

Supplementary Information

Self-powered visual ultraviolet photodetector with prussian blue electrochromic display

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Experimental Section

Reagents: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was obtained from National Chemical Reagent Company (Shanghai, China). Titanium foil (purity > 99.7%) was purchased from Aldrich. The ITO plates (surface resistance of 30-60 Ω/cm^2) were purchased from Nanbo Display Technology Co., Ltd. (Shenzhen, China). Hydrofluoric acid, nitric acid, acetone and absolute ethanol were of analytical grade from Beijing Chemical Reagent Company (China) without further purification. Ultrapure water from Water Purifier (Sichuan Water Purifier Co., Ltd., China) was used in all the experiments.

Preparation of Pt-modified TiO_2 nanotube electrode (Pt/TNT): The ordered TiO_2 nanotubes were prepared by a potentiostatic anodization in a two-electrode electrochemical cell. A 0.25-mm-thick titanium foil with a size of 0.5 cm \times 0.5 cm was used as a working electrode, and a platinum foil with the same size served as a counter electrode. The interval between working electrode and counter electrode was about 2 cm. Prior to anodize, the titanium foil was chemically etched by immersing in a mixture of HF and HNO_3 (volume ratio of HF: HNO_3 : H_2O in 1:4:5) for 40 s. Then the titanium foil was rinsed with acetone, absolute ethanol and water for 10 min, respectively. The substrate was then dried in air at room temperature. The voltage was applied by a

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DC power supply (SK1730SL1A, Sanke Technologies). The TiO₂ NTs were formed by anodizing the Ti foil in 40 mL of 0.5 wt% HF solution at 20 V for 20 min with magnetic agitation, which is the same as the reported method.^[1] During anodization, the color of the titanium oxide layer normally changed from purple to blue, light green, and then finally light red. Anodized titanium foils were annealed in at 500 °C for 3 h in air atmosphere, heating and cooling rates were kept at 1 °C min⁻¹.

The Pt/TNT electrode was prepared by electrodeposited Pt nanoparticles on the TiO₂ NTs support at room temperature in a three-electrode cell system. CVs were carried out in electrolyte solution 10 mM H₂PtCl₆ from -0.4 to 0.5 V at a scan rate of 10 mV s⁻¹. The structure and loading of the Pt nanoparticles are adjusted by changing the number of the potential cycles.

Preparation Prussian Blue (PB)/ITO film (PB/ITO): PB/ITO was prepared according to our previous reports.^[2] Before modification, the ITO chips were washed with acetone, ethanol, and water in ultrasonic bath sequentially. Then ITO chips were immersed in a solution of 1:1 (v/v) ethanol/NaOH (1 M) for 15 min to active the surface. After rinsed with pure water and dried under N₂ flow, the ITO electrodes were electropolymerized with PB in a freshly prepared solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM K₃[Fe(CN)₆], and 2.5 mM FeCl₃ by applying a controlled potential of 0.4 V for 300 s. The obvious color and absorbance change were conformed the successful preparation of the PB film. The modified electrode was thoroughly rinsed with water to remove the physically adsorbed species, and then dried in 100 °C overnight.

Instruments: SEM images were taken with a XL30 field-emission scanning electron microscope at an accelerating voltage of 15 kV. XRD patterns were collected by a D8 ADVANCE (Germany) with Cu K α radiation ($\lambda=1.54056$ Å) in the range of 20-80° (2 θ). Photoelectrochemical (PEC)

studies were carried out in a conventional three electrode system with a platinum foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. All electrochemical measurements were recorded by a CHI 832C electrochemical workstation (Chenhua Co., Shanghai). Absorption measurements were performed on a Cary 500 UV-Vis-NIR spectrometer (Varian). PB was connected with Pt/TiO₂ NTs by resistant and copper wire constructing photoelectrochemical cell to switch the absorbance of PB.

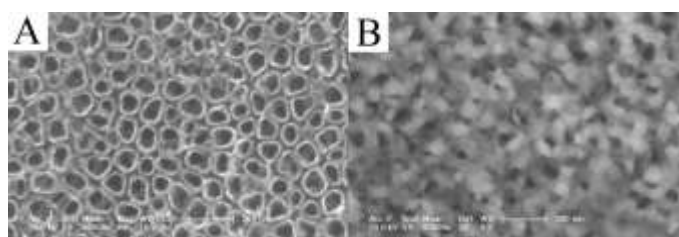


Fig. S1 The typical SEM images of the as-prepared TiO₂ nanotube (A) and Pt/TiO₂ nanotube (B).

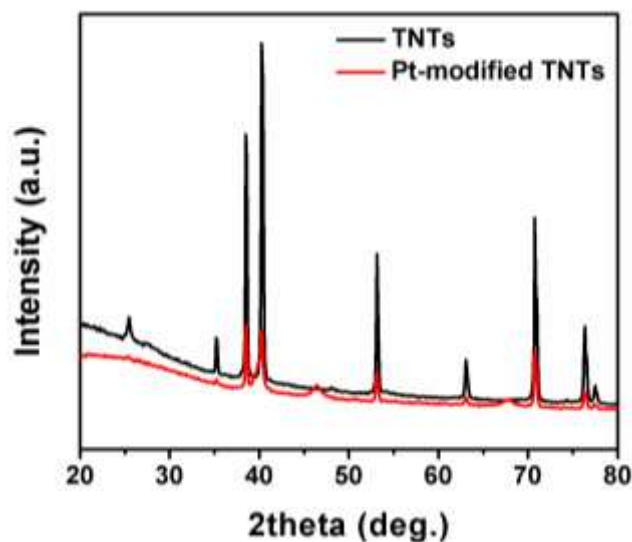


Fig. S2 The typical XRD patterns of the as-prepared TiO₂ nanotube and Pt/TiO₂ nanotube.

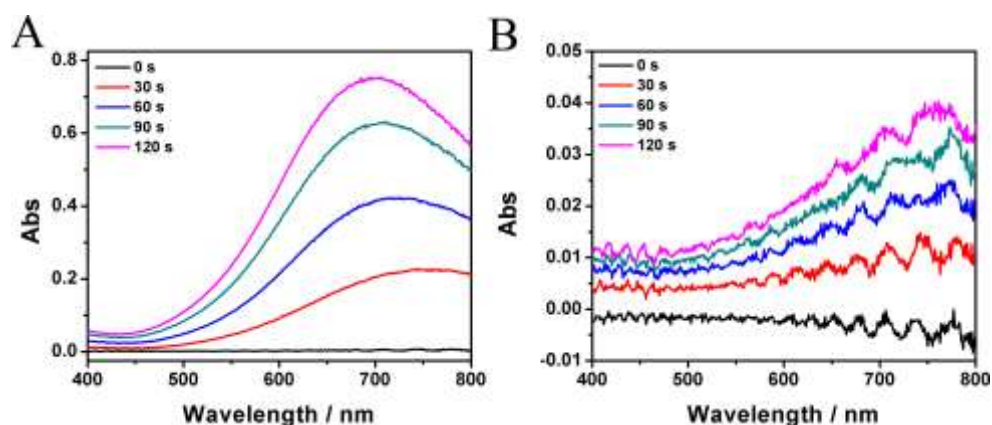


Fig. S3 The comparison of the performance of the device in the presence (A) and absence (B) of Pt. Note: The absorbance of Prussian white (PW) as baseline.

As shown in Fig. S3, it could be observed that the rate of recovery in the presence of Pt is superior to that in the absence of Pt although the self-recover can be observed in the absence of Pt.

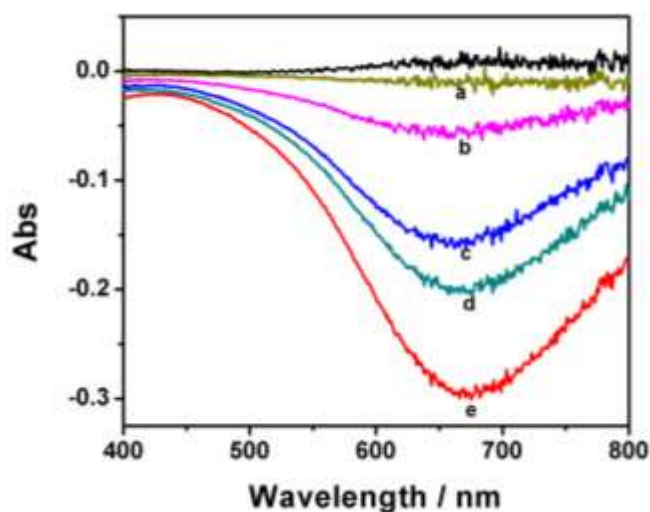


Fig. S4 The absorbance change of PB under light irradiation of varying intensity with 10 s at 365 nm: 2 mW/cm² (a), 4 mW/cm² (b), 10 mW/cm² (c), 20 mW/cm² (d), 40 mW/cm² (e). Note: The absorbance of Prussian blue (PB) as baseline.

Reference

1. L. Han, L. Bai, C. Zhu, Y. Wang, S. Dong, *Chem. Commun.* 2012, **48**, 6103.
2. L. Jin, Y. Fang, L. Shang, Y. Liu, J. Li, L. Wang, P. Hu, S. Dong, *Chem. Commun.* 2013, **49**, 243.