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Supporting Information

Ag size-dependent visible-light-responsive photoactivity of Ag-TiO₂ nanostructure based on surface plasmon resonance

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Experimental Section

Materials

Tetrabutyl titanate (Ti(OBu)₄, 98%), hydrofluoric acid (37%), titanium powder (Ti, 4N) and silver nitrate (AgNO₃, 99.8%), isopropanol, triethanolamine (TEOA), p-benzoquinone (BQ), are purchased from Sinopharm Chemical Reagent Co., Ltd., Sodium iodate (99%) is purchased from Aladdin Industrial Corporation. All reagents were used directly without further purification.

Synthesis of TiO₂ Nanocrystals.

Anatase TiO₂ nanocrystals with co-exposed {001} and {101} facets was hydrothermally prepared via a procedure similar to the previous report. ¹⁹ Typically, 10 mL of Ti(OBu)₄ and 1.2 mL of hydrofluoric acid solution were mixed in a dried Teflon autoclave with a capacity of 50 mL, and then kept at 180°C for 24 h. After cooling to room temperature, the white power was washed by ethanol and deionized water for three times, then the white powder was collected by filtration. Finally, it was dried at 80 °C overnight.

Synthesis of PAg-TiO₂.

In a typical experimental procedure, 100 mg of the as-prepared TiO₂ and a calculated mass fraction (5wt%) of metal precursor AgNO₃ was added into 50 mL deionized water, then the suspension was irradiated by a UV lamp (λ =365 nm) under continuous stirring. After 30 min photodeposition, the suspension was filtered, washed with deionized water and ethanol three times, and then dried at 30 °C for 24 h.

Synthesis of SAg-TiO₂

In a typical experimental procedure, 100 mg of the as-prepared TiO₂, a calculated mass fraction (5wt%) of metal precursor AgNO₃ and a certain amount of NaIO₃ were added into 50 mL deionized water, after stirred in the dark condition for 1h, then the suspension was irradiated by a UV lamp (λ =254 or 365 nm) under continuous stirring for different time (15, 30, 45, 60 min) at 0, 10 and 20 °C to find the optimum conditions. Subsequent processing was similar to that of the PAg-TiO₂. AgIO₃-TiO₂ power for XRD and DRS test was obtained as the same as SAg-TiO₂ but without UV lamp irradiation.

Material Characterization

X-Ray diffraction patterns (XRD) of the samples were performed by a Bruker D8 advance X-ray diffractometer using Cu K α radiation at room temperature and the scan rate of 2° min⁻¹ in the 2 θ range from 10° to 80°. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2100 FEF Field Emission Electron Microscope with its operating at an accelerating voltage of 200 KV. UV-vis diffuse reflectance spectra (DRS) were

recorded using a Shimadzu UV-3600 spectrometer by using $BaSO_4$ as a reference. The oxidation states of arsenic on the surfaces of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) which was operated on a VG Multilab 2000 spectrometer (Thermo Electron Corp.) with an Mg-K α X-ray source, and the spectra were calibrated to the C 1s peak at 284.6 eV. The photoluminescence (PL) spectra were obtained using a Jasco FP-6500 with λ exc=310 nm. The time-resolved photoluminescence (PL) spectra were recorded by a Multifunction Steady State and Transient State Fluo-rescence Spectrometer (FES920, Edinburgh Instruments) at 398 nm with 330 nm excitation at room temperature.

Photoactivity Test

The photoactivity were carried out by the degradation of RhB under visible light ($\lambda \ge 420$ nm) irradiation, The visible light was emitted by a 500 W, high-pressure xenon lamp (Changzhou Yuyu Electro-Optical Device Co., Ltd. China) equipped with a 420 nm cutoff filter to guarantee the needed irradiation light. Typically, the aqueous RhB-catalyst suspension was prepared in this way: A 30 mg catalyst was dispersed in 50 ml of aqueous suspension containing RhB dye (C₀= 10 mg/L), the suspension was sonicated for 5 min, then the mixture was stirred for 0.5 h in the dark to reach desorption-adsorption equilibrium before the irradiation. The suspensions were maintained under constant air-equilibrated conditions during irradiation. A 5 mL suspensions was drawn from the system at 15min interval during the experiment and centrifuged by TGL-16G centrifuge (Shanghai Anting Scientific Instrument Factory, China) at 10,000 rpm for 15 min to remove the catalyst particles. The upper clear liquid of RhB was analyzed on the basic of its characteristic optical absorption at 554 nm, using a Shimadzu UV-3600 spectrophotometer.



Fig. S1 TEM images of SAg-TiO₂ derived from different photoreaction conditions. (A) 365 nm light irridiation at 0° C; (B) 365 nm light irridiation at 10° C; (C) 365 nm light irridiation at 20° C; (D) 254 nm light irridiation at 10° C.



Fig. S2 UV-Vis diffuse reflectance spectra (DRS) of the $AgIO_3$ -TiO₂ power and the SAg-TiO₂ derived from different irradiation times.



Fig. S3 High-resolution XPS spectrum of SAg-TiO $_2$ (A) Ag 3d ; (B)I 3d



Fig. S4 (A) XRD patterns of AgIO₃-TiO₂ before {red line} and after {black line} irradiation by 365 nm light irradiation at 10°C for 30 min; (B) High-resolution XPS spectra of SAg-TiO₂ obtained by 365 nm light irradiation.



Fig.S5 Cycling degradation curve for for SAg–TiO₂ (1 nm).