

# Photocatalytic mineralisation of herbicide 2,4,5-Trichlorophenoxyaceticacid: Enhanced performance by triple junction Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O and the underlying reaction mechanism

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## 1. Morphology and composition of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O junction

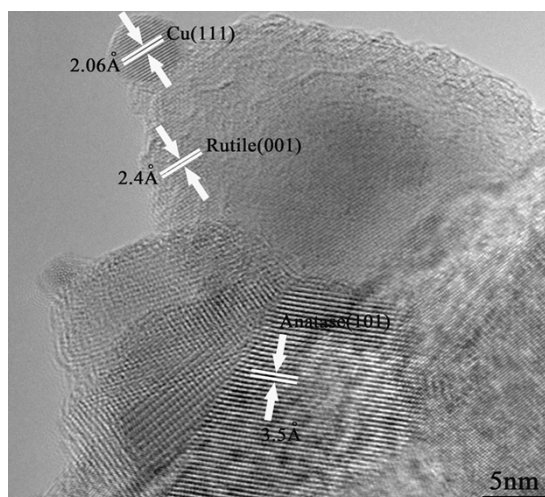


Figure S1 HR-TEM image of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O junction

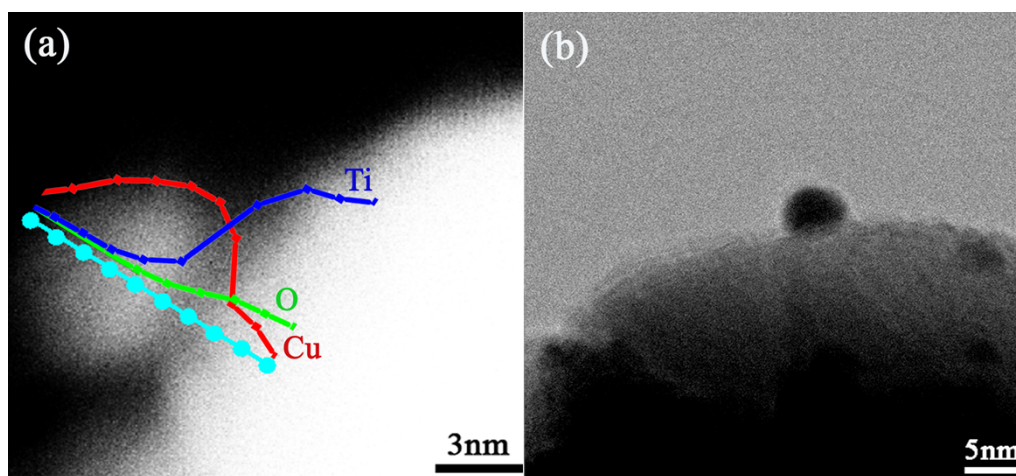
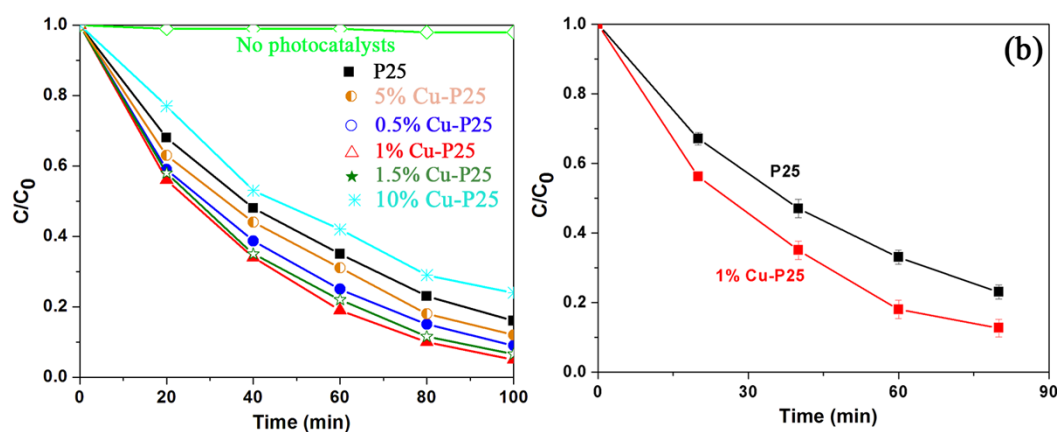


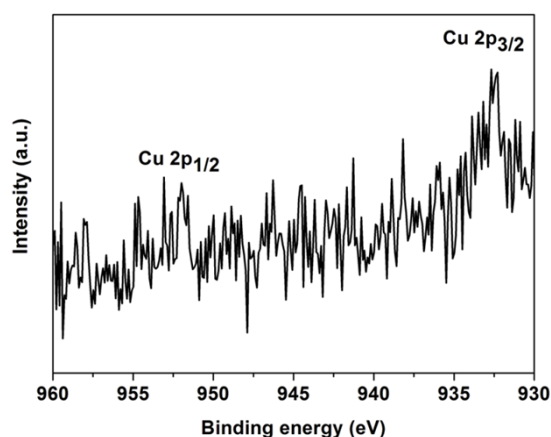
Figure S2 HAADF-STEM image of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O composite; (b) ABF-STEM image of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O composite.

## 2. Photocatalytic removal of 2,4,5-T over photocatalysts



**Figure S3** (a) Process of photocatalytic degradation of 2,4,5-T over P25 and Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O; (b) Photocatalytic degradation results with error bar.

## 3. XPS spectrum of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O fabricated from Cu(NO<sub>3</sub>)<sub>2</sub>

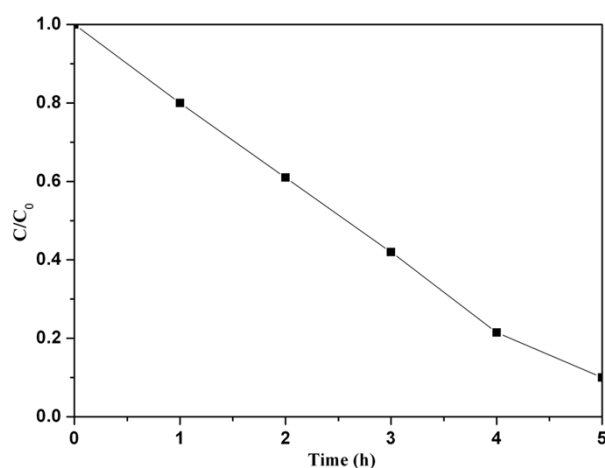


**Figure S4** Cu 2p spectrum of 1% Cu loaded P25 fabricated from Cu(NO<sub>3</sub>)<sub>2</sub>.

## 4. Photodegradation of 2,4,5-T by Cu<sub>2</sub>O photocatalyst

Cu<sub>2</sub>O photocatalyst was fabricated via the following procedure:<sup>[1]</sup> 0.4 g Cu(OAc)<sub>2</sub> was dissolved in 30 mL water. Then, 40 mL of NaOH aqueous solution (0.2 M) and 20 ml of ascorbic acid aqueous solution (0.1 M) were successively added into the solution. After stirring for 30 minutes at 50 °C, the precipitate of Cu<sub>2</sub>O was filtered, washed with water and dried at 70 °C in a vacuum oven.

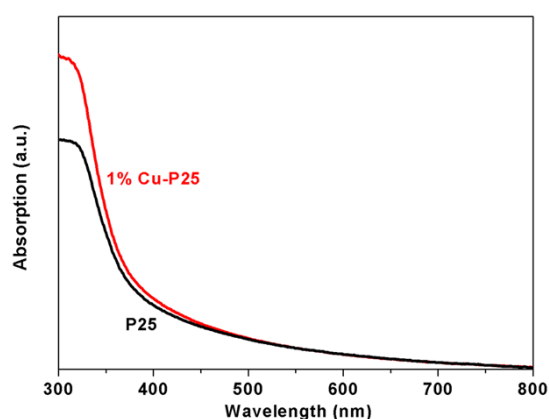
For the photocatalytic test, 30 mg of  $\text{Cu}_2\text{O}$  photocatalysts were suspended in 100 mL of 10 ppM aqueous solution of 2,4,5-T. The suspension was stirred in the dark for 2 hours to achieve the equilibrium adsorption. Then the stirred suspension was illuminated with a 300W xenon lamp.



**Figure S5** Photodegradation of 2,4,5-T over  $\text{Cu}_2\text{O}$  photocatalysts.

## 5. UV-vis spectra of samples

As shown in Figure S5, the loading of Cu species on the surface exhibits negligible influence on the absorption edge of  $\text{TiO}_2$ . However, the slightly increased absorption in the visible region is due to the presence of Cu-related species in the product.

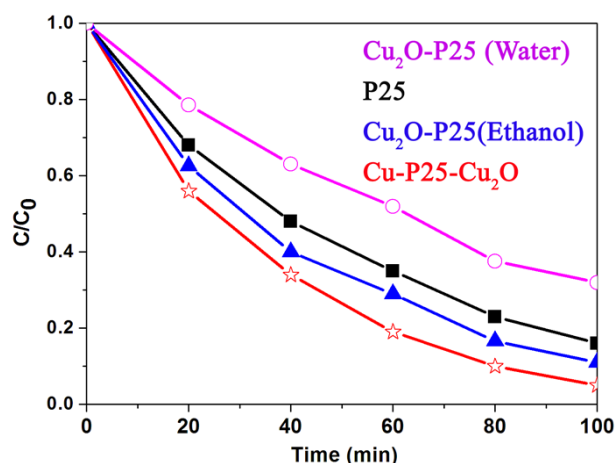


**Figure S6** UV-vis absorption spectra of P25 and Cu loaded P25

## 7. Activity of $\text{Cu}_2\text{O-TiO}_2$ photocatalysts

An impregnation method was used to fabricate 1% Cu<sub>2</sub>O loaded TiO<sub>2</sub>. Firstly, 100 mg P25 and a certain amount of Cu(OAc)<sub>2</sub> were added to 100 mL absolute ethanol under vigorous stirring. Then, NaOH and ascorbic acid dissolved in absolute ethanol were added. After the ethanol was evaporated and the sample was dried at 50 °C, Cu<sub>2</sub>O loaded photocatalysts were washed in water and dried at room temperature. In the control experiment, water was used as solvent during the impregnation process.

As shown in Figure S5, 1% Cu<sub>2</sub>O loaded P25 prepared in ethanol exhibits higher photocatalytic activity than bare P25. However, a remarkable decrease was observed when water was used as solvent during the evaporation process. This result indicates that the type of solvent has a significant influence on the activity of nanoparticles. As we know, agglomeration in ethanol is usually alleviated, resulting in a higher performance during photodegradation. The higher activity of Cu-P25-Cu<sub>2</sub>O than Cu<sub>2</sub>O-P25 also confirms the superiority of this triple junction.

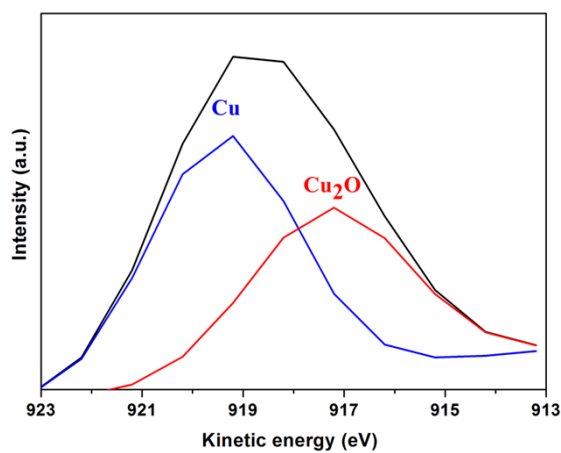


**Figure S7** Photodegradation of 2,4,5-T over different Cu loaded samples.

**8. Cycling tests:** Here, 50 mg of 1% Cu loaded P25 was suspended in 100 mL of 50 ppM aqueous solution of 2,4,5-T. After the photocatalytic reaction, the suspension was filtered, washed thoroughly with water and dried at room temperature. Due to the loss of powders during the

filtration process, the catalyst collected from several parallel photocatalytic reactions were combined and 50mg was used for the next cycle.

### 9. Auger spectrum of Cu-TiO<sub>2</sub>-Cu<sub>2</sub>O after photocatalytic reaction



**Figure S9** The Cu L<sub>3</sub>VV Auger spectrum of 1% Cu loaded P25 collected after photocatalytic reaction.

### References

- [1] B. Li, T. Liu, L. Hu, Y. Wang, J. Phys. Chem. Solids 2013, 74, 635.