# Electronic Supplementary Information

# $Sn_3O_4$: A novel heterovalent-tin photocatalyst with hierarchical 3D nanostructures under visible light

Yunhui He, Danzhen Li*, Jing Chen, Yu Shao, Jiangjun Xian, Xiuzhen Zheng and Peng Wang

Research Institute of Photocatalysis, State Key Laboratory Breeding Base of Photocatalysis,
Fuzhou University, Fuzhou, 350002, P. R. China.

Fax: +86-591-8377-9256; E-mail address: dzli@fzu.edu.cn.

**Sample preparation procedure:** All chemicals used in this study were analytical grade (Sigma-Aldrich) without further purification. Distilled water was applied for all synthesis. In a typical fabrication, 0.90 g of $SnF_2$ was added into a 100 mL autoclave Teflon vessel containing 50 mL distilled water and 25 mL ethanol with stirring for 1 h, to form a white suspension. The resulting aqueous precursor suspension was then hydrothermally treated at 180 $^{o}$C for 6 h to form tin oxide sample. The obtained solid sample was filtered and washed with water for three times, then dried at 80 $^{o}$C without further treatment. $SnO_2$, $Sn_3O_4$ and SnO were simply synthesized by controlling the pH values of the suspensions. NaOH and HCl with concentrations of 1 mol/L solutions were added to adjust pH values of the suspensions. When the pH value of the precursor was 1, white $SnO_2$ nanopartical was prepared. Once the pH increased to 3, pure hierarchical yellow $Sn_3O_4$ could be obtained. At pH 13, under alkaline conditions, the black SnO was synthesized. N-doped $TiO_2$ was synthesized by a traditional method [1] through calcination of P 25 at 550 °C under dry $NH_3$ flow for 3 h.

**Characterization:** The crystal phase was analyzed by X-ray diffraction with Cu Kα radiation (XRD, Bruke D8, German). X-ray photoelectron spectroscopy with monochromatized Al Kα X-rays (hν = 1486.6 eV) radiation (XPS, ThermoFisher Scientific Co. ESCALAB 250, USA) was used to investigate the surface properties. The shift of the binding energy was corrected using the C1s level at 284.6 eV as an internal standard. Scanning electron microscope (FESEM, FEI Nova NANOSEM 230, operated at an accelerating voltage of 15 kV) was used to characterize the morphology of the samples. The morphology and structure were examined by transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN, operated at an accelerating voltage of 200 kV). The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV-vis spectrophotometer (DRS, Cary-50, Varian Co., USA) equipped with an integrating sphere assembly, using $BaSO_4$ as reflectance sample. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 150 $^{o}$C prior to measurements. The photoelectrochemical experiment was measured on an electrochemical system (CHI-660D, China). The catalysts were deposited as a film on a 0.5 cm × 0.5 cm indium−tin−oxide conducting glass to obtain the working electrode. Ag/AgCl and Pt served as the reference electrode and the counter electrode, respectively. The electrolyte was 0.1 M $Na_2SO_4$ solution. The Mott−Schottky experiments were conducted on a Precision PARC workstation. Electron spinresonance (ESR) spectra were obtained using a Bruker model A300 spectrometer with a 500W Xe-arc lamp equipped with an IR-cutoff filter ( $\lambda < 800$ nm) and an UV-cutoff ( $\lambda > 420$ nm) as a visible light source. The settings were center field, 3512 G; microwave frequency, 9.86 GHz; power, 20 mW.

**Photocatalytic activity:** In the test, 0.04 g of $Sn_3O_4$ powder was added into 80 mL of MO solution (10 ppm) or 4-Phenylazophenol (20 ppm) in a 100 mL Pyrex glass vessel. To obtain the adsorbed equilibrium states, the suspension was kept in the dark for 120 min with continuing agitation prior to irradiation. $O_2$ was bubbled through the suspension to ensure that the reaction was operated under $O_2$ saturation conditions. The reactors were then irradiated with visible light emitted by a 500 W halogen lamp (Philips Electronics) with 420 and 800 nm cutoff filters. The system was cooled by a fan and water, which were used to maintain the system at room temperature. At given time intervals, 3 mL aliquots were extracted and centrifuged to remove the catalysts. The filtrates were analyzed by recording variations of the maximum absorption band ($\lambda = 464$ nm of MO and 374 nm of 4-Phenylazophenol) in the UV-vis spectra using UV-vis spectrophotometer. After degradation, the catalysts were centrifuged from the suspensions and dried to reuse.

**In situ XPS analysis:** In the present work, visible light irradiation was carried out in XPS preparation chamber (base pressure ~ $5.0 \times 10^{-8}$ mbar), and the sample was then transferred to XPS analysis chamber (base pressure ~ $8.0 \times 10^{-10}$ mbar) without being exposed to air. This “in situ” setting makes the samples possible to eliminate the possibility of the influence of environmental pollutions, thereby permitting the detection of the intrinsic surface reaction under visible light irradiation. A

Mercury–Xenon lamp (LC8, HAMAMATSU, 200 W, Japan) with 420 and 800 nm cutoff filters was used as an excitation light source, and introduced into the XPS preparation chamber though a sapphire window. Prior to the illumination of the sample, $CH_3OH$ was adsorbed onto the surface of the sample by vacuum drying of the suspension. After the irradiation in XPS preparation chamber, the photoinduced holes were quenched by the photocatalytic oxidation of $CH_3OH$, whereas photoexcited electrons remained in $Sn_3O_4$. Thus, the differential spectrum between before and after irradiation was attributed to the electrons in $Sn_3O_4$.[2]

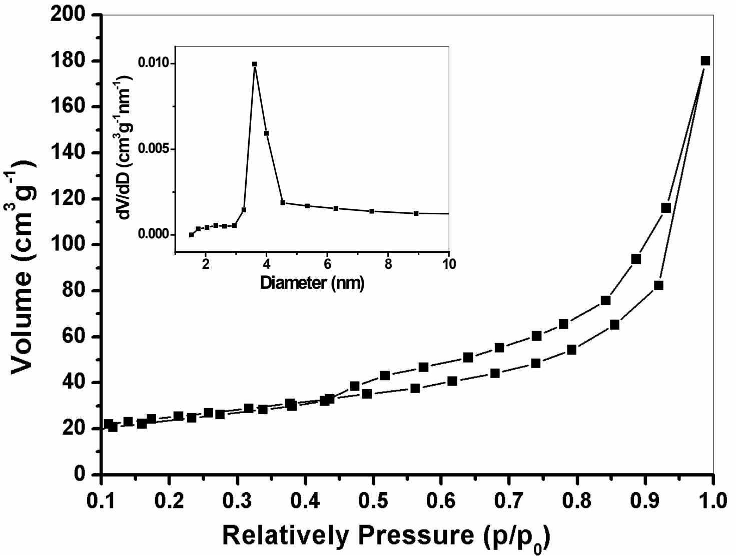

**Fig. S1** The nitrogen adsorption–desorption isotherm and pore size distribution (inset) of $Sn_3O_4$

Note: The isotherm of the $Sn_3O_4$ samples is types IV, indicating the pore-size distribution in the mesoporous regions. The shapes of hysteresis loops are of type $H_3$, associated with mesopores formed due to aggregation of plates-like particles.

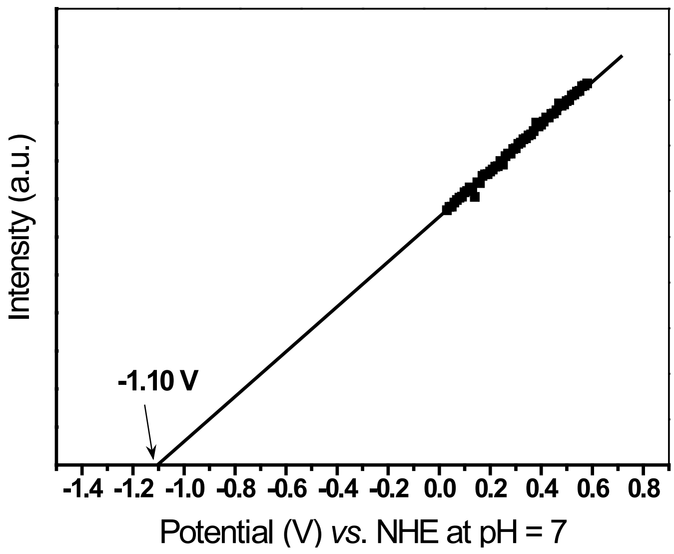

**Fig. S2** Mott-Schottky plot of $Sn_3O_4$

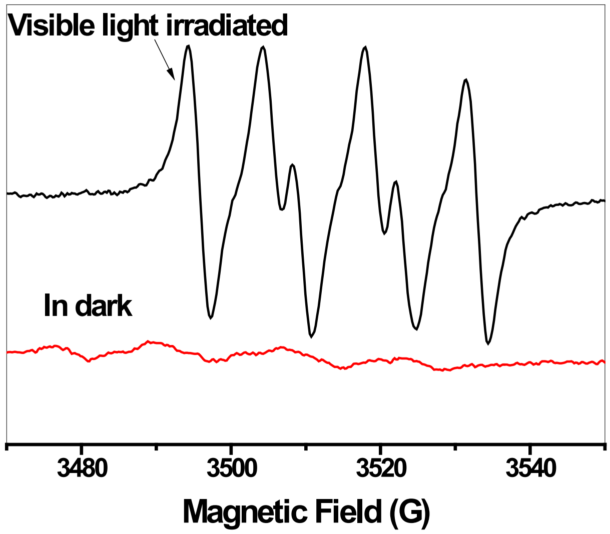

**Fig. S3** DMPO spin-trapping ESR spectra in $Sn_3O_4$ methanolic dispersion for DMPO- $O_2\bullet^-$.

Note: ESR spin-trap with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) technique [4] was used in this experiment.

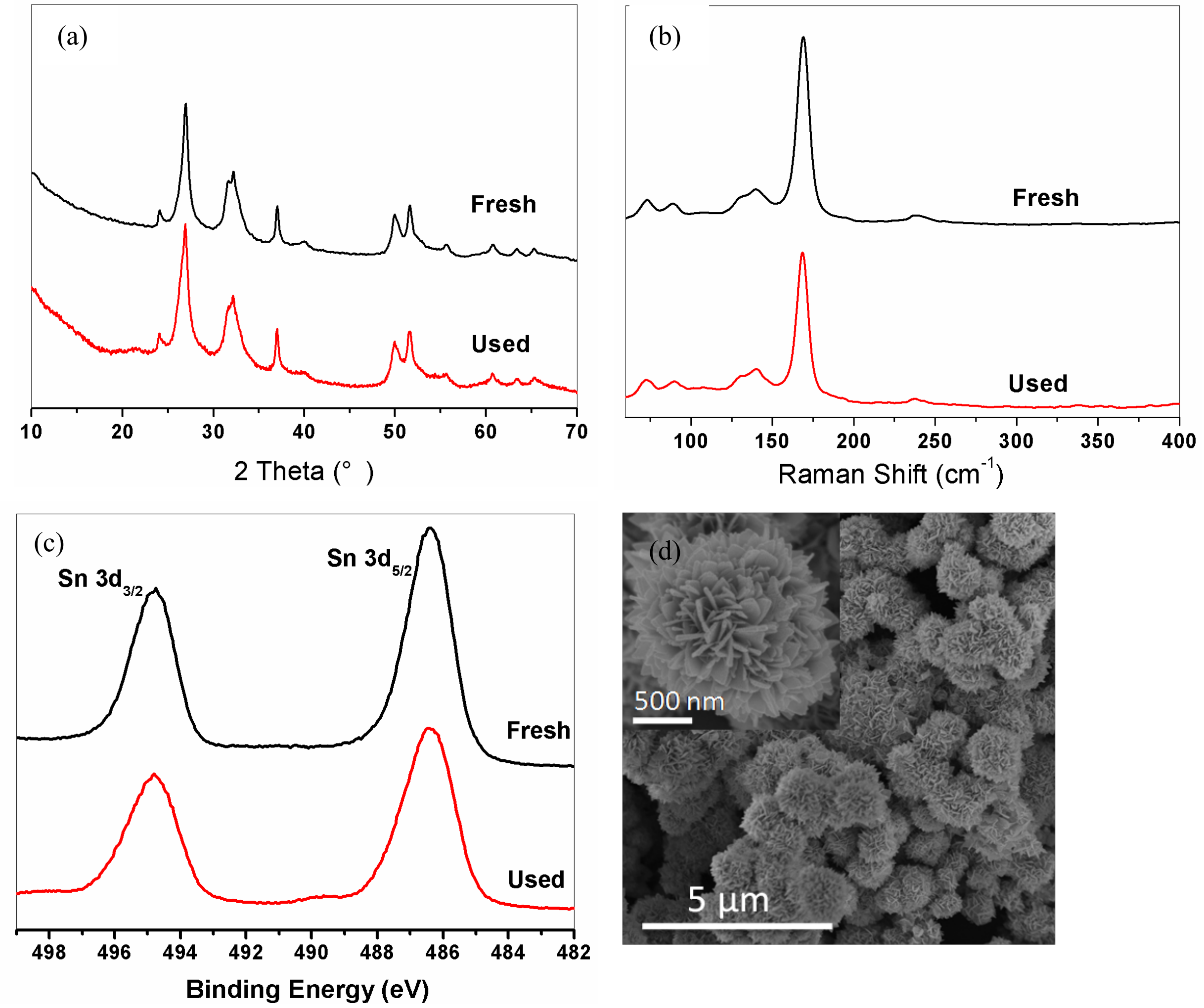

**Fig. S4** XRD patterns (a), Raman spectra (b) and XPS (c) of fresh and used $Sn_3O_4$, and SEM images of used $Sn_3O_4$ (d). Inset of (d) shows magnifying hierarchical 3D nanostructure of $Sn_3O_4$.

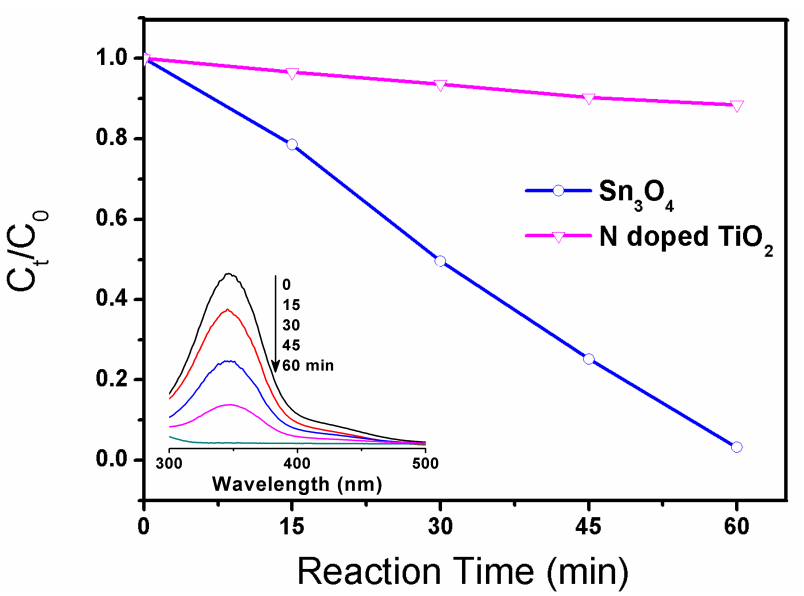

**Fig. S5** (a) Photocatalytic degradation of 4-Phenylazophenol over the as-prepared catalysts under visible light irradiation. Insert shows UV-vis spectral changes of 4-Phenylazophenol as a function of reaction time.

**Table S1.** In-situ XPS analysis of the $Sn_3O_4$ irradiated by visible light in vacuum

| **Irradiation time / min** | **$Sn3d_{5/2}$** | | **$Sn3d_{3/2}$** | | **Assignment** | **Ratio /At.%** |
|---|---|---|---|---|---|---|
| | **Position / eV** | **FWHM / eV** | **Position / eV** | **FWHM / eV** | | |
| 0 | 486.4 | 1.54 | 494.8 | 1.54 | Sn(II)-O | 66.2 |
| | 487.0 | 1.54 | 495.5 | 1.54 | Sn(IV)-O | 33.8 |
| 10 | 486.4 | 1.54 | 494.8 | 1.54 | Sn(II)-O | 65.6 |
| | 487.0 | 1.54 | 495.5 | 1.54 | Sn(IV)-O | 25.8 |
| | 484.8 | 1.54 | 492.6 | 1.54 | Sn(0) | 8.6 |
| 20 | 486.4 | 1.54 | 494.8 | 1.54 | Sn(II)-O | 64.5 |
| | 487.0 | 1.54 | 495.5 | 1.54 | Sn(IV)-O | 19.4 |
| | 484.8 | 1.54 | 492.6 | 1.54 | Sn(0) | 16.1 |
| 30 | 486.4 | 1.54 | 494.8 | 1.54 | Sn(II)-O | 62.9 |
| | 487.0 | 1.54 | 495.5 | 1.54 | Sn(IV)-O | 15.6 |
| | 484.8 | 1.54 | 492.6 | 1.54 | Sn(0) | 21.5 |

## References:

1. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*， 2001, **293**, 269–271.

2. K. Yamanaka, T. Morikawa, *J. Phys. Chem. C,* 2012, **116**, 1286-1292.

3. C. C. Chen, P. X. Lei, H. W. Ji, W. H. Ma, J. C. Zhao, *Environ. Sci. Technol.* 2004, **38**, 329.