Supporting information

Heterostructured ZnO/SnO_{2-x} Nanoparticles for Efficient Photocatalytic Hydrogen Production

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Experimental Section:

Preparation of samples: The ZnO/SnO_{2-x} powders were synthesized by a two-step reaction. At first, 1 mmol of $SnCl_2 \cdot 2H_2O$ was added into 40 ml mixed aqueous solution, consisted of ethanol solution and di-ionized water in a 1:1 volume ratio. The obtained mixture was magnetically stirred for 1 h, and then the white suspension was transferred to autoclave and heated at 120 °C for 6 h. The yellow powder was collected after centrifugation and dried at 60 °C for 8 h [1]. 100 mg as-prepared SnO_{2-x} sample was soaked into 10 ml ethanol aqueous solution containing $Zn(NO_3)_2$ for 30

min under vigorous stirring. After the immersion, the product was dried in an oven at 60 °C under ambient temperature for 8 h, and was pyrolyzed in N_2 atmosphere (denoted as ZnO/SnO_{2-x}) at 350°C for 3 h. The weight ratio of pristine SnO_{2-x} : $Zn(NO_3)_2 \cdot 6H_2O$ is 5:1. Meanwhile, the yellow powder was directly annealed in N_2 atmosphere (denoted as SnO_{2-x}) at the same temperature to get the better crystallinity. The procedure of stoichiometric SnO_2 NPs was identical with that for the pristine SnO_{2-x} NPs except for using $SnCl_4 \cdot 5H_2O$ as the tin source to replace $SnCl_2 \cdot 2H_2O$ and annealing in air atmosphere to replace nitrogen. Commercial TiO_2 (P25) and commercial ZnO NPs (Guangzhou Chemical Reagent Factory, Specific Surface Area = 40 m^2/g) were employed directly without any treatment.

Materials characterizations: The surface structure, morphology and composition of the samples were characterized by scanning electron microscope (SEM, Quanta 400), X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu Kα radiation (λ = 1.5418 Å), and transmission electron microscopy (TEM, JEM2010-HR). The X-ray Photoelectron Spectroscopy (XPS, ESCALab250) with a 200W Al Kα radiation was used to measure the chemical bonding state and chemical state of the samples. The C 1s peak at 284.8 eV from adventitious carbon was regarded as the energy reference. The optical properties of the products were measured with a UV-Vis-NIR Spectrophotometer (UV, Shimadzu UV-3150). Rome temperature photoluminescence (PL) spectra were measured using a combined fluorescence lifetime and steady state spectrometer (FLS920, EDINBURGH) and the exaction wavelength was 280 nm. Nitrogen adsorption/desorption isotherms at 77 K were conducted on an ASAP 2020

V3.03 H instrument. All samples (powders) were outgassed at 100 ^{o}C for 5 h under flowing nitrogen before measurements. The specific surface areas of SnO_2, SnO_{2-x} and ZnO/SnO_{2-x} NPs calculated by the Brunauer-Emmett-Teller (BET) method are similar. They are about 24.7, 23.4 and 25.1 m^2/g, respectively.

Electron Paramagnetic Resonance (EPR) Measurements: EPR spectra were studied on powdered products by a conventional Bruker spectrometer (Bruker, A300-10-12) operating at X-band frequency and magnetic field modulation of 100 kHz, with a microwave power of 2.25 mW and modulation amplitude of 1 G at 88 K. The resonance lines were simulated by the Bruker WINEPR SimFonia program.

Photocatalytic and electrochemical measurements: The photocatalytic H_2 evolution reaction was operated in a Pyrex reactor with an entry window of optical flat quartz glass. The 80 mg as-prepared sample was dispersed in the reaction cell with 100ml of 0.1 M Na_2S and 0.1 M Na_2SO_3 mixed aqueous solution. A 300W Xe lamp (Beijing Changtuo, PLS-SXE-300UV) supplying the full wavelength light illumination was used as the light source. The distance between the light and liquid level remains stable in every time when the detection was carried out. The distance between the light and solution is about 10 cm and the power of light illumination is about 180 mW/cm^2. The amount of H_2 evolution was analyzed using on-line gas chromatography with a thermal conductivity detector and N_2 gas carrier. In the stability test, the photocatalytic experiment was stopped for each cycle (5 h) by turning off the light and evacuating the reactor. Photoelectrochemical (PEC) measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the

photoelectrode surface. The F-doped SnO_2 coated glasses (FTO) are the working electrodes with a light irradiation area of 1.0 cm^2, which subjected to drop the ethanol solution containing the identical weight of products on the conductive surface and then dry at 60 °C for 12 h, while a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Donor density calculation: The ZnO/SnO_{2-x} displayed the smallest slope compared to other samples, suggesting the ZnO/SnO_{2-x} NPs possess the most donor densities according to the Mott-Schottky equation:

$$N_d = (2/e_0\varepsilon\varepsilon_0)[d(1/C^2)/dV]^{-1}$$

where N_d is the donor density, e_0 the electron charge, ε the dielectric constant of SnO_2 (ε = 12.7), ε_0 the permittivity of vacuum, and V the applied bias at the electrode. The carrier densities of the SnO_2, SnO_{2-x} and ZnO/SnO_{2-x} samples are calculated to be 6.0×10^{19} cm^{-3}, 9.9×10^{19} cm^{-3} and 2.9×10^{20} cm^{-3}, respectively.

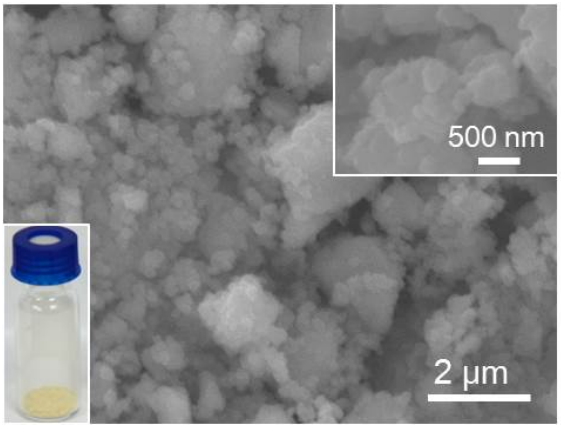

Fig. S1 SEM image of as-prepared SnO_{2-x}

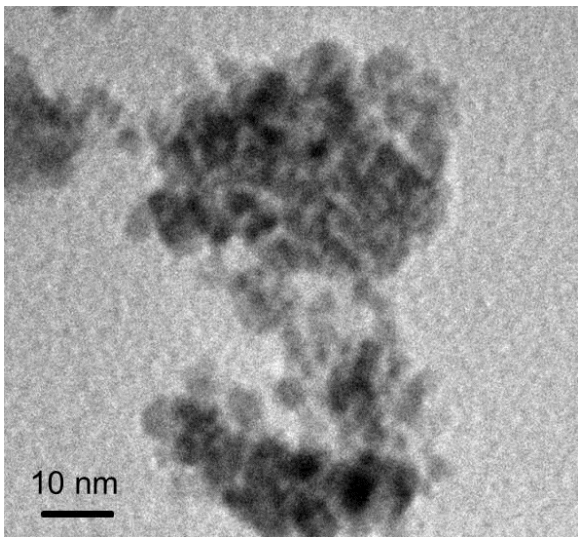

Fig. S2 TEM images of Calcined SnO_{2-x}.

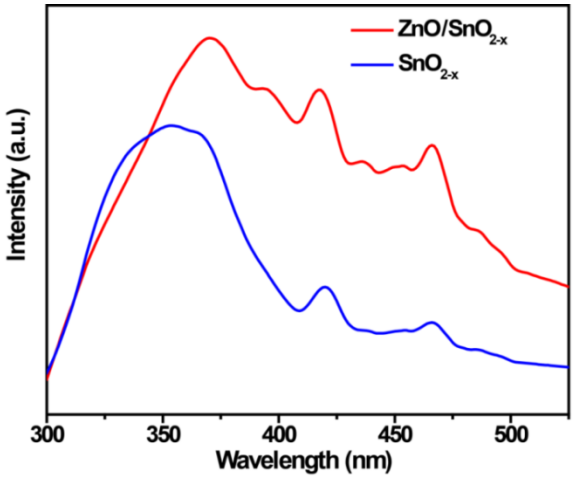

Fig. S3 Room temperature PL spectra of SnO_{2-x} and ZnO/SnO_{2-x} studied at the excitation wavelength of 280 nm.

In both samples broad PL bands mainly peak at about 350 nm were observed, which ascribed to the presence of point defects, such as oxygen vacancy.[2] Due to the increasing number of oxygen vacancy, the spectrum of ZnO/SnO_{2-x} NPs has higher intensity than that of SnO_{2-x} NPs at the main peak. We also recorded other peaks at

393, 418, and 466 nm, which are utilized for detecting the concentration and chemical state of oxygen vacancy by earlier reports [3-5].

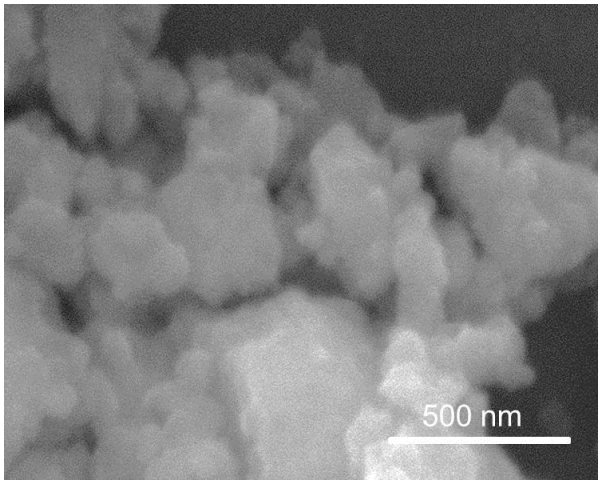

Fig. S4 SEM image of ZnO NPs, showing they are made up of NPs with a diameter of 300-400 nm.

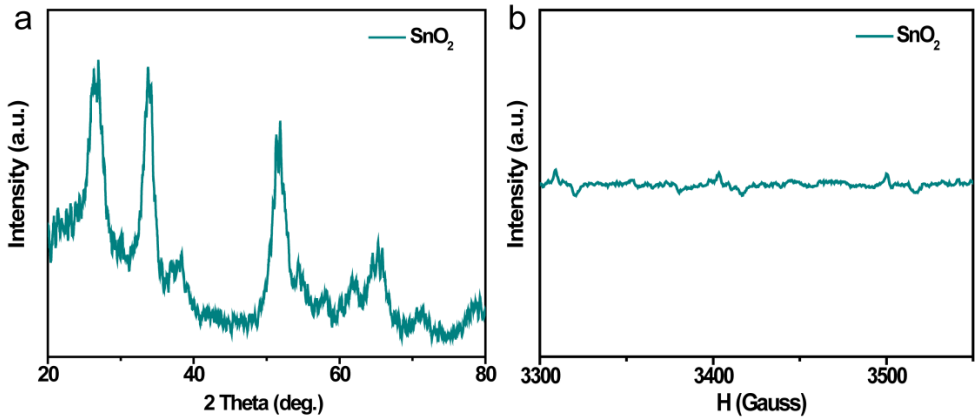

Fig. S5 (a) XRD pattern of SnO_2;(b) EPR spectrum of SnO_2 powders recorded at 88 K.

References:

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