

Electronic Supplementary Information for

Quantum-dot-embedded Ionomer-derived Films with Ordered Honeycomb Structures via Breath Figure

Jing Wang, Cai-Feng Wang, Hai-Xia Shen, and Su Chen*

State Key Laboratory of Material-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China.

*To whom correspondence should be addressed. E-mail: chensu@njut.edu.cn

1. Experimental

Materials. All reagents were of analytical grade and commercially available. Solvents: N, N'-dimethylformamide (DMF), methanol and chloroform were all used as received without any further purification. Monomers: Methyl methacrylate (MMA) was firstly washed by NaOH solution (30 wt %) until it become colorless to remove inhibitors, then dried over anhydrous sodium sulfate (Na_2SO_4), and finally distilled under reduced pressure. was obtained by Ar. Initiators: 2, 2'-azobisisobutyronitrile (AIBN) were purified by recrystallization from ethanol twice. Cadmium acrylate ($\text{Cd}(\text{AA})_2$) and sulfur source sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) (purity, 99%) were purchased from the Aldrich Chemicals Company and hydrochloride solution (HCl) (1 mol/L) was titrated by sodium hydroxide (NaOH).

Synthesis of PMMA/ $\text{Cd}(\text{AA})_2$ ionomers. A typical free-radical copolymerization was performed as follows. Firstly, 62 g DMF containing 0.05 g AIBN was introduced into a 250 mL of four-neck flask equipped with a reflux condenser and a mechanical stirrer. Then, the reaction mixture was immersed in water bath at 60 °C. An amount of MMA (19 g, 0.19 mol) monomer together with $\text{Cd}(\text{AA})_2$ (1 g, 0.004 mol) in 19 g DMF solvent was added drop-wisely in about 30 min. The polymerization process was carried out at 80 °C for 4 hours under a nitrogen atmosphere. Finally, the PMMA/ $\text{Cd}(\text{AA})_2$ solution was washed with methanol to remove excessive free MMA

monomer, dried under vacuum overnight at 60 °C and redissolved in chloroform (CHCl₃).

Preparation of PMMA/CdS QD-polymer *in situ*. the hydrogen sulfide (H₂S) gas was obtained by the reaction of Na₂S·9H₂O (1.5 g) with HCl (40 g, 1 mol/L) and dried by calcium chloride anhydrous (CaCl₂). PMMA/Cd(AA)₂ (1 g) was dissolved in CHCl₃ (10 mL) with continuous stirring to form a homogeneous solution, followed by exposure in H₂S atmosphere, where the colorless solution turned yellow after about 5 min. The sample was then regarded as PMMA/CdS QD-polymer.

Formation of honeycomb-patterned films. A drop of PMMA/Cd(AA)₂ or PMMA/CdS QD-polymer solution (solvent: CHCl₃) was cast onto a cleaned glass substrates at ambient conditions (85 % relative humidity). These polymer solutions were left in the humidity chamber for 1.5 min. After the solvent and water droplets were evaporated completely, the thin films turn non-transparent. Comparable pure PMMA film was formed at the same concentration in the same way.

2. Characterization

SEM images were recorded on a JEOL 6320F. Transmission electron microscope (TEM) observation was performed with a JEOL JEM-2100 transmission electron microscope. Samples were dispersed in DMF, and a drop of the solution was placed on a copper grid that was left to dry before transferring into the TEM sample chamber. Photoluminescence (PL) spectra were measured on a Varian Cary Eclipse spectrophotometer at room temperature. A 360 nm laser beam was chosen as the excited light source from Xe-lamp with the tube voltage 600 V and the excitation and emission slits both 5 nm. Optical transmission and fluorescence microscopy were performed on a Carl-Zeiss Axiophot microscope equipped with a high-resolution charge coupled device (CCD) camera (Sony DKC 5000), which was connected to a frame grabber and a personal computer for image processing.

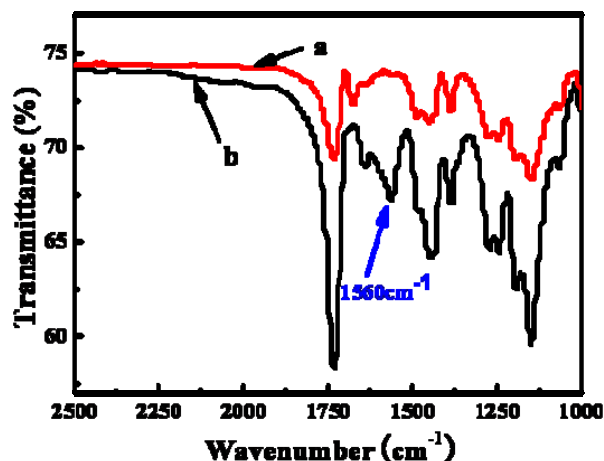


Fig. S1 FT-IR spectra of (a) pure PMMA control sample, MMA wt % = 20 wt %, AIBN/MMA = 0.3 % (wt/wt) and (b) PMMA/Cd(AA)₂ ionomer, Cd(AA)₂/MMA = 11 % (wt/wt), DMF wt % = 80 wt %, AIBN/(MMA, Cd(AA)₂) = 0.3 % (wt/wt). Solution: *N, N'*-Dimethylformamide (DMF), reaction time: 4 h, reaction temperature: 80 °C. Compared with Fig. S1a, Fig. S1b clearly exhibits a new characteristic peak of carboxylate appearing at 1560 cm⁻¹, indicating that Cd(AA)₂ has been successfully polymerized into the PMMA chains.

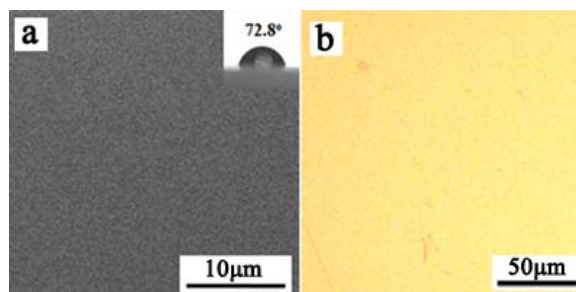


Fig. S2 SEM image and the optical transmission microscopy image of PMMA/CdS film without honeycomb structures. Fig S2a obviously shows that honeycomb structures do not exist in the PMMA/CdS film obtained at dry conditions, with its water contact angle 72.8° shown in the inset. Fig S2b displays a single color exhibited by the PMMA/CdS films without honeycomb structures.

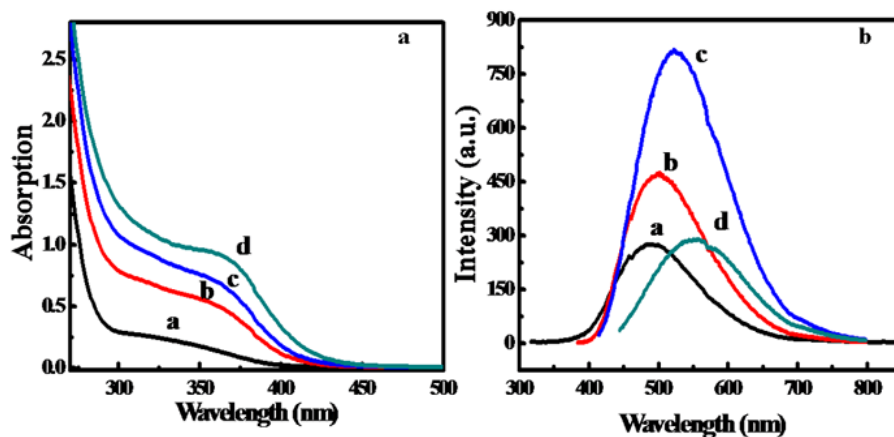


Fig. S3 (a) UV-vis spectra and (b) fluorescence emission spectra of PMMA/CdS QD-polymer solutions ($\lambda_{\text{ex}} = 360 \text{ nm}$) by exposing PMMA/Cd(AA)₂ solutions in the H₂S atmosphere at different intervals: (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min, respectively. Obvious red shift of the absorption characteristic peaks in Fig. S3a and PL emission peaks in Fig. S3b from (a) to (d) is observed. This is ascribed to the particle growth of CdS NCs when the molar ratios of Cd²⁺ to S²⁻ getting lower by extending the exposure time in the H₂S atmosphere.