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Supporting Information

Construction of TiO_2-MnO_2 0D-2D nanostructured heterojunction for enhanced photocatalytic hydrogen production

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Experimentation

1. Synthesis of TiO_2-MnO_2

The TiO_2 nanoparticles were synthesized by a standard sol-gel approach. Typically, tetrabutyl titanate ($Ti(OC_4H_9)_4$, 98%, 5 mL) was slowly added into 20 mL of anhydrous ethanol (C_2H_5OH) under stirring. Then, 0.75 mL of hydrochloric acid (HCl, 36.0~38.0%) solution was added into the mixed solution. Finally, 10 mL of the mixed deionized water and C_2H_5OH solution (1:1, V/V) was added dropwise under continuously stirring for 1 h to obtain sol. The resultant sol was dried at 180 ºC for 4 h in an oven and the brown powders were obtained. The powders were rinsed by water and ethanol, centrifuged at 10,000 g for 4 min, dried at 80 ºC for 4 h, and grounded in a mortar. According to our previous work, the size of the TiO_2 particles was not uniform. The nanoparticles with 5-20 nm size were purified and used in this work. For fine interaction, the TiO_2 nanoparticles were annealed at 180 ºC for 4 h in flowing N_2 (30 sccm, purity >99.999%).

The MnO_2 nanosheets were synthesized by the chemical co-deposition technique. First, 1.0 g of potassium permanganate ($KMnO_4$, 99.9%) was dissolved in 500 mL of deionized water under stirring. Then, 500 mL of anhydrous ethanol (C_2H_5OH) was added dropwise under continuous stirring for 2 h. Finally, the precipitation was collected by suction filtration and washed repeatedly by water and ethanol, dried at 80 °C for 12 h and grounded in a mortar to obtain the powdered sample.

MnO_2 powder (0.16 g) was added into 40 mL deionized water and ultrasonic treatment for 0.5 h and then 0.25 g TiO_2 was added into the solution. The mixture solution was ultrasonic for 1 h. The mixture was then dried under 80 °C and heated at 300 °C for 4 h. The obtained composite was denoted as TiO_2-MnO_2.

For photoelectrochemical (PEC) characterizations, the powders were fabricated into film-like electrodes by a doctor blade method using fluorine-doped tin oxide (FTO) as substrate (Adv. Energy Mater. 4 (5) (2014) 1300995). The working geometric surface area was fixed to 0.16 cm^2. Briefly, 0.3 g TiO_2-MnO_2 nanocomposite powder was dispersed in isopropyl alcohol (0.5 mL). Then, macrogol-6000 (0.05 g) was added to the system, and finally, 0.05 mL acetylacetone was added. After each operation, the mixture treated by an ultrasonic process for 30 min and stirring for 30 min. The last step includes continuously stirring for 24 h to make the solution uniform. FTO glasses pieces (1.0 cm × 1.5 cm) were used as the substrates for the sample films. Before coating the active films, the FTO substrates were pre-cleaned by sonicating in acetone, ethyl alcohol and deionized water for 30 min, successively. Sample films were prepared by a doctor blade method using scotch tape as the spacer. Following drying in the air for 24 h, then the films were sintered at 300 °C for 4 h followed by furnace cooling. The working geometric surface area of the sample film was approximately 0.4 cm × 0.4 cm, where the remaining area was covered with epoxy resin.

2. Characterization

X-ray diffraction (XRD) patterns of all samples were collected in the 2θ range of 20-80° using a Philips X' Pert-PRO diffractometer (Cu Kα 0.154056 nm), operated at 40 kV and 100 mA. Raman spectra were collected on a Fourier transform infrared-Raman spectrometer (HR800, Jobin Yvon, France). The morphologies were characterized by transmission electron microscopy (TEM, JEOL JEM 2100F). The instrument employed for X-ray photoelectron spectroscopy (XPS) studies was a Kratos AXIS Ultra DLD XPS instrument with Al Kα radiation operated at hv = 1486.6 eV. The energy levels were evaluated by using ultraviolet photoelectron spectroscopy (UPS, Kratos AXIS Ultra DLD). A gas discharge lamp was used for UPS, with helium gas admitted and the He (I) (hv = 21.22 eV) emission line employed. The optical absorption spectra of the samples were measured using a UV-vis-NIR Spectrophotometer (HITACHI, U-3900H, Japan) with the FTO substrate as the reference.

3. Photoelectrochemical Measurements

All the PEC properties were measured under a three-electrode system equipped with a quartz window to facilitate illumination of the sample surface. The electrolyte was 50 mL of 0.5 M sodium sulfate. A 550 W Xe lamp with an AM 1.5 G filter was used as the simulated solar illumination in the PEC characterization step. The incident light intensity was calibrated to 100 mW cm^{-2} via standard silicon solar cells. The thin film served as a working electrode, a piece of platinum gauze and an Ag/AgCl (Saturated KCL) was used as counter electrode and reference electrode, respectively. The working electrode was exposed to an electrolyte with an actual geometric area of 0.16 cm^2. All the electrochemical measurements were performed at room temperature on an electrochemical workstation (RST5200, Zhengzhou Shiruisi Instrument Technology Co., Ltd., China). The photocurrent was measured with a scan range from -0.8 V to 1.8 V (vs. Ag / AgCl). The amplitude and applied bias during the electrochemical impedance (EIS) measurements were 10 mV and 1.0 V vs. Ag/AgCl.

4. Photocatalytic activity evaluation

H_2 production activity of the samples was characterized under simulated sunlight illumination. The hydrogen generation rates of the samples were estimated in a LabSolar-III-AG inline hydrogen production system equipped with a gas chromatograph. Before photoreactions, the system was completely degassed to remove O_2 and CO_2. For the half-reaction, 80 mL DI water and 20 mL methyl alcohol were used for photocatalytic H_2 production. A 300 W Xe lamp was used as the light source.

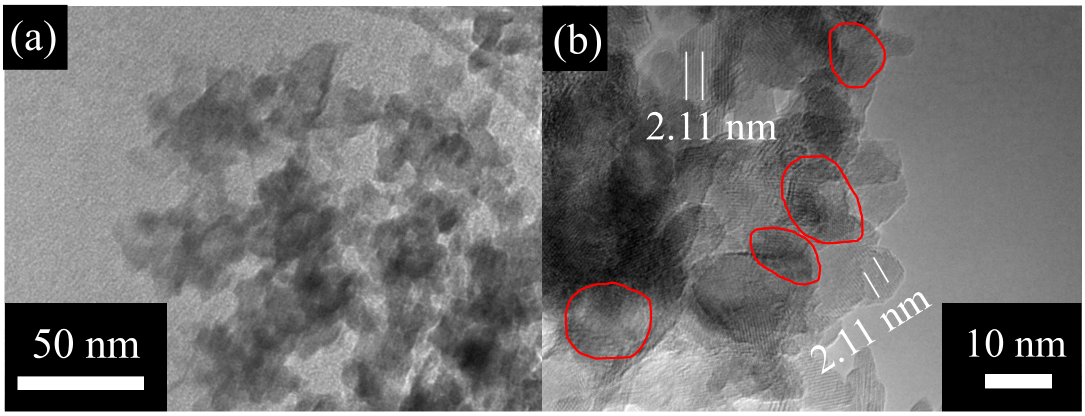

Figure S1: (a) The TEM images of TiO_2-MnO_2 powders. (b) The HRTEM images of TiO_2-MnO_2 powders.

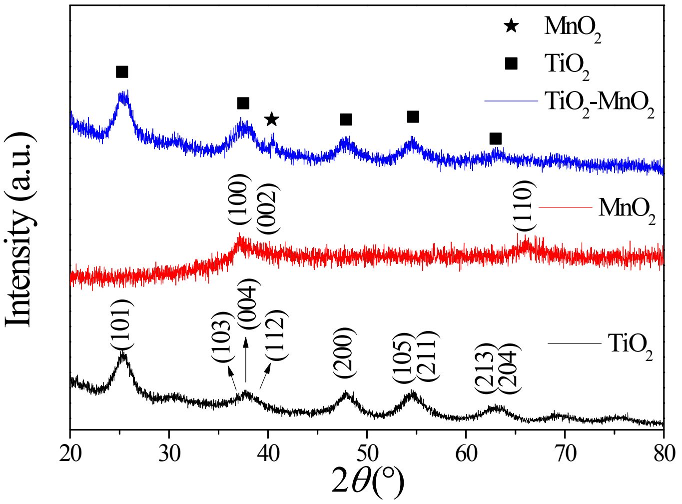

Figure S2: X-ray diffraction (XRD) patterns of TiO_2, MnO_2 and TiO_2-MnO_2 powders.

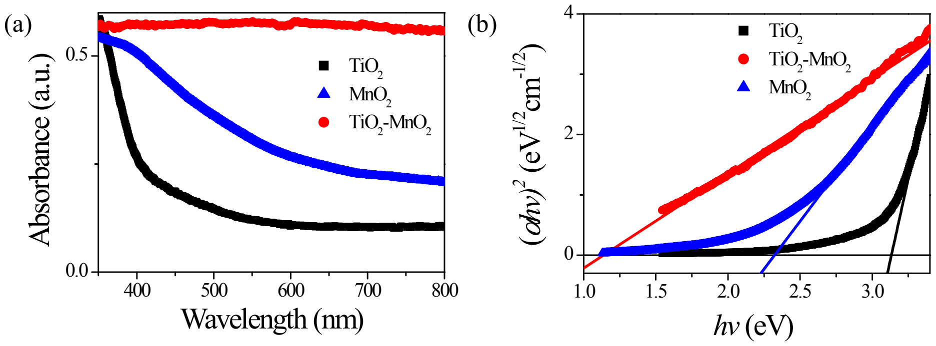

Figure S3. UV-visble absorption spectra (a) and plots of the band gap energy (b) of TiO_2, MnO_2 and TiO_2-MnO_2 powders.