Supplementary Information

Facile synthesis of ultrathin $SnNb_2O_6$ nanosheets towards improved visible-light photocatalytic H_2-production activity

Chao Zhou,[a] Yufei Zhao,[a] Lu Shang,[a] Run Shi,[ab] Li-Zhu Wu,[a] Chen-Ho Tung[a] and Tierui Zhang*[a]

[a]*Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.*

[b]*University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.*

**Corresponding author. Tel.: +86 10 82543428. E-mail: tierui@mail.ipc.ac.cn*

Experimental Section

Preparation of $SnNb_2O_6$ nanosheets. All chemicals were used as received without further purification. Ultrathin $K_4Nb_6O_{17}$ nanosheets were prepared following a similar procedure reported previously by us using Nb_2O_5 and KOH as precursors.[1] Bulk $K_4Nb_6O_{17}$ powders were prepared by a conventional solid state reaction.[2] In a typical synthesis process, 0.15 g of $K_4Nb_6O_{17}$ and 0.087 g of $SnCl_2$ were mixed, added into 16 mL deionized water and ultrasonicated for 5 min. In order to prevent the oxidation of Sn^{2+} to Sn^{4+} during the hydrothermal process, the above suspension was first saturated by N_2 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, finally dried at ambient temperature.

Preparation of bulk $SnNb_2O_6$ powders. For comparison, bulk $SnNb_2O_6$ powders were also prepared by the conventional high temperature solid state reaction method.[3] In a typical synthesis process, a mixture of the starting materials, SnO and Nb_2O_5, was calcined at 900 °C for 6 h in flowing N_2 using an alumina boat.

Preparation of N doped TiO_2. For comparison, N-doped TiO_2 was prepared by calcination of commercial TiO_2 and urea at 500 °C for 2 h. After being cooled to room temperature, the as-obtained yellow powders were washed with distilled water and ethanol for three times, repectively, then dried at 60 °C for 12 h.

Preparation of Pt loaded $SnNb_2O_6$. 0.3 wt.% Pt loaded $SnNb_2O_6$ samples were prepared by a facile photodeposition method. 50 mg of $SnNb_2O_6$ powders were suspended in a 50 mL quartz tube with 20 mL 20 vol.% lactic acid aqueous solution. Then, 41.6 μL of H_2PtCl_6 solution (10 mmol/L) was 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 CuKα 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 (HRTEM) 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 150 °C for 12 h. The total specific surface areas of samples were calculated using the Brunauer-Emmett-Teller(BET) method. X-ray photoelectron spectroscopy (XPS) analysis was obtained on a PHI Quantro SXM instrument. All binding energies were referenced to the C 1s peak (284.8 eV) arising from carbon impurities.

Electrochemical impedance spectra (EIS) and photoelectrochemical response measurements. The EIS measurements were carried out on a CHI660e instrument (Shanghai Chenhua) by using a three-electrode cell. The pristine $SnNb_2O_6$ powders without Pt loading and ethanol were mixed homogeneously (100 mg mL^{-1}), and the obtained paste was spread on the ITO substrate with a glass rod, then calcined at 300 °C for 2 h to improve mechanical stability and electrical contact with ITO substrate. Finally, the resultant films with a thickness of *ca.*3 μm and 1 cm^2 active area were obtained. The resultant electrode served as the working electrode, with a platinum sheet as the counter electrode and a Ag/AgCl (saturated KCl) electrode as the reference electrode. The EIS measurements were performed in the presence of a 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1 : 1) mixture as a redox probe in 0.1 M KCl solution. The impedance spectra were recorded with the help of ZPlot/ZView software under an ac perturbation signal of 5 mV over the frequency range of 1 MHz to 100 mHz.

Photocurrent-time response spectra were performed in a standard three-electrode system on a CHI660e electrochemical workstation (Shanghai Chenhua). The as-obtained $SnNb_2O_6$ samples coated on the ITO substrate served as the working electrode with a working area of about 1 cm^2 and a thickness of about 3 μm, and a platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The electrolyte was 0.1 M Na_2SO_4 aqueous solution. A 300 W Xenon lamp with an ultraviolet cut-off filter ($\lambda >$ 400 nm) was utilized as the visible-light source.

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, $v_{water}/v_{lactic\ acid}$ = 4:1) in aquartz 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 (PLS-SXE300C photochemical reactor, Perfect Light Ltd, Beijing) 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 5Å, TCD detector). The apparent quantum yields of those $SnNb_2O_6$ samples were evaluated using a 300 W Xe lamp equipped with a 420 nm bandpass filter. The apparent quantum yield is defined by Eqs 1.

$$\begin{aligned}\text{Apparent quantum yield (AQY, \%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{2 \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%\end{aligned} \tag{1}$$

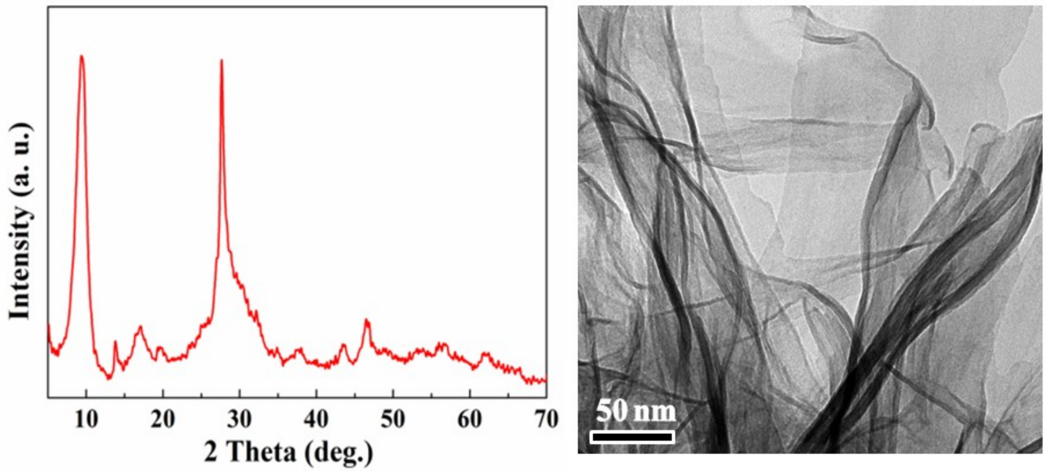

Fig. S1 XRD pattern (left) and TEM image (right) of ultrathin $K_4Nb_6O_{17}$ nanosheets.

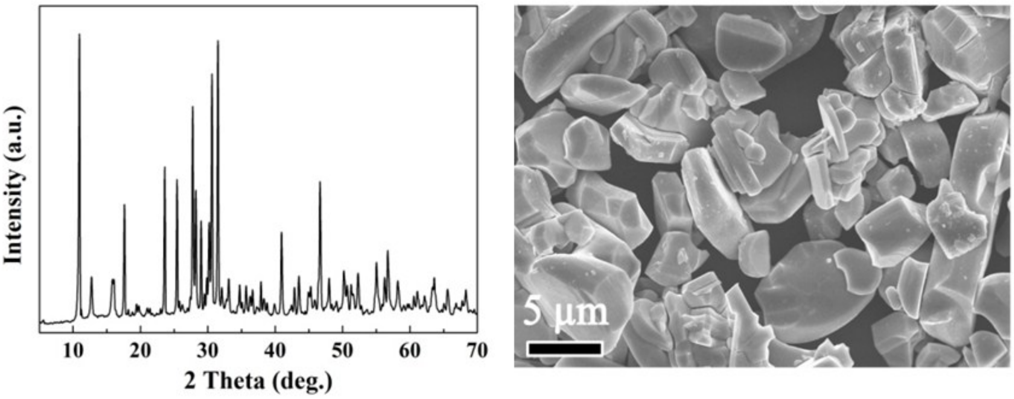

Fig. S2 XRD pattern (left) and SEM image (right) of bulk $K_4Nb_6O_{17}$ powders.

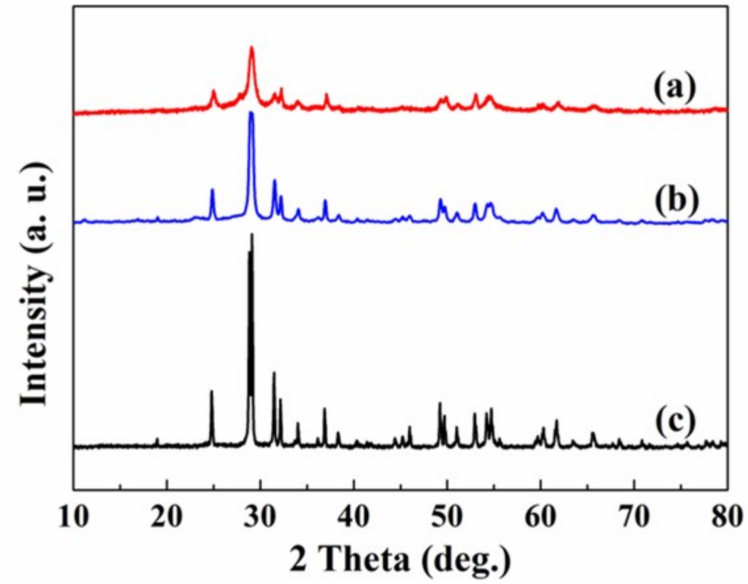

Fig. S3 XRD patterns of (a) $SnNb_2O_6$-3, (b) $SnNb_2O_6$-50 and (c) $SnNb_2O_6$-SSR.

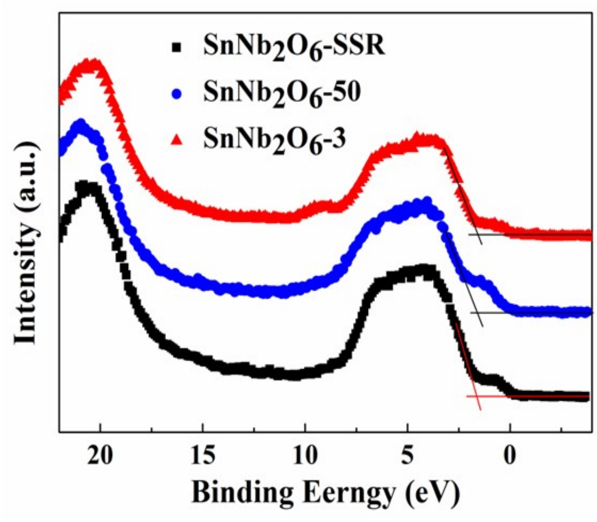

Fig. S4 High resolution valence band XPS spectra of $SnNb_2O_6$-SSR, $SnNb_2O_6$-50 and $SnNb_2O_6$-3.

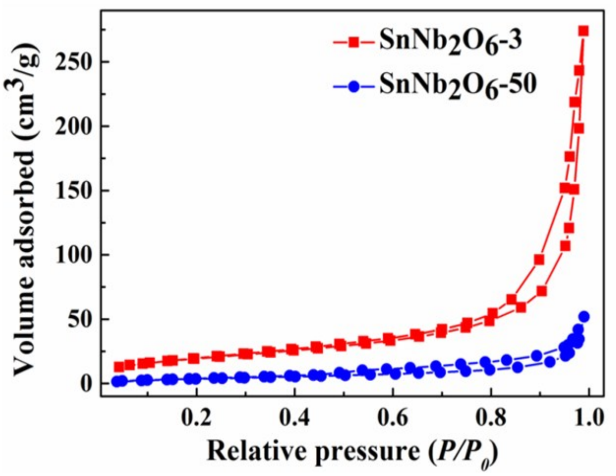

Fig. S5 N_2 adsorption-desorption isotherms of $SnNb_2O_6$-3 and $SnNb_2O_6$-50.

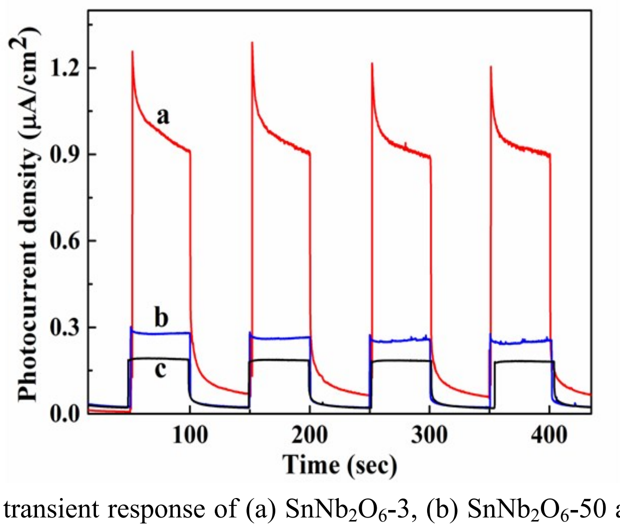

Fig. S6 Photocurrent transient response of (a) $SnNb_2O_6$-3, (b) $SnNb_2O_6$-50 and (c) $SnNb_2O_6$-SSR in 0.1 M Na_2SO_4 solution without bias under visible light irradiation ($\lambda > 400$ nm).

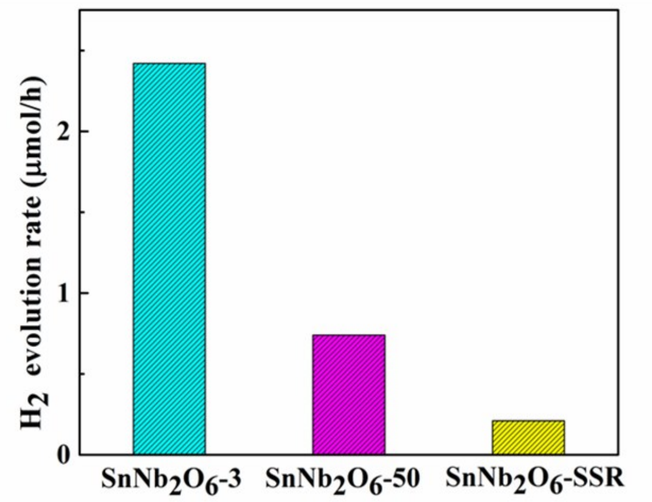

Fig. S7 Photocatalytic H_2 evolution of pristine $SnNb_2O_6$-3, $SnNb_2O_6$-50 and $SnNb_2O_6$-SSR without Pt loading from lactic acid aqueous solutions under visible light irradiation (λ > 400 nm).

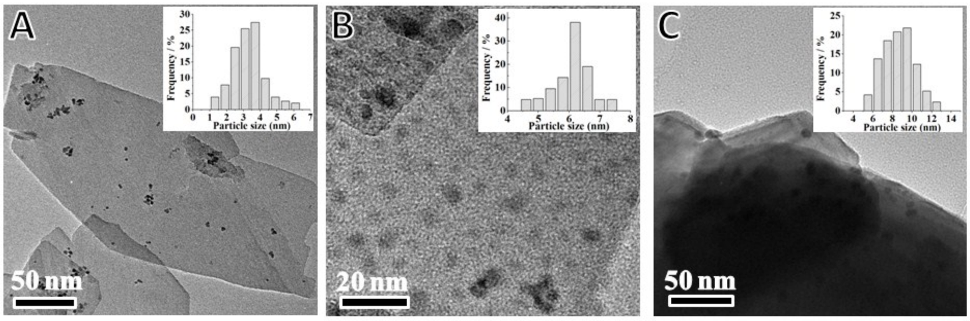

Fig. S8 TEM images of 0.3 wt.% Pt loaded (A) $SnNb_2O_6$-3, (B) $SnNb_2O_6$-50 and (C) $SnNb_2O_6$-SSR *via* an *in-situ* photodeposition method.

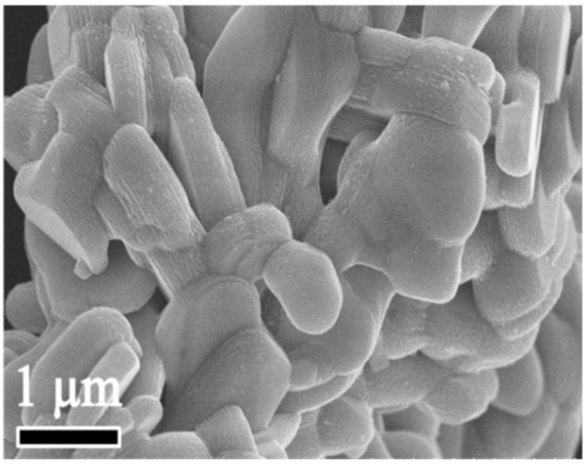

Fig. S9 SEM image of $SnNb_2O_6$-SSR.

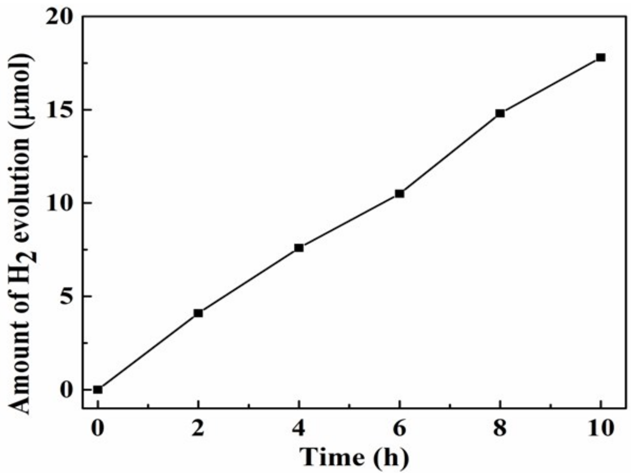

Fig. S10 Photocatalytic H_2 evolution of 0.5 wt.% Pt loaded N-doped TiO_2 from lactic acid aqueous solutions under visible light irradiation ($\lambda > 400$ nm).

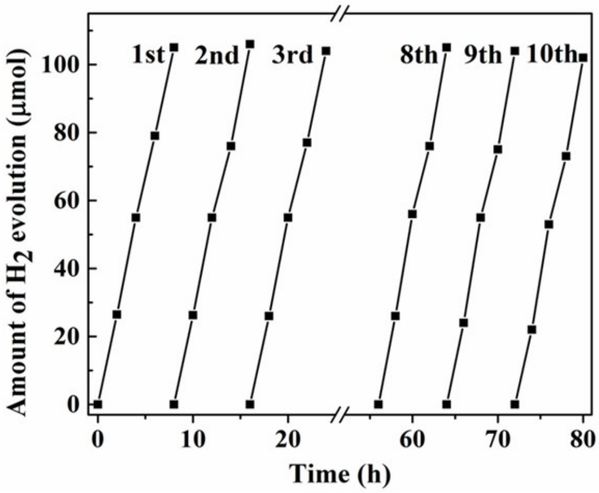

Fig. S11 Time course of hydrogen evolution over 0.3 wt.% Pt loaded ultrathin $SnNb_2O_6$-3 nanosheets from lactic acid aqueous solutions under visible light irradiation ($\lambda > 400$ nm).

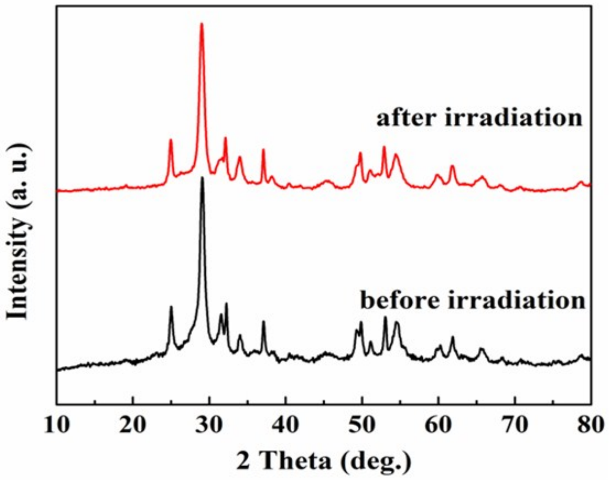

Fig. S12 XRD patterns of ultrathin $SnNb_2O_6$-3 nanosheets before and after visible light irradiation ($\lambda > 400$ nm).

References

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2. M. C. Sarahan , E. C. Carroll , M. Allen , D. S. Larsen , N. D. Browning and F. E. Osterloh, *J. Solid State Chem.,* 2008, **181**, 1678-1683.
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