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RESEARCH ARTICLE

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Preparation and properties of polymer and quantum dot composites

Abstract Quantum dots (QDs) were prepared in an organic system through a simple and low-cost wet chemistry method. Polymer beads with a diameter of 60–70 nm and specific functional groups were synthesized by a particular seeded emulsion polymerization technique. QDs were embedded in the polymer beads with the specific functional groups through dissolving and swelling method, which provided the condition for the conjunction of biomolecules and QDs as fluorescent probes. The prepared composites were characterized with UV-Vis, PL, TEM, FTIR, CLSM and conductance titration etc. The results show that QDs are successfully embedded in polymer beads, which breaks the limitation that the conjunction of biomolecules and QDs can be achieved only for those synthesized in aqueous system.

Keywords quantum dots (QDs), polymer beads, fluorescence, seeded emulsion

1 Introduction

Semiconductor nanocrystals, also known as quantum dots, have drawn intense research interest as fluorescence label in biotechnology. The properties of QDs result from quantum-size confinement, which occurs when metal and semiconductor particles are smaller than their exciton Bohr radii (about 1 to 5 nm). Regardless of the excitation wavelength, a narrow emission peak is observed, and the emission wavelength is size-dependent. Different-sized QDs can be simultaneously excited by a single wavelength, because each type of QD exhibits a specific emission peak. All of these features give quantum dots advantages over organic dyes (such as rhodamine 6G and other organic dyes [1]) and make quantum dots a promising chromophore for many applications [2]. In contrast, traditional fluorescent organic dyes suffer from photobleaching and technical difficulties with their simultaneous excitation for multiple-target labeling, which make experimentation cost higher and analysis more complex. However, these luminescent QDs are prepared in organic solvents and not suitable for biological application [3]. In order to attach biomolecules to a QD, some functional groups were bound to a QD to render the QDs water solubility. The free functional group is also available for covalent coupling to various biomolecules (such as proteins, peptides, and nucleic acids) by cross-linking to reactive amine groups.

Here, we embedded QDs prepared in an organic system in polymer beads through a dissolving and swelling method to gain QDs/polymer beads composites that are suitable for biological applications. During the formation process of polymer beads by seeded emulsion polymerization, we gained the product by controlling the mixing ratio of reactants and the reaction time. Compared with micron-sized particles, nanosized particles go beyond the limit of optical scattering. As a result, the ratio of the fluorescence strength of particles to background can be augmented and background's influence on image spatial resolution is greatly reduced [4].

2 Experimental

2.1 Materials

Cadmium oxide (CdO), oleic acid, selenium(99.5%), chloroform, methanol, styrene, divinylbenzene, acrylic acid, potassium persulfate (KPS), poly(vinylpyrrolidone K30) (PVP), sodium dodecyl sulfate (SDS), etc. were supplied by China National Pharmaceutical Group Corporation and Shanghai Chemical Reagent Corporation. All chemicals were analytical grade and used directly without further purification;

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trioctylphosphine was supplied by Aldrich (TOP, 90%, 117854).

2.2 Synthesis of CdSe quantum dots

1.25 mmol selenium (98.7 mg) reacted with 2.25 mL TOP to form TOPSe under stirring. In a 100 mL three-necked flask, 1.75 mL cadmium oxide (224.7 mg) was dissolved in 30 mL oleic acid under stirring. The mixture was heated to 180°C under nitrogen atmosphere, into which the TOPSe solution was swiftly injected. Samples at different periods of reaction time were gained. After washing with methanol and centrifugation, the products were separated in chloroform.

2.3 Preparation of polymer beads with specific functional groups by seeded emulsion polymerization technique

The seed latexes were prepared by seeded emulsion polymerization carried out in a three-necked separator flask, equipped with a stirrer, a spiral condenser, a dropping funnel with a nitrogen inlet, and a nitrogen inlet. 0.3 g SDS was added into the reactor then heated to 78°C under nitrogen atmosphere and stirring. After 30 min, the mixture of 49 mL styrene and 1 mL divinylbenzene was fed in the dropping funnel slowly. The initiator solution was then heated for another 30 min. Then 20 mL KPS (w = 0.02) and 0.5g PVP were added into the reactor and pH of the system was tuned up to 8 by $NaHCO_3$ solution. After reacting at 80°C for 7 h, seed latex was obtained.

100 mL seed latex diluted in 300 mL water was mixed with 10 mL acrylic acid and 0.14 g KPS. The mixture reacted under protection of nitrogen atmosphere for 4 h at 80°C. Then the mixture was distilled under reduced pressure at 55°C until no liquid outflow existed, and then dispersed in water after washed by ethanol twice.

2.4 Encapsulation of quantum dots into polymer beads

0.18 g polymer beads and 0.27 mg CdSe quantum dots were dispersed in solvent (propyl alcohol: chloroform=9:1, *V*/*V*), then swelled for 24 h at room temperature. The size of the polymer beads increased during the reaction period, and the orange quantum dots were embedded into polymer beads gradually. Polymer beads-QDs composites were obtained finally. The deposition at the bottom was orange composites, while the superstratum was clear liquid. The suspension was mixed uniformly and characterized.

2.5 Characterizations

A Unicam-UV 300 ultraviolet-visible (UV-Vis) spectrophotometer and a PerkinElmer LS 55 photoluminescence (PL) spectra were used to characterize the optical properties, and the optical measurements were carried out under room temperature. The particle morphologies and size distribution were examined by Philip 120 transmission electron microscopy at an accelerating voltage of 80 kV; a DDSJ2308A conductivity meter (Shanghai Leisi Xinjing Equipment CO. LTD) was used to measure the carboxyl content of polymer beads; an EQU INOX 55 FT-IR Spectrometer (German BRU KER CO.) was used to characterize the surface functional groups of polymer beads; a Meta 510 confocal loser scanning microscope (Ceiss CO.) was used to compare fluorescence of polymer beads with that of polymer/QDs composites.

3 Results and discussion

3.1 The absorption spectra of CdSe nanoparticles

Figure 1 presents the UV-Vis absorption spectra of CdSe nanoparticles dispersed in chloroform. It shows that with the reaction time increasing, the absorption edge shifts to longer wavelength (from 499 to 538 nm), and the size of CdSe particles also increases. The shift of the absorption edge in Fig. 1 [5] indicates that the size of the particles increases from 2.2 to 3 nm with the growth time from 3 to 45 min.

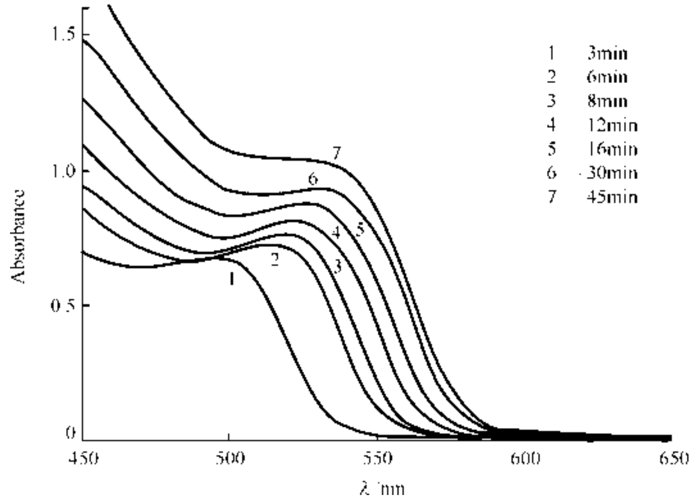

Fig. 1 The absorbance spectra of CdSe nanoparticles in chloroform

3.2 The photoluminescent spectra of CdSe nanoparticles

Figure 2 presents the photoluminescent spectra of CdSe nanoparticles dispersed in chloroform (excitated at 500 nm). In contrast to the absorption spectra, Fig. 2 shows the shift of the emission peak from 533 nm to 564 nm with the reaction time increasing from 3 min to 45 min. It further proves that the size of CdSe particles increases with the increase in reaction time. The PL intensity decreases while the half peak width of the emission spectra increases (from 37 nm to 45 nm) with the increase of the particle size.

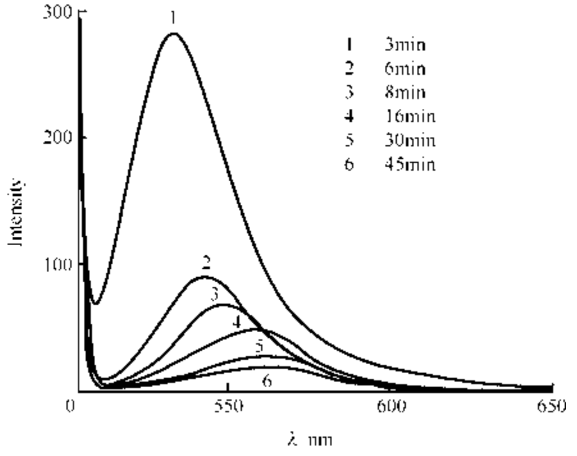

Fig. 2 The fluorescence spectra of CdSe nanoparticles in chloroform

3.3 TEM analysis

The diameter and size distribution of the CdSe nanocrystals synthesized in this work were determined by TEM. A representative example is presented in Fig. 3, for a sample of CdSe quantum dots grown for 45 min. The mean particle diameter (3 nm) calculated from the TEM photo was found to be in good agreement with the size estimated from UV-Vis, and the size distribution is quite narrow.

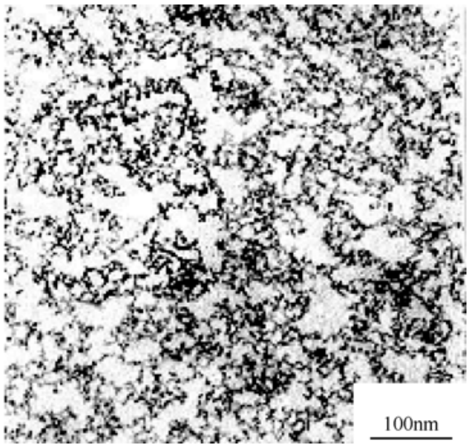

Fig. 3 The TEM image of CdSe nanoparticles (*t*=45 min)

3.4 The FTIR of seed emulsion and polymer beads

Specific functional groups of polymer beads were characterized with FTIR, Fig. 4(a) shows the FTIR spectra of seed emulsion, and Fig. 4(b) shows the FTIR spectra of synthesized polymer beads after adding acrylic acid to seed emulsion, Fig. 4(c) shows the partly enlarged graph to compare Fig. 4(a) with Fig. 4(b). Figure 4(c) shows characteristic signal for carboxyl (ν(C=O) at 1750–1700 cm^{-1}) after the introduction of acrylic acid, which indicates that the carboxyl groups are attached to the surface of polymer beads during polymerization. Comparison between Fig. 4(a) and Figure 4(b) shows obvious characteristic signals for both C=O (stretching vibration of C=O at 1350–1180cm^{-1}) and OH (non-planar variable-angle vibration of OH at 950–900 cm^{-1}) groups, which further implies that carboxyl groups are attached to the surface of polymer beads.

3.5 Content analysis of carboxylic groups linked to the surface of polymer beads

Figure 5 shows the result of carboxylic group content by the method according to reference [6]. Surface carboxylic group content can be calculated by the expression:

$$c_{\mathrm{COOH}} = c_{\mathrm{NaOH}} \Delta V / m$$

According to c_{NaOH} (standard NaOH concentration) = 0.01 mol/L, ΔV(volume of consumed alkali solution)=10 mL, m(weight of polymer beads)=191.7 mg, the c_{COOH} was calculated to be 522 μmol/g.

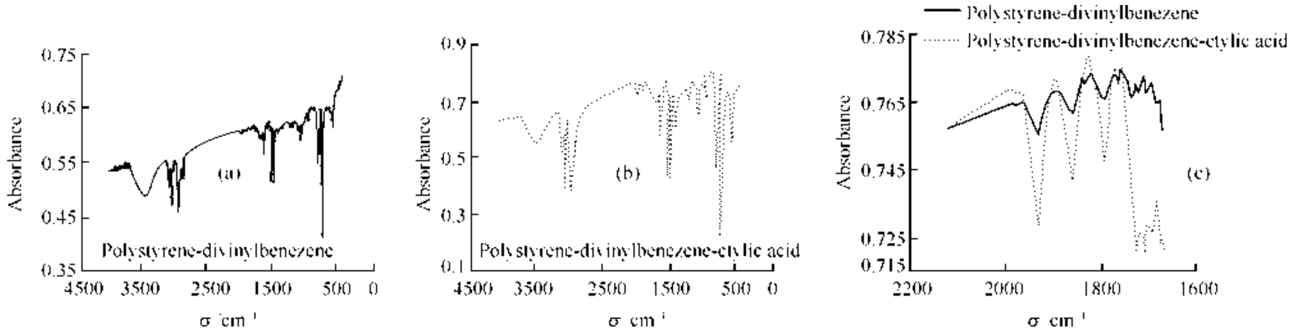

Fig. 4 The FTIR of seed emulsion and polymer beads with special functional groups

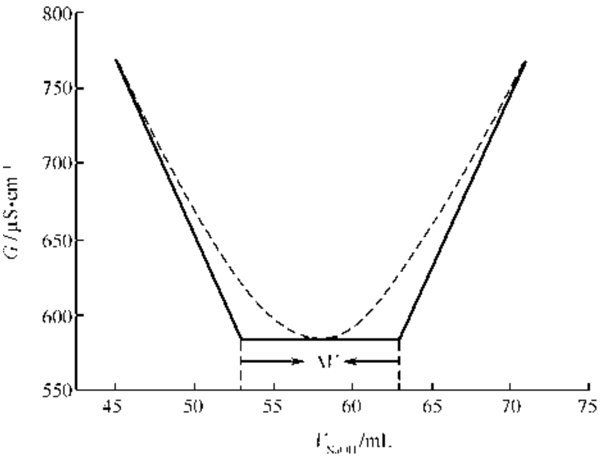

Fig. 5 The conductivity titration curve of polymer beads linked with acrylic acid

3.6 Comparison between the TEM image of seed emulsion and polymer beads

Transmission electron microscope was used to illustrate the size, surface morphology and dispersed state of beads. Figure 6 shows the TEM images of polymer beads before and after the introduction of acrylic acid in the process of seeded emulsion polymerization technique. It can be seen from Fig. 6 that all the particles are regular spheres and exhibit a narrow particle size distribution. The diameter of polymer beads was about 63 nm. After the introduction of acrylic acid, the diameter of polymer beads was about 70 nm. These results imply that the diameter of beads get bigger after the addition of acrylic acid because of the coating of carboxyl functional groups onto polymer beads' surfaces.

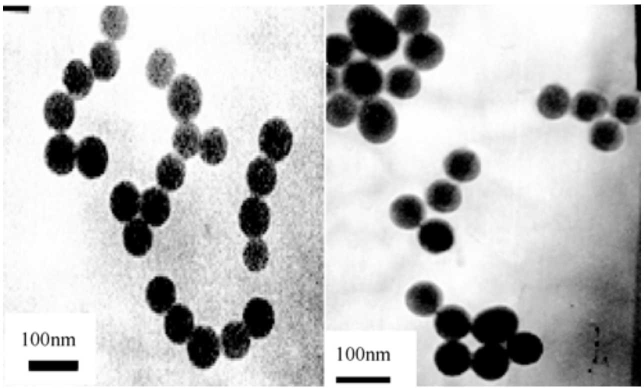

Fig. 6 The TEM image of polymer beads: (a) seed latex, (b) polymer beads

3.7 Fluorescence micrography of QDs embedded into polymer beads

Confocal laser scanning microscope was used to draw a fluorescence comparison between the polymer beads and their composites with QDs. Figure 7(a) shows the fluorescence micrograph of polymer beads before QDs were embedded; no fluorescence dot is found. Figure 7(b) shows the fluorescence micrograph of polymer beads-QDs composites; obvious round fluorescence dots are found. The comparison implies that QDs were successfully embedded in polymer beads through dissolving and swelling for 24 h under room temperature.

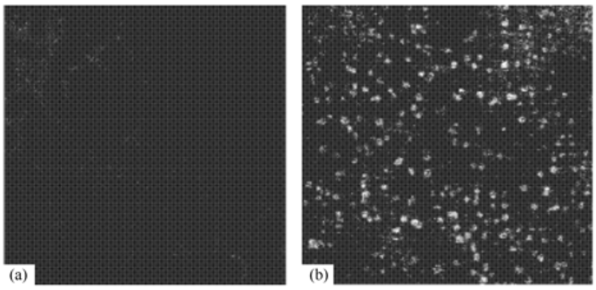

Fig. 7 The fluorescence micrographs of (a) polymer beads, (b) polymer beads embedded QDs

4 Conclusion

QDs, a new kind of fluorescence nanoparticles that have drawn intense research interest in cell biology and iatrology [7], were prepared through a wet chemistry method. This method is simple and the cost is low. Polymer beads with a diameter of 60–70 nm and specific functional groups were synthesized by a particular seeded emulsion polymerization technique. The size is about one order of magnitude less than the results that have been reported. QDs are successfully embedded in polymer beads with the specific functional groups through the dissolving and swelling method. The fluorescence intensity and width of emission peak are reasonably maintained during the forming process. The results reported herein open up new opportunities of QDs for further binding with biomolecules as fluorescence tags, which breaks the limitation that the conjunction of biomolecules and QDs can be achieved only for the QDs synthesized in aqueous system.

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