A controlled approach for synthesizing CdTe quantum dots polyamidoamine nanocomposites

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ABSTRACT

We develop a controllable approach to prepare ordered–CdTe quantum dots (QDs) polyamidoamine (PAMAM) nanocomposites (NCPs) by self-assembly growth of simple CdTe– PAMAM in aqueous solution. The sphere and network CdTe NCPs were obtained at pH 4.7 for growing 15 h and 79 h respectively. As the NCPs ceased growing over pH 8 immediately, we can conveniently control their size and morphology by adjusting pH of the solution to tune the growth time. The morphology change of CdTe-PAMAM nanocomposites was characterized by TEM images. The fluorescent intensity and photostability of ordered–CdTe–PAMAM have been improved significantly.

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1. Introduction

The controllable synthesis of nanomaterials with desired size and morphology has evolved into an important research field in nanoscience, since the size and shape of nanomaterials greatly influence their fundamental properties and practical applications [1,2]. Quantum dots (QDs) (CdS, CdSe and CdTe) are highly emissive and show great promise for use in future applications such as biotechnology, photovoltaic devices and solar cell devices [3–5]. Due to their size or shaped-dependent properties, a large number of controllable approaches, such as template, self-assembly, size-selective photoetching treatment, solvent growth [6–8] have been employed in control synthesis of QDs successfully in the last decades. Importantly, the extent of particle interaction in the network is a direct function of the dimensionality of the ordered structure. Now the use of polymers is a prominent method for the synthesis of nanoparticles [9–11], because the polymer matrices provide for processability, solubility, and control of the growth and morphology of the nanoparticles. Dendrimers are new kinds of nanotechnological polymers with highly branched molecules that form in well-defined patterns (generations) that allow control over morphology, size and terminal functionality [12]. For example, the fourth-generation (G 4) Poly(amidoamine) (PAMAM) with a particle size of ca. 4 nm [13] possesses 64 surface amine groups per particle and shows a high capacity of carrier materials and an excellent water-solublility. Recently these excellent properties of PAMAM have drawn great attention and have widely applied in the synthetic protocols for ordered morphology, well size-controlled and highly catalytic composites such as dendrimer–metal and dendrimer–semiconductor composites [14–16].

In this paper, we present a facile and effective method to control synthesis ordered–CdTe–PAMAM nanocomposites (NCPs) in two steps. First, CdTe-PAMAM simple NCPs were prepared by the reaction between PAMAM and thiolglycolic acid modified CdTe in aqueous solution. Then, the control growth of simple NCPs self-assembly forms ordered–CdTe–PAMAM NCPs *via* adjusting the growth time and pH of the aqueous solution.

2. Experimental

2.1. Reagents and apparatus

Tellurium powder (40 mesh, 99.997%), Cd(ClO$_4$)$_2$·6H$_2$O, thiolglycolic acid (TGA) and NaBH$_4$ (99%) were from Aldrich(USA). Doubly distilled water was used for all chemical procedures. PAMAM was synthesized according to reported procedure [17]. A

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methanol solution of 20% G 4–NH_2 (64 end groups) PAMAM was purified by dialyzing.

The high-resolution TEM measurements were carried out using a JEOL 2010F analytical electron microscope with a field emission source. The accelerating voltage was 100 kV. Fluorescence spectra were measured on a FL 4500 fluorescence spectrometer (Perkin–Elmer).

2.2. TGA coating of CdTe nanoparticles

The colloidal CdTe solutions were prepared according to the synthetic route reported earlier [18,19]. A pure CdTe QDs sedimentation was obtained by separating with a 16,000 rpm centrifugal sedimentation and washing with water four to five times. An aqueous solution of 0.1% (calculated according to cadmium) CdTe QDs solution was obtained by sonicating dispersing the fresh sedimentation immediately.

2.3. Synthesis of ordered– CdTe QD–PAMAM nanocomposites

An appropriate volume of 0.1% CdTe QDs solution was added into 0.05% PAMAM aqueous solution with rapid stirring. First, the QDs reacted with PAMAM in aqueous solution to form simple nanocomposites (NCPs), and then the simple NCPs grew to larger ones. Finally, the self-assembly growth of larger spherical NCPs formed ordered–CdTe QD–PAMAM NCPs at pH 4–6 and room temperature in dark for days.

3. Results and discussions

3.1. Controlling synthesis of ordered–QDs–PAMAM nanocomposites

PAMAM is an organic alkali and proton accepter. At acidic solution, polyamidoamine will accept several protons and form positive charged PAMAM. However, PAMAM exists in neutral molecule at basic solution. While TGA, a carboxylic acid (pK_a,TGA = 3.61), is a proton donor. TGA exists in its acidic form and in de-proton (acid radical, TGA^-) form at lower pH and high pH, respectively. When the pH is higher than 3.6, thiolglycolic acid exists in TGA^- form, hence, at higher pH, QDs particles repel each other as the negative charge on the surface of the quantum dots. In contrast, when the pH of the solution is lower than 3.6, the predominant form is thiolglycolic acid, and the QDs will link one and another by the hydrogen bond.

The CdTe QDs modified with TGA were very uniform and with a diameter about 4 nm, as seen from Fig. 1. When QDs mixture with diluted PAMAM (QDs: PAMAM = 4:1 in particles), the carboxyl of TGA on the QDs will link with the amine group to form simple QDs–PAMAM composites under acidic condition. And most of PAMAM molecules (particles) will surround by QDs in the simple composites. Hence, the hydrogen bond and electrostatic effect on the surface of QDs are the main driving force for the simple composites self-assemble growth. In other words, the simple composites grow to large one as the hydrogen-bonding interaction and electrostatic effect on the surface of the QDs. Therefore, the size and morphology of the NCPs depend on the growth time and pH of the solution.

The influence of acidity of the solution was investigated from pH 2 to 10. At lower pH, the NCPs grow very fast but their size and shape can not easily be controlled as there is the strong driving force of the hydrogen bond on the surface of QDs. In contrast, the NCPs grow slowly at higher pH because of electronegative repelling on their surface. At pH 4–6, the composite grow fast and well-ordered. Hence, the following self-assembly growth was performed at pH 4.7 aqueous solution. NCPs cease growing at pH over 8. QDs and
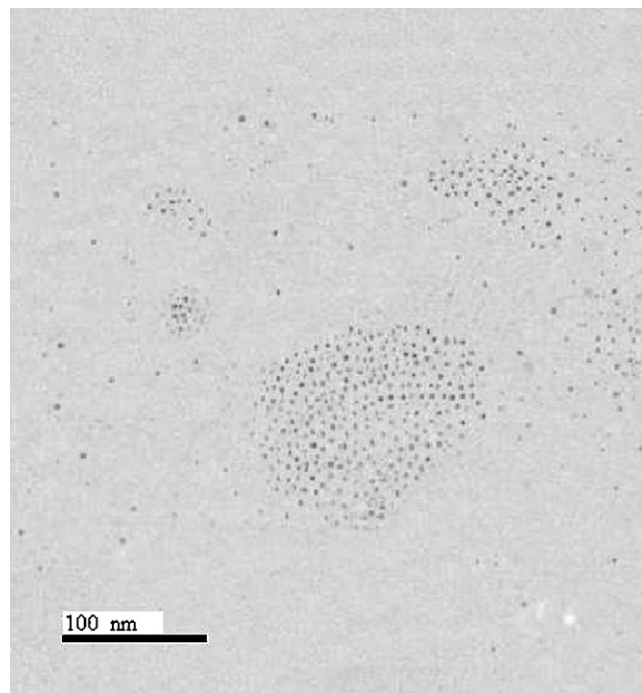

Fig. 1. TEM imagine for CdTe quantum dots, maginification of 300,000, at 100 V.

their PAMAM nanocomposites have strong fluorescence emission around pH 8.5. Therefore, it is convenient to control their size and morphology, and further using in practice by adjusting pH of the solution.

The growth process of QDs–PAMAM was monitored by TEM method. TEM image captures several ordered nanocomposites, as shown in Fig. 2. Fig. 2A is the TEM image for the simple nanocomposites grown for 15 h at pH 4.7, and one can notice that the predominant size of the QDs-PAMAM composites is about 14 ± 3 nm. They stop growing immediately only simply adjusting the pH over 8. Their size, morphology and the photo-properties keep unchanged for three months at pH 8.5 at room temperature in dark.

Fig. 2B and C are the TEM images at different growth for 26 h and 50 h at pH 4.7, respectively. From Fig. 2B, one can notice that the smaller sphere particles ordered assemble to larger one first, then, the particles have a tendency to outspread assembly. With the growing of the NCPs, the nanocomposites tend to self-assemble to form network structure obviously, as seen in Fig. 2C. After the NCPs growth for 79 h at pH 4.7 in the solution, one can observe a novel ordered water soluble QD-PAMAM NCPs with the network tri–dimension perfectly (as shows in Fig. 2D).

With the NCPs growing, the spherical nanoparticles trend to self-assemble in order. Briefly, the small simple NCPs grow to larger spherical NCPs at the beginning, and then the further growth of larger NCPs form a series of TSM-NCPs. Finally, the TSM-NCPs assemble regularly and construct ordered–QDs–PAMAM nanocomposites gradually, as shown in Scheme 1.

3.2. The photoproperty of the CdTe nanomaterials

Some previous research indicated that polyamidoamine dendrimers and polyethylenimine reduced the quantum yields (QY) of QD [20,21]. On the contrary, the phenomenon that enhance the fluorescent intensity of QD has been observed previously by other literatures [15,19,9]. In our work, the QY of the QDs-PAMAM nanocomposties has enhanced obviously.
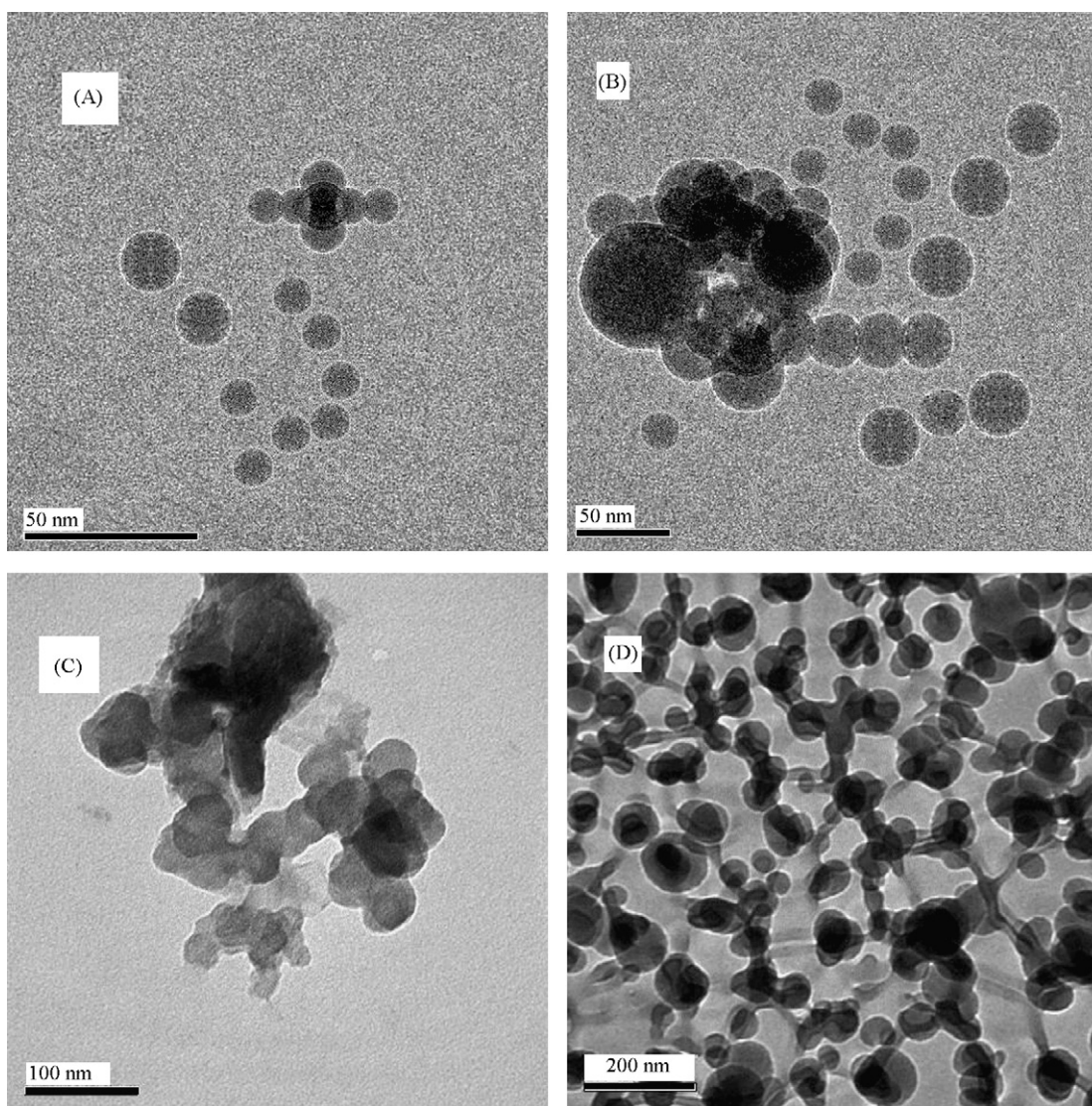
Fig. 2. The TEM imagines of CdTe PAMAM nanocomposites at different growth time at pH 4.7, (A) 15 h, (B) 26 h, (C) 50 h and (D) and 79 h.

The luminescence QY of CdTe QDs and the QDs-PAMAM nanocomposties formed at different growth time were measured by referring to Rhodamine 6G (QY 95%) with the method described in Ref. [22]. The QY of CdTe QDs, CdTe-PAMAM NCPs grown for 15 h were of 13.6% and 66.2% respectively. And the QY of NCPs grown for 57 and 79 h were 68.5% and 69.2% respectively, which indicates that the luminescence property CdTe QDs has improved greatly.

QY continuously increases greatly with the forming of QDs-PAMAM nanocomposites as mentioned above. There are several

stages to enhance the PL intensity of QDs, including the surface passivation and energy transfer between nanoparticles and polymers and so on. Early research reported that Lewis bases are perfect surface passivators and can enhance fluorescent intensity of QDs obviously [23–25]. Recently research showed that the QY of CdS enhanced from 30.3 to ca. 95% with PEI modification. In the present study, we adopted the strategy that PAMAM interacted with performed CdTe (thiolglycolic acid as surfactant). G 4–NH$_2$ (64 end groups) is a kind of Lewis base and an excellent QD surface pas-
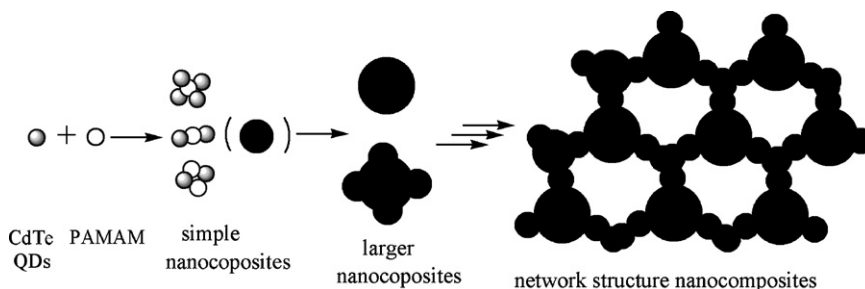
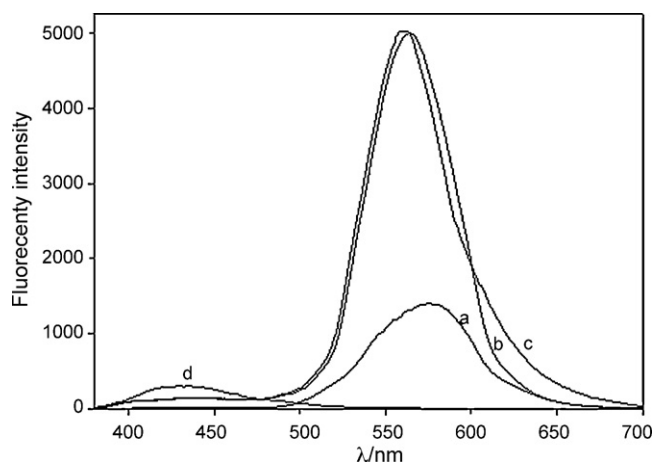**Scheme 1.** The growth process of CdTe QD-PAMAM nanocomposites.

Fig. 3. Curves of fluorescent spectra: (a) diluted (1:500) original QDs aqueous solution, (b) 1 ml of diluted (1:500) original QDs aqueous solution mixed with 2 μl of 2% PAMAM aqueous solution and QDs-PAMAM composites in 1 ml aqueous solution containing 2 μl of 2% PAMAM aqueous solution growth for (c) 15 h and (d) 79 h.

sivator. The dangling bonds arouse surface traps that facilitate nonradiative recombination that causes QY reduction. When the surface is passivated with PAMAM, nonradiative recombination decreases or vanishes, resulting in QY enhancement.

The controlled experiments [15] showed that PAMAM is a kind of high efficient passivator. The research [15] reported that a significant decrease of nonradiative recombination and a great enhancement of the QY were occurred after oxidation passivation. A comparison of fluorescence curves was obtained from CdTe QDs, CdTe–PAMAM composites (growth 15 and 79 h) and PAMAM, as shown in Fig. 3. The peak emissions of QDs–TGA and QDs–PAMAM locate at 575 and 560 nm, the blue shift indicates that QDs were oxidized and passivated. As a result, fluorescence emission of the QDs nanocomposites increased.

As depicted in Fig. 3, one observes that the QDs (1/500 original concentration) have a strong symmetric emission spectrum centered at 564 nm. This emission band is attributed to the electron–hole recombination in the CdTe nanocrystals as a result of the quantum size effect. PAMAM also shows a relatively weak fluorescence emission band with a maximum at 435 nm. An interesting phenomenon is observed that the fluorescence of CdTe QDs–PAMAM enhances substantially. Notice that the fluorescence spectrum of QD–PAMAM composites has an enhanced major peak corresponding to the CdTe nanocrystals with a partially quenched shoulder peak arising from PAMAM. One could infer that the fluorescence enhancement of QD–PAMAM composites seems to be assigned to the energy transfer from PAMAM donor to QDs acceptor. Hence, it is obvious that both the surface passivation and energy transfer occur in the QD-PAMAM nanocomposites and led to the increase of QY in our present work.

The fluorescence intensity of the QDs–PAMAM composites retains of its 95% original value over 2 weeks at 30 W (centre 365 nm). The effective protection and energy transfer from PAMAM is great benefit to the stability and fluorescence intensity of the QDs–PAMAM nanocomposites.

4. Conclusions

In summary, a novel water-soluble, ordered and tunable CdTe–PAMAM NCPs are prepared by simply adjusting the pH and growth time. The growth processes of QD-PAMAM nanocomposites were characterized by TEM images, which show that the CdTe–PAMAM NCPs possess different sizes and morphologies at different growth time. The NCPs can cease growing immediately over pH 8. Therefore, one can easily control the growth time precisely and prepare the NCPs with optional structure for various purposes by changing the pH of the solution. The fluorescence intensity of QDs–dendritic NCPs has been improved significantly arisen from the surface passivation (surface oxidation passivation and modified with PAMAM) and the energy transfer existing in CdTe QDs and PAMAM. The QY of the nanocomposites is as five times as that of pure QDs. The high quality composites have a great potential application in photoelectric and sensing devices, solar cell and biotechnology.

Acknowledgments

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