Easy preparation and characterization of highly fluorescent polymer composite microspheres from aqueous CdTe nanocrystals

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Abstract

Fluorescent microspheres were easily fabricated from aqueous CdTe nanocrystals (NCs). The NCs, which had negative charges on the surface, were first extracted to chloroform by cationic surfactant octadecyl-p-vinyl-benzyldimethylammonium chloride (OVDAC) and then swollen into performed polystyrene (PS) microspheres. Through this method, strong photoluminescence (PL) of aqueous NCs was inherited in the resultant composite microspheres. Moreover, the NCs were firmly stabilized in the microspheres, withstanding not only polar solvents but also nonpolar solvents. UV–vis spectrum, PL spectrum, TEM, and confocal fluorescence microscopy were used to characterize the product.

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1. Introduction

Due to quantum confinement effects, semiconductor nanocrystals (NCs) show special optical and electronic properties that depend strongly on the size of the NCs. For example, when the size of CdSe NCs is varied from 2 to 6 nm, the photoluminescence (PL) covers the whole visible spectrum [1]. Semiconductor NCs with different emission colors can be excited simultaneously by a single excitation source and distinguished, which make them important materials for biological applications [2]. Incorporation of fluorescent NCs into inert microspheres will generate new composite fluorescent markers with enhanced stability and versatile surface functionalities [3–5]. Controllable incorporation of different-sized NCs into the same microsphere is also expected to realize high-capacity intensity–color multiplexed optical encoding and fast detection [6–8].

Various approaches to semiconductor NC-tagged fluorescent microspheres have been developed rapidly in recent years, including the modified Stöber method [9], the swelling method [6], and the inverse microemulsion technique [10]. Most recently, Bawendi and co-workers reported a robust procedure for incorporating CdSe/ZnS core/shell NCs into a silica or titania shell on silica microspheres [11]. Gao and co-workers successfully embedded CdTe NCs into poly(isopropyl acrylic amide) hydrogel microspheres via hydrogen bond interaction [12]. Although great progress has been achieved, the controllable incorporation of NCs into microspheres with both bright PL emission and long-time stability is still difficult. The swelling method first proposed by Nie and co-workers, in which no complicated reaction is needed, the emission intensities can be precisely controlled, and the PL emission of resultant microspheres can be kept for a long time, is thought to be ideal. By this method, both single-color and multicolor microspheres have been prepared with high reproducibility [6]. Unfortunately, this strategy has been limited so far to hydrophobic NCs, since aqueous NCs cannot be swollen into hard organic microspheres owing to their inherent insolubility in organic solutions. However, NCs prepared by aqueous synthesis have so many merits [13], such as lower cost, less toxicity, and scale-up preparation, that it is important to develop methods to prepare hard fluorescent microspheres from aqueous NCs. To this aim, surface modification is practicable [14]. In this paper, highly fluorescent composite microspheres with long-time stability were prepared by combining surface modification of aqueous NCs and a swelling technique. Surprisingly, the
NCs were concreted into the microspheres even without sealing the microspheres using a polymer or silica layer. UV–vis spectrum, PL spectrum, TEM, and confocal fluorescence microscopy were used to characterize the product.

2. Experimental

2.1. Synthesis and surface modification of CdTe NCs

A series of negatively charged CdTe NCs with PL emission colors from green to red were prepared according to the references [13,15]. The cationic surfactant octadecyl-p-vinylbenzyl(dimethyl)ammonium chloride (OVDAC) was synthesized according to the references [15,16]. A portion of 1 mg OVDAC was added to 1 ml CdTe aqueous solution (0.00125 N according to Cd²⁺) to coat the surface of NCs under vigorous stirring; subsequently, 1 ml chloroform was added to extract OVDAC-coated CdTe NCs, and the chloroform phase was separated for swelling use.

2.2. Synthesis of PS microspheres

Cross-linked polymer microspheres were prepared by emulsifier-free emulsion polymerization [6,17,18]. Typically, the mixture of 10 ml styrene (St), 0.1 ml divinylbenzene (DVB), 0.2 ml acrylic acid (AA), 60 mg potassium persulfate (KPS), and 100 ml water were stirred in a three-neck flask at 70 °C for 10 h with N₂ protection, and the diameter of the resultant polystyrene (PS) microspheres was 625 nm. By controlling the amount of St, DVB, and AA added to the reaction system, the diameter of the microspheres had been tuned from 200 nm to several micrometers.

2.3. Preparation of fluorescent composite microspheres via swelling

Microspheres of 5 mg PS (198 nm in diameter) were separated from the supernate using a centrifuge and then redispersed in 5 ml of isopropanol, to which 0.1 ml of chloroform solution of OVDAC-coated CdTe was added dropwise under ultrasonic treatment for swelling. The composite microspheres were separated out and washed several times using the mixture of isopropanol and chloroform. Under such preparation conditions, the swelling process was complete within 3 min, and the ratio of CdTe NCs to PS microspheres was calculated to be about 2 × 10². By increasing the amount of chloroform solution containing CdTe NCs, more NCs were embedded into PS microspheres. Repeated swelling was also applicable to increase the concentration of NCs in the microspheres.

2.4. Characterization

UV–vis absorption spectra were recorded using a Shimadzu 3100 UV–vis–near-IR spectrophotometer. Fluorescence experiments were performed with the help of a Shimadzu RF-5301 PC spectrofluorimeter. Transmission electron micrograph was recorded by a JEOL-2010 electron microscope operated at 200 kV. An Olympus BX-51 fluorescence microscope was used to examine the composite microspheres. Specimens were excited using an ultraviolet source.

3. Results and discussion

Fig. 1 presents the overall procedures for the production of fluorescent polymer microspheres starting from aqueous CdTe NCs. Differently from NCs prepared by the organometallic route [19,20], CdTe NCs prepared by aqueous synthesis were negatively charged [13,21], thus providing an electrostatic interaction with cationic surfactants, such as octadecylbenzyl(dimethyl)ammonium chloride (OBDAC), octadecyl-p-vinylbenzyl(dimethyl)ammonium chloride (OVDAC), and cetyltrimethylammonium bromide (CTAB). With the coating of these surfactants, CdTe NCs could be extracted to organic solvents, including chloroform, toluene, and styrene. Then a conventional swelling method can be applied to the NCs. In the following parts, we took OVDAC-coated CdTe for discussion.

Fig. 2 indicates the UV–vis absorption and PL spectra of a series of aqueous CdTe NCs that were stabilized by 3-mercaptopropionic acid (MPA). The sizes of these NCs were from 2.5 to 4.0 nm, which covered the emission range from 520 to 650 nm (emission peaks). These aqueous CdTe NCs were highly luminescent, and the PL quantum yields (QY) of some samples were up to 30% [13]. The coating of CdTe NCs with OVDAC relied on electrostatic interaction. By adjusting the
molar ratio of OVDAC to NCs, nearly all NCs could be extracted into chloroform solution. The proper molar ratio was 1 mmol OVDAC to 0.7 mmol NCs (referring to the MPA concentration in the NC solution). The operation was also important for the extraction efficiency. Currently, first OVDAC was dissolved in aqueous solution to coat CdTe NCs, and then chloroform was added to the mixture under vigorous stirring to extract OVDAC-coated CdTe NCs. From UV–vis absorption and PL spectra of OVDAC-coated CdTe in chloroform, we could see that the fluorescence properties of the NCs hardly change (Fig. 3). This was one advantage of our strategy over the previous method, named surface ligand exchange [22], in which the PL emission was more or less quenched.

OVDAC-coated CdTe NCs were soluble in the mixture of chloroform and isopropanol, and swollen into PS microspheres that were previously dispersed in this mixture. The original white PS microspheres were tinted in CdTe NCs’ emission colors under UV light, which indicated the implantation of CdTe NCs. The optimized swelling conditions also enabled a near 100% efficiency of embedding NCs into PS microspheres, which was confirmed by the fact that no fluorescent signals were detected in the supernate after the microspheres were centrifuged out. So we could calculate the average number of NCs per microsphere by dividing the total number of NCs by the total number of polymer microspheres. Take 198-nm PS microspheres, for example; the maximum number of CdTe NCs in per microsphere was up to $5 \times 10^3$. Thus, strong PL emission was inherited by these microspheres.

Fig. 4 presents the real PL image of the resultant composite microspheres that were simultaneously excited by the same UV light excitation source. The microspheres were about 625 nm in diameter by optical microscopy under a bright field. Four different-sized CdTe NCs with PL emission peaks at 529, 564, 603, and 648 nm were swollen into PS microspheres through routine operation. Under excitation, composite microspheres embedded with four different-sized NCs were all excited and distinguishable. It is worth noting that simultaneous excitation of multiple emission colors is a unique character of semiconductor NCs, which makes intensity–color multiplexed optical coding possible. In these images, the microspheres were very bright as a result of the high loading levels, and the brightness of every microsphere was uniform to the eyes. This result means that the swelling process is homogeneous in each microsphere, which is crucial for producing uniform multicolor multiplexed optical coding possible. In these images, the microspheres were very bright as a result of the high loading levels, and the brightness of every microsphere was uniform to the eyes. This result means that the swelling process is homogeneous in each microsphere, which is crucial for producing uniform multicolor multiplexed optical coding possible. In these images, the microspheres were very bright as a result of the high loading levels, and the brightness of every microsphere was uniform to the eyes. This result means that the swelling process is homogeneous in each microsphere, which is crucial for producing uniform multicolor multiplexed optical coding possible.

The distribution of CdTe NCs in composite microspheres was investigated by transmission electron microscopy (TEM). Fig. 5a shows the TEM images of bare PS microspheres before NC swelling. These microspheres had smooth surfaces. After PS microspheres were swollen with OVDAC-coated CdTe, small particles about 3 nm could be clearly seen located on the surface layers of the microspheres, and the size of these particles was consistent with the size of aqueous CdTe NCs. CdTe NCs were observed only in the outer layers of microspheres, which also implied that they were incorporated into microspheres by swelling. The shape of the composite microspheres remained spherical and the size did not change greatly, since they were cross-linked. More NCs were observed with increasing the concentration of NCs for swelling. Although the admittance of NCs in microspheres was saturated, the distribution of CdTe NCs was very uniform, and no apparent aggregates of NCs were observed under TEM (Fig. 5d).
To confirm that CdTe NCs in the microspheres were well dispersed, PL spectra were investigated (Fig. 6), since the aggregation of CdTe NCs would result in red-shift of the emission peak and broadening of FWHM. The PL spectra of a series of 198-nm PS microspheres with different concentrations of CdTe NCs were recorded. When the concentrations were below $3 \times 10^3$ NCs per microsphere, the PL spectra of CdTe NCs in microspheres were nearly identical to that of aqueous CdTe. From the PL spectra, we can deduce that no or very minor aggregations occurred in the microspheres. As the concentration of NCs continued to increase, the PL emission peaks began to red-shift. When the concentration of the NCs got to the maximum, the emission peak red-shifted about 16 nm compared with that of aqueous CdTe NCs. This might be caused by aggregation of CdTe NCs or Förster energy transfer. As the distance between neighboring NCs became shorter than 10 nm, Förster energy transfer occurred due to the NCs having a size distribution \[23\]. The fact that the FWHM became narrower excluded the speculation of aggregation of the NCs and confirmed the occurrence of Förster energy transfer. We believe that the inter-leaving polymer chains and the long chains of OVDAC around the surface of NCs separated CdTe NCs effectively to prevent them from aggregating. This is consistent with the result that no apparent aggregates of NCs were found from TEM images. So the concentration of CdTe NCs per microsphere should be controlled below the critical concentration for Förster energy transfer to maintain their original fluorescence properties.

We had mentioned that all CdTe NCs with different emission colors from green to red could be swollen into microspheres at controlled intensities. Besides, multicolored NCs could also be incorporated into the same microsphere with controlled intensity ratios in the same way by premixing the chloroform solutions of different-sized NCs at expected intensity ratios (Fig. 7). The amount of CdTe totally incorporated into the microspheres was kept below the critical concentration for Förster energy transfer. After different-colored CdTe NCs were swollen into
the same microsphere, the emission peaks did not change for the CdTe two samples compared to those in chloroform. At the same time, the intensity ratios slightly changed. The results also indicated that CdTe NCs dispersed in the microspheres separately and Förster energy transfer did not occur, since Förster energy transfer would cause not only the enhancement of emission intensity for larger NCs with decreased emission intensity for smaller ones, but also red shift of the emission peak positions of both samples [12]. We could also conclude that the micropores of the polymer microspheres were so large that the size of the NCs did not influence their penetration into the microspheres. This was very important for the preparation of multiplexed optical coding. NCs with more emission colors could be embedded into the microspheres and still distinguishable on the condition that the FWHM was narrow enough.

An interesting fact of our investigation was that CdTe NCs rooted in the composite microspheres even without blocking NCs in the microspheres [24]. When the composite microspheres were subject to repeated washing in water or organic solvents under ultrasonic treatment for 5 min each time, the fluorescence intensity of the microspheres did not change, and no PL signals was detected in the washing solvents after the microspheres were separated out. The organic solvents could be dimethyl formamide (DMF), alcohol, isopropanol, a mixture of chloroform and isopropanol (1:2 v/v), and even chloroform. A soaking experiment was also done to investigate long-time stability of the NCs in the microspheres. No leakage of CdTe NCs was found when the composite microspheres were soaked in water or isopropanol for more than half a year. We attributed this result to the strong hydrophobic interaction between OVDAC and the PS matrix. The long chains of OVDAC molecules around CdTe NCs were fully twisted with the cross-linked long chains of polymer to prevent the NCs from leaking out of polymer microspheres. The same stability of OBDAC- or CTAB-capped CdTe NCs was found in the microspheres, which confirmed that the concretion of CdTe NCs in polymer matrix was due to hydrophobic interaction rather than covalent bonding or π–π interaction. Moreover, the PL emission of these composite microspheres was dramatically stable. The PL intensity of the microspheres did not change any more even after 6 months’ storage at room temperature as the microspheres were precipitated out and kept in vial in the form of powder.

In summary, polymer composite microspheres with strong PL emission were fabricated by swelling cationic surfactant-coated aqueous CdTe NCs into preformed PS microspheres. Through this strategy, both single-color and multicolor fluorescent microspheres with controlled PL intensities could be obtained. The hydrophobic interaction between the surfactants and the cross-linked chains of polymer was strong enough to prevent NCs from leaking when the fluorescent microspheres were exposed to polar solvents. It proved that aqueous NCs were good alternatives to prepare fluorescent composite microspheres by swelling method after proper surface coating. The current method may be extended to other aqueous nanocrystals for the preparation of functional microspheres.

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References