Facile Preparation of CdS Quantum Dots Using Hyperbranched Poly(amidoamine)s with Hydrophobic End-Groups as Nanoreactors

Yunfeng Shi,[1,2] Lanbo Liu,[3] Chunlai Tu,[2] Lijuan Zhu,[2] Deyue Yan,[2]
Guolin Li,[2,4] Fulin Guo,[4] Xinyuan Zhu[2]

[1]School of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000,
People's Republic of China
[2]School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites,
Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[3]Clinical Medical College, Shanghai Jiao Tong University, Shanghai 200025, People's Republic of China
[4]Department of Oral and Maxillofacial Surgery, The First Affiliated Hospital of Harbin Medical University,
Nangang District, Harbin 150001, People's Republic of China

ABSTRACT: Hyperbranched poly(amidoamine)s with methyl ester terminals (HPAMAM) were synthesized by one-pot approach and subsequently used as nanoreactors to prepare CdS quantum dots (QDs). HPAMAM could bind Cd^{2+} through their internal amines, while the external methyl ester groups prevented the aggregation of polymers. After reaction with S^{2-}, CdS QDs sequestered within individual hyperbranched polymers were obtained. The resulting CdS/HPAMAM nanocomposites were characterized by dynamic light scattering, transmission electron microscopy, ultraviolet-visible spectroscopy, photoluminescence spectroscopy, and Fourier transform infrared spectroscopy, confirming the formation of CdS QDs with small particle size and narrow size-distribution. Furthermore, the effects of Cd^{2+}/S^{2-} ratio and aging time on the photoluminescence of CdS QDs were also investigated. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1077–1083, 2011

Key words: hyperbranched; CdS quantum dots; nanocomposites; nanoreactors; luminescence

INTRODUCTION

Quantum dots (QDs), also referred to semiconductor nanocrystals, have currently drawn much attention for applications in light-emitting devices,[1–4] nonlinear optical devices,[5] solar cells,[6] and biolabeling.[7,8] At present, various ways have been developed to synthesize high-quality QDs, such as the nonaqueous trioctyl phosphine oxide/trioctyl phosphine technique[9–11] and the aqueous route with different thiols[12–15] or polymers[16–20] as stabilizers. However, to realize the successful applications of these fluorescent QDs, at least two aspects need to be concerned about. First, the optical properties, which usually depend on several factors, such as size, size-distribution, shape, and chemical/biological stability of QDs, should be improved. Second, these inherently instable particles should be stabilized by matrix materials and aggregation of QDs in this process must be prevented.

In the recent years, dendritic polymers[17–20] have been extensively applied as stabilizers and template/nanoreactors to prepare QDs that have narrow size-distribution without aggregation. The dendritic polymers have three-dimensional globular architecture, numerous cavities, and plenty of peripheral functional groups, which offer dendritic polymers the capability of *in situ* preparing QDs with controlled size. Recently, various nanoreactors based on supramolecular multiarm hyperbranched polymers[20] and covalent dynamic hyperbranched polymers[21] were also reported to prepare smart QDs with pH response. The QDs prepared within dendritic polymer may integrate the characteristic properties of QDs and polymers together, and they are easy

to form films or to assemble on substrates. Furthermore, many dendritic polymers such as poly (amidoamine) have been widely used in biomedical science.[22] Therefore, the surface coating with these dendritic polymers might improve the bioapplication of QDs for biolabeling. However, due to the existence of many functional end-groups such as amines, the aggregation of QDs/dendritic polymers nanocomposites happens frequently. To prevent such an aggregation, surface modification of dendritic polymers[21] is usually adopted, which makes the preparation of nanocrystals complicated. If water-soluble dendritic polymeric template with hydrophobic end-groups can be prepared by a simple one-pot synthesis, the preparation of nonaggregated QDs/dendritic polymers nanocomposites will become much easy.

In the present work, a kind of hyperbranched poly (amidoamine) with methyl ester-terminal groups (HPAMAM) was synthesized and used as nanoreactors to prepare CdS QDs. Cd^{2+} ions did not complex with exterior methyl ester groups but only complexed with the inner amines in HPAMAM, thus the resulting CdS QDs could be segregated in the cavities of hyperbranched polymers. Moreover, the size and size-distribution of CdS QDs could be well controlled by this kind of nanoreactors.

EXPERIMENTAL

Materials

Ethylenediamine (EDA), methyl acrylate (MA), methanol, and cadmium chloride hemipentahydrate ($CdCl_2 \cdot 2.5H_2O$) were from Sinopharm Chemical Reagent Co. MA was purified under reduced pressure before use. Anhydrous sodium sulfide (Na_2S) was purchased from Alfa Aesar. The ultrapure water with 18.2M Ω/cm was used in all experiments.

Synthesis of HPAMAM

HPAMAM is a typical kind of hyperbranched polymer, which can be synthesized from commercially available AB and C_n types of monomers (3/1 mol ratio) by one-pot polymerization via the couple-monomer methodology. About 6.61 g (0.11 mol) EDA and 5 mL methanol were added into a flask placed in cryohydrate bath, and then 28.41 g (0.33 mol) MA mixed with 20 mL methanol was dropwise added into the flask under stirring. The reaction was kept at room temperature for 120 h to get an intermediate. ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K) δ = 1.7–1.9 (NH), 2.39–2.46 (NHCH$_2$CH_2CO, NCH$_2$CH_2CO), 2.46–2.48 (NCH_2CH$_2$N), 2.48–2.57 (NHCH_2CH_2N), 2.62–2.67 (NHCH_2CH$_2$N), 2.69–2.72 (NHCH_2CH$_2$NH), 2.72–2.78 (NCH_2CH$_2$CO), 2.85–2.91 (NHCH_2CH$_2$CO), and 3.62–3.68 (CH_3O).

The intermediate in the flask was fixed onto rotary evaporator to remove the methanol under the vac-

uum. The rotate speed was set as 65 revolutions per minute. After reacting for 1 h at 60°C, 2 h at 100°C, 2 h at 120°C, and 2 h at 140°C on the rotary evaporator under vacuum, slightly yellow HPAMAM was gained.[23] It is worth mentioning that water pump was replaced by oil pump for the reaction at 120 and 140°C to improve the vacuum degree and the polymerization degree subsequently. The molecular weight of HPAMAM measured by gel permeation chromatography was about 3.4×10^3, and the molecular weight polydispersity was 1.1. ^{1}H-NMR (400 MHz, CDCl$_3$, 298 K) δ = 2.26–2.33 (NH), 2.33–2.48 (COCH_2), 2.48–2.65 (NCH_2CH$_2$CO), 2.65–2.82 (CH$_2$CH_2N), 2.82–2.96 (NHCH_2CH$_2$O), 3.18–3.34 (CH_2CH$_2$N), 3.34–3.49 (NCH_2CH$_2$CO), and 3.49–3.75 (OCH_3).

Synthesis of CdS QDs within HPAMAM nanoreactors

Typically, 5 mL aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1.5 mM) was added into 15 mL aqueous solution of HPAMAM (3 mg/mL) in a conical flask and vigorously stirred for 48 h. Then, the flask was deaerated with N_2 for 20 min, followed by adding 2 mL aqueous solution of oxygen-free Na_2S dropwise (1.25 mM). Herein, the Cd^{2+}/S^{2-} molar ratio was set as 3 : 1. The mixture was stirred for 1 h at room temperature, and optically clear CdS QDs aqueous solution was obtained.

Measurements

^{1}H-NMR measurements were carried out on a Varian Mercuryplus 400 NMR spectrometer with CDCl$_3$ as solvent. Element analysis was done on Perkin–Elmer 2400 II. Dynamic light scattering (DLS) measurements were performed in aqueous solution at 25°C by using Zetasizer Nano S (Malvern Instruments, Malvern, Worcestershire, UK). Ultraviolet-visible spectroscopy (UV–vis) spectra were recorded on a Perkin–Elmer Lambda 20/2.0 UV–vis spectrometer. Emission spectra were collected using a Varian Cary spectrometer. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL 2010 microscope with energy-dispersive X-ray spectrometer (EDS) at an accelerating voltage of 200 kV. Grids were prepared by dropping aqueous solution of the QDs onto carbon-coated copper grids. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bruker Equinox-55 FTIR spectrometer.

RESULTS AND DISCUSSION

Synthesis and characterization of HPAMAM nanoreactors

The synthesis of HPAMAM was based on a two-step reaction, which was depicted in Scheme 1. First,
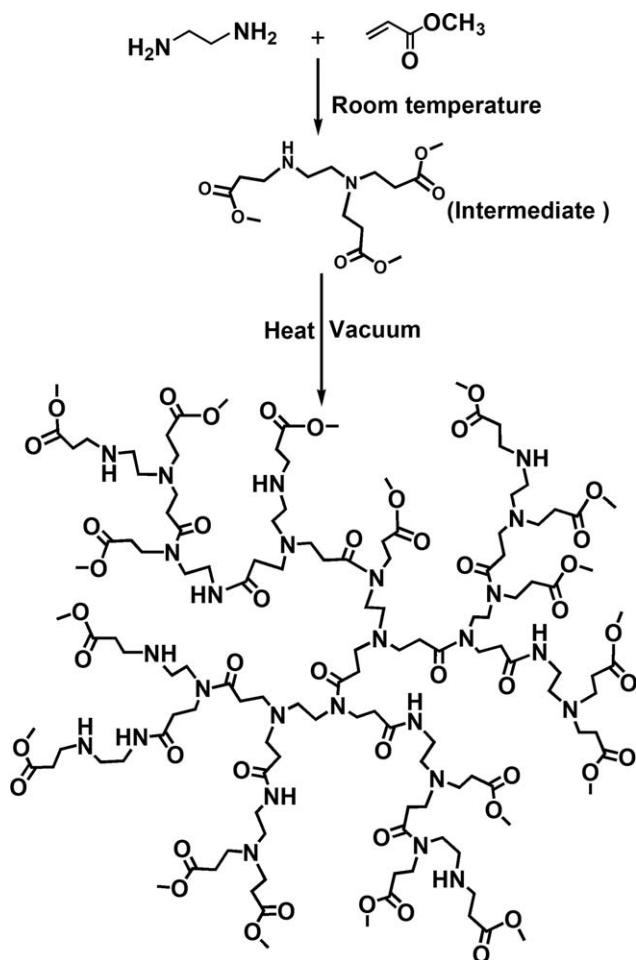
Scheme 1   Reaction scheme of HPAMAM.

Michael addition of MA to EDA gives intermediate at room temperature. Element analysis shows that the content of N and C elements in this intermediate is 9.3 and 52.5 wt %, respectively. ^{1}H-NMR was used to estimate the structure of this intermediate.
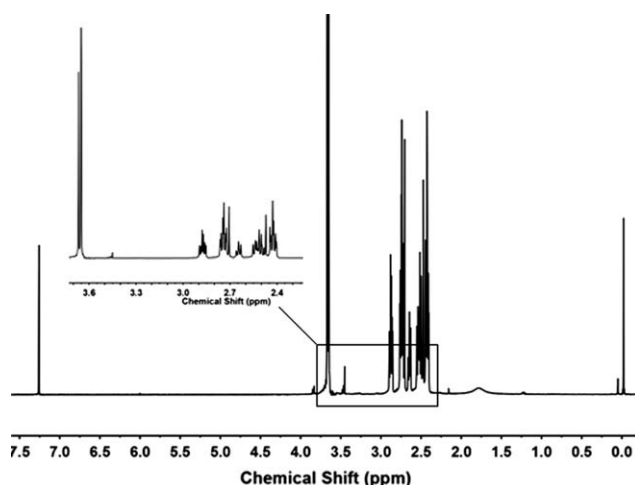

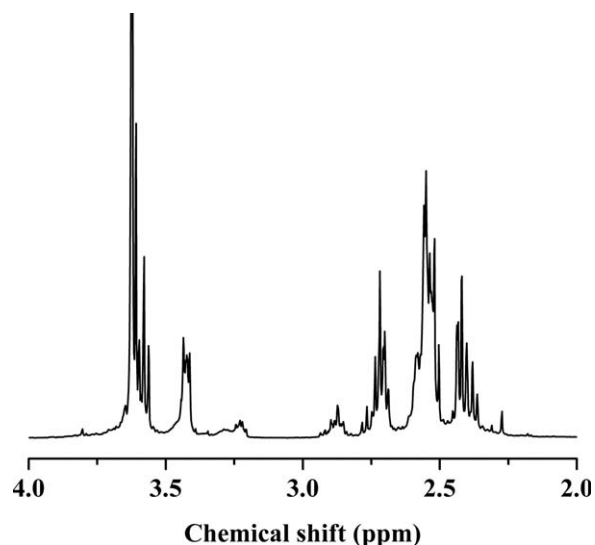**Figure 1** ^{1}H-NMR spectrum of HPAMAM intermediate (400 MHz, in CDCl$_3$, 298 K).

**Figure 2** ^{1}H-NMR spectrum of HPAMAM (400 MHz, in CDCl$_3$, 298 K).

The peaks corresponding to double bond of MA are not found in ^{1}H-NMR spectrum (Fig. 1), indicating that all the double bond of MA has reacted with amines. Second, increasing temperature and vacuum degree drive the intermediate to form the HPAMAM by amidation reaction. The polymer structure of methyl ester terminated HPAMAM was analyzed by ^{1}H-NMR (Fig. 2). The signals at about 3.49–3.80 ppm in the ^{1}H-NMR spectrum are consistent with methoxyl groups of MA. This confirms the existence of methoxyl groups, which could prevent the aggregation of HPAMAM in solvents. The very weak signals between 2.26 and 2.33 ppm are assigned to the amine groups in the molecular chain, implying that almost all the amines are reacted in polymerization.

Preparation of CdS QDs within HPAMAM nanoreactors

The preparation of CdS QDs using HPAMAM as stabilizers and reactors was illustrated in Scheme 2. HPAMAM has numerous amines and methyl ester terminals. The existence of amines gives the opportunity to chelated Cd^{2+} ions, while the methyl ester terminals can prevent the agglomeration between polymers. Cd^{2+} ions were first chelated by HPAMAM under vigorous stirring. After reaction with S^{2-}, nonaggregated CdS QDs stabilized by individual HPAMAM were obtained.

Characterization of CdS QDs

The hydrodynamic diameters of HPAMAM and CdS/HPAMAM nanocomposites were measured by means of DLS technique. Figure 3 shows that the initial diameter of HPAMAM nanoreactors is 2.9 nm,
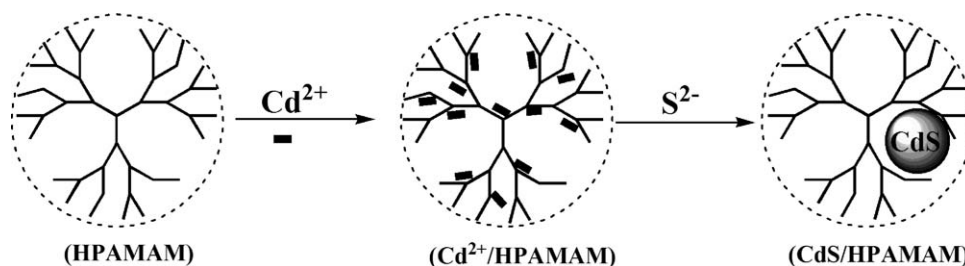
Scheme 2 Schematic illustration for the preparation of CdS QDs using HPAMAM nanoreactors.

while it shrinks slightly to 2.7 nm after encapsulating CdS QDs. This indicates that CdS/HPAMAM nanocomposites do not aggregate, and CdS QDs should be restricted into the interior of HPAMAM. Crooks and coworkers[17] also reported that dendrimer radius shrank slightly in the presence of the encapsulated CdS QDs, which is agreement with our observation.

Figure 4 displays the absorption spectrum of CdS/HPAMAM nanocomposites. The CdS QDs exhibit an absorption plateau at 340 nm. Upon UV light irradiation (365 nm), CdS/HPAMAM aqueous solution displays intense yellow–green emission. The size of CdS QDs can be estimated from the absorption peak using Peng's empirical formula.[24] The wavelength at 340 nm corresponding to the midpoint of the absorption plateau is chosen as the maximum wavelength to apply in the Peng's formula. From the absorption plateau, the Peng's empirical formula predicts that the diameter of CdS QDs is about 1.9 nm. Figure 5 displays the photoluminescence spectrum of CdS/HPAMAM nanocomposites. Upon excitation at wavelength of 340 nm, the prepared CdS QDs show a relatively strong emission spectrum with a maximum at 420 nm. The relative

quantum yield (QY) of CdS QDs was measured according to the method described in the reference.[25] Coumarin 1 in ethanol with a reported QY of 0.73 was used as a QY standard, the absorbance for the standard and the CdS sample at the excitation wavelengths of 340 nm and the fluorescence spectra of the same solutions were measured, respectively. A relative QY of 0.17 was obtained by this comparison. The relatively low photoluminescence of QDs prepared within polymers can be attributed to the quenching effect of polymers with amine groups.[26,27]

TEM was used to investigate the morphology of the as-prepared CdS QDs. Figure 6(a) shows a typical TEM image of CdS QDs obtained within HPAMAM nanoreactors. The size-distribution of nanoparticles is rather narrow with an average diameter of 2.2 nm. The SAED pattern of CdS QDs inside Figure 6(a) appears as broad diffuse rings due to the small particle size, and the lattice parameters fit to the cubic zinc blend structure of bulk CdS crystals. The corresponding EDS analysis in Figure 6(b) corroborates the existence of Cd and S elements in the nanocomposites.

Figure 7 shows a comparison of the FTIR spectra between 4000 and 500 cm^{-1} of the neat HPAMAM and CdS/HPAMAM nancomposites. The band positions and their assignments are listed in Table I. The
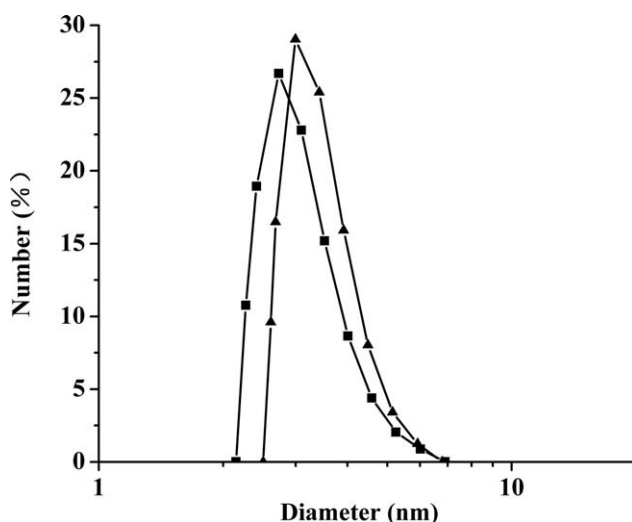

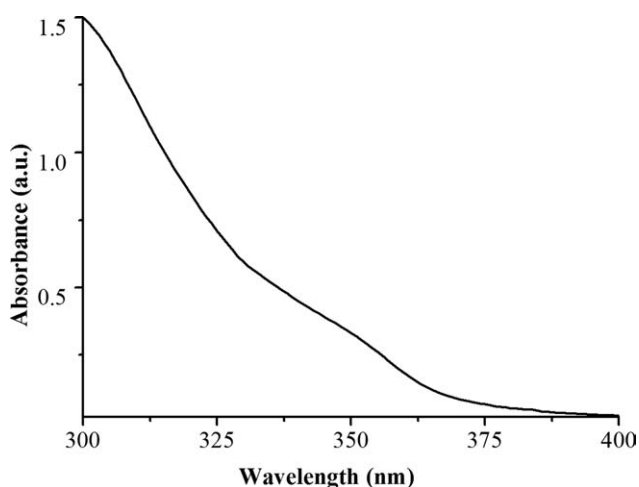**Figure 3** Size-distribution of HPAMAM (triangles) and CdS/HPAMAM nanocomposites (squares), measured by DLS.

Figure 4 UV–vis spectrum of CdS/HPAMAM nanocomposites.
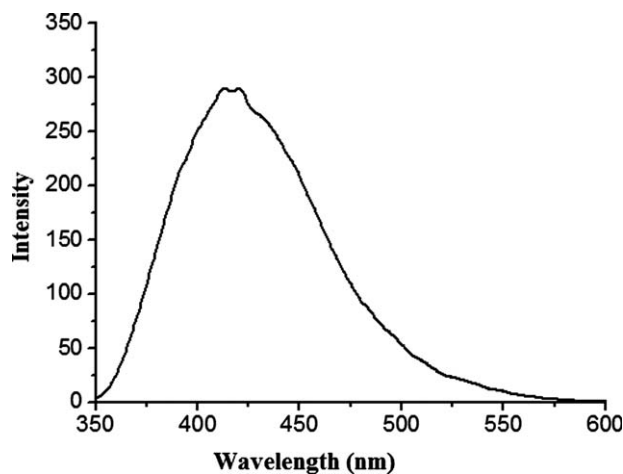
Figure 5 PL spectrum of CdS/HPAMAM nanocomposites.

bands at 3440 cm^{-1} correspond to the NH stretching vibration. An observation of the spectra shows a slight shift of the NH stretching frequency to 3446
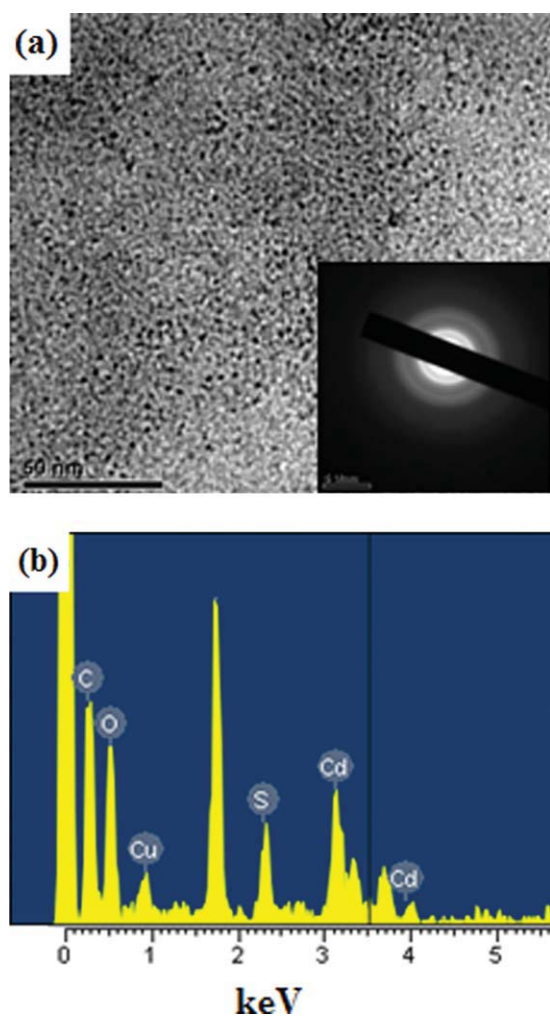

Figure 6 (a) TEM image (scale bar: 50 nm) (Inset: SAED patterns) and (b) EDS of CdS QDs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
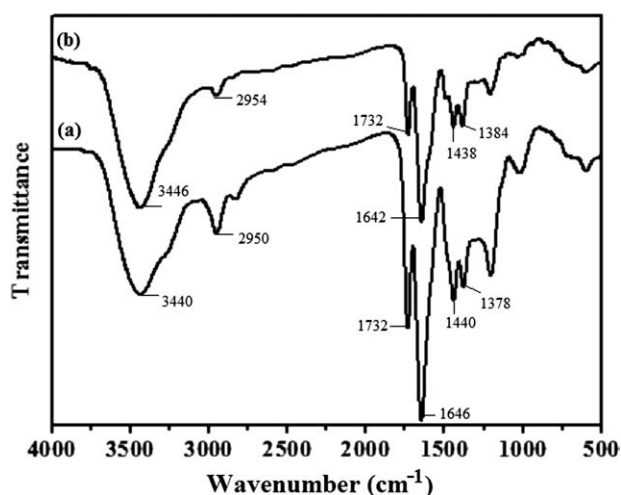

Figure 7 FTIR spectra of (a) HPAMAM and (b) CdS/HPAMAM nanocomposites.

cm^{-1} after the adsorption on the CdS QDs. The characteristic bands assigned to amides I and III in HPA-MAM are at 1646 and 1378 cm^{-1}, while the band positions of amides I and III slightly shift to 1642 and 1384 cm^{-1} in the CdS/HPAMAM nancomposites. At the same time, the carbonyl band position at 1732 cm^{-1} seems to be invariant. These changes indicate that coordination interactions exist between CdS QDs and HPAMAM through its inner amines, while the carbonyl groups actually do not interact with CdS QDs due to its lower complex capability compared to amines.

Effect of Cd^{2+}/S^{2-} ratios on the photoluminescence

We found that the photoluminescence of CdS QDs was sensitive to the Cd^{2+}/S^{2-} ratios. Figure 8 shows the variations of UV–vis and photoluminescence spectroscopy (PL) properties upon changing the Cd^{2+}/S^{2-} ratio. The absorption plateau has no significant change, while the PL intensity is enhanced gradually for Cd^{2+}/S^{2-} ratios from 1 : 2 to 3 : 1. This means that the QY of CdS QDs enhances with

TABLE I
FTIR Bands for HPAMAM and CdS/HPAMAM Nanocomposites

Assignment	Band position (cm^{-1})	
	HPAMAM CdS	HPAMAM
N—H stretching	3440	3446
CH$_2$ antisymmetric stretching	2950	2954
CH$_2$ symmetric stretching	2842	2854
C=O stretching	1732	1732
Amide I	1646	1642
CH$_2$ scissoring	1440	1438
Amide III	1378	1384

increasing Cd^{2+}/S^{2-} ratios and tends to saturate at higher ratios.

Aging of the CdS/HPAMAM nanocomposites

CdS QDs prepared under Cd^{2+}/S^{2-} ratio of 3 : 1 were used to investigate the optical properties upon aging at 5°C, as shown in Figure 9. The absorption plateau and the emission peak of CdS QDs have no obvious changes, which mean that CdS QDs have no significant growth during the aging time. However, the PL intensity increases accompanying with prolonging the aging time, because more compact surface coating of HPAMAM on CdS QDs can be achieved, and the surface defect is eliminated during the aging process.

CONCLUSIONS

In the present work, HPAMAM with hydrophobic methyl ester end-groups was synthesized by one-pot approach and subsequently used as nanoreactors to prepare CdS QDs with small particle size and narrow size-distribution. HPAMAM could bind Cd^{2+} through their internal amines, while the external
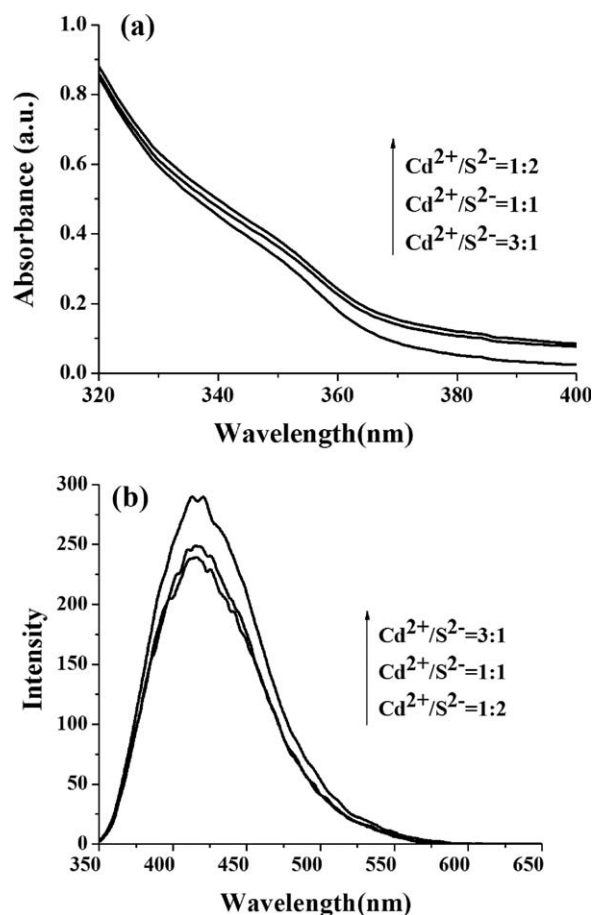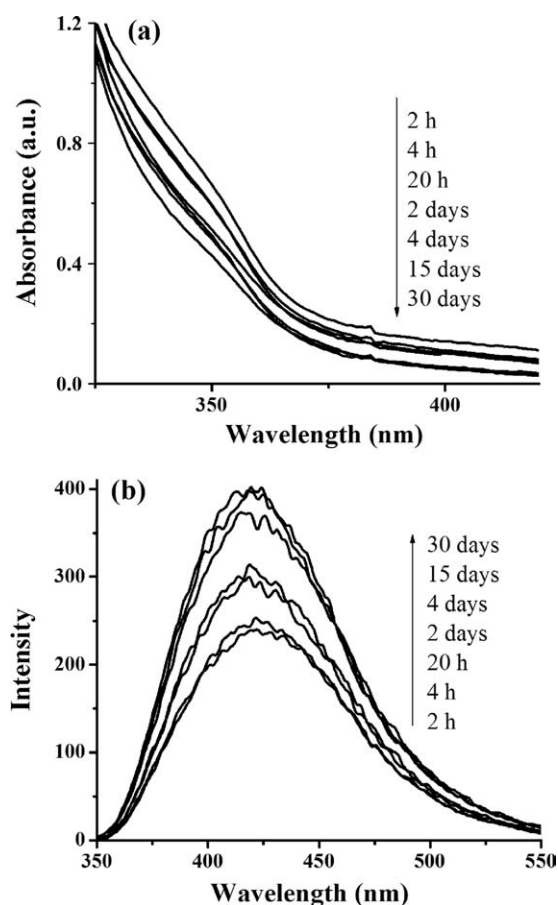
Figure 9 (a) Evolution of absorption spectra and (b) the corresponding evolutions of PL spectra of CdS/HPAMAM nanocomposites prepared under Cd^{2+}/S^{2-} ratio of three after storage at 5°C.

methyl ester groups prevented the aggregation of polymers; thus, nonaggregated CdS QDs sequestered by individual HPAMAM were obtained. Benefiting from the repulsive interactions among the methyl ester groups, HPAMAM nanoreactors were proved to be effective in controlling the size and size-distribution of CdS QDs. The resulting CdS/HPAMAM nanocomposites were characterized by DLS, TEM, UV–vis, PL, and FTIR, confirming the formation of CdS QDs with small particle size and narrow size-distribution. The effects of Cd^{2+}/S^{2-} ratio and aging time on the photoluminescence of CdS QDs were also investigated. The resulting QDs/hyperbranched polymer nanocomposites might offer an attractive platform for fabricating thin photoluminescent films or biolabeling.

Figure 8 Optical properties of CdS/HPAMAM nanocomposites prepared under different Cd^{2+}/S^{2-} ratio.

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