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Covalent linking of quantum dots to polymer for inorganic-inorganic luminescence films via layer-by-layer assembly with clay

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## Experimental

## **Chemicals and Materials**

All chemicals used were analytical-reagent grade. 2-Mercaptoethylamine hydrochloride (MA, 99 %) was purchased from Sigma-Aldrich (St. Louis, MO). Tellurium powder (Te, 99.999 %), thioglycolic acid (TGA, 90 %), CdCl<sub>2</sub>·2.5H<sub>2</sub>O, Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (99.5 %) and NaBH<sub>4</sub> (98 %) were purchased from Tianjin Chemical Reagent Company (Tianjin, China). Potassium tellurite (K<sub>2</sub>TeO<sub>3</sub>, 98 %) and poly(allylamine hydrochloride) (PAH, MW 10,000-20,000) were obtained from Beijing HWRK Chem. Co. Ltd. (Beijing, China). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 98 %) and N-hydroxysuccinimide (NHS, 98 %) were received from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). NaOH, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (30 %, v/v) were supplied by Beijing Chemical Reagent Company (Beijing, China). Sodium montmorillonite (MMT) clay from Nanocor Inc. (Arlington Heights, IL, USA) was employed without further purification. The deionized water from a Millipore water purification system was used throughout the experiments.

## Apparatus

The solid UV-vis absorption spectra were acquired on a Shimadzu UV-3600 spectrophotometer (Tokyo, Japan). The fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) with the excitation wavelength of 365 nm. The excitation slit and the emission slit were both maintained at 5.0 nm with a scanning rate of 1200 nm/min. Transmission electron microscopy (TEM) images of QDs were obtained with Tecnai G<sup>2</sup>20 TEM (FEI, USA) operated at 200 kV. X-ray diffraction (XRD) patterns of the (PAH-QDs/MMT)<sub>n</sub> UTFs were recorded on a Rigaku D/max-2500VB2+/PC diffractometer using Cu K<sub>a</sub> radiation with the following operating parameters: 50 mA, 40 kV, 2 $\theta$  scanning from 0.5° to 8°. The scanning electron microscope (SEM) was performed on a Hitachi S-3500 SEM with an accelerating voltage of 20 kV. Atomic force microscopy (AFM) in tapping mode was carried out on a NanoScope IIIa (Digital Instruments Co., Santa Barbara, CA, USA) instrument. Fluorescence microscope images were recorded on an Olympus IX71 fluorescence microscope (Olympus, Japan). The photobleaching was measured by the UV lighting with CHF-XQ 500W.

#### **Preparation of MMT Nanosheets**

MMT particles were dispersed in deionized water at a concentration of 0.1 wt %. After gentling stirring for 48 h, the dispersion was centrifuged at 10,000 rpm for 5 min to remove the unexfoliated particles. The resulting clear supernatant was collected for subsequent use. The concentration of exfoliated MMT nanosheets (2.86 g/L) was determined by measuring the residual solid content.

# Synthesis of MA-Capped CdTe QDs

MA-capped CdTe QDs were prepared as described with a slight modification.<sup>1</sup> Briefly, freshly prepared NaHTe solution was added to nitrogen saturated CdCl<sub>2</sub> solution (0.1142 g CdCl<sub>2</sub>·2.5H<sub>2</sub>O was dissolved in 100 mL ultrapure water) at pH 5.6-5.9 in the presence of MA as a stablilizing agent. In our experiments the typical molar ratio of Cd<sup>2+</sup>: HTe<sup>-</sup>: MA was 1: 0.5: 2.4. After vigorously stirring the mixture for 10 min, it was refluxed at 90 °C under nitrogen flow for suitable time to control the growth of the CdTe QDs.

#### Synthesis of TGA-Capped CdTe QDs

TGA-capped CdTe QDs were synthesized in aqueous phase according to the literature procedure (Cd<sup>2+</sup>: TGA: TeO<sub>3</sub><sup>2-</sup> was 1: 1.0: 0.2).<sup>2</sup> In a typical synthesis, 0.0533 g Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was dissolved into 50 mL deionized water in a stand-up flask. Then 18  $\mu$ L TGA stabilizer was added, followed by adjusting the pH value of the mixed solution to 10.5-11.0 with 1 M NaOH. After stirring for 5 min at room temperature, 0.0108 g K<sub>2</sub>TeO<sub>3</sub> dissolved in 50 mL deionized water was added to the above mixture solution. Then 0.08 g of NaBH<sub>4</sub> was added into the precursor solution. After stirring for another 5 min, the mixture was refluxed at 100 °C under open-air conditions to produce CdTe QDs with desired sizes by controlling the refluxing time. The crude CdTe QDs solution was purified with dialysis to remove excessive thiols, free cadmium ions and by-products. The purified CdTe QDs were stocked for further use.

#### Surface Modification of CdTe QDs with PAH

Covalently modified CdTe QDs (PAH-QDs) were prepared by adding purified CdTe QDs to PAH solution (0.1 wt %, pH = 7.5) in a volume ratio of 1: 5, and then EDC/NHS (1 mg/mL) was added (EDC/NHS: PAH = 1: 1 by volume). EDC and NHS were used for the formation of amide bond between the carboxylic group of the TGA-capped CdTe QDs and the amino group of PAH. In contrast, electrostatic modification of CdTe QDs (PAH@QDs) was achieved via similar method in the absence of EDC/NHS.

#### Fabrication of Multilayer Ultrathin Films of QDs/MMT

The quartz glass slides were treated with piranha solution (concentrated  $H_2SO_4$ :  $H_2O_2 = 7: 3$  by volume) for 30 min. Then the slides were cleaned in pure water with sonication for 30 min, followed by thorough rinsing with deionized water. The multilayer UTFs of QDs/MMT were fabricated using a layer-by-layer (LBL) assembly method. The glass was dipped into 0.1 % PAH solution in 0.5 M NaCl for 10 min and thoroughly washed with deionized water, resulting in a positively charged substrate. The substrate was dipped into the negatively charged of MMT nanosheet suspension for 10 min and thoroughly washed with deionized water, and then was dipped into the positively charged QDs solution (MA-QDs or PAH@QDs or PAH-QDs) for 10 min and washed with deionized water. These procedures were repeated for n cycles to fabricate multilayer UTFs of (QDs/MMT)<sub>n</sub>. The resulting UTFs were dried with nitrogen at room temperature. The (QDs/PAH)<sub>n</sub> UTFs were obtained by LBL assembly of TGA-capped CdTe QDs and PAH.

### References

- 1 Shi, L. X.; Hernandez, B.; Selke, M. J. Am. Chem. Soc. 2006, 128, 6278.
- 2 Wu, S. L.; Dou, J.; Zhang, J.; Zhang, S. F. J. Mater. Chem. 2012, 22, 14573.

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# **Supporting Figures**



**Fig. S1** (A) XRD patterns of MMT and MMT nanosheet colloids in water; (B) TEM image of the obtained MMT nanosheets and their Tyndall light scattering in aqueous suspension.



Fig. S2 Tapping-mode AFM image of the obtained MMT nanosheets



**Fig. S3** TEM images of CdTe QDs (A) before and (B) after covalently modified with PAH and UV-vis absorption spectra and fluorescence spectra of CdTe QDs aqueous solution (C) before and (D) after addition of PAH in the presence of EDC (inset: photoemission under UV irradiation).



Fig. S4 (A) UV-vis absorption spectra of the  $(PAH-QDs/MMT)_n$  UTFs (n = 6-30) (inset: absorbance at 485 nm as a function of bilayer number n) and (B) their photographs under daylight.



Fig. S5 Side-view SEM images of the  $(PAH-QDs/MMT)_n$  UTFs (n = 6, 12, 18, 24, respectively).



Fig. S6 Top-view SEM images of the  $(PAH-QDs/MMT)_n$  UTFs (n = 6, 12, 18, 24, respectively).



**Fig. S7** Photostability of (A) the (PAH-QDs/MMT)<sub>30</sub> UTF and (B) (QDs/PAH)<sub>30</sub> UTF under UV irradiation for various time (inset: the normalized luminescence intensity as a function of irradiation time).



**Fig. S8** Storage stability of (A) the  $(PAH-QDs/MMT)_{30}$  UTF and (B)  $(QDs/PAH)_{30}$  UTF recorded weekly in one month (inset: the normalized luminescence intensity as a function of storage time).



**Fig. S9** Normalized fluorescence spectra of the  $(PAH-QDs/MMT)_{30}$  UTF by dipping in water for 10 s and repeating the process for 100 cycles.



**Fig. S10** Fluorescence spectra of the TGA-capped CdTe QDs solution in the temperature range 25-75 °C (inset: the emission intensity as a function of temperature).



**Fig. S11** Maximum emission wavelengths of  $(PAH-QDs/MMT)_{30}$  UTF as a function of heatingcooling cycles between 25 °C ( $\blacklozenge$ ) and 75 °C ( $\blacklozenge$ ).