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Supporting information

Facile synthesis of 3D flower-like $Cu_{2-x}Se$ nanostructures via sacrificing template method and the excellent antibacterial activities

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Content

1. Experimental

1.1. Preparation of 3D flower-like $Cu_{2-x}Se$ film

Firstly, a 3D flower-like CuO film with nanosheet hierarchical structure was prepared by referring to our previous work,[1] where a piece of copper foil ($10 \times 20 \times 0.15$ mm^3) was immersed in a solution (prepared using 2.8 g of NaOH, 1.026 g of $(NH_4)_2S_2O_8$ and 18 mL deionized water) for 2 h at room temperature. The obtained black CuO film was used as a sacrificing template for synthesis of the flower-like $Cu_{2-x}Se$ film. Then, a claret Se^{2-} solution was prepared by adding 2 g NaOH, 0.114 g $NaBH_4$ and 0.12 g Se powder into 20 mL deionized water in a 100 mL of round bottom flask and refluxing at 100°C for 1 h under constant stirring. After it was naturally cooled down to room temperature, it was transferred into a 100 mL of conical beaker. Subsequently, the 3D flower-like CuO film precursor was immersed in the claret Se^{2-} solution and reacted for 8 h to obtain the 3D flower-like $Cu_{2-x}Se$ film. The product was washed by distilled water and ethanol, respectively, for several times and dried in an oven at 60 °C for 6 h.

1.2. Characterizations

The SEM images were taken on a scanning electron microscope (ZEISS MERLIN Compact, Germany). The TEM and HRTEM images were taken on a transmission electron microscope (Tecnai G^2F20, FEI). The XRD was performed on a Rigaku Ultima IV diffractometer with a Cu Kα radiation source (λ=1.5418 nm) operated at 40 kV and 40 mA. The XPS spectra were recorded on a ESCALAB 250Xi system. The UV-vis diffuse reflectance absorption spectrum was recorded on a Hitachi/U-3900 UV-visible spectrophotometer in the wavelength range of 200−1400 nm.

1.3. Photocatalytic activity tests

The photocatalytic activities of the 3D flower-like $Cu_{2-x}Se$ film were assessed by photodegradations of MB, MO and RhB dye solutions under UV-vis light source (CEL-HXF300 Xe lamp equipped with a VisREF filter, 350−780 nm, 900 mW/cm^2). A 25 mL of photocatalytic reactor contains a piece of flower-like $Cu_{2-x}Se$ film catalyst

(10×20 mm^2), 0.1 mL of H_2O_2 and 8 mL of single or mixed dye solution with concentrations of 1.25×10^{-4} M for MB or MO solutions, and 2.09×10^{-5} M for RhB solution. After the reactor was kept ventilating for about 30 min in dark to reach the adsorption equilibrium, the solution was illuminated by the light source which was located 10 cm above the reactor to induce photodegradation reactions. The reaction temperature was maintained at 6 °C by circulating cooling water using a cooling and circulating water pump (LX300). The sampling analyses on organic dye solutions were carried out every ten minutes by a UV-2100 UV-visible spectrophotometer. The photocatalytic degradation ratio (DR) was calculated by the following formula:

$$DR = (1 - A_i/A_0) \times 100\%$$

where A_0 is the initial absorbency of MB at 627 nm, MO at 464 nm and RhB at 554 nm, while A_i is the absorbency at certain reaction time accordingly.

1.4. Antibacterial activity tests

The antibacterial activities of the 3D flower-like $Cu_{2-x}Se$ were evaluated by using Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli*. We firstly incubated the bacterial strains at 37 °C for 16 hours in Luria-Bertani broth medium (LB) to obtain 5 mL of 10^9 CFU mL^{-1} of bacteria. Then 0.5 mL, 10^9 CFU mL^{-1} of the bacterial solution was taken and quantified to 10^5 CFU mL^{-1} using a 10-fold gradient dilution method, which was used for the antibacterial activity tests. Finally, certain amount of $Cu_{2-x}Se$ powder scraped from the as-prepared film or $Cu_{2-x}Se$ film was put into 2 mL of bacteria solution (0.1 mL of 10^5 CFU mL^{-1} bacteria + 1.9 mL LB medium) and incubated for 16 hours at 37 °C. A blank bacteria solution without the $Cu_{2-x}Se$ sample was operated in the same way. The concentrations of bacteria after incubation for 16 h were examined by measuring the absorbance of the bacterial solution at the wavelength of 600 nm. The antibacterial ratio was calculated as follows:

$$AR = (1 - A_{bi}/A_{b0}) \times 100\%$$

where A_{b0} is the absorbance of the blank bacteria, while A_{bi} is the absorbance of the bacteria in the presence of the $Cu_{2-x}Se$ sample. Because both the bacteria and Cu(II)

ions solution can absorb the light at 600 nm, we must take out the absorbance caused by Cu(II) ions solution to obtain the absorbance caused by pure bacteria. Thus, a micro-filtration membrane was applied to remove the bacteria from the solution since the diameter of the bacteria (0.8 μm) is greater than the pores of the micro-filtration membrane (0.22 μm). The absorbance of the filtrate was measured, which was caused by the Cu(II) ions solution.

Reference 1: F. Gao, L. Zhu, H. Li and H. Xie, *Mater. Res. Bull.* 2017, **93**, 342.

2. Crystal structure and morphology of the flower-like CuO precursor

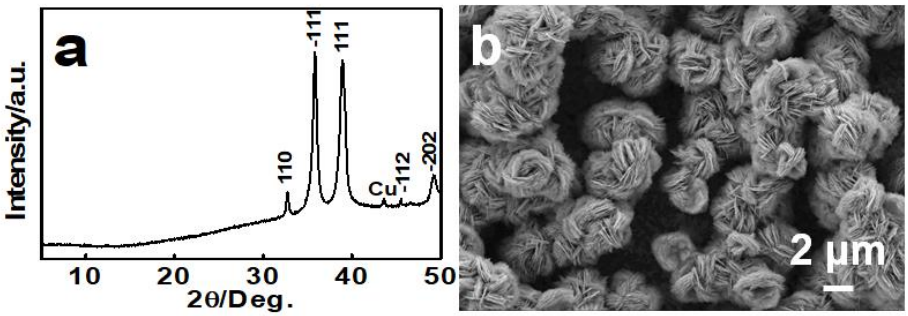

Fig. S1. (a) SEM image and (b) XRD pattern of the as-prepared 3D flower-like CuO film precursor on a Cu foil substrate.

The XRD result in Fig. S1a demonstrates that all diffraction peaks of the as-prepared precursor film on a Cu foil substrate match well with a monoclinic CuO (JCPDS: 65-2309) except a weak peak at 43.5°, originated from the Cu substrate (JCPDS: 01-1241). The corresponding SEM image (Fig. S1b) shows that this CuO film is composed of 3D flower-like microstructures assembled by nanosheets, which was used as a sacrificing template for preparation of the 3D flower-like $Cu_{2-x}Se$ with hexagonal nanosheet hierarchical structure.

3. XPS spectra of the flower-like $Cu_{2-x}Se$

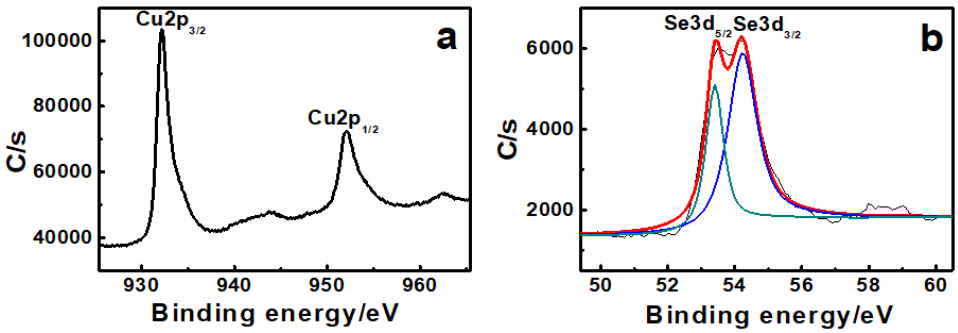

Fig. S2. XPS spectra of (a) Cu 2p and (b) Se 3d for the as-prepared 3D flower-like $Cu_{2-x}Se$ film.

4. NaOH quantity effect on product morphology and crystal phase

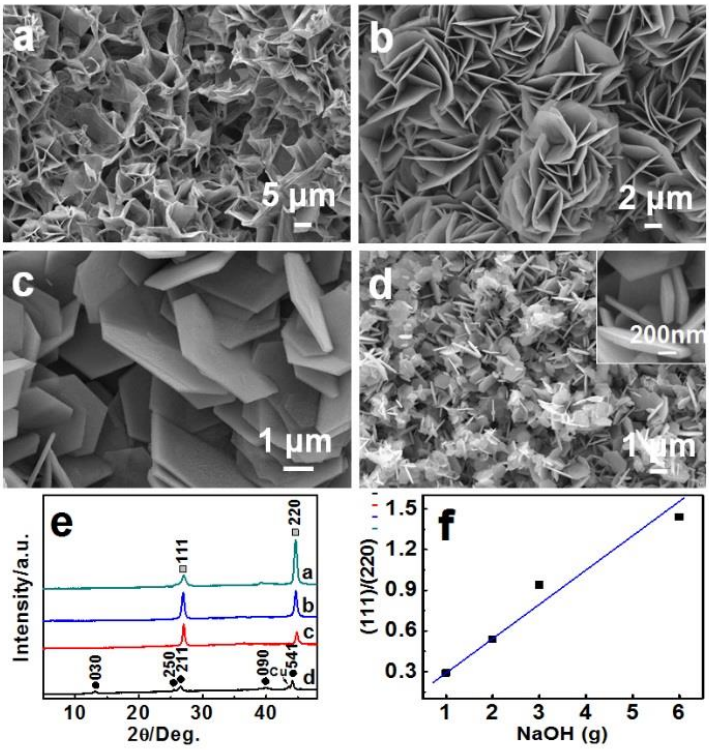

Fig. S3. SEM images of the product films prepared at room temperature using different NaOH quantity: (a) 1 g, (b) 3 g, (c) 6 g and (d) 9 g. (e) Corresponding XRD patterns and (f) plot of (111)/(220) peak intensity ratios versus NaOH quantities.

The relationship of the (111)/(220) peak intensity ratios and NaOH quantities was investigated. As shown in Fig. S3f, the ratio of the (111) / (220) peaks underwent a successive distinct change, nearly linearly increasing from 0.29 (for 1g NaOH product) to 1.43 (for 6g NaOH product). The TEM and HRTEM images in Fig. S4 confirm a solid nature of the $Cu_{2-x}Se$ nanoplate and the same growth habit as the 3D flower-like $Cu_{2-x}Se$ (Fig. 1f). Further increasing NaOH quantity to 9 g led to formation of pure orthorhombic phase of Cu_2Se_x hexagonal nanoplates. The size of the nanoplates is much smaller (~1 μm) and the crystallinity is much lower.

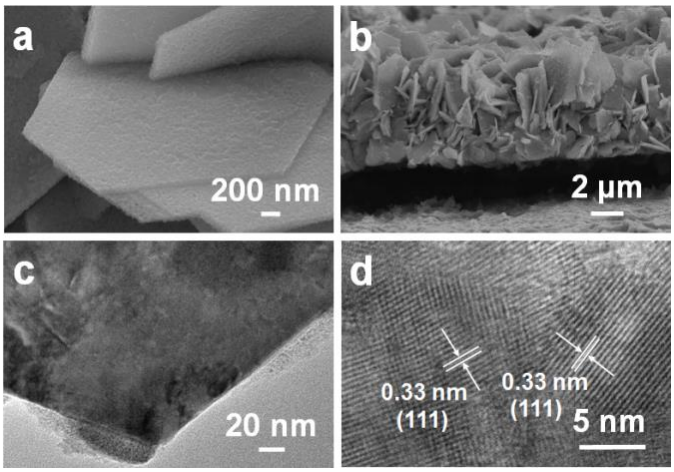

Fig. S4. (a) high-magnification SEM, (b) side view SEM (c) TEM, and (d) HRTEM images of the as-obtained hexagonal $Cu_{2-x}Se$ nanoplate array film prepared using 6 g of NaOH at room temperature.

5. Time dependent morphology evolutions

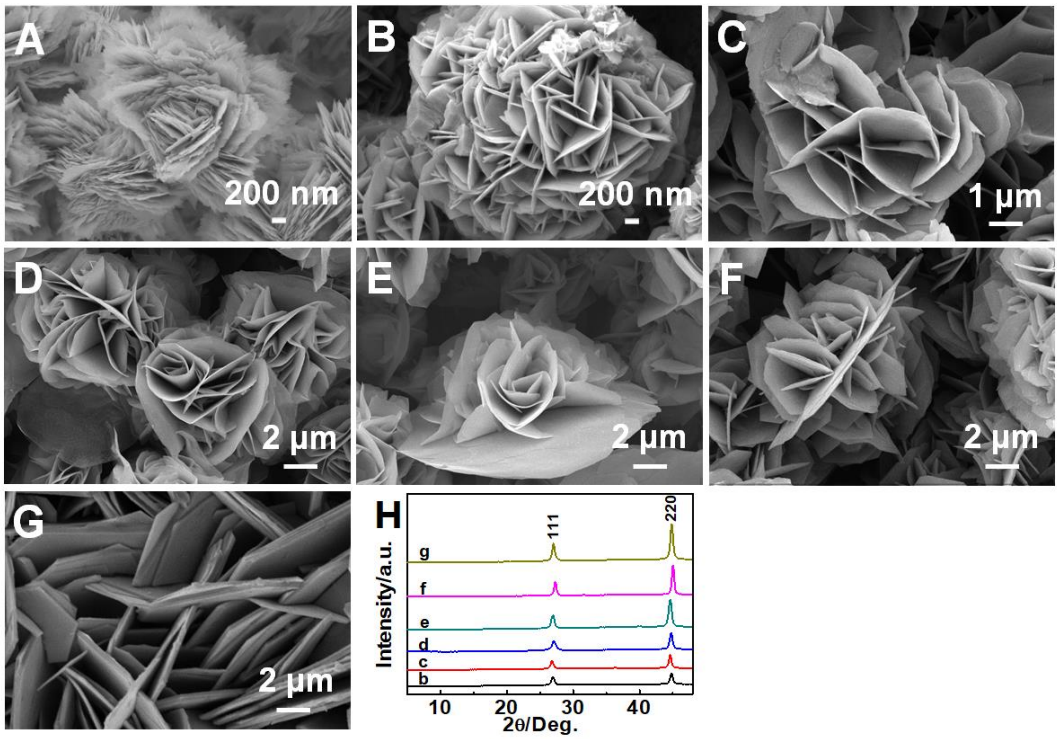

Fig. S5. (A) SEM image of the 3D flower-like CuO precursor; (B-G) SEM images of the $Cu_{2-x}Se$ nanostructure films prepared at room temperature for different reaction times: (B) 10 min, (C) 30 min, (D) 2 h, (E) 4 h, (F) 6 h and (G) 10 h; (H) Corresponding XRD patterns of the $Cu_{2-x}Se$ nanostructure films.

At 30 min, the flower-like $Cu_{2-x}Se$ microstructures assembled by tortuous larger sizes of nanosheets were obtained. From 30 min to 2 h, the product morphology changed slightly, but the crystallinity increased obviously. With further increasing reaction time, the tortuous nanosheets gradually became flat, accompanying with gradual formation of the hexagonal shape of nanosheets. Compared to the XRD result for the 2 h product, the $Cu_{2-x}Se$ peak intensities of the 4 h and 6 h products increased distinctly, indicating that the as-formed $Cu_{2-x}Se$ layer became much thicker with enhanced crystallinity. Further increasing reaction time (10 h) resulted in formation of massive hexagonal nanoplates array which grew perpendicular to the

Cu substrate, intercrossed each other and uniformly covered over the entire surface. Several nanoplates tended to attach each other face to face, forming thicker plates and the crystallinity of the film product was further enhanced. Therefore, suitable reaction time is required to obtain 3D flower-like $Cu_{2-x}Se$ assembled by hexagonal nanosheets with high crystallinity.

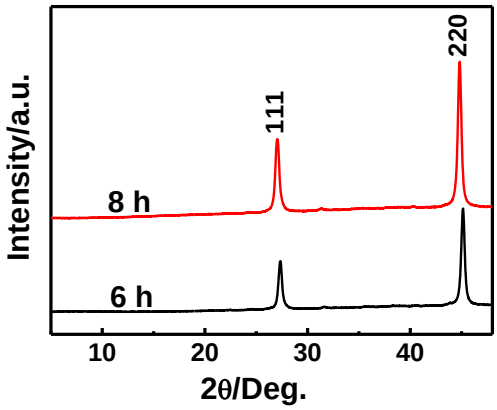

Fig. S6. XRD patterns of the $Cu_{2-x}Se$ film products obtained at 6 h and 8 h, using 2 g of NaOH at room temperature.

6. UV-vis absorption spectra of the three dye solutions

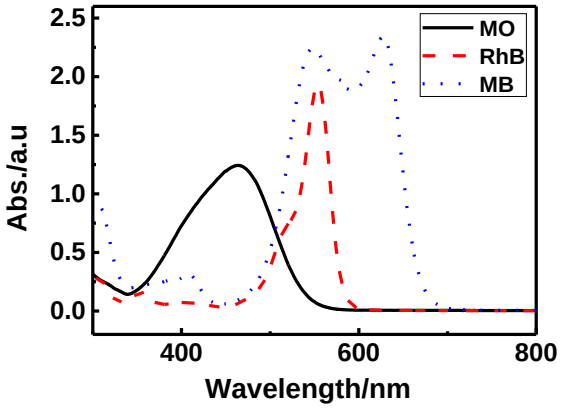

Fig. S7. UV-vis absorption spectra of the three kinds of dye solutions with concentrations of 1.25×10^{-4} M for methyl blue and methyl orange, and 2.09×10^{-5}M for RhB.

7. Standard curves of the bacteria

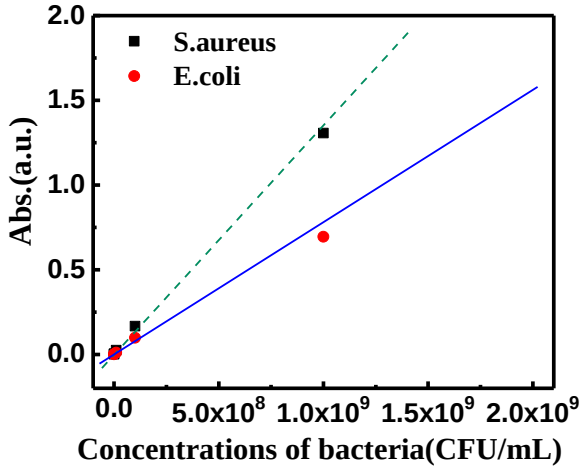

Fig. S8. Relationship of absorbances and concentrations of bacteria.

8. Standard curve of Cu^{2+} ions

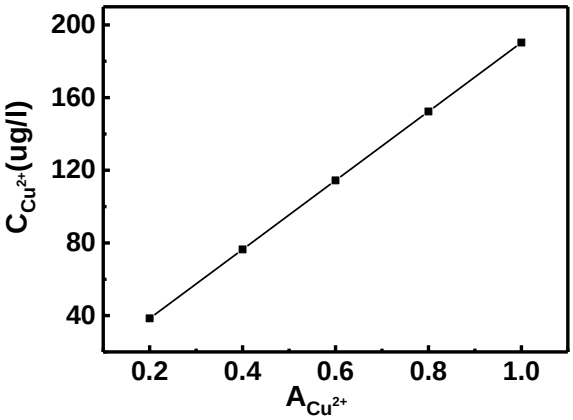

Fig. S9. Standard curve of the Cu^{2+} concentrations and absorbances.

9. Effect of incubation time on antibacterial rate and absorbance of Cu(II) ions

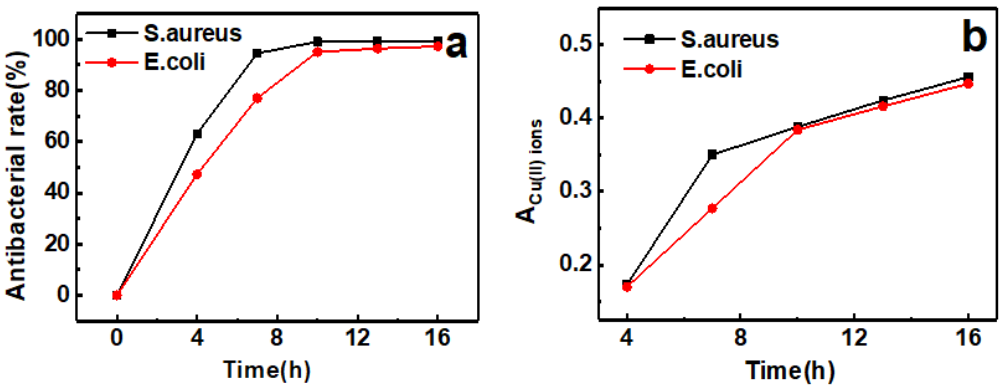

Fig. S10. The effects of incubation time on (a) antibacterial rates and (b) absorbances of Cu(II) ions.