

Electronic Supplementary Information (ESI)

Hydrogenated titania: synergy of surface modification and morphology improvement for enhanced photocatalytic activity

Zhaoke Zheng,^a Baibiao Huang,^{*a} Jibao Lu,^b Zeyan Wang,^a Xiaoyan Qin,^a Xiaoyang Zhang,^a Ying Dai,^b and Myung-Hwan Whangbo^c

^a *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China,*

^b *School of Physics, Shandong University, Jinan 250100, China*

^c *Department of Chemistry, North Carolina State University, Raleigh, USA*

E-mail: bbhuang@sdu.edu.cn

Experimental Details

Preparation. H-TiNT microspheres were prepared using the alkali hydrothermal method described in our previous report.¹ In a typical procedure, 5.1 g Ti(OBu)₄ was mixed with 75 mL absolute ethanol under vigorous stirring. After that, 0.33 mL sulfuric acid (98%) and 0.3 mL deionized water was added. The resulting solution was transferred in a dried Teflon autoclave, and then kept at 180 °C for 4 h. After being cooled to room temperature, the white precipitate was collected, washed with ethanol for several times, and dried at 40 °C. 0.5 g of the precipitate were mixed with 50 mL of 10 M NaOH aqueous solutions, followed by hydrothermal treatment at 150 °C in a Teflon autoclave for 24 h. Then the filtered sample was dispersed into 600 mL of 0.1 M HCl aqueous solution for 12 h, and washed thoroughly with deionized water. The powder was collected and dried at 60 °C to give the H-TiNT microspheres.

Preparation of hydrogenated TiO₂ (TiO₂-H) nanowire-microspheres. The as-prepared H-TiNT microspheres were transferred to a quartz boat located at the

center of a quartz tube, which was horizontally placed in a tubular furnace. Then the mixture was heated to 500 °C at a rate of 5 °C /min under a flow of H₂ (5 % in N₂) at 300 sccm and was kept at 500 °C for 4 h. At the end of the heating period, the quartz tube was cooled to room temperature naturally. The hydrogen flow was continued until the quartz tube had reached 150 °C. For comparison, common TiO₂ microspheres (TiO₂-air) were also prepared by annealing the H-TiNT microspheres at 500 °C for 4 h in air atmosphere.

Co-catalyst loading. Pt species were loaded onto the above-prepared TiO₂ samples by impregnating them (0.4 g) in 80 mL of H₂PtCl₆·6H₂O aqueous solution (0.25 mM). The suspensions were stirred and followed by UV illumination (300 W Xe arc lamp) for 20 min at room temperature. After that, the precipitates were collected and dried in an oven at 80 °C for 12 h. The nominal weight ratios of Pt to TiO₂ was 1 wt %.

Structure characterization. XRD patterns were obtained using a Bruker D8 advanced X-ray powder diffractometer with Cu K α radiation (λ = 1.5418 Å). The morphologies of the samples were examined by SEM (Hitachi S-4800 microscope) and HRTEM (JEOL JEM-2100). The surface areas were measured by using the Brunauer-Emmett-Teller method with a Builder 4200 instrument at liquid nitrogen temperature. The pore volume and the pore size distribution were derived from the absorption branch of the absorption-desorption isotherms by using the Barrett-Joyner-Halenda method.²⁻³ FTIR spectra were measured with a Nexus 670 infrared (IR) spectrophotometer over the range of 500–4000 cm⁻¹. The diffuse reflectance spectra were measured on a Shimadzu UV 2550 UV/Vis spectrophotometer. Laser Raman spectra were collected under ambient conditions using an HR LabRaman 800 system. A green laser beam (λ = 532 nm) was used for excitation. Thermogravimetric analysis (TGA) curves were recorded using a SDT Q600 simultaneous analysis system.

Photocatalytic measurements. Photocatalytic hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. In a typical photocatalytic experiment, 0.1 g of catalyst was suspended in 100 ml aqueous solution containing 20 % methanol in volume. The reaction temperature

was maintained at 5 °C. The amount of H₂ evolved was determined by using a gas chromatograph (Varian GC3800). The light source in the above photoreactivity experiment was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd).

2,4-dichlorophenol (2,4-DCP) was chosen to evaluate the photocatalytic properties of the TiO₂ microspheres. In a typical reaction, 50 mg of as-prepared samples were dispersed in a Pyrex glass reactor (with the cross section of 30 cm² and the height of 5 cm) containing 50 mL 2,4-DCP solutions with concentration of 40 mgL⁻¹. Prior to irradiation, the suspensions were stirred in the dark for 30 min to ensure the adsorption/desorption equilibrium. At given time intervals, about 5 ml of the suspension was taken for the following analysis after centrifugation. The optical system for detecting the catalytic reaction consists of a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd), and the degradation of 2,4-DCP was monitored by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai).

The formation of active hydroxyl radicals (•OH) upon irradiation was also chosen to evaluate the photocatalytic properties. In a typical reaction, various photocatalysts were suspended in 100 mL of aqueous solution containing 0.01 M NaOH and 3.0 mM terephthalic acid. Prior to the light irradiation, the suspension was stirred in the dark for 1 h to obtain the equilibrium adsorption state. Then, 5.0 mL of solution was taken out every 30 min, and the TiO₂ was separated from the solution with a centrifugation method. The remaining clear liquid was used for fluorescence spectrum measurements. During the photoreactions, no oxygen was bubbled into suspension. The employed excitation light in recording fluorescence spectra is 320 nm.

Computational details. Our first-principles density functional calculations were carried out by using the Vienna *ab initio* simulation package (VASP).⁴ The exchange–correlation potential was described by GGA (generalized gradient approximation)⁵ with the Perdew–Burke–Ernzerhof (PBE)⁶ scheme. The (101), (001), and (100) surfaces of TiO₂ are modeled by the 1 × 1 surface cells consisting of 30, 18, and 7 atomic layers and the thickness of vacuum layer above each slab is 20 Å, which was found to be well converged. The 7×10×1, 10×10×1, and 9×4×1 Γ -centered *k*-points⁷ set was used to sample the Brillouin zones of the (101), (001), and (100)

surfaces, respectively. The plane-wave cutoff energy was set as 500 eV and the relaxation cycles were terminated when all atomic-force components were smaller than 10^{-2} eÅ⁻¹.

References

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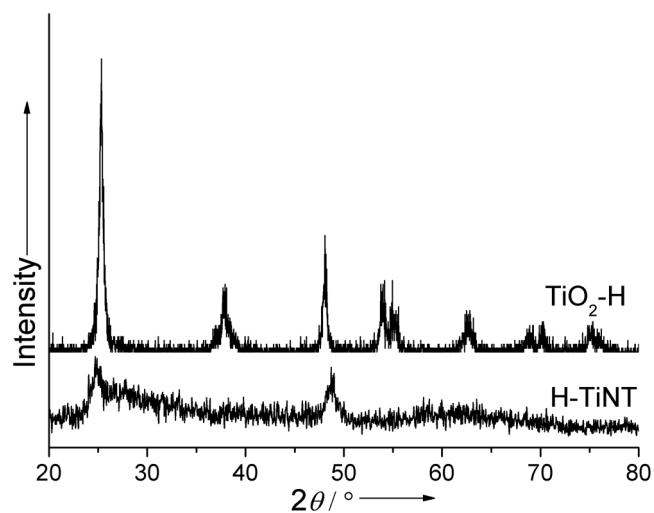


Fig. S1 XRD pattern of H-TiNT and $\text{TiO}_2\text{-H}$ microspheres.

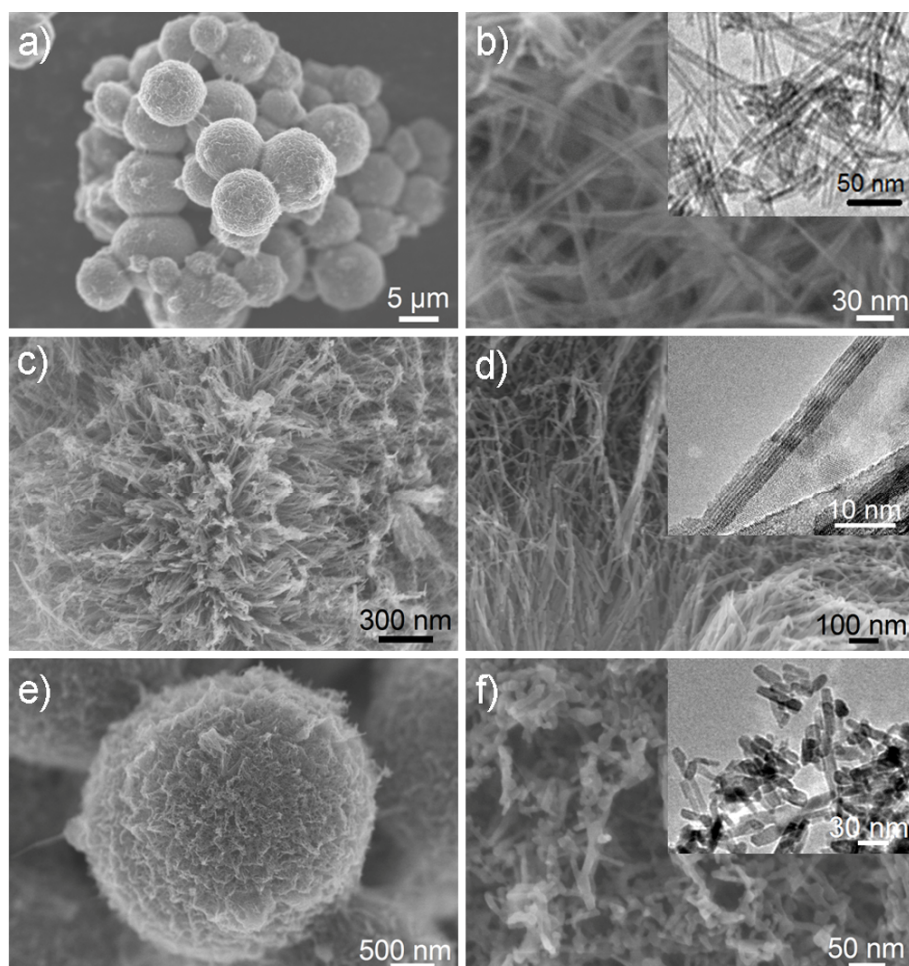


Fig. S2 SEM and TEM (inset) images of (a,b) H-TiNT, (c,d) $\text{TiO}_2\text{-H}$, and (e,f) $\text{TiO}_2\text{-air}$ microspheres.

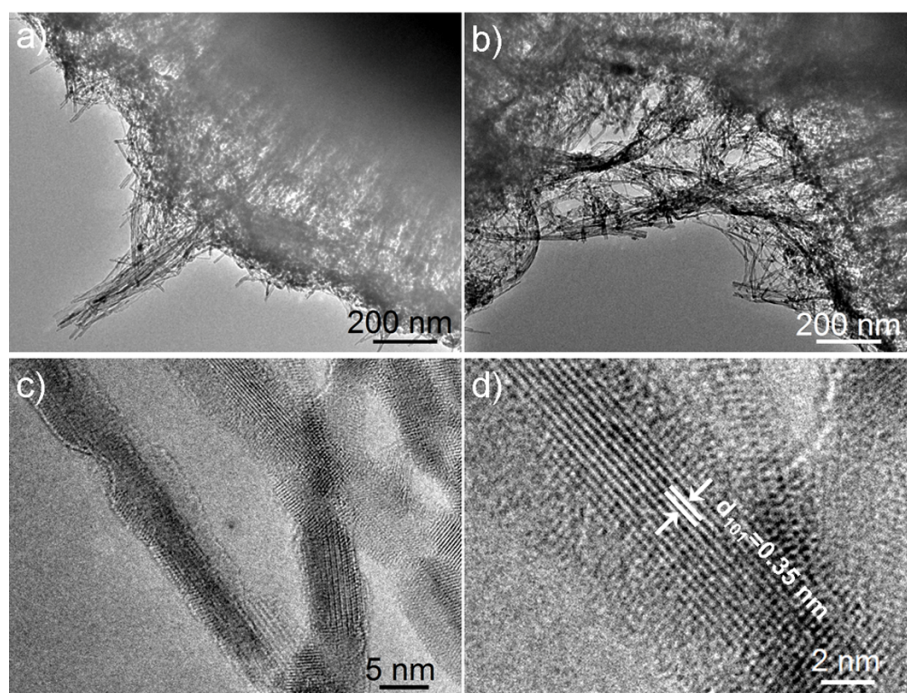


Fig. S3 TEM and HRTEM images of $\text{TiO}_2\text{-H}$ nanowire-microspheres.

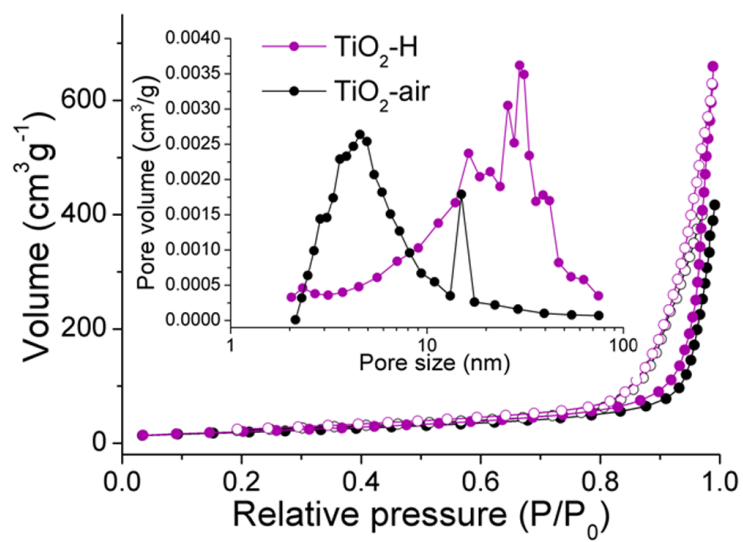


Fig. S4 Nitrogen adsorption (●) –desorption (○) isotherm and pore-size distribution curves measured for $\text{TiO}_2\text{-H}$ and $\text{TiO}_2\text{-air}$ microspheres.

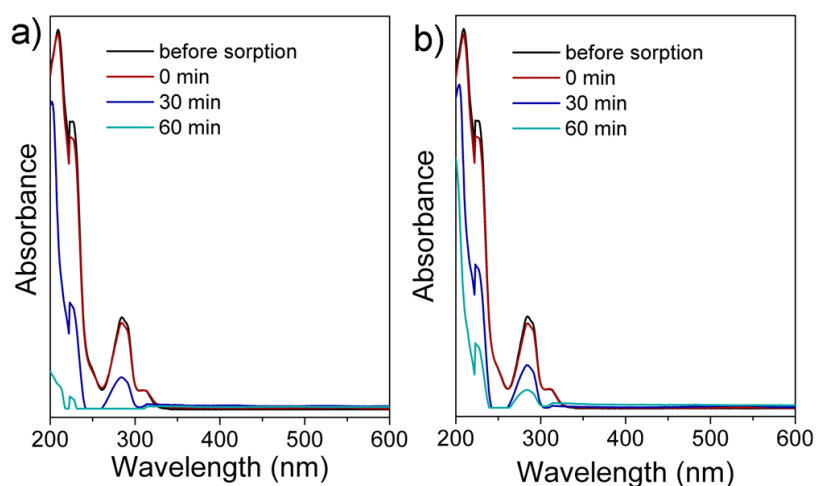


Fig. S5 Photodegradation of 40 mgL^{-1} 2,4-DCP over (a) TiO_2 -H nanowire-microspheres and (b) TiO_2 -air microspheres. Prior to the light irradiation, the 2,4-DCP solution mixed with the catalyst was kept in the dark for 30 min to obtain the equilibrium adsorption state.

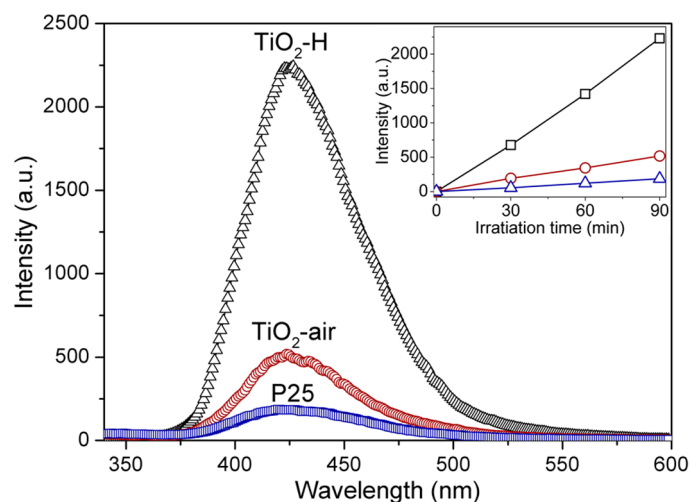


Fig. S6 Fluorescence spectra of the visible-light irradiated TiO_2 samples in terephthalic acid (3 mM) after irradiation for 90 min; inset: the time dependences of fluorescence intensity at 426 nm, TiO_2 -H ($\square$), TiO_2 -air ($\circ$), P25 (Δ).

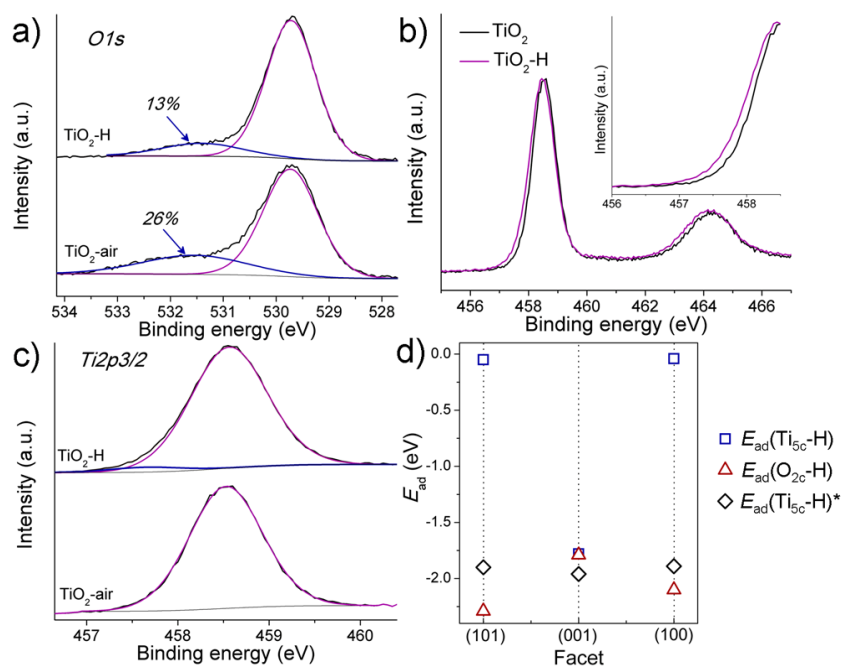


Fig. S7 (a) O 1s XPS spectra and (b,c) Ti 2p XPS spectra of TiO₂-H and TiO₂-air. (d) Calculated energy E_{ad} of H-adsorption on the Ti_{5c} and O_{2c} sites on different facets, $E_{ad} = [E(\text{adsorbed}) - E(\text{clean}) - n(H)\mu(H)]/n(H)$. Here $E(\text{adsorbed})$ and $E(\text{clean})$ represent the energies of H-adsorbed and clean surfaces, respectively, $n(H)$ the number of adsorbed H atoms, and $\mu(H)$ the chemical potential of one isolated H atom. $E_{ad}(Ti_{5c}-H)^*$ means the adsorption energy of H atoms on the Ti_{5c} sites on the surfaces with H atoms adsorbed on the O_{2c} sites, where $E_{ad} = [E(Ti_{5c}-H + O_{2c}-H) - E(O_{2c}-H) - n(H)\mu(H)]/n(H)$.

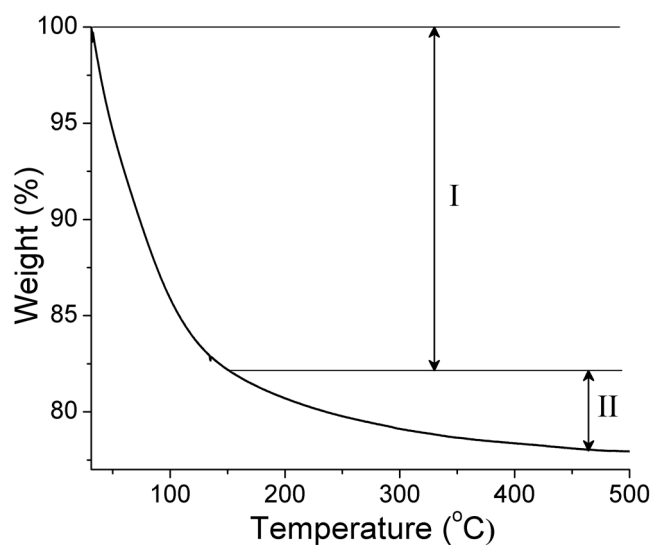


Fig. S8 TGA curve for H-TiNT microspheres measured at a heating rate of 10 °C/min.

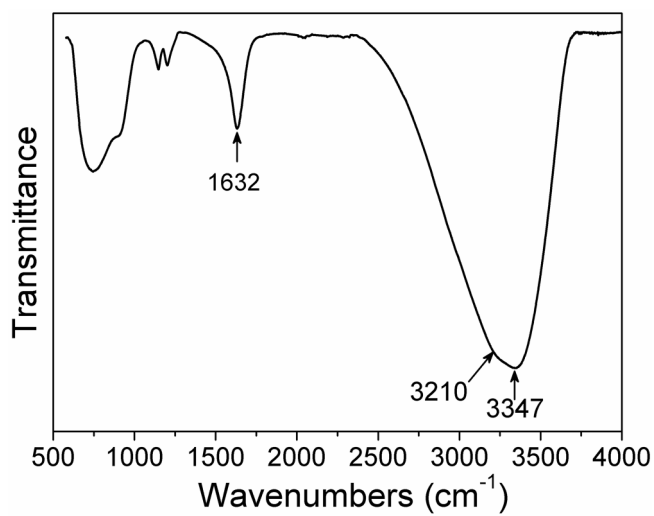


Fig. S9 FTIR spectra of H-TiNT microspheres.

Table S1. Pore structure information of H-TiNT, TiO₂-H and TiO₂-air microspheres.

Microspheres	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore size (nm)
H-TiNT	325.3	0.50	6.18
TiO ₂ -H	75.0	1.02	27.3
TiO ₂ -air	61.1	0.29	18.7