Supporting Information for

Reversible regulation CdTe quantum dots fluorescence intensity based on the Prussian blue with high anti-fatigue performance

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EXPERIMENTAL SECTION

Materials. Mercaptosuccinic acid (MSA) was obtained from Aldrich. $NaBH_4$ was purchased from Acros. Na_2TeO_3 was bought from Schering-Kahlbaum in Germany. $CdCl_2$, KCl, HCl, $K_3[Fe(CN)_6]$, $FeCl_3$ and NaOH were acquired from Beijing Reagent Company. All other chemicals were of analytical grade. All aqueous solutions were prepared with ultrapure water (18.2 MΩ).

Methods. Spectroelectrochemical measurements were carried out in a modified fluorescence cell. A home-made Teflon plate acted as the electrode holder. The ITO electrode, platinum wire electrode and Ag/AgCl electrode (saturated KCl solution) were used as the working electrode, the counter electrode and the reference electrode, respectively. The ITO plates (surface resistance is about 20 Ω/cm^2) were obtained from Nanbo Display Technology Co. Ltd. (Shenzhen, China). The electrochemical measurements were conducted on the CHI832 electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). Fluorescence measurements were carried out on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France) with excitation slit width of 5 nm and emission slit width of 10 nm. Absorption measurements were implemented on a Cary 500 UV-Vis-NIR spectrometer (Varian).The excitation peak wavelength is 360 nm.

Preparation of PB Film. ITO plate was rinsed with acetone, ethanol and double-distilled water successively in ultrasonic bath. The active solution was made of 1:1 (v: v) ethanol/ NaOH (1 M), and then the ITO was immerged in the above active solution for 15 min. Followed by the ultrasonic operation in water to remove the foreign ions adsorbed on the ITO. Then the ITO plates were dried under N_2 stream. Finally, the active ITO chips were prepared. The electrodeposition solution was prepared: first, 50 mL double-distilled water was added in the centrifuge tube. Immediately 450 μL HCl solution (mass fraction solution 37%) was injected in. Then 0.37 g KCl (0.1 M), 0.034 g $FeCl_3$ (2.5 mM) and 0.041 g $K_3[Fe(CN)_6]$ (2.5 mM) were added to the mixed solution, respectively. The mixed solution should be shaken thoroughly every time when chemical reagent was put in. The active ITO electrode was electrodeposited with PB in a freshly electrodeposition solution by applying 0.4 V constant potential for 480 s. And the i-t curve was exhibited in Fig. S1. The evident color (blue) and the absorbance change were verified the successful synthesis of the PB film. Besides, the SEM characterization of the PB was further demonstrated that the electrochromic material PB was prepared as expected (Fig. S2). The modified ITO/PB electrode was adequately washed with water to remove the foreign adsorbed species. The ITO/PB electrodes were finally reinforced in 100 ℃ for 8 h.

Synthesis of the CdTe QD$_S$. CdTe QD$_S$ protected by MSA were prepared according to the previous report. The most important point is to prepare with CdTe QDs suitable wavelength based on FRET. The specific synthesis method was as follows: first, 50 mL double-distilled water was filled in 100 mL round-bottom flask; and then under stirring, 4 mL 0.04 M $CdCl_2$, 100 mg $C_6H_5Na_3O_7{\cdot}2H_2O$, 1 mL 0.01 M Na_2TeO_3 and 50 mg MSA were added, successively. The solution should be mixed intensively for 5 min. Finally, 100 mg $NaBH_4$ was added in above solution and mixed the solution acutely. After the solution became reseda, it should be heated immediately to 100 ℃ and refluxed under open system for 24 h. At the same time the color of solution was getting pale red until ultima orange red. The final step was centrifuged and cleaned the prepared CdTe QD$_S$ protected by MSA. In more detail, the ethylalcohol was added in the above solution with the volume ratio of 1:1. And next the mixed solution was centrifuged at the 8000 rpm for 10 min, which removed the supernatant. Finally the CdTe QDs should be dried at 80 ℃ for 6 h.

Preparation of ITO/PB/CdTe Fluorescence Switching. PB film was electrodeposited on the ITO plate. Then the CdTe QD$_S$ were put on the surface of PB by layer-by-layer self-assembly technology to form the ITO/PB/CdTe hybrid film structure. The detail is as follows: the 0.005 mg/mL CdTe QDs were assembled on the surface of PB to from the ITO/PB/CdTe hybrid structure. And the ITO/PB/CdTe electrode was moored under ultraviolet lamp. Then the electrode was washed with water to remove the unfixed CdTe

QDs, and dried in N_2 stream. The above procedures was repeated twice. The ITO/PB/CdTe electrode was successfully assembled.

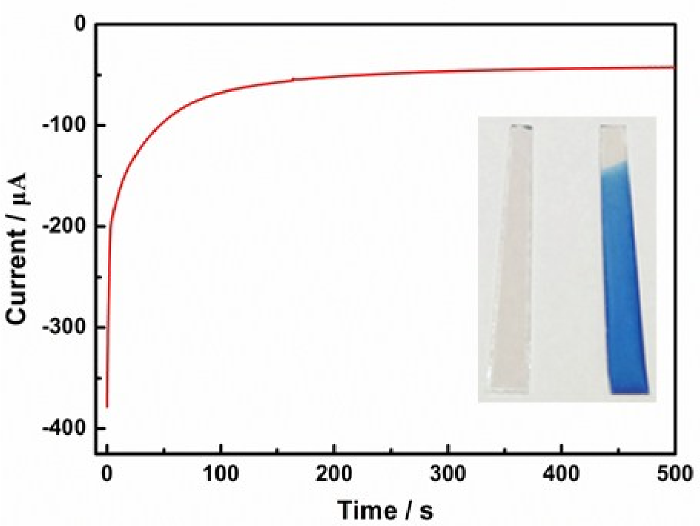

Fig. S1 The i-t curve of the electrodespotion PB.

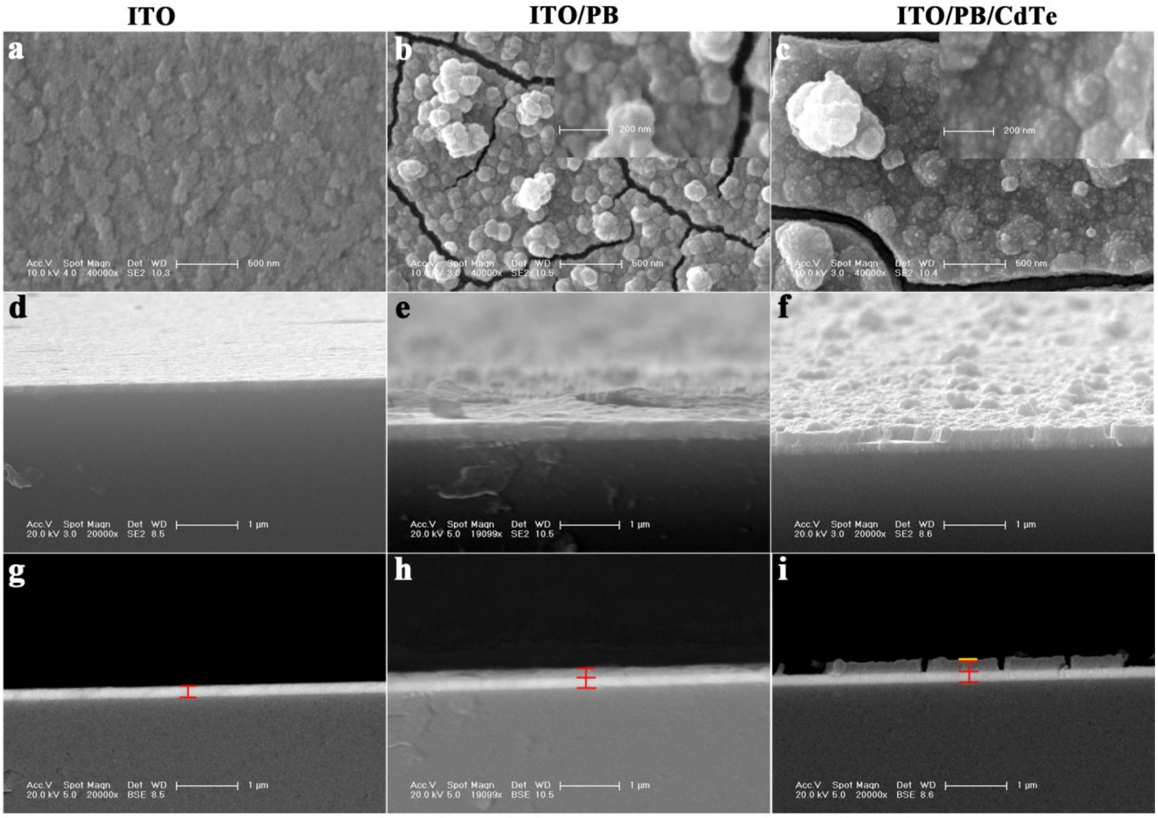

Fig. S2 The surface SEM images of the ITO(a), ITO/PB (b) and ITO/PB/CdTe(c), the across-section SEM images (SE model) of the ITO (d), ITO/PB (e) and ITO/PB/CdTe (f), the across-section SEM images (BSE model) of the ITO (g), ITO/PB (h) and ITO/PB/CdTe (i).

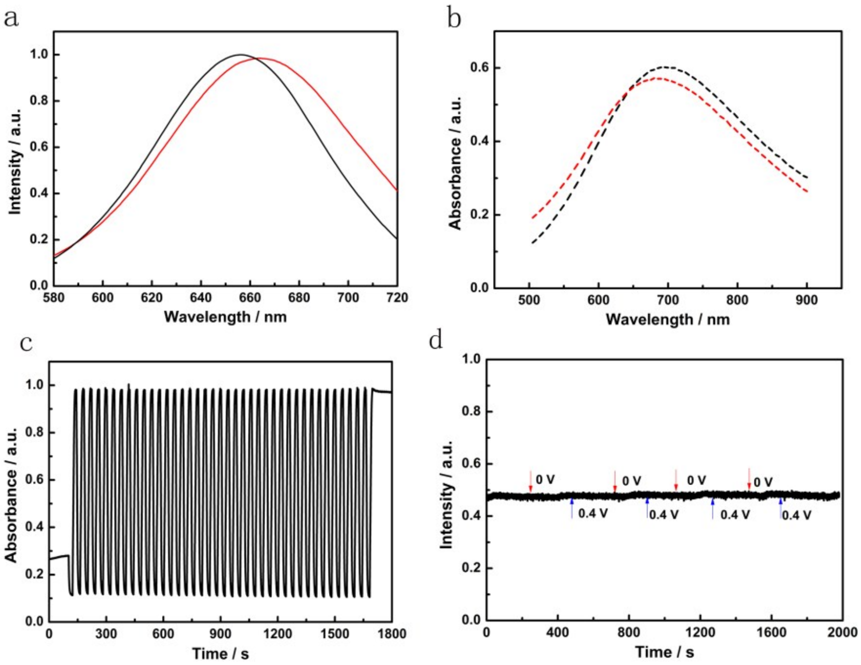

Fig. S3 (a) Emission spectra of the solution state (black line) and solid state (red line) CdTe QDs; (b) absorption spectra of ITO/PB (black line) and ITO/PB/CdTe (red line) electrodes; (c) the reversibility of ITO/PB electrode under double-potential steps of 0 V and 0.4 V; (d) the luminescence intensity variation of ITO/CdTe electrode under double-potential steps of 0 V and 0.4 V.

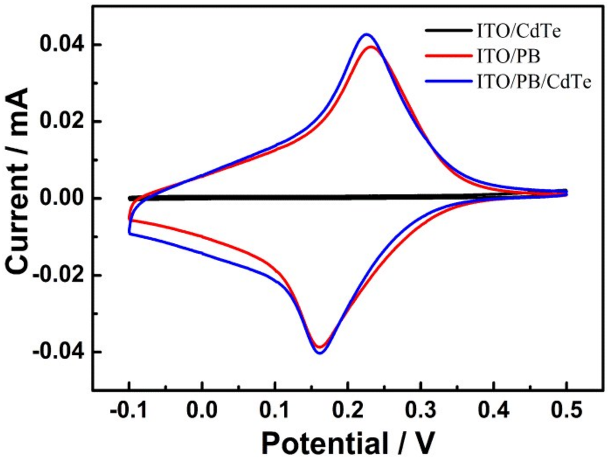

Fig. S4 The CV curves of the ITO/CdTe, ITO/PB and ITO/PB/CdTe electrodes. In the electrochemical testing, the area of the working electrode was decreased to ~7 mm^2.

The CV curves of the ITO/PB/CdTe almost overlapped with that of ITO/PB.

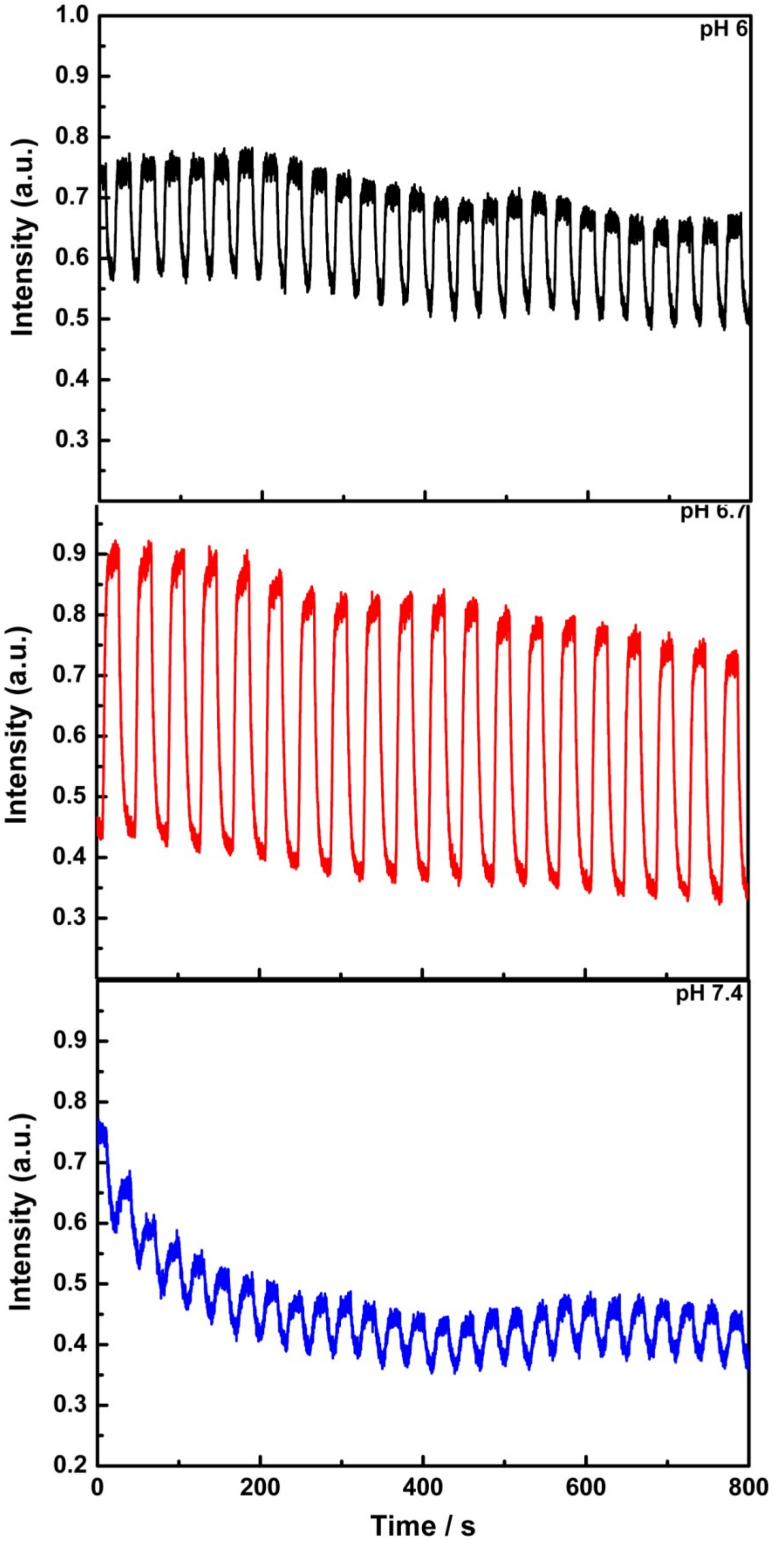

Fig. S5 Comparison of ITO/PB/CdTe electrodes fluorescence intensity under pH 6 (black line), pH 6.7 (red line) and pH 7.4 (blue line) 0.1 M PBS.

Table S1 The cycle performance comparison with other published works.

Number	Title	Cycles	Reference
1	Reversible modulation of quantum dot photoluminescence using a proteinbound photochromic fluorescence resonance energy transfer acceptor	4	1
2	Water-souble, thermostable, photomodulated color-switching quantum dots	11	2
3	Reversible modulation of gold nanoclusters photoluminescence based on electrochromic poly(methylene blue)	20	3
4	Self-powered fluorescence controlled switch systems based on biofuel cells	10	4
5	Self-powered fluorescence display devices based on a fast self-charging/recharging battery (Mg/Prussian blue)	13	5
6	A high performance fluorescence switching system triggered electrochemically by Prussian blue with upconversion nanoparticles	47	6
7	An electroswitchable fluorescence thin-film based on a luminescent polyoxometalate clusters	7	7
8	Fluorescence modulation in bilayer containing fluorescent and photochromic dopants	20	8
9	Electroswitchable fluorescent thin film controlled by polyoxometalate	9	9
10	Modulation of a fluorescent switch based on a controllable photochromic diarylethene shutter	20	10
11	Reversibly electroswitched quantum dot luminescence in aqueous solution	20	11
12	Combination of a fluorescent conjugated polymer, photochromic dye, and UV-curable acryl oligomer for fluorescence switching applications	10	12
13	An azobenzene-based photochromic liquid crystalline amphiphile for a remote-controllable light shutter	10	13
14	Electrochemical switching fluorescence emission in rhodamine derivatives	8	14
15	Gold nanocluster-based electrochemically controlled fluorescence switch surface with prussian blue as the electrical signal receptor	30	15
16	Reversible regulation CdTe quantum dots fluorescence intensity based on the Prussian blue with high anti-fatigue performance	133	The proposed work

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