

CuO/CuSCN valence state heterojunction with visible light enhanced and ultraviolet light restrained photocatalytic activities

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Experimental Details

Synthesis of the CuO/CuSCN. The CuO/CuSCN nanostructural photocatalyst was prepared via a one-step low temperature method. In a typical synthetic approach, 0.01 mol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolves in 100 ml deionized water with constant stirring, and then a certain amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added until clarifying dark blue solution formed. The mixed solution was heated in an oil bath at 80 °C after 0.02 mol NaSCN powder was introduced into this copper ammonia solution. The result precipitates were collected until the residual solution was about 30 ml and washed with deionized water and absolute ethanol several times and then dried at 60 °C at ambient condition for overnight. The amount of CuO in CuO/CuSCN composite samples could be controlled by the ratio of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaSCN. Pure CuSCN was synthesized by a simple method: 0.01 mol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolves in 100 ml deionized water, and 0.01 mol NaSCN was added. The white precipitations were obtained after 12 hours constant stirring. We could obtain pure CuO powder according to Tu's report with tiny modification [1], 200 ml copper ammonia solution were heated at 80 °C for 12 hours, and the black precipitates were collected after washing and drying.

Characterization of the samples. The X-ray powder diffraction (XRD) patterns of the as-prepared products were characterized by using a Bruker AXS D8 advance powder diffractometer (Cu $K\alpha$ X-ray radiation, $\lambda=0.154056$ nm). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific Escalab 250 spectrometer with monochromatized Al $K\alpha$ excitation, and C1s (284.6 eV) was used to calibrate the peak positions of the elements. Scanning electron microscopy (SEM, Hitachi S-4800 microscope) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100, 200 kV) were employed to observe the morphologies and micro-structures. The photoluminescence (PL) measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. UV-Vis diffuse reflectance spectra were obtained for the dry-pressed disk samples by using a Shimadzu UV 2550 recording spectrophotometer, which was equipped with an integrating sphere and BaSO_4 was used as a reference.

Photocatalytic Reaction. The photocatalytic activity of the as-prepared samples was characterized by decomposing methylene blue (MB) under visible light irradiation at room temperature. The visible light source ($\lambda > 420$ nm) comes from a 300 W Xe arc

lamp (PLS-SXE300, Beijing Trusttech Co., Ltd) equipped with an ultraviolet cutoff filter and UV+Vis light source is achieved by removing the ultraviolet cutoff filter. The distance between the liquid surface of suspension and the light source was set about 15 cm. The photocatalytic activity experiments were carried out with the sample powder (0.1 g) suspended in MB solution (100 mL, 20 mg L⁻¹) with constant stirring. Prior to the irradiation, the suspensions were magnetically stirred in the dark for 1 h to establish the adsorption/desorption equilibrium. At the given time intervals, about 5 mL of the suspension was taken for further analysis after centrifugation. MB photodegradation was analyzed at 664 nm as a function of irradiation time on a UV-vis spectrophotometer (Shimadzu UV 2550).

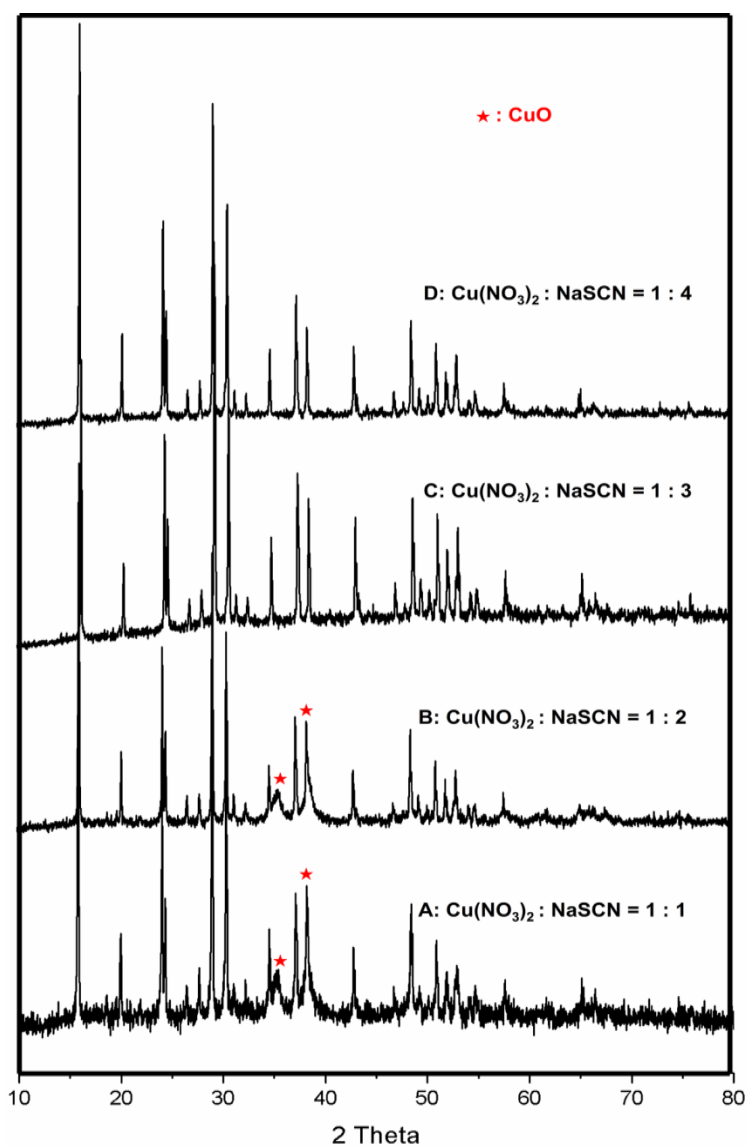


Fig. S1 XRD patterns of CuO/CuSCN composite obtained by different Cu(NO₃)₂ and NaSCN molar ratio.

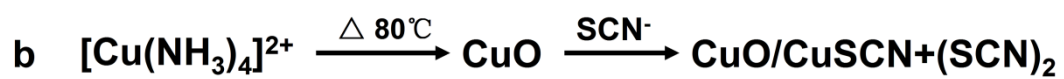


Fig. S2 The formed process of CuO/CuSCN composite

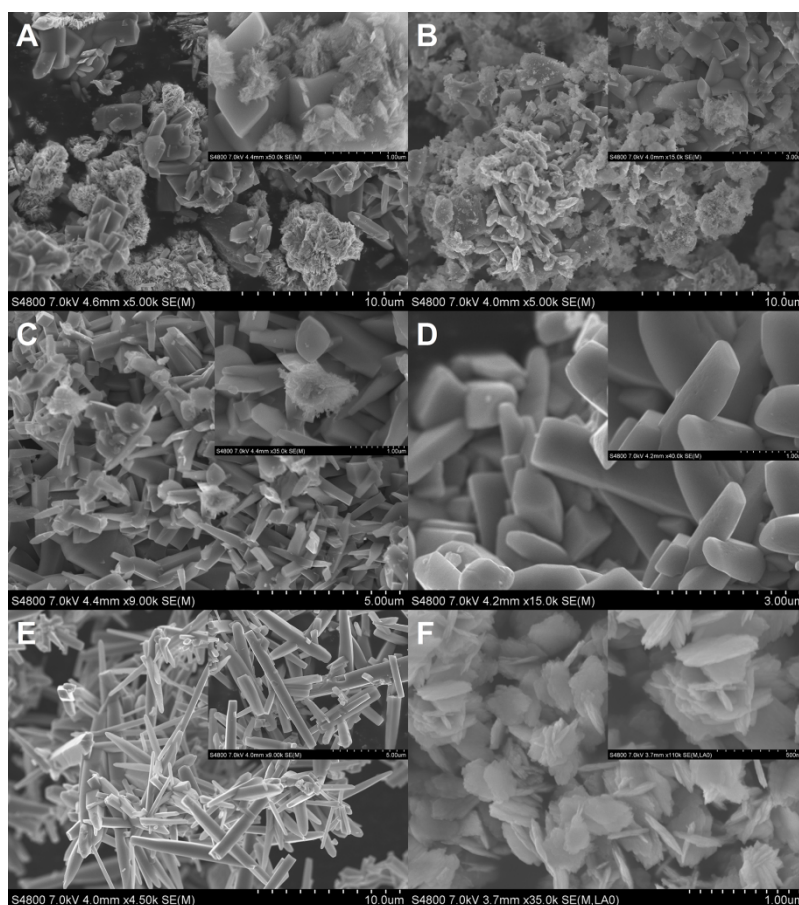


Fig. S3. SEM images of different samples. A is $\text{Cu}(\text{NO}_3)_2 : \text{NaSCN} = 1:1$, B is $\text{Cu}(\text{NO}_3)_2 : \text{NaSCN} = 1:2$, C is $\text{Cu}(\text{NO}_3)_2 : \text{NaSCN} = 1:3$, D is $\text{Cu}(\text{NO}_3)_2 : \text{NaSCN} = 1:4$, E is pure CuSCN, F is pure CuO.

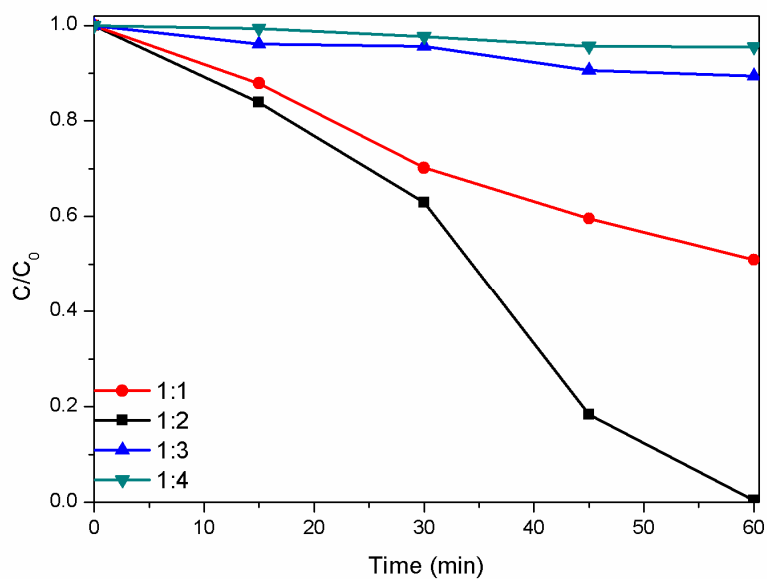


Fig. S4. The photocatalytic activities of the samples obtained via different molar ratio between $\text{Cu}(\text{NO}_3)_2$ and NaSCN.

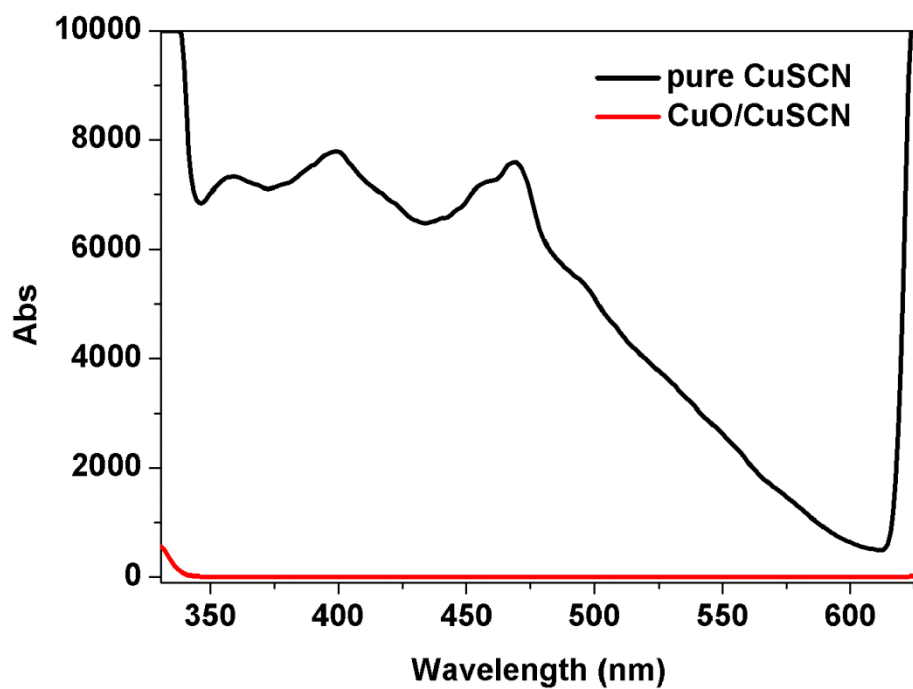


Fig. S5. PL spectra of the CuO/CuSCN composites and pure CuSCN samples ($\lambda=320$ nm)

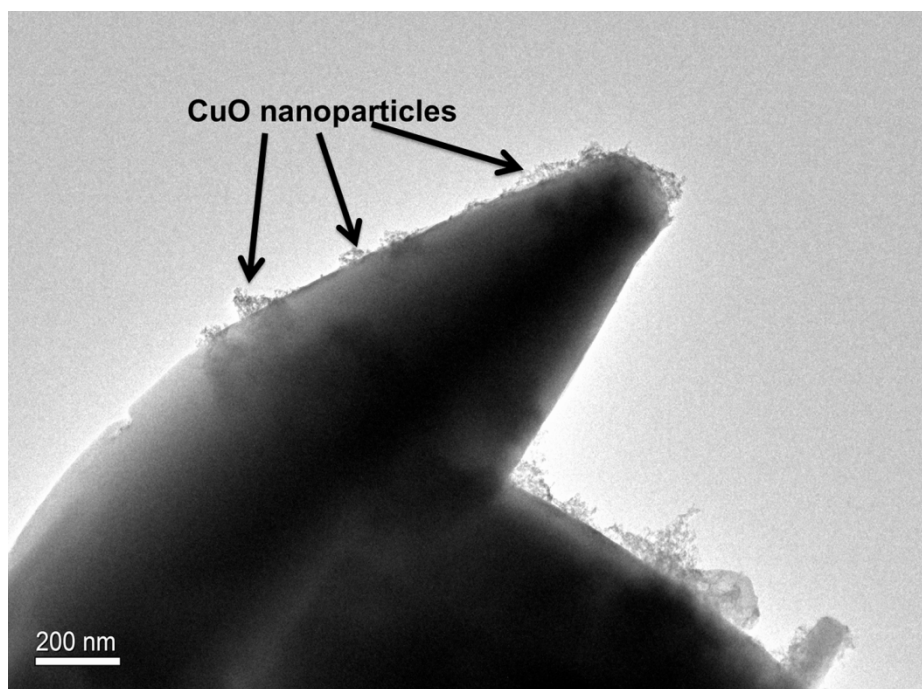


Fig.S6. TEM image of CuO/CuSCN composites

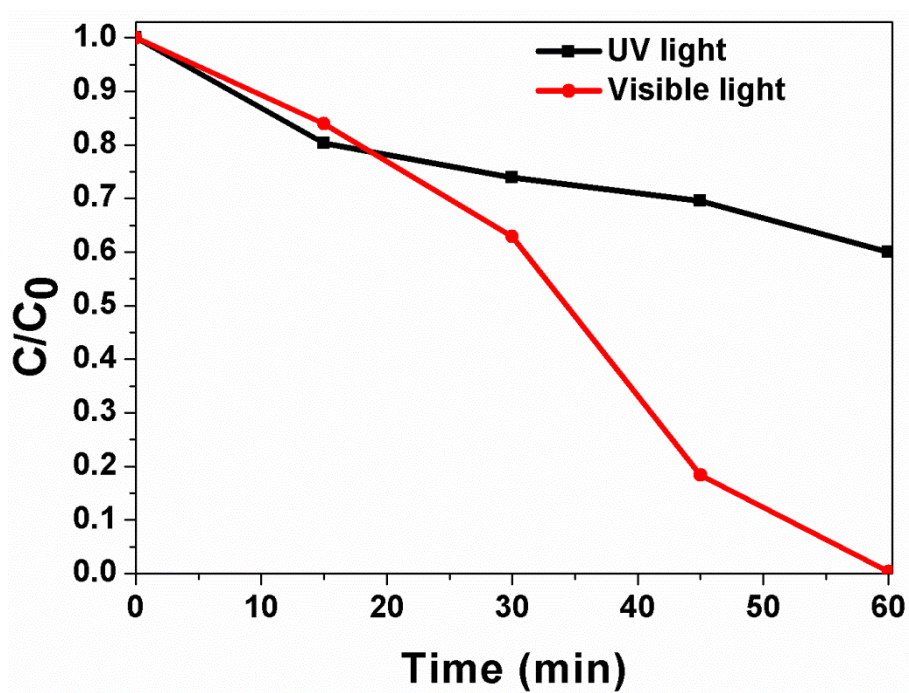


Fig.S7. The comparison of CuO/CuSCN composites photocatalytic activities under UV ($\lambda < 300$ nm) and Visible light ($\lambda > 420$ nm) irradiation

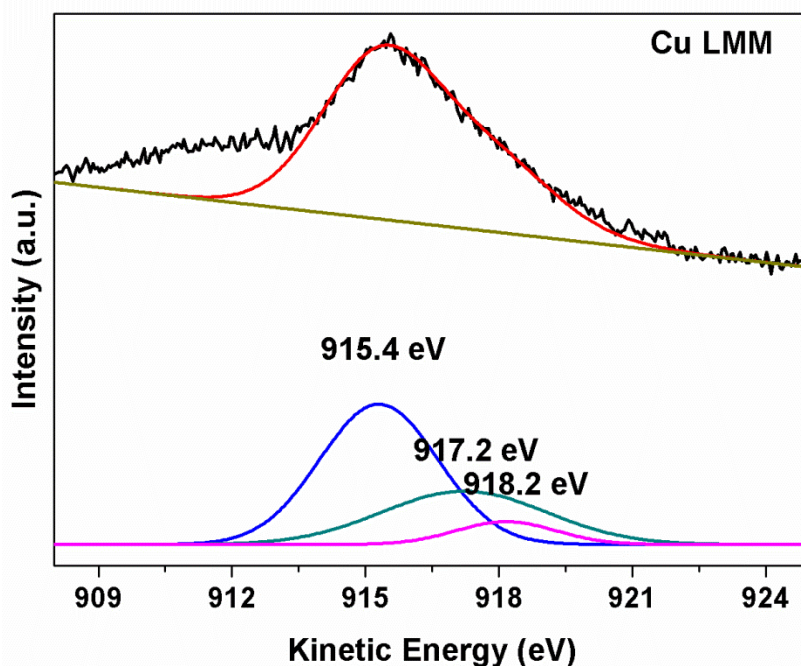


Fig.S8. XPS spectra of Cu LMM of CuO/CuSCN composites after photocatalytic process under N₂ (without O₂).

In order to support the photocatalytic mechanism which we proposed in the manuscript, we added an experiment to verify the existence of Cu⁰ during the photocatalytic process. 0.2 g CuO/CuSCN was dispersed in 200 ml MB (20 mg/L) solution, and then irradiation under visible light for 2 hours with constant injection of pure N₂. The sample was separated, dried and collected for XPS measurement. Cu⁰ cannot be distinguished by Cu 2p XPS spectra, because of their spectral overlap [2]. The further characterization was carried out by Cu L₃M_{4,5}M_{4,5} Auger spectra. As shown in Fig.S8, the Auger spectra of Cu LMM exhibit a broadening peak, which can be divided into three peaks centered at 918.2 eV, 917.2 eV and 915.4 eV by Gaussian fitting. According to the literature, the peak with a kinetic energy of 918.2 eV is attributed to Cu⁰ [3], while the peaks at 915.4 eV and 917.2 eV are Cu⁺ [4] and Cu²⁺ [5], respectively.

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