

Electronic Supporting Information

for

Efficient Visible-Light Photocatalytic Heterojunctions Coupled by Plasmonic Cu_{2-x}Se and Graphitic Carbon Nitride

Jing Han,^{ab} Hong Yan Zou,^{ab} Ze Xi Liu,^a Tong Yang,^b Ming Xuan Gao^b and Cheng Zhi Huang,^{ab}

^aKey Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Pharmaceutical Science, Southwest University, Chongqing, 400715, P. R. China. E-mail: chengzhi@swu.edu.cn, Tel: (+86) 23 68254659, Fax: (+86) 23 68367257.

^bCollege of Chemistry and Chemical Engineering, Southwest University C, Chongqing 400716, China

1. Experimental section

Characterization

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) was performed with an S-4800 scanning electron microscope (Hitachi, Japan). Transmission electron microscopy (TEM) measurements were obtained from a Tecnai G2 F20 S-TWIN microscopy (FEI, USA). The X-ray photoelectron spectroscopy (XPS) analysis was conducted by an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA). The samples for XPS were made by the deposition of a nanocrystal suspension in water on Si substrate. A Fourier transform infrared (FT-IR) spectrophotometer (FTIR-8400S, Shimadzu, Japan) was employed to measuring the FT-IR spectrum. UV-vis-NIR absorption spectra were obtained using a Hitachi U-3600 spectrophotometer. Steady-state fluorescence spectra and fluorescence anisotropy were measured with an F-2500 fluorescence spectrophotometer (Hitachi, Japan) with the nanoparticles dispersed in reagents.

2. Results and discussion

2.1 Structure and property analysis

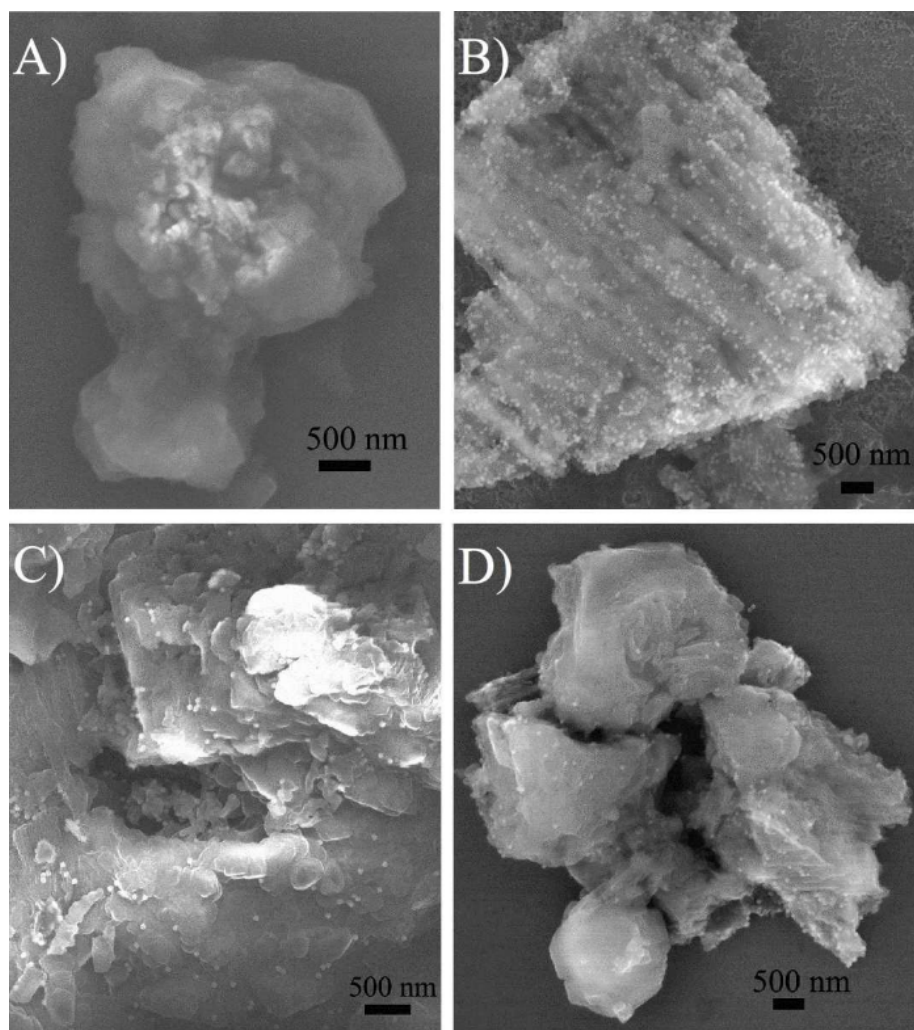


Fig. S1 SEM images of g-C₃N₄ (A), 60 wt% Cu_{2-x}Se/g-C₃N₄ (B), 40 wt% Cu_{2-x}Se/g-C₃N₄ (C) and 20 wt% Cu_{2-x}Se/g-C₃N₄ (D).

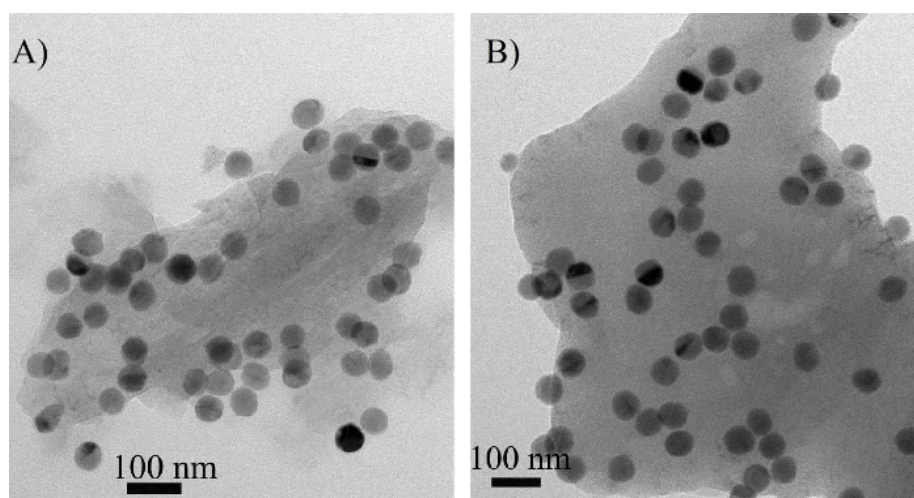


Fig. S2 TEM images of 40 wt% Cu_{2-x}Se/g-C₃N₄ (A) and 20 wt% Cu_{2-x}Se/g-C₃N₄ (B).

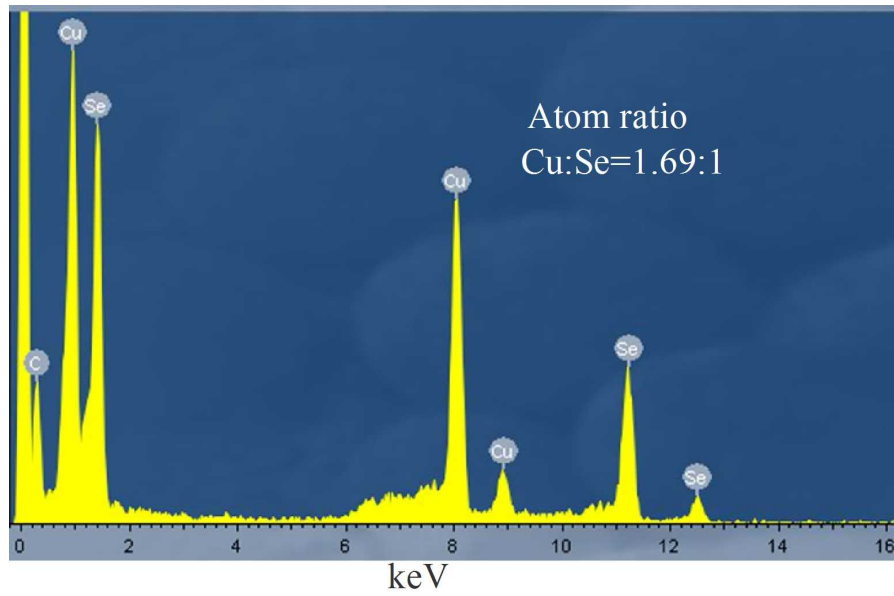


Fig.S3 EDS image of the Cu_{2-x}Se .

Calculation of band gap energy

The band gap energies of semiconductors can be estimated by Kubelka–Munk transformation,¹

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (1)$$

Where α represents the absorption coefficient, ν is the light frequency, E_g is the band gap energy, A is a constant and n depends on the characteristics of the transition in a semiconductor. For Cu_{2-x}Se and $\text{g-C}_3\text{N}_4$, the value of n is 4 for the indirect transition. Thus, as shown in Figure 5 (inset), the band gap energies of Cu_{2-x}Se and $\text{g-C}_3\text{N}_4$ is 1.35 eV and 2.64 eV, respectively.

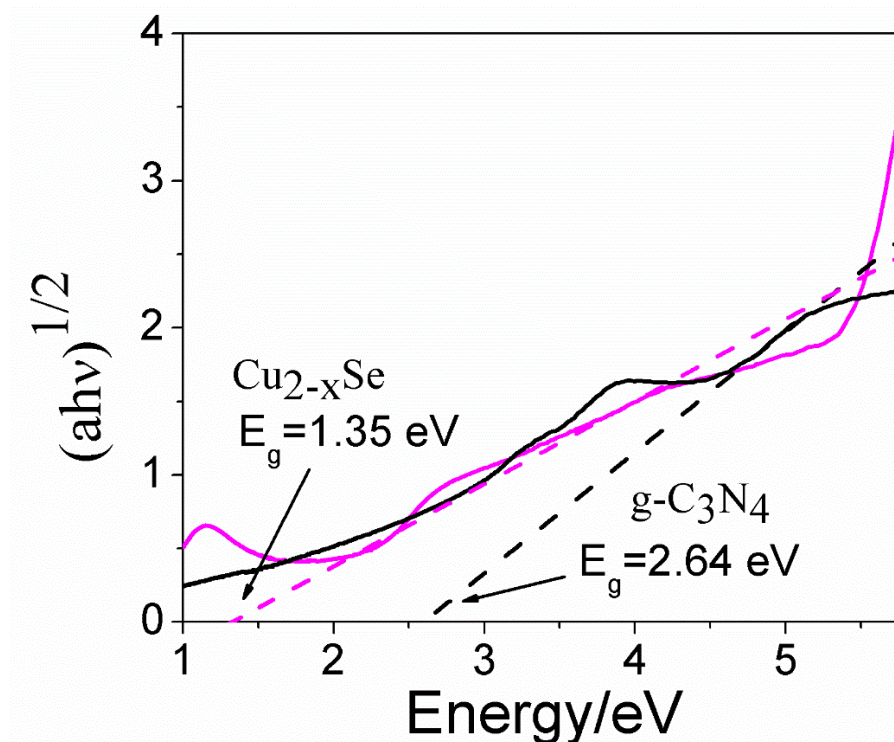


Fig. S4 The band-gap energy of Cu_{2-x}Se and $\text{g-C}_3\text{N}_4$

2.2 Photocatalytic Performances

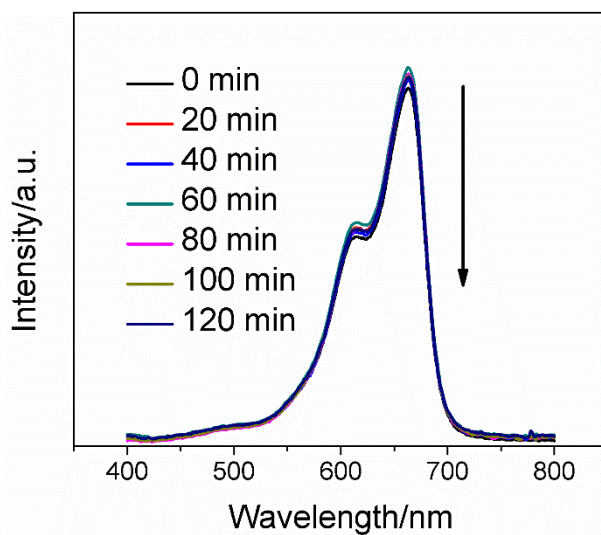


Fig. S5 The UV-vis spectra change during the MB photodegradation without photocatalysts

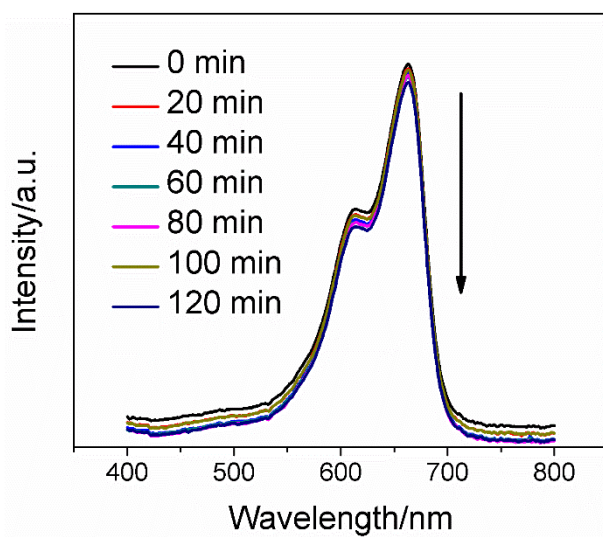


Fig. S6 The UV-vis spectra change during the MB photodegradation by 12 mg 60 wt% $\text{Cu}_{2-x}\text{Se}/\text{g-C}_3\text{N}_4$ photocatalysts without light.

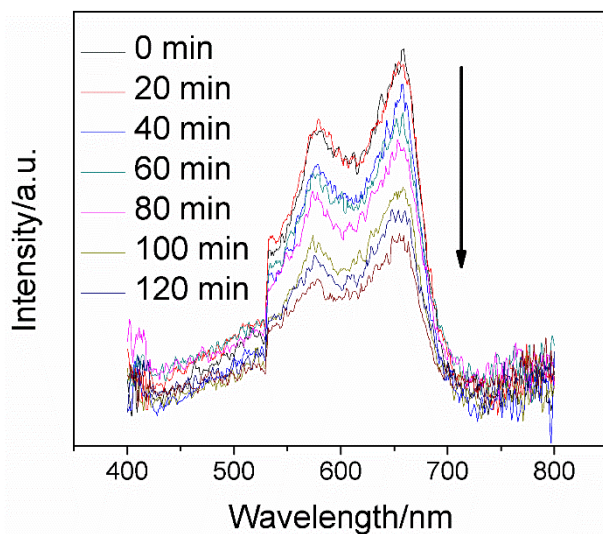


Fig. S7 The UV-vis spectra change during the MB photodegradation by 12 mg Cu_{2-x}Se under visible-light irradiation.

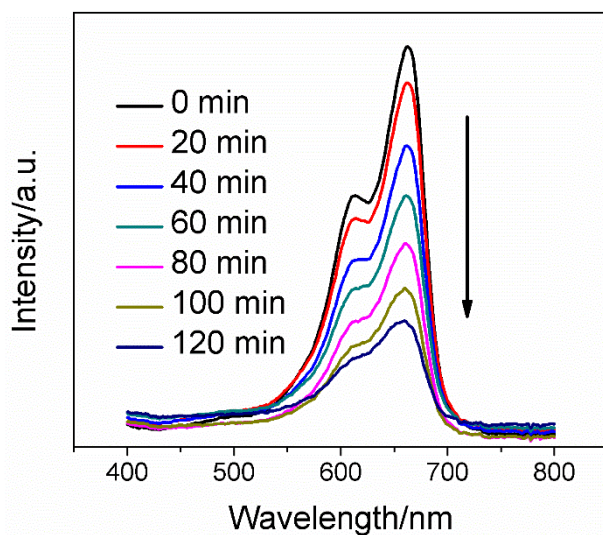


Fig. S8 The UV-vis spectra change during the MB photodegradation by 12 mg g-C₃N₄ under visible-light irradiation.

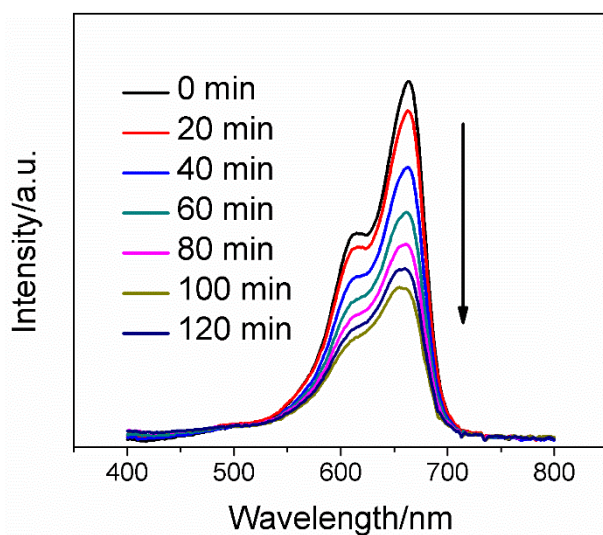


Fig. S9 The UV-vis spectra change during the MB photodegradation by 12 mg mechanical mixtures of Cu_{2-x}Se and g-C₃N₄ with the mass ratio of 3:2 under visible-light irradiation.

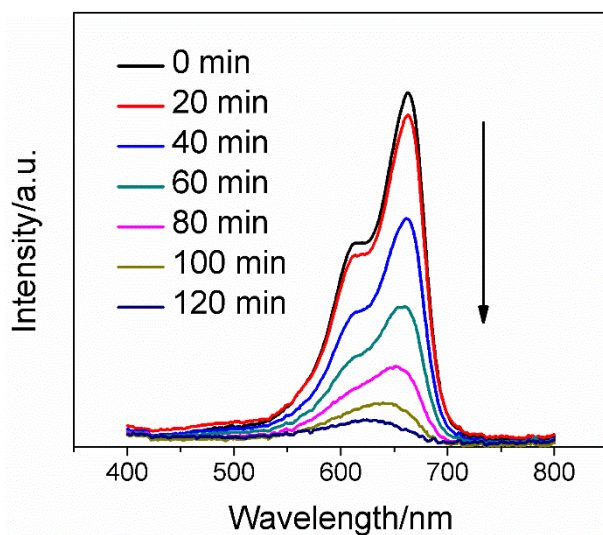


Fig. S10 The UV-vis spectra change during the MB photodegradation by 12 mg 60 wt% Cu_{2-x}Se/g-C₃N₄ heterojunctions under visible-light irradiation.

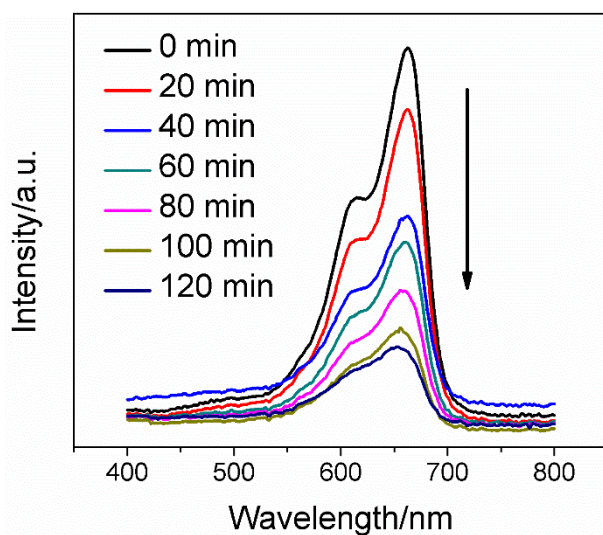


Fig. S11 The UV-vis spectra change during the MB photodegradation by 12 mg 40 wt% Cu_{2-x}Se/g-C₃N₄ heterojunctions under visible-light irradiation.

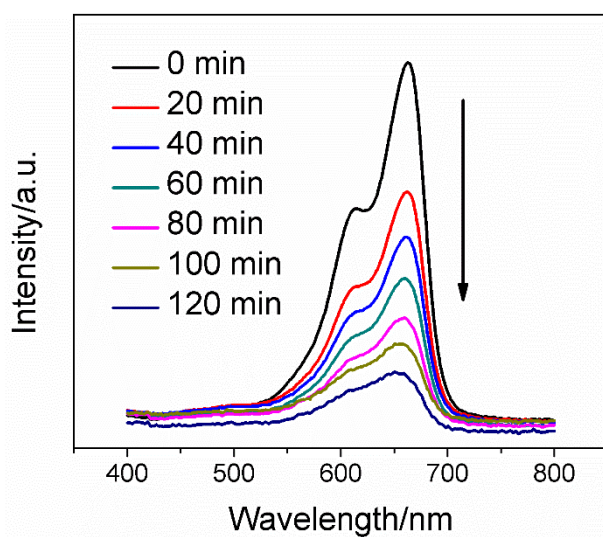


Fig. S12 The UV–vis spectra change during the MB photodegradation by 12 mg 20 wt% $\text{Cu}_{2-x}\text{Se}/\text{g-C}_3\text{N}_4$ heterojunctions under visible-light irradiation.

Table S1. Surface and Photocatalytic Characterization of $\text{Cu}_{2-x}\text{Se}/\text{g-C}_3\text{N}_4$ Heterojunctions

Sample	BET (m^2/g)	k (min^{-1})
No Light	/	0.00023
Cu_{2-x}Se	/	0.00455
C_3N_4	5.68	0.00998
Mechanical mixtures	/	0.00732
20 wt%	9.38	0.011
40 wt%	5.56	0.01234
60 wt%	6.29	0.0276

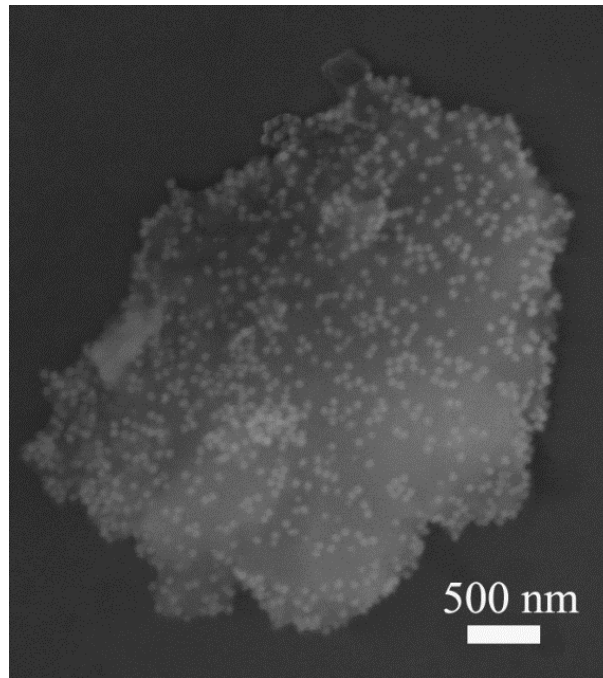


Fig. S13 The SEM image of 60 wt% $\text{Cu}_{2-x}\text{Se}/\text{g-C}_3\text{N}_4$ recycled used for three times in the same photocatalytic process.

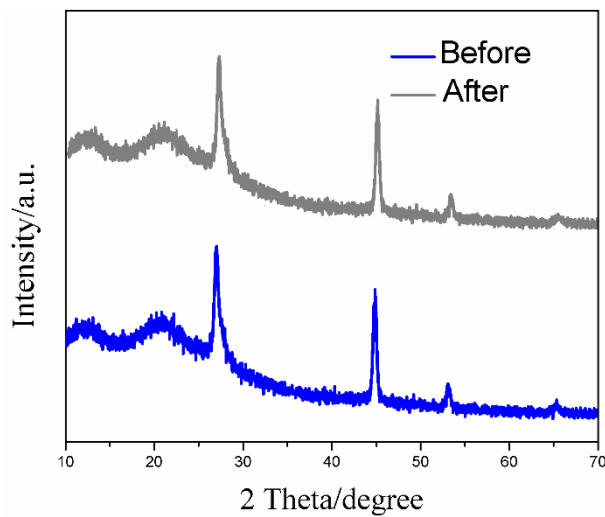


Fig. S14 The XRD of 60 wt% $\text{Cu}_{2-x}\text{Se}/\text{g-C}_3\text{N}_4$ before and after three cycles in the photocatalytic process.

References

- 1 J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721.