

## Supporting Information

### **Solar-driven co-production of C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> from CO<sub>2</sub> and H<sub>2</sub>O**

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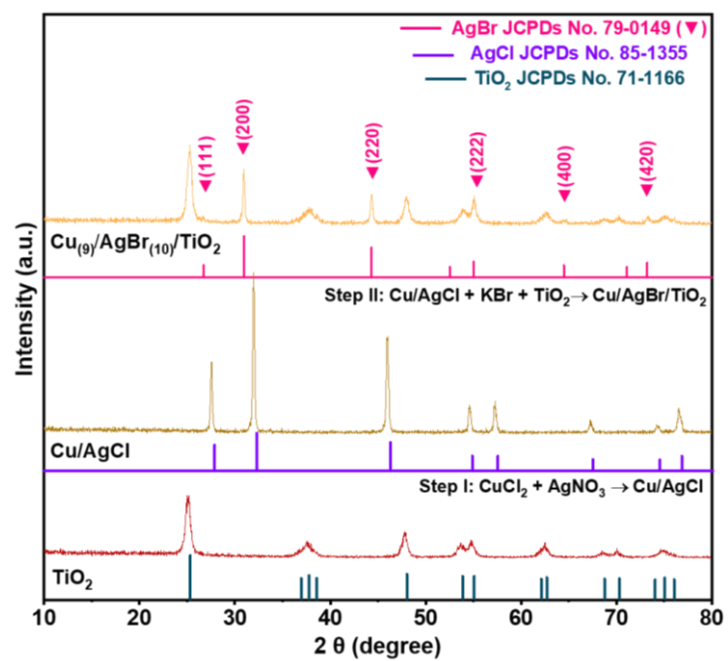


Figure S1. Structural analysis by XRD pattern. XRD patterns of the as-prepared samples.

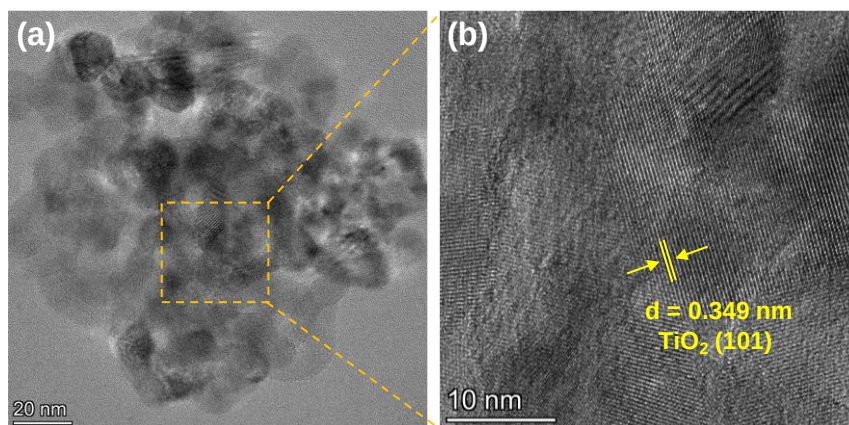


Figure S2. Morphological structure characterization of TiO<sub>2</sub>. (a) HRTEM of TiO<sub>2</sub>. (b) Magnifying area in (a).

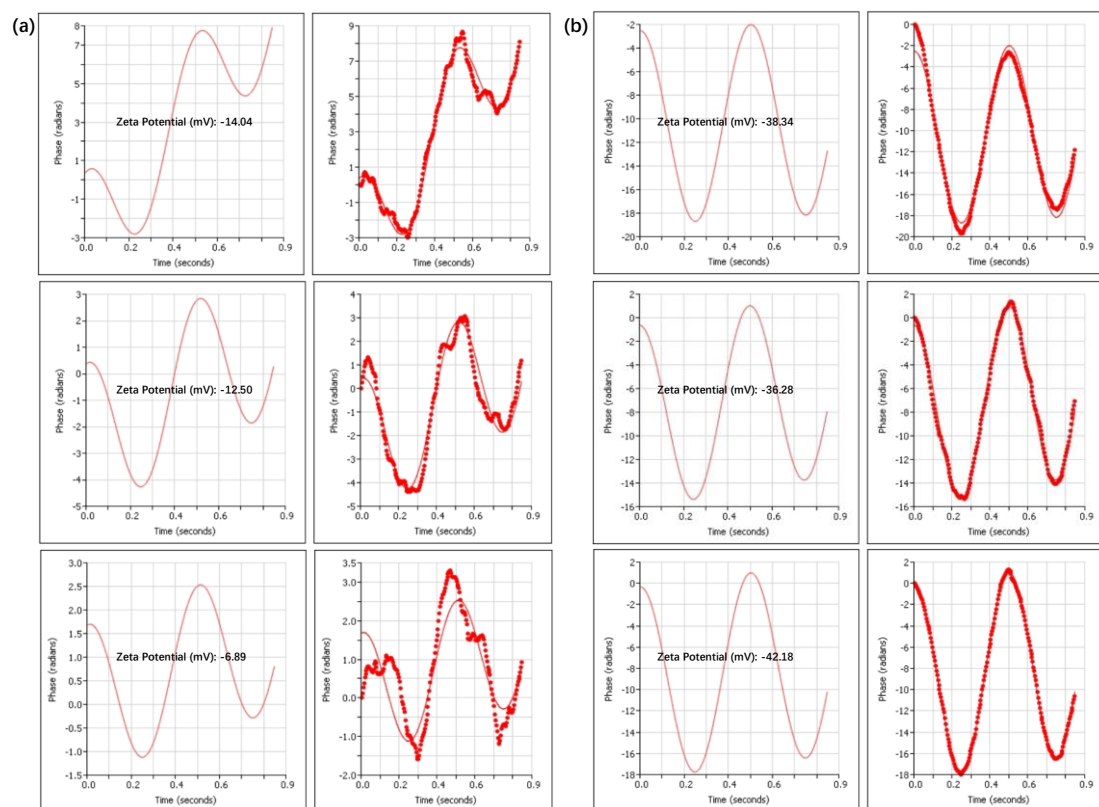


Figure S3. Surface potential changes during catalyst synthesis. (a) Phase diagram of AgCl without KBr addition. (b) Phase diagram of AgCl with KBr addition.

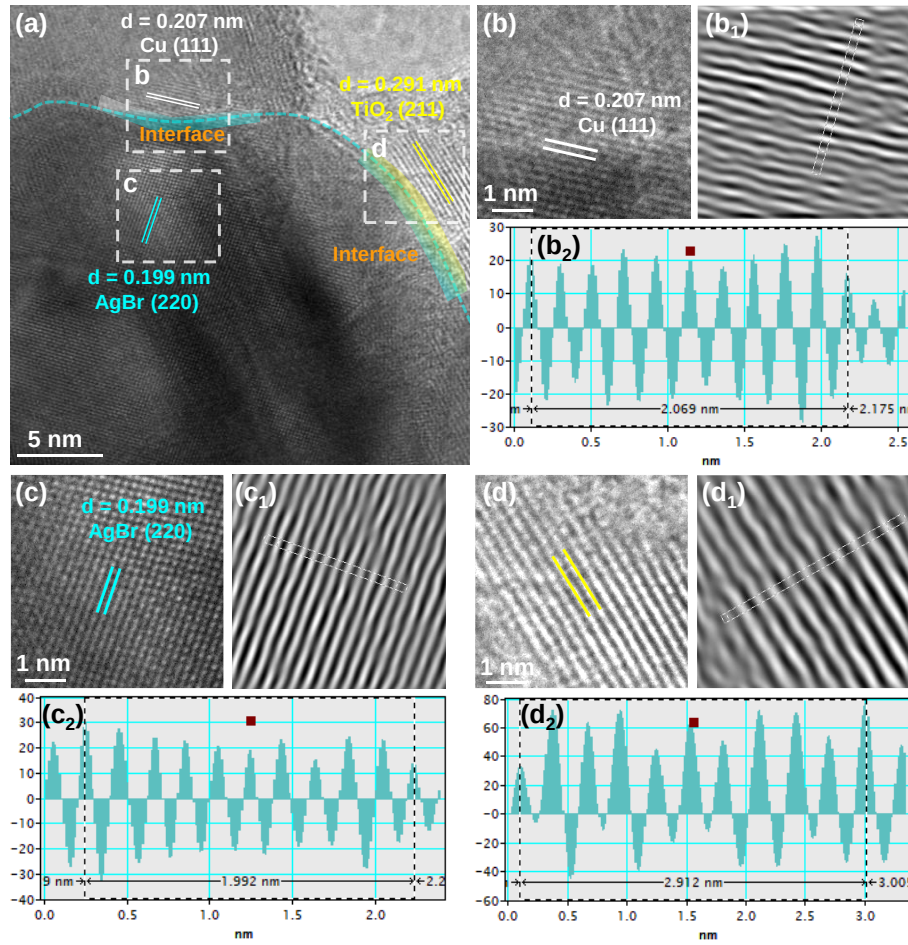
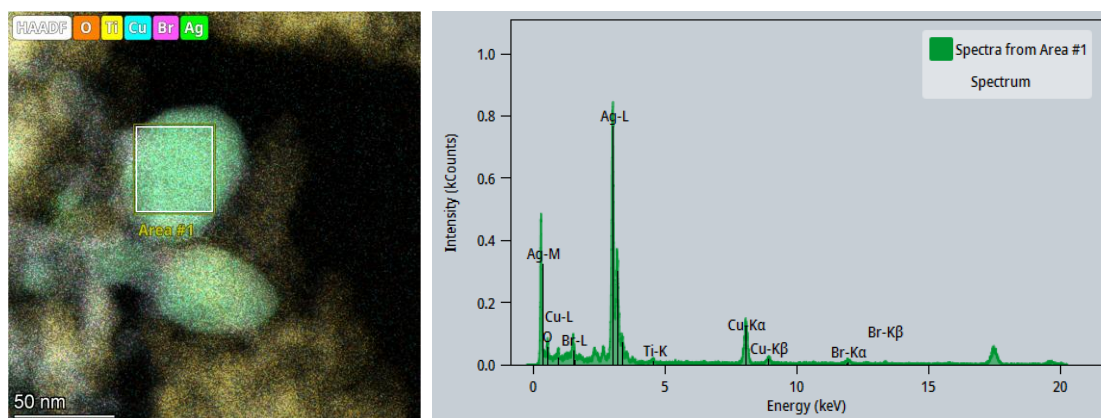


Figure S4. Morphological structure characterization of  $\text{Cu}_9/\text{AgBr}_{10}/\text{TiO}_2$ . (a) HRTEM of  $\text{Cu}_9/\text{AgBr}_{10}/\text{TiO}_2$ . (b), (c), and (d) Magnifying HRTEM area in (a). (b<sub>1</sub>), (c<sub>1</sub>), and (d<sub>1</sub>) Fast fourier transform (FFT) in (b), (c), and (d). (b<sub>2</sub>), (c<sub>2</sub>), and (d<sub>2</sub>) Brightness intensity of the blue line profile in (b<sub>1</sub>), (c<sub>1</sub>), and (d<sub>1</sub>).



| Element Family | Atomic Fraction (%) | Atomic Error (%) | Mass Fraction (%) | Mass Error (%) | Fit Error (%) |
|----------------|---------------------|------------------|-------------------|----------------|---------------|
| O              | 9.78                | 0.81             | 1.75              | 0.17           | 1.05          |
| Ti             | 1.13                | 0.21             | 0.61              | 0.12           | 3.20          |
| Cu             | 17.84               | 2.52             | 12.67             | 1.98           | 0.39          |
| Br             | 3.11                | 0.47             | 2.78              | 0.44           | 1.64          |
| Ag             | 68.15               | 3.05             | 82.19             | 2.26           | 0.19          |

Figure S5. Elemental distribution of  $\text{Cu}_9/\text{AgBr}_{10}/\text{TiO}_2$ . EDS spectrum and detailed elements distribution configuration of the selected area in the  $\text{Cu}_9/\text{AgBr}_{10}/\text{TiO}_2$  overlap EDS elemental mapping.

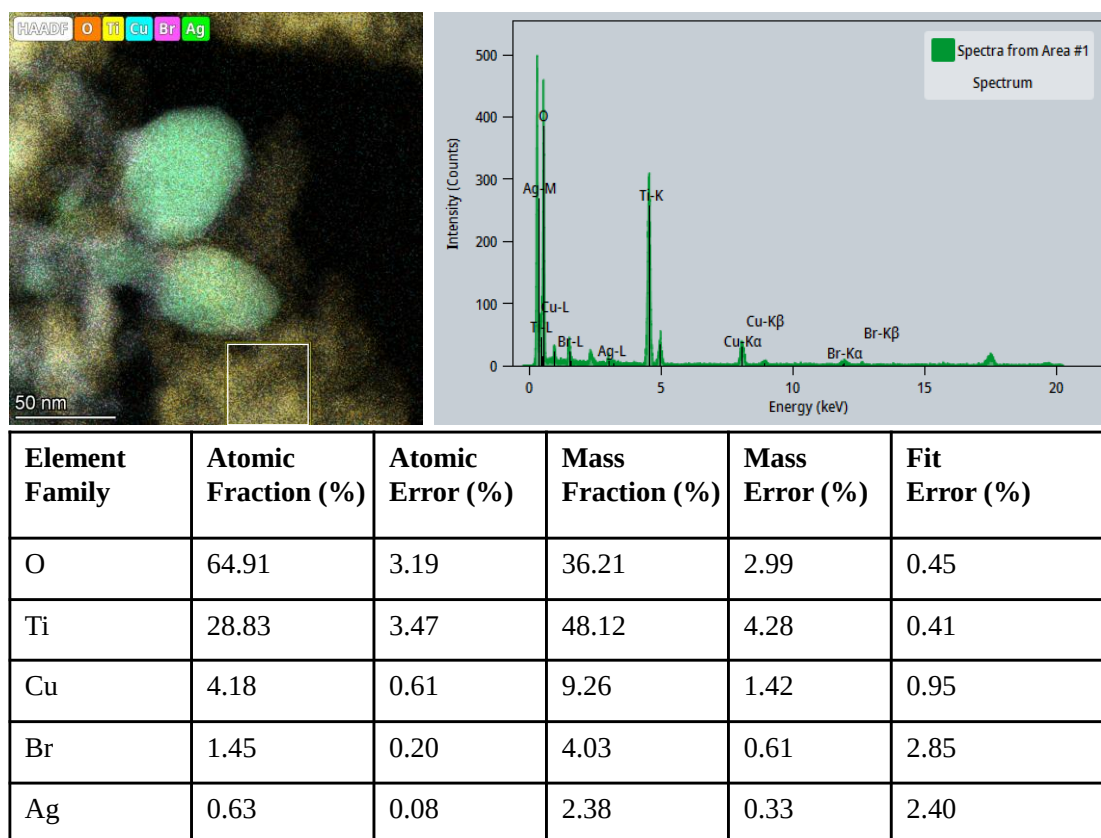


Figure S6. Elemental distribution of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ . EDS spectrum and detailed elements distribution configuration of the selected area in the  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  overlap EDS elemental mapping.

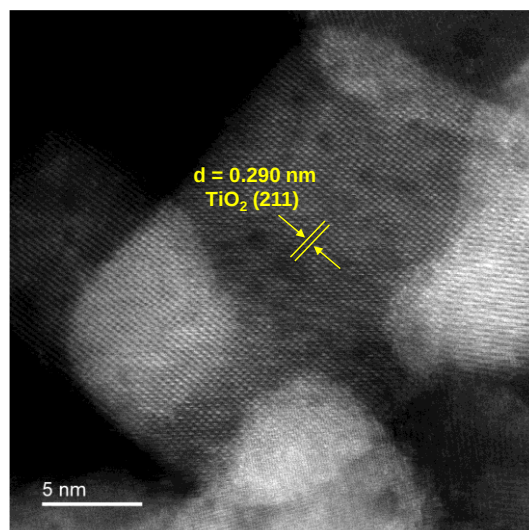


Figure S7. Atomic-level configuration of Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>. AC-HAADF-STEM of selected TiO<sub>2</sub> species in Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>.

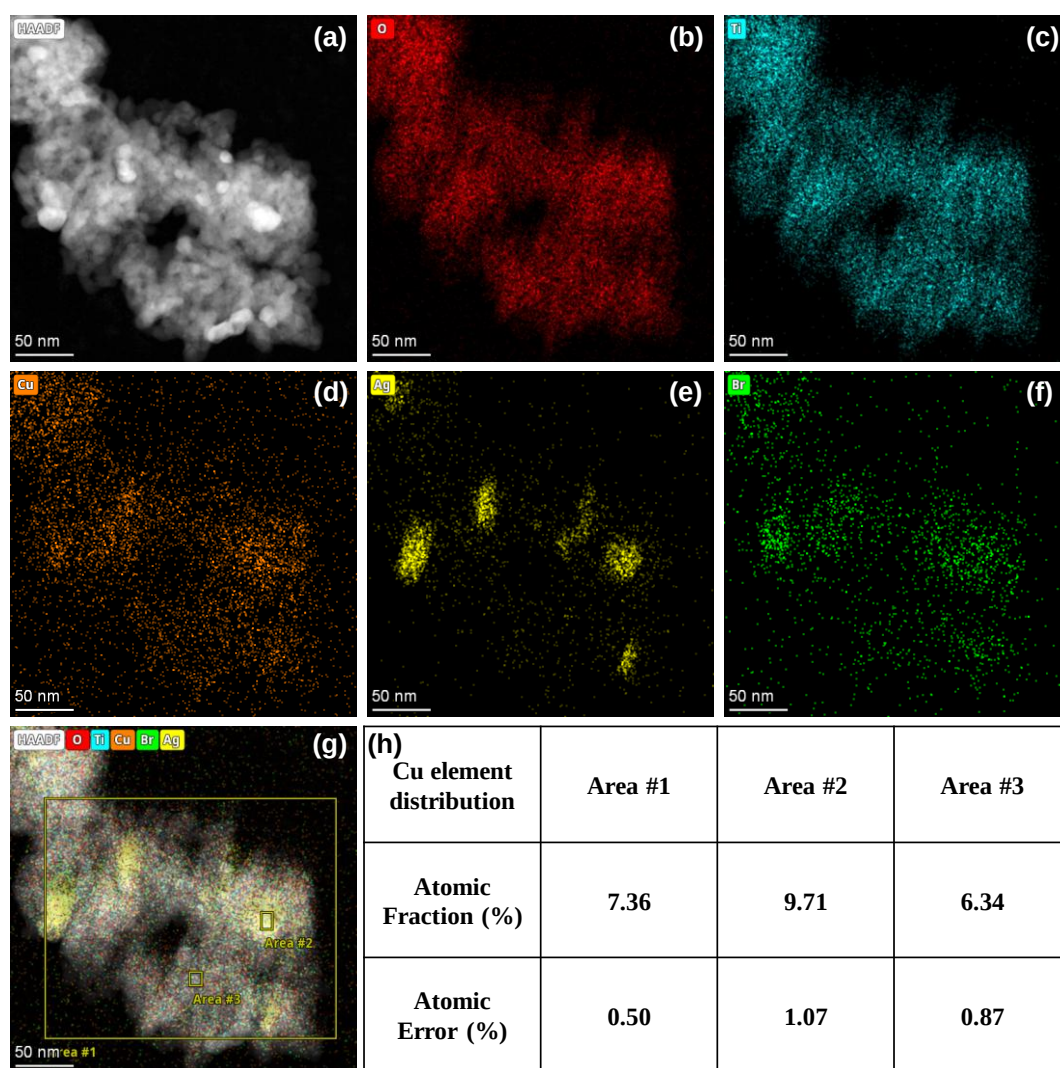


Figure S8. Elemental distribution of AgBr/TiO<sub>2</sub>. HAADF-STEM (a) and the corresponding EDS element mappings (b-f) images of Cu decorated AgBr/TiO<sub>2</sub>. (g) Overlapping EDS elemental mapping images and (h) the corresponding Cu element distribution configuration in different areas of Cu decorated AgBr/TiO<sub>2</sub>.

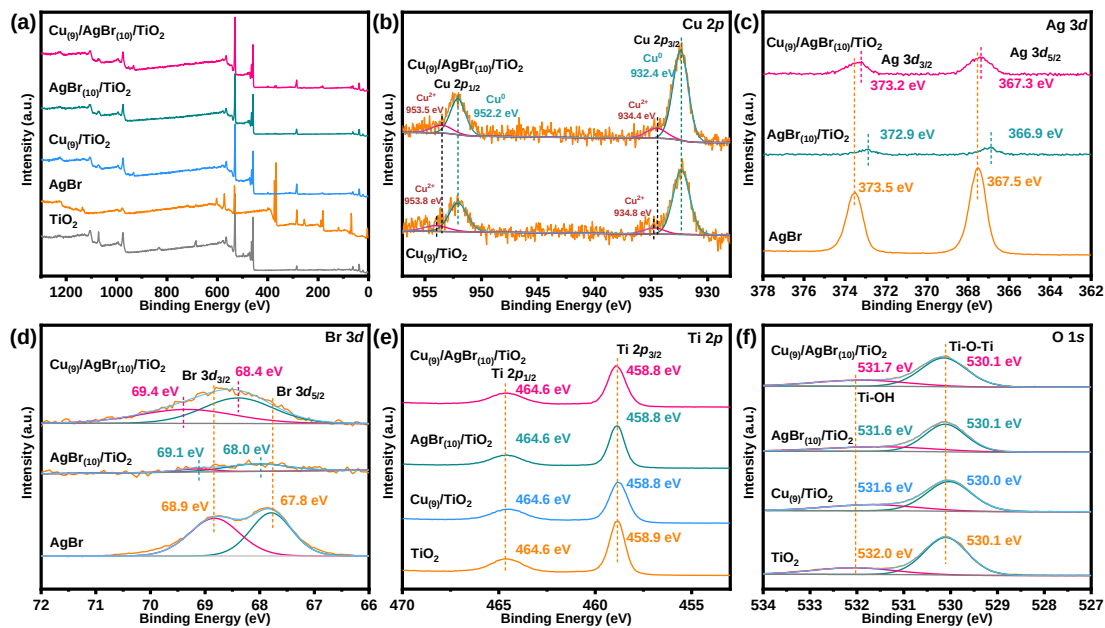


Figure S9. Elemental valence analysis of different catalysts. (a) Survey XPS spectra of the as-prepared samples. (b) Cu 2p, (c) Ag 3d, (d) Br 3d, (e) Ti 2p, and (f) O 1s XPS spectra of the as-prepared samples.

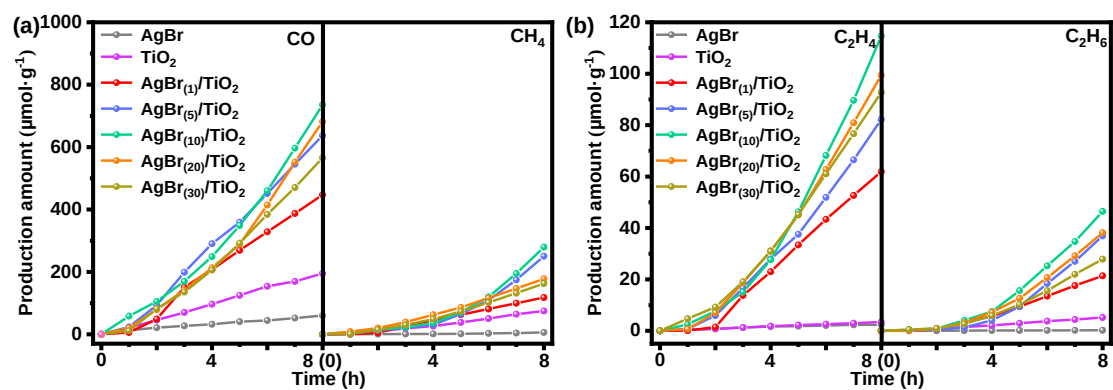


Figure S10. Time-resolved analysis of photocatalytic performance. (a) Time-dependent CO and CH<sub>4</sub> evolution over different AgBr<sub>(x)</sub>/TiO<sub>2</sub>. (b) Time-dependent C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> evolution over different AgBr<sub>(x)</sub>/TiO<sub>2</sub>.

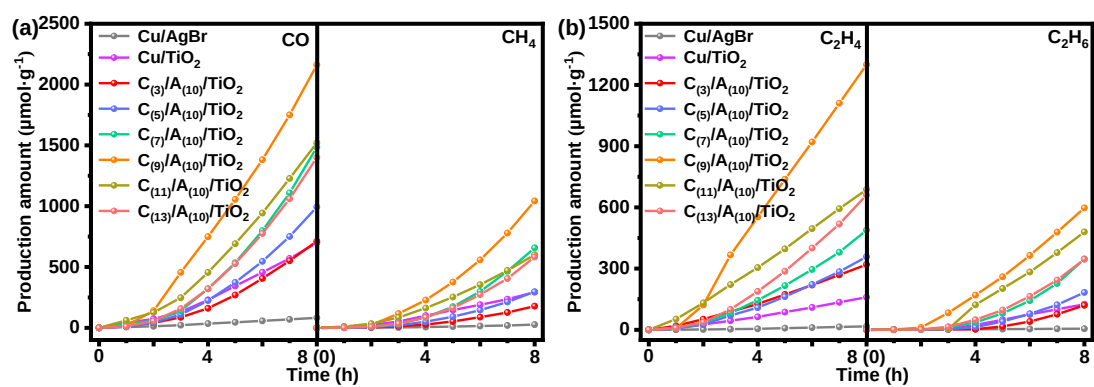


Figure S11. Time-resolved analysis of photocatalytic performance. (a) Time-dependent CO and CH<sub>4</sub> evolution over different Cu<sub>(x)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>. (b) Time-dependent C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> evolution over different Cu<sub>(x)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>.

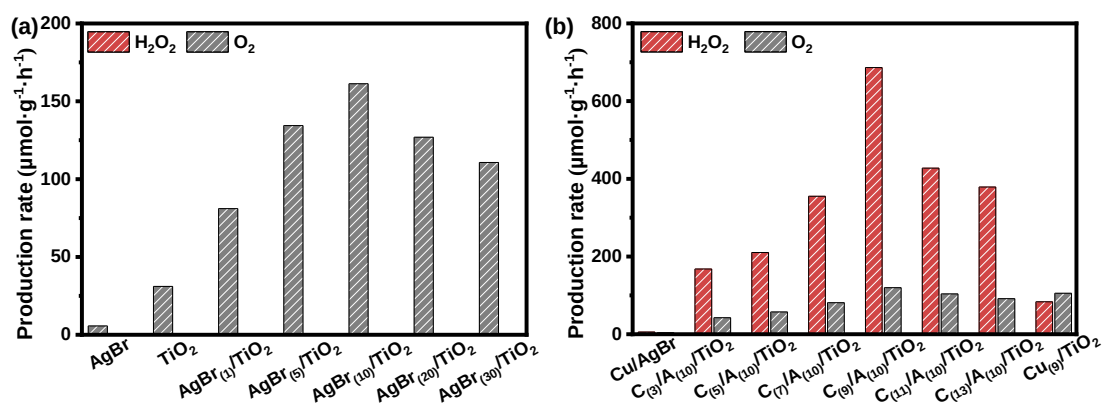


Figure S12. Oxidation-product performance on different catalysts.  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  production rates of the as-prepared samples analyzed from different phases.

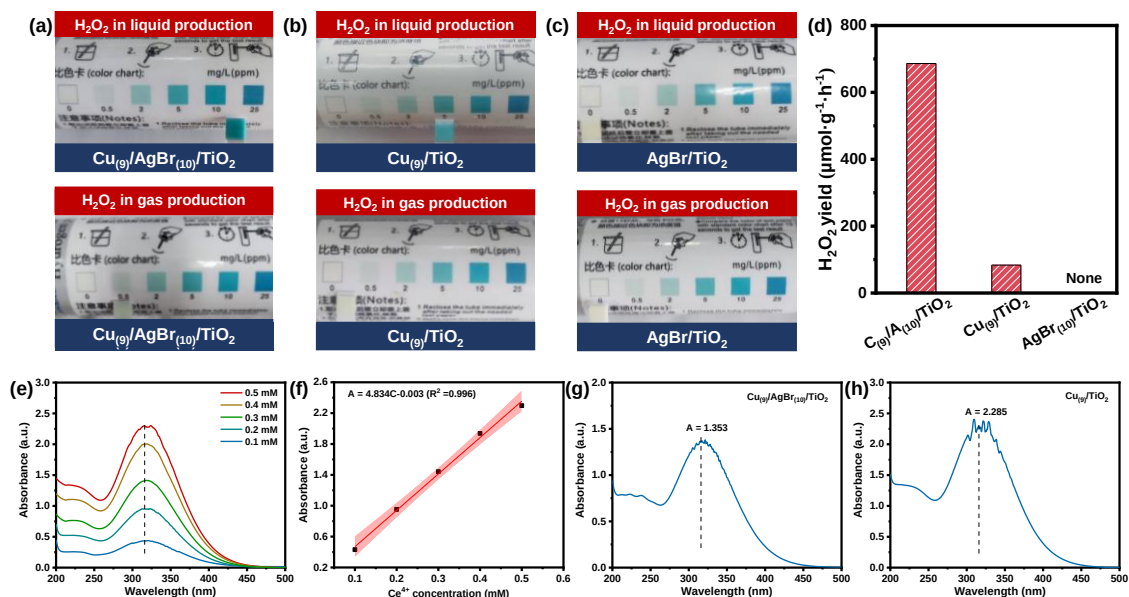


Figure S13.  $\text{H}_2\text{O}_2$  product analysis on different catalysts. Images of  $\text{H}_2\text{O}_2$  test strips used for both gas-phase and liquid-phase product detection over (a)  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ , (b)  $\text{Cu}_{(9)}/\text{TiO}_2$ , and (c)  $\text{AgBr}_{(10)}/\text{TiO}_2$ . (d)  $\text{H}_2\text{O}_2$  production rates of the as-prepared samples. (e) UV-vis absorption spectra of  $\text{Ce}^{4+}$  solution in different concentrations (0.1-0.5 mM). (f) The concentration standard curve of  $\text{Ce}^{4+}$  solution. UV-vis absorption spectra of  $\text{Ce}^{4+}$  solution (0.5 mM) mixed with the generated  $\text{H}_2\text{O}_2$  over (g)  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  and (h)  $\text{Cu}_{(9)}/\text{TiO}_2$ .

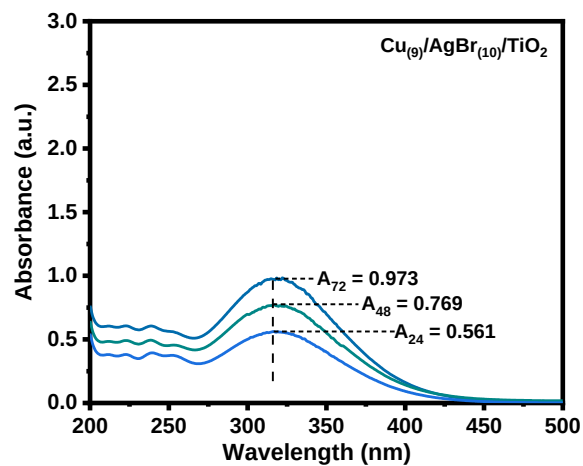


Figure S14.  $\text{H}_2\text{O}_2$  product analysis after the stability test. UV-vis absorption spectra of  $\text{Ce}^{4+}$  solution (0.5 mM) mixed with the generated  $\text{H}_2\text{O}_2$  over  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  after 72 h reaction.

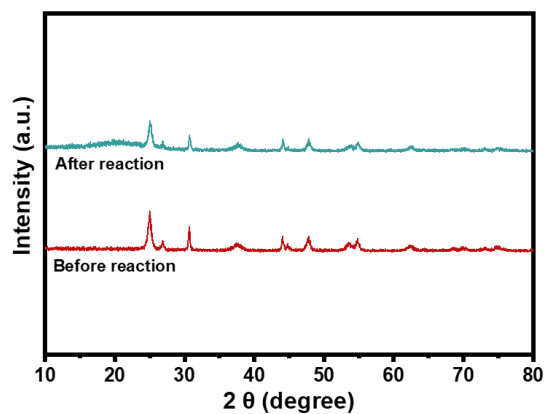


Figure S15. Structural analysis after the stability test. XRD patterns of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  before and after 24 h irradiation for 3 times repeated tests.

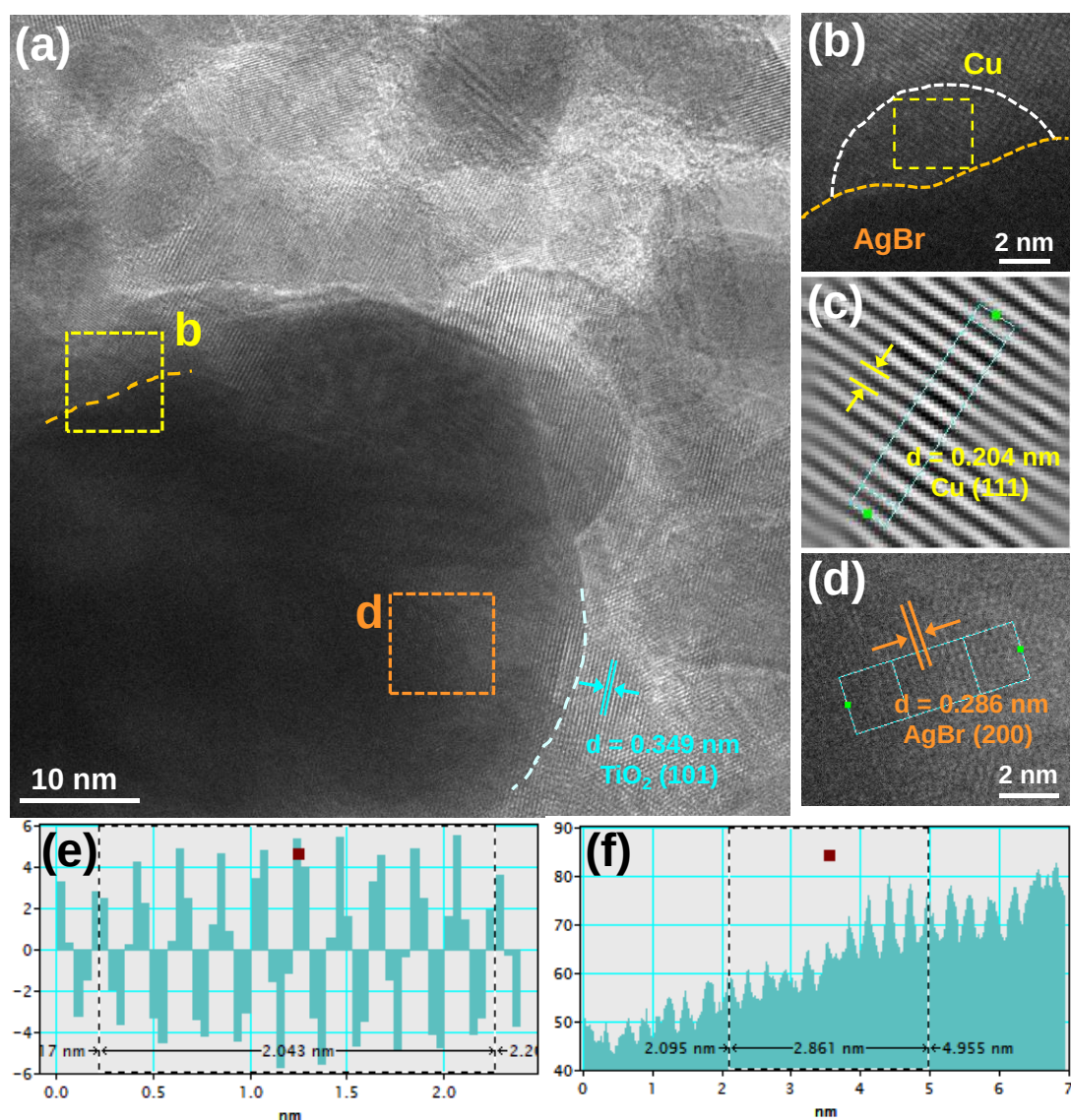


Figure S16. Morphological structure analysis after the stability test. (a) HRTEM of  $\text{Cu}_9/\text{AgBr}_{10}/\text{TiO}_2$  after 24 h irradiation for 3 times repeated tests. (b) Magnifying area in (a). (c) Fast fourier transform (FFT) of the yellow area in (b). (d) Magnifying area in (a). (e) Brightness intensity of the blue line profile in (c). (f) Brightness intensity of the blue line profile in (d).

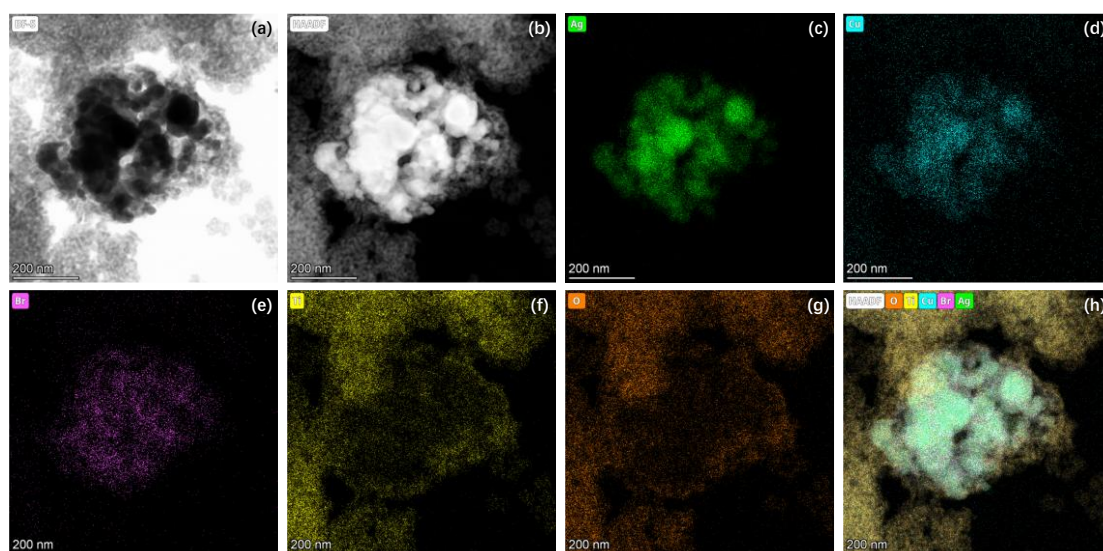


Figure S17. Morphological structure and elemental distribution analysis after the stability test. (a) TEM, (b) HAADF-STEM image, and (c-h) the corresponding EDS element mappings of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  after 24 h irradiation for 3 times repeated tests.

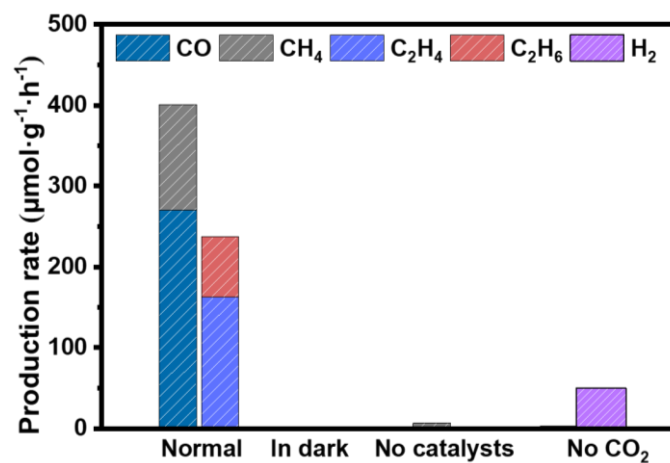


Figure S18. Source analysis of carbon-containing products. CO<sub>2</sub> photoreduction performance of Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub> under different conditions.

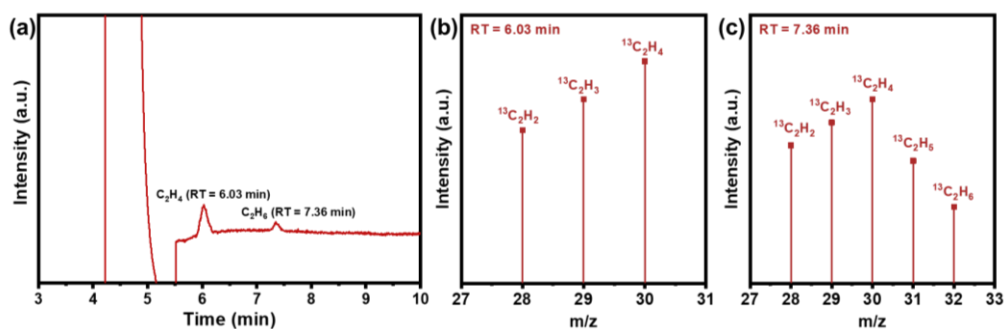


Figure S19. Source analysis of carbon-containing products. (a) GC spectra of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ , and MS spectra of (b)  $\text{C}_2\text{H}_4$  and (c)  $\text{C}_2\text{H}_6$  from the photocatalytic reduction of  $^{13}\text{CO}_2$  over  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ .

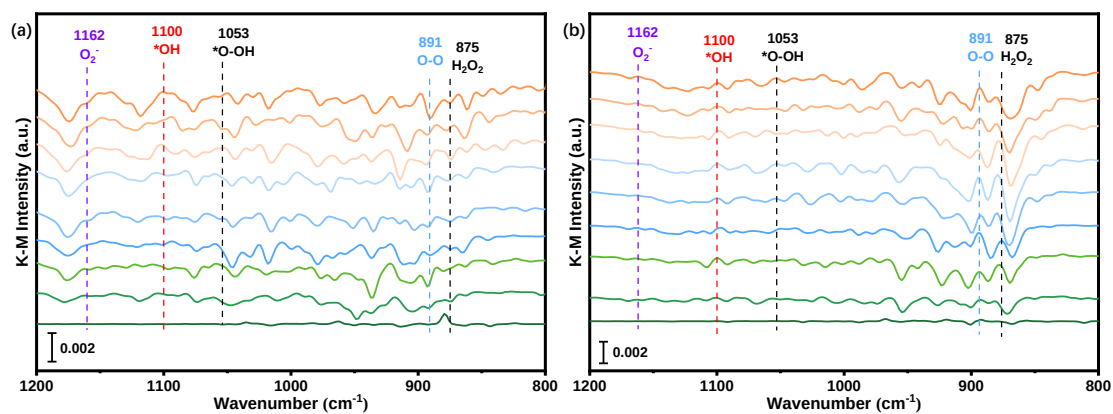


Figure S20. Analysis of generated H<sub>2</sub>O<sub>2</sub> pathways. *In situ* DRIFTS spectra of AgBr<sub>(10)</sub>/TiO<sub>2</sub> (a) and Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub> (b).

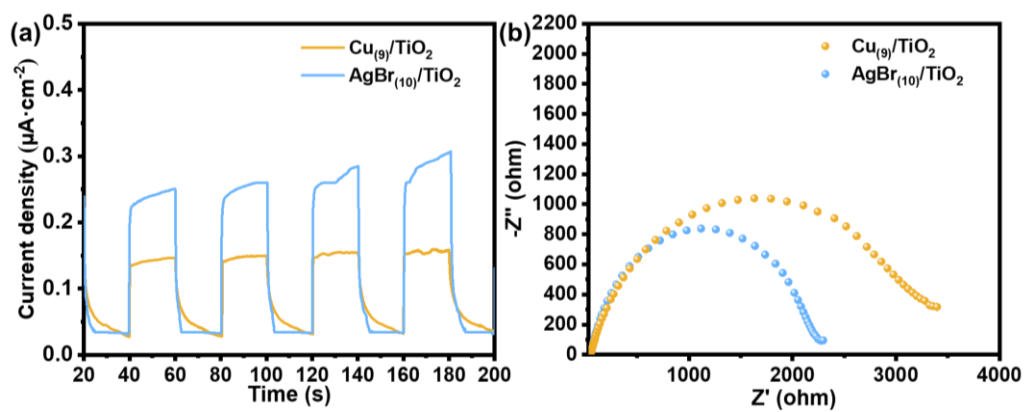


Figure S21. Dynamics analysis of photogenerated charge carrier. (a) Photocurrent response and (b) EIS measurements of  $\text{Cu}_{(9)}/\text{TiO}_2$  and  $\text{AgBr}_{(10)}/\text{TiO}_2$ .

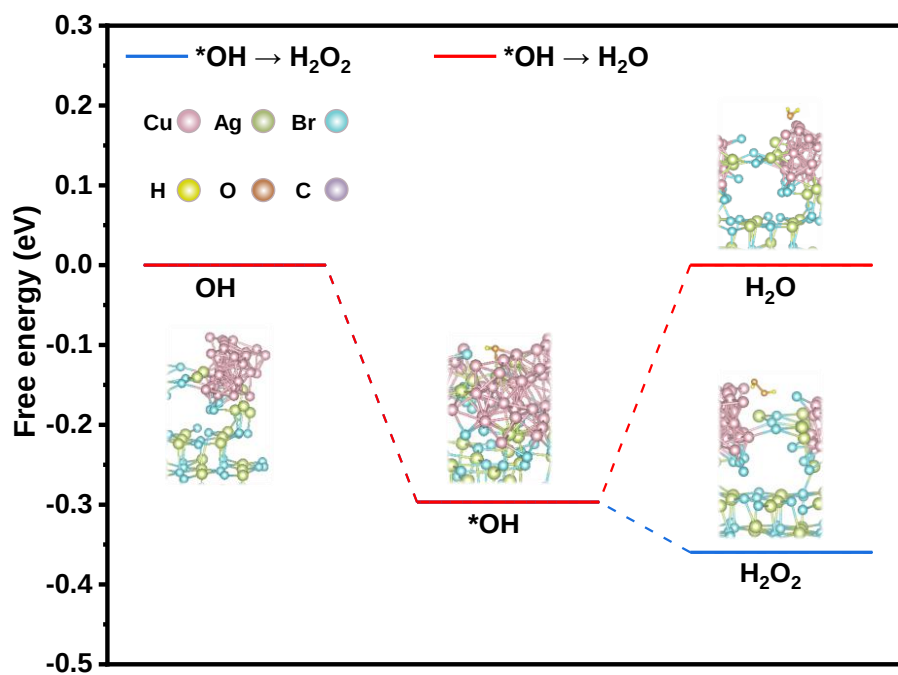


Figure S22. Theoretical analysis of generated  $\text{H}_2\text{O}_2$  pathways. The free energy diagram of  $^*\text{OH}$  conversion to  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$ .

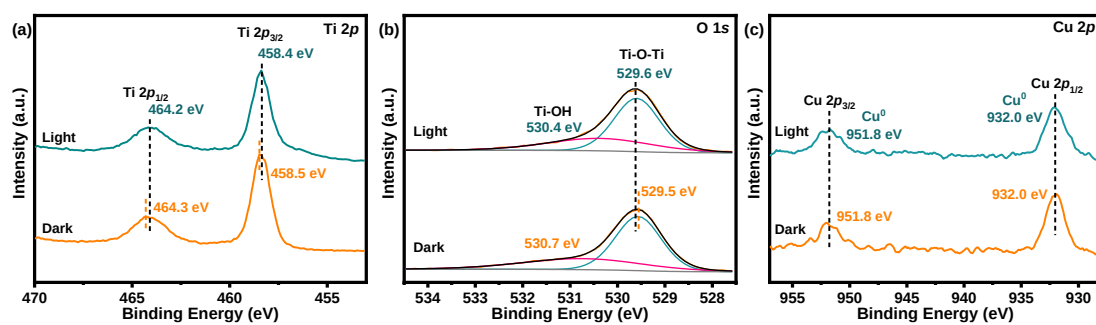


Figure S23. Analysis of photogenerated charge transfer pathways. *In situ* irradiated XPS spectra for Ti 2p (a), O 1s (b), and Cu 2p (c) of  $\text{Cu}_9/\text{TiO}_2$  in the dark or under irradiation.

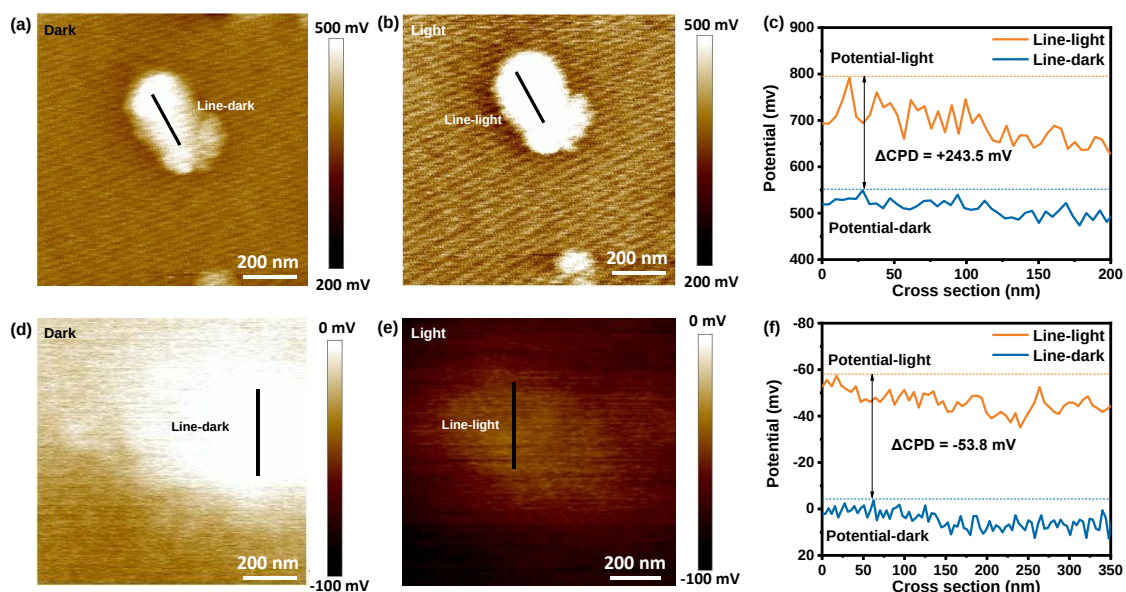


Figure S24. Analysis of photogenerated charge transfer pathways. (a) KPFM potential image of  $\text{TiO}_2$  under dark. (b) KPFM potential image of  $\text{TiO}_2$  under illumination. (c) Cross-sectional SPV of  $\text{TiO}_2$  acquired from KPFM potential images under dark and illumination. (d) KPFM potential image of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  under dark. (e) KPFM potential image of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  under illumination. (f) Cross-sectional SPV of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$  acquired from KPFM potential images under dark and illumination.

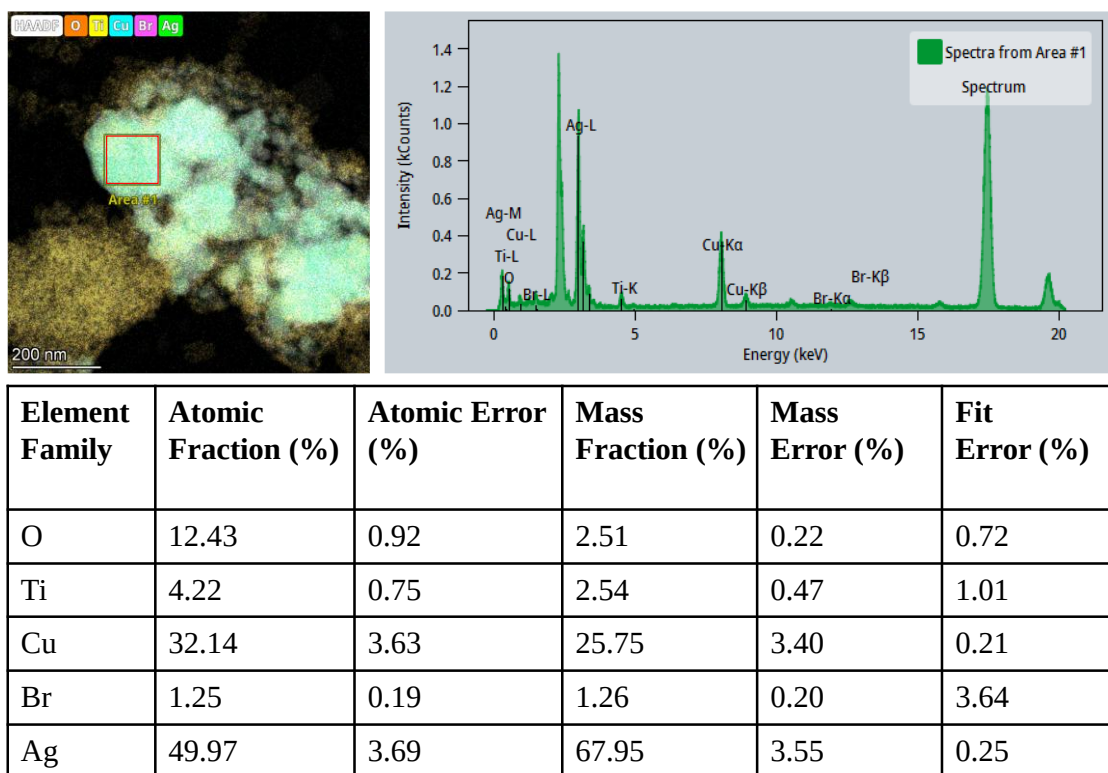


Figure S25. Elemental distribution analysis of Cu photodeposited AgBr/TiO<sub>2</sub>. EDS spectrum and detailed elements distribution configuration of the selected area in the Cu photodeposited AgBr/TiO<sub>2</sub> overlap EDS elemental mapping.

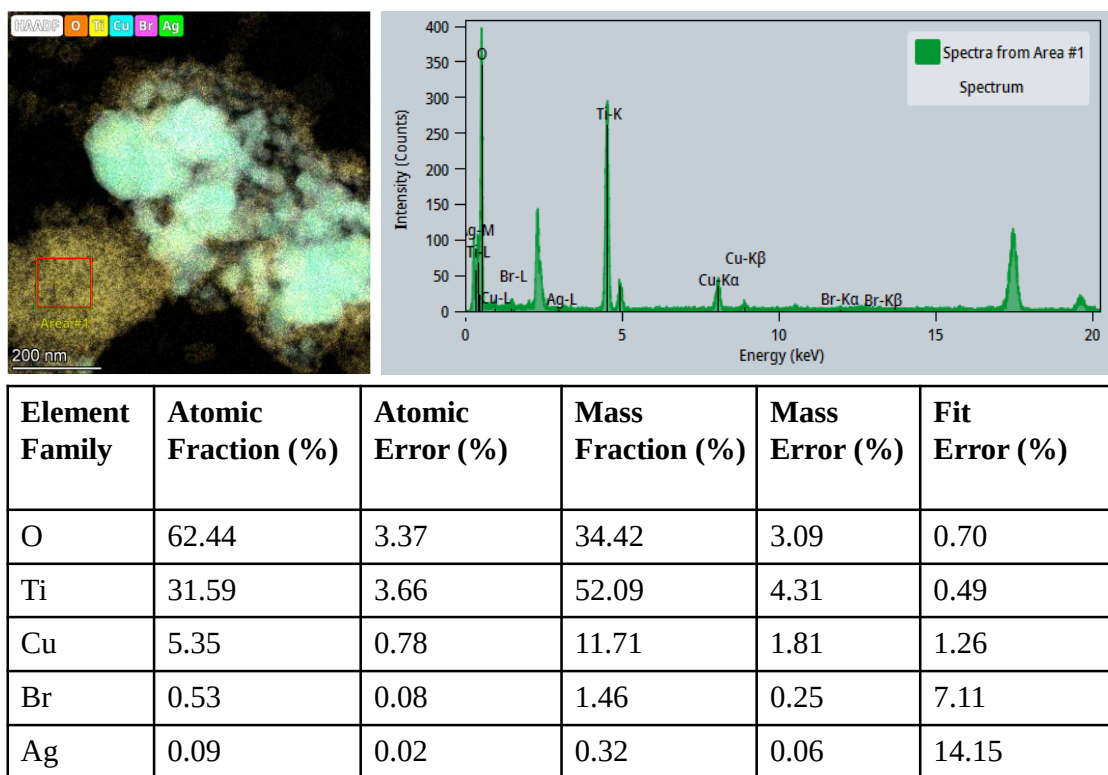


Figure S26. EDS spectrum and detailed elements distribution configuration of the selected area in the Cu photodeposited AgBr/TiO<sub>2</sub> overlap EDS elemental mapping.

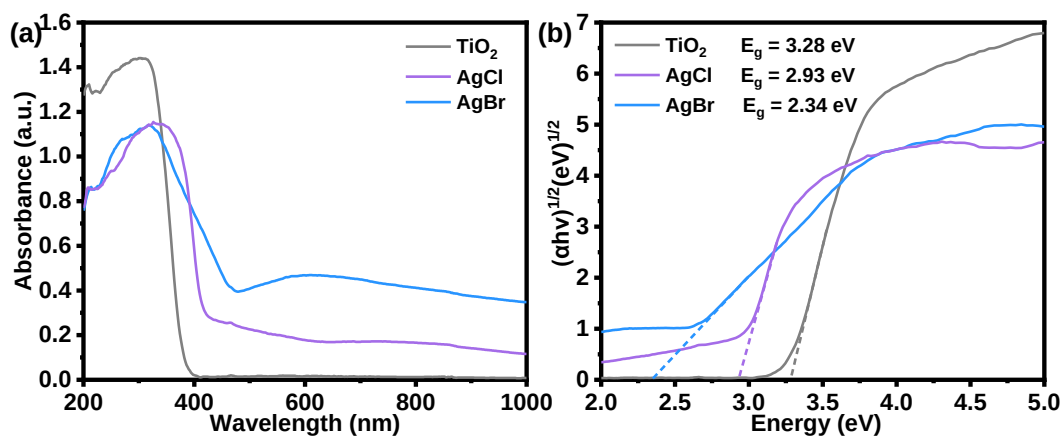


Figure S27. Analysis of photo absorption performance and band structure.

(a) UV-vis-NIR DRS spectra of TiO<sub>2</sub>, AgCl, and AgBr. (b) Plot of  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  for the bandgap energy of TiO<sub>2</sub>, AgCl, and AgBr.

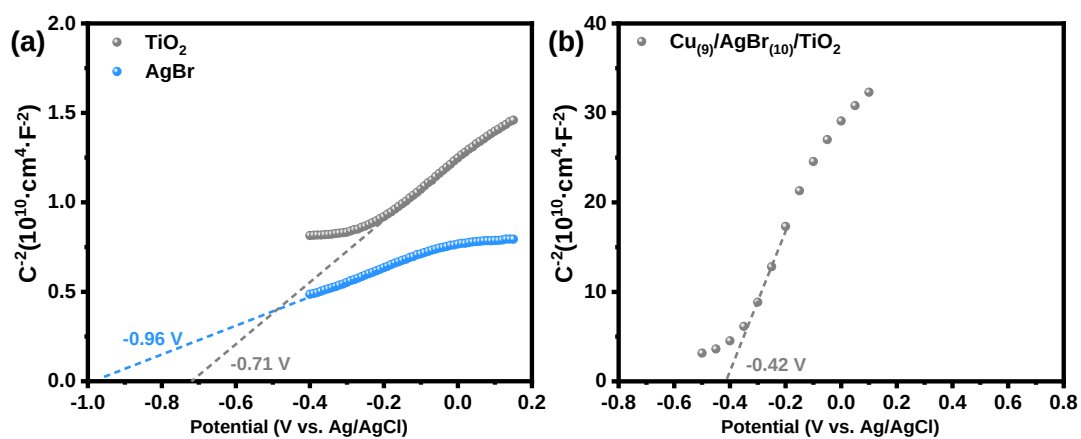


Figure S28. Analysis of band structure. (a) Mott-Schottky plots of  $\text{TiO}_2$  and  $\text{AgBr}$ . (b) Mott-Schottky plots of  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ .

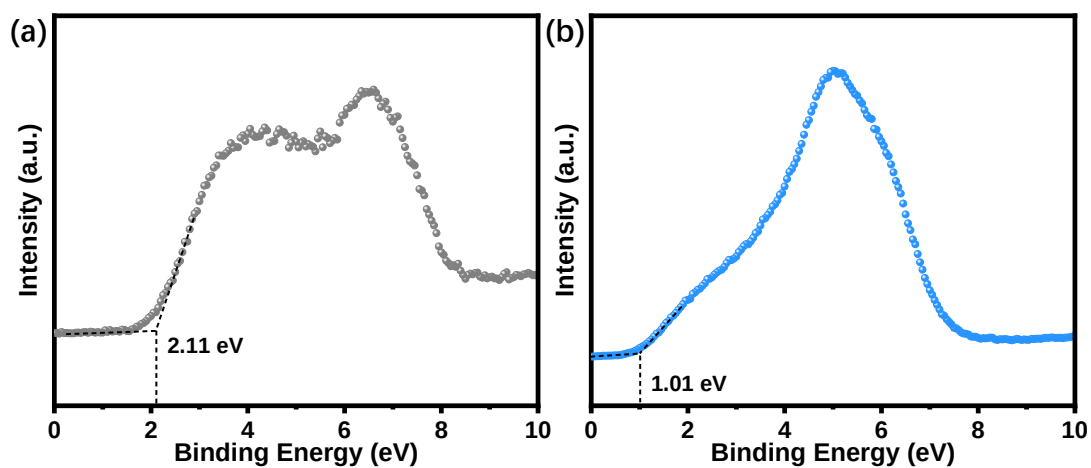


Figure S29. Analysis of band structure. The survey XPS spectrum of valence band spectrum of (a)  $\text{TiO}_2$  and (b)  $\text{AgBr}$ .

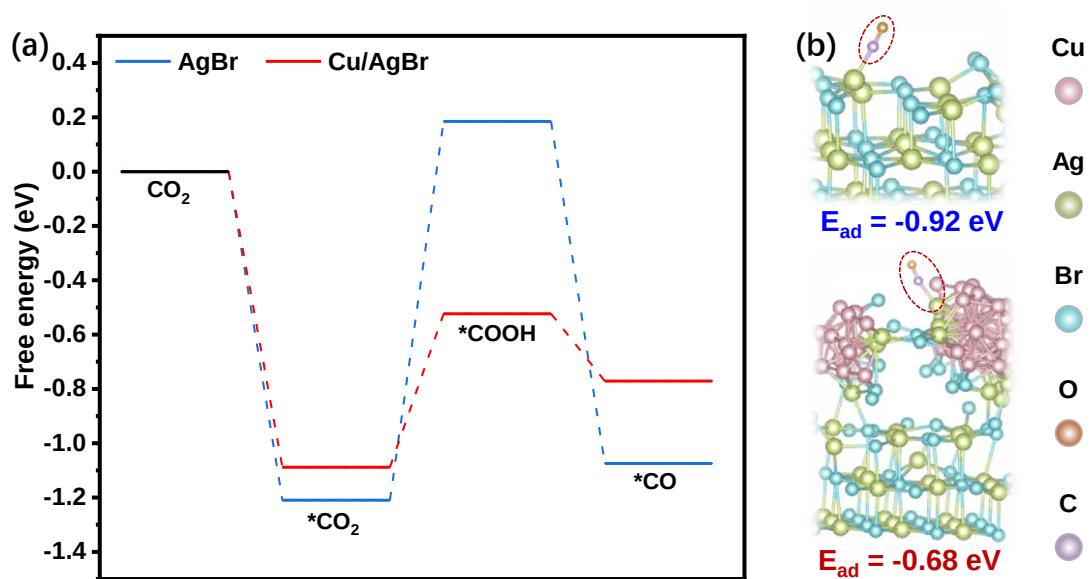


Figure S30. Theoretical analysis of  $\text{CO}_2$  conversion pathways. (a) The free energy diagram for  $\text{CO}_2$  conversion to  $^*\text{CO}$  over AgBr and Cu/AgBr. (b) Optimized structures of CO absorbed on AgBr and Cu/AgBr, and their adsorption energies.

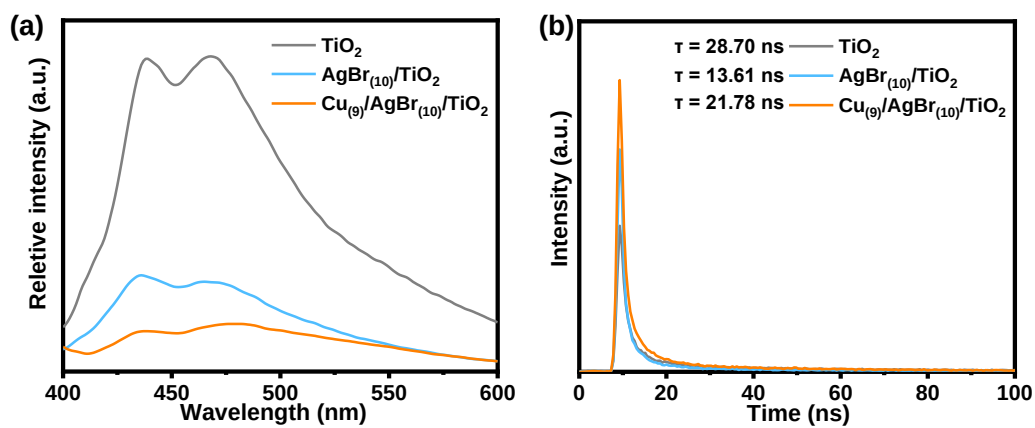


Figure S31. Dynamics analysis of photogenerated charge carrier. Steady-state PL spectra (a) and time-resolved transient PL spectra (b) over the as-prepared photocatalysts.

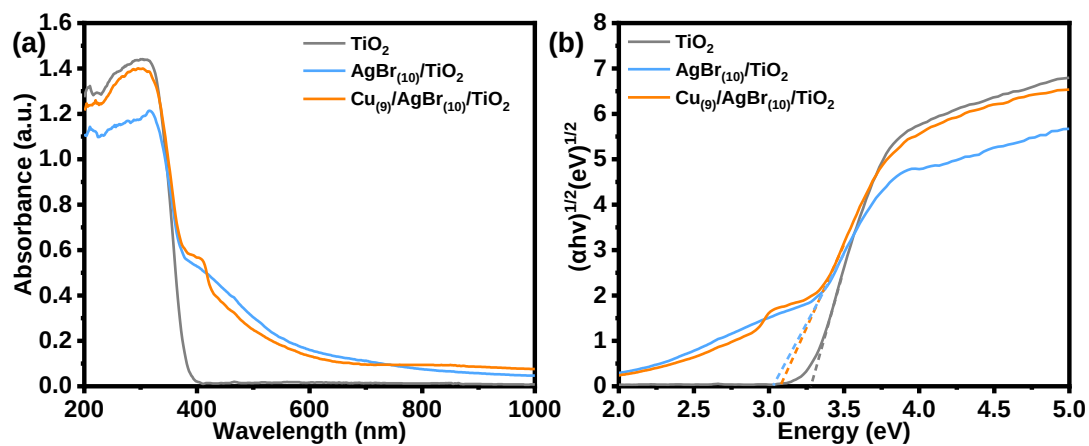


Figure S32. Analysis of photo absorption performance and band structure.

(a) UV-vis-NIR DRS spectra of TiO<sub>2</sub>, AgBr<sub>(10)</sub>/TiO<sub>2</sub>, and Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>. (b) Plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  for the bandgap energy of TiO<sub>2</sub>, AgBr<sub>(10)</sub>/TiO<sub>2</sub>, and Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub>.

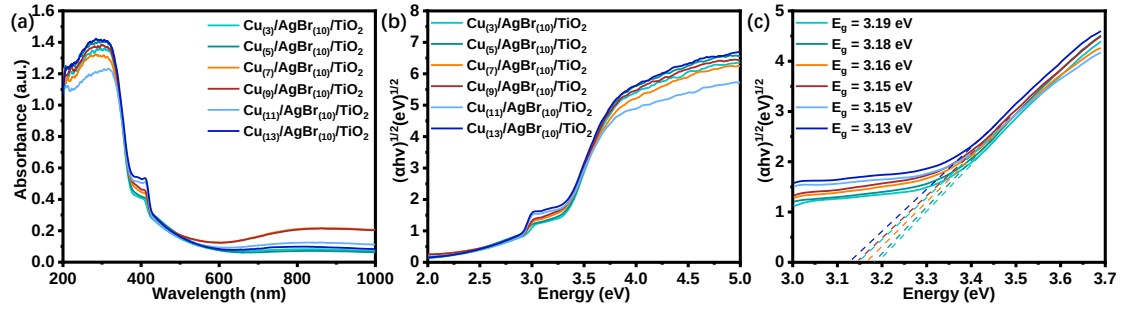


Figure S33. Analysis of photo absorption performance and band structure.

(a) UV-vis-NIR DRS spectra of different Cu loading amounts of  $\text{Cu}_{(x)}/\text{AgBr}_{(10)}/\text{TiO}_2$ . (b) Plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  for the bandgap energy of different Cu loading amounts of  $\text{Cu}_{(x)}/\text{AgBr}_{(10)}/\text{TiO}_2$ . (c) Magnifying plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  in (b).

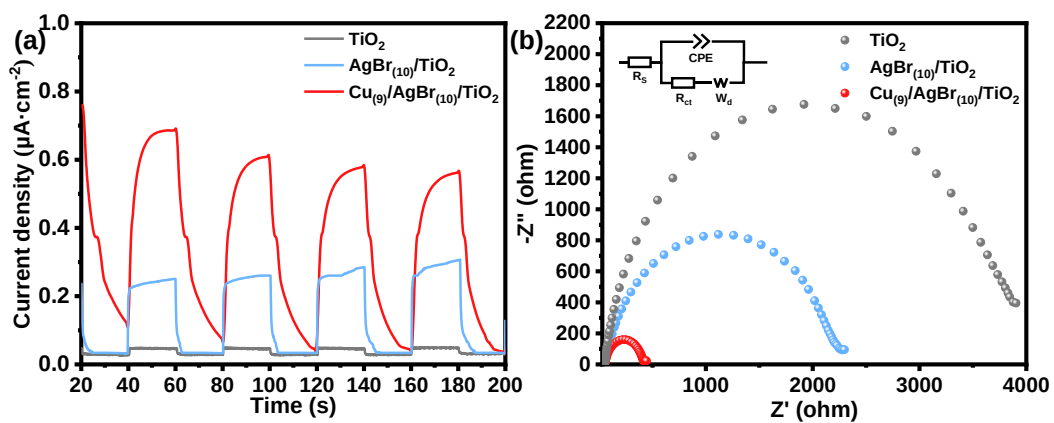


Figure S34. Dynamics analysis of photogenerated charge carrier. Photocurrent response (a) and EIS measurements (b) of  $\text{TiO}_2$ ,  $\text{AgBr}_{(10)}/\text{TiO}_2$ , and  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ .

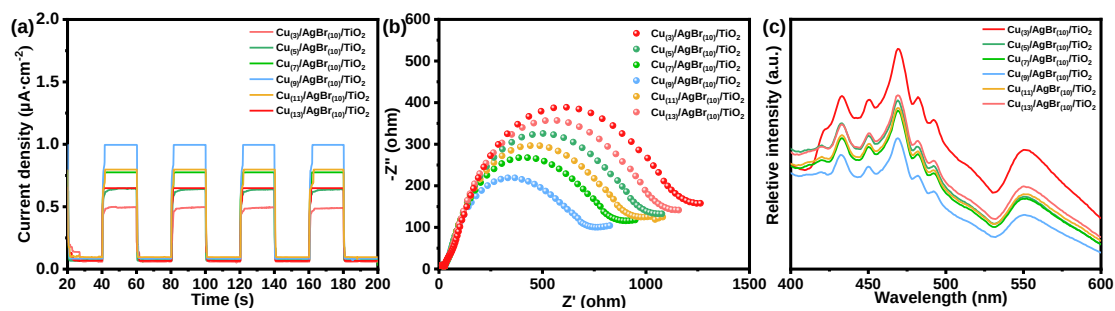


Figure S35. Dynamics analysis of photogenerated charge carrier. Photocurrent response (a), EIS measurements (b), and steady-state PL spectra (c) over the as-prepared photocatalysts.

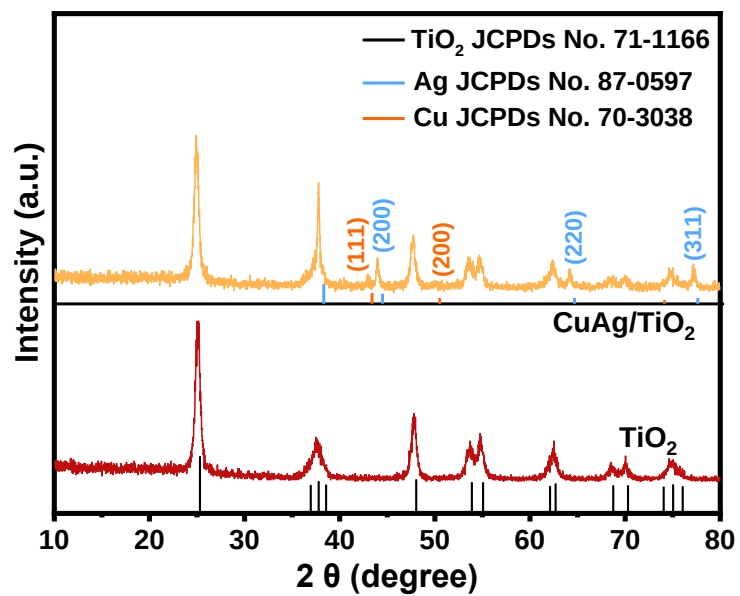


Figure S36. Structural analysis by XRD pattern. XRD patterns of  $\text{TiO}_2$  and  $\text{CuAg/TiO}_2$ .

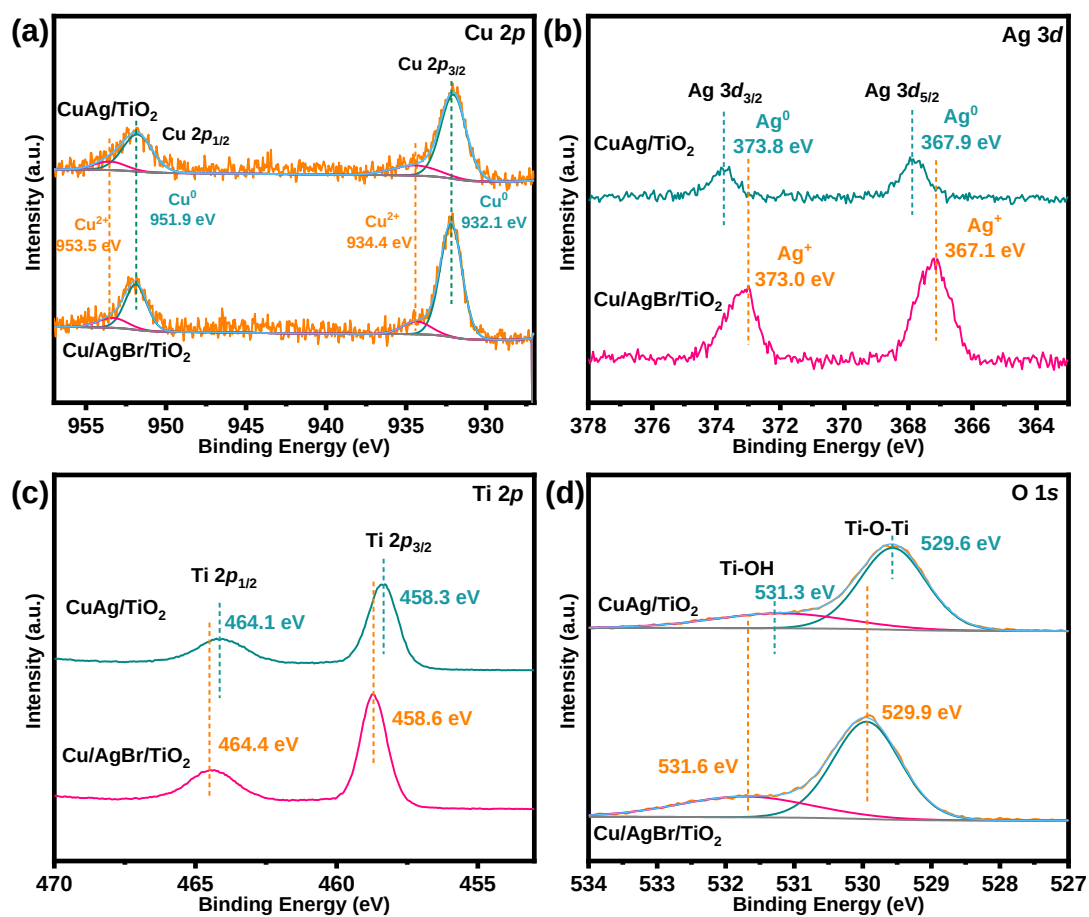


Figure S37. Elemental valence analysis of different catalysts. (a) Cu 2p, (b) Ag 3d, (c) Ti 2p, and (d) O 1s XPS spectra of Cu/AgBr/TiO<sub>2</sub> and CuAg/TiO<sub>2</sub>.

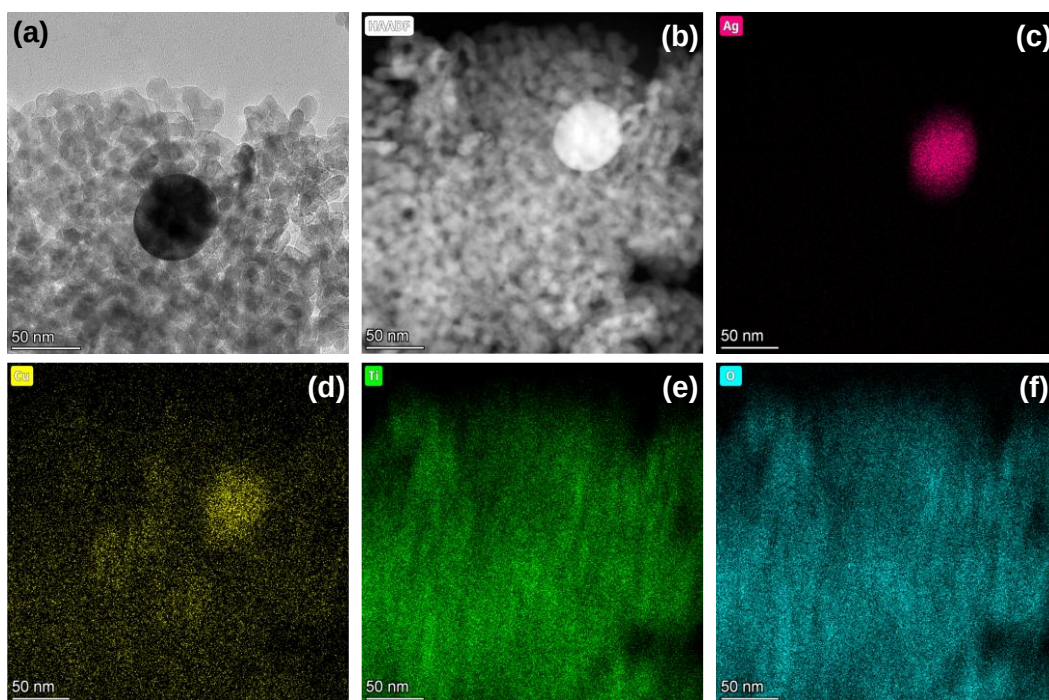


Figure S38. Morphological structure characterization of CuAg/TiO<sub>2</sub>. (a) TEM, (b) HAADF-STEM image, and (c-f) the corresponding EDS element mappings of CuAg/TiO<sub>2</sub>.

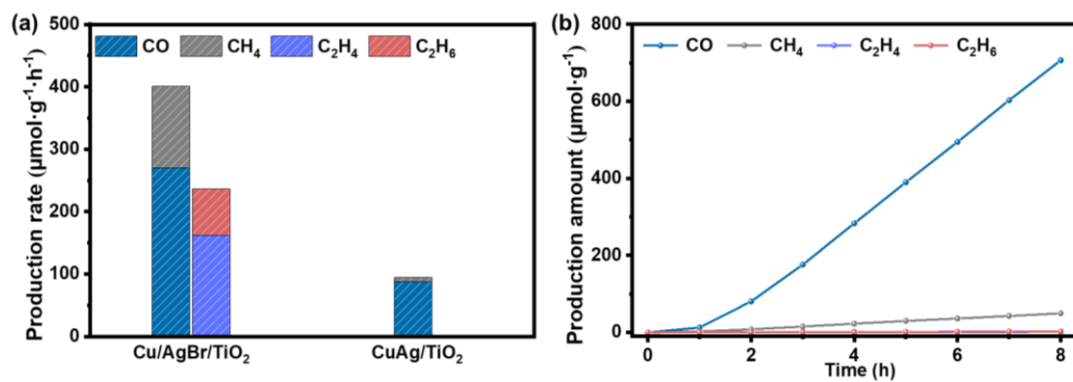


Figure S39. Time-resolved analysis of photocatalytic performance. (a) Products evolution rates over  $\text{Cu/AgBr/TiO}_2$  and  $\text{CuAg/TiO}_2$ . (b) Time-dependent C-based products evolution over  $\text{CuAg/TiO}_2$ .

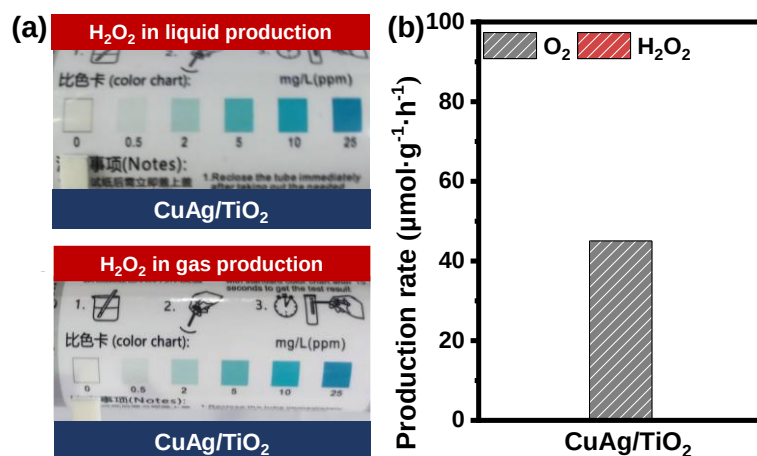


Figure S40. Analysis of oxidation-product performance on CuAg/TiO<sub>2</sub>. (a) Images of H<sub>2</sub>O<sub>2</sub> test strips used for both gas-phase and liquid-phase product detection. (b) O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> production rates of the as-prepared samples.

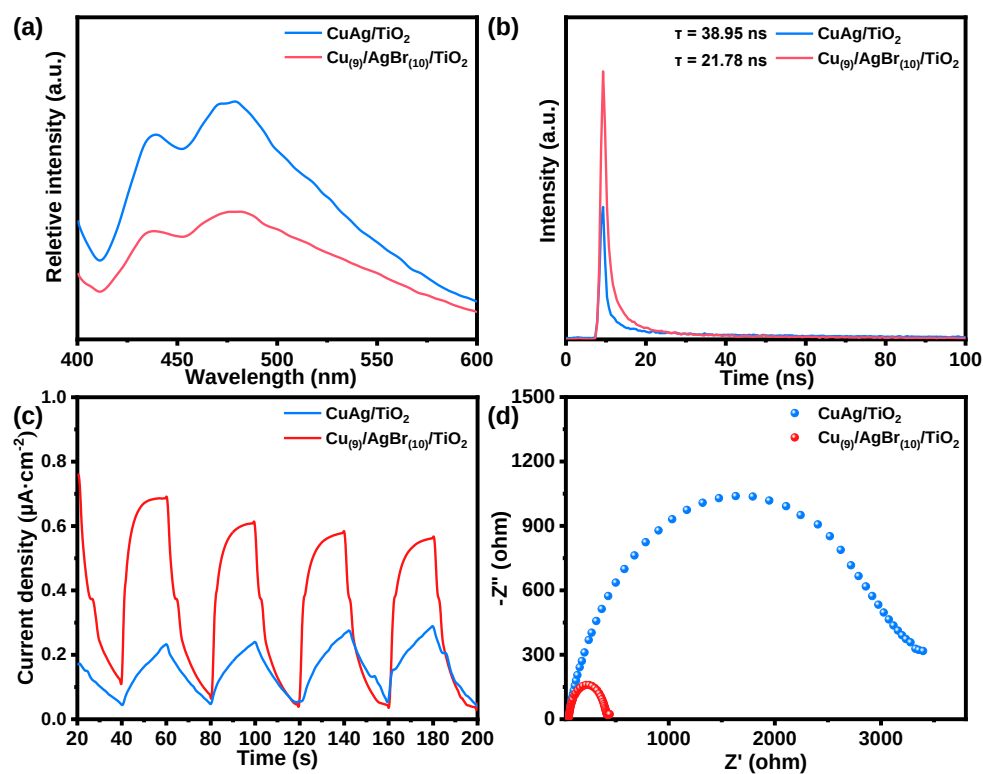


Figure S41. Dynamics analysis of photogenerated charge carrier. Steady-state PL spectra (a), time-resolved transient PL spectra (b), photocurrent response (c), and EIS measurements (d) of  $\text{CuAg/TiO}_2$  and  $\text{Cu}_{(9)}/\text{AgBr}_{(10)}/\text{TiO}_2$ .

Table S1. Zeta potential of AgCl before and after KBr addition.

| Sample     | Zeta Potential<br>(mV) | Mobility<br>( $\mu$ s)/(V/cm) | Conductance<br>( $\mu$ S) | Sample<br>Count (kcps) | Ref. Count<br>(kcps) |
|------------|------------------------|-------------------------------|---------------------------|------------------------|----------------------|
| AgCl       | -11.14                 | -0.87                         | 9                         | 878                    | 1032                 |
| AgCl + KBr | -38.93                 | -3.04                         | 66                        | 646                    | 885                  |

Table S2. Cu contents of as-prepared ternary hybrid structures in 4 mL solution determined by ICP-AES.

| Catalysts                                                  | Concentration | Content   |
|------------------------------------------------------------|---------------|-----------|
| Cu <sub>(3)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub>  | 12.4 µg/mL    | 2.48 wt%  |
| Cu <sub>(5)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub>  | 20.7 µg/mL    | 4.14 wt%  |
| Cu <sub>(7)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub>  | 29.5 µg/mL    | 5.90 wt%  |
| Cu <sub>(9)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub>  | 41.7 µg/mL    | 8.34 wt%  |
| Cu <sub>(11)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub> | 46.9 µg/mL    | 9.38 wt%  |
| Cu <sub>(13)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub> | 53.6 µg/mL    | 10.72 wt% |

Table S3. EXAFS fitting parameters at the Cu K-edge ( $S_0^2=0.880$ ).

| Sample  | Shell | $CN^a$ | $R(\text{\AA})^b$ | $\sigma^2(\times 10^{-3} \text{\AA}^2)^c$ | $\Delta E_0(\text{eV})^d$ | $R$ factor |
|---------|-------|--------|-------------------|-------------------------------------------|---------------------------|------------|
| Cu foil | Cu-Cu | 12*    | 2.54              | 8.7                                       | 4.8                       | 0.002      |
| Sample  | Cu-Cu | 8.4    | 2.51              | 11.1                                      | -7.9                      | 0.02       |
|         | Cu-Ag | 5.1    | 2.89              | 19.8                                      | -9.9                      |            |

<sup>a</sup> $CN$ , coordination number; <sup>b</sup> $R$ , distance between absorber and backscatter atoms; <sup>c</sup> $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders; <sup>d</sup> $\Delta E_0$ , inner potential correction;  $R$  factor indicates the goodness of the fit.  $S_0^2$  was fixed to 0.880, according to the experimental EXAFS fit of Cu foil by fixing  $CN$  as the known crystallographic value. Fitting range:  $2.5 \leq k (\text{\AA}) \leq 12.5$  and  $1.0 \leq R (\text{\AA}) \leq 3.0$  (Cu foil);  $3.0 \leq k (\text{\AA}) \leq 11$  and  $1.0 \leq R (\text{\AA}) \leq 3.0$  (Cu/AgBr/TiO<sub>2</sub>). A reasonable range of EXAFS fitting parameters:  $0.700 < S_0^2 < 1.000$ ;  $CN > 0$ ;  $0.02 > \sigma^2 > 0.003 \text{\AA}^2$ ;  $|\Delta E_0| < 10 \text{ eV}$ ;  $R$  factor  $< 0.02$ .

Table S4. EXAFS fitting parameters at Ag K-edge ( $S_0^2=0.827$ ).

| Sample  | Shell | $CN^a$ | $R(\text{\AA})^b$ | $\sigma^2(\times 10^{-3} \text{\AA}^2)^c$ | $\Delta E_0(\text{eV})^d$ | $R$ factor |
|---------|-------|--------|-------------------|-------------------------------------------|---------------------------|------------|
| Ag foil | Ag-Ag | 12*    | 2.86              | 9.4                                       | 1.47                      | 0.0078     |
| Sample  | Ag-Br | 7.0    | 2.95              | 7.5                                       | 8.17                      | 0.012      |
|         | Ag-Cu | 5.1    | 2.96              | 3.8                                       | 0.13                      |            |

<sup>a</sup> $CN$ , coordination number; <sup>b</sup> $R$ , distance between absorber and backscatter atoms; <sup>c</sup> $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders; <sup>d</sup> $\Delta E_0$ , inner potential correction;  $R$  factor indicates the goodness of the fit.  $S_0^2$  was fixed to 0.827, according to the experimental EXAFS fit of Ag foil by fixing  $CN$  as the known crystallographic value. Fitting range:  $2.0 \leq k (\text{\AA}^{-1}) \leq 12.0$  and  $1.0 \leq R (\text{\AA}) \leq 3.0$  (Ag foil);  $2.0 \leq k (\text{\AA}^{-1}) \leq 10$  and  $1.0 \leq R (\text{\AA}) \leq 3.5$  (Cu/AgBr/TiO<sub>2</sub>); A reasonable range of EXAFS fitting parameters:  $0.700 < S_0^2 < 1.000$ ;  $CN > 0$ ;  $0.02 > \sigma^2 > 0.003 \text{\AA}^2$ ;  $|\Delta E_0| < 10 \text{ eV}$ ;  $R$  factor  $< 0.02$ .

Table S5. C<sub>2</sub>H<sub>4</sub> evolution rates of Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub> in comparison with recent reports in photoreduction CO<sub>2</sub> with H<sub>2</sub>O.

| Photocatalysts                                                 | Reaction feedstock                                                     | Reaction conditions                                    | Yield (μmol·g <sup>-1</sup> ·h <sup>-1</sup> ) | Selectivity (%) | Stability (h) | Ref.      |
|----------------------------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------|------------------------------------------------|-----------------|---------------|-----------|
| Cu/AgBr/TiO <sub>2</sub>                                       | 2 mg catalysts<br>90 kPa CO <sub>2</sub><br>1 mL H <sub>2</sub> O      | 300 W Xe lamp<br>400 mW·cm <sup>-2</sup>               | 162.4                                          | 42.5            | 8             | This work |
| Cu/AgBr/TiO <sub>2</sub>                                       | 2 mg catalysts<br>90 kPa CO <sub>2</sub><br>1 mL H <sub>2</sub> O      | 300 W Xe lamp<br>400 mW·cm <sup>-2</sup>               | 181.1                                          | 33.1            | 24            | This work |
| S <sub>v</sub> -CdS@ZIF-8                                      | 20 mg catalysts<br>80 kPa CO <sub>2</sub><br>2 mL H <sub>2</sub> O     | 300 W Xe lamp<br>λ > 420 nm                            | 0.8                                            | 12.1            | 3             | [12]      |
| CuACs/PCN                                                      | 5 mg catalysts<br>100 kPa CO <sub>2</sub><br>45 mL H <sub>2</sub> O    | 300 W Xe lamp                                          | 1.57                                           | /               | 3             | [13]      |
| CuO <sub>x</sub> @p-ZnO                                        | 5 mg catalysts<br>500 kPa CO <sub>2</sub><br>H <sub>2</sub> O vapor    | 300 W Xe lamp<br>320-780 nm<br>100 mW·cm <sup>-2</sup> | 2.7                                            | 32.9            | 8             | [14]      |
| Mo-COF                                                         | 10 mg catalysts<br>1 mL CO <sub>2</sub><br>5 mL H <sub>2</sub> O       | 300 W Xe lamp<br>λ > 420 nm                            | 3.57                                           | 42.92           | 2             | [15]      |
| C@Fe <sub>2</sub> C/TiO-2                                      | 10 mg catalysts<br>70 kPa CO <sub>2</sub><br>90 mL H <sub>2</sub> O    | 300 W Xe lamp<br>λ > 420 nm<br>2 °C                    | 4.48                                           | /               | 5             | [16]      |
| Cu <sup>δ+</sup> /CeO <sub>2</sub> -TiO <sub>2</sub>           | 10 mg catalysts<br>100 kPa CO <sub>2</sub><br>30 mL H <sub>2</sub> O   | 300 W Xe lamp<br>320-850 nm<br>200 mW·cm <sup>-2</sup> | 4.51                                           | 73.9            | 5             | [17]      |
| BW-3                                                           | 10 mg catalysts<br>100 kPa CO <sub>2</sub><br>0.4 mL H <sub>2</sub> O  | 300 W Xe lamp                                          | 5.92                                           | /               | 5             | [18]      |
| Bi <sub>2</sub> S <sub>3</sub> @In <sub>2</sub> S <sub>3</sub> | 5 mg catalysts<br>100 kPa CO <sub>2</sub><br>1 mL H <sub>2</sub> O     | 300 W Xe lamp<br>320-780 nm<br>112.3 °C                | 9.57                                           | 90              | 5             | [19]      |
| V <sub>s</sub> -SAL                                            | 4-5 mg catalysts<br>100 kPa CO <sub>2</sub><br>0.4 mL H <sub>2</sub> O | 300 W Xe lamp                                          | 18.3                                           | 88.9            | 6             | [20]      |
| CuGaS <sub>2</sub>                                             | 10 mg catalysts<br>100 kPa CO <sub>2</sub><br>20 mL H <sub>2</sub> O   | 450 W Xe lamp                                          | 20.6                                           | 92.7            | 8             | [21]      |
| CuInP <sub>2</sub> S <sub>6</sub>                              | 4-5 mg catalysts<br>100 kPa CO <sub>2</sub><br>0.4 mL H <sub>2</sub> O | 300 W Xe lamp<br>AM 1.5G                               | 20.89                                          | 74.6            | 5             | [22]      |
| Cu <sub>2</sub> ZnSnS <sub>4</sub>                             | 10 mg catalysts<br>100 kPa CO <sub>2</sub><br>2 mL H <sub>2</sub> O    | 300 W Xe lamp<br>λ > 420 nm<br>50 mW·cm <sup>-2</sup>  | 25.16                                          | 72.4            | 12            | [23]      |
| WO <sub>3-x</sub> -2                                           | 5 mg catalysts<br>100 kPa CO <sub>2</sub><br>0.2 mL H <sub>2</sub> O   | 300 W Xe lamp                                          | 61.6                                           | 89.3            | 3             | [24]      |

Table S6. H<sub>2</sub>O<sub>2</sub> evolution rates of Cu<sub>(9)</sub>/AgBr<sub>(10)</sub>/TiO<sub>2</sub> in comparison with recent reports in photoreduction CO<sub>2</sub> with H<sub>2</sub>O.

| Photocatalysts                                                                       | Reaction feedstock                                                                                 | Reaction conditions                                        | Yield (μmol·g <sup>-1</sup> ·h <sup>-1</sup> ) | Ref.      |
|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------------------------------|------------------------------------------------|-----------|
| Cu/AgBr/TiO <sub>2</sub>                                                             | 2 mg catalysts<br>90 kPa CO <sub>2</sub><br>1 mL H <sub>2</sub> O                                  | 300 W Xe lamp<br>400 mW·cm <sup>-2</sup>                   | 686.3                                          | This work |
| NH <sub>2</sub> -MIL-125-Ti/WO <sub>3-x</sub>                                        | 20 mg catalysts<br>80 kPa CO <sub>2</sub><br>50 mL H <sub>2</sub> O                                | 300 W Xe lamp<br>5 °C                                      | 8.41                                           | [6]       |
| Cs <sub>4</sub> Mn(Bi <sub>1-x</sub> Sb <sub>x</sub> ) <sub>2</sub> Cl <sub>12</sub> | 10 mg catalysts<br>100 kPa CO <sub>2</sub><br>30 μL H <sub>2</sub> O                               | 300 W Xe lamp<br>AM 1.5G                                   | 14.69                                          | [7]       |
| Ag <sub>27</sub> TPyP-Fe                                                             | 1 mg catalysts<br>100 kPa CO <sub>2</sub><br>20 mL H <sub>2</sub> O                                | 300 W Xe lamp<br>25 °C                                     | 35.9                                           | [8]       |
| Ag-MnO <sub>x</sub> /CaTiO <sub>3</sub>                                              | 300 mg catalysts<br>0.5 M NaHCO <sub>3</sub><br>100 kPa CO <sub>2</sub><br>350 mL H <sub>2</sub> O | 100 W high-pressure mercury lamp<br>44 mW·cm <sup>-2</sup> | 46                                             | [9]       |
| TPE-PT                                                                               | 20 mg catalysts<br>100 kPa CO <sub>2</sub><br>1 mL H <sub>2</sub> O                                | 300 W Xe lamp<br>25 °C                                     | 259.1                                          | [10]      |
| Cu <sub>2</sub> O-Ag-TiO <sub>2</sub>                                                | 5 mg catalysts<br>100 kPa CO <sub>2</sub><br>17 mL H <sub>2</sub> O                                | 300 W Xe lamp<br>300 mW·cm <sup>-2</sup>                   | 350                                            | [11]      |

Table S7. The time-resolved fluorescence spectra of as-prepared samples.

| <b>Photocatalysts</b>                                     | <b>B<sub>1</sub></b> | <b>τ<sub>1</sub>, ns</b> | <b>B<sub>2</sub></b> | <b>τ<sub>2</sub>, ns</b> | <b>τ, ns</b> |
|-----------------------------------------------------------|----------------------|--------------------------|----------------------|--------------------------|--------------|
| TiO <sub>2</sub>                                          | 4026.71              | 2.33                     | 234.30               | 49.89                    | 28.70        |
| AgBr <sub>(10)</sub> /TiO <sub>2</sub>                    | 6115.14              | 1.69                     | 202.90               | 32.38                    | 13.61        |
| Cu <sub>(9)</sub> /AgBr <sub>(10)</sub> /TiO <sub>2</sub> | 6999.73              | 2.15                     | 317.88               | 43.25                    | 21.78        |
| CuAg/TiO <sub>2</sub>                                     | 2301.40              | 2.05                     | 232.38               | 53.04                    | 38.95        |