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A facile layer-by-layer assembly method for the fabrication of fluorescent polymer/quantum dot nanocomposite thin films[†]

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We demonstrated an efficient and robust approach for the preparation of polymer/quantum dot (QD) nanocomposite thin films in nonpolar media. By employing photopolymerization based on the thiol-ene reaction, thiol-containing polymer with affinity groups for CdSe@CdS QDs was produced for the buildup of the polymer/CdSe@CdS QD nanocomposite thin films utilizing layer-by-layer assembly. The polymer/QD nanocomposite films were characterized by SEM, TEM, fluorescence spectrometry, thermogravimetric analysis, confocal laser scanning microscopy and time-resolved fluorescence spectrometry. The resulting free-standing polymer/QD nanocomposite films exhibit high fluorescent intensity, moderate transparency, good photostability and thermal stability. We further applied photolithographic patterning in conjunction with an LBL assembly method to fabricate a polymer/CdSe@CdS QD nanocomposite pattern on a flexible substrate. This versatile and facile method provides prospects for the design of novel photonic devices based on the polymer/QD nanocomposite thin films.

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1. Introduction

Polymer/quantum dot (QD) nanocomposite thin films are of great importance for their applications in photonic and optoelectronic devices, such as light-emitting diodes,^{1,2} photovoltaic cells,^{3,4} biological sensors,^{5,6} and so forth. The common methods for producing polymer/QD nanocomposite thin films include layer-by-layer (LBL) assembly,^{7,8} Langmuir–Schäfer deposition,⁹ and self-assembly of block copolymer,¹⁰ in which the QDs were incorporated into polymer matrix. Among these approaches, LBL assembly is the most versatile and robust protocol to create the nanocomposite thin films with controlled morphology, thickness, functionality, and unique properties.¹¹ Numerous polymer/QDs nanocomposite thin films have been fabricated utilizing the LBL assembly approach based on the complementary interactions, including electrostatic attraction,¹² hydrogen-bonding,¹³ and covalent bonds.¹⁴

Traditional LBL assembly is carried out in polar solvent, mainly in water and/or alcohol, in which cationic and anionic layers are alternatively adsorbed on the substrate.¹⁵ Aqueousbased LBL approach is not suitable for the buildup of thin films containing uncharged polymer and hydrophobic QDs, which are usually synthesized in nonpolar solvents using organic capping ligands. As a result, LBL assembly of polymer/ QD thin films often involves the phase transfer of QDs from nonpolar media to aqueous solution through ligand exchange.¹⁶ This may lead to some drawbacks: (i) the photoluminescence (PL) of the resultant nanocomposite films would be diminished due to the poor surface passivation during the phase transfer and/or self-assembly.¹⁷⁻¹⁹ (ii) Chemical degradation will occur for QDs irradiated under the humidity environment due to the residual moister during LBL assembly.²⁰

Hence, LBL assembly of polymer/QD thin films is preferable to be carried out in the nonpolar solvents to preserve the

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[†] Electronic supplementary information (ESI) available: Experimental procedures for the preparation of stock solutions. Synthesis route of trimethylolpropane tris(3-mercaptopropionate) (Scheme S1), ¹H NMR spectrum of trimethylolpropane tris(3-mercaptopropionate) (in CDCl₃) (Fig. S1); high resolution TEM image of CdSe@CdS QDs (Fig. S2); EDS of the PMMA with and without thiol group after QDs solution immersion (Fig. S3), molecular structures of the components of the photopolymerizable resin (Fig. S4); FTIR spectra of PMMA-SH, OA-CdSe@CdS QDs, and PMMA-SH/CdSe@CdS films with different bilayer number (Fig. S5); photograph of free-standing PMMA-SH/CdSe@CdS QDs nanocomposite film under ambient light and UV light (Fig. S6); TEM image of the PMMA-SH/CdSe@CdS QDs nanocomposite film (Fig. S7); PL spectra of the (PMMA-SH/CdSe@CdS)7 film before and after CW laser irradiation (Fig. S8); photographic images of the patterned PMMA-SH/CdSe@CdS nanocomposite microdots on different substrates, e.g. glass, ITO, Si and plastics (Fig. S9). Biexponential fitting results of the CdSe@ CdS QDs toluene solution and PMMA-SH/CdSe@CdS QDs nanocomposite film, respectively (Table S1). See DOI: 10.1039/c4ra04779f

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original optical properties of the QDs. Lee and coauthors have demonstrated the LBL growth of polymer/CdSe@ZnS QD nanocomposite multilayers in organic media through LBL assembly adopting a two-step grating approach.^{21,22} Alternatively, polymer/QD thin films could also be fabricated through direct affinity interaction between QDs and polymers containing terminal anchoring moieties in nonaqueous solution.²³ However, growth of highly fluorescent polymer/QDs thin films with hydrophobic properties in nonpolar media has not yet been reported based on the one-step LBL assembly employing the QDs and functionalized polymers with affinity groups.

In this study, we proposed a robust and versatile approach for the growth of polymer/QDs nanocomposite thin films via LBL assembly in nonpolar media. The LBL assembly was carried out utilizing the affinity interaction between the CdSe@CdS QDs and photopolymerized PMMA containing thiol groups introduced by thiol-ene reaction. Free-standing PMMA-SH/ CdSe@CdS QDs nanocomposite thin films with bright PL were successfully fabricated without the necessity of ligand exchange and the substrate's surface functionalization before the deposition of the first layer. The nanocomposite films exhibit highly luminescent property, good photostability and thermal stability, and moderate transparence. In addition, microstructured patterns of PMMA-SH/CdSe@CdS QDs nanocomposite on flexible substrate were fabricated employing photolithography processing in conjugated with an LBL assembly approach. The present work provides the potential prospects for the development of novel photonic and optoelectronic devices such as flexible light-emitting diodes.

2. Materials and methods

2.1. Materials

1-Octadecene (ODE, tech. 90%), cadmium oxide (CdO, 99.998%), polymethylmethacrylate (PMMA) and 3-mercaptopropanoic acid (MPA, 97%) were purchased from Alfa Aesar. Rhodamine 6G (R6G) was purchased from Sigma. Trioctylphospine (TOP, tech. 90%) was purchased from Fluka. Deuteriochloroform (CDCl₃) was purchased from J&K Chemical Ltd. Benzil and 2-benyl-2-(dimethylamino)-4'-morpholinobutyrophenone (BDMBP) were purchased from Sigma-Aldrich. Pemaerythritol-triacrylate (PE-3A) was purchased from Kyoeisha Chemical Co. Ltd., Japan. Trioctylamine (TOA, 95%) was purchased from Shanghai Indole Biological Technology Co., Ltd. Selenium dioxide (SeO2, AR) was purchased from Zhengzhou Kefeng Chemical reagent Co., Ltd. Anhydrous methanol (CH₃OH, AR), anhydrous ethanol (CH₃CH₂OH), sodium hydroxide (NaOH, AR), acetone (CH₃COCH₃, AR), toluene $(C_6H_5CH_3, AR)$, myristic acid (MA, AR), anhydrous magnesium sulfate (MgSO₄, AR), oleic acid (OA, 90%), sulphur (S, AR), hexane (CH₃(CH₂)₄CH₃, AR), sulfuric acid (H₂SO₄, 98%), methyl methacrylate (MMA, AR), chloroform (CHCl₃, AR) and 1,1,1tris(hydroxymethyl) propane (TMP, AR) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd and used without further purification.

2.2. Synthesis of CdSe@CdS QDs

CdSe@CdS ODs were synthesized according to the previously reported procedure with minor modification.24-26 First, CdSe QDs were synthesized and purified.^{25,26} In a typical synthesis, SeO₂ (1 mmol), cadmium myristate (1 mmol, ESI[†]), and ODE (63 mL) were added and stirred in a 150 mL three-neck round flask, and the reaction was performed at 240 °C in the air atmosphere. Three minutes after the temperature reached to 240 °C, 1 mL of OA was added dropwise into the reaction solution to further stabilize the CdSe QDs. The reaction was stopped by cooling down the flask to room temperature. CdSe QDs were purified by adding excess amount of acetone and centrifugation. The resultant CdSe QDs were dispersed in hexane for the further measurement and preparation of CdSe@CdS core-shell QDs. Second, CdSe@CdS QDs were synthesized using one-pot injection approach.²⁴ In a typical synthesis, 2 mL of hexane solution of CdSe QDs (35 µM), 8 mL of trioctylamine, and 600 µL of cadmium oleate (0.5 M, ESI[†]) in OA were degassed at 70 °C during 1 h. The solution was then heated to 260 °C under nitrogen atmosphere, and a mixture of 3.4 mL of TOA, 600 µL of TOPS (0.5 M, ESI[†]) in TOP, and 1 mL of OA was injected in 4 h. After the reaction, CdSe@CdS QDs were purified by ethanol precipitation followed by centrifugation. The resultant CdSe@CdS QDs were dispersed in toluene for the further measurement and LBL assembly.

2.3. Synthesis of trimethylolpropane tris(3-mercaptopropionate)

Trimethylolpropane tris(3-mercaptopropionate) (denoted as trithiol) was synthesized according to the reported procedure (Scheme S1[†]).²⁷ In brief, 1,1,1-tris(hydroxymethyl) propane (6.715 g, 0.05 mol), toluene (40 mL), and H₂SO₄ (0.401 g) were added and mixed in a three-neck flask equipped with reflux condensing tube, constant pressure drop funnel, and Dean-Stark trap. 3-mercapto-propanoic acid (17.504 g, 0.15 mol) was dropped slowly into the reaction system through the constant pressure drop funnel. The reaction was carried out by heating the flask to 130 °C. Four hours later, the reaction was terminated by cooling down to room temperature. Then, the reaction solution was washed with deionized water to neutrality. The organic phase was separated, and dried over anhydrous MgSO4. The resultant product was obtained by the removal of toluene using the rotary evaporator. Viscous transparent liquid was collected and kept in the moister-proof cabinet for the further measurement and preparation of the photopolymerizable resin. Yield = 92%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.9 (m, 3H, CH₃), 1.45 (m, 2H, CH₂), 1.65 (m, 3H, SH), 2.65 (S, 6H, -CH₂-CO-), 2.8 (S, 6H, -CH₂-S-), 4.1 (S, 6H, -CH₂-O-) (Fig. S1⁺).

2.4. Preparation of photopolymerizable resins

Photopolymerizable resin containing thiol groups was prepared according to the previously reported procedure.²⁸ In brief, methyl methacrylate (MMA), trithiol, PE-3A, benzil, and BDMBP were mixed overnight in the dark room to make the photopolymerizable resin. For comparison, photopolymerizable resin

 Table 1
 Components of the photopolymerizable resins with and without trimethylolpropane tris(3-mercaptopropionate) (trithiol)

	MMA	Trithiol	PE-3A	Benzil	BDMBF
Resin 1 (wt %)	64.7	0	33.3	1.0	1.0
Resin 2 (wt %)	28.4	31.4	38.3	1.1	0.8

without thiol groups was also prepared under the same experimental condition. The components of the photopolymerizable resins are shown in Table 1.

2.5. Preparation of PMMA-SH/CdSe@CdS QDs nanocomposite films

The preparation of PMMA-SH/CdSe@CdS QDs nanocomposite thin films was shown in Scheme 1. First, transparent PMMA film containing thiol groups (PMMA-SH) was produced by photopolymerization of the thiol-containing resin based on the thiol-ene reaction.29 The spin-coating of the photopolymerizable resin was carried out on the KW-4 spin-coater over 4000 rpm for 60 s. The photopolymerizable resin was polymerized by exposing to the UV light (320 W high-pressure Hg Arc lamp) for 4 min. Second, the PMMA-SH film was immersed in the toluene solution of CdSe@CdS QDs (QDs concentration: 0.55 g L^{-1}) for the adsorption of the QDs on the surface of the PMMA-SH film. The substrate was then removed from the QDs solution, rinsed with toluene and dried. Third, PMMA-SH/CdSe@CdS QDs nanocomposite multilayers were obtained by repeating the first and second step for several cycles. The resultant film is denoted as "(PMMA-SH/ CdSe@CdS)_n", which means the film is fabricated from PMMA-SH and CdSe-CdS QDs with a bilayer (assembly cycle) number of *n*.

2.6. Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were collected using a JEM 2100F (JEOL) instrument working at 200 kV. Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) were obtained with a FE-SEM equipped with an EDS (Hitachi S-4800). The absorption and PL spectra were collected by using Shimadzu UV-2550 spectrometer and Hitachi F-4500 fluorescence spectrometer, respectively. X-ray diffraction (XRD) measurements were performed on a D8 focus Powder X-ray Diffractometer (XRD,



Scheme 1 Schematic diagram showing the fabrication of PMMA-SH/CdSe@CdS QDs nanocomposite thin films adopting LBL assembly.

Bruker, Cu K α radiation, $\lambda = 1.5406$ Å). ¹H NMR spectra were recorded on an Avance II-400 spectrometer (Bruker) using CDCl₃ as a solvent and all shifts are referred to tetramethylsilane (TMS). Vibrational absorbance spectra were characterized using FTIR spectroscopy (Excalibur 3100, Varian). Thermogravimetric analysis (TGA) was measured by using a SDT Q600 system (TA instrument) with a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen atmosphere. Time-resolved photoluminescence decays were recorded using single-photon count fluorescence spectrometer (F900, Edinburgh Instrument Co.). The specimens were excited at 488 nm with a pulsed laser (150 ps pulse duration), and the recorded emission wavelength was 626 nm. The photoluminescence decays exhibited a multiexponential decay and were fitted with a biexponential function, and we reported the resulting average lifetime τ_{avg} (ESI[†]).³⁰ Steady state and time resolved fluorescence spectrometer (FLSP920, Edinburgh Instruments) equipped with integrated sphere was used to determine the absolute photoluminescence quantum yield (PLQY) of CdSe@CdS QDs toluene solution and PMMA-SH/ CdSe@CdS QDs nanocomposite film, respectively. For the PLQY measurement, the excitation wavelength was fixed at 550 nm, and the optical density of the CdSe@CdS QDs toluene solution was tuned to 0.1 at the excitation wavelength.

A confocal laser scanning microscope (A1R MP, Nikon) was used to investigate the photostability of the PMMA-SH/CdSe– CdS QDs nanocomposite film, and the morphologic and fluorescent performance of the nanocomposite patterns. For the photostability measurement, the samples were excited on the confocal laser scanning microscope A1R MP by using continuous-wave (CW) 561 nm diode-pumped solid-state laser (Coherent Sapphire). The laser beam was focused using an objective with a numerical aperture of 0.5 ($20 \times$, NA = 0.5, Nikon). The PL was collected with PMT (32 channels) through the same objective. The PL spectra were taken at 1s intervals during the laser exposure. The excitation laser power was recorded with Newport optical power meter (Model 1916 R), equipped with the detector (Model 818-SL). All of the measurements were carried out at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of CdSe@CdS QDs

Zinc blende (ZB) CdSe@CdS QDs were synthesized using the seed-growth method. First, nearly monodispersed ZB CdSe QDs about 3.4 nm were acquired, as shown in Fig. 1a. The ZB structure of the CdSe QDs was recognized by the HR-TEM image (inset of Fig. 1a). The lattice spacing was 0.35 nm, which was consistent with the value of ZB CdSe (111) (International center for diffraction data, no. 19-0191).

Second, CdSe@CdS QDs were synthesized employing the 3.4 nm CdSe QDs as seeds. As shown in Fig. 1b, cubic and tetrahydral CdSe@CdS QDs were obtained, which were the typical morphology of ZB crystal structure. The deposition of CdS shell on the CdSe seeds was verified by the HR-TEM image (inset of Fig. 1b). The lattice spacing was 0.29 nm, which was consistent with the ZB CdS (200) (International center for diffraction data, no. 41-1049). Growth of the CdS shell on the CdSe seeds resulted



Fig. 1 TEM images of (a) CdSe and (b) CdSe@CdS QDs. The insets are the corresponding high-resolution TEM images of the CdSe and CdSe@CdS QDs, respectively. Scale bar in the inset is 5 nm. (c) XRD patterns of the CdSe and CdSe@CdS QDs, respectively. (d) Absorption (dashed line) and photoluminescence (solid line) spectra of the CdSe and CdSe@CdS QDs, respectively.

in the increase of size from 3.4 nm to 7.3 nm. Owing to the monodispersed property, the CdSe@CdS QDs could be assembled into a two-dimensional ordered structure when dropped on the carbon-supported copper grid (Fig. 1b).

The powder XRD patterns of CdSe and CdSe@CdS QDs are plotted in Fig. 1c. CdSe QDs show sharp reflection peaks at $2\theta =$ 25.3°, 42.2°, and 49.7°, which are consistent with the (111), (220), and (311) planes of the bulk ZB CdSe (JCPDS 19-0191). After the growth of CdS shell, the diffraction features appearing at $2\theta = 26.5^{\circ}$, 44°, and 52.1° correspond to the (111), (220), and (311) planes of the bulk ZB CdS (JCPDS 10-0454). The growth of the CdS shell induced the narrowing of the diffraction patterns owing to the smaller lattice constant compared to that of the ZB CdSe core, which is consistent with the reported result.³¹

The absorption and PL spectra of the CdSe and CdSe@CdS QDs are shown in Fig. 1d. The absorption and PL peaks of the CdSe QDs located at 565 and 578 nm, respectively. The growth of CdS shell led to a red-shift of the first excitonic transition and PL peaks to 615 and 626 nm, respectively, due to the delocalization of the electron wave function into CdS shell, which agreed well with the previously reported result.³² The growth of CdS shell also induced some broadening of the PL spectrum, in which the full width at half-maximum increased from 25 to 32 nm. The CdSe@CdS QDs with good surface passivation and bright fluorescence provide prospective applications in constructing functional organic–inorganic nanocomposite thin films.

3.2. LBL assembly of the PMMA-SH/CdSe@CdS QDs nanocomposite thin films

To demonstrate the effect of thiol groups on the adsorption of the CdSe@CdS QDs, we characterized the PL spectra of the PMMA films with and without thiol groups after dipping them

in the toluene solution of CdSe@CdS QDs for 30 min. An obvious PL band centered at the wavelength of 626 nm was observed for PMMA-SH film after dipping, as shown in Fig. 2a. The PL band was consistent with that of the toluene solution of CdSe@CdS QDs, indicating that CdSe@CdS QDs were successfully adsorbed on the surface of the PMMA-SH film. In contrast, we did not observe any noticeable PL emission for the PMMA film without thiol groups under the identical condition. The bright red colour of the polymer film with thiol groups under UV light also verified that CdSe@CdS QDs were anchored on the surface of the PMMA-SH film (Fig. 2b). The absorption of the CdSe@CdS QDs on the surface of PMMA-SH film was further confirmed by the EDS spectra, in which the emergence of the Cd and Se atoms corroborated the introduction of the CdSe@CdS ODs on the PMMA-SH film (Fig. S3[†]). Therefore, thiol group is critical for the adsorbing of the CdSe@CdS QDs, owing to the strong affinity interaction between Cd atoms and



Fig. 2 (a) PL spectra of the PMMA and PMMA-SH films immersed into the toluene solution of CdSe@CdS QDs. Photographs of the PMMA and PMMA-SH/CdSe@CdS QDs films under (b) 365 nm UV light and (c) ambient light, respectively.

thiol groups.^{33,34} FTIR characterization further suggested that the LBL assembly could be ascribed to the in-site ligand exchange between oleic acid and thiol moieties of polymer (Fig. S5†), which is similar to the previously reported results for metal (or metal oxide) nanoparticles LBL assembly.^{35,36} Meanwhile, the polymer film maintained transparency after the adsorption of the CdSe@CdS QDs as shown in Fig. 2c, indicating the well dispersion of CdSe@CdS QDs on PMMA-SH film.

In sequence, the influence of immersion time on the adsorption of the CdSe@CdS QDs was studied to optimize the assembly condition. Fig. 3a presents the PL spectra of the PMMA-SH films dipped in the toluene solution of CdSe@CdS QDs for different time. The PL emission intensity of the polymer films increased monotonically with the prolonged immersion time. Accordingly, the emission colour changed from weak to strong with the ascending immersion time, as shown in the inset of Fig. 3a. Fig. 3b shows that the PL intensity firstly increases with the immersion time, and then gradually approaches saturation. The phenomenon is probably ascribed to the Langmuir absorption isotherm, which has been observed



Fig. 3 (a) PL spectra and photograph of PMMA-SH/CdSe@CdS QDs with the increasing of the immersion time from 2 min to 60 min. (b) The plot of the fluorescence intensity at 626 nm *versus* time.

in the LBL assembly of QDs in previous report.³⁷ Furthermore, SEM images of the PMMA-SH films immersed in CdSe@CdS QDs toluene solution for different time were presented in Fig. 4. For the immersion time of 2 min, only a spot of surface of the PMMA-SH film was covered by the CdSe@CdS QDs. Nevertheless, majority of the surface of the polymer film was covered by the QDs for the immersion time of 20 min, and 30 min, respectively. Consequently, the immersion time was optimized to be 30 min in order to obtain PMMA-SH/CdSe@CdS QDs nanocomposite film with high PL intensity in appropriately short time.

Furthermore, the dependence of the assembly of the CdSe@CdS QDs on assembly cycles (n) was monitored by the UV-vis absorption and PL spectra measured after each deposition cycle. As shown in Fig. 5a, the absorbance at 615 nm (the first excitonic transition of the CdSe@CdS QDs) increased monotonically with the increase of n. The linear relationship between this absorption peak and n (inset of Fig. 5a) suggests that the growth process is well controlled, leading to stepwise, uniform, and layer to layer deposition.²¹ This can be further verified by the monotonic increase of the PL intensity at 626 nm (Fig. 5b). The inset of Fig. 5b shows the photograph of (PMMA-SH/CdSe@CdS)7 under 365 nm excitation, demonstrating a bright red emission from the nanocomposite thin film. Meanwhile, a blue-shift of the PL peaks is observed during the preparation of the polymer/CdSe@CdS QDs multilayers. The phenomenon is attributed to the oxidation of the CdSe@CdS QDs upon the UV irradiation during the polymerization of the photopolymerizable resin, which is consistent with the similar QDs/polymer nanocomposites.38,39 It's worth noting that freestanding polymer/QDs nanocomposite film can be obtained by stripping the multilayer film from the glass substrate (Fig. S6[†]). As a result, mechanically stable polymer/CdSe@CdS QDs nanocomposite films with different PL intensities and thickness can be easily assembled by optimizing the deposition cycles.



Fig. 4 SEM images of the PMMA-SH film immersed in CdSe@CdS QDs solution for (a) 0 min, (b) 2 min, (c) 20 min, and (d) 30 min, respectively. The scale bar is 150 nm.



Fig. 5 (a) UV-vis absorption and (b) photoluminescence spectra of (PMMA/SH-CdSe@CdS QDs)_n measured with increasing the bilayer number from 1 to 7. Dashed lines are the UV-vis and photo-luminescence spectra of the PMMA-SH film without CdSe@CdS QDs deposition for comparison. The inset in panel (a) shows the linear increase of absorbance measured at 615 nm wavelength as a function of the deposition cycles (*n*). The inset in panel (b) shows the photograph of (PMMA/SH-CdSe@CdS QDs)₇ under the 365 nm UV light irradiation.

3.3. Photophysical properties of the PMMA-SH/CdSe@CdS QDs nanocomposite film

We investigated the photophysical properties of the PMMA-SH/ CdSe@CdS QDs nanocomposite film, including the PLQY, radiative dynamics and photostability. Self-assembly of the CdSe@CdS QDs on the PMMA-SH film resulted in the decrease of the absolute PL QY of the CdSe@CdS QDs from 45.8% to 16.9%. The decline of the PL QY of the CdSe@CdS QDs was mainly attributed to the quenching effect of thiol groups through QDs surface trap states, which suppressed the radiative recombination of the photogenerated exciton.^{40,41} The PL quenching result is consistent with the reported phenomenon that the PL intensity of thiol capped CdSe@CdS QDs.⁴²

In order to gain further insight into the effects of the thiol groups on the exciton recombination of the CdSe@CdS QDs, we studied radiative dynamics of the PMMA-SH/CdSe@CdS QDs nanocomposite film. Time-resolved decay curves were measured to determine the PL lifetimes of the CdSe@CdS QDs toluene solution and the (PMMA-SH/CdSe@CdS)₇ film, respectively. Fig. 6 plots the PL decay curves of the CdSe@CdS QDs toluene solution and (PMMA-SH/CdSe@CdS)₇ film, respectively. Biexponential fitting results are shown in Table S1.† The average PL lifetime of the CdSe@CdS QDs in diluted toluene solution is determined to be 25.67 ns, which is similar to the value in previous study.^{43,44} The relative short PL lifetime is attributed to the thin CdS shell.^{45,46}

After assembly into the polymer matrix, the PL lifetime of the CdSe@CdS QDs is reduced to 16.93 ns, which is shorter than that of the pristine CdSe@CdS QDs. The declined radiative lifetime was attributed to the interaction of the polymer with the CdSe@CdS QDs surface. In CdSe@CdS QDs, the small conduction band offset allows for partial delocalization of the electron wave function from core into the shell.⁴⁷ Photogenerated holes will transfer quickly from the QDs to thiol groups in the polymer matrix. Charge separation at the interface between the CdSe@CdS QDs and thiol groups resulted in shorter radiative lifetime, which is consistent with the previous study.⁴¹ The accelerated radiative decay agrees well with the reduced PLQY after LBL assembly, both arising from the carrier transfer from the QDs to the thiol groups in the polymer matrix.

The photostability of the PMMA-SH/CdSe@CdS QDs nanocomposite film is a crucial issue for the practical applications. We further investigated the photostability of the PMMA-SH/ CdSe@CdS QDs nanocomposite film under laser excitation. Fig. 7 shows the time-resolved PL intensities of the (PMMA-SH/ CdSe@CdS)₇ film excited with a CW laser irradiation at 561 nm under ambient condition. The power intensity of the laser irradiation was 0.508 kW cm⁻² (ESI[†]). For comparison, time-



Fig. 6 PL decays of the CdSe@CdS QDs (black) and PMMA-SH/ CdSe@CdS QDs nanocomposite film (red), respectively.

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Fig. 7 PL intensity *versus* laser irradiation time for PMMA-SH/CdSe@CdS QDs nanocomposite film (red) and R6G doped PMMA film (black), respectively.

resolved PL intensity of R6G doped PMMA (R6G/PMMA = 0.5wt%, ESI[†]) was also measured under the same condition. All the PL intensities are normalized with their initial values at t = 0. As shown in Fig. 7, the PL intensity of the (PMMA-SH/CdSe@CdS)₇ film shows a monotonic decrease under the CW laser exposure for 2 h. The PL intensity declined to 92% of the initial value at the beginning 5 min, and then kept stable during the remained evolution time. For R6G doped PMMA film, the PL intensity decreased dramatically to only 20% of the initial value after 2 h laser exposure. The PL intensity decrease of the composite film was attributed to the photobleaching and/or photoinduced fluorescence dark of the CdSe@CdS QDs under laser exposure, which is consistent with the previously reported results.48,49 The proportion of the PL much smaller than that of the R6G doped PMMA film, which suggests that the PMMA-SH/CdSe@CdS QDs nanocomposite film possesses much better photostability than the commonly used organic dye- doped polymer film. Although slight photobleaching occurred for PMMA-SH/CdSe@CdS QDs nanocomposite film under laser irradiation, the PL spectra of the composite film almost kept constant after laser exposure (Fig. S8[†]). The photostability of the PMMA-SH/CdSe@CdS QDs nanocomposite film can benefit numerous applications from solid-state lasers to light emitting diodes (LEDs).

3.4. Transparent and thermal properties of the PMMA-SH/ CdSe@CdS QDs nanocomposite film

We further investigated the transparent and thermal properties of the PMMA-SH/CdSe@CdS QDs nanocomposite film. The optical transmittance spectra of the PMMA-SH and PMMA-SH/ CdSe@CdS nanocomposite films were plotted in Fig. 8a. The PMMA-SH film without CdSe@CdS QDs has a transmission of 95% across the range of 450–800 nm, with a significant transmittance drop between 300–450 nm due to the absorption of the residual photo initiator and photosensitizer. For the (PMMA-SH/CdSe@CdS)₇ film, the optical transmittance spectrum shows a similar transmission of 95% between 650–800 nm, and



Fig. 8 (a) Transmittance spectra of the PMMA-SH film and (PMMA-SH/CdSe@CdS)₇ nanocomposite film, respectively. Inset is the photograph of the (PMMA-SH/CdSe@CdS)₇ nanocomposite film. (b) TGA curves of the PMMA-SH film and PMMA-SH/CdSe@CdS nanocomposite film, respectively.

decreased transmission between 450 and 650 nm due to the absorption of the CdSe@CdS QDs. The red arrow in Fig. 8a shows the dip caused by the absorption of the CdSe@CdS QDs, which agrees well with the absorption spectrum of the toluene solution of CdSe@CdS QDs (Fig. 1d). The inset of Fig. 8a shows the photograph of the (PMMA-SH/CdSe@CdS)₇ nanocomposite film under ambient light. The clear film with orange color verifies the transparency of the nanocomposite film containing CdSe@CdS QDs.

The thermal stability of the PMMA-SH/CdSe@CdS QDs nanocomposite has been investigated by the TGA analysis. As shown in Fig. 8b, the decomposition temperature of the PMMA-SH/CdSe@CdS QDs film is 330 °C (here the decomposition temperature is defined as the temperature of 10 wt% weight loss under nitrogen at a heating rate of $10 \,^{\circ}$ C min⁻¹). In addition, TGA curves also indicate that about 2.04 wt% of CdSe@CdS QDs is incorporated in the PMMA-SH/CdSe@CdS QDs nanocomposite film through the LBL assembly. The thermal stability of PMMA-SH/CdSe@CdS QDs is better than that of the bare PMMA-SH film after 340 °C. The improvement of the thermal stability of the PMMA-SH/CdSe@CdS QDs nanocomposite



Fig. 9 (a) Schematic for the preparation of the PMMA-SH/CdSe@CdS QDs nanocomposite pattern on the flexible substrate. (b) Photographic image of the patterned PMMA-SH/CdSe@CdS QDs nanocomposite microdots on the flexible substrate. (c) Optical and (d) fluorescent microscopic images of single PMMA-SH/CdSe@CdS QDs nanocomposite microdot. The size of the patterned dot is about 400 μ m.

could be assigned to the interaction between the CdSe@CdS QDs and PMMA-SH polymer chains.⁵⁰ The further crosslinking in the PMMA-SH/CdSe@CdS QDs nanocomposite hindered the movement of the PMMA-SH chains and prevented its thermal decomposition. The superior thermal stability of the PMMA/ QDs nanocomposite is of great importance for applications in device manufacturing.

3.5. Microstructured patterns of PMMA-SH/CdSe@CdS QDs nanocomposite on flexible substrate

Fluorescent microstructures of PMMA-SH/CdSe@CdS QDs nanocomposite could be patterned *via* a photolithographic process in conjugation with the LBL assembly. As illustrated in Fig. 9a, patterned dots with a feature size of 400 μ m could be fabricated on the substrates. First, thiol-containing photopolymerizable resin is deposited on a substrate through spin-

coating. Second, the resin film is photocross-linked by UV irradiation through a shadow mask. Third, the patterned PMMA-SH microstructures are immersed in the toluene solution of CdSe@CdS QDs for 30 min. Finally, the fluorescent pattern is obtained after the removal of the unadsorbed CdSe@CdS QDs. As shown in Fig. 9b, highly fluorescent dots (9 \times 9) are patterned on the flexible plastic film. Optical and fluorescent microscopic images show that the size of the patterned dot is about 400 µm with bright fluorescence. The pink color is attributed to the combination of the red color of the CdSe@CdS QDs and the blue colour of the plastic film. Similarly, the fluorescent structures could be also patterned on other substrates, such as glass, ITO, and silicon (Fig. S9[†]). These patterned structures open up the prospect in the design and construction of advanced optical devices such as flexible display panel and LEDs.

4. Conclusions

We have demonstrated a facile and efficient approach for the fabrication of polymer/QDs nanocomposite thin films adopting LBL assembly. The key feature is the use of the thiol-ene reaction to incorporate thiol groups in polymer network, which will adsorb the CdSe@CdS QDs through the thiol-cadmium affinity *via in situ* ligand exchange process. Highly fluorescent nanocomposite thin films are obtained with good photostability, thermal stability, and optical transparency. Furthermore, patterned fluorescent structures can be constructed based on the combination of photolithographic process and LBL assembly of CdSe@CdS QDs. Therefore, this work solves the problem of the self-assembly of hydrophobic QDs in nonpolar media and provides a robust strategy for fabricating functional polymer/QDs nanocomposite films for the purpose of promising applications in optical and optoelectronic devices.

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