Supplementary Information

Facile preparation of black Nb^{4+} self-doped $K_4Nb_6O_{17}$ microspheres with high solar absorption and enhanced photocatalytic activity

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Experimental Section

Preparation of white $K_4Nb_6O_{17}$ microspheres.

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 40 mL of 3 mol/L KOH solution was pretreated at 200 ℃ for 12 h in a sealed Teflon stainless autoclave until a clear solution was obtained. Then, 3 g urea was added into the above clear solution (18 mL), and the KOH concentration was adjusted to 1.5 mol/L by adding deionized water. This mixed clear solution was loaded into a 50 mL Teflon stainless autoclave. After the sealed Teflon stainless autoclave was heated at 200 ℃ 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.

Preparation of black Nb^{4+} self-doped $K_4Nb_6O_{17}$ microspheres.

Black Nb^{4+} self-doped $K_4Nb_6O_{17}$ microspheres were prepared by a facile photoreduction method. In a typical synthesis procedure, 100 mg of white $K_4Nb_6O_{17}$ powder was dispersed in a 50 mL quartz tube with 20 mL 20 vol% methanol aqueous solution. Then, 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 12 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. The resultant black powder was centrifuged, washed with distilled water three times, and dried at 40 ℃ under vacuum for 3 h.

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). UV-vis diffuse reflection spectra were recorded using a Varian spectrophotometer (Cary 5000) with an integrating sphere using $BaSO_4$ as reflectance sample and were converted from reflection to absorption spectra by the Kubelka–Munk method. 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. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. The electron paramagnetic resonance (EPR) spectra were collected using a Bruker ESP 500 spectrometer at 90 K.

Photocatalytic H_2 production activities. The photocatalytic H_2 evolution from methanol aqueous solutions was conducted in a 50 mL quartz tube with a rubber septum. The photocatalyst powders (100 mg) were dispersed in a water/methanol 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 ($\lambda \geq 400$ nm). The amount of evolved H_2 was determined by a Shimadzu GC-2014 gas chromatography (N_2 carrier gas, molecular sieve 5 Å, TCD detector).

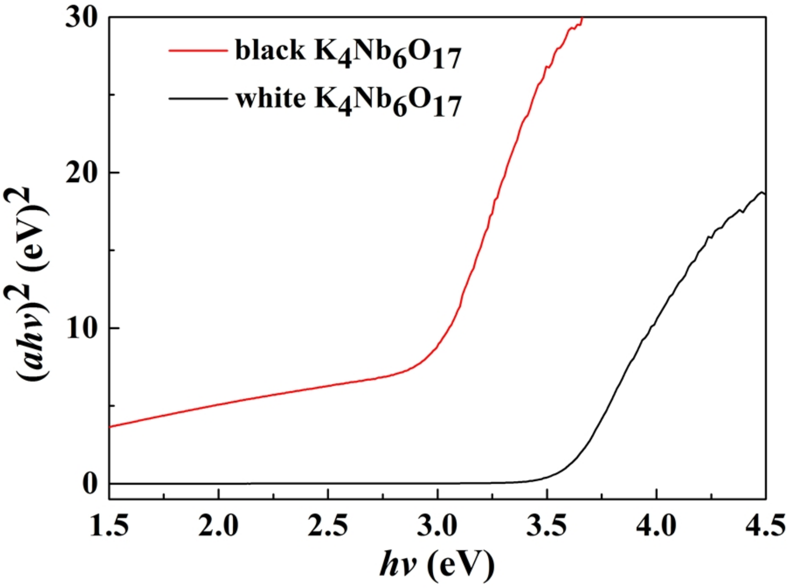

Fig. S1 Bandgap estimation based on the Kubelka-Munk function for the white and black K4Nb6O17 samples.

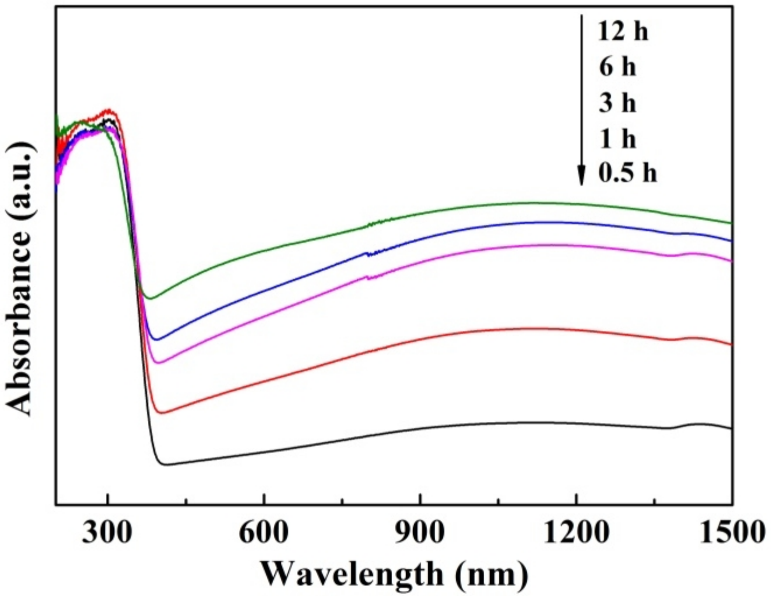

Fig. S2 UV-Vis diffuse reflectance spectra of the black Nb^{4+} self-doped $K_4Nb_6O_{17}$ microspheres prepared by UV light irradiation for different time.

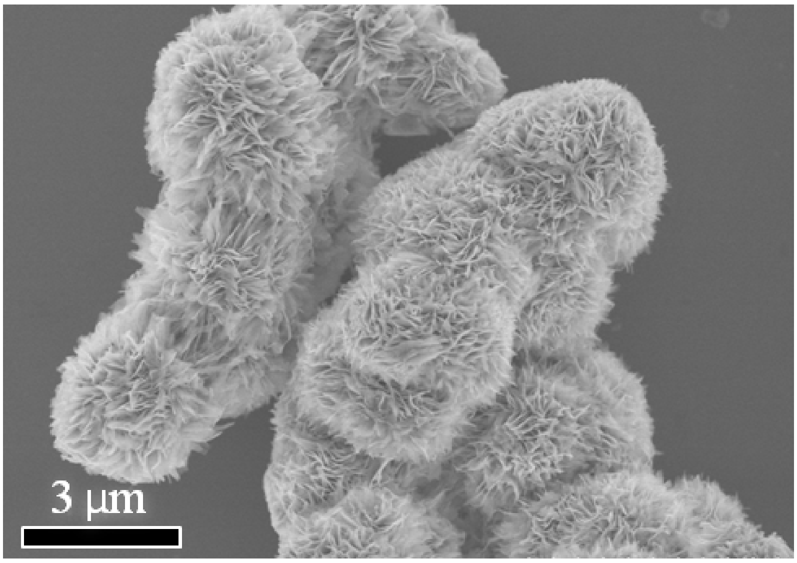

Fig. S3 SEM image of the black Nb^{4+} self-doped $K_4Nb_6O_{17}$ sample.

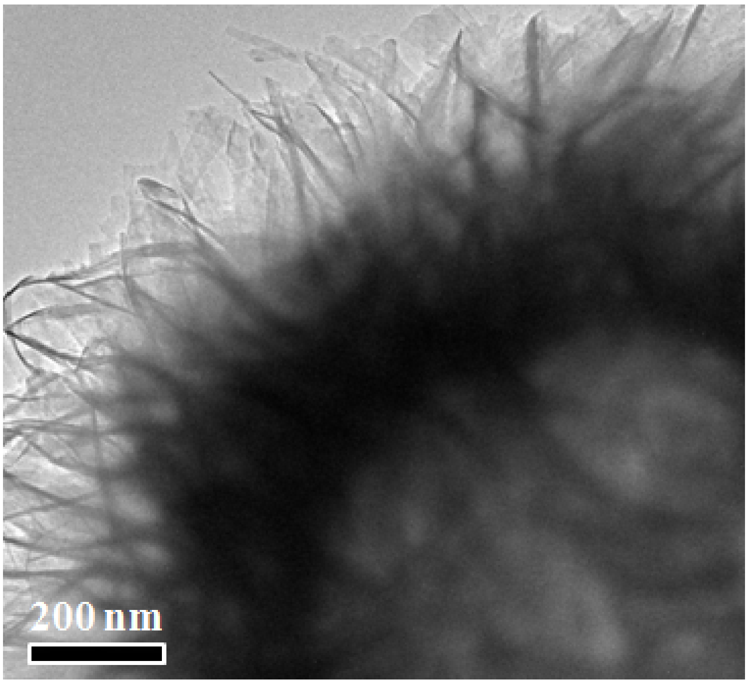

Fig. S4 TEM image of the black Nb^{4+} self-doped $K_4Nb_6O_{17}$ sample.

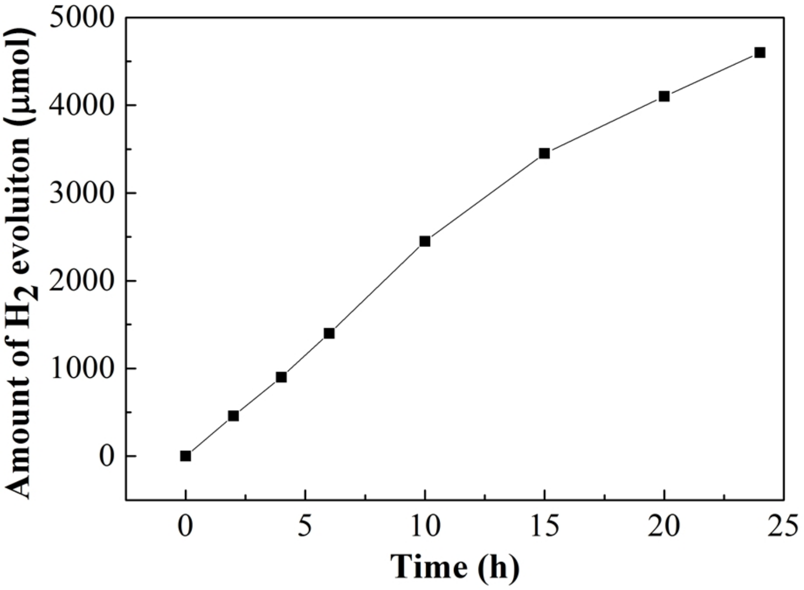

Fig. S5 Time course of photocatalytic H_2 production of the black Nb^{4+} self-doped $K_4Nb_6O_{17}$ sample under full-spectrum light irradiation ($\lambda \geq 320$ nm).