**Electronic Supplementary Information (ESI)** 

## Cu/TiO<sub>2</sub> octahedral-shell photocatalysts derived from metal-organic framework @ semiconductor hybrid structures

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**Chemicals.** 1,3,5-Benzenetricarboxylic acid (H<sub>3</sub>BTC), poly(vinyl pyrrolidone) (PVP, M.W.=29,000 or 55,000) and cupric chloride (CuCl<sub>2</sub>) were purchased from Aldrich. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All the chemical reagents and organic solvents were commercially purchased and used as received.

**Synthesis of Cu nanoparticles.** The Cu nanoparticles were prepared using the same procedure as that for Cu/TiO<sub>2</sub>-AA hybrid structure, except that the 7-mg  $Cu_3(BTC)_2@TiO_2$  was substituted by 5-mg bare  $Cu_3(BTC)_2$ .



**Fig. S1** TEM images of  $Cu_3(BTC)_2@TiO_2$  core-shell structures (a) after soaked in water for 24 hours; (b) after soaked in HCl for 5 seconds; (c) and (d) after soaked in 10% HCl solution for 5 seconds.



Fig. S2 EDS spectrum of the synthesized Cu/TiO<sub>2</sub>-AA hybrid structure taken from the region in Fig. 2a.



Fig. S3 (a) TEM images and (b) XRD patterns of the Cu nanoparticles obtained using the same procedure as that for Cu/TiO<sub>2</sub>-AA hybrid structure, except that the 7-mg  $Cu_3(BTC)_2@TiO_2$  was substituted by 5-mg bare  $Cu_3(BTC)_2$ .