

## Electronic Supplementary Information (ESI)

### Strongly visible-light responsive plasmonic shaped AgX:Ag (X= Cl, Br) nanoparticles for efficient reduction of CO<sub>2</sub> to methanol

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### The calculation of quantum yields:

The photon flow was measured by the ferrioxalate actinometer method.<sup>1, 2</sup> The actinometer solution was prepared as follows. In a volumetric flask of 100 mL, 5 ml of an aqueous solution of 0.2 M  $\text{Fe}_2(\text{SO}_4)_3$  and 5 ml of an aqueous solution of 1.2 M  $\text{K}_2\text{C}_2\text{O}_4$  were added and then diluted to 100 ml with distilled water. 40 mL of the above actinometer solution was irradiated under visible light for 20 s.

The ferrous ion concentration is subsequently determined via a UV-*vis* spectrophotometric determination of its phenanthroline complex at 510 nm. The analytical procedure was as follows. In a flask of 100 ml, 1 ml of the actinometer solution after irradiation, 2 ml of an aqueous solution 0.2 wt % of 1,10 phenanthroline and 0.5 ml of a buffer solution of pH = 4-5 were added and diluted to 100 ml with distilled water, then the solution was kept in the dark for 30 min. After the reaction, absorbance of the solution at 510 nm was measured using a UV-*vis* spectrophotometer.

Comparison test was conducted similar to the above procedure except the actinometer solution without irradiation. And the ferrous ion concentration was also measured by UV-*vis* spectrophotometric at 510 nm.

The buffer solution was prepared by adding 41 g of  $\text{CH}_3\text{COONa}\cdot\text{H}_2\text{O}$  to 5 ml of  $\text{H}_2\text{SO}_4$  and by diluting to 500 mL with distilled water. The blank value was determined with the same procedure but without irradiating the actinometer solution and was subtracted from the values obtained by irradiating.

### References

1. M. Schiavello, V. Augugliaro, V. Loddo, M. J. López-Muñoz, L. Palmisano, *Res. Chem. Interned.* 1999, **25**, 213.
2. Y. J. Zhang, L. J. Guo, W. Yan, L. Zhao, H. H. Yang, M. T. Li, Y. B. Xu, *Acta Energ. Solar. Sinica*, 2006, **27**, 1113.

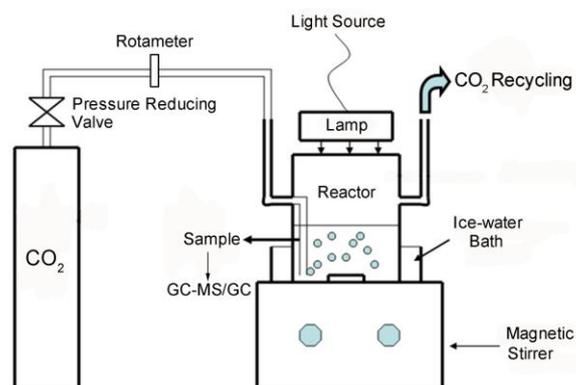


Figure S1. Schematic diagram of the as-used home-made photocatalytic reduction system.

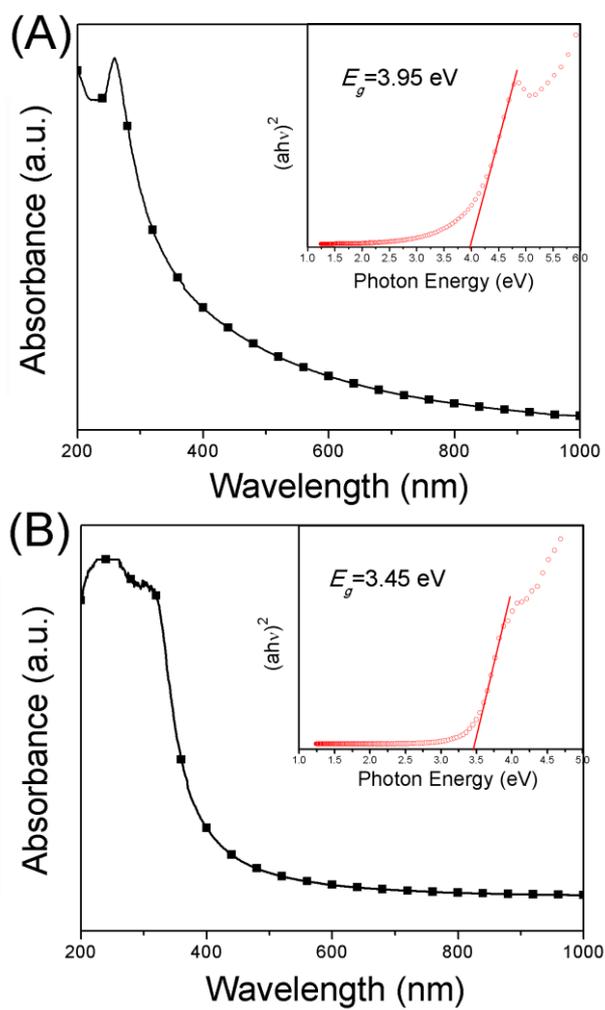


Figure S2. UV-vis spectra and band gap estimation of the as-prepared AgCl (A) and AgBr (B) nanoparticles.

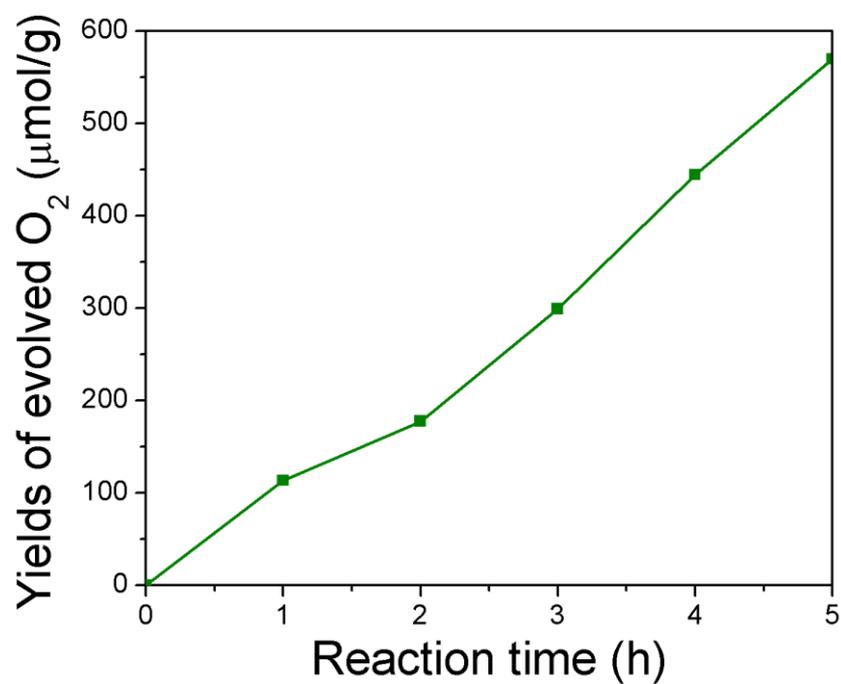


Figure S3 Amount of oxygen evolution during photocatalytic oxidation of water using AgCl:Ag nanoparticles without CO<sub>2</sub> under visible light irradiation. The yield is relatively larger than that produced in photoreduction of CO<sub>2</sub> (Equation 2) due to the limitation of the reactor system.

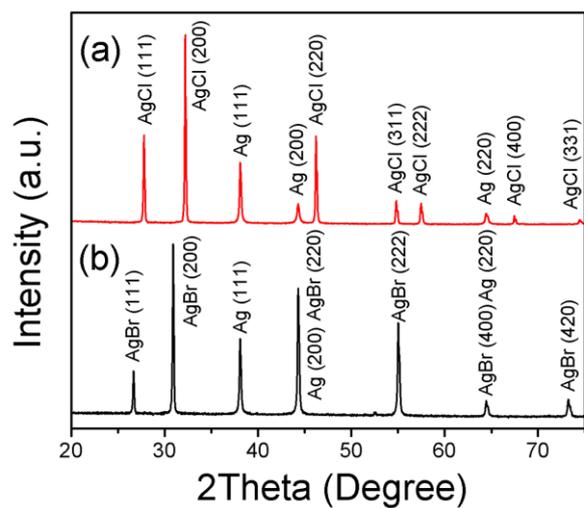


Figure S4. XRD patterns of (A) AgCl:Ag and (B) AgBr:Ag after three repeated reactions of reduction of CO<sub>2</sub>.