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A Temperature Sensor Based on CdTe Quantum Dots/Layered Double

Hydroxide Ultrathin Films *via* Layer-by-Layer Assembly

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Experimental section:

Reagents and materials: Poly dimethyldiallylammonium chloride (PDDA, Mw = 100,000–200,000), Al₂(Te)₃, Cd(ClO₄)₂·6H₂O, mercaptosuccinic acid were purchased from Sigma Chemical. Co. Ltd. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH, C₂H₅OH, H₂SO₄ are of analytical grade and used without further purification. The deionized and decarbonated water was used in all the experimental processes.

of MgAl-NO₃-LDH nanosheets: The synthesis and exfoliation Synthesis of MgAl-NO₃-LDH were similar to that described in our previous work.^[1] Typically, $Mg(NO_3)_2 \cdot 6H_2O$ (0.002 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.001 mol) and urea (0.012 mol) were dissolved in aqueous solution (70 cm³). The mixture was sealed in a teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. The resulting MgAl-CO₃-LDH was washed with water and dried in air at 60 °C. The transformation from MgAl-CO3-LDH to MgAl-NO₃-LDH was achieved by the following method: a sample of MgAl-CO₃-LDH (0.3 g) was treated with 300 cm^3 of an aqueous solution containing NaNO₃ (0.50 mol) and HNO₃ (0.0015 mol) whilst purging with nitrogen gas, and was shaken for 1 day at ambient temperature (25 °C). The resulting MgAl-NO₃-LDH was washed with hot distilled water, and then dried in vacuum at 60 °C. Subsequently, 0.1 g of this sample was shaken in 100 cm³ of formamide solution for 24 h to produce a colloidal suspension of exfoliated MgAl-LDH nanosheets.

Preparation of CdTe QDs: The aqueous synthesis of mercaptosuccinic acid modified CdTe QDs was referred to the reported method.^[2] In a typical synthesis, 0.985 g (2.35 mmol) of $Cd(ClO_4)_2 \cdot 6H_2O$ was dissolved in water (125 mL); 0.278 g of mercaptosuccinic acid

stabilizer was added under stirring, followed by adjusting the pH value to be 11 with addition of a NaOH solution (1.0 M). The solution was placed in a three-necked flask fitted with a septum valves and was deaerated by N₂ bubbling for 30 min. Under stirring, H₂Te gas generated by Al₂(Te)₃ and H₂SO₄ was purged into the solution together with a slow nitrogen flow, and CdTe QD precursor was formed at this stage. The formation and growth of QDs proceed upon refluxing at 100 °C under open-air conditions with an attached condenser. The fluorescent color of CdTe QDs solution changes from green to red upon increasing refluxing time.

Assembly of CdTe QDs/LDH UTFs: The quartz glass substrate was cleaned in concentrated NH₃/30% H₂O₂ (7:3) and concentrated H₂SO₄ for 30 min each, and then was washed thoroughly with deionic water. The substrate was dipped into a colloidal suspension of MgAl-LDH nanosheets (1.0 g dm⁻³) for 10 min followed by washing thoroughly, and then was treated with CdTe QDs aqueous solution (0.25 g dm⁻³) for another 10 min. Multilayer UTFs of (CdTe QDs/LDH)_n were fabricated by repeating the above deposition process for *n* cycles. The resulting UTFs were dried with a nitrogen gas flow for 2 min at 25 °C. The fabrication of (CdTe QDs/PDDA)_n UTFs is similar to that of the (CdTe QDs/LDH)_n UTFs.

Techniques of characterization: The solid UV-vis absorption spectra were collected in the range from 400 to 800 nm on a Shimadzu U-3000 spectrophotometer, with the slit width of 1.0 nm. The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer with the excitation wavelength of 360 nm. The fluorescence emission spectra are in the range from 400 to 700 nm, and the width of both the excitation and emission slit is 3 nm. XRD patterns of CdTe QDs/LDH UTFs were recorded using a Rigaku 2500VB2+PC

diffractometer under the conditions: 40 kV, 50 mA, Cu K α radiation with step-scanned in step of 0.04° (2 θ) in the range from 0.5 to 10° using a count time of 10 s/step. The morphology of UTFs was investigated by using a scanning electron microscope (SEM Hitachi S-3500) equipped with an EDX attachment (EDX Oxford Instrument Isis 300), and the accelerating voltage applied was 20 kV. The surface roughness data were obtained by using a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. TEM images were recorded on a JEOL JEM-2100 transmission electron microscope with the accelerating voltage of 200 kV. Fluorescence image was observed using an OLYMPUS-BX51 fluorescence microscope. The photobleaching was tested by the UV lighting with CHF-XQ 500W. Photoluminescence quantum yield was measured using a Nanolog FL3-2iHR infrared fluorescence spectrometer equipped with an integrating sphere.



Scheme S1. Schematic representation for the LBL fabrication of multilayer luminous UTF based on mercaptosuccinic acid modified CdTe QDs and LDH nanosheets.



Figure S1. (A and B) TEM images of the CdTe QDs; UV-vis absorption spectrum and fluorescence spectrum of (C) CdTe QDs aqueous solution (the inset shows its photoemission under UV irradiation) and (D) rhodamine 6G. Quantum yield of CdTe QDs was determined to be 53% against rhodamine 6G in ethanol ($QY_{R6G}=95\%$).



Figure S2. UV-vis absorption spectra of the $(CdTe QDs/LDH)_n$ UTFs (A) and their photographs under daylight (B).



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18, 24, 30 bilayers

п	6	12	18	24	30
rms roughness (nm)[a]	5.40	6.78	8.89	10.27	12.75
SEM thickness (nm)[b]	~71	~144	~216	~288	~357

[a] The statistical rms roughness values were obtained by AFM.

[b] The SEM thickness values were obtained from the side-view of CdTe QDs/LDH UTFs.



Figure S6. The fluorescence microscope image of the $(CdTe QDs/LDH)_{30}$ UTF in a heating–cooling cycle in the temperature range 23–80 °C.

$T(^{o}C)$	23	80	23	
2θ (°)	0.716	0.878	0.732	
d_{003} (Å)	12.33	10.50	12.06	

Table S2. 2θ degree and d_{003} value for the (CdTe QDs/LDH)₃₀ UTF in a heating–cooling cycle



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References:

- [1] D. P. Yan, J. Lu, M. Wei, J. B. Han, J. Ma, F. Li, D. G. Evans and X. Duan, Angew. Chem. Int. Ed., 2009, 48, 3073.
- [2] N. P. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski,A. Eychmüller and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 7177.