

Supporting information

Constructing WO₃/TiO₂ composite structure towards sufficient use of solar energy

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Experimental Details:

Preparation of WO₃/TiO₂ colloids. Colloidal WO₃ and TiO₂ nanoparticles in acidic aqueous solution were prepared with sodium tungstate and titanium tetra-n-butoxide as precursors. WO₃ was synthesized according to the literatures.² Briefly, Na₂WO₄ (0.5790 g) was dissolved in 100 mL H₂O and bubbled with N₂ for 15 min. Then 2.0 mL concentrated HCl was added dropwise into the solution without stirring and the white precipitate was washed by water at 0 °C under N₂ atmosphere.

The preparation of TiO₂ colloid was based on our previous report.⁷ In a typical procedure, 3 mL titanium tetra-n-butoxide was dispersed in 25 mL absolute ethanol, and then the mixture was added dropwise into 30 mL water by dropping funnel under vigorous magnetic stirring. After complete addition by absolute ethanol washing, the suspension was heated to 70 °C while stirring for about 90 min. Then 70 mL HNO₃ solution was added to adjust the pH value (~ 1.0) and the mixture was kept on stirred at 70 °C for 4 h in airproof condition. For comparison, a series of colloidal WO₃/TiO₂ systems were obtained via three ways as follows.

(i) Physical mixture. The WO₃ precipitate was dissolved in hot acidic solution under sonication to form semitransparent colloidal suspensions at first. The solvent (oxalic acid) was replaced by acetic acid (30 %), which possesses relatively lower ionic strength and has less influence on the stability of TiO₂ colloid. After addition of TiO₂ colloid, the two types of semiconductor were mixed with each other via magnetic stirring.

(ii) Ultrasonic dispersion. The WO₃ precipitate was uniformly dispersed in the TiO₂ colloid under ultrasonication to form a colloidal mixture.

(iii) Composite structure. Stoichiometric ratio of titanium tetra-n-butoxide and Na₂WO₄ was dispersed in absolute ethanol. Thus the hydrolysis of Na₂WO₄ occurred accompanying with the peptization of amorphous TiO₂ in nitric acid medium. By varying the amount of Na₂WO₄, WO₃/TiO₂ nanocomposites with different molar percentage were produced and labeled with 4%, 8%, 16%, and 24% according to the nominal concentration of W.

Double-distilled water was used throughout the preparation of TiO₂ and the colloidal products were diluted to 100 mL in volumetric flask for further use.

Characterization of WO₃/TiO₂ composite. All powder samples were obtained by adjusting pH value to about 7.0 when the sedimentation of colloid occurred. Then the precipitation was collected by centrifugation, washing and vacuum drying at 60 °C for 6 h. Finally, the products were milled into fine powders. X-ray photoelectron spectroscopy (XPS) measurements were performed with PHI 5700 ESCA system (Physic Electronics) using a monochromatic Mg source (Mg K α 1253.6 eV, 200 W) and a standard peak of C1s (284.6 eV). Crystalline phases of the as-prepared powders were investigated by an X-ray diffraction method (XRD-6000 X-ray diffractometer (Shimadzu) with a Cu K α radiation source and a fixed power source (40 kV and 40 mA)). The samples were scanned over a range of 10-70°, which covers the main characteristic diffraction peaks of anatase TiO₂ and WO₃. The morphology of the colloid TiO₂ nanoparticles were directly examined using transmission electron microscopy (TEM, FEI Tecnai G2 T20 S-Twin) operating at an accelerating voltage of 200 kV. As further evidence, high-resolution transmission electron microscopy (HRTEM) was employed and the corresponding fast Fourier transform (FFT) was obtained by Gatan Digital Micrograph software (Gatan Inc., America).

Photocatalytic activity. Photocatalytic activities of samples were determined by the

decomposition rate of methylene blue (MB) dye in an aqueous solution. A high-pressure 100 W mercury (Hg) lamp and a 500 W halogen lamp (Institute of Electric Light Source, Beijing) were used as UV-light and Vis-light source. A Pyrex vessel was filled with circulating water to cool the reaction system. While reacting with target pollutants (MB) under halogen lamp, a cutoff filter was settled to completely remove any radiation below 420 nm and to ensure illumination by visible light. At given time intervals, the mixture was sampled to analyze by a TU 1900 UV-vis spectrophotometer (Puxi Inc., Beijing) equipped with 1 cm quartz cell. Changes of UV-vis absorption spectra as well as values of maximum absorption versus irradiation time ($A/A_0 \sim t$) were recorded, which reflected the decrease of dye concentration.

(1) UV pre-irradiation. 1 mL colloidal photocatalyst was diluted to 10.00 mL with water (pH ~ 2.0) and the mixture was irradiated for 4 h under UV-light.

(2) Comparison between dark reaction and visible photoactivity. After 4 h irradiation, 40 μ L 0.2% MB was added for degradation in the darkness (“dark reaction”, to evaluate the function of energy storage) or under halogen lamp with $\lambda \geq 420$ nm (“visible irradiation”, to evaluate the Vis-light photoactivity). The mixture was kept under constant air-equilibrated conditions before and during the irradiation.

(3) Lasting of visible photoactivity. Attenuation of the Vis-light photoactivity was examined by tracking the MB degradation at given residence time (t_r), which represented the period experienced in the darkness before reacting with MB dye. The value of t_r varied from 0 day to 10 days.

(4) Visible photoactivity with pre-irradiation by different UV/Vis proportion. Photocatalysts are pre-irradiated by mixed light (Hg lamp + halogen lamp) with fixed total intensity and UV/Vis proportion of 1/25, 1/12.5, 1/5, respectively. A 500 W Xenon (Xe) lamp was used for simulating solar light with UV/Vis of $\sim 1/15$ (about 3% UV and 44% Vis). The subsequent visible photoactivity measurements were conducted following the same method as above (with pure UV pre-irradiation).

Important experimental details of special labels in the photocatalytic reaction are listed and compared in Table S1.

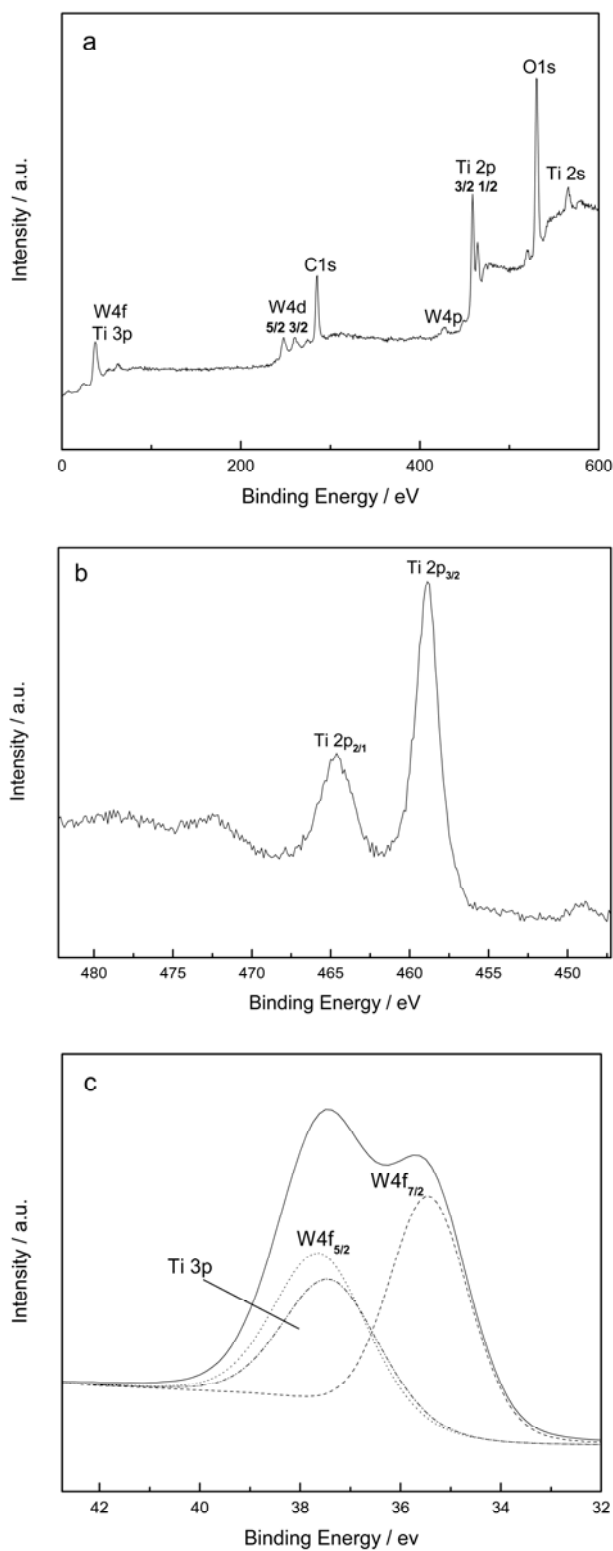


Fig. S1 (a) XPS survey spectrum of the 16 % WO₃/TiO₂ composite system; (b) High-resolution XPS spectrum of Ti 2p region; (c) simulated Gaussian line shapes in high-resolution spectrum of Ti 3p and W 4f regions.

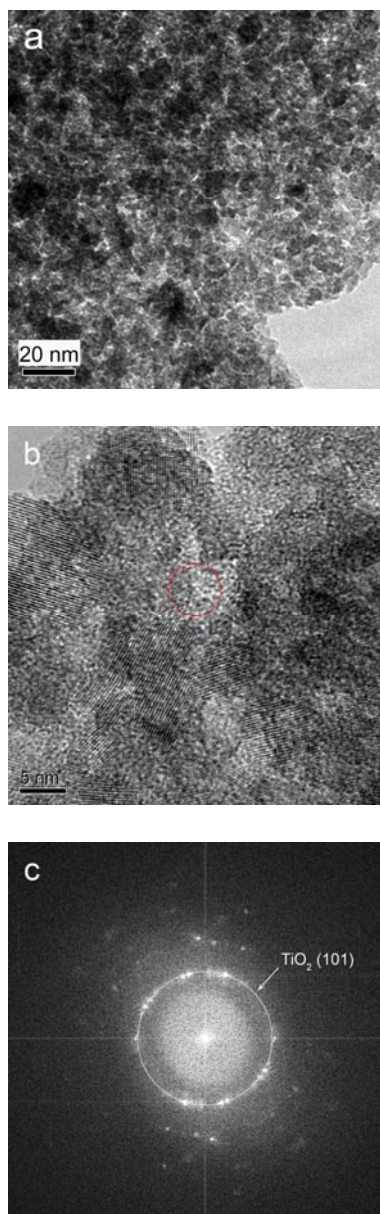


Fig. S2 (a) TEM image of 16% WO_3/TiO_2 nanocomposite at low resolution; (b) High-resolution TEM of 16% WO_3/TiO_2 nanocomposite. Amorphous WO_3 particles are indicated by red circle e; (c) The corresponding FFT pattern.

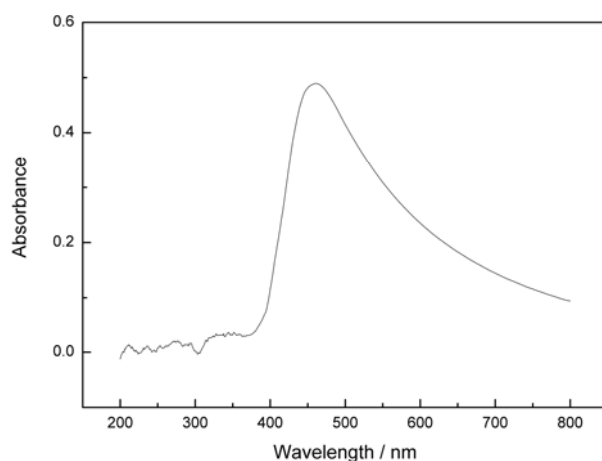
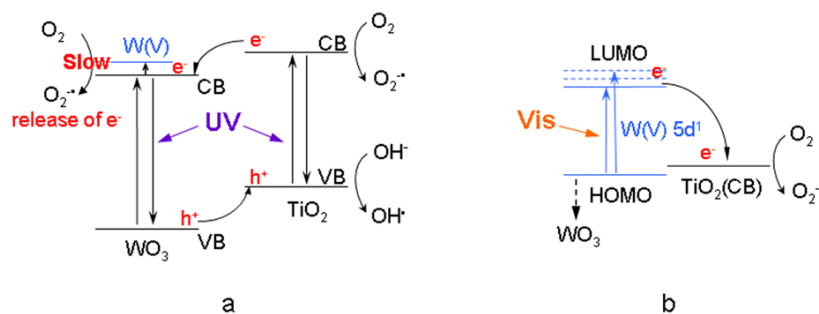


Fig. S3 Absorption spectrum of WO_3/TiO_2 composite colloid after 4 h UV-light irradiation. The reference solution is the pristine sample without UV-light pre-irradiation. Nominal concentration of Ti in the colloids, 8.81 mM; pH~1.0.



Scheme S1 Scheme of electron transfer between WO_3 and TiO_2 under UV pre-irradiation (a) and the subsequent visible irradiation (b).

Table S1 Comparison of experimental details in the photocatalytic reaction.

| process | I. pre-irradiation | | II. energy release in the darkness | III. photocatalysis under visible light |
|--|-----------------------------------|-----------------------------------|---------------------------------------|--|
| | UV light | UV/Vis mixed lights | | |
| dark reaction | WO ₃ /TiO ₂ | -- | adding MB dye for degradation | -- |
| visible irradiation | WO ₃ /TiO ₂ | -- | -- | adding MB dye for degradation |
| visible irradiation with given t_r (residence time)* | WO ₃ /TiO ₂ | -- | experiencing in the darkness | adding MB dye for degradation |
| mixed lights pre-irradiation | -- | WO ₃ /TiO ₂ | -- | adding MB dye for degradation |

*Three parallel experiments are conducted for comparison, including natural attenuation, N₂ gas protection, and UV re-irradiation. Experiment of N₂ gas protection is introduced to remove the dissolved O₂ to delay energy release in process II. And that of UV re-irradiation is operated by repeating process I after process II.

Table S2 WO₃ molar percentage of as-prepared samples.

| sample | WO ₃ (mol %) | |
|--------|-----------------------------|-----------------------------|
| | N ₁ ^a | N ₂ ^b |
| 1 | 8% | 6.5% |
| 2 | 16% | 11.9% |
| 3 | 24% | 16.1% |

^a N₁ as nominal value. ^b N₂ as value measured by XPS.