

# Preparations of bifunctional polymeric beads simultaneously incorporated with fluorescent quantum dots and magnetic nanocrystals

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Received 9 November 2007, in final form 2 January 2008

Published 13 February 2008

Online at [stacks.iop.org/Nano/19/105601](http://stacks.iop.org/Nano/19/105601)

## Abstract

Bifunctional polystyrene beads simultaneously incorporated with fluorescent CdTe quantum dots (Q-dots) and superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanocrystals were prepared by a modified mini-emulsion polymerization method, in which polymerizable surfactants were used as both phase transfer agent for aqueous colloidal nanoparticles and emulsifier. In addition, silica coating was also introduced to Fe<sub>3</sub>O<sub>4</sub> nanocrystals for regulating the internal structure of the composite beads. Transmission electron microscopy, confocal fluorescence microscopy and conventional spectroscopy were used to characterize the composite beads, as well as the polymerizable surfactant-coated CdTe Q-dots and silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Different mixing methods were also attempted in order to vary the size of the resultant bifunctional beads.

## 1. Introduction

Both fluorescent quantum dots (Q-dots) and superparamagnetic nanocrystals have received intensive investigation over the past few years due to their substantial applications in the biological and biomedical fields [1, 2]. The fluorescent Q-dots, as a new type of biolabeling material, have been proven to be superior to conventional dyes due to their excellent optical properties such as high fluorescence quantum yield, sharp emission profile with broad excitation range, color tunable fluorescence and strong resistance to photobleaching [3]. The magnetic nanocrystals also show great potentials in cell tagging, tracking and imaging [4–6], targeted drug delivery [7], as well as hyperthermia treatment of cancers, etc [8, 9]. Therefore, to combine the optical properties of Q-dots with the superparamagnetic properties of magnetic nanocrystals will undoubtedly lead to a new type of bifunctional nanomaterial useful for bioapplications [10].

So far, three strategies have been developed for combining these two types of nanomaterials. The first one is to couple

fluorescent Q-dots with magnetic nanoparticles at the single-particle level by forming bifunctional heterodimers [11, 12], and the second one is to deposit thin films containing both fluorescent and magnetic nanocrystals via a layer-by-layer self-assembly technique on polymeric beads [13, 14] or deposit thin layer-by-layer films containing Q-dots on preformed magnetic microspheres incorporated with iron oxide nanocrystals [15]. The third one is to simultaneously integrate these two types of nanocrystals within microspheres of inert materials [16, 17]. In comparison with the first two types of approaches, the third one not only offers protection for nanocrystals against the harsh chemical environments, but also allows manipulation of the optical properties of the bifunctional beads by varying the ratios among the different types of fluorescent Q-dots incorporated [18–20]. However, to the best of our knowledge, there are only a few successful examples of such bifunctional beads [15–17], especially using hydrophobic polymers as the bead matrices. Even though to load fluorescent Q-dots into swollen polystyrene latex has been proven to be an effective approach for preparing fluorescent beads [20], the limited pore size in the cross-linked polystyrene matrix

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may prevent larger magnetic nanocrystals from entering the beads, while relatively larger magnetic particles are preferred for producing high magnetic susceptibility in the resultant beads.

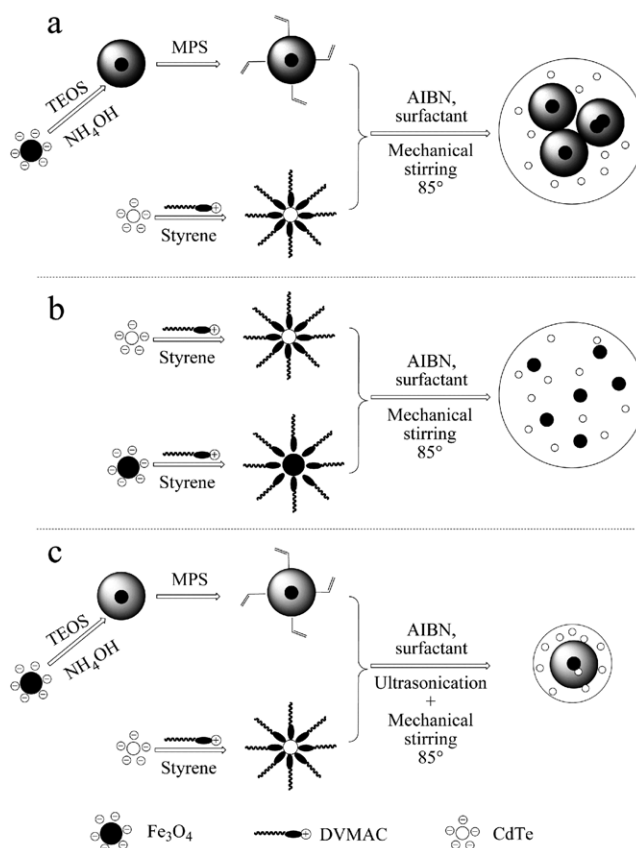
An alternative approach towards the preparation of polystyrene beads doped with functional inorganic nanocrystals is a modified mini-emulsion polymerization method, by which we have recently demonstrated that different types of water soluble inorganic nanocrystals, independent of their chemical natures, can be encapsulated into polystyrene beads by using polymerizable surfactants as both phase transfer agent for aqueous colloidal nanoparticles and emulsifier. The polymerizable nature of the phase transfer agent can effectively prevent the incorporated nanocrystals from agglomeration in the hydrophobic matrix, while the use of polymerizable emulsifier is critical for effectively entrapping inorganic nanocrystals within the resultant polystyrene beads [21].

Following on from this study, we further extended the modified mini-emulsion polymerization method to preparations of fluorescent–magnetic bifunctional polystyrene beads by simultaneously encapsulating both CdTe Q-dots and Fe<sub>3</sub>O<sub>4</sub> nanocrystals. Similar to our previous investigation, didecyl-p-vinylbenzylmethylammonium chloride (DVMAC), a polymerizable surfactant, was used as the phase transfer agent to, on the one hand, transfer both water soluble CdTe Q-dots and Fe<sub>3</sub>O<sub>4</sub> nanocrystals into styrene, and, on the other hand, to bind vinyl groups to the particle surface. Polymerizable octadecyl-p-vinylbenzyltrimethylammonium chloride (OVDAC) was chosen as emulsifier during the following mini-emulsion polymerization. As magnetic iron oxide particles have strong featureless absorptions covering nearly the whole visible range, a composite structure with magnetic nanocrystals positioned in the inner part of the composite beads should be helpful for gaining higher fluorescence brightness out of the composite beads. To achieve such a composite structure, silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) were prepared and used after vinyl groups were grafted onto the particle surface. The effect of the silica coating for Fe<sub>3</sub>O<sub>4</sub> nanocrystals on the fluorescence intensity of the bifunctional beads was investigated by comparing with those based on Fe<sub>3</sub>O<sub>4</sub> nanocrystals without the silica coating. Further decreasing the size of the composite bifunctional beads was also attempted by using ultrasonication for better emulsifying the immiscible system.

## 2. Experimental details

Triton® X-100, tetraethyl orthosilicate (TEOS, purity: 98%) and 3-(trimethoxysilyl)propyl methacrylate (MPS, purity: 98%) were purchased from Aldrich and used as received. Styrene was purified by distillation under reduced pressure. Reagent grade hexadecane and aqueous ammonia (25 wt%) were used without further purification. Didecyl-p-vinylbenzylmethylammonium chloride (DVMAC) and octadecyl-p-vinylbenzyltrimethylammonium chloride (OVDAC) were synthesized according to [22].

In general, three synthetic routes were developed for achieving fluorescent–magnetic bifunctional polystyrene beads as illustrated in scheme 1. In all these synthetic routes (a, b



**Scheme 1.** Different synthetic routes adopted in the current investigations for achieving fluorescent–magnetic bifunctional polystyrene beads based on differently sized fluorescent CdTe Q-dots and superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanocrystals.

and c), CdTe Q-dots were capped by DVMAC. In contrast, two types of Fe<sub>3</sub>O<sub>4</sub>-based magnetic particles were prepared for the following polymerization. The first type was obtained by first coating the Fe<sub>3</sub>O<sub>4</sub> nanocrystals with silica and then grafting vinyl groups onto the silica shell. The average size of the silica-coated magnetic particles was about 100 nm. Compared with the first type of magnetic particles, the second type of magnetic particles was prepared by directly capping Fe<sub>3</sub>O<sub>4</sub> nanocrystals with DVMAC. In fact, the difference between these two types of magnetic particles is not only the way the vinyl groups were bonded. The larger size of the former ones was also expected to be helpful for getting stronger photoluminescence out of the bifunctional beads, which will be discussed in detail in the following section. In addition to the difference in the form of the Fe<sub>3</sub>O<sub>4</sub> nanocrystals, the following polymerization was also carried out by different mixing methods, i.e. mechanical stirring (routes a and b) and a combination of ultrasonic mixing and mechanical stirring (route c). More details on synthetic route c are described in the appendix.

In detail, aqueous colloidal CdTe nanocrystals were first synthesized according to previous reports [23] and then transferred into styrene using DVMAC as phase transfer agent [18, 21]. Typically, 60 mg DVMAC was used for transferring as-prepared CdTe Q-dots from 2 ml aqueous solution ( $1.84 \times 10^{-7}$  M) into 1.5 ml styrene. The resultant

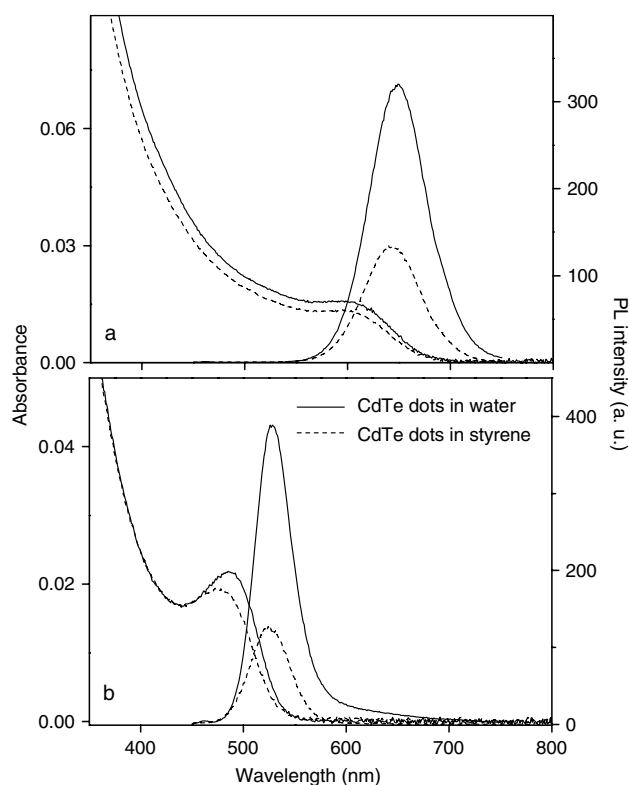
styrene solution of CdTe Q-dots was extracted after the aqueous phase became colorless using a separating funnel.

$\text{Fe}_3\text{O}_4$  nanocrystals used in the current investigations were then prepared according to one of our previous publications [24]. In brief, the  $\text{Fe}_3\text{O}_4$  nanocrystals were synthesized by pyrolyzing ferric triacetylacetonate in 2-pyrrolidone ( $3.5 \times 10^{-2}$  M). The reaction was initiated by refluxing the 2-pyrrolidone solution for about half an hour and then terminated by cooling the reaction mixture to room temperature. After that, three fold of methanol was introduced to precipitate the  $\text{Fe}_3\text{O}_4$  nanocrystals which were subsequently washed three times by acetone before further experiments. The average size of the resultant particles was  $10.3 \pm 2.3$  (s.d.: standard deviation) nm measured by TEM. The silica-coated  $\text{Fe}_3\text{O}_4$  particles were prepared by hydrolyzing TEOS in the presence of 10 nm  $\text{Fe}_3\text{O}_4$  nanocrystals. Typically, 0.3 g as-prepared magnetite nanocrystals were dispersed in 180 ml ethanol/water (8:1) mixture followed by addition of 7 ml ammonia aqueous solution (25 wt%). Under mechanical stirring, 1.2 ml TEOS was consecutively introduced. The whole reaction lasted typically for 24 h at room temperature to obtain the silica-coated  $\text{Fe}_3\text{O}_4$  nanoparticles. Then, 1 ml MPS was added to the reaction mixture for further functionalizing the silica-coated nanoparticles with vinyl groups [25]. The following reaction was allowed for 24 h at  $45^\circ\text{C}$ . Vinylated  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  particles obtained were isolated by centrifugation and then washed by a mixture of ethanol and water (V:V = 1:1) three times.

Since the resultant  $\text{Fe}_3\text{O}_4$  powder could be well dispersed in basic solution ( $\text{pH} \approx 12$ ), the following phase transfer process was enabled for producing the second type of magnetic particles using DVMAC as phase transfer agent. Typically, 129 mg DVMAC dissolved in 1 ml styrene was used to extract 1.5 mg  $\text{Fe}_3\text{O}_4$  nanocrystals from 0.5 ml aqueous solution. The phase transfer efficiency was determined to be 69% by the phenanthroline method [26].

Then subsequent mini-emulsion polymerization following the first synthetic route was carried out as below. 15 ml deionized water was added to a three-necked flask. Then, 1.5 ml as-prepared styrene solution of DVMAC-capped CdTe dots was introduced. In this styrene solution, 10 mg vinylated  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  was pre-dispersed by ultrasonication and 0.015 g AIBN was dissolved. After that, 0.075 g OVDAC and 0.075 g Triton<sup>®</sup> X-100 were introduced as emulsifier. The polymerization was initiated at  $85^\circ\text{C}$  under mechanical stirring and lasted for 6 h. The bifunctional beads were finally obtained via magnetic separation followed by cleaning procedures with water and ethanol. In a similar way, the second synthetic route adopted the  $\text{Fe}_3\text{O}_4$  directly transferred from aqueous solution into styrene using DVMAC, instead of the silica-coated particles. The third synthetic route ran generally the same as the first one except that the reaction mixture was subjected to ultrasonication (200 W) for 60 s before it was heated up to  $85^\circ\text{C}$  for further polymerization.

The UV-vis absorption spectra were recorded with a Cary 50 UV-vis spectrophotometer. The fluorescence spectra were obtained with a Cary Eclipse fluorescence spectrophotometer. TEM images were recorded by a JEM-100CX II microscope

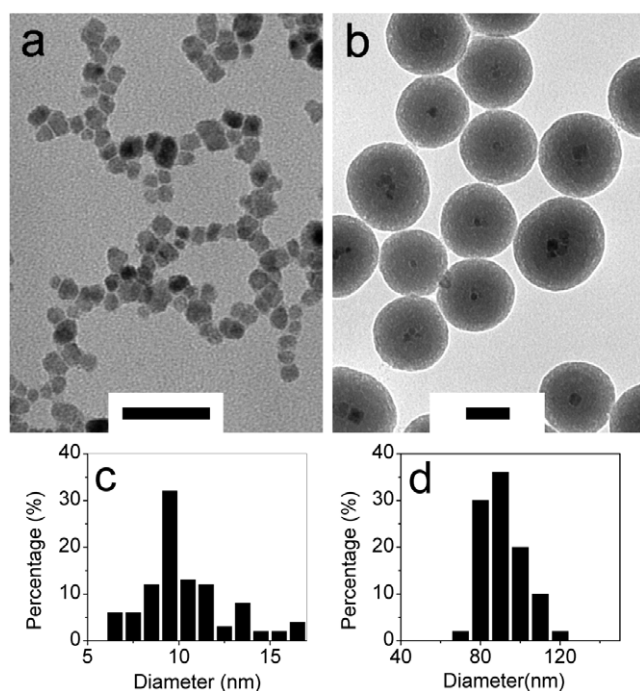


**Figure 1.** Absorption and fluorescence spectra of the red (a) and green (b) CdTe Q-dots recorded before (solid curves) and after (dashed curves) they were transferred from aqueous solution into styrene using DVMAC as phase transfer agent. The excitation wavelength for fluorescence measurements was fixed at 400 nm.

operating at 100 kV. The confocal fluorescence image was taken with a Leica confocal scanning system mounted on a Leica Aristoplan and equipped with a 1006 oil immersion objective with a numerical aperture (NA) of 1.4. The morphology of the bead samples was characterized with a JEOL JSM-6700F field emission scanning electron microscope (SEM). FTIR spectra were taken on a Bruker EQUINOX55 FTIR spectrometer.

### 3. Results and discussion

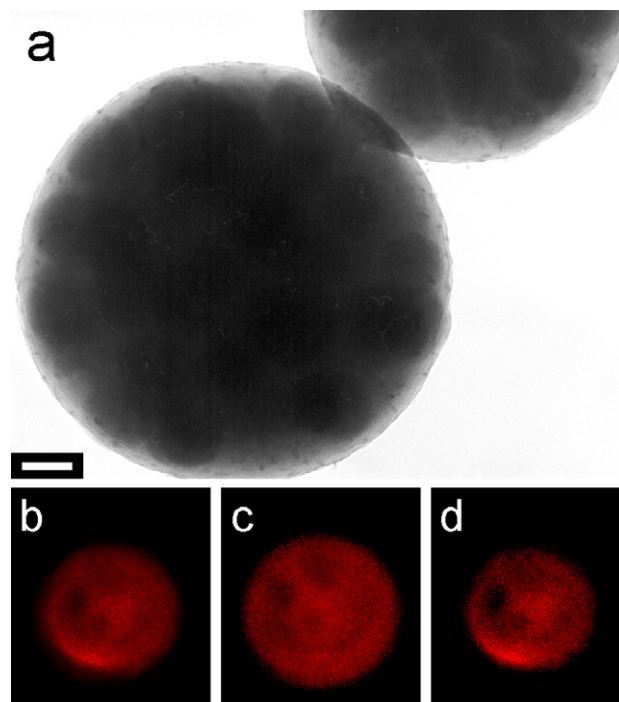
Two differently sized CdTe Q-dot samples, with central photoluminescence peaking at 530 nm (green CdTe Q-dots) and 652 nm (red CdTe Q-dots), respectively, were used in the current investigations. Both fluorescence and absorption spectra of these two samples were recorded before and after they were transferred into styrene. The results shown in figure 1 demonstrate that DVMAC is an effective phase transfer agent for CdTe Q-dots, taking effect nearly independently of particle size. Under the aforementioned conditions, the phase transferring efficiency for red and green CdTe Q-dots was about 83% and 89%, respectively. Moreover, the phase transferring process for CdTe nanocrystals did not alter their optical properties except for a certain loss in fluorescence quantum yield, i.e. 50% for the red CdTe Q-dots and 64% for the green CdTe Q-dots, respectively. It should be pointed out that the DVMAC-coated CdTe nanocrystals remained highly



**Figure 2.** TEM images of the as-prepared  $\text{Fe}_3\text{O}_4$  nanoparticles (a) and the vinylated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  composite particles (b). The scale bar corresponds to 50 nm. Panels (c) and (d) present the corresponding particle size distributions.

dispersible in styrene as no light scattering appears in the long wavelength range below the absorption threshold.

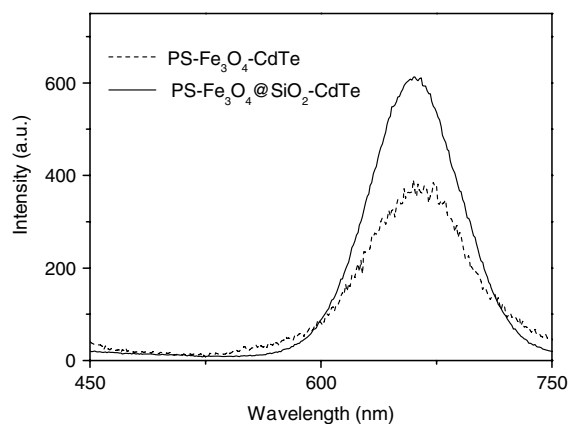
Figure 2(a) shows a transmission electron microscopy (TEM) image of the as-prepared  $\text{Fe}_3\text{O}_4$  nanocrystals. The electron diffraction measurement (see the appendix figure A.1) reveals that the iron oxide nanoparticles possess a highly crystalline structure with  $d$ -spacing values being very well in agreement with those for the bulk magnetite (see table A.1). Because the surface of  $\text{Fe}_3\text{O}_4$  nanocrystals has a strong affinity to silica, especially in the alkaline range [27], the silica coating was realized in an ethanol/water mixture via the hydrolysis and condensation of TEOS by a modified Stöber method. The resultant  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles were then used as cores for further grafting vinyl groups via the hydrolysis of 3-(trimethoxysilyl)propyl methacrylate (MPS). The vinylated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles show very clear core-shell structures (figure 2(b)) with a diameter of  $96.0 \pm 10$  nm. Fourier-transformed infrared spectroscopy (FTIR) results (see figure A.2) demonstrated that vinyl groups were successfully grafted onto the particle surface. As a result, the vinylated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles were expected to form covalent bonds with radical polymers upon further polymerization, and consequently firmly fixed in the resultant polymer beads. The histograms shown in figures 2(c) and (d) depict size distributions of both as-prepared  $\text{Fe}_3\text{O}_4$  nanocrystals and the vinylated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles. It is quite obvious that the particle size distribution of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles is much smaller than that for the as-prepared  $\text{Fe}_3\text{O}_4$  nanocrystals, indicating that the general morphologies of the former particles were governed by the Stöber process.



**Figure 3.** (a) TEM image of polystyrene beads simultaneously incorporated with red CdTe QDs and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles (the scale bar corresponds to 100 nm); (b)–(d), three confocal fluorescence microscopy images acquired by a successive scan along the  $z$  axis of the presented composite bead.

The way to graft vinyl groups onto  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles also led to a hydrophobic surface for the vinylated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles, which were readily dispersed in styrene forming a relatively stable dispersion, usually stable for hours. Such colloidal metastability is expected to be useful for controlling the internal structures of the composite polymeric beads since it will drive the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles to form aggregates during polymerization. At the initial stage of the mini-emulsion polymerization, the shear force introduced by mechanical stirring will force the oil droplets to spin while they are circling in the flask. Due to the higher density in comparison with styrene, the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  particles tend to stay in the central area of the oil droplet. As polymerization goes on, they will form aggregates and eventually are fixed in the inner part of the beads. Such a composite structure might be helpful for maximizing the fluorescence intensity of the composite beads, on the one hand by reducing the re-absorption of the fluorescence from Q-dots by  $\text{Fe}_3\text{O}_4$  nanocrystals and, on the other hand, by decreasing the energy transfer probability between these two types of particles due to the existence of the thick enough silica shell.

To provide experimental evidence for the hypothesis regarding the internal structure of the bifunctional composite beads, TEM and confocal fluorescence microscopy measurements were carried out. Due to the solid structure of the composite beads, an electron beam is not able to pass through polystyrene beads several micrometers thick; therefore, relatively small beads were selected and pictured under TEM for better showing the internal structures. As shown in figure 3(a), the  $\text{SiO}_2@ \text{Fe}_3\text{O}_4$  particles aggregate within the poly-

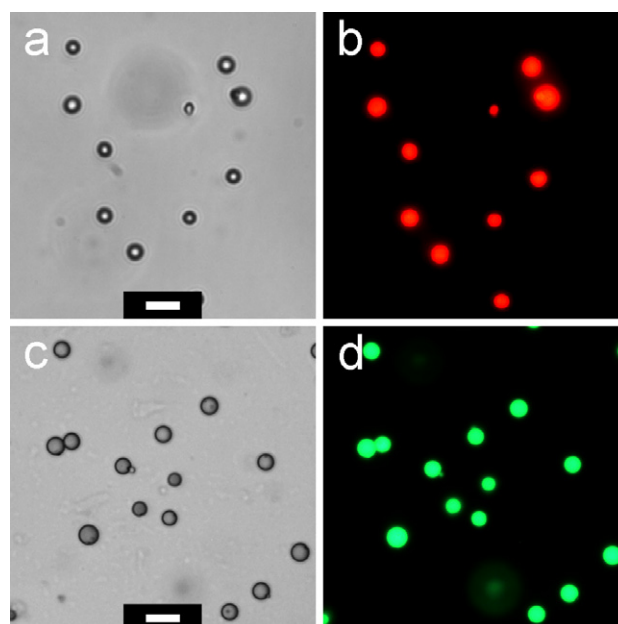


**Figure 4.** Fluorescence spectra recorded from aqueous dispersions of the bifunctional beads prepared using vinylated  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  composite particles (solid line) and  $\text{Fe}_3\text{O}_4$  nanocrystals capped by DVMAC (dashed line), respectively. The excitation wavelength for the fluorescence measurements was fixed at 400 nm.

meric bead, forming a ‘guava-like’ structure. Such structure can more clearly be seen from a smaller bead. Further confocal fluorescence microscope images shown in figures 3(b)–(d) strongly support such a ‘guava-like’ structure.

To provide experimental support for the hypothesis that stronger fluorescence intensity may come out of the ‘guava-like’ beads, a bifunctional bead sample was prepared via the second synthetic route shown in scheme 1 simply for comparison. Before the control experiment was performed, the contents of  $\text{Fe}_3\text{O}_4$  nanoparticles in the as-prepared styrene solution and powder of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  were carefully determined by the phenanthroline method. It was demonstrated that 56.3  $\mu\text{l}$  freshly prepared styrene solution of  $\text{Fe}_3\text{O}_4$  nanocrystals capped by DVMAC contained equal amounts of  $\text{Fe}_3\text{O}_4$  nanocrystals to 18 mg vinylated  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles. According to this ratio, two parallel preparations for the bifunctional beads were carefully carried out by using the same amount of CdTe Q-dots freshly transferred into styrene.

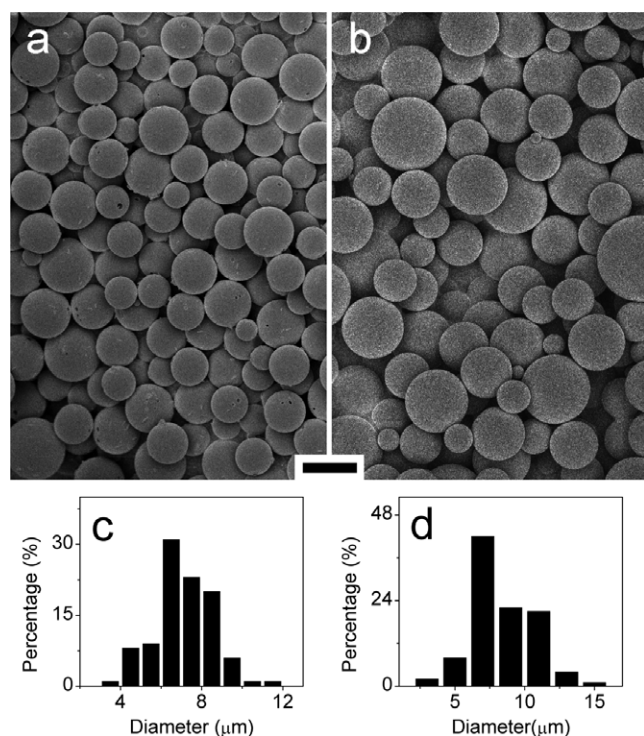
The subsequent conditions for polymerization, including the amount of initiator, stirring speed and heating rate, were controlled exactly the same for both systems. The fluorescence intensity of the resultant aqueous dispersions of these two types of bifunctional beads was measured and compared in figure 4. It is quite obvious that the beads with a ‘guava-like’ structure exhibit higher fluorescence intensity than that based on DVMAC-capped  $\text{Fe}_3\text{O}_4$  particles. Assuming that the inorganic nanocrystals were evenly distributed throughout the bead matrix, the statistical distance between  $\text{Fe}_3\text{O}_4$  and CdTe nanocrystals is far below that required for energy transfer [19]. Nevertheless, close contacts between these two types of particles may not be completely excluded in the reference beads. In this context, the introduction of the silica shell will be helpful for decreasing the energy transfer probability between CdTe and  $\text{Fe}_3\text{O}_4$ . Apart from this effect, the confocal fluorescence microscopy results strongly suggest that the magnetic particles are successfully positioned in the inner part of the beads, which is also helpful for reducing the re-absorption of the fluorescence by  $\text{Fe}_3\text{O}_4$  particles.



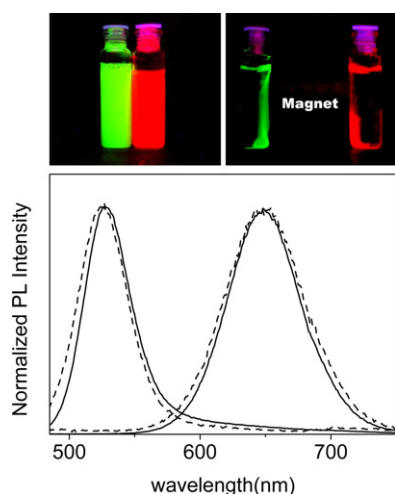
**Figure 5.** Microscopic images of bifunctional composite beads incorporated with red CdTe Q-dots ((a), (b)) and green Q-dots ((c), (d)), respectively. Photographs (a) and (c) are bright-field images, whereas photographs (b) and (d) are fluorescence images. The scale bars in the bright-field images correspond to 10  $\mu\text{m}$ .

The bifunctional beads prepared using both red and green CdTe dots in combination with the silica-coated  $\text{Fe}_3\text{O}_4$  particles were also characterized by conventional fluorescence microscopy. The results shown in figure 5 prove that CdTe nanocrystals have successfully been incorporated, independent of their initial size, into the polystyrene beads which present a perfect one-to-one correspondence between the bright-field image and the fluorescence image, suggesting that almost all polymeric beads were loaded with Q-dots. The general morphologies of the beads incorporated with either red or green CdTe Q-dots can more clearly be seen under a scanning electron microscope, as shown in figure 6. The corresponding histograms for the composite beads present slightly different average bead sizes, i.e. 7.2  $\mu\text{m}$  for red beads and 8.7  $\mu\text{m}$  for green beads. In spite of the slight difference in size, these two types of beads present strong fluorescence and quick response to external magnetic fields, as shown in figure 7. The upper panel presents photographs of aqueous dispersions of these two types of bifunctional beads taken under ultraviolet light before and after being subjected to an external magnetic field. It turned out that the composite beads exhibited strong response to magnetic fields. Only a few minutes were required to attract most of the bifunctional beads to the sidewall of the small glass vials by a 0.5 T permanent magnet. The fluorescence spectra of the green beads and the red beads in diluted suspensions were recorded and compared with the corresponding parent CdTe dots.

As shown in figure 7, little difference in fluorescence is present between the parent CdTe Q-dots and those incorporated in the composite beads, suggesting that the current approach could also be used for preparing multiplexed optical encoding beads with magnetic properties [18, 21].

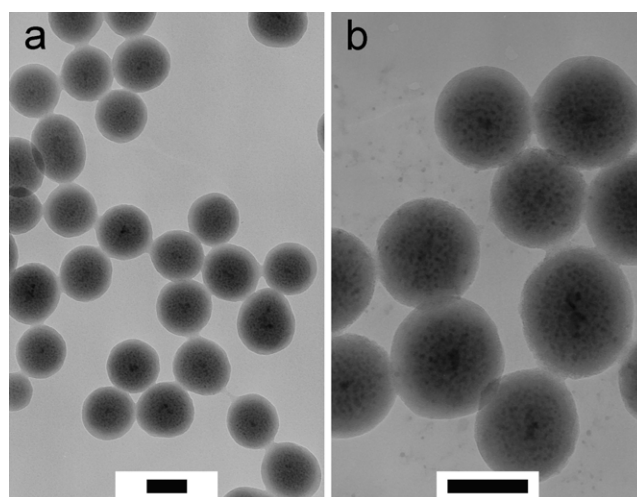


**Figure 6.** SEM images of bifunctional composite beads incorporated with red CdTe Q-dots (a) and green CdTe Q-dots (b), respectively. The scale bar inserted corresponds to 10 μm. The histograms of these types of composite beads are presented in frames (c) and (d), respectively.



**Figure 7.** Upper panel: photographs of aqueous dispersions of the bifunctional beads incorporated with red and green CdTe dots, respectively, apart from the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles. The photographs were taken in ultraviolet light before and after a permanent magnet (0.5 T) was fixed in between. Bottom panel: normalized fluorescence spectra recorded from the above aqueous dispersions (dashed line) together with those of their parent CdTe Q-dots (solid line).

One of the most important driving forces of the current investigations is to develop a new synthetic route for fluorescent–magnetic bifunctional polystyrene beads potentially useful for biological applications. Therefore,



**Figure 8.** TEM images of the bifunctional composite beads prepared via synthetic route c shown in scheme 1. Part of image (a) was enlarged and shown as image (b) to better show the internal structures of the composite beads. All the scale bars correspond to 100 nm.

further decreasing the bead size is not only interesting but also welcome in practice as tagging cells for either optical labeling or magnetically separating purposes, smaller beads of 100 nm may introduce much less stress to cells than micrometer beads. It is known that a microemulsion is thermodynamically stable with an interfacial tension at the oil/water interface close to zero. In contrast, the interfacial tension is much large than zero in a mini-emulsion; high shear is required to reach a steady state in mini-emulsion polymerization [28, 29]. Therefore, to further decrease the size of oil droplets in the current system for reducing the size of the resultant beads, according to synthetic route c in scheme 1, the reaction system was first subjected to ultrasonication of 200 W for about a minute before it was transferred to an oil bath for further polymerization. In addition, hexadecane was imported into the oil phase as a hydrophobe to suppress Ostwald ripening. The resultant beads were carefully collected by centrifugation and magnetic separation, then washed by ethanol and water for three times. TEM results shown in figure 8 demonstrate that the average bead size was successfully reduced to  $136.3 \pm 8.4$  nm, remaining larger than the initial  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles ( $96.0 \pm 10$  nm). Consequently, the ‘guava-like’ structure is replaced by a core ( $\text{Fe}_3\text{O}_4$ )–shell ( $\text{SiO}_2$ )–shell (PS) structure. CdTe Q-dots, however, were located mainly in the layer of PS but near to the  $\text{SiO}_2$ –PS interface. Moreover, there is no obvious change with respect to the PL emission in comparison with their parent CdTe Q-dots (see figure A.3).

#### 4. Conclusions

In summary, we have successfully prepared a new type of bifunctional beads whose fluorescent and magnetic properties are endowed by CdTe Q-dots and superparamagnetic  $\text{Fe}_3\text{O}_4$  nanocrystals, respectively. Moreover, these two types of inorganic nanoparticles are chemically trapped in a polystyrene matrix by forming covalent bonds between the polymer

backbone and the vinyl groups modified on the nanoparticle surfaces. The silica coating on the  $\text{Fe}_3\text{O}_4$  nanocrystals, however, turns out to be important for regulating the internal structure of the bifunctional beads by forming a ‘guava-like’ structure, and consequently giving rise to higher fluorescence intensity in comparison with those beads prepared based on  $\text{Fe}_3\text{O}_4$  nanocrystals without the silica shell. This enhancement effect could be attributed to the minimization of re-absorption of the fluorescence emitting from the CdTe Q-dots by  $\text{Fe}_3\text{O}_4$  nanocrystals, as well as elimination of possible energy transfer between CdTe and  $\text{Fe}_3\text{O}_4$  nanocrystals. Furthermore, it was demonstrated that ultrasonication is very helpful for dramatically reducing the size of the bifunctional beads, apart from suppressing their size distribution.

## Acknowledgments

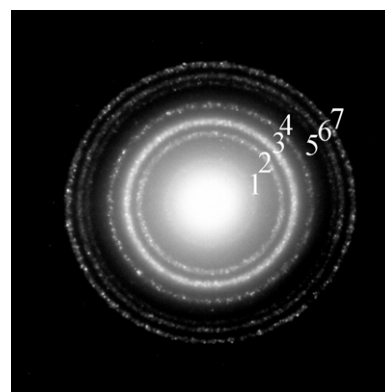
The current investigations were jointly supported by projects (NSFC, 20673128; MOST, 2006AA03Z319) and partly supported by the National Center for Nanoscience and Technology, China. We are grateful to Ms Weijun Tong for confocal measurements.

## Appendix

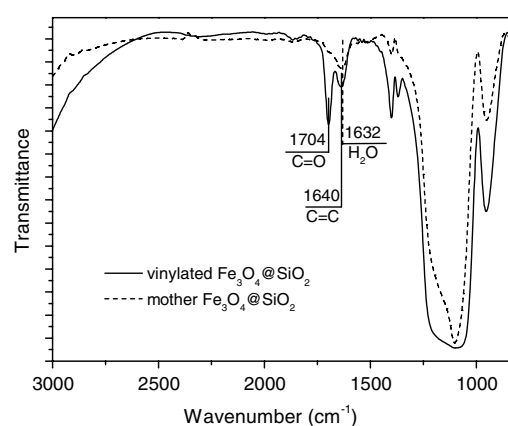
Synthesis of bifunctional polystyrene beads was via synthetic route c shown in scheme 1. The synthesis was performed as follows. 1.5 ml CdTe-styrene solution was prepared by transferring the as-prepared CdTe nanocrystals from 1 ml aqueous solution using 32 mg DVMAC, into which 10 mg vinylated  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles was then dispersed followed by addition of 15 mg AIBN, and 80  $\mu\text{l}$  hexadecane. In parallel, another 15 ml aqueous solution containing 0.08 g OVDAC and 3 mg  $\text{NaHCO}_3$  was prepared. After that, the aforementioned two solutions were mixed by mechanical stirring for 30 min. Then the whole reaction mixture was subjected to ultrasonication for 60 s at 200 W (JY92-II ultrasonic pulverizer manufactured by Shanghai Xinzhi Biological Technology Institute) in an ice bath. Right after the ultrasonication-assisted emulsification, the temperature of the reaction system was raised to 85 °C and maintained at this temperature for 5 h. After the reaction was completed, the reaction mixture was subjected to centrifugation. The resultant precipitate was subsequently re-dispersed in water for further magnetic separation. The product isolated by magnetic

**Table A1.** The experimental  $d$ -spacing values calculated from the electron diffraction pattern shown in figure A.1 together with the standard values for bulk  $\text{Fe}_3\text{O}_4$  from JCPDS card 19-0629.

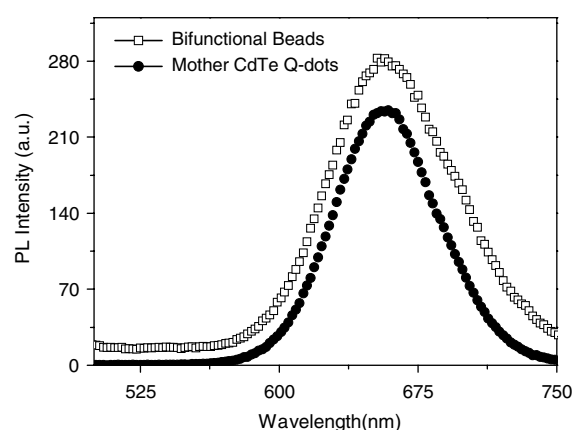
| Ring | Calculated $d$ spacing | JCPDS data for $\text{Fe}_3\text{O}_4$ | $hkl$ |
|------|------------------------|----------------------------------------|-------|
| 1    | 0.4851                 | 0.4852                                 | 111   |
| 2    | 0.3000                 | 0.2967                                 | 220   |
| 3    | 0.2528                 | 0.2532                                 | 311   |
| 4    | 0.2107                 | 0.2099                                 | 400   |
| 5    | 0.1716                 | 0.1714                                 | 422   |
| 6    | 0.1617                 | 0.1615                                 | 511   |
| 7    | 0.1484                 | 0.1484                                 | 440   |



**Figure A.1.** Electron diffraction pattern of the as-prepared  $\text{Fe}_3\text{O}_4$  nanocrystals.



**Figure A.2.** FTIR spectra of the vinylated  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles together with the mother  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles.



**Figure A.3.** Fluorescence spectra of mother CdTe nanocrystals and bifunctional polystyrene beads prepared via synthetic route c shown in scheme 1.

separation was rinsed with ethanol and water three times before further characterizations. The optical properties of the resultant beads were mainly characterized by fluorescence spectroscopy. The results are shown in figure A.3.

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