Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Acquired pH-responsive and Reversible Enrichment of Organic Dyes by Peroxide Modified Ultrathin TiO_2 Nanosheets

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Experimental Section

Chemicals Titanous sulfate solution ($Ti_2(SO_4)_3$, 15%~18%), titanium trichloride ($TiCl_3$, 15%-20%), hydrogen peroxide (H_2O_2, 30%) and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of TiO_2(B) Nanosheets In a typical synthetic procedure, 1mL $TiCl_3$ aqueous solution and 1ml deionized water were mixed with 30 mL ethylene glycol in a 40 mL Teflon-lined autoclave. After stirred for 10 s with a glass rod, the mixture was sealed and then kept at 140 ^oC for 4 h in an oven.

Modifying TiO_2(B) nanosheets by peroxide As-prepared TiO_2(B) nanosheets from ethylene glycol were washed with water and ethanol for 5 times. To modified the product, it was mixed with 1 mL H_2O_2 at room temperature, and then further washed with water for 3 times.

Synthesis of peroxide modified anatase nanosheets (PMAN) In a typical synthesis of PMAN, 1 mL $Ti_2(SO_4)_3$ solution (~15%) and 1 mL H_2O_2 solution (30%) were mixed with 30 mL deionized water in a beaker, immediately forming a red solution. After sealed with polyethylene membrane, the beaker was kept at 95 ^oC for 1 h in an oven, then yellow products could be collected at the bottom. The products were washed with water for 3 times to remove unreacted H_2O_2.

Adsorption of organic dyes To characterize the enhanced and pH responsive adsorption of organic dyes, 0.050 g PMAN was dispersed in 15 mL water, and was then mixed with 1.0 mL dye solutions with a concentration of 1mmolL^{-1}, including methyl red (MR), methyl blue (MB), fluorescein sodium (FS), rhodamine B (RhB), methyl orange (MO), methyl violet (MV) and methylene blue (MeB) (pH=7). These dyes can be removed from solutions by natural sedimentation. The pH responsive adsorption and desorption cycle was repeatedly adjusted using HCl and NaOH at pH=3 and 7, respectively.

Characterization Crystal structure of the as-prepared sample was determined from X-ray diffraction (XRD) pattern, which was recorded on a Rigaku diffractometer using Cu Kα radiation (λ =1.5418 Å), operating at 40 kV and 200 mA and a scanning rate of 6° per minute. Morphologies of the products were investigated on a high-resolution transmission electron microscopy (HRTEM) of FEI Tecnai F20 with an accelerating voltage of 200 kV. XPS measurements were performed on a PHI 550 EACA/SAM photoelectron spectrometer using Al Kα (1486.6 eV) radiation. Thermogravimetric Analysis (TGA) was carried out on a Mettler-Toledo TG/SDTA 851 thermal analyzer under static air atmosphere, and the heating rate was 10 K/min with a temperature range from 25 ^oC to 800 °C. The absorption spectra were obtained on a Hitachi U-3010 UV-vis spectrometer.

Figure S1. Structure of TiO_2(B) nanosheets. (a) TEM images of TiO_2(B) nanosheets. (b) Original HRTEM with real scale. (c) Size distribution of TiO_2(B) nanosheets in water characterized by Dynamic Light Scattering (DLS), (d) BET surface area data of TiO_2(B) nanosheets. (e) XRD pattern of TiO_2(B) nanosheets. (f)TEM image of TiO_2(B) nanowires.

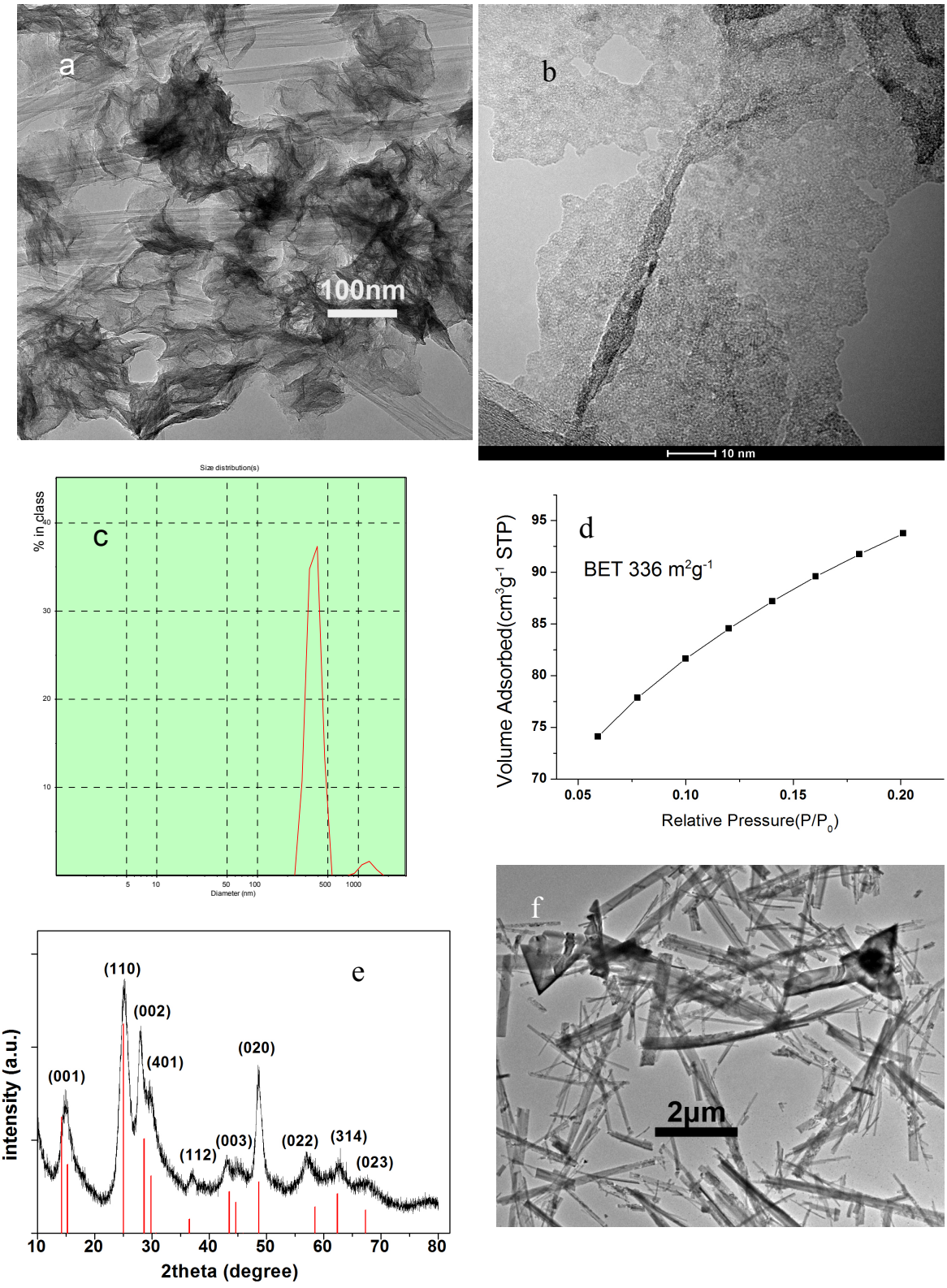

Figure S2. (a-e) TEM images of peroxide modified anatase nanosheets (PMAN). (f) BET surface area data of PMAN, after pretreated at 250 ^{o}C for 5 h.

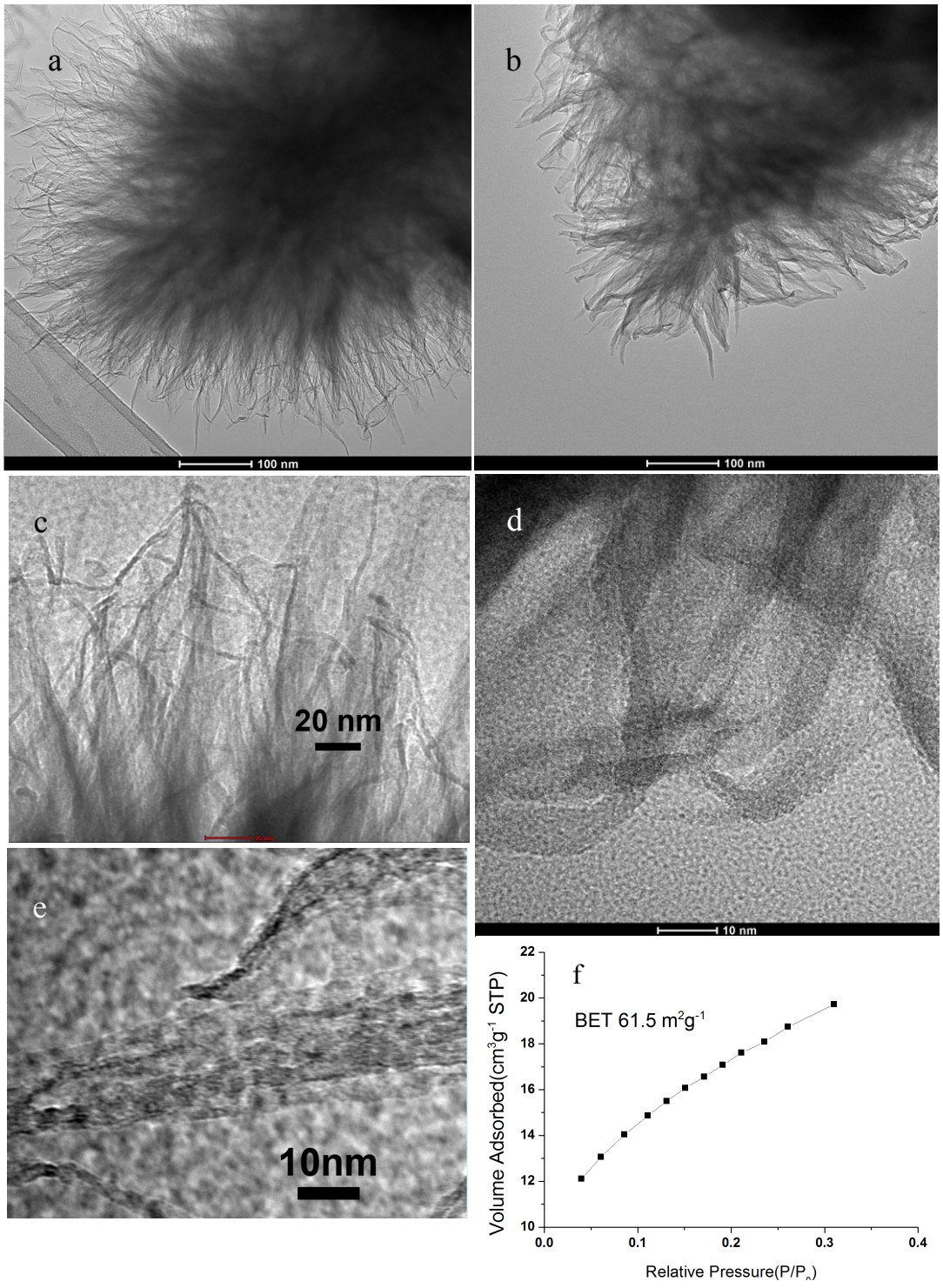

Figure S3. (a) Survey XPS curve of PMAN and (b) Ti2p.

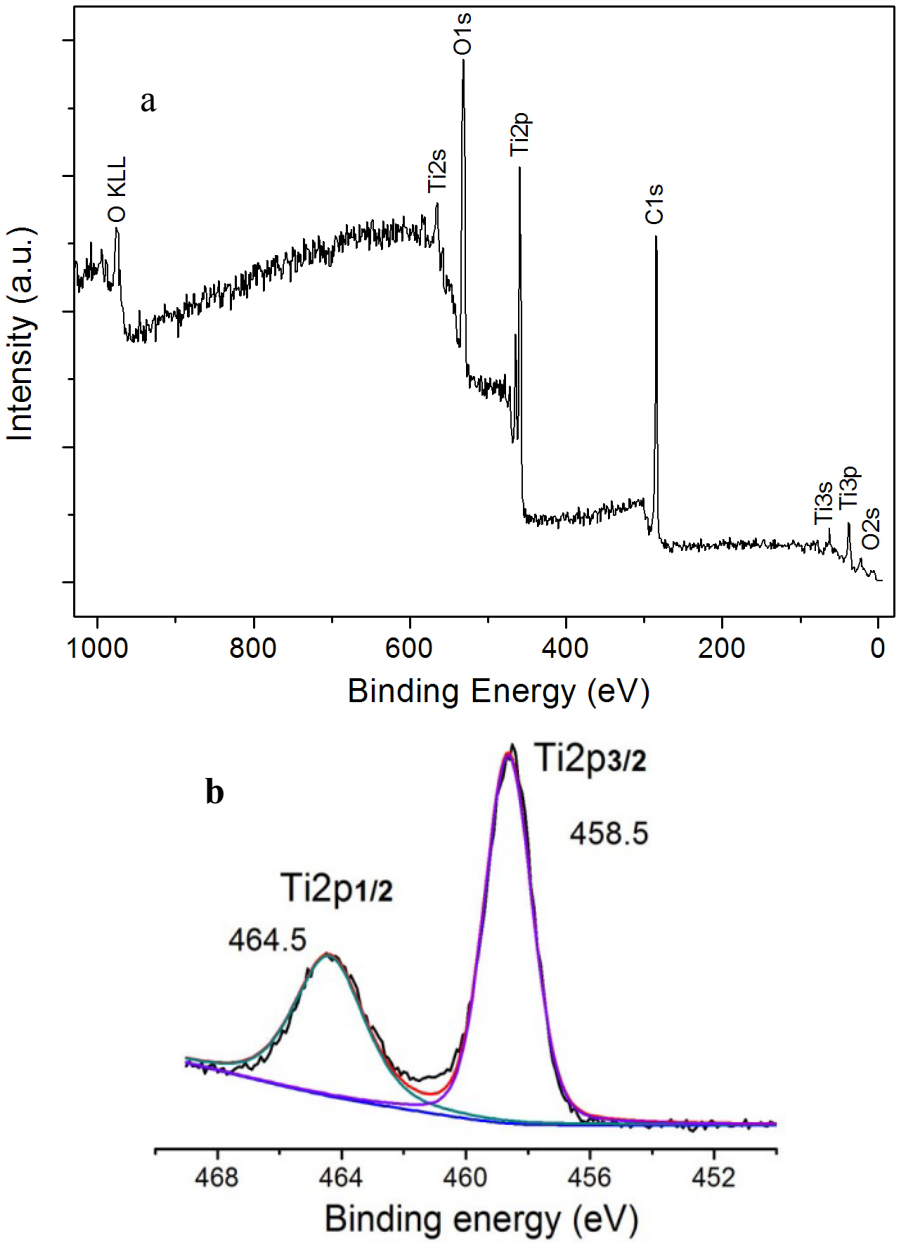

Figure S4. Optical absorption of organic dye solutions before and after adding PMAN.

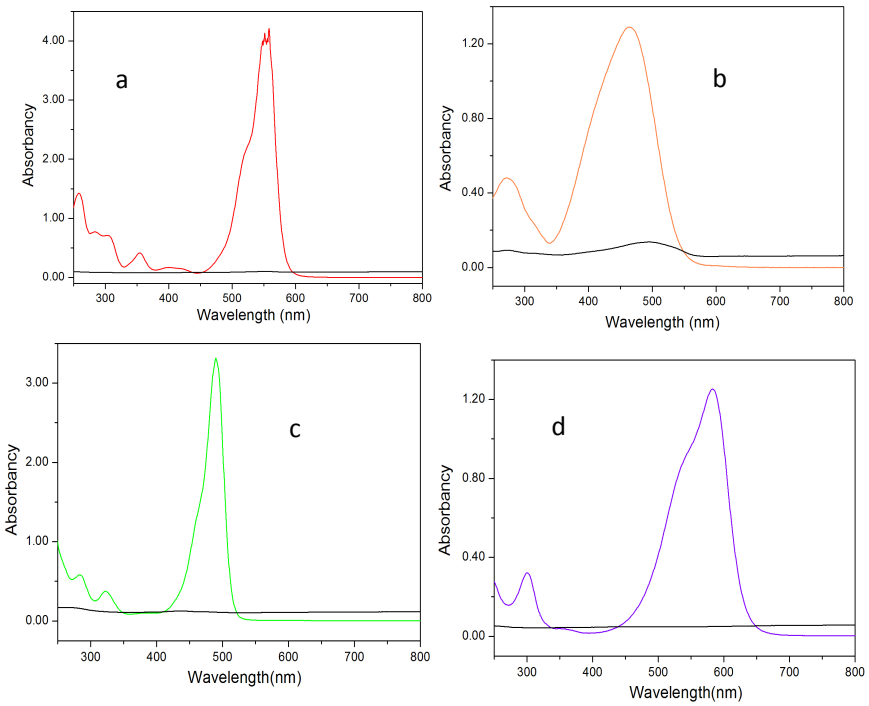

Figure S5. Camera images showing the adsorption results of dyes by PMAN in comparison with P25 (a-c). (d) The adsorption result of RhB by peroxide modified TiO_2(B) nanosheets compared with unmodified sample.