Supplementary material

Hierarchical Z-scheme 1D/2D architecture with TiO$_2$ nanowires decorated by MnO$_2$ nanosheets for efficient adsorption and full spectrum photocatalytic degradation of organic pollutants

Jiejing Zhang,[1a] Yajie Hu,[1a] Hong Zheng [*a] and Pengyi Zhang [*b]

a Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China
b State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

[1] The first coauthors

* Corresponding authors.

Tel.: +86 10 82322974 (H. Zheng), +86-10-62796840-601 (P. Zhang)
Fax: +8610 82322974 (H. Zheng), +86-10-62796840-602 (P. Zhang)
E-mail addresses: zhengh@cugb.edu.cn (H. Zheng), zpy@tsinghua.edu.cn (P. Zhang)

1. Experimental section

1.1 Preparation of the samples

TiO$_2$ nanowires were synthesized using a hydrothermal method reported by Pan et al. [1] with a small modification. Typically, after 2.4 g P25 nanoparticle powders were added into 80 mL of 10 M KOH aqueous solution and stirred for 30 min until a homogeneous suspension was gained. The suspension was transferred to a Teflon-lined stainless-steel autoclave (100 mL) and the autoclave was kept at 200 ℃for 24 h. The obtained products were successively washed with 0.1 M HCl aqueous solution for several times until the pH was about to 7, and then they were immersed in 0.1 M HCl aqueous solution and kept for 5 min under continuous stirring. Then the precipitate was immediately washed with deionized water for some times until the pH value was equal to 7. After being recovered by vacuum filtration, the product was dried at 70 ℃ for 6 h, then heated at the heating rate of 5 °C/min and kept at 550 ℃ for 2 h in a muffle furnace.

The MnO$_2$ nanosheets were hydrothermally fabricated using the method reported by Rong et al. [2]. Briefly, 20 mmol of KMnO$_4$ and 10 mmol of $(NH_4)_2C_2O_4 \cdot H_2O$ were fully dissolved in 70 mL deionized water under vigorous magnetic stirring. Subsequently, the above mixture solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and the autoclave was kept at 90 ℃ for 24 h. After the autoclave cooled down naturally to room temperature, the precipitates were collected by centrifugation, and washed with deionized water for several times and then dried at 105 ℃. Before being used to prepare the composite, the precipitates were added into deionized water and sonicated for 3 h and the MnO$_2$ nanosheets sol were obtained.

1.2 Characterization of the samples

The X-ray diffraction (XRD) measurements were performed by a Bruker D8 advance diffractometer with Cu Kα radiation (λ= 0.15418 nm) at 40 kV and 100 mA. The Raman spectra were collected on a laser confocal Raman spectrometer (Invia, Renishaw, UK) with 2 cm^{-1} acquisition resolution, using Ar$^+$ laser (532 nm) as the excitation light source. SEM image of the as-prepared composite was observed on a ISM-IT300 scanning electron microscope of Japan Electronics Co., Ltd. The morphology of TiO$_2$ nanowires was recorded on a JSM-7001F field-emission scanning electron microscopy (FESEM, Japan) operated at 10.0 kV. TEM image of MnO$_2$ nanosheets was obtained on a Hitachiht 7700 transmission electron microscope (TEM) operated at 100kV. The high resolution transmission electron microscopy (HRTEM) image of the as-prepared composite was obtained on a JEM-2011F field emission transmission electron microscopy (JEOL, Japan) with an accelerating voltage of 200 kV. The surface elemental composition and chemical states of all samples were examined by an X-ray photoelectron spectrometer (ESCA PHI-5300 XPS) with a pass energy of 50 eV and an X-ray excitation source of Al Kα. The values of binding energies were calibrated with respect to C1s peak at 284.80 eV. The light absorption properties of the samples were observed by UV–visible diffuse reflectance spectra (UV–vis DRS) through a Hitachi UV-3100 UV-Vis spectrophotometer. N$_2$ adsorption-desorption data of the samples were obtained at 77.35 K using a Quantachrome ASIQM0002-4 BET analyzer. And their pore size distribution was acquired from the N$_2$-desorption branch using the BJH method. The FT-IR spectra were acquired on a PerkinElmer Frontier infrared spectrometer to determine the content of RhB on the composite surface. The spectral range was recorded from 4000 cm^{-1} to 400 cm^{-1} by the KBr pellet technique. Photoluminescence (PL) spectroscopy was collected on a Hitachi F-4600 florescence spectrophotometer with the excitation 300nm. Electrochemical impedance spectroscopy (EIS) were collected under visible light and ultraviolet light irradiation via an electrochemical analyzer (CHI760E, China) in the standard three-electrode system using as-prepared samples as the working electrode, a silver chloride electrode as reference, a platinum wire parallel as a counter electrode and 0.1 M sodium sulfite as electrolyte. Electronic spinning resonance (ESR) signals were obtained on the Japanese electron JES-FA200 ESR spectrometer using 5,5-Dimethyl-l-pyrroline N-oxide (DMPO) as trapping agent in aqueous suspension solution and dimethyl sulfoxide suspension solution. Mott-Sckottky spectroscopy were obtained by an a electrochemical analyzer (CHI660B, China) to determine the flat-band potential of working electrodes (pristine TiO$_2$ nanowires and

sole MnO_2 nanosheets) in a standard three-electrode configuration with a Pt wire, Hg/Hg_2Cl_2 (in saturated KCl) and Na_2SO_4 (0.1 M) as the counter electrode, a reference electrode and aqueous solution electrolyte, respectively, in darkness.

Table S1 S_{BET} of pristine TiO_2 nanowires, sole MnO_2 nanosheets and the composite

Samples	TiO_2	MnO_2	Composite
S_{BET} (m^2/g)	54.3	116.4	130.9
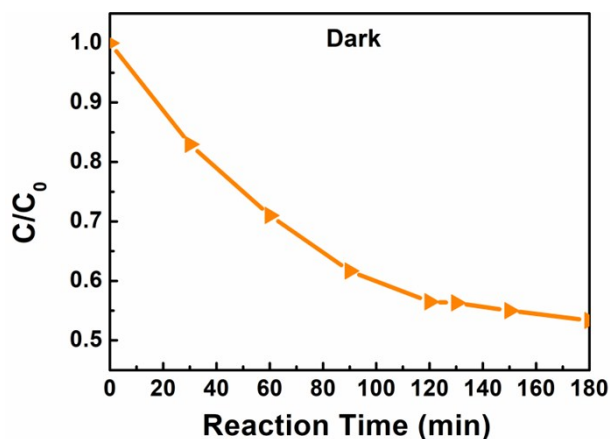
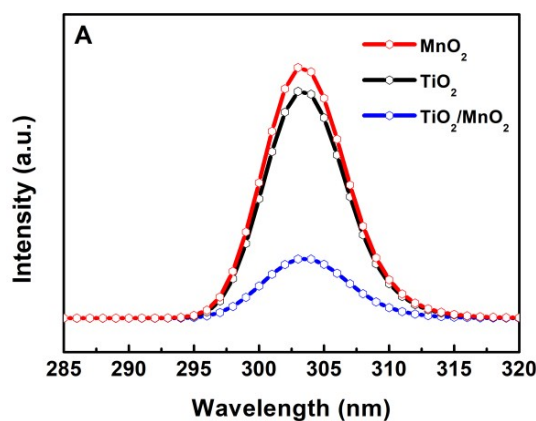Fig. S1 The adsorption of RhB by the as-prepared composite.
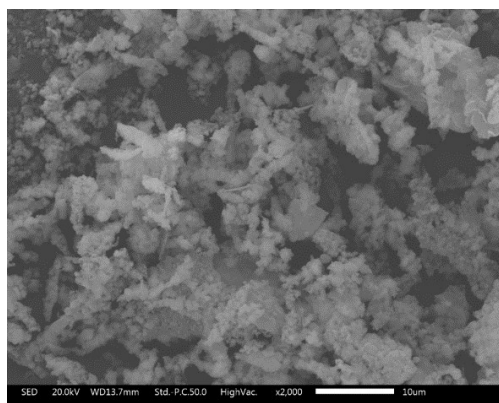
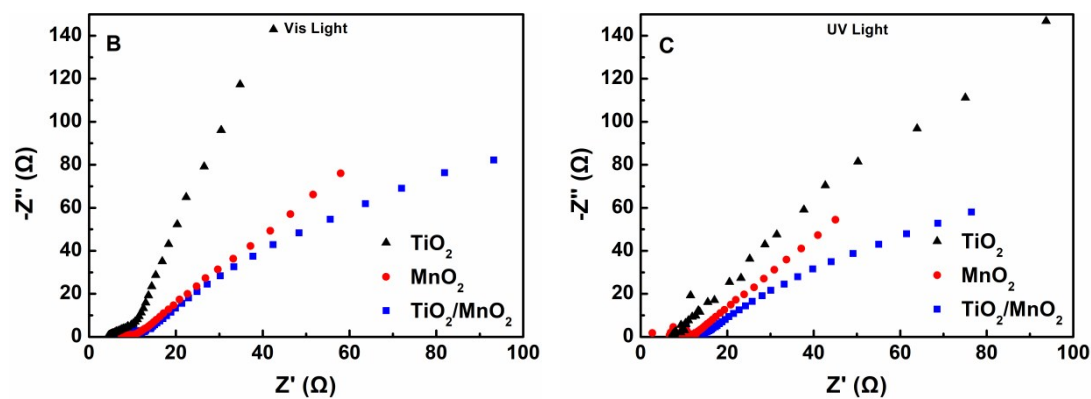Fig. S2 The SEM images of the composite after the cycle test under visible light irradiation.

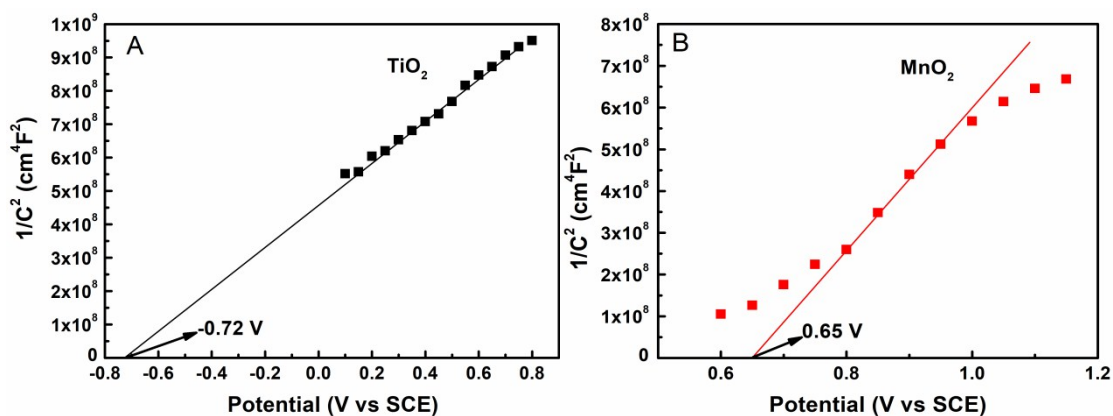Fig. S3 PL (A) and EIS spectra of the samples under visible (B) and UV light (C) irradiation.

Fig. S4 Mott−Schottky plots for (A) TiO_2 nanowires and (B) MnO_2 nanosheets.

References

1. X. Pan, Y. Zhao, S. Liu, C. L. Korzeniewski, S. Wang and Z. Y. Fan, *ACS Appl. Mater. Inter.*, 2012, **4**, 3944−3950.
2. S. P. Rong, K. Z. Li, P. Y. Zhang, F. Liu and J. Y. Zhang, *Cataly. Sci. Technol.*, 2018, **8**, 1799−1812.