Electronic Supplementary Information

Facile synthesis of high-efficient In_2S_3 photocatalysts for the removal of dye with size-dependent photocatalysis

Chaofan Zheng [a,†], Ziyao Wang [a,†], Jialong Yuan [a], Qingfeng Xu [a], Haixin Li [a], Xiaoyi Lu [a], Jiangang Gao [a,b,*] and Wenjin Yue [a,b,*]

[a] School of Chemical and Environmental Engineering, Anhui Polytechnic University, Wuhu, 241000, P. R. China

[b] Anhui Laboratory of Clean Energy Materials and Chemistry for Sustainable Conversion of Natural Resources, Wuhu, 241000, P. R. China

*Corresponding author.

Email address: gaojiangang@ahpu.edu.cn (Jiangang Gao)

yuewenjin_79@163.com (Wenjin Yue)

[†] These authors contributed equally to this work.

S1. Photocatalysis experiments

In_2S_3-5, In_2S_3-10 and In_2S_3-15 were suspended in rhodamine B (RhB) solution to obtain the suspension with the concentration of 60 mg/L, respectively. Then the suspension was kept in the dark for 30 min to reach the adsorbed equilibrium before the photoreaction. Artificial solar light used 300 W Xenon lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd., China) loaded with Cut 420 filter which emitted visible light in 400–780 nm. The distance between Xenon lamp and the suspension was 10 cm away, getting the intensity approximately constant at 220 mW/cm^2. 3 mL suspension was taken out and centrifuged to remove In_2S_3 particles at intervals, the filtrates were tested by UV-vis absorption spectrum to record the variation of the maximum absorption band of RhB at λ=554 nm. Moreover, the photodegradation of crystal violet (CV), malachite green (MG), methyl orange (MO), congo red (CR) and acid red (AR) with In_2S_3-10 were carried out as the similar procedure, except that the maximum

absorption band of CV at λ=590 nm, MG at λ=617 nm, MO at λ=465 nm, CR at λ=498 nm and AR at λ=511 nm.

S2. Electrochemical measurements

In electrochemical experiments, Pt wire and saturated calomel electrode (SCE) electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry (C-V) measurement was carried out in N_2 atmosphere at a scan rate of 50 mV/s with tetrabutylammonium perchlorate dissolved in acetonitrile (0.1 M) as the supporting electrolyte. 4 mg In_2S_3 was dispersed in the mixed solvent containing 1.5 mL deionized water and 0.5 mL ethanol to carry out ultrasound treatment for 60 min followed by the addition of 60 μL Nafion glue. Dry *ca. 15-20* μL mixture on carbon substrate to make the working electrode for C-V measurement. In linear sweep voltammetry (LSV), transient photocurrent-time (I—t) curves and electrochemical impedance spectroscopy (EIS) measurements, the working electrodes were prepared as follows. 5 mg In_2S_3 which dispersed in the mixed solvent containing 0.5 mL water and 0.5 mL alcohol had a ultrasound treatment for 120 min, followed by 20 mL Nafion glue adding into the mixture, then *ca.* 300-400 μL mixture was dried on ITO conductive glass. 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. 300 W Xe lamp with an optical cut-off filter ($\lambda \geq 420$ nm) was used as the light source. EIS measurement was carried out at open circuit potential in 10^5-10^{-2} Hz frequency range.

S3. Calculation of band edge potential based on empirical equation and C-V measurement

Based on the value of $E_{g\text{-}O}$, the valence band edge potential (E_{VB}) of a semiconductor at the point of zero charge can be calculated by the following empirical equation: $E_{VB} = X - E^e + 0.5E_{g\text{-}O}$, where X is the electronegativity of the semiconductor (the value for In_2S_3 is 4.7 eV), E^e is the energy of free electrons on the hydrogen scale (~4.5 eV). Furthermore, the conduction band edge potential (E_{CB}) can be determined by $E_{CB} = E_{VB} - E_{g\text{-}O}$. The calculated results of different In_2S_3 are shown as Table 1 in main body.

C-V measurements are also helpful for determination of the ionization potential (IP) and the electron affinity (EA) of nanoparticles that are equal to E_{VB} and E_{CB}. With SCE reference electrode, it is expected that the nanoparticles have $IP = -(E_{ox} + 0.245)$ eV and $EA = -(E_{red} + 0.245)$ eV, where E_{ox} and E_{red} are the onset potentials of oxidation and reduction peaks. The value of 0.245 was the potential

of SCE electrode versus the normal hydrogen electrode (NHE). The results of different In_2S_3 are shown as Table 1 in main body.