

Supporting Information for

## Enhanced Photocatalytic Properties of Biomimetic Ag/AgCl Heterostructures

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### Experimental Section

#### 1 Synthesis of Ag nanowires

The Ag nanowires were prepared by a modified polyol process. In a typical synthesis, 1,3-butylene glycol (1, 3 BG, 10mL) that contained poly (vinyl pyrrolidone) (PVP,  $M_w \approx 50000$ , 150 mM as calculated in terms of the repeating unit) was placed in a 25-mL vial, capped, and heated with stirring in an oil bath at 160 °C for 1 h. 1 mL Na<sub>2</sub>S solution (1 mM in 1, 3 BG) was then quickly added. After 5 min, AgNO<sub>3</sub> (0.15 M solution in 1, 3 BG) were added with drop by drop to the stirring solution. The vial was then capped and heated at 160 °C for 30 min. After injection of the AgNO<sub>3</sub> solution, the color of reaction mixture changed from dark to blue, then to light yellow, and other color. The samples for morphology and structure analysis were washed with acetone and water to remove excess polyols and PVP via centrifugation, finally was dissolved in water.

#### 2 Synthesis of Ag/AgCl nanocable-AgCl nanoplate hierarchical structures

In a typical Ag/AgCl hierarchical structures synthesis, the reaction mixture containing the as-synthesized Ag nanowires (10 mg) solution was added to aqueous solution (PVP 50 mM). Aqueous CuCl<sub>2</sub> (0.02M) was slowly added dropwise to this Ag nanowire solution. The resulting mixture was maintained at room temperature until its color became brown. Vigorous stirring was employed throughout the synthesis. The obtained samples for morphology and structure analysis were washed with water and ethanol to remove the CuCl<sub>2</sub> and PVP via centrifugation. Finally, the obtained Ag/AgCl samples were dissolved in water.

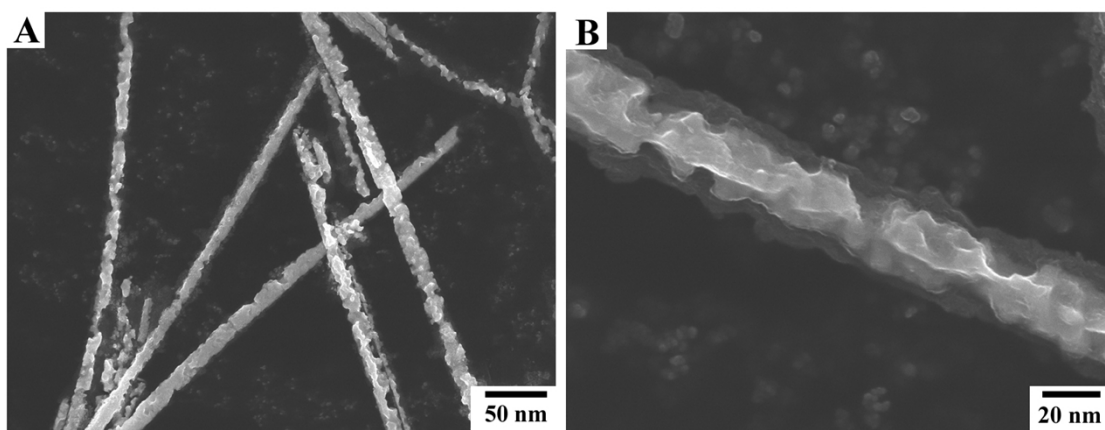
#### 3. Photocatalytic Reactions

In all catalytic activity of experiments, the samples (0.2 g) were put into a solution of RhB dyes (100 ml, 8 mg/L), which was then irradiated with a 300W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with  $\lambda \geq 420$  nm. The degradation of organic dyes was monitored by UV/Vis spectroscopy (UV-2550, Shimadzu). Before the spectroscopy measurement, these photocatalysts were removed from the photocatalytic reaction systems by a dialyzer.

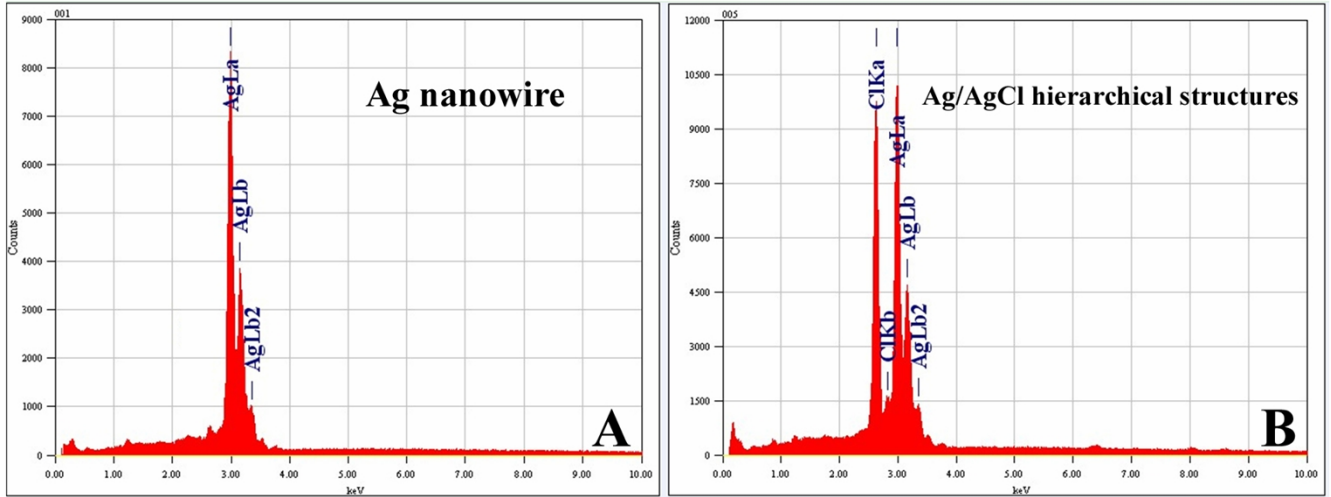
#### 4. Characterizations

SEM images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. An energy-dispersive (ED) detector was equipped with this field-emission scanning electron microscope and operated at an accelerating voltage of 15 kV. The X-ray diffraction spectra (XRD) measurements were performed on a Philips X'pert MPD instrument using Cu K $\alpha$  radiation (50 kv). The XRD patterns were recorded from 10° to 90° with a scanning rate of 0.067°/s. UV/Vis absorption spectra were taken at room temperature on a UV-2550 (Shimadzu) spectrometer.

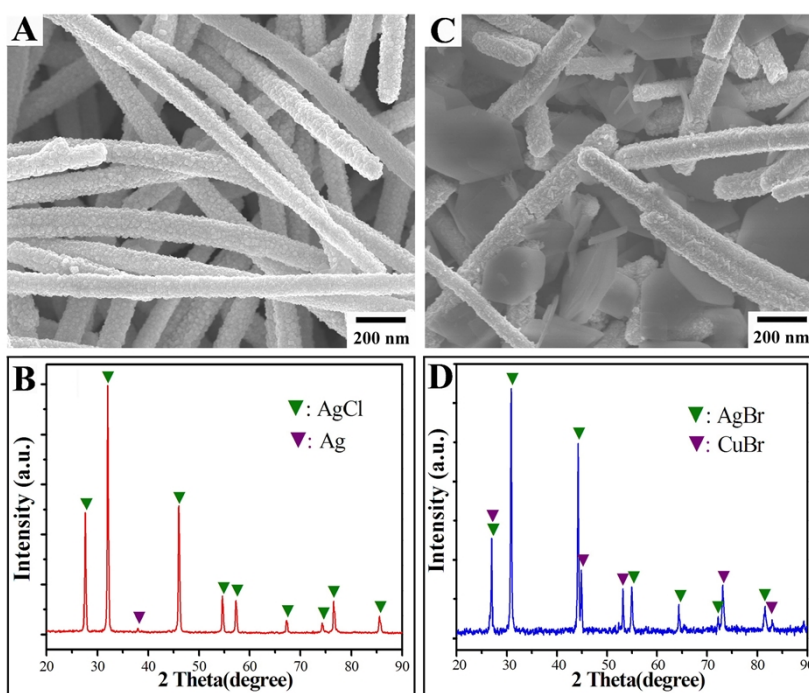
Additional figures



**Fig. S1.** (A, B) SEM images of Ag core nanowires obtained from the resolution Ag/AgCl nanoplate-nanowire hierarchical structures with  $\text{NH}_3 \cdot \text{H}_2\text{O}$ .



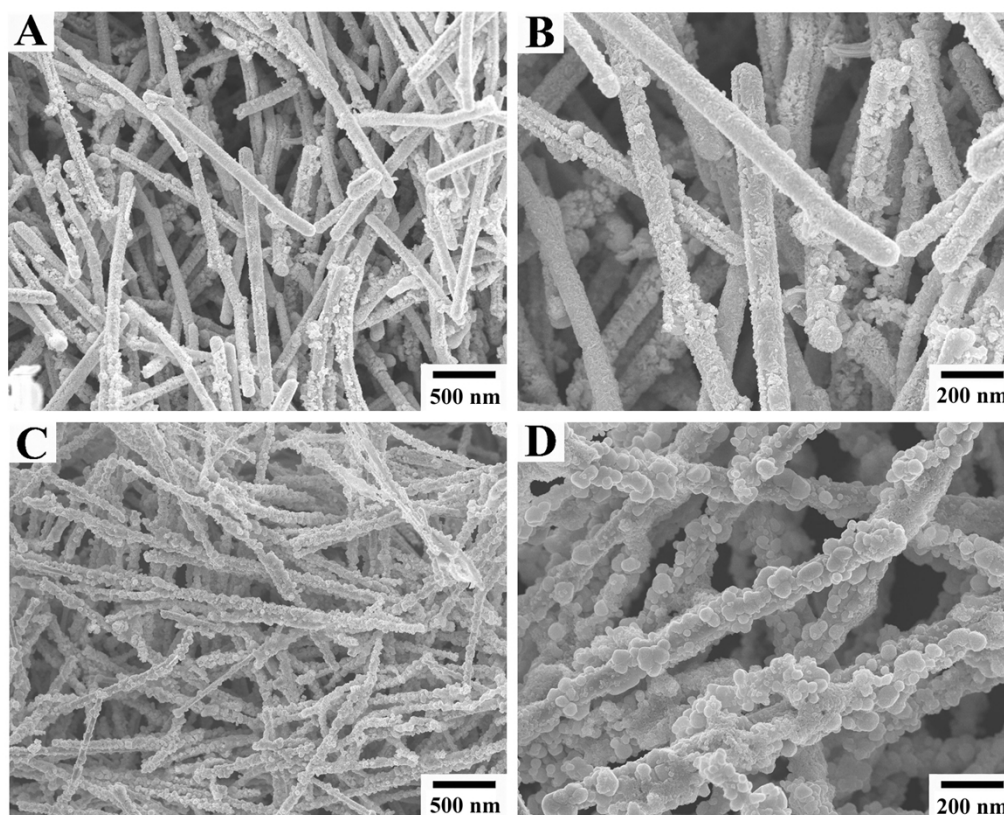
**Fig. S2** (A) EDS patterns of Ag nanowires and (B) EDS patterns of Ag/AgCl nanoplate-nanowire hierarchical structures



**Fig. S3** (A,B) SEM images and XRD patterns of as-prepared Ag/AgCl heterostructures by reacting Ag nanowires with FeCl<sub>3</sub>; (C,D) SEM images and XRD patterns of as-prepared Ag/AgBr/CuBr heterostructures by reacting Ag nanowires with CuBr<sub>2</sub>.

### Results and discussion

The oxidation reaction over metallic Ag nanowires with other metal cations or haloids anions has also been studied. As shown in the Fig. S3AB, when CuCl<sub>2</sub> has been replaced by FeCl<sub>3</sub> in this synthesis system, only conventional Ag/AgCl core-shell nanowires with relatively uniform diameters have been fabricated, while no any AgCl nanoplate have been formed. Herein, we consider that in the presence of FeCl<sub>3</sub>, Fe<sup>3+</sup> ions could rapidly the surfaces Ag atoms of Ag nanowires into AgCl nanocrystals, which have been reduced into Fe<sup>2+</sup> ions. It is well known that FeCl<sub>2</sub> could be well resolved in the aqueous solution, which only produces Ag/AgCl core-shell nanowires in this reaction system. On the other hand, we have also studied the structures and compositions of nanoproducs synthesized by replacing Cl anions with Br anions. As shown in Fig. S3C,D, only a mixture of AgBr nanowires and hexagon CuBr nanoplates has been obtained in the presence of CuBr<sub>2</sub>. It has been considered that after the oxidation of Ag atoms, Cu<sup>2+</sup> ions have been reduced to Cu<sup>+</sup> ions, which react with Br<sup>-</sup> ions to form CuBr nanoplates. However, it is well known that the stability of CuBr is relatively high, which can not be oxidized into Cu<sup>2+</sup> ions by the O<sub>2</sub> in the atmosphere. Thereby, the CuBr nanoplates can not be replaced by Ag<sup>+</sup> to form AgBr nanoplates as a result of lower K<sub>sp</sub> of AgBr than that of CuBr, and only a mixture of AgBr nanowires and hexagon CuBr nanoplates has been obtained. The above demonstrations suggest that the redox potential of both metal cations and haloids anions play crucial roles in successfully fabricating the Ag/AgCl nanoplate/nanowires hierarchical structures.



**Fig. S4.** (A, B) SEM images of the Ag/AgCl nanoproducts prepared in the absence of PVP; (C, D) SEM images of the Ag/AgCl nanoproducts prepared in the presence of CTAC.

### Results and discussion

It should be noted that the PVP play a crucial role in determining the morphologies and structures of the Ag/AgCl nanoproducts. As shown in Fig. S4A,B in the absence of PVP, only irregular AgCl nanoparticles formed on the Ag nanowires to construct Ag/AgCl core-shell nanowires, and no any AgCl nanoplate have been observed in the final products. On the other hand, when PVP was replaced by hexadecyl-trimethylammonium chloride (CTAC), some large AgCl nanoparticles with an average of 100 nm have been formed on the surfaces of Ag nanowires (Fig. S4C,D). Accordingly, we speculate that the particular adsorption and structure induction of PVP may promote the heteroepitaxial growth of AgCl nanoplates on the surface of Ag/AgCl core-shell nanowires and cause the resultant products with uniform Ag/AgCl hierarchical nanostructures.

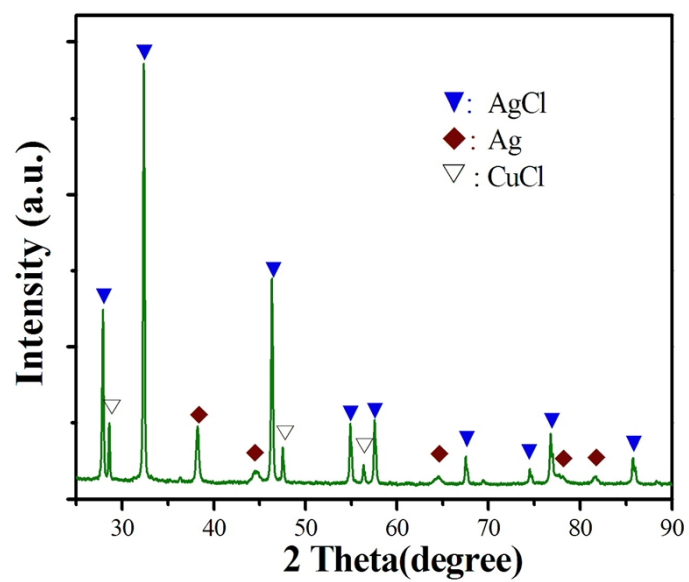
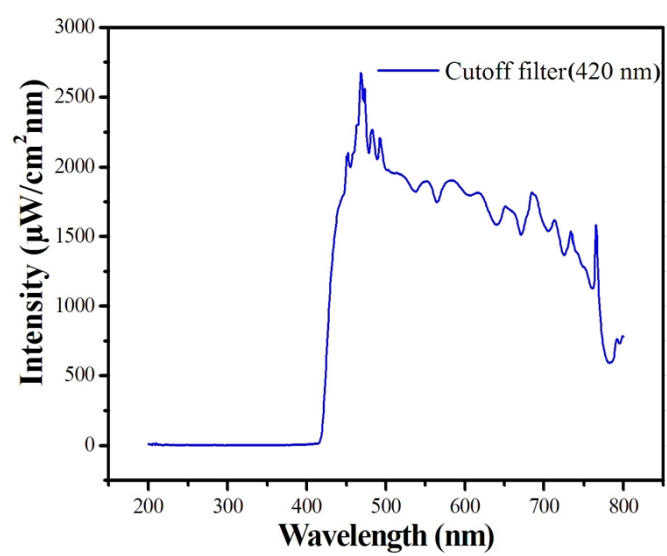


Fig. S5. XRD pattern of the Ag/AgCl/CuCl nanoproducts prepared in pure N<sub>2</sub> atmosphere.



**Figure S6.** The intensity and spectral distribution of the light source employed in the degradation experiments.

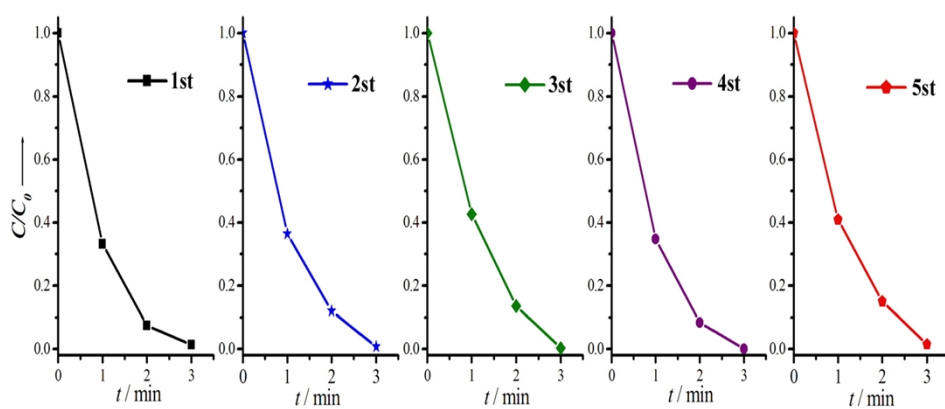


Fig. S7 Photocatalytic activities of Ag/AgCl nanoplate-nanowire hierarchical structures for the degradation of RhB (B) dyes under visible light irradiation ( $\lambda > 420$  nm) for five cycles.



