Supplementary Information

High Performance Fluorescence Switching System Trigged Electrochemically by Prussian Blue with Upconversion Nanoparticles

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Experimental Section

Chemicals

NaF, KCl, HCl, $K_3[Fe(CN)_6]$, $FeCl_3$, NaOH and trisodium citrate dehydrate were bought from Beijing Reagent Company (Beijing, China). While, Y_2O_3, Yb_2O_3, Er_2O_3, and $TmCl_3 \cdot 6H_2O$ were bought Aladdin. All other chemicals were of analytical grade and all water used during the experiments was ultrapure water (>18 MΩ). Phosphate buffer solution (PBS) consisting of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 (pH = 6.0) was used as the electrolyte throughout the experiments.

Instrumentation

All the electrochemical experiments were carried out on a CHI832C electrochemical work station (Shanghai Chenhua Instrument Corporation, China). Transmission electron microscope (TEM) images were gained with a TECNAI G2 high-resolution TEM operating at 200 kV. Scanning electron microscopy (SEM) images were operated in a Philips XL-30 ESEM. The X-ray diffraction (XRD) measurement was operated on a D8 Focus diffractometer (Bruker) with Cu Kα radiation (λ=0.15405 nm) range from 10-90°（2θ）. Luminescence measurements were performed on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France) with emission slit width of 2.5 nm by using a 980 nm laser (with the current of 1.00 A) as an excitation light source. The 980 nm laser was bought from Hi-Tech Optoelectronics Co., Ltd. During the whole experiments the current of the 980 nm laser was 1.00 A. Absorption measurements were conducted with a Cary 500 UV vis NIR spectrometer (Varian). Spectroelectrochemical measurements were determined with a modified fluorescence cell according to the previous report (1 cm-length quartz cell) at room temperature. A Teflon plate was used as a cap of the cell as well as the electrode support. Platinum wire, ITO electrode, and Ag/AgCl (saturated KCl) were used as the counter electrode, the working electrode, and the reference electrode, respectively. The ITO plates (geometric area of ～ 1 cm * 5 cm) with surface resistance of 30-60 Ω /cm^2 were purchased from Nanbo Display Technology Co., Ltd. (Shenzhen, China).

Synthesis of β-UCSMs hexagonal crystals

The β-UCSMs were prepared according to the previous literature[20] with some modifications. In order to make the emission band of β-UCSMs overlap greatly with the absorption band of PB oxidation states, we changed the doping proportionality of the rare earth element to manipulate the ratio of the green and red emission. A total 5 mL of $Y(NO_3)_3$, $Yb(NO_3)_3$, $Er(NO_3)_3$, and $TmCl_3$ were added into 10 mL of sodium citrate solution and stirred for 1 h to form a homogeneous solution. Then a solution of 20 mL NaF (0.525g) was added at 30 ℃ under magnetic stirring for 30 min. Subsequently, the pH of the solution was adjusted to 3 by adding sufficient HNO_3 (98 %). Straight after that, the solution was ultrasonically agitated for 10 min and transferred into two 50 mL autoclaves, sealed, as well as hydrothermally treated for 2 h under 180 ℃. Finally, the above obtained solution was cooled to room temperature and separated by centrifugation to obtain the white precipitates. After washed with deionized water and ethanol for several times to remove the excess reactant, the white precipitates were dried for 12 h under 80 ℃.

Preparation of PB Film on the ITO Electrode

Before modification, the ITO plates were washed with acetone, ethanol and water with an ultrasonic bath for 20 minutes sequentially. Then in order to activate the ITO plates, the plates were immersed in a solution of 1:1 (v/v) ethanol/NaOH (1 M) for 15 min. Afterwards the ITO plates were washed with pure water for several times and dried under N_2 flow. After that, the ITO plates used as working electrodes were electropolymerizated with PB by a freshly prepared solution consisting of 0.1 M HCl, 0.1 M KCl, 2.5 mM $FeCl_3$, and 2.5 mM $K_3[Fe(CN)_6]$ with a controlled potential of 0.4 V for 480 s. The successful preparation of the PB film was proved with the obvious changes of the colour, from transparent to blue and absorbance. Before being used, the PB ITO electrode was thoroughly washed with deionized water several times to remove the physically adsorbed species and then dried with N_2 flow. Finally the PB ITO electrode was dried in 100 ℃ for 8 h and saved in centrifuge tubes for following use.

Preparation of β-UCSMs on PB film ITO Electrode

Before preparation, the as synthesized β-UCSMs were dispersed into deionized water with the concentration of 2 mg / mL and ultrasonically agitated for 20 min. Afterwards, the as obtained solution (10 μL) was dropped onto the above obtained PB film ITO electrode, and dried under ultraviolet lamp for 30 min. Eventually, 5 μL Nafion solution (0.2 %) was dropped onto the surface of the β-UCSMs and dried under ultraviolet lamp for 30 min too.

Procedures for preparing and sensing sulfite and other species by fluorescence and UV measurement

Typically, 2 mL of PB NPs aqueous solution (0.96 mM) containing 0.1 mg/mL of β-UCSMs was served as the probe solution. Sodium sulfite solution (Na_2SO_3) was freshly prepared with the concentration of 2.0 mM, while other interferential ion solutions were prepared at 10.0 mM. After adding these species into the probe solution for 15 min at 25 ℃, the fluorescence emission spectra were recorded in the range from 400 nm to 750 nm using the 980 nm laser as the excitations and the emission slit width was 20 nm. Meanwhile, the UV absorption spectra of every sample were also recorded.

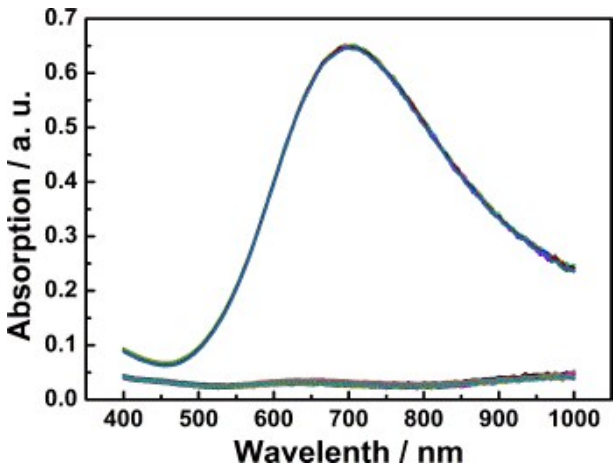

Fig. S1. Absorption spectra of the ITO/PB/β-UCSMs electrode under alternating applied potential with -0.3 V (bottom lines) and 0.4 V (top lines) for 20 cycles.

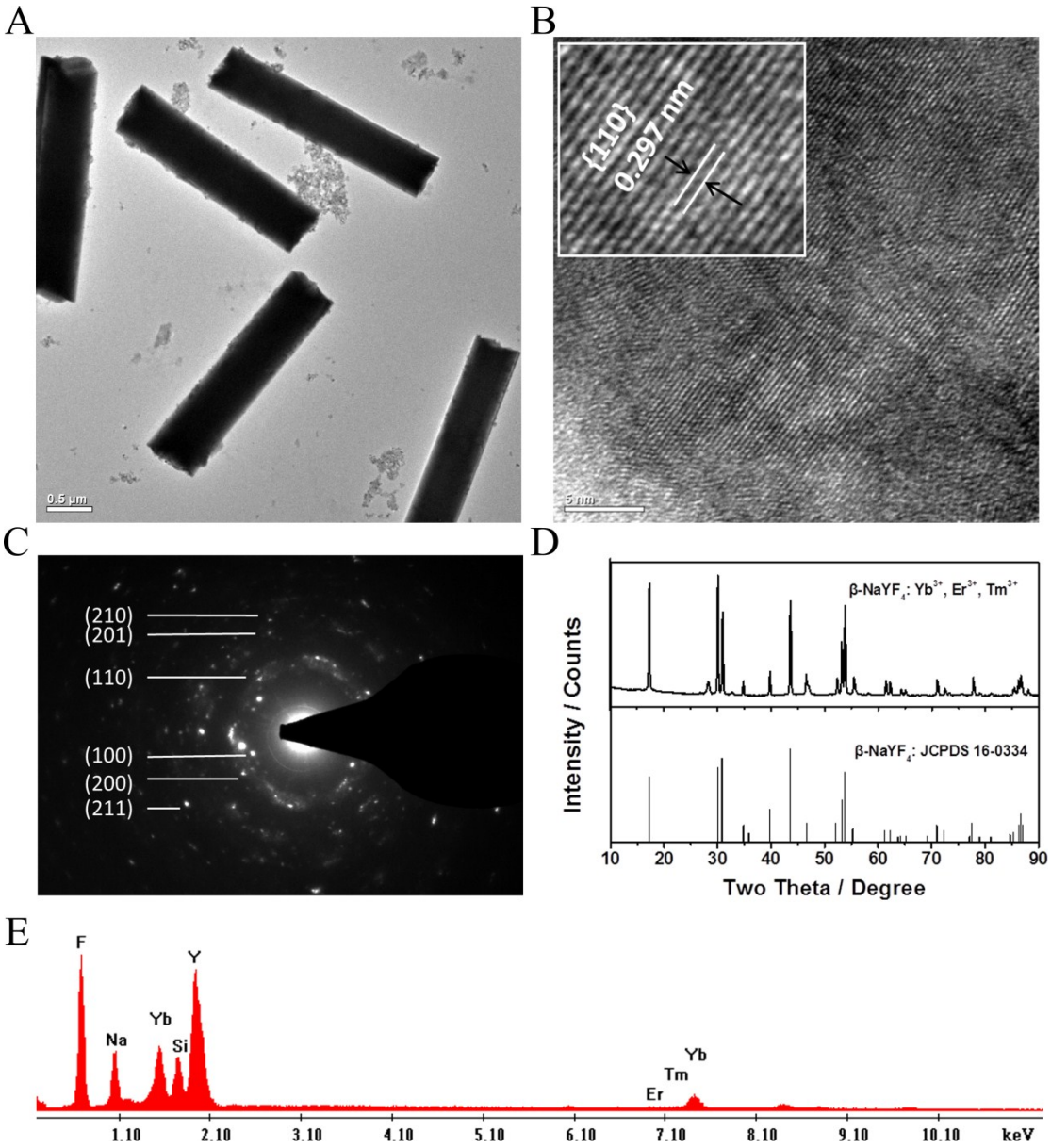

Fig. S2. (A) The TEM image of the β-UCSMs. And the β-UCSMs have an average diameter of 400 nm with the length of 2 μM judging from the TEM data. (B) The HRTEM image of the β-UCSMs. The inset shows the lattice distance is around 0.29 nm, which matches well with the $d_{(110)}$ of the β-$NaYF_4$. (C) The selected area electron diffraction (SAED) image of the β-UCSMs. (D) The XRD patterns for the β-UCSMs. (E) The EDX image of the β-UCSMs.

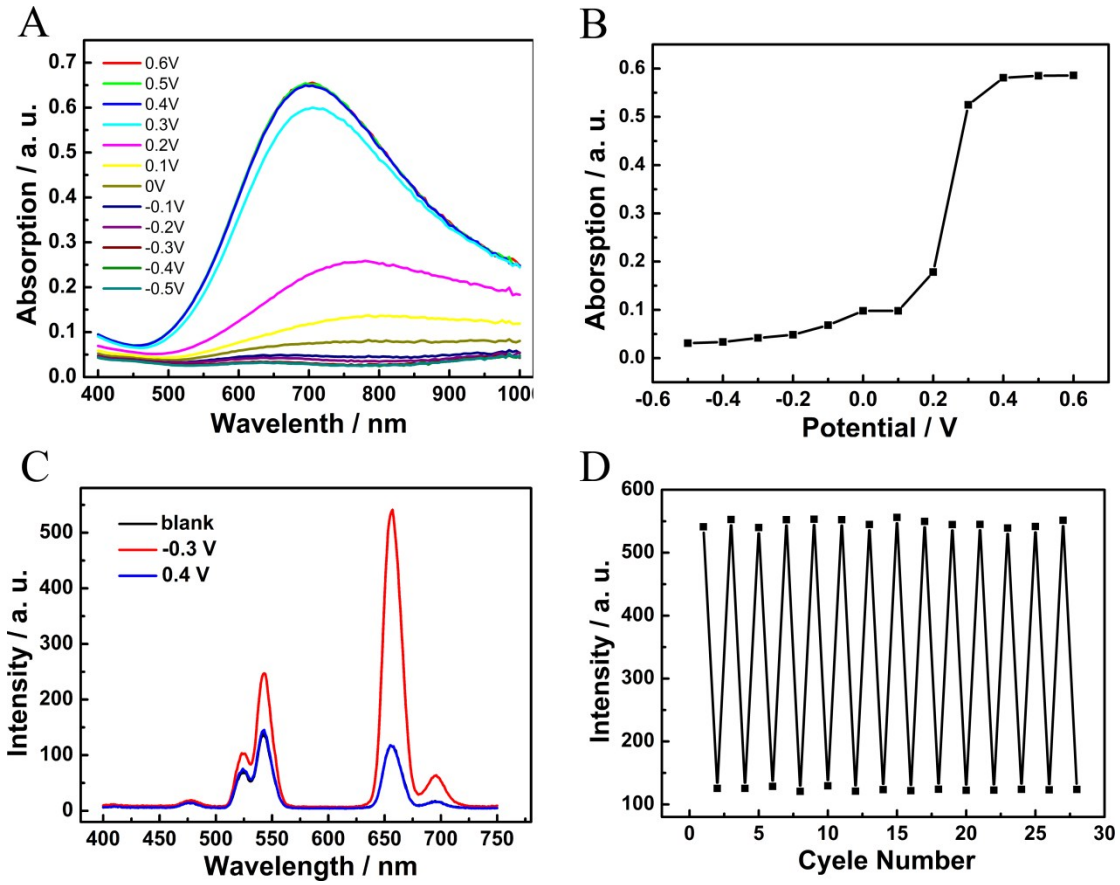

Fig. S3.(A) Absorption spectra of the ITO/PB electrode at different potentials, from top to bottom: 0.5, 0.4, 0.3, 0.2, 0.1, 0, -0.1, -0.2, -0.3, -0.4 and -0.5 V. (B) The absorption intensity at 650 nm of the ITO/PB electrode as a function of the applied potentials. (C) Emission spectra of the ITO/PB/β-UCSMs electrode under alternating applied potential with -0.3 V (top lines) and 0.4 V (bottom lines). (D) Reversible fluorescence (653 nm) on–off cycles as a function of the applied potentials.

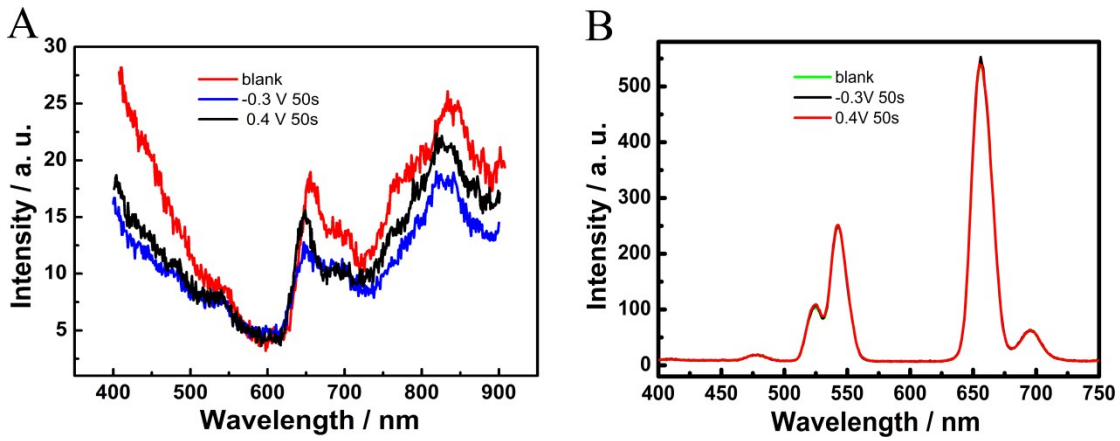

Fig. S4. (A) The fluorescence intensity of the PB ITO electrode with and without applying potential (-0.3 V, 0.4V) for 50 s excited by 980 nm laser. And it outs out no switch phenomenon without the β-UCSMs film. (B) The fluorescence intensity of the

β-UCSMs ITO electrode with and without applying potential (-0.3 V, 0.4V) for 50 s excited by 980 nm laser, which also outs out no switch phenomenon without the PB film.

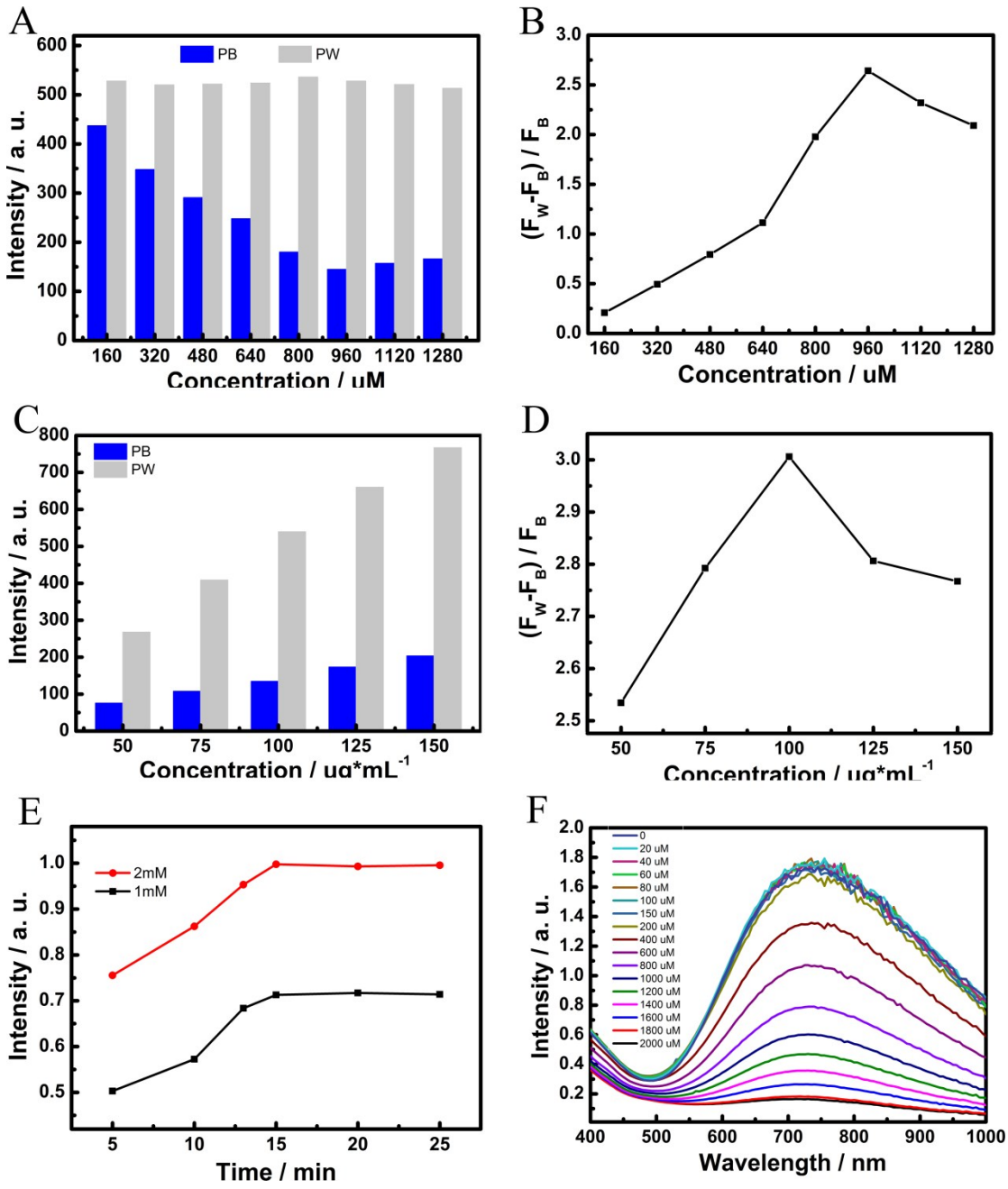

Fig. S5. (A) The fluorescence intensity (at 653 nm) of the β-UCSMs solution (0.1 mg/mL) with different concentration of PB and PW, respectively. (B) The plot of the fluorescence intensity of β-UCSMs solution as a function of the PB and PW concentration. F_B and F_W are the intensity of β-UCSMs with the same concentration of PB and PW respectively. $(F_W - F_B)/F_B$ is the fluorescent contrast. (C) The fluorescence intensity (at 653 nm) of the PB and PW solution (0.96 mM) with different concentration of β-UCSMs respectively. (D) The plot of the fluorescence intensity of

the solution of PB and PW with different concentration of β-UCSMs. (E) The fluorescence intensity (at 653 nm) of the probe solution (0.96 mM PB and 0.1 mg/mL β-UCSMs) with adding 2 mM sulfite and 1 mM sulfite as a function of time respectively. (F) The UV response of the probe solution (containing 0.96 mM PB NPs and 0.1 mg/mL β-UCSMs) as a function of sulfite concentration (0, 20, 40, 60, 80, 100, 150, 200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800 and 2000 μM).

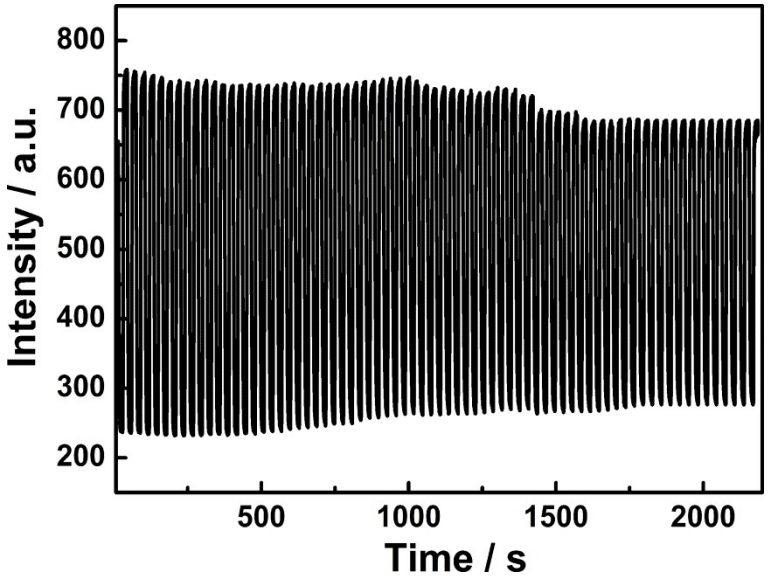

Fig. S6. Reversible fluorescence (653 nm) on–off cycles as a function of the applied potentials.