Supplementary Information

S-Cu-FC/CuS modified GO carboxymethyl cellulose hydrogel for enhanced photocatalytic sterilization through homo-heterojunction interface accelerated charge transfer

Bo Huang,‡[a,f] Wei Guan,‡[b] Chaofeng Wang,[c] Shuilin Wu,*[b,d,f] Zhenduo Cui,[b] Yufeng Zheng,[d] Zhaoyang Li,[b] Shengli Zhu,[b] Hui Jiang,[b] Paul K. Chu,[e] and Xiangmei Liu,*[c]

College of pharmacy, Guangxi University of Chinese Medicine, Nanning 530022, China.
School of Materials Science & Engineering, the Key Laboratory of Advanced Ceramics and Machining Technology by the Ministry of Education of China, Tianjin University, Tianjin, 300072, China.
School of Health Science and Biomedical Engineering, Hebei University of Technology, Tianjin, 300401, China. E-mail: Liuxiangmei1978@163.com (X. M. Liu)
School of Materials Science & Engineering, Peking University, Beijing, 100871, China. E-mail: slwu@pku.edu.cn (S. L. Wu)
Department of Physics, Department of Materials Science and Engineering, and Department of Biomedical Engineering, City University of Hong Kong, Kowloon, Hong Kong, 999077, China.
Biomedical Materials Engineering Research Centre, Hubei University, Wuhan 430062, China.
‡These authors contribute equally to this paper.

1. Preparation of S-Cu-FC/CuS/GO

It is now known that the following reactions would occur in the presence of sulphite in acidic solutions:

$CuFeS_2+4H^+=Cu^{2+}+Fe^{2+}+2H_2S$, $2Fe^{3+}+H_2S=2Fe^{2+}+S+2H^+$, $CuFeS_2+2H^+=CuS+Fe^{2+}+H_2S$. So, it could be determined that the reaction between CuFC and TAA was mainly a complexation reaction between Cu^{2+} and S^{2-} or HS^-. Based on the principle of this reaction, then, the product of the reaction between TAA and CuFC ($Cu_2[Fe_2(CN)_6]$) was assumed as: $Cu_x[Fe(CN)_6]$-Cu_yS (x+y=2). It followed that when all Cu^{2+} participated in the reaction, x=2 and y=0, the product was still CuFC ($Cu_2[Fe_2(CN)_6]$). It also followed that when Cu^{2+} did not participate in the reaction, x=0 and y=2, the product was all CuS. Therefore, we assumed that the reaction proceeds according to the most ideal situation, only a part of Cu^{2+} in CuFC were involved in the formation of CuS and the producxt might be (2-y){$Cu_2[Fe(CN)_6]$}-yCuS. Meanwhile, based on the mass of the raw material in the reaction, the following equations could be obtained:

$N(Cu)_x+N(Cu)_y=2N(Cu_2[Fe(CN)_6])_{Raw}=N(Cu)(2-y)\{Cu_2[Fe(CN)_6]\}$-yCuS

$2N_A×n((2-y)\{Cu_2[Fe(CN)_6]\})+N_A×n(yCuS)=2N_A×n(Cu_2[Fe(CN)_6])_{Raw}$.

We further assumed that CuFC was mixed up with CuS powders and a complex with the same number of copper atoms as the ideal reaction product could be obtained:

$2N_A×n((2-y)\{Cu_2[Fe(CN)_6]\})=2N_A×n(Cu_2[Fe_2(CN)_6])_{Direct\ mixing}$,

$N_A \times n(yCuS) = N_A \times n(CuS)_{\text{Direct mixing}}$

$2N_A \times n(Cu_2[Fe(CN)_6])_{\text{Direct mixing}} + N_A \times n(CuS)_{\text{Direct mixing}} = N(Cu)_{(2-y)\{Cu_2[Fe_2(CN)_6]\}-yCuS}$

$2N_A \times m(Cu_2[Fe(CN)_6])/M(Cu_2[Fe(CN)_6]) + N_A \times m(CuS)/M(CuS) = 2N(CuFC)_{\text{Raw}}$

$2N_A \times m(CuFC)/(340 \text{ g mol}^{-1}) + N_A \times m(CuS)/(80 \text{ g mol}^{-1}) = 2N_A \times m((2-y)\{Cu_2[Fe(CN)_6]\}-yCuS)_{\text{Raw}}/M((2-y)\{Cu_2[Fe(CN)_6]\}-yCuS)$

If the suitation was optimal, 50% of the copper atoms were involved in the reaction:

$2N_A \times m(CuFC)/(340 \text{ g mol}^{-1}) + N_A \times m(CuS)/(80 \text{ g mol}^{-1}) = 2N(Cu[Fe(CN)_6]-CuS) = 2N_A \times m(\text{S-Cu-FC/CuS})/M(\text{S-Cu-FC/CuS}) = 2N_A \times m(\text{S-Cu-FC/CuS})/(356 \text{ mg mol}^{-1})$

$m(CuFC)/170 + m(CuS)/80 = m(\text{S-Cu-FC/CuS})/178$.

Let $m(CuFC) = A$, $m(CuS) = B$, $m(\text{S-Cu-FC/CuS}) = C$, it could be obtained: $1.047A + 2.225B = C$ (for TEM, XRD and electrochemical test, S, C was set to the usual mass of 3 mg). So, $1.047A + 2.225B = 3$ mg. If $C = 3$ mg and $A + B$ was in the vicinity of 3 mg, A and B was set up as 1.433 mg and 0.674 mg, respectively. Therefore, CuFC (1.433 mg) and CuS (0.674 mg) were mixed and grounded. The mixture was treated with ultrasound for 2 h and dispersed in ethanol and lyophilized to obtain CuFC/CuS.
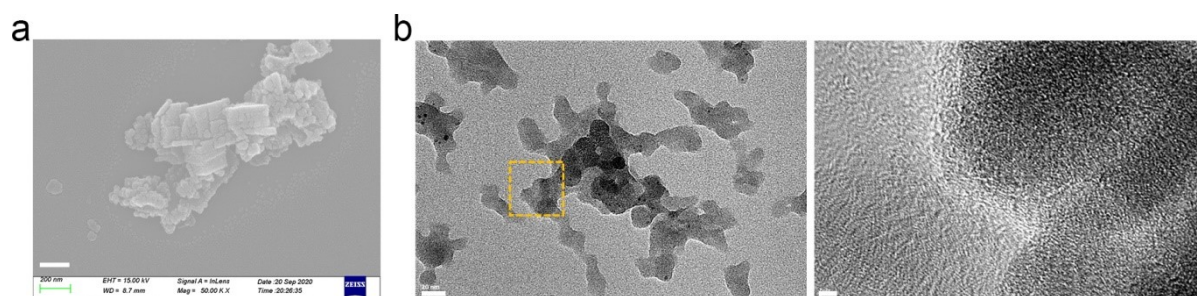
2. Supplementary Figures

Figure S1. (a) SEM images of CuFC. The scale bar is 200 nm. (b) TEM images of CuFC (left scale bar = 20 nm and right scale bar = 20 nm).
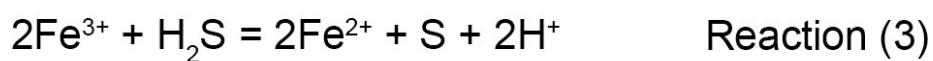
$$CuFeS_2 + 4H^+ = Cu^{2+} + Fe^{2+} + 2H_2S \quad \text{Reaction (1)}$$

$$4Fe^{2+} - 4e = 4Fe^{3+} \quad \text{Reaction (2)}$$

$$2Fe^{3+} + H_2S = 2Fe^{2+} + S + 2H^+ \quad \text{Reaction (3)}$$

$$CuFeS_2 + 2H^+ = CuS + Fe^{2+} + H_2S \quad \text{Reaction (4)}$$

Figure S2. Mechanisms of the dissolution of chalcopyrite ($CuFeS_2$) in acidic sulfate aqueous solution.

The dissolution of $CuFeS_2$ in acidic solutions could be split into the above reaction processes. As the shown in Reaction (1), the $CuFeS_2$ was initially dissolved by acidic solutions into ions (Cu^{2+} and Fe^{2+}) and H_2S generated. Ferrous ions were unstable and easily oxidized leading to Reaction (3) to produce Fe^{3+}. However, the reductive H_2S would react with Fe^{3+} to reduce the latter to Fe^{2+}. Generally, the reactions ultimately exhibited by the dissolution of chalcopyrite could be summarized as Reaction (4).[1-15]
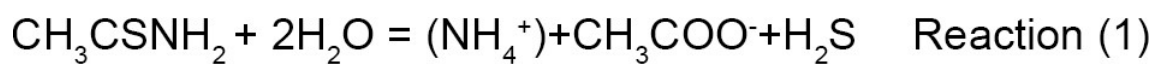
$$CH_3CSNH_2 + 2H_2O = (NH_4^+) + CH_3COO^- + H_2S \quad \text{Reaction (1)}$$

$$H_2S = HS^- + H^+ \quad \text{Reaction (2)}$$

Figure S3. Mechanisms of the hydrolysis of thioacetamide in acidic solution.

Thioacetamide could be hydrolyzed in acidic solutions to form H_2S or HS^-, so it was often used in analytical chemistry as a group reagent or precipitation reagent for metal cations instead of the toxic and odorous H_2S. Therefore, in order to ensure that a part of Cu^{2+} in CuFC would react with TAA and material not be dissolved because of the excessive oxidation at high temperatures or strong acids, the reaction of CuFC and TAA was carried at 60 °C for only 30 min in a slightly acidic solution (pH = 5).[16,17]
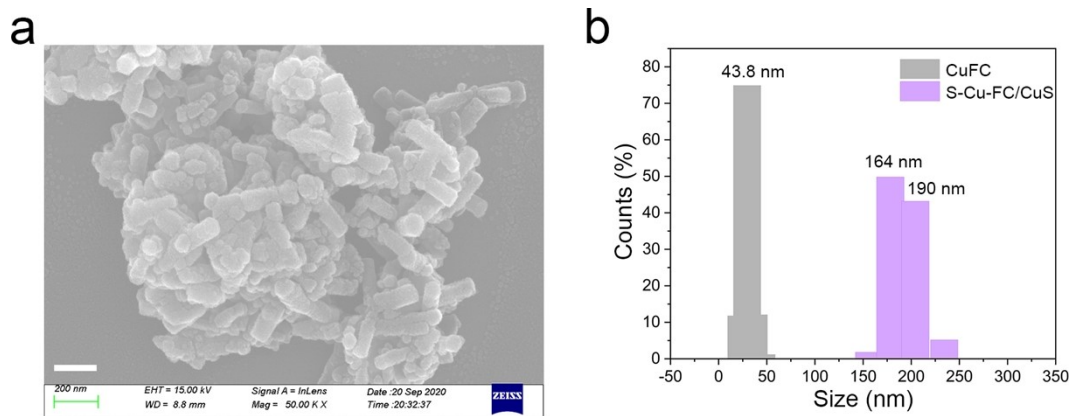
Figure S4. (a) SEM images of S-Cu-FC/CuS. Scale bar is 200 nm. (b) Particle sizes of CuFC and S-Cu-FC/CuS.
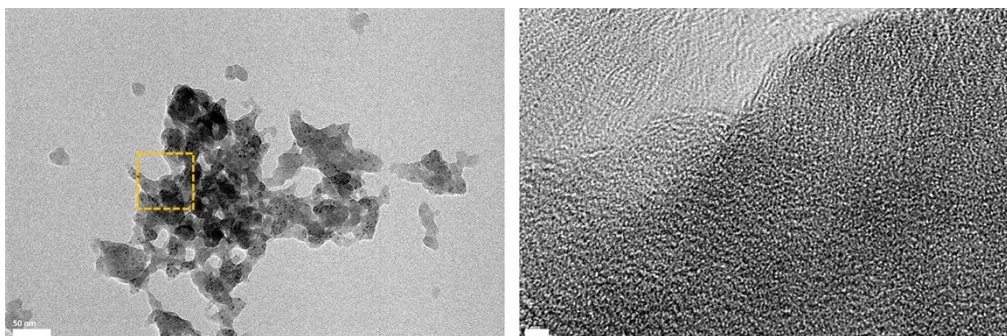
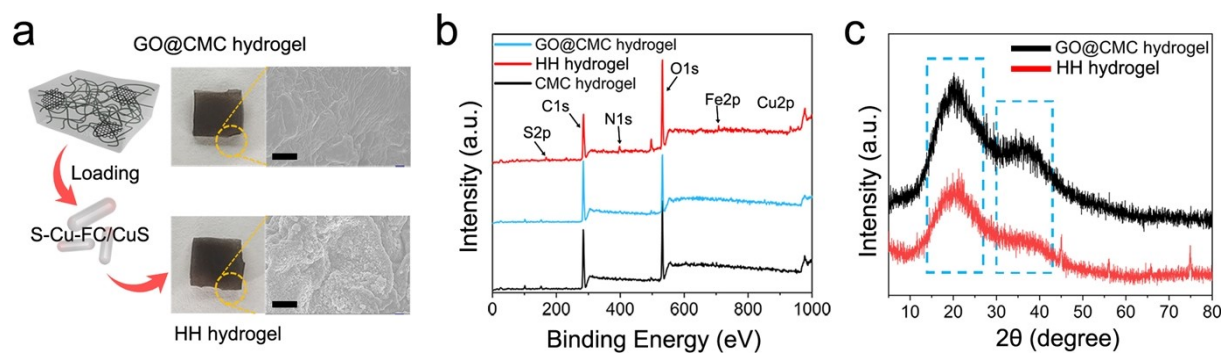**Figure S5.** TEM images of CuFC/CuS (left scale bar = 50 nm and right scale bar = 2 nm).

Figure S6. (a) Schematic diagram of the preparation of the HH hydrogel and SEM images of GO@CMC hydrogel and HH hydrogel. Scale bars are all 20 μm. (b) XPS spectra of CMC hydrogel, GO@CMC hydrogel, and HH hydrogel. (c) XRD of GO@CMC hydrogel and HH hydrogel.
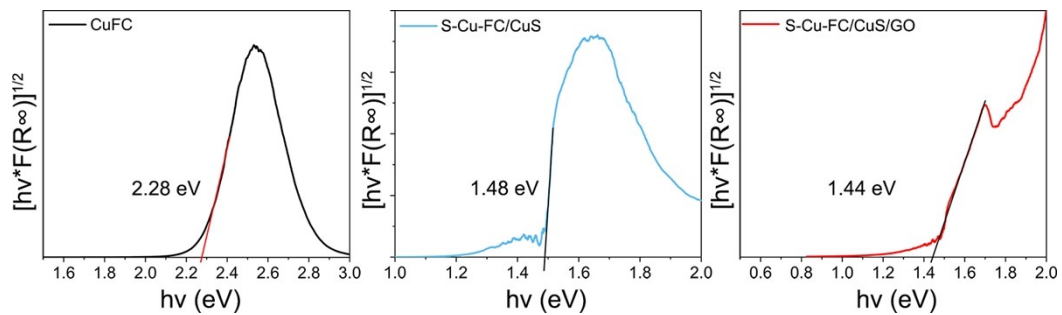
Figure S7. Energy gaps calculated from UV-*vis*-NIR diffuse reflectance spectra.

The energy gap (E_g) can be obtained by the equation: $(\alpha h v)^n = B(h v - E_g)$. And CuS is a direct semiconductor (n = 2).
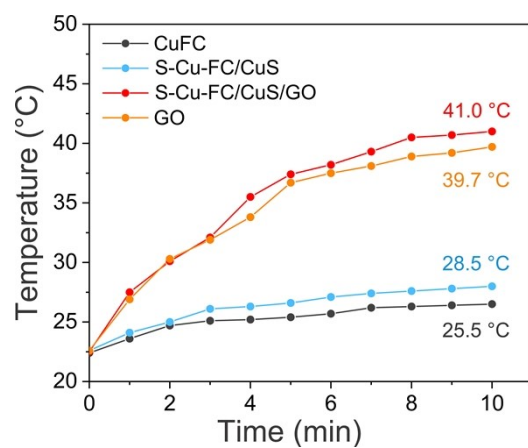
Figure S8. Temperature changes of GO, CuFC, S-Cu-FC/CuS, and S-Cu-FC/CuS/GO under 808-nm NIR irradiation (0.6 W cm^{-2}, distance = 5 cm, 10 min).
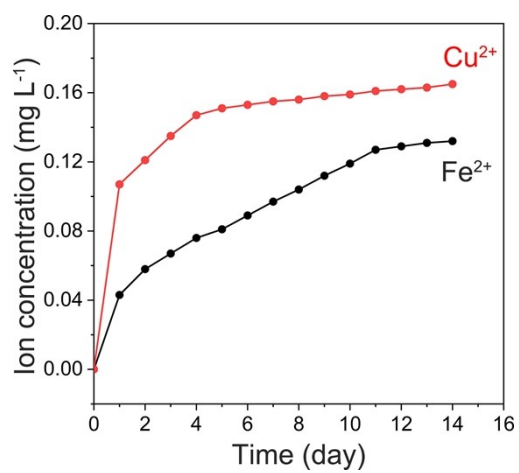
Figure S9. ICP test of the Cu^{2+} and Fe^{2+} released from HH hydrogel in 14 days.
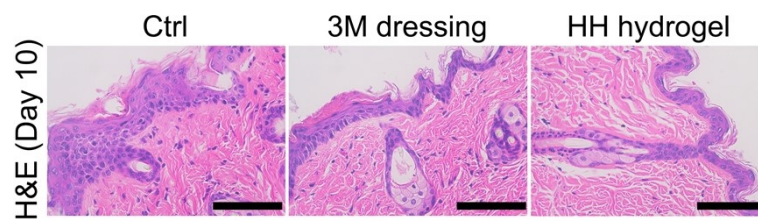
Figure S10. H&E staining images of different group at day 10. Scale bars are all 200 μm.

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