Fabrication of a quantum dot-polymer matrix by layer-by-layer conjugation

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Abstract

A polymer-quantum dot (QD) composite matrix was fabricated by a simple layer-by-layer (LBL) covalent conjugation of cadmium selenide (CdSe) QDs to poly(dimethylsiloxane) (PDMS) films. LBL covalent conjugation was preferred in the current work for avoiding possible phase separation of QDs into microdomains when directly mixed with polymers. A PDMS film was fabricated by thermal curing of a pre-polymer mixture and was silanized using 3-mercaptopropyltrimethoxy silane (3MPS). A monolayer of CdSe QDs was conjugated to the polymer film through thiol coupling. By repeating the fabrication of PDMS film on the QD layer, silane coupling, and QD conjugation we have successfully prepared an optically transparent multilayer polymer-QD matrix. We selected PDMS as a host polymer considering (1) photoluminescence (PL) of QDs was not affected by PDMS, (2) simple chemical conjugation of QDs to PDMS, (3) flexible structural fabrication, and (4) optical transparency. Formation of individual layers of polymer and QDs was characterized using atomic force microscopy (AFM) imaging, and the presence of QD layers inside the PDMS matrix was identified from fluorescence imaging. Besides a simple demonstration of LBL conjugation of QDs to PDMS, the preparation of an optically transparent polymer-QD matrix where PL properties of QDs are intact would be useful during the construction of QD based optical and optoelectronic devices supported in host matrixes.
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1. Introduction

Semiconductor quantum dots (QDs) are attractive materials for their unique optical properties including extended absorption in the UV–vis region, narrow emission band, size tunable optical emission, brightness, and photostability [1–4]. Recent advancements in syntheses and understanding of surface chemistry of cadmium selenide (CdSe) QDs provided several advantages including easy preparation [5–8], availability in multicolor [3,4,9], and compatibility in organic and aqueous phases due to surface modifications using different ligands [2,4,9,10]. Furthermore, simple synthetic approaches and advanced optical and electronic properties make QDs a promising material for applications in photovoltaic cells [11,12], sensors [13–16], light emitting diodes [17], and bio-labeling [4,18]. However, incor-

poration of QDs in supporting matrixes is a prerequisite for real devices.

Compatibility of QDs in different host matrixes is under investigation. Introduction of methods for regular arrangement and high-density homogeneous distribution of QDs in host materials would considerably shape their applications in photovoltaic, optoelectronic, and sensor devices. The key to select a host matrix is intact photoluminescence (PL) efficiency and band gap of QDs when integrated into the matrix. However, quenching of PL quantum yield due to carrier diffusion in photovoltaic systems comprising QDs and conducting polymers is unavoidable [19,20]. Other properties such as optical transparency, physical and chemical stability, and easy molding of host materials are favorable for advanced applications. In this regard, several polymers are potential candidates for preparing supporting host matrixes for QDs. Different strategies including simple mixing of QDs and polymers [16,19,21–24], and covalent and non-covalent conjugation of QDs to polymers [25–34] were used for preparing polymer-QD composites. Nevertheless,

simple mixing of QDs and a polymer is not always preferred due to phase segregation and aggregation of QDs observed from time-to-time [16,22,23]. The obscurities associated with uniform distributions of QDs in polymers were resolved to a certain level recently by covalent and non-covalent conjugation of QDs to polymers such as ligand integrated polynorbornenes [25,27], polyamines [34], thiolated polyphenols [26], and functionalized ionic polymers [28,30]; presence of microdomains due to phase segregation was observed in certain cases though [25,27].

In general, host materials for QDs may be classified into two: (1) active semiconductor hosts for photovoltaic and opto-electronic applications where the host electronically interacts with QDs and perturb the PL properties of QDs, and (2) passive wide band-gap hosts which provide only supporting roles without altering optical and electronic properties of QDs. For both the classes of hosts covalent conjugations of QDs to host materials are preferred for reducing phase segregation. In the current work, we chose to investigate compatibility of CdSe QDs in poly(dimethylsiloxane) (PDMS) and compared the PL properties of QDs in PDMS and another polymer, namely poly(vinyl pyrrolidone) (PVP). PDMS has several advantages [35–39] including easy molding into various structural forms, structural flexibility when molded, efficient covalent conjugation to silanes those can bridge other molecules/systems to PDMS, optical transparency, and electrical and thermal insulations. Furthermore, PL properties of CdSe QDs was intact in the presence of PDMS; several other polymers are potential quenchers of PL [20,23,27]. For avoiding phase segregation during the preparation of a PDMS-QD matrix we have selected a simple method of silane coupled layer-by-layer (LBL) conjugation, and prepared a multilayer PDMS-QD matrix.

2. Materials

CdSe QDs were synthesized following literature methods [5–8]; however, certain variations to ligands and experimental conditions were employed in the current work. In a typical synthesis of CdSe QDs, a mixture of cadmium oleate (1.2 mL, 1.2 M solution in oleic acid) and trioctylphosphine selenide (TOPSe, 1 mL, 1.36 M solution in trioctylphosphine) was reacted at 120 °C for 2 h in the presence of hexadecyl amine (2 g) and trioctylphosphine oxide (TOPO, 2 g). Cadmium oleate solution (1.2 M in oleic acid) was prepared by dissolving required amount of cadmium oxide (CdO) in oleic acid at 200 °C for 2 h, and TOPSe solution (1.36 M in trioctylphosphine) was prepared by dissolving required amount of Se shots in trioctylphosphine at 150 °C for 2 h. The reaction between cadmium oleate and TOPSe yielded CdSe QDs with narrow size distribution (3.5–5 nm) and bright PL ($\phi_f = 0.25$). We characterized the size distribution of CdSe QDs from spectral measurements and transmission electron microscopy (TEM) imaging. Typical absorption and PL spectrums of CdSe QDs dispersed in chloroform are shown in Fig. 1A (traces 'a' and 'b', respectively). TEM image of a CdSe QD sample, prepared by dispersing a n-butanol solution of QDs on a carbon coated copper grid, is shown in Fig. 1B. Relatively narrow size distribution of the CdSe QDs (average particle diam-
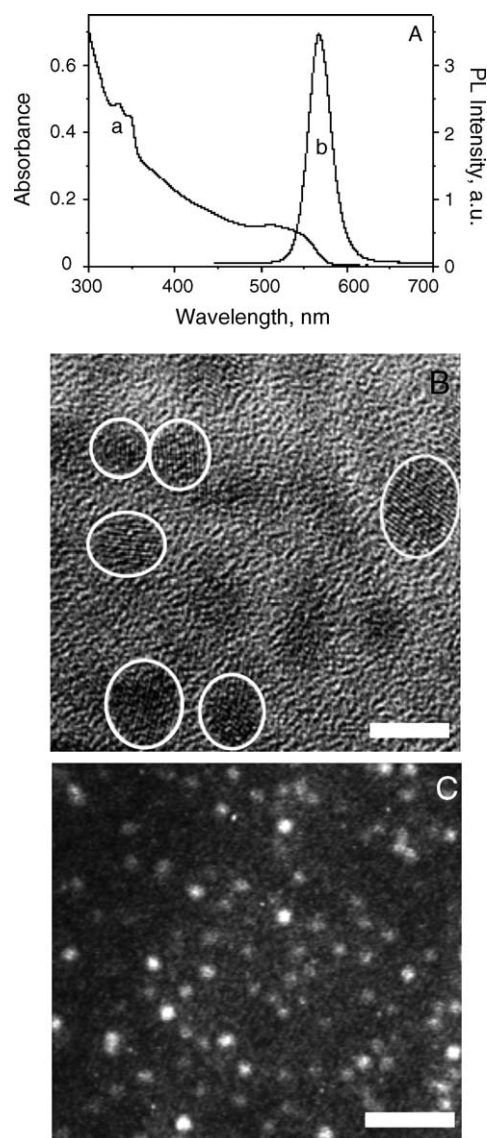

Fig. 1. (A) Absorption (a) and PL (b) spectrums of CdSe QD solutions in chloroform. PL measurement was carried out after adjusting optical density of a QD solution to 0.1 at 450 nm. PL spectrum was recorded by exciting the sample at 450 nm; (B) TEM image of a CdSe QD sample, the sample was prepared by dispersing a n-butanol solution (∼50 pM) of CdSe QDs on a carbon coated copper grid followed by drying under vacuum; and (C) fluorescence image of single CdSe QDs in a sample prepared by spin-coating a 0.1 nM chloroform solution on a slide glass. The fluorescence image was collected by exciting at 532 nm. The scale bars in (B) and (C) are 5 nm and 10 μm, respectively.

eter ∼ 4 nm) was relevant from the emission band (full width at half maximum (*fwhm*) = 35 nm) and the TEM image. Furthermore, the brightness of PL was characterized using single-QD fluorescence imaging. Typical fluorescence image of isolated CdSe QDs in a sample prepared by spin coating a 0.1 nM CdSe QD solution on a slide glass is shown in Fig. 1C. It may be noted that PL intensities vary from dot to dot. Different PL intensities of single-QDs are likely due to an average effect of inherent PL intensity fluctuations ('on' and 'off' blinking) within an integration time of 30 ms. A possibility that groups of QDs are included in some fluorescent spots is also not completely ruled out.

Selenium shots, cadmium oxide, trioctylphosphine, TOPO, oleic acid, and PVP were obtained from Aldrich and used as supplied. PDMS pre-polymer and curing agent (Sylgard 184), and 3-mercaptopropyltrimethoxy silane (3MPS) used for LBL matrix preparation were obtained from Dow Corning and AZmax, respectively. Spectroscopic grade chloroform and ethanol were obtained from Wako and were used as supplied during surface modification of PDMS films, conjugation of QDs to PDMS films, and spectral measurements.

Reference samples for PL measurements were prepared by dispersing QDs in chloroform solutions containing PDMS or PVP (up to 50 mg/mL).

2.1. Instruments used

Absorption and PL spectrums were recorded using a Hitachi-4100 spectrophotometer and a Hitachi-4500 spectrofluorometer, respectively. Topography images of PDMS and QD conjugated PDMS were recorded using a MFP-3D atomic force microscope (Asylum Research). Size distribution of CdSe QDs was characterized by TEM imaging (JEOL JEM-3010, 300 kV). Fluorescence images of layered PDMS-QD samples were recorded using a wide-field video microscopy system; a combination of an inverted optical microscope (Olympus IX70) equipped with a band-pass filter (560/50M, Chroma Technology Corp.), a 40× objective lens (Olympus UPlanFl, NA 0.7), an image intensifier (Hamamatsu C8600), and a CCD camera (Hamamatsu C5985) was used. Excitation sources used for fluorescence imaging were either second harmonics (532 nm) of a diode-pumped continuous wave Nd:YVO$_4$ laser (Spectra Physics Millennia IIs) or a band pass (460–490 nm) filtered light from a Xenon lamp. Laser intensity used for imaging was ~320 mW/cm^2.

3. Results and discussion

3.1. Fabrication of a multilayer PDMS-QD matrix

We prepared a multilayer polymer-QD matrix by LBL fabrication of thin PDMS polymer films and conjugation of CdSe QDs to individual layers. Steps involved in the preparation of the polymer-QD matrix are shown in Fig. 2, and the details are discussed here. PDMS polymer films were prepared from a mixture (10:1 w/w) of PDMS pre-polymer and curing agent. A stock of the mixture was prepared by thoroughly mixing 4 g PDMS pre-polymer and 400 mg curing agent. Trapped air bubbles were carefully removed by placing the mixture in a vacuum chamber for 30 min. A base film was fabricated by placing 200 μL of the mixture in a glass bottle followed by heating at 65 °C for 1 h in a water bath. The glass bottle was horizontally placed in the water bath such that a top-flat polymer base film was formed. The glass bottle containing the PDMS base film was cooled to room temperature, and a monolayer of thiol-ended silane was coupled to the top surface of the film by uniformly placing a 200 μL solution of 3MPS (100 μM in ethanol). PDMS is known to react with silanes such as 3MPS. The silane coupling reaction was allowed for 20 min at room temperature and the 3MPS left unreacted was removed by repeated (three times) washing using ethanol. Residual ethanol present in the bottle was removed by drying in a vacuum chamber. A monolayer of thiol-ended silane was formed on the PDMS film, and the thiol functional group was used for conjugation to QDs. For this, 200 μL of a CdSe QD solution (~100 μM) in chloroform was carefully placed on the silanized PDMS film for 3 min. We have tested a range of concentrations of 3MPS and CdSe QDs and reaction time for identifying ideal conditions of high-density QD coverage on the PDMS film. Unbound QDs were removed by washing using
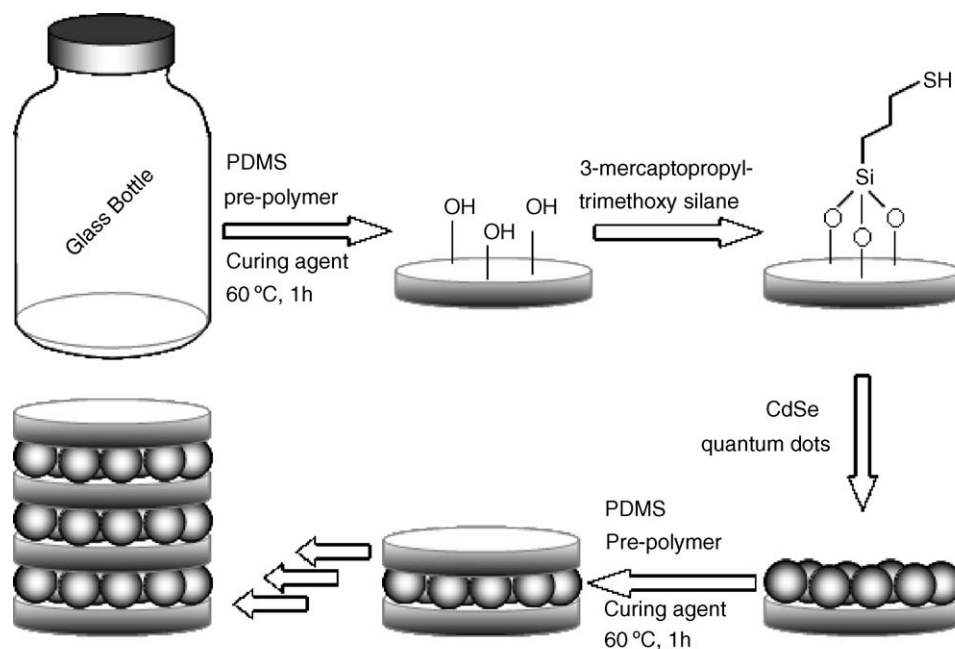

Fig. 2. Schematic presentation of steps involved in the LBL conjugation of CdSe QDs to PDMS films. The LBL conjugation was carried out in a glass bottle of 2 cm diameter.

chloroform and ethanol, and the film was dried under vacuum. A second layer of PDMS film was prepared on the QD conjugated base film by placing 50 μL of the pre-polymer mixture followed by curing at 65 °C for 1 h. The amount of the pre-polymer mixture was reduced to 50 μL for obtaining a thin film; on the other hand, 200 μL of the pre-polymer mixture used in the first step was helpful for filling non-flat base of the glass bottle. Silane couplings, QD conjugations, and preparation of polymer over layers on QDs were repeated until a multilayer PDMS-QD matrix was formed. All the steps involving QDs were carried out in the dark for minimizing photo-darkening of QDs.

The covalent LBL conjugation method selected in the current work was advantageous for preparing QD monolayers compared to widely known electrostatic LBL assembling of multilayer films. In conventional LBL electrostatic assembly methods [30,31,39–41], repeated layers are assembled by dipping a supporting glass or a metal plate alternately in solutions of cationic and anionic molecules/nanoparticles. Fabrications of multilayer matrixes by electrostatic LBL assembling were demonstrated for different combinations of systems among polyelectrolytes, metal nanoparticles, QDs, organic molecules, and biomolecules. The advantages of the electrostatic LBL assembly are fast processing and the use of different molecular systems; however, this method is limited to charged molecules and particles. Also, the presence of defects due to incomplete or non-uniform electrostatic depositions can affect the quality of films [31]. On the other hand, covalent LBL conjugations have several advantages including (1) charged and neutral molecules or nanoparticles with a functional group can be laid into films, (2) covalent conjugation reduces possible defects in film morphology, (3) phase segregation of component materials can be avoided, and (4) layer thickness can be defined on the basis of reaction conditions. Phase segregation and the formation of microdomains observed in previous reports [25,27] in the case of polymer-QD composites were due to ligand integrated conjugation methods; i.e. QDs were stabilized in phosphine side-chains of polymers without strong covalent bonding. On the other hand, it was possible to obtain a polymer-QD matrix with uniform fluorescence intensity distribution when prepared in the presence of relatively large amount of unbound ligands [24]; the effect of large amount of ligand in the polymer-QD matrix on the physical and mechanical properties of the composite was not investigated in detail though. In the current work the use of mercaptosilane coupled covalent conjugation of QDs to PDMS was helpful for not only strong binding of QDs to PDMS layers but also avoiding unbound ligands in the matrix.

3.2. Characterization of QD conjugated PDMS films using AFM and optical imaging

We characterized the conjugation of CdSe QDs to the silane coupled PDMS film using AFM imaging and fluorescence imaging. Samples containing one PDMS layer and one QD layer were used in AFM imaging; however, we tested different coverage of QDs on silane coupled PDMS films by using samples prepared from CdSe QD solutions of a range of concentrations. Typical tapping mode AFM images collected in air of samples prepared
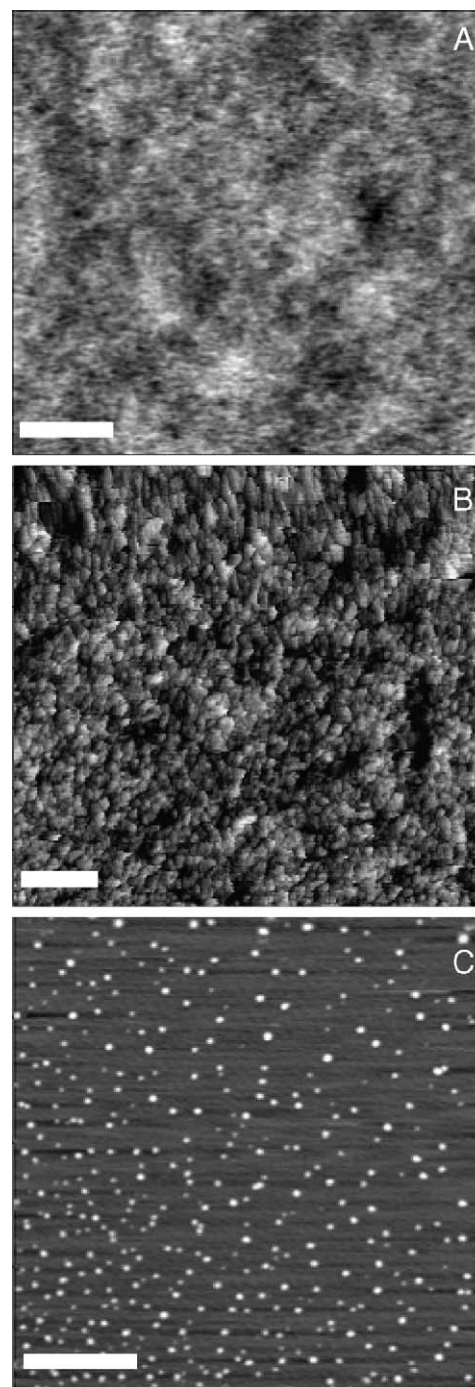

Fig. 3. Tapping mode AFM images of a silane coupled PDMS film (A), and high (B) and low (C) density distributions of CdSe QDs on a PDMS film. The high and low density distributions of CdSe QDs on PDMS films were obtained by using 100 μM and 100 nM QD solutions for conjugation reactions. The scale bars are 2 μm (A), 100 nm (B) and 500 nm (C).

using 100 μM and < 100 nM QD solutions are shown in Fig. 3B and C, respectively. Topography of a silane coupled PDMS film is shown in Fig. 3A for reference. The concentrations of 3MPS used for preparing samples imaged in Fig. 3B and C were 100 and 10 μM, respectively. The use of different concentrations of silane and QDs was helpful for identifying ideal conditions for a high density distribution of QDs. Conjugation of CdSe QDs

to a silanized PDMS film was characterized from concentration dependent surface coverage. Uniform distribution of QDs was observed for samples prepared from low concentrations of QD solutions (<100 nM, Fig. 3C), and a high density and uniform surface coverage was observed for sample prepared from high concentrations of QD solutions (>10 μM). Indeed, the surface coverage is also dependent on reaction time; prolonged conjugation reaction of QDs on a silanized PDMS film was avoided considering gradual dissolution/swelling of PDMS in the presence of chloroform.

The presence of different layers of QDs and PDMS in a multilayer PDMS-QD matrix was confirmed from optical imaging of different planes. Typical bright field optical images of three PDMS layers in a PDMS-QD matrix collected by varying the focal plane of a objective lens are shown in Fig. 4A–C. Presence of dark spots, likely dust particles trapped inside the matrix during intervals of layer preparations, was helpful for identifying individual layers within the matrix. Different QD layers on individual PDMS layers were identified from fluorescence imaging. Typical fluorescence image collected from one of the QD layers is shown in Fig. 4D. The fluorescence image was selected using a band pass filter (560/50M) for CdSe QD emission ($\lambda_{max} = 567$ nm). We observed uniform distribution of bright fluorescence from different QD layers in the matrix, confirming a high density and a homogeneous distribution of QDs. The presence of different layers of QDs in the matrix was further characterized from fluorescence image of a cross-section of the matrix. For this, the matrix was carefully sectioned using a sharp knife, and a thin sample obtained was turned 90° in such a way that the layers of PDMS and QDs are visible from top and bottom surfaces of the sectioned sample. Typical fluorescence image of a cross-section of the matrix is shown in Fig. 4E. The QDs layers were identified as bright stripes in the fluorescence image. Also, the fluorescence image of the cross-section was helpful for determining approximate thickness of PDMS layers; average thickness of PDMS layers was 75 μm. Although we were able to demonstrate LBL formation of a polymer-QD matrix, technical difficulties associated with sample deformation during slicing prevented us from imaging several layers in sectioned samples. Furthermore, we have identified distribution of QDs inside PDMS layers in samples containing three or more layers of QDs. This is likely due to swelling of PDMS and diffusion of QDs under repeated exposure to chloroform. Efforts are underway for obtaining PDMS-QD composites without exposing the polymer to sensitive solvents such as chloroform.

3.3. Photoluminescence properties of CdSe QDs in the presence of PDMS

We examined the effect of polymer environments on the PL properties of CdSe QDs. For this, PL spectra of QDs were
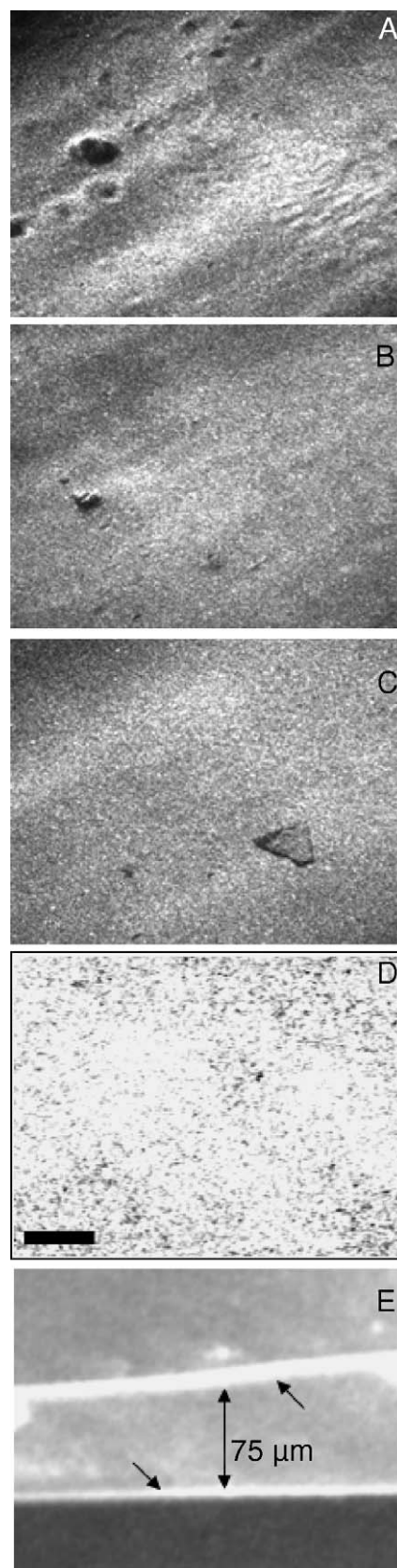

Fig. 4. Optical microscopic images of a PDMD-QD multilayer matrix: (A–C) transmittance images collected by changing focal plane (z-axis) under the same x–y coordinates in the multilayer sample; (D) fluorescence image of a QD conjugated PDMS layer in the matrix; and (E) fluorescence image of a cross-section of a PDMS-QD matrix. The bright lines in (E) are QD layers in the sample. Scale bar is 50 μm in D and is common to A–D.
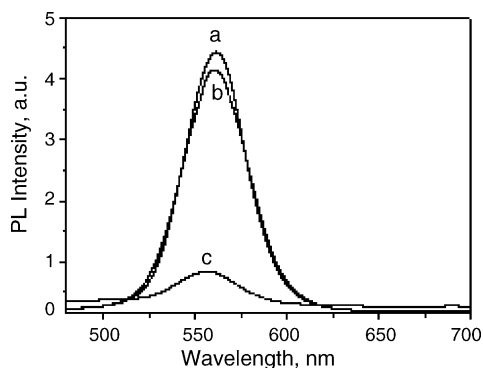
Fig. 5. PL spectra of chloroform solutions of CdSe QD samples: (a) without polymer, (b) in the presence of 50 mg/mL PDMS, and (c) in the presence of 50 μg/mL PVP. Optical densities of the samples were adjusted to 0.1 at the excitation wavelength (450 nm).

recorded in the presence of different concentrations of PDMS and PVP. Typical PL spectra of CdSe QDs recorded in the presence of PDMS and PVP are shown in traces 'a' and 'c', respectively in Fig. 5; samples for PL measurements were prepared by dissolving QDs in chloroform followed by adding polymer solutions in chloroform. Interestingly, we observed that PL intensity and spectral maximum of CdSe QDs was not considerably affected in the presence of PDMS. Also, increase in the concentration of PDMS had little effect on the PL properties of QDs; PL spectrum of QDs recorded in the presence of 50 mg/mL of PDMS in chloroform is shown in Fig. 5 (trace 'b'). A slight decrease in the PL intensity of QDs was likely due to reduced absorbance; background scattering in the presence of a high concentration of PDMS was observed from absorption spectrum. Nevertheless, the PL intensity of a CdSe QD solution was considerably reduced and the spectrum was slightly blue-shifted in the presence of even a small amount of PVP (50 μg/mL). The quenching of PL intensity and blue-shift of PL spectrum were likely due to interaction between PVP and surface energy states of QDs. It has been known in the literature that surface capping agents and solvent polarity play roles in stabilizing excitons in QDs. [42,43] Quenching of PL intensity and blue-shift of PL spectrum observed for QDs in the presence of PVP is likely due to reduced stability of surface states in QDs in the presence of PVP. Although the effects of PDMS and PVP on the PL properties of QDs has been attributed to difference in the stability of surface states, detailed time resolved PL investigations are necessary for clearly understanding the origin of the difference.

Exchange of surface ligands and incorporation of electron donor or acceptor moieties on the surface of QDs were known to affect the PL properties of QDs; simple examples are quenching of PL quantum efficiency of QDs when mixed with π-conjugated polymers such as polyvinyl carbazole [19] and polythiophene [20]. The quenching of PL quantum efficiency was due to changes in the surface oxidation states of QDs during ligand exchange and carrier diffusion in the presence of π-conjugated polymers; quenching of PL intensity of QDs observed in the presence of PVP also likely falls under the former category. Compared to several other polymers the PL of QDs was intact in the presence of PDMS, and PDMS may be considered as a

passive polymer host for QDs. Considering the passive nature, optical transparency, and structural flexibility PDMS would be a promising host material during the construction of QD based materials and devices.

4. Conclusions

In the current work we have demonstrated a simple LBL conjugation method for integrating CdSe QDs into PDMS films, and constructed a multilayer polymer-QD matrix. PDMS was selected considering several basic advantages required for a host material such as optical transparency, easy molding into various structural forms, structural flexibility when molded, and simple chemical conjugation. Furthermore, unlike in the case of several other polymers PDMS was found to preserve the PL properties of CdSe QDs. The current work is a combination of the fundamental advantages of PDMS polymer and the LBL covalent conjugation method for fabrication of a polymer-QD matrix. The current method was useful for avoiding phase separation of QDs, defects in the distribution of QDs, and inhomogeneous film thickness. Rather than demonstrating a simple preparation of an optically transparent polymer-QD matrix, the current method would be useful during incorporation of QDs in optical and optoelectronic devices supported in a PDMS matrix.

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