Supplementary Information

Bubble template synthesis of $Sn_2Nb_2O_7$ hollow spheres for enhanced visible-light-driven photocatalytic hydrogen production

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Experimental Section

Preparation of $Sn_2Nb_2O_7$ hollow spheres. All chemicals were used as received without further purification. In a typical synthesis process, a mixture of 0.5 g Nb_2O_5 power and 45 mL of 3 mol/L KOH solution was pretreated at 200 °C for 12 h in a sealed Teflon stainless autoclave until a clear solution was obtained, which was also reported in our previous work.[1,2] The XRD pattern of the powders obtained from the above evaporated clear solution demonstrates the formation of a soluble potassium niobate $K_8Nb_6O_{19}\cdot 10H_2O$. Then 0.38 g $SnCl_2$ and 3 g urea were added into the above clear solution (16 mL) and ultrasonicated for 5 min. In order to prevent the oxidation of Sn^{2+} to Sn^{4+} during the hydrothermal process, the clear solution was first saturated by nitrogen gas for at least 30 min to eliminate oxygen and then transfered into a 20 mL Teflon stainless autoclave. After the sealed Teflon stainless autoclave was heated at 200 °C for 12 h in an oven, the final products were collected by filtration, washed with deionized water and absolute ethanol for several times, and dried at ambient temperature. This sample was labled as HT-SNO. For comparison, a control experiment without urea was also carried out under the same hydrothermal conditions.

Preparation of bulk $Sn_2Nb_2O_7$ powders. For comparison, the bulk $Sn_2Nb_2O_7$ was also

prepared by the conventional high temperature solid state reaction method according to the reference.[3] This sample was labled as SSR-SNO.

Preparation of Pt loaded $Sn_2Nb_2O_7$. Pt loaded $Sn_2Nb_2O_7$ samples were prepared by a facile photodeposition method. 50 mg of $Sn_2Nb_2O_7$ powder was suspended in a 50 mL quartz tube with 20 mL 20 vol% lactic acid aqueous solution. Then, various amounts of H_2PtCl_6 solution (10 mmol/L) were added. Subsequently, the quartz tube was purged with N_2 for at least 30 min to remove air and then sealed with a rubber septum. The suspension was irradiated with a 500 W high-pressure mercury lamp for 1 h under magnetic stirring (XPA-7 photochemical reactor, Nanjing Xujiang Machine-electronic Plant). The temperature of the suspension during irradiation was maintained at 298 K using a thermostatically controlled water bath.

Characterization. The powder X-ray diffractometer (XRD) patterns of samples were performed on a Bruker D8 Focus X-ray diffractometer with monochromated Cu Kα radiation (λ = 0.15418 nm). Field emission scanning electron microscopic (FESEM) images were obtained on a Hitachi S-4800 microscope. Transmission electron microscopic (TEM) and high resolution TEM (HR-TEM) images were obtained using a JEOL-2011F microscope. UV-vis diffuse reflection spectra of samples were recorded using a Varian spectrophotometer (Cary 5000) with an integrating sphere. N_2 adsorption-desorption isotherms and pore-size distributions were obtained on a Quadrasorb SI MP apparatus at 77 K. Prior to the experiments, samples were degassed in vacuum at 200 ^{o}C for 12 h. The total specific surface area of samples was calculated using the Brunauer-Emmett-Teller (BET) method.

Surface photovoltage (SPV) measurement. The SPV measurement system is composed of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell, and a computer. A 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power) and a double-prism monochromator (Zolix SBP500) provided monochromatic light as the source light. The samples were studied without further treatment, and the contact between samples and indium tin oxide electrode was not ohmic during the SPV measurement.

Photocatalytic H_2 production activities. The photocatalytic hydrogen evolution from lactic

acid aqueous solutions was conducted in a 50 mL quartz tube with a rubber septum. The photocatalyst powders (50 mg) were dispersed in a water/lactic acid solution (20 mL, *v*/*v* = 4:1) in a quartz tube using a magnetic stirrer. The solution was then purged with N_2 for at least 30 min to remove O_2 and then sealed with a rubber septum. The light source was a 300 W Xenon lamp (CEL-HXF 300, Beijing CEL Tech. Co., Ltd) equipped with an ultraviolet cut-off filter (λ > 400 nm). The amount of evolved hydrogen was determined by a Shimadzu GC-2014 gas chromatography (N_2 carrier gas, molecular sieve 5 Å, TCD detector).

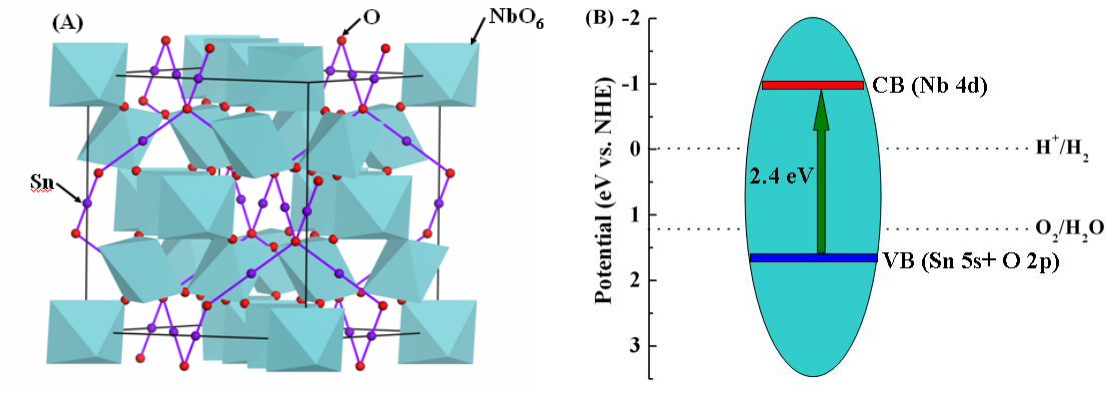

Fig. S1 The crystal structure (A) and energy band structure (B) of $Sn_2Nb_2O_7$.[4]

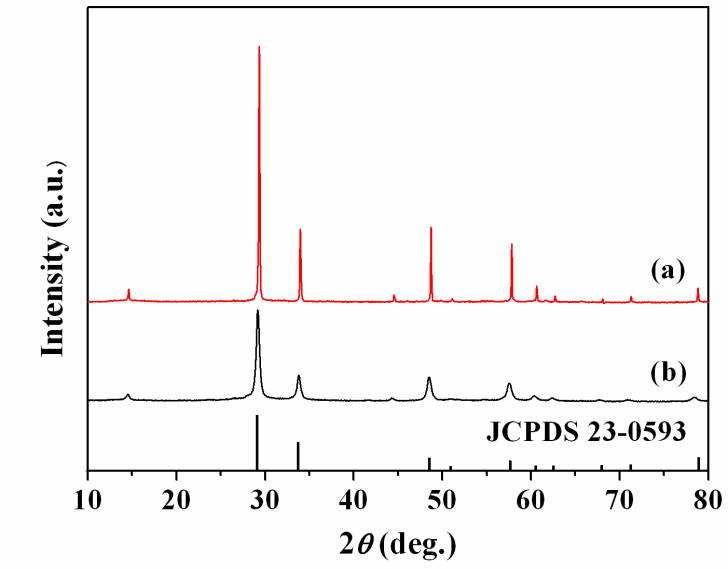

Fig. S2 XRD patterns of SSR-SNO (a) and HT-SNO (b).

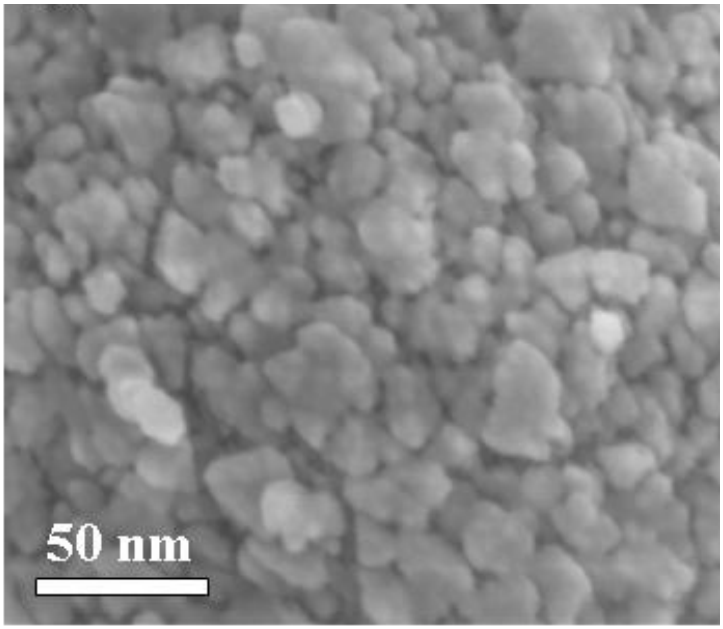

Fig. S3 FESEM image of HT-SNO hollow spheres.

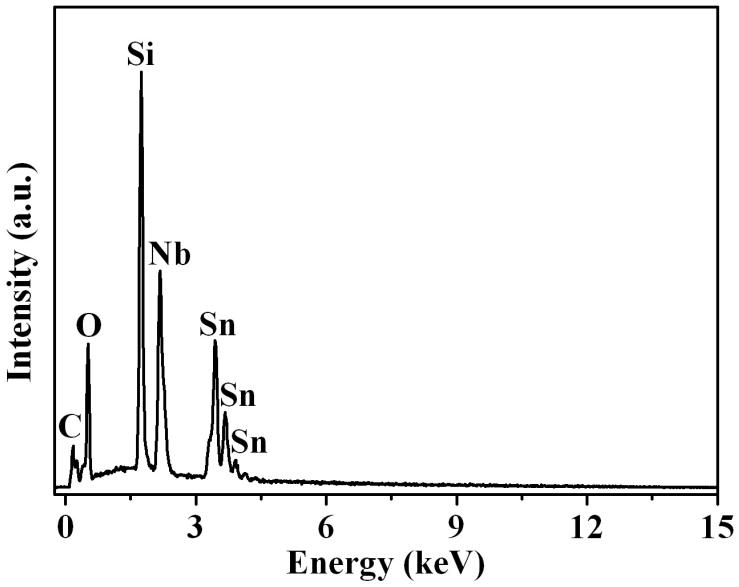

Fig. S4 EDS pattern of HT-SNO.

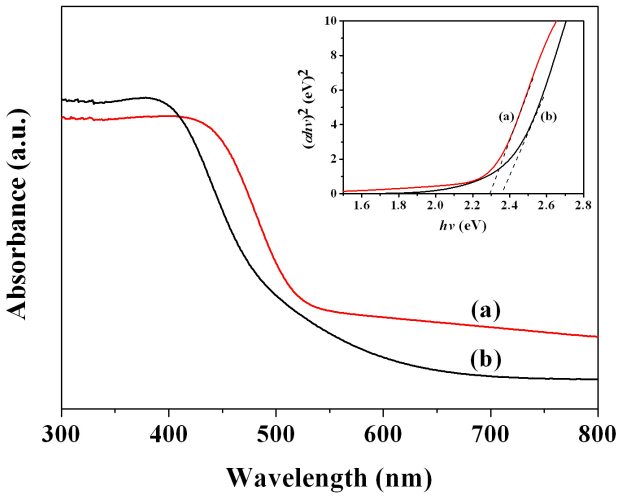

Fig. S5 UV-vis diffuse reflectance spectra of SSR-SNO (a) and HT-SNO (b).

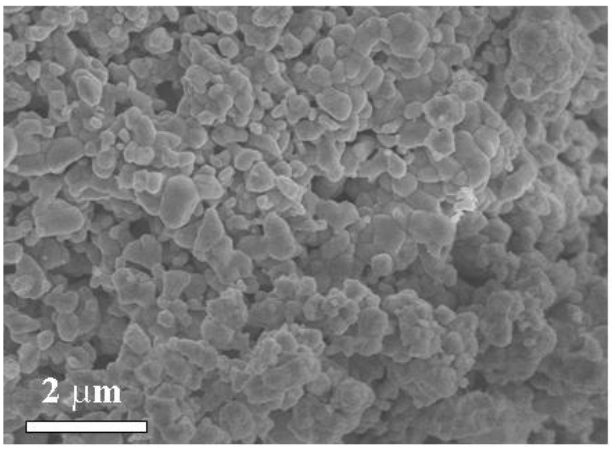

Fig. S6 FESEM image of SSR-SNO.

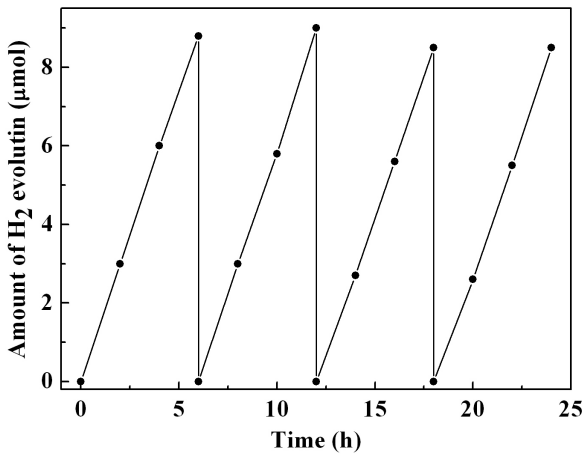

Fig. S7 Time course of hydrogen evolution over 0.3 wt% Pt loaded HT-SNO from lactic acid aqueous solutions under visible light irradiation (λ > 400 nm).

References

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4. Y. Hosogi, Y. Shimodaira, H. Kato, H. Kobayashi and A. Kudo, *Chem. Mater.*, 2008, **20**, 1299-1307.