPAMAM-PC unimolecular micelles.

QDs with various Cd/S molar ratios were obtained by the addition of different amount of aqueous S^{2-} to the chloroform solution. For CdS QDs with a Cd/S ratio of 1, they were prepared by just the addition of excess aqueous S^{2-} solution, as redundant S^{2-} could not react with the Cd^{2+} ions in the chloroform solution. The resulting CdS QD solution was colorless because of their extremely small size and glowed bright blue under UV illumination. The product showed a high stability against aggregation for several months.

This two-phase nanoreactor system for preparing CdS QDs possessed these advantages:

1. The ratio of Cd^{2+} ions to amphiphilic HPAMAM-PC no longer needed to be of concern and excessive Cd^{2+} could be added. This was because the loading capability of HPAMAM-PC to Cd^{2+} ions was fixed and redundant Cd^{2+} ions in the aqueous phase were not extracted into the interiors of HPAMAM-PC in chloroform solution.
2. Excessive S^{2-} could be added. After all of the Cd^{2+} in HPAMAM-PC reacted with S^{2-}, the redundant S^{2-} still remained in the aqueous phase and could be easily removed by water/chloroform phase separation.

Characterization of the CdS QDs

The hydrodynamic diameters of the HPAMAM-PC and CdS/HPAMAM-PC nanocomposites were measured by means of DLS. Figure 2 shows that the initial

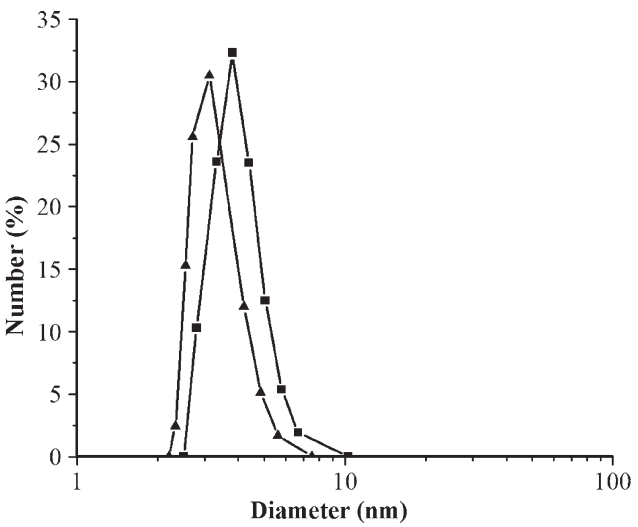


Figure 2 Size distribution of (▲) HPAMAM-PC and (■) CdS/HPAMAM-PC nanocomposites as measured by DLS.

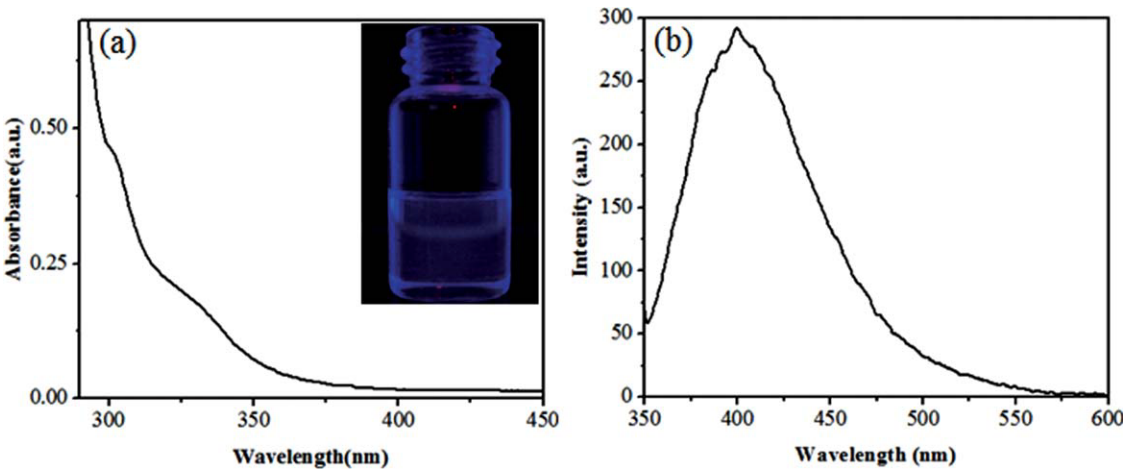


Figure 3 (a) UV–vis and (b) PL spectra of CdS/HPAMAM-PC nanocomposites in chloroform. Inset: Photographs of the CdS/HPAMAM-PC nanocomposites in chloroform illuminated with a UV lamp (365 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diameter of the unimolecular HPAMAM-PC was 3.2 nm in chloroform, whereas it increased a little to 3.7 nm after the CdS QDs were incorporated. This indicated that the CdS QDs were restricted to the interior of HPAMAM-PC and, thus, had no significant influence on the hydrodynamic size of HPAMAM-PC.

Figure 3 displays the absorption and photoluminescence (PL) spectra of the CdS/HPAMAM-PC nanocomposites in chloroform. The CdS QDs exhibited an absorption plateau at 328 nm, as shown in Figure 3(a). Upon UV light irradiation (365 nm), the CdS/HPAMAM-PC chloroform solution emitted intense blue light [inset, Fig. 3(a)]. The size of the CdS QDs was estimated from the absorption peak with the Brus effective mass model.[27] From the absorption plateau, the Brus model predicted that the diameter of the CdS QDs was about 2.5 nm. Upon excitation at a wavelength of 340 nm, the prepared CdS QDs showed a relatively strong emission spectrum with a maximum at 400 nm [Fig. 3(b)]. The relative QY of CdS QDs was measured according to the method described in ref. 28. Coumarin 1 in ethanol with a reported QY of 0.73 was used as a QY standard; the absorbance for the standard and CdS sample at the excitation wavelength of 340 nm and the fluorescence spectra of the same solutions were measured. A relative QY of 0.19 was obtained by this comparison. This value was close to the reported QY of CdS QDs prepared with PAMAM dendrimers in methanol.[18] The relatively low PL of the QDs prepared within polymers was attributed to the quenching effect of polymers with amine groups.[29,30] Compared to QDs tightly coated with small molecular stabilizers, the surface of the QDs functionalized by polymers was imperfect, and many defects existed. When these QDs/polymers nanocomposites were excited, plenty of excitons were trapped, and thus, QY decreased greatly.

TEM was used to investigate the morphology of the as-prepared CdS QDs. Figure 4(a) shows a typical TEM image of the CdS QDs obtained within HPAMAM-PC unimolecular micelles. The size distribution of nanoparticles was rather narrow, with an average diameter of 2.6 nm. Figure 4(b,c) gives the HRTEM image and the selected area electron diffraction (SAED) pattern of the CdS QDs. The lattice planes on the HRTEM image further confirmed the existence of the CdS QDs. The SAED pattern appeared as broad diffuse rings because of the small particle size, and the lattice parameters fit the cubic zinc blended structure of the bulk CdS crystals. The corresponding EDS analysis, shown in Figure 4(d), corroborated the existence of the Cd and S elements in the nanocomposites.

The FTIR spectra of the neat HPAMAM-PC and CdS/HPAMAM-PC nanocomposites are shown in Figure 5. The bands at 2921 and 2851 cm^{-1} in both curves corresponded to the asymmetric —CH_2— stretching vibrations and symmetric —CH_2— stretching vibrations, respectively. The characteristic bands assigned to amides I and II in HPAMAM-PC were at 1643 and 1546 cm^{-1}, respectively whereas the band positions of amides I and II slightly shifted to 1637 and 1549 cm^{-1}, respectively, in the CdS/HPAMAM-PC nanocomposites. These changes indicated that coordination interactions existed between the CdS QDs and HPAMAM-PC through its inner amine groups. A previous report on the synthesis of nanocrystals with a dendrimer template also showed that the interactions between dendrimers and nanocrystals led to the frequency shifts in the FTIR spectra.[31]

The composition of the CdS/HPAMAM-PC nanocomposites was measured by TGA, as shown in Figure 6. The measurement indicated that both the HPAMAM-PC and CdS/HPAMAM-PC nanocomposites

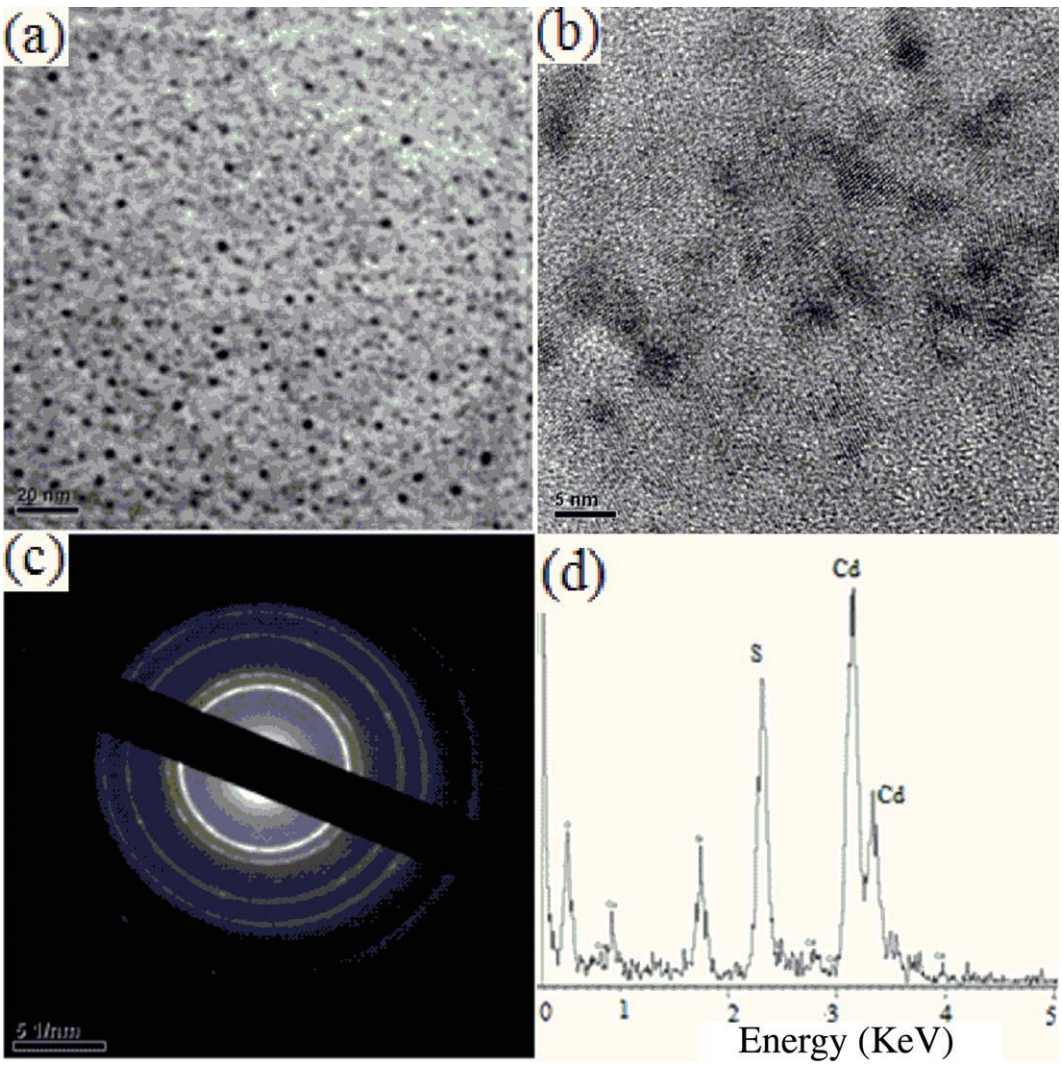


Figure 4 (a) TEM image (scale bar = 20 nm), (b) HRTEM image (scale bar = 5 nm), (c) SAED patterns, and (d) EDS of the CdS/HPAMAM-PC nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

began to decompose close to 300°C, and the existence of CdS QDs slightly increased the decomposition temperature of HPAMAM-PC. At 800°C, the weight loss of CdS/HPAMAM-PC (96.9 wt %) was lower than that of neat HPAMAM-PC (100 wt %); this was attributed to the existence of 3.1 wt % of CdS QDs in the CdS/HPAMAM-PC nanocomposites. The content of the CdS QDs was low because the molecular weight of HPAMAM-PC was not high enough and, hence, limited their encapsulation capability.

Preparation of the metal nanocrystals

As the topological structure and complexation interactions between amines and metal ions are predominant in the process of incorporating metal ions into the internal cavities of HPAMAM-PC, our procedure was successfully extended to prepare other nanoparticles, such as Au and Ag nanocrystals (Fig. S2, see

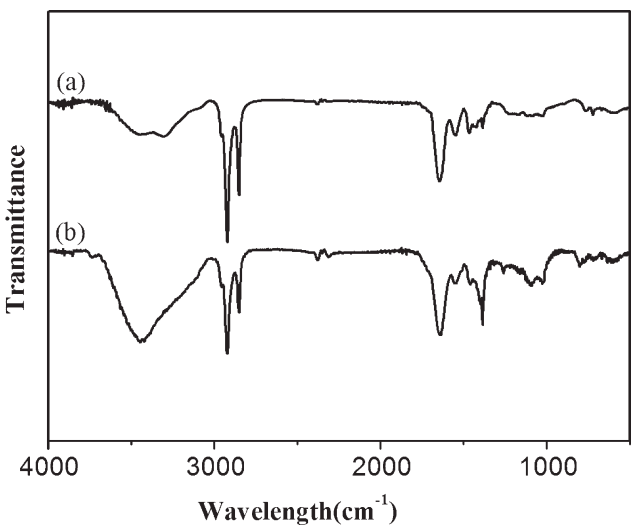


Figure 5 FTIR spectra of the (a) HPAMAM-PC and (b) CdS/HPAMAM-PC nanocomposites.

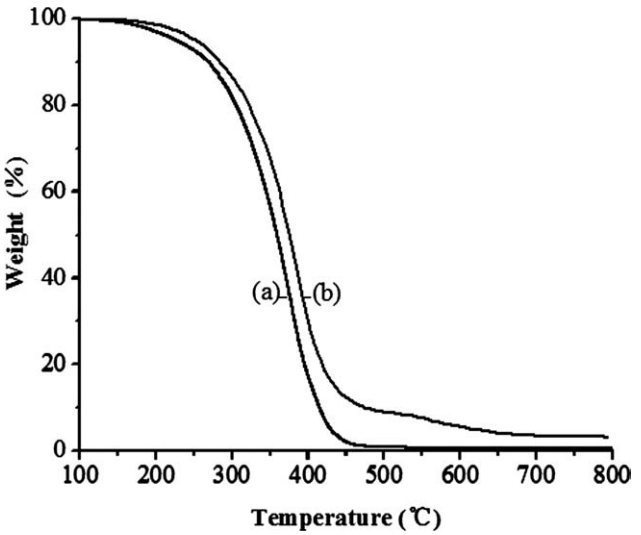


Figure 6 TGA weight loss curves of the (a) neat HPAMAM-PC and (b) CdS/HPAMAM-PC nanocomposites. The heating rate was 20°C/min.

Supporting Information). For example, similar to the aforementioned procedure for CdS QDs, Au nanocrystals smaller than 2 nm in size were prepared by the transfer of aqueous $AuCl_4^-$ ions to the cavities of HPAMAM-PC in the chloroform phase, followed by $NaBH_4$ reduction.

CONCLUSIONS

In this study, a facile two-phase route for preparing CdS QDs with amphiphilic HPAMAM-PC as a unimolecular nanoreactor was developed. With a hydrophilic dendritic core and hydrophobic arms, the amphiphilic hyperbranched polymers formed stable unimolecular micelles in chloroform and were used as nanoreactors and stabilizers to synthesize CdS QDs. Benefiting from the repulsive interactions among the hydrophobic shells, the amphiphilic unimolecular micelles were proven to be effective in controlling the size and size distribution of the CdS QDs. Moreover, this simple and versatile strategy was successfully extended to the preparation of other nanoparticles, such as Au and Ag nanocrystals. Thanks to the amphiphilic nature of polymeric matrices, the resulting nanocrystals/hyperbranched polymer nanocomposites prepared by this strategy might be used to fabricate thin photoluminescent films or to prepare highly ordered hierarchical structures with potential applications in photovoltaics and optoelectronics.

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