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*Supplementary Material*

# Cu Nanoparticles Modified Step-Scheme $Cu_2O/WO_3$ Heterojunction Nanoflakes for Visible-Light-Driven Conversion of $CO_2$ to $CH_4$

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## S1. Catalytic Experiment for $CO_2$ Photoreduction

Photocatalytic activity for $CO_2$ reduction with water vapor was evaluated in a stainless-steel cylindrical vessel with a length of 15 cm and a volume of 180 mL, and the light source was a 300 W Xenon arc lamp (PLS-SXE 300, Beijing Trust tech Co. Ltd., China) with a UV cutoff filter ($\lambda > 400$ nm). The catalyst was put on a glass sheet (1.8 × 2 cm) equipped with a quartz window. Before lighting, the reaction setup was vacuum-treated, and then high purity $CO_2$ gas (99.995%) was purged into the reaction system several times. The compressed high purity $CO_2$ gas passed through a water bubbler to generate a mixture of $CO_2$ and $H_2O$ vapor. After illumination, the gaseous products were quantifiably identified by offline analysis using a GC-7890IIgas chromatograph (Techcomp Corp., China) equipped with FID and TCD detectors, and the columns were TDX-01 and Porapak-Q, respectively. Then, the hydrocarbon product was further analyzed by GC-MS (Agilent 7890A-5975C) equipped with a DB-FFAP capillary column. In order to evaluate the stability of the synthesized composites, the $Cu/Cu_2O/WO_3$ model sample was refreshed by electrochemical treatment before washing and drying, and its photocatalytic performance was reassessed.

**Table S1.** ICP-AES analysis of $Cu_2O/WO_3$ and $Cu/Cu_2O/WO_3$ samples.

| Sample | Ratio of Cu/W atoms (%) |
|---|---|
| $WO_3$ | 0.00 |
| $Cu_2O/WO_3$ | 16.66 |
| $Cu/Cu_2O/WO_3$ | 18.22 |
| $Cu/Cu_2O$ | 100 |
| $Cu_2O$ | 100 |

**Table S2.** Band gaps of pure $WO_3$, $Cu_2O$, $Cu_2O/WO_3$ and $Cu/Cu_2O/WO_3$ samples.

| Sample | Band gap( eV ) |
|---|---|
| $WO_3$ | 2.83 |
| $Cu_2O/WO_3$ | 2.32* |
| $Cu/Cu_2O/WO_3$ | 2.09* |
| $Cu_2O$ | 2.03 |

* The above value was apparent band gap of the sample.

**Table S3.** Comparison of performance $CO_2$ conversion of the obtained material with other reported catalysts.

| Catalyst | Experimental Conduction | Performance | Reference |
|---|---|---|---|
| $Cu/Cu_2O/g\text{-}C_3N_4$ | 300W Xe lamp | CO: 10.8 μmol/$g_{cat}$/h<br>$CH_4$: 3.1 μmol/$g_{cat}$/h<br>$CH_4$/CO: 0.29 | Carbon, 2022, 193, 272-284. |
| $Cu/CuO_x/TiO_2$ | 56 mW/cm² LED (425 nm) | CO: 0.7 μmol/$g_{cat}$/h<br>$CH_4$: 1.2 μmol/$g_{cat}$/h<br>$CH_4$/CO: 1.71 | Nanomaterials, 2022, 12, 1584. |
| $Cu\text{-}Ti_3C_2Tx/g\text{-}C_3N_4$ | 300W Xe lamp (170 mW/cm², 400nm cutoff filter) | CO: 1225.5 μmol/$g_{cat}$/h<br>$CH_4$: 90 μmol/$g_{cat}$/h<br>$CH_4$/CO: 0.07 | Chem. Eng. J., 2022, 446, 137028. |
| $1\%CuO_x/TiO_2(101)$ | 300 W Xe lamp | CO: 0.32 μmol/$g_{cat}$/h<br>$CH_4$: 2.29 μmol/$g_{cat}$/h<br>$CH_4$/CO: 7.15<br>$H_2$: 2.96 μmol/$g_{cat}$/h | Appl. Surf. Sci., 2021, 564, 150407. |
| $Cu_2O/Ti_3C_2T_x$ | 300 W Xe lamp | CO: 17.55 μmol/$g_{cat}$/h<br>$CH_4$: 0.96 μmol/$g_{cat}$/h<br>$CH_4$/CO: 0.05 | Appl. Surf. Sci., 2021, 542, 148685. |
| $Cu_2O@Cu_3(BTC)_2$ | 500 W Xe lamp (400nm cutoff filter), Thin film on copper mesh | CO: 0.73μmol for 8h | Angew. Chem. Int. Ed., 2021, 6, 8455-8459. |
| $Cu/Cu_2O/WO_3$ | 300 W Xe lamp (170 mW/cm², 400nm cutoff filter, ) | After 24 h illumination<br>$CH_4$: 101.2 μmol/$g_{cat}$/h<br>$H_2$: 13.3 μmol/$g_{cat}$/h<br>$O_2$: 143.7 μmol/$g_{cat}$/h | This work |

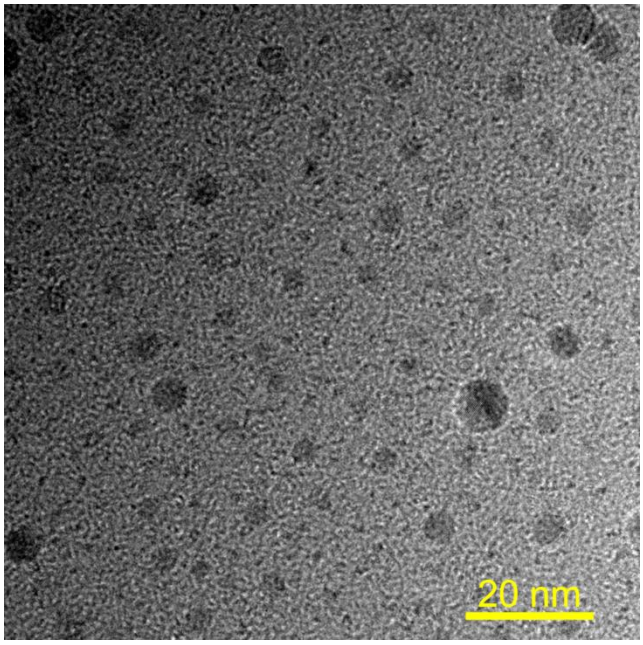


**Figure S1.** TEM image of Cu nanoparticles in $Cu/Cu_2O/WO_3$ sample.

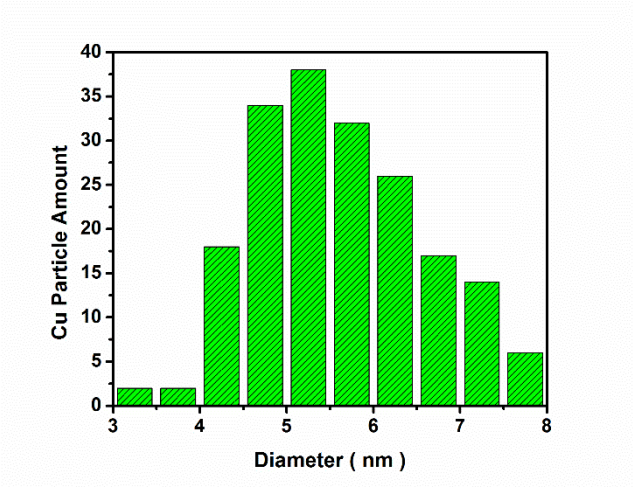


**Figure S2.** Size distribution histogram of Cu nanoparticles.

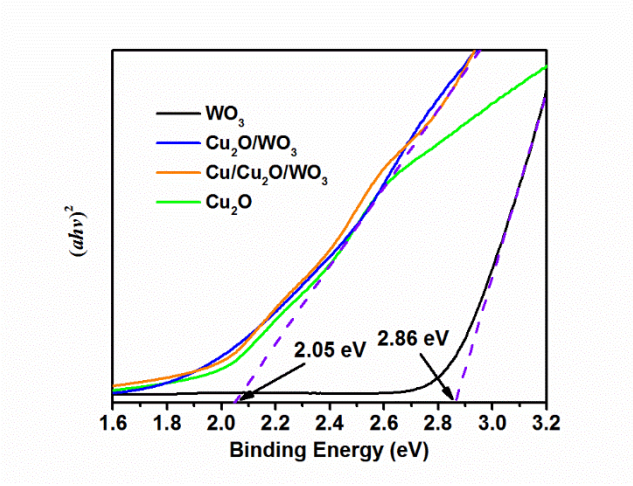


**Figure S3.** The curves of $(\alpha h\nu)^2$ versus photo energy ($h\nu$).

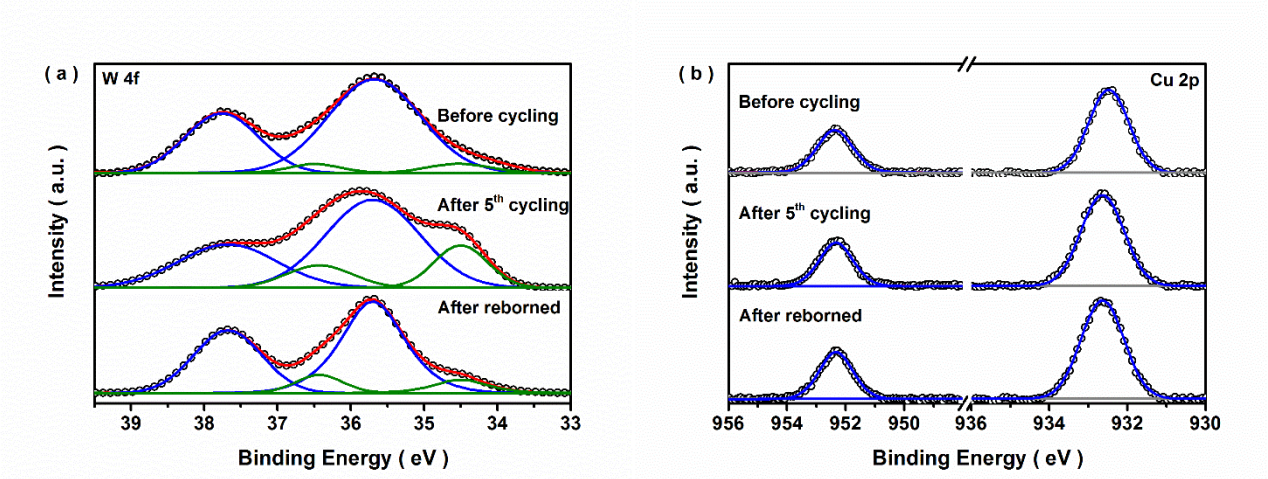


**Figure S4.** XPS spectra of Cu/Cu2O/WO3 in the cycling tests **(a)** W 4f and **(b)** Cu 2p.