Electronic Supplementary Information

A Novel Phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ Heterogeneous Nanorod for High Efficiency Photocatalytic Hydrogen Production

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Experimental Section

Preparation for the phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ heterogeneous particles: Pure MgTiO$_3$ and MgTi$_2$O$_5$ were purchased form Aldrich. All the chemicals were analytical-grade and used without further purification. In typical synthesis of phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ particles, commercial MgTiO$_3$ and MgTi$_2$O$_5$ particles with molar ratio 1:1 were dispersed in 50 mL of 0.01 M phosphoric acid aqueous solution with magnetic stirring at room temperature (about 25 °C) for 12 h and then centrifugalized and dried at 60 °C for 4 h. The dry white powder was calcined at 400°C for 2 h to obtain phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ nanoparticles. Phase-pure MgTiO$_3$, MgTi$_2$O$_5$ and phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ nanoparticles were donated to MT, MDT and MT-MDT, respectively. MT&MDT indicated sample of mechanically mixed and 400 °C calcined with a 1:1 ratio of MgTiO$_3$ and MgTi$_2$O$_5$.

Fabrication of phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ heterogeneous nanorods: Magnesium acetate (Mg(CH$_3$COO)$_2$).4H$_2$O and tetra-n-butyl titanate (Ti(OC$_4$H$_9$)$_4$) with different molar ratio were dissolved in 60 mL ethylene glycol (EG) to form a clean solution, then the solution was stirred at room temperature (about 25 °C) for about 10 min, a white precipitation appeared and increased gradually. The stirring was continued 1 h to ensure the complete reaction. The white precipitation was recovered and purified by centrifugation three times and redispersion cycles with ethanol, and dried under vacuum at 60 °C for 4 h. Finally, the white precipitation was calcined at 600 °C for 2 h in air to obtain the phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ heterogeneous nanorods.

Photocatalytic hydrogen production: The photocatalytic hydrogen production experiment was conducted in an online photocatalytic hydrogen production system (AuLight, Beijing, CEL-SPH2N) at ambient temperature (20 °C). 0.1 g catalyst was suspended in a mixture of 80 mL distilled water and 20 mL methanol in the reaction cell by using a magnetic stirrer. 1 wt.% Pt loaded photocatalysts were prepared by known standard method of in-situ photodeposition method.
using $\text{H}_2\text{PtCl}_6$ aqueous solution. Prior to the reaction, the mixture was deaerated by evacuation to remove $\text{O}_2$ and $\text{CO}_2$ dissolved in water. The reaction was carried out by irradiating the mixture with UV light from a 300 W Xe lamp with a 200-400 nm reflection filter which means the wavelength of light is approximately 200-400 nm. Gas evolution was observed only under photoirradiation, being analyzed by an on-line gas chromatograph (SP7800, TCD, molecular sieve 5 Å, $\text{N}_2$ carrier, Beijing Keruida Limited).

The determination of the apparent quantum efficiency for hydrogen generation was performed using the same closed circulating system under illumination of a 300 W Xe lamp with bandpass filter (313, 365 and 420 nm) system. The light intensity was measured using a Si photodiode (oreal 91105V). The total light intensities were 11.3 mW·s$^{-1}$ (313 nm), 7 mW·s$^{-1}$ (365 nm), and 1.5 mW·s$^{-1}$ (420 nm). The irradiation area was around 7 cm$^2$. Apparent quantum efficiency (AQE) at different wavelengths was calculated by the following equation.

$$
\text{AQE} = \frac{2 \times \text{the number of evolved } H \text{ molecules}}{\text{the number of incident photons}} \times 100\%
$$

**Characterization:** X-ray powder diffraction (XRD) patterns were obtained by Bruker D8. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument operating at 15 KV. The transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. Raman measurements were performed with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The laser beam was focused with a 50 × objective lens to a ca. 1 μm spot on the surface of the sample. The pyrolysis experiments of phase-mixed $\text{MgTiO}_3/\text{MgTi}_2\text{O}_5$ heterostructure nanorods precursor were carried out in TG (TA, Q600) under a stream of air at a heating rate of 10 °C min$^{-1}$. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method using a Tristar II 3020 surface area and porosity analyzer (micromeritics). UV-visible absorption spectroscopy was recorded using a UV-visible spectrophotometer (SHIMADZU UV-2550). The surface photovoltage spectroscopy measurement was carried out with a home-built apparatus which was described elsewhere.$^1$ The valence-band spectra were examined by X-ray Photoelectron Spectroscopy (XPS) using a Kratos-AXIS ULTRA DLD apparatus with Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious
carbon (binding energy = 284.6 eV). The X-ray absorption data were recorded at room temperature in transmission mode by using ion chambers or in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (111) double-crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150 and 210 mA. The photon energy was calibrated with Ag metal foil. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTEMIS. The beamline covered an energy range from 100 to 1000 eV, with an energy resolution at 0.2 eV.


Figure S1. The crystal structure and the band gap of MgTiO₃ (A, B) and MgTi₂O₅ (C, D). The calculations were performed within the framework of density functional theory (DFT) framework embedded in the CASTEP code. The exchange-correlation energy is treated with generalized gradient approximation (GGA), using spin-polarized Perdew-Burke-Ernzerhof (PBE) functional.
Figure S2. The UV-vis diffuses absorbance spectra, valence-band XPS and illustration of charge transfer cross the heterogeneous phase junction of MgTiO$_3$ and MgTi$_2$O$_5$.

Figure S3. SEM images of commercial MgTiO$_3$ (A) and MgTi$_2$O$_5$ nanoparticles (B) and their photocatalytic hydrogen production activity (C).
Figure S4. HRTEM image of phase-mixed MgTiO₃/MgTi₂O₅ heterogeneous nanoparticles.

Figure S5. H₂ production activity of MgTiO₃ (MT), MgTi₂O₅ (MDT), phase-mixed MgTiO₃/MgTi₂O₅ heterogeneous particles (MT-MDT) and mechanically mixed sample with a 1:1 ratio of MgTiO₃/MgTi₂O₅ (MT&MDT).
Figure S6. Raman spectra of pure MgTiO$_3$ (MT) and MgTi$_2$O$_5$ (MDT).

Figure S7. SEM images of phase-mixed MgTiO$_3$/MgTi$_2$O$_5$ nanorods precursor. R-MT-1 (A), R-MT-2 (B) and R-MT-3 (C).

Figure S8. XRD pattern (A) and FT-IR curve (B) for the precursor of R-MT-2.
Figure S9. TG curve of the precursor of R-MT-2.

Figure S10. SEM images of the crashed R-MT-2 with low (A) and high magnification (B). (the sample is crashed by milling using a agate mortar)

Figure S11. UV-vis spectra of MT, R-MT-1, R-MT-2, R-MT-3 and MDT.
Figure S12. Nyquist plots in the three-electrode system of MT, MDT, MT-MDT and R-MT-2 electrodes in 0.5 M Na₂SO₄ solution, Ag/AgCl reference electrode and Pt foil as counter electrode in dark (A) and under AM 1.5 irradiation (100 mW/cm²) (B). EIS was performed in the frequency range between 1 MHz and 10 mHz with an ac voltage amplitude of 10 mV at a DC bias of 0 V. The impedance spectra were interpreted by a nonlinear least squares fitting procedure using commercial software (ZsimpWin).

Figure S13. Transient photocurrent responses of MT, MDT, MT-MDT and R-MT-2 electrodes in 0.5 M Na₂SO₄ solution, Ag/AgCl reference electrode and Pt foil as counter electrode at a potential of 0.2 V.
Figure S14. The N\textsubscript{2} adsorption-desorption isotherms and the corresponding BJH pore-size distribution plots (inset) of R-MT-1, R-MT-2 and R-MT-3.

Figure S15. TEM images of R-MT-1 (A) and R-MT-3 (B).

Figure S16. PHP activity of R-MT-2 and broken R-MT-2.
Figure S17. The selected area electron diffraction (SAED) of R-MT-2.