

Supporting Information

Combination of alkali treatment and Ag_3PO_4 loading effectively improves the photocatalytic activity of TiO_2 nanoflowers

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1. Experimental section

1.1. Materials

Isopropyl alcohol (IPA), isopropyl titanate (TTIP), ethanol (C₂H₅OH) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co., VLtd. Sodium dihydrogen phosphate (Na₂HPO₄) and silver nitrate (AgNO₃) were purchased from Maclin Reagent Co., Ltd. Diethylenetriamine (DETA) was purchased from Aldrich. All reagents employed were of analytic grade and without further purification.

1.2. Synthesis of TiO₂ nanoflowers

0.05 mL of diethylenetriamine was added to 71 mL of isopropyl alcohol drop by drop and stirred for 10 min. 3.35 mL of isopropyl titanate was slowly dropped into the above solution and stirred in a magnetic agitator for 30 min. The solution was put into a 100 mL Teflon-lined stainless-steel autoclave and then placed in a blast drying oven at 200 °C for 24 h. When the autoclave cools naturally to room temperature, the autoclave was removed from the drying oven. The turbid solution and precipitate at the bottom were put into a centrifuge tube and centrifuged at 6000 RPM for 5 min. Anhydrous ethanol was added to the precipitate and centrifuged twice. The precipitate was transferred to a petri dish and dried at 60 °C for 24 h. The dried sample was thoroughly ground with a mortar and transferred to a corundum boat. The pure TiO₂ nanocrystalline flower samples with better crystal properties were obtained by a heating rate of 6 °C/min to 550 °C for 4 h.

1.3. Synthesis of TiO₂/OH

40 mg of TiO₂ nanoflowers were added to 30 mL of NaOH solution (1 M) and stirred for a period of time. The alkali-treated titanium dioxide was cleaned with deionized water and placed in a drying oven. TiO₂/OH composites were obtained after drying at 60 °C for 3 h, and named as TiO₂/OH-10, TiO₂/OH-30, TiO₂/OH-50 and TiO₂/OH-70, respectively.

1.4. Synthesis of TiO₂/OH/Ag₃PO₄

40 mg of TiO₂/OH was added to 100 mL of ultra-pure water and stirred for 10 min, then 270 mg of AgNO₃ was added and stirred evenly. 179 mg of Na₂HPO₄ was stirred in a 50 mL beaker for 10 min, and then slowly added dropwise to the above solution and stirred for 2 h. After stirring, TiO₂/OH/Ag₃PO₄-1 was prepared by centrifugation with ultra-pure water for 2 times and then with anhydrous ethanol for 2 times. The preparation method of other TiO₂/OH/Ag₃PO₄ materials is the same as that of TiO₂/OH/Ag₃PO₄-1. The addition of 540, 810, 1080 mg of AgNO₃ and 358, 537, 716 mg of Na₂HPO₄ were labeled as TiO₂/OH/Ag₃PO₄-2, TiO₂/OH/Ag₃PO₄-3 and TiO₂/OH/Ag₃PO₄-4, respectively.

1.5. Characterization of TiO₂/OH/Ag₃PO₄

The Cu K α radiation source in the X-ray diffractometer was used to analyze the crystal phase of the sample. The surface morphology and structure of the sample can be observed by field emission scanning electron microscope (FESEM, JEOL, JSM-6700F). High-resolution transmission electron microscope (HRTEM, JEOL, JEM-2200FS) was used to observe the chemical composition of the sample. The UV-Vis

absorption spectrum of the sample in the range of 200-800 nm was tested with an ultraviolet-visible spectrophotometer (Shimadzu uv-3600). The chemical state of the elements of the sample was tested by X-ray electron spectroscopy (XPS). The photoluminescence spectra of the samples were studied on the F-380 fluorescence spectrophotometer with an excitation wavelength of 325 nm, and the recombination efficiency of photo-generated charges was analyzed. CHI 660E electrochemical workstation was used to conduct electrochemical impedance spectroscopy (EIS) and Mott-Schottky tests on the samples.

1.6. Evaluation of photocatalytic activities of THS/APO photocatalyst

The RhB solution was prepared by adding 3 mg of RhB to 1 L of ultra-pure water and stirring for 1 h. 20 mg of photocatalyst was added to 100 mL of RhB solution, and stirred for 30 min under dark conditions, so that the photocatalyst could perform sufficient dark adsorption and reach adsorption-desorption equilibrium. Using a 300 W xenon lamp as the light source, 7.5 mL of the reaction solution was taken at 15 min intervals and centrifuged to obtain the supernatant. The supernatant obtained by centrifugation was measured on an ultraviolet-visible spectrophotometer (uv-3600) to measure its absorption spectrum. In the capture experiment, 1 mM of IPA, EDTA, and BQ were used as capture agents, which were added to 100 mL of RhB solution and catalytic sampling was performed.

1.7. Photoelectrochemical measurements

The electrochemical measurement was carried out in Chenhua CHI 660E

electrochemical workstation. A three-electrode system consisting of Ag/AgCl as the reference electrode, platinum wire as the counter electrode and photoanode was used to measure the samples. The electrolyte was prepared by adding 6.006 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 4.11 g of Na_2SO_3 to 100 mL of ultra-pure water. 5 mg of sample and 0.5 mL of nafion solution were taken into 1 mL of ethanol, and sonicated for 30 min. The dispersion was evenly coated on a 1 cm^2 ITO sheet and dried in a blast drying oven for 2 h. The Mott-Schottky and Electrical impedance spectra of the sample were measured under the solar simulator.

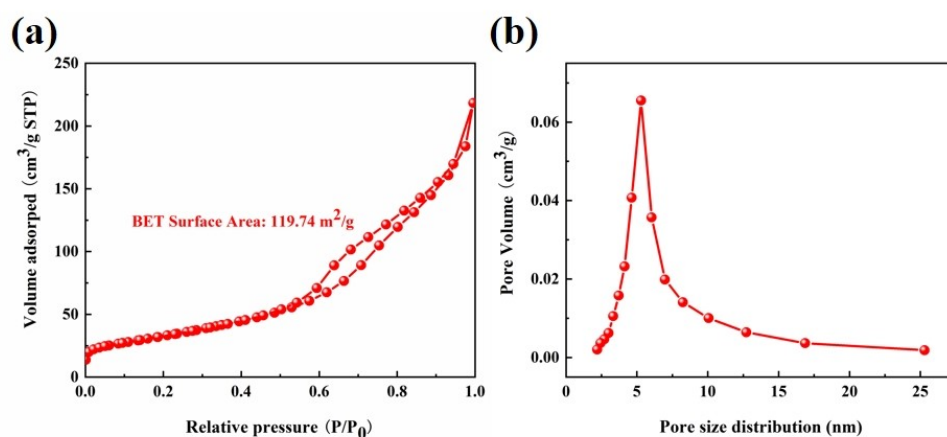


Fig. S1. (a) N_2 adsorption-desorption isotherm and (b) corresponding pore size distribution curves of TiO_2 .

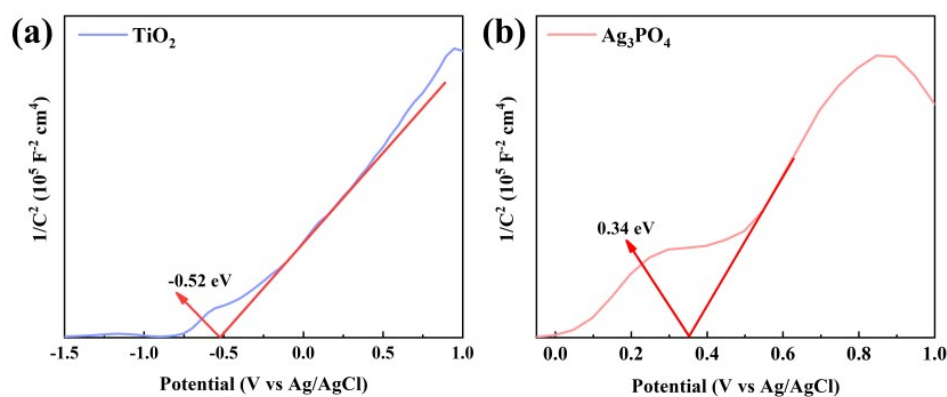


Fig. S2. Mott-Schottky plots of TiO_2 and $\text{TiO}_2/\text{OH}/\text{Ag}_3\text{PO}_4$.

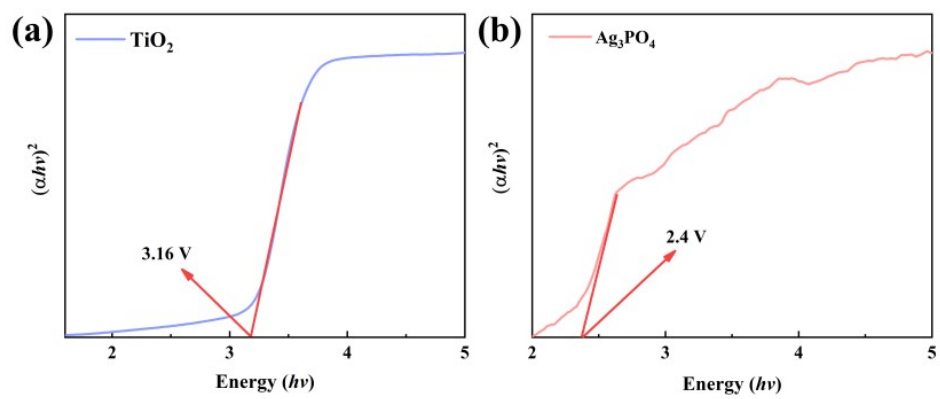


Fig. S3. Tauc plots of TiO_2 , TiO_2/OH and $\text{TiO}_2/\text{OH}/\text{Ag}_3\text{PO}_4$.