

Supporting information for:

**A Series of High Efficient Photocatalysts for Organic Contaminants Degradation
under Visible Light Irradiation**

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1. Experimental Section

1.1 Sample preparation

The antimonite acid sample was synthesized via Sb_2O_3 and H_2O_2 at 65 °C for 30h and then drying at room temperature as reported previously [Zarbin, A.; Alves, O.; Amarilla, J.; Rojas, R.; Rojo, J. *Chem. Mater.* **1999**, *11*, 1652]. The N-doped antimonite acid sample was obtained after drying the washed product prepared by heating antimonite acid powders with urea at weight ratio of 1: 2 at 400 °C for 2 h at a furnace.

1.2 Characterizations

The crystal structures of samples were determined by an X-ray diffractometer (DX-2500 diffractometer, Fangyuan) with Cu $K\alpha$ radiation ($\lambda=0.154145$ nm). Fourier transform infrared spectroscopy (FTIR) was taken with a BIO-RAD (TFS-135) spectrophotometer. In the case of X-ray photoelectron spectroscopy (XPS) (ESCALAB 250), an Al anode with a monochromator was used to significantly reduce the background signal. The binding energy was referenced to the C 1s peak

taken at 284.8 eV. The diffuse reflectance spectrum was recorded with a UV-Vis spectrophotometer (Varian Cary 5000) and transformed to the absorption spectra according to the Kubelka-Munk relationship. The photoluminescence (PL) spectra were performed at room temperature with a Fluorolog Tau-3 spectrofluorometer (Jobin Yvon/SPEX Horiba).

1.3 Photocatalytic activity evaluation

The photocatalytic activity of the as-prepared sample was evaluated by the Rhodamine B (RhB) photodegradation under visible light irradiation, which was emitted from 300-W Xe lamps with L-42 cut-off filter. The photocatalytic reaction was carried out with 0.2 g powder sample suspended in a 100 ml RhB solution in a glass cell. The initial concentration of RhB solution was about 2.5 mg L⁻¹. The variation in RhB concentration was recorded using a UV-Vis spectrophotometer by measuring the absorbance at 554 nm. The initial concentration of phenol solution was about 0.05 mM. The undegraded phenol was analyzed fluorimetrically. The excitation and emission wavelengths were set at 259 and 298 nm, respectively. [Karunakaran C., Dhanalakshmi R., Anilkumar P., *Journal of Hazardous Materials*, **2009**, 167, 6648]

1.4 •OH radicals determination

In recent years, Ishibashi et al. [Ishibashi, K.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol., A* **2000**, 134, 139] have developed a photoluminescence technique by TAPL to detect •OH selectively. Therefore, the method of photoluminescence technique with TA-PL was used to detect the generation of •OH. [Liu, G.; Wang, L.; Sun, C.; Yan, X.; Wang, X.; Chen, Z.; Smith, S.; Cheng, H.; Lu, G. *Chem. Mater.* **2009**, 21, 1266; Chen, Z.; Li, D.; Zhang, W.; Shao, Y.; Chen, T.; Sun, M.; Fu, X. *J. Phys. Chem. C* **2009**, 113, 4433.]

The measurements of the amount of $\cdot\text{OH}$ were conducted according to the literature.[Ishibashi, K.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol., A* **2000**, *134*, 139;] The reaction principle was that terephthalic acid (TA) readily reacted with $\cdot\text{OH}$ radicals to produce highly fluorescent product, 2-hydroxyterephthalic acid (TAOH), which emitted photoluminescence at around 426 nm on the excitation of its own 312 nm absorption band. The intensity of the peak attributed to TAOH was known to be proportional to the amount of $\cdot\text{OH}$ radicals formed. The experimental process was described below. Two-hundred milligrams of photocatalyst was suspended in 100 mL of aqueous solution containing 20 mM NaOH and 6 mM terephthalic acid. Before exposure to visible light irradiation, the suspension was stirred in the dark for 30 min. Then, 5 mL of the solution was taken out every 20 min and filtered for fluorescence spectrum measurements.

2. Results and discussion

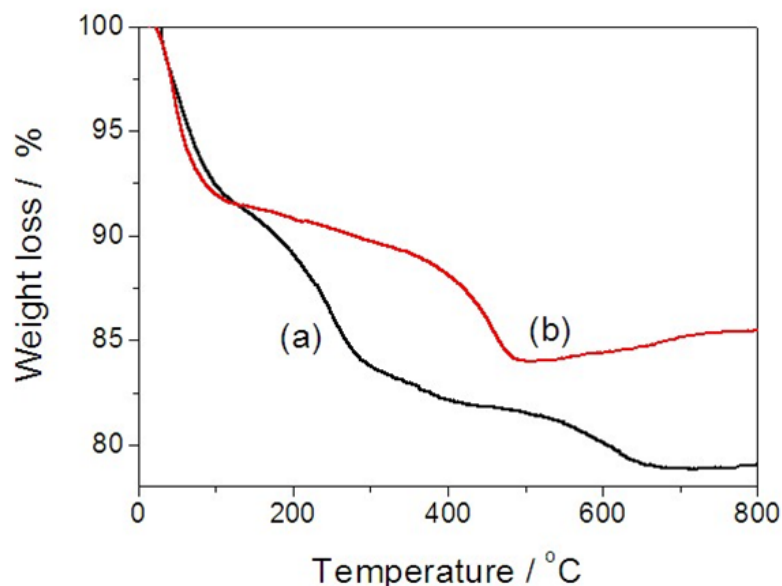


Figure S1. TG curves recorded for antimonic acid (a) and the product after heating with urea at 400 °C (b).

TG curves recorded for antimonite acid (a) and the product after heating with urea at 400 °C (b) are shown in Figure S1. Three well-defined weight losses and one plateau are observed on the antimonite acid. The first weight loss region ranges from room temperature to 120 °C, the second one ranges from 120 to 300 °C, the third weight loss goes from 300 to 700 °C, and the plateau takes place above 700 °C. The former two weight losses are caused by water vapor. The adsorbed and crystalline water bring the first and second weight loss, respectively. Two well-defined weight losses are observed on the product after heating with urea at 400 °C. The first weight loss at range from room temperature to 120 °C, which is caused by removing the adsorbed water. The second weight loss from 300 to 500 °C is possibly attributed to the decomposition of antimonite acid and releasing N₂. According to the above results, the formula of antimonite acid and the product after heating with urea at 400 °C are estimated to be H₂Sb₂O₆•3.6H₂O and H₂Sb₂O_{5.9}N_{0.1}•2.1H₂O, respectively.

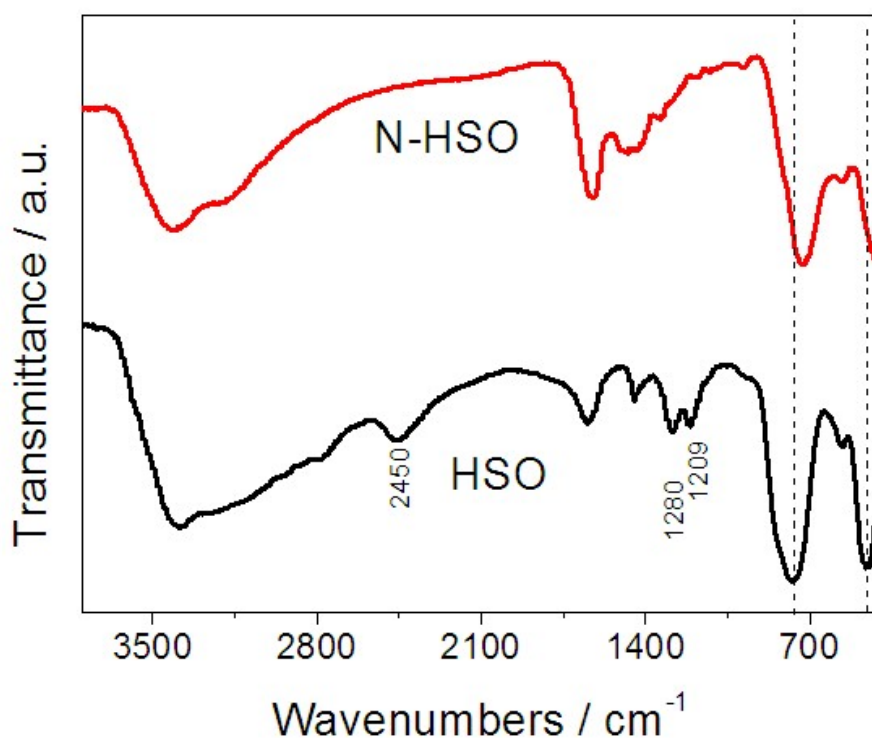


Figure S2. FTIR spectra of HSO and N-HSO.

Figure S2 shows the FTIR spectra of HSO and N-HSO. Obviously, the negative peaks at 770 and 450 nm of N-HSO shift to shorter wavelength in comparison with these of HSO. A functional relationship between the IR frequencies and the metal–oxygen bond length in the local structure has been established, in which the lower frequencies of the IR band correspond to the longer bond lengths. The observation indicates that the Sb–O bond lengths are increased due to the substitution of nitrogen atom for oxygen atom because of the larger ion radius of nitrogen. Other band at 2450, 1280 and 1209 could be caused by the crystalline water.

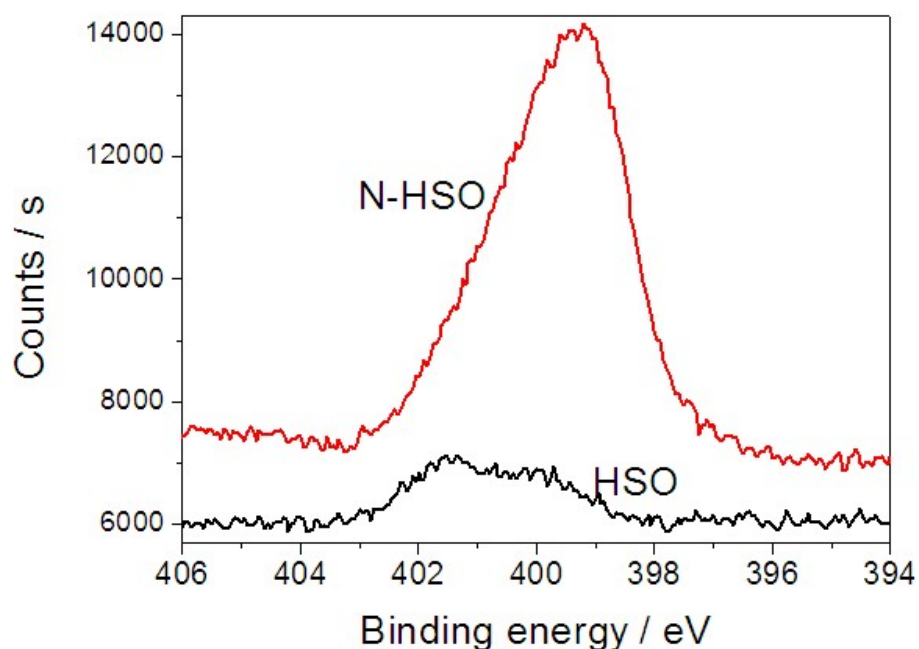


Figure S3 N 1s XPS line obtained from the HSO and N-HSO samples.

From Figure S3, it could be seen that the obvious N 1s line exists in N-HSO sample. In HSO sample, there is a small peak at ~401.5 eV, which is caused by the adsorbed N₂.

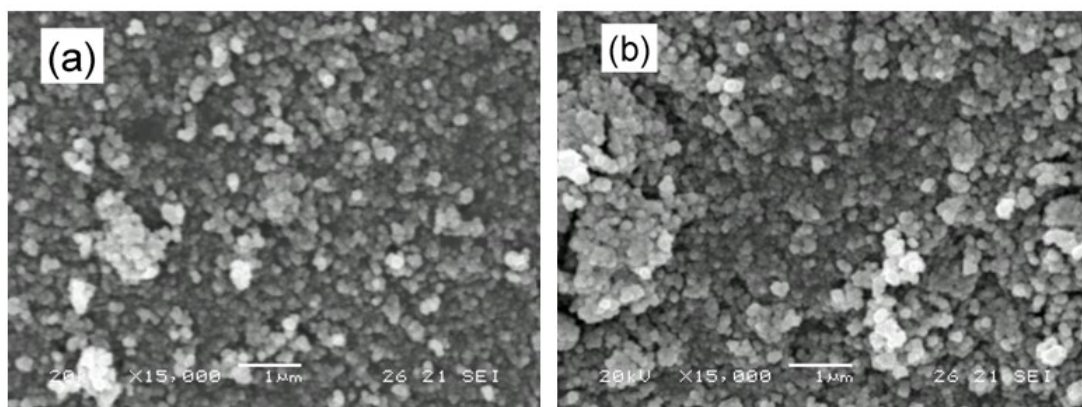


Figure S4 SEM images of the HSO (a) and N-HSO (b).

From Figure S4, it is no obvious difference in morphology and particle size, indicating that the obvious difference in photocatalytic activity is not caused by the morphology and particle size.

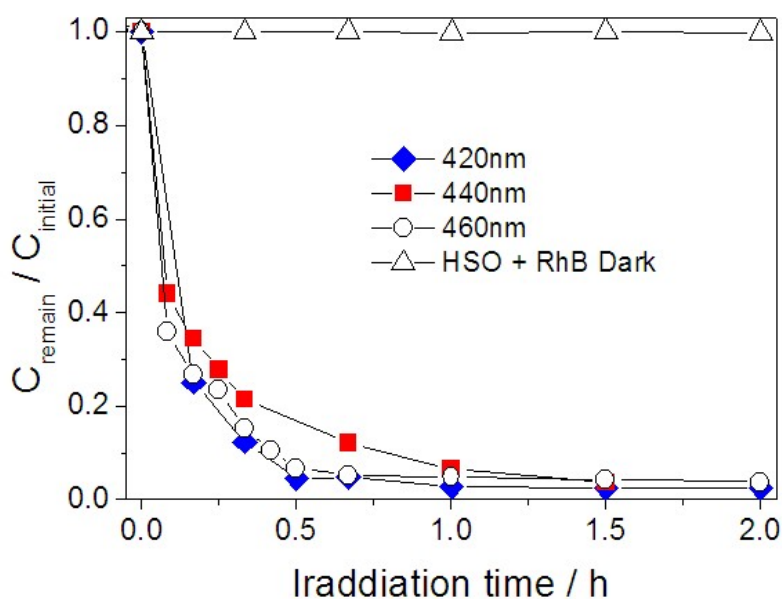


Figure S5 Normalized concentration changes versus the irradiation time in presence of HSO under the different cut-off filters.

The smallest light wavelength could be controlled by the cut-off filter. Figure S5 shows the normalized concentration changes versus the irradiation time in presence of HSO under the different cut-off filters and dark reaction. Obviously almost the same activities under 420, 440 and 460 nm cut-off filters and no degradation in the dark

reaction are observed, indicating that RhB degradation is caused by the self-sensitized degradation and not by the oxidation.

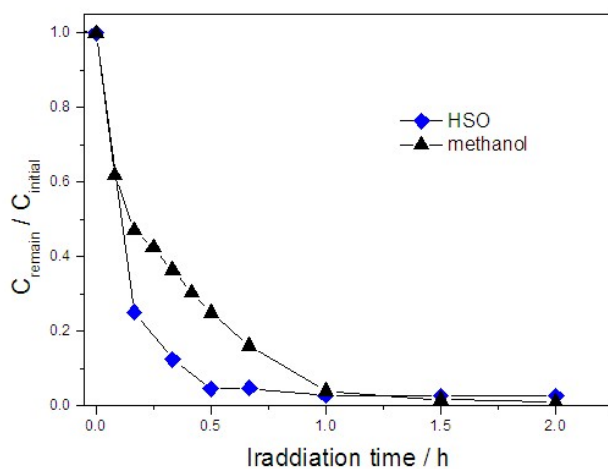


Figure S6 Normalized concentration changes versus the irradiation time in presence of HSO with and without the hole sacrifice (methanol).

A slight lower activity is observed in the presence of hole sacrifice over HSO, indicating that photogenerated hole has a little contribution on the RhB degradation.

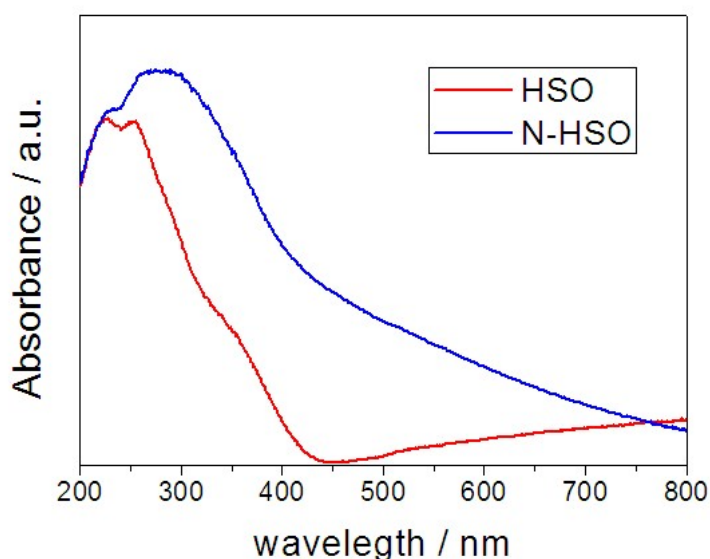


Figure S7 UV-vis spectra of HSO and N-HSO.

Figure S7 displays the UV-vis spectra of HSO and N-HSO. It is apparent that the N-HSO could absorb more visible light and HSO has an absorption tail in visible light

region.

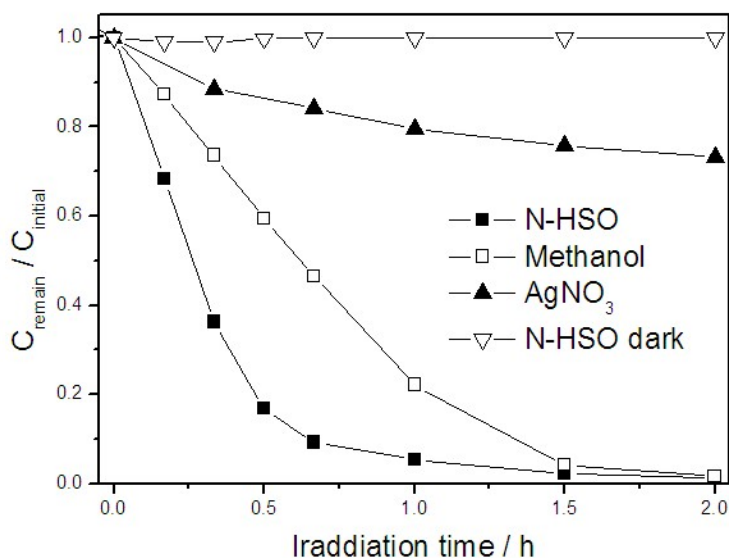


Figure S8 Normalized concentration changes versus the irradiation time in presence of N-HSO with and without the sacrifice reagents (AgNO_3 and methanol) in comparison with the dark reaction.

The sacrifice reagents could terminate one reaction path way in the reaction. AgNO_3 and methanol could sacrifice the photogenerated electrons and holes. After the introduction of these sacrifice reagent, the activity dramatically decreases, indicating that both the photogenerated electrons and holes have contribution to the RhB degradation under visible light irradiation ($\lambda > 400 \text{ nm}$).

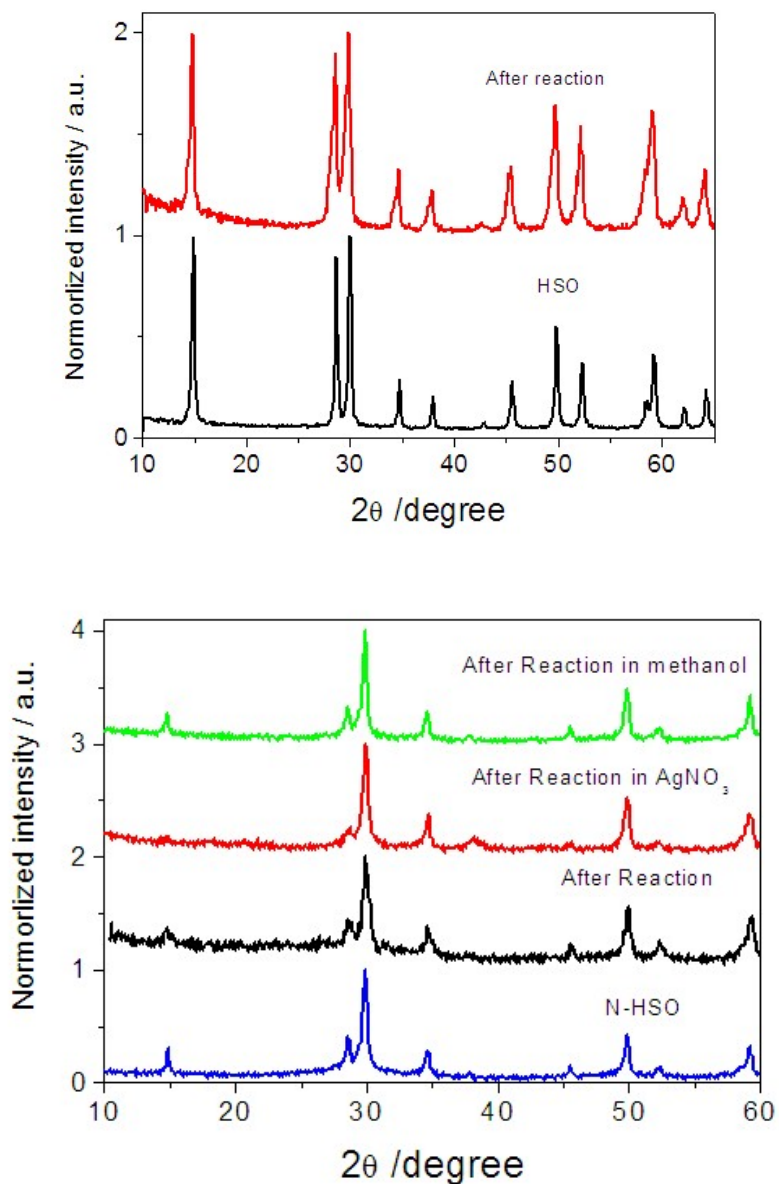


Figure S9 X-ray patterns of HSO and N-HSO before and after vary reactions.

From figure S9, it can be seen that the crystal structure of HSO and N-HSO before and after reaction is almost the same, implying that the crystal structure is stable for the reactions.