Microwave-Assisted Deposition of Metal Sulfide/Oxide Nanocrystals onto 3D Hierarchical Flower-Like TiO_2 Nanostructure with Improved Photocatalytic Activity

Liyuan Mao,[a] Yanrong Wang,[a] Yijun Zhong,[a] Jiqiang Ning [b] and Yong Hu*[a]

Experimental Section

Synthesis of hierarchical flower-like TiO_2 nanostrucutres:

In a typical experimental procedures, 2 mL of 0.17 M $Ti(SO_4)_2$ and 3 mL of 0.27 M NaOH stock solution in distilled water were mixed with 35 mL of EG under magnetic stirring for 10 min, forming a clear solution. Then, the resulting mixture was transferred into a 50 mL of Teflon-lined stainless steel autoclave and heated at 180 °C for 10h. After collection by centrifugation, the products were washed with ethanol and distilled water three times before being dried at 60 °C for 8 h. The final pure TiO_2 nanoflowers were obtained after calcination of the above samples at 450 °C in static air for 3 h.

Synthesis of TiO_2-based metal sulfide/oxide hetero-nanostructures:

In a typical synthesis, 0.1 mmol of metal salt ($CdCl_2 \cdot 2.5H_2O$, $ZnCl_2$ or $Ce(NO_3)_3 \cdot 6H_2O$) was added into a round bottom flask and dissolved in a solvent of 20 mL of water to form a clear solution with the assistance of ultrasonication. Then, 30 mg of the as-prepared pure TiO_2 nanoflowers were added and well dispersed into the above solution under vigorous stirring at 60 °C for 3h. To obtain TiO_2-CdS (ZnS) hetero-nanostructures, 0.3 mmol of TAA was added into the above solution and then placed in a microwave refluxing system and irradiated at 300 W for 30 min. For TiO_2-ZnO (CeO_2) hetero-nanostructures, 0.5 mmol of HMT was added before microwave irradiation. The final products were collected and washed by ethanol and

distilled water for several times, and dried in an oven at 60 °C for 4h.

Characterization:

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using Cu Kα radiation at a scanning rate of 0.06 deg s^{-1}. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted at 200 kV with a JEM-2100F field emission TEM. Samples for TEM measurements were prepared for TEM by dispersing the products in ethanol and placing several drops of the suspension on holey carbon films supported by copper grids. UV-vis diffuse reflectance spectra (UV-vis DRS) of the as-prepared samples were recorded over the range of 200-800 nm in the absorption mode using a Thermo Nicolet Evolution 500 UV-vis spectrophotometer equipped with an integrating sphere attachment. The absorption spectra were measured using a PerkinElmer Lambda 900 UV-vis spectrophotometer at room temperature.

Photocatalytic test:

Photocatalytic activities of TiO_2-CdS hetero-nanostructures were evaluated by the photodegradation of MO under visible-light irradiation using a 500 W Xe lamp with a 420 nm cutoff filter. The reaction cell was placed in a sealed black box with the top opened and the cutoff filter was placed to provide visible-light irradiation. In a typical process, 20 mg of the photocatalyst was added into 20 mL of MO solution (5 mg L^{-1}). After being dispersed in an ultrasonic bath for 5 min, the solution was stirred for 2 h in the dark in order to reach adsorption equilibrium between the catalyst and the solution and was then exposed to visible-light irradiation. The photocatalysts were

removed by centrifugation at given time intervals, and the MO concentration was measured colorimetrically at 464 nm using the UV-vis spectroscopy.

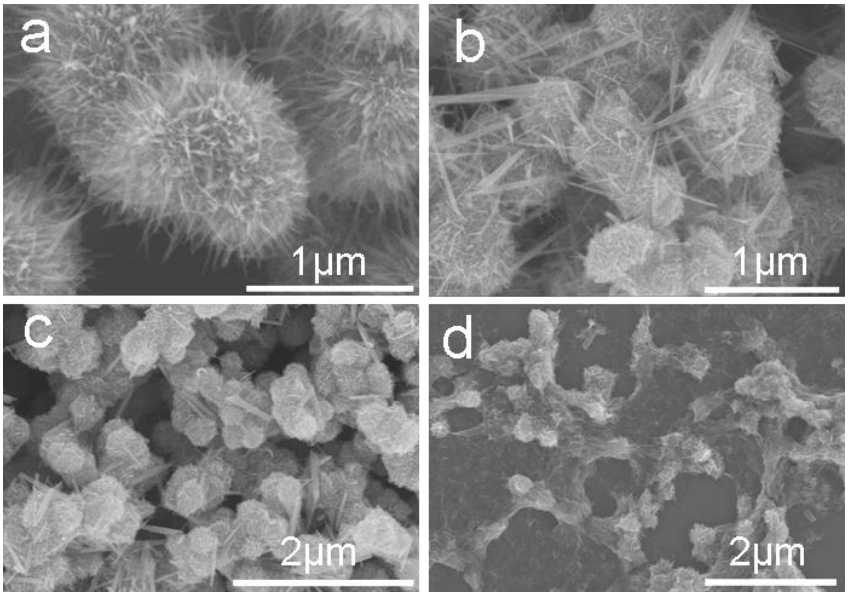


Fig. S1. SEM images of the as-prepared TiO_2 nanostructures synthesized with different volumes of EG added in reaction system: (a) 30 mL, (b) 20 mL, (c) 10 mL, (d) 0 mL.

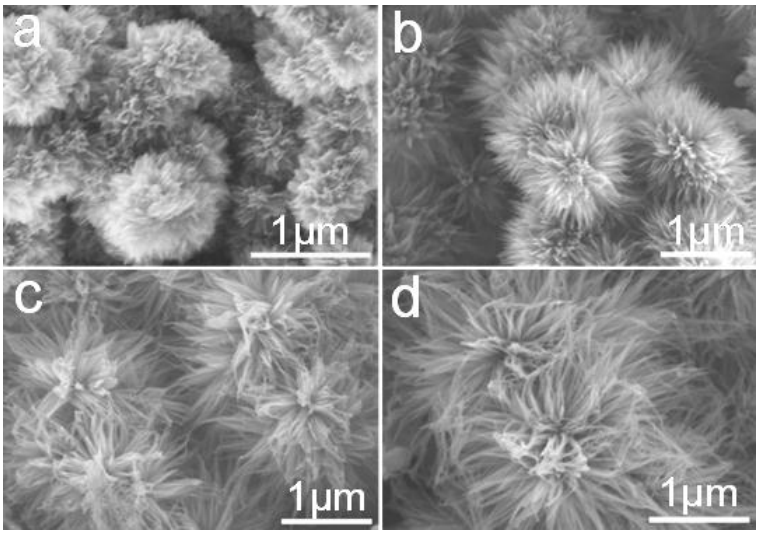


Fig. S2. SEM images of TiO_2 nanostructures obtained after different reaction durations: (a) 2, (b) 8, (c) 12, (d) 24 h.

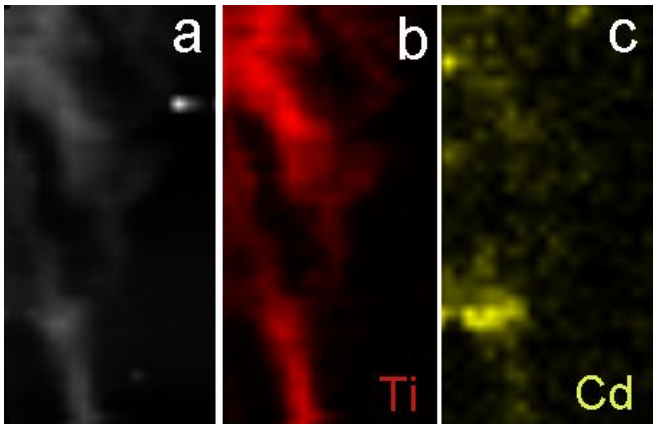


Fig. S3 (a) TEM image of a section of TiO_2-CdS hetero-nanostructures, and the elemental mapping EDS images of Ti (b) and Cd (c).

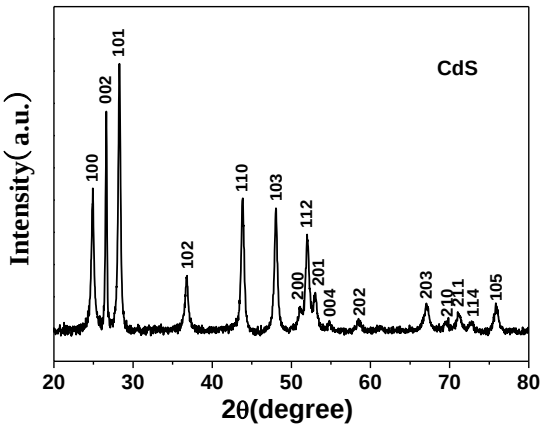


Fig. S4. XRD patterns of the pure CdS via a microwave-assisted method (JCPDF card no. 41-1049).

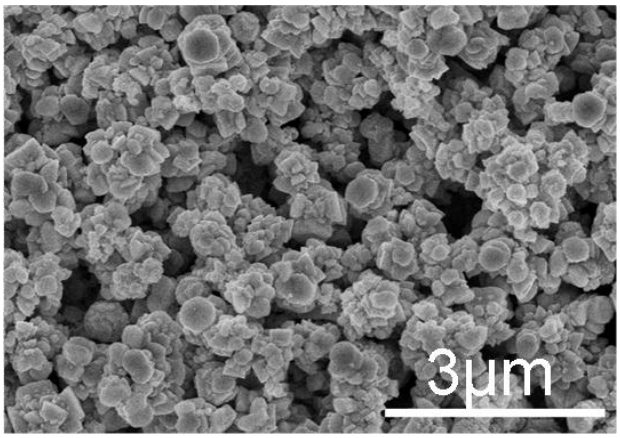


Fig. S5 SEM image of pure CdS via a microwave-assisted method.

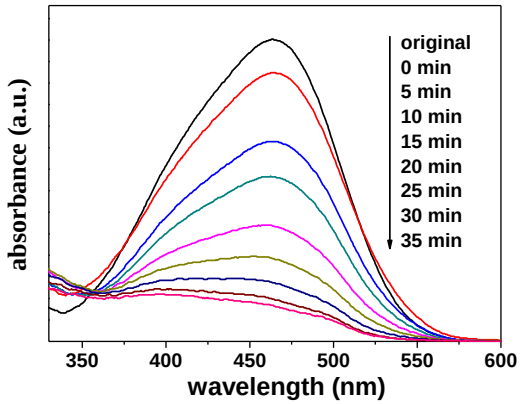


Fig. S6 The absorption spectra of the MO solution at different exposure time using the as-prepared TiO_2-CdS hetero-structures as catalyst under visible-light irradiation.

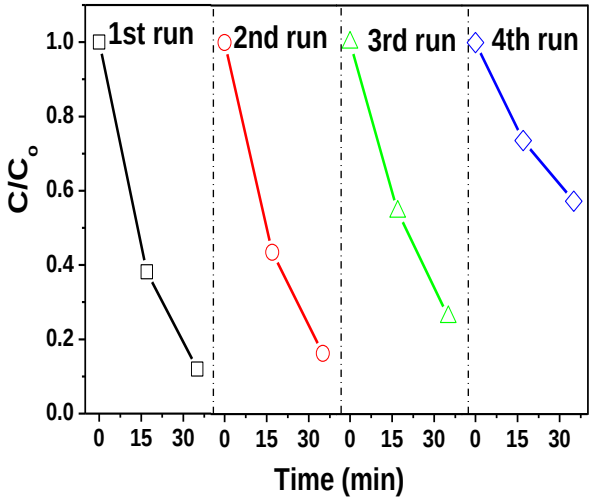
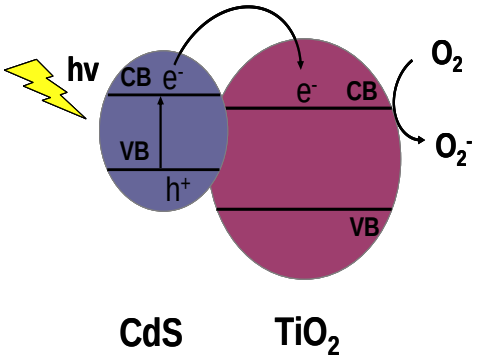


Fig. S7 4 cycles of photodegradation of MO using the as-prepared TiO_2-CdS hetero-nanostructures.



Scheme S1 Schematic diagram representing the charge-transfer process in the TiO_2-CdS hetero-nanostructures.