Electronic Supplementary Information (ESI)

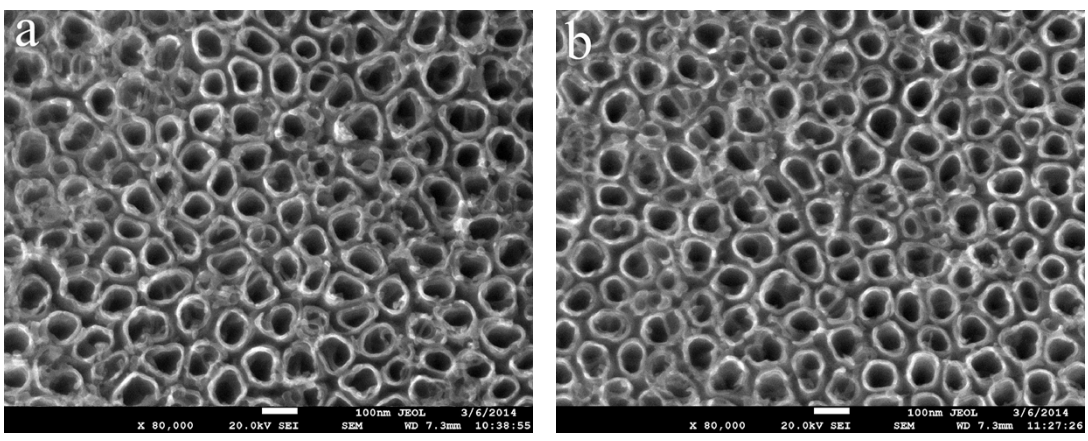
Experimental Section

Fabrication of TiO_2 Nanotubes (TiO_2-NTs): TiO_2-NTs were prepared by an electrochemical anodization in fluoride-contained electrolyte. Typically, smooth Ti sheets (Aldrich) with a geometric size of 1×2.5 cm^2 was anodized at a constant voltage of 20 V for 20 min in 0.5% HF aqueous solution. A Pt foil with a size of 2×2 cm^2 was used as a cathode. The anodized Ti sheets were then washed with deionized water and dried in the air spontaneously, which was followed by annealed at 450 °C for 3 h to realize anatase crystallization of TiO_2 nanotubes. TiO_2-NTs formed on smooth Ti sheet were denoted as S-TiO_2-NTs. In order to obtain hierarchical TiO_2-NTs, porous Ti sheet (1×2.5 cm^2) made of irregular microscale Ti particles (Baoji Jinkai Co., Ltd, China) was anodized at a constant voltage of 30 V for 20 min in 0.5% HF aqueous solution. The anatase crystallization of TiO_2 nanotubes was realized by calcination at 450 °C. The resulting TiO_2-NTs were denoted as H-TiO_2-NTs.

Synthesis of MoS_2 Nanoparticles on TiO_2-NTs by Photocatalysis: Layered MoS_2 nanoparticles were deposited directly on TiO_2-NTs by photocatalytic reduction of $(NH_4)_2MoS_4$ precursor. S-TiO_2-NTs or H-TiO_2-NTs were placed in 15mL of $(NH_4)_2MoS_4$ precursor in H_2O/C_2H_5OH mixed solvent with volume ratio of 9:1. Before photocatalytic reaction, the precursor solution was deaerated with N_2 for 30 min, and then TiO_2-NTs was irradiated with 10 mW/cm^{-2} of 365-nm ultraviolet (UV) light from a high-pressure mercury lamp. The irradiated TiO_2-NTs were washed with deionized water and dried with N_2 airflow. The resulting MoS_2 nanoparticles on TiO_2-NTs could be used as an electrode for HER directly.

Electrocatalytic Activity for Hydrogen Evolution Reaction (HER): The electrocatalytic activities of MoS_2 nanoparticulate electrode were evaluated by measuring the polarization curves in 0.5 M H_2SO_4 electrolyte using a three-electrode configuration. The Tafel curves were calculated from the polarization curves by subtracting the background current. The MoS_2 electrode with a geometric area of 1 cm^2 was used for a working electrode and a Pt wire acted as a counter electrode. The reference electrode was Ag/AgCl electrode in 3.5 M KCl solution (φ=0.205 V vs. Standard Hydrogen Electrode, SHE). The potential was supplied by a CHI660D electrochemical workstation (Shanghai Chenhua Apparatus Co., China), which were calibrated to be against SHE based on an equation of φ (V vs. SHE) = φ (V vs. Ag/AgCl)+0.205 V. The scanning rate was fixed to be 5 mV/s for the measurements.

Characterizations: The morphologies of TiO_2-NTs and MoS_2 nanoparticles were characterized using a field emission scanning electron microscope (SEM, JSM-7500F) at 20 kV. The surface chemical compositions were studied using an X-ray photoelectron spectroscopy (XPS) measurement (PHI Quantera). High resolution morphologies of MoS_2 nanoparticles were obtained using a transmission electron microscope (TEM, JEOL JEM-3000F) at 300 kV. In this case, TiO_2-NTs were prepared by anodization of Ti foil at 60 V for 30 min in ethylene glycol (Beijing Chemical Factory, China) consisting of 0.25 wt % ammonium fluoride (Beijing Chemical Factory, China) and 2 vol% Milli-Q water. After MoS_2 deposition, TiO_2-NTs were scraped from Ti foil for TEM measurements.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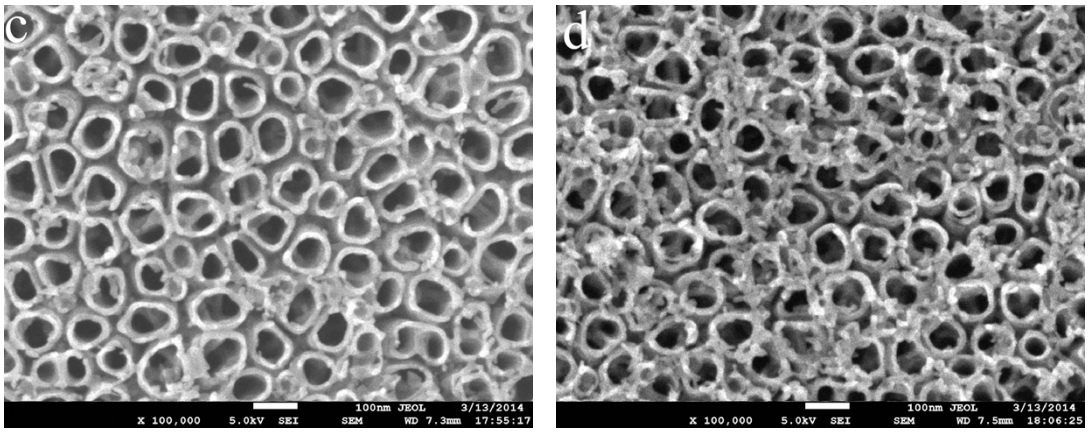

Figure S1. High-resolution SEM images of TiO_2-NTs before (a) and after photocatalytic reaction for 1 h (b), 4 h (c) and 8 h (d).