

Supporting Information

Highly enhanced plasmonic photocatalytic activity of Ag/AgCl/TiO₂ by CuO co-catalyst

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Synthesis equations for CuO/Ag/AgCl/TiO₂

- $2\text{AgNO}_3 + \text{CaCl}_2 \longrightarrow 2\text{AgCl} + \text{Ca}(\text{NO}_3)_2$ (i)
- $\text{Ag}(\text{I}) + \text{Reductant} \longrightarrow \text{Ag}$ (ii)
- $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \longrightarrow \text{Cu}(\text{II})$ (iii)
- $\text{Cu}(\text{II}) + \text{Reductant} \longrightarrow \text{Cu}$ (iv)
- $\text{Cu} \xrightarrow{\text{Calcination at } 500^\circ\text{C in air}} \text{CuO}$ (v)
- $\text{TTIP} \xrightarrow{\text{Alcoholysis/Condensation}} \text{TiO}_2$ (vi)

Synthesis of Ag/TiO₂

Ag/TiO₂ was synthesized with some modifications in the method described in the manuscript. In short, 6.738 g of Brij-58 was taken in a two-neck flask. The temperature was kept at 50 °C throughout the experiment. No CaCl₂ was used to avoid the formation of AgCl. 2 mL pure EG was added to the melted Brij-58. 1.2 mL 0.5 M AgNO₃, complexed by 0.38 mL ETA and dissolved in acetonitrile was added. The solution turned yellowish. Then the solution was evaporated to remove acetonitrile. 30 mL cyclohexane was added and stirred for 15 min, followed by the addition of 0.140 g NaBH₄. The solution turned to dark brown. After stirring for 30 min, 0.3 mL of ammonium hydroxide (NH₃·H₂O, 25%~28%, Sinopharm Chemical Reagent Co., Ltd.) was added. 20 min later, 0.5 mL TTIP was added in successive additions of 0.2 mL, 0.15 mL, and 0.15 mL having a gap of 15 min each. After 1 h of the last TTIP addition, 30 mL IPA was added and the precipitate was separated by centrifugation followed by washing with IPA and cyclohexane. The precipitate was dried at 100°C for 10 h and then calcined at 500°C for 2 h to obtain the powder.

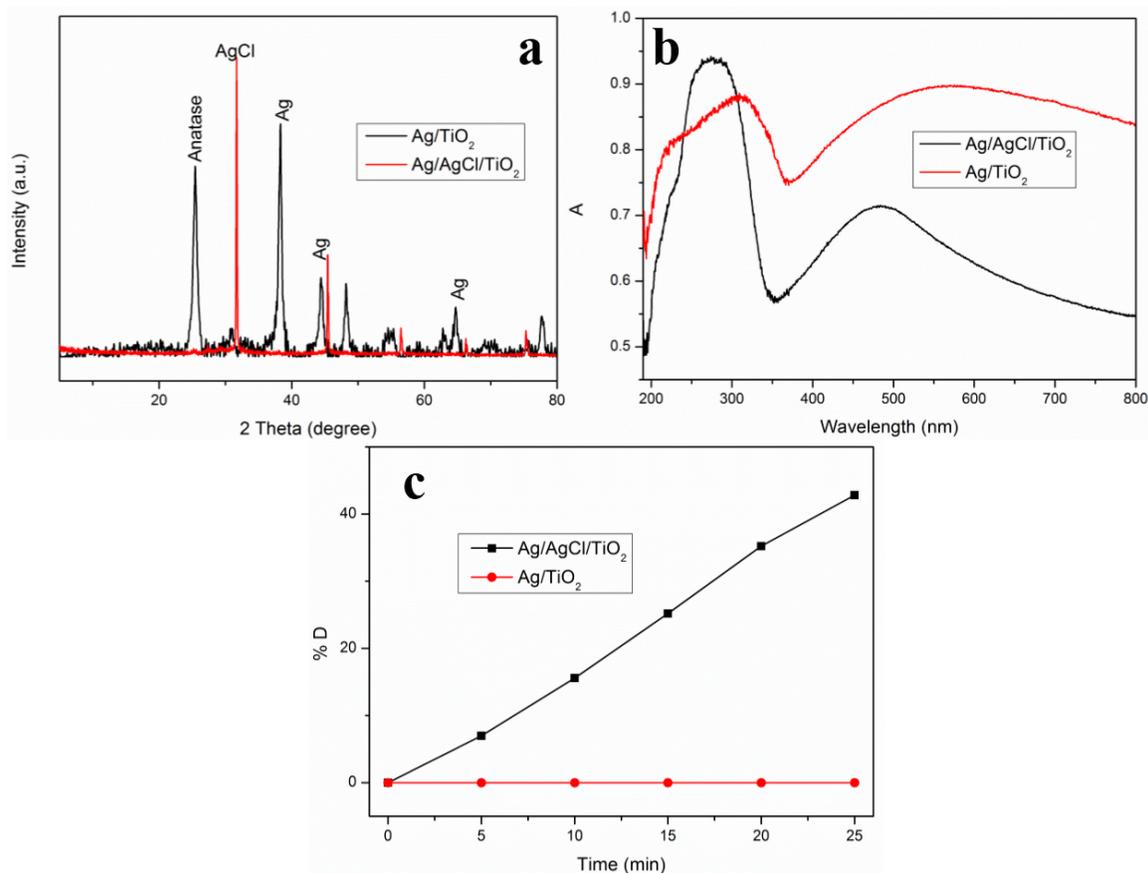


Figure S1: (a) XRD patterns, (b) UV-Vis spectra of Ag/TiO₂ and Ag/AgCl/TiO₂, and (c) MO degradation over Ag/TiO₂ and Ag/AgCl/TiO₂ under visible light.

Band gap calculations

The band gap of TiO₂ in various catalyst was calculated by

$$E_g^{\text{nano}} = hc/\lambda$$

Where, E_g^{nano} is the energy band gap of nanoparticles, h is plank's constant, c is the speed of light, and λ is the cut off wave length obtained from the absorption spectrum (Figure S2). As can be seen in Figure S2, TiO₂ band gap in P25, Ag/TiO₂, CuO/TiO₂,

Ag/AgCl/TiO₂, and CuO/Ag/AgCl/TiO₂ was found to be 3.01 eV, 2.30 eV, 2.36 eV, 3.07 eV, 3.07 eV, and 3.13 eV respectively.

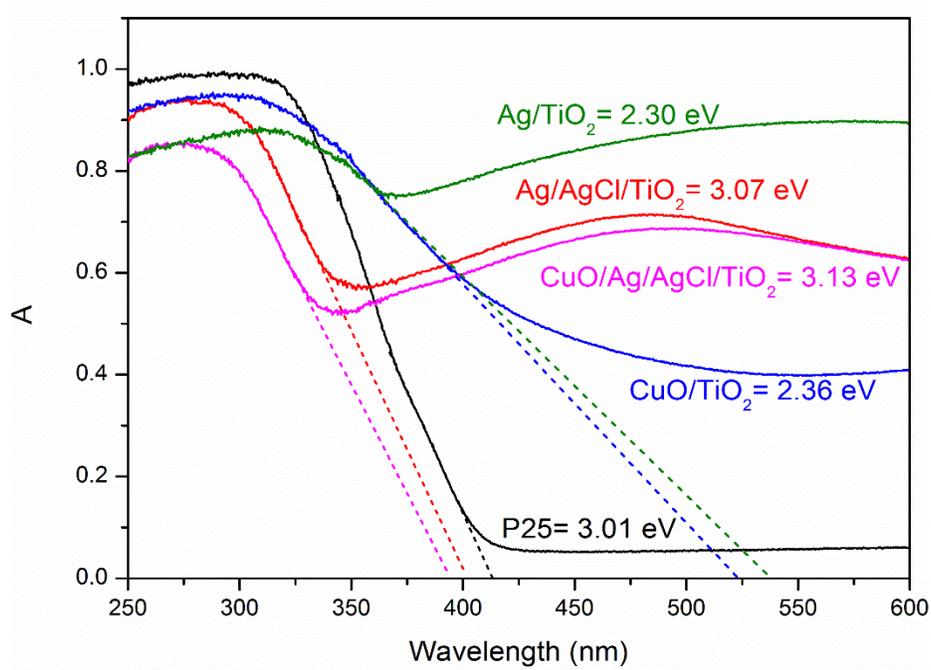


Figure S2: Band gap calculations by using hc/λ , where λ for P25, Ag/TiO₂, CuO/TiO₂, Ag/AgCl/TiO₂, and CuO/Ag/AgCl/TiO₂ is 412 nm, 539 nm, 525 nm, 403 nm, and 396 nm, respectively.

Stability of the photocatalyst

The stability of a photocatalyst can be evaluated for three consecutive cycles^{1,2}, therefore, we carried out only three consecutive cycles for stability of CuO/Ag/AgCl/TiO₂. The result is shown below:

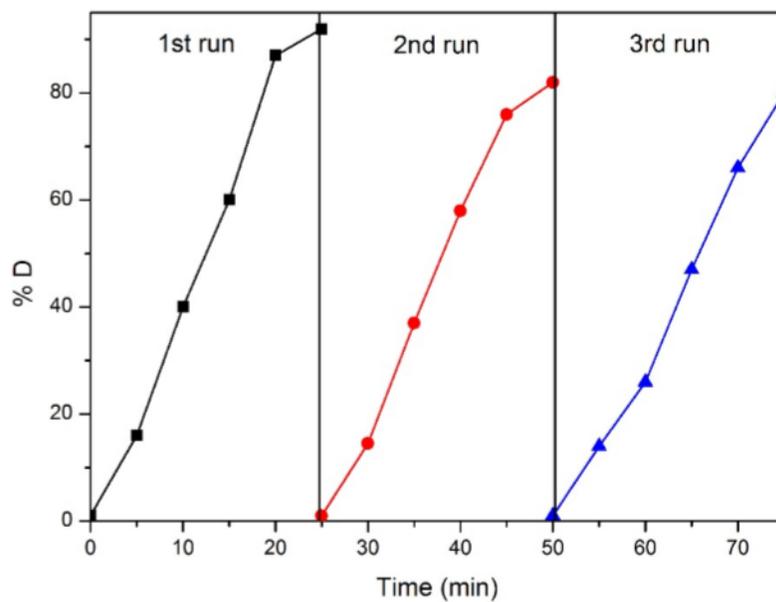


Figure S3: Recycling studies of the CuO/Ag/AgCl/TiO₂ for the visible light photodegradation of MO.

1. W. Ong, L. Tan, S. Chai and S. Yong, *Dalton. Trans.*, 2015, DOI: 10.1039/C4DT02940B.
2. J. Zeng, S. Liu, J. Cai and L. Zhang, *J. Phy. Chem. C*, 2010, **114**, 7806-7811.