

Supporting Information for

Two-dimensional dendritic Ag_3PO_4 nanostructures and their photocatalytic properties

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Experimental Section

1. Synthesis of rectangular silver nanowires

The silver nanowires were firstly prepared by a modified polyol process. In a typical synthesis, 1, 2-Propylene glycol (1, 2 PG, 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 NaCl solution (1 mM in 1, 2 PG) was then quickly added. After 5 min, AgNO_3 (0.15 M solution in 1, 2 PG) were added with drop by drop to the stirring solution. The vial was then capped and heated at 160 °C for 40 min. After injection of the AgNO_3 solution, the color of reaction mixture changed from milkiness to light yellow, and silvery white. The reaction solution was cooled to room temperature. Finally, the as-prepared Ag nanowire samples were washed with distilled water for several times to remove excess polyols and PVP via centrifugation, and dried at room temperature.

2. Synthesis of dendritic Ag_3PO_4 nanowires

The dendritic Ag_3PO_4 nanostructures were prepared by using rectangular Ag nanowires as the silver ions source and starting materials. In a typical synthesis, Ag nanowires (0.2 g) were added in aqueous solution containing the PVP (0.3 M) and NaH_2PO_4 (0.2 M), which was stirred for 10 min. Then, H_2O_2 aqueous solution (10% *V/V*) was added with drop by drop to the above solution until its colour became yellow. The obtained Ag_3PO_4 samples for morphology and structure analysis were washed with water to remove the NaH_2PO_4 and PVP and dried under atmosphere. For comparison, the oxidation reactions of Ag nanocubes and bulk Ag belts have also been performed under the same synthetic conditions as the above Ag_3PO_4 sample.

3. Photocatalytic Reactions

In all catalytic activity of experiments, the samples (0.2 g) were put into a solution of RhB dye (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 RhB dye 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 and FE-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 Rigaku RINT-2000 instrument using Cu K α radiation (40 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

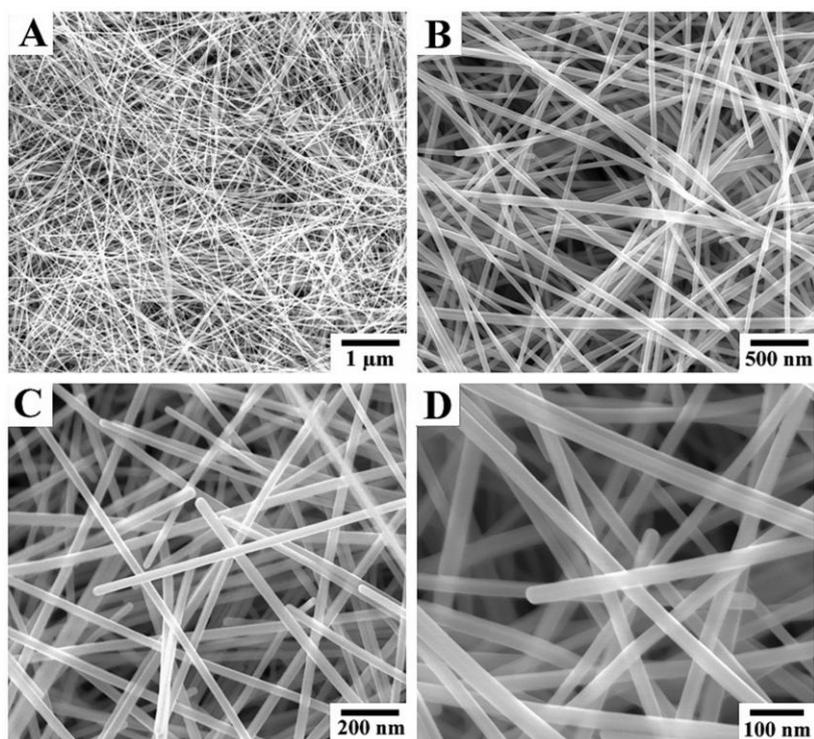


Fig. S1. (A-D) SEM images of Ag nanowires with different magnifications synthesized by 1,2 PG reduction.

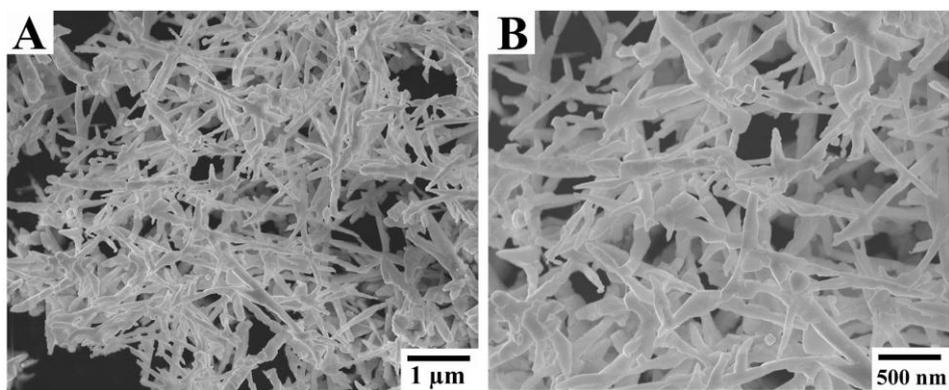


Fig. S2. (A,B) SEM images of the dendritic Ag_3PO_4 nanowires with different magnifications synthesized by oxidation of Ag nanowires.

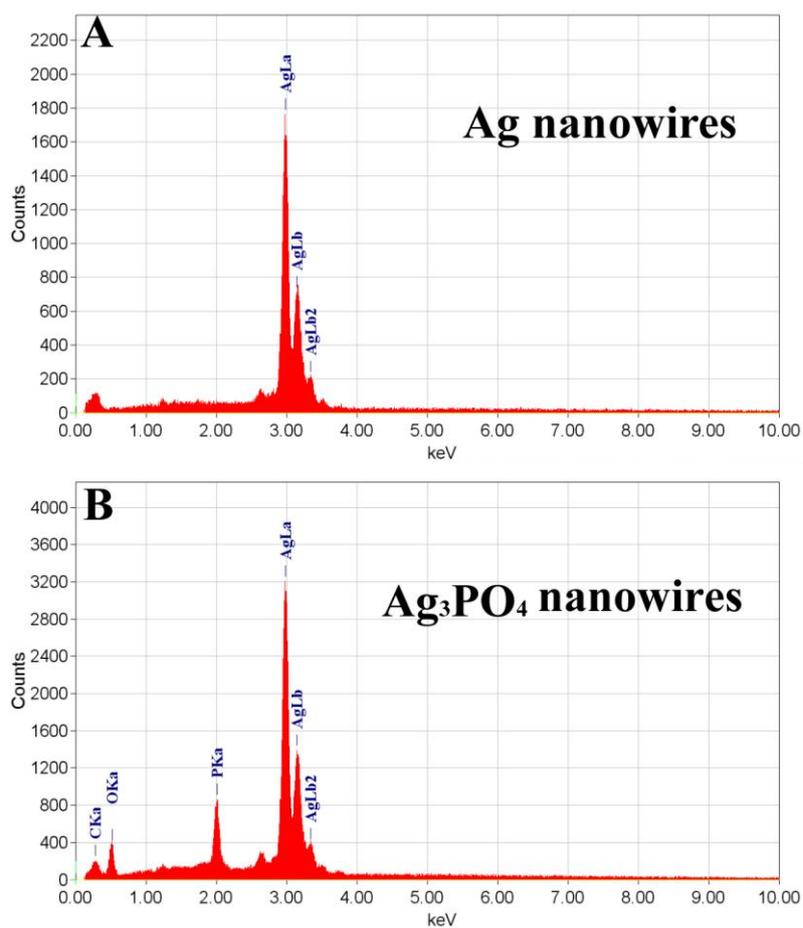


Fig. S3. (A) EDS pattern of Ag nanowires, (B) EDS pattern of dendritic Ag₃PO₄ nanowires.

Results and discussion

Moreover, the energy dispersive X-Ray spectroscopy (EDS) has also been performed and the results have been shown in Fig. S3. Before the oxidation process, only the peaks of Ag element have been detected. However, when these Ag nanowires were reacted with H₂O₂ and NaH₂PO₄, except for the Ag element, the O and P elements have been evidently observed, proving that Ag₃PO₄ products has been formed after this oxidation reaction.

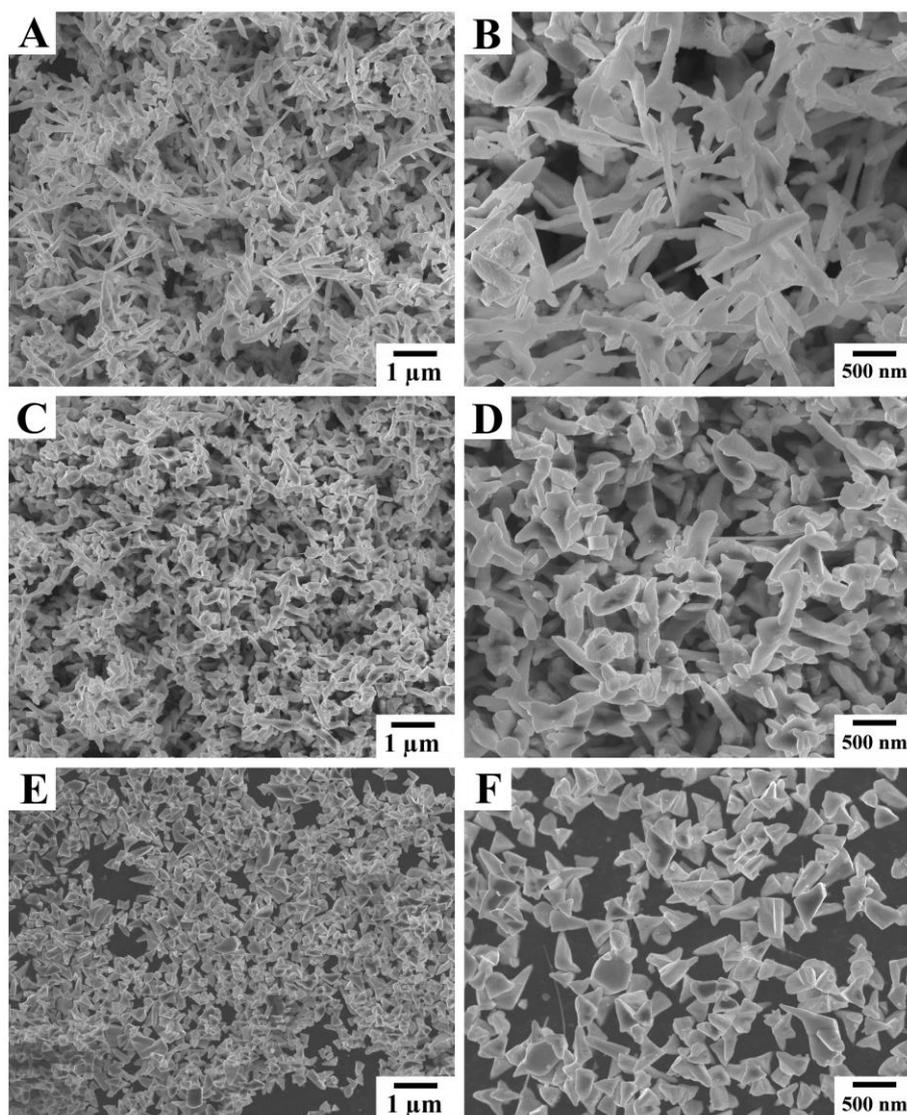


Fig. S4. SEM images of Ag_3PO_4 products prepared with different concentrations of PVP: (A,B) 0.2 M, (C,D) 0.1 M, (E,F) without PVP.

Results and discussion

Based on the present results, we consider that PVP absorbed on the surface of the Ag nanowires through Ag-O coordination might control the oxidation reaction between Ag nanowire and H_2O_2 , which may change the growth rates of Ag_3PO_4 nanocrystals and induce the oriented attachment into 2D dendritic structures. However, with decreasing the PVP concentrations, the formation rate of Ag_3PO_4 nanocrystals has been remarkably increased and the structure-induce function of PVP has been correspondingly reduced. Thereby, the 2D dendritic structure has gradually disappeared as a result of the rapid growth of Ag_3PO_4 nanocrystals, and irregular morphology has been finally formed.

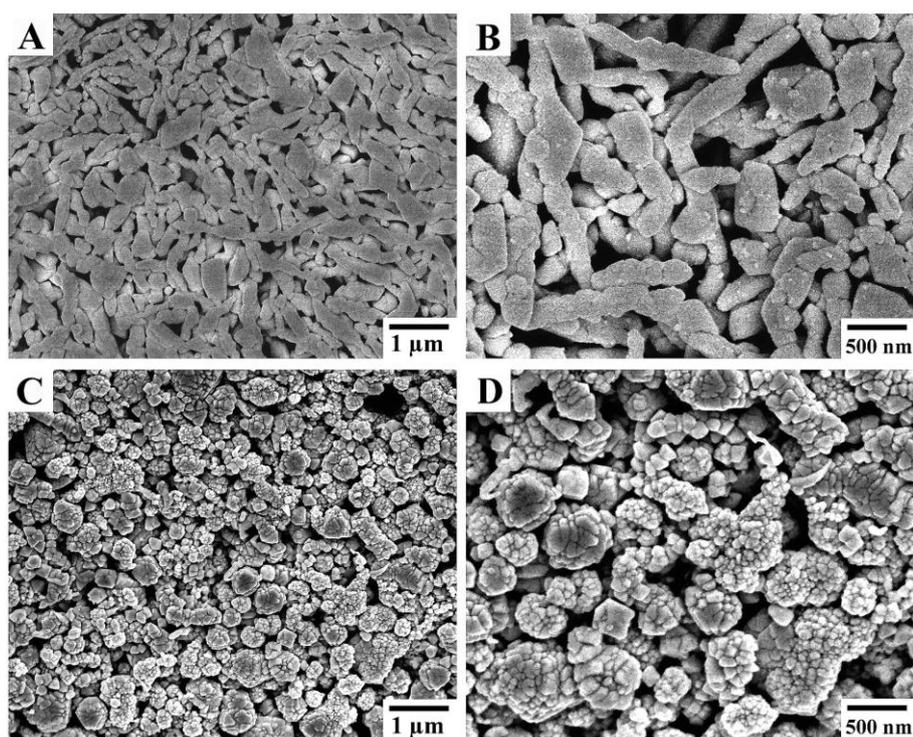


Fig. S5. (A,B) SEM images of irregular AgCl nanoproductions prepared by directly reacting Ag nanowires with H₂O₂ and NaCl in the presence of PVP solution, (C,D) SEM images of AgBr nanoproductions prepared by directly reacting Ag nanowires with H₂O₂ and NaBr in the presence of PVP solution.

Results and discussion

This oxidation growth process can also be used to prepare other semiconductor materials. As shown in Fig. S5A,B, when NaH₂PO₄ was replaced by NaCl to react with Ag nanowires in this synthesis system, irregular AgCl nanorods have been formed. Moreover, it should be noted that the quantities and layer thickness of the obtained AgCl nanorods were lower than that of the Ag₃PO₄ nanostructures, which may be due to the fast growth rates derived from the redox potential of AgCl/Ag pair (0.223V). Furthermore, in the presence of NaBr solution, AgBr nanoparticles with large dimensions have been synthesized. We consider that the much lower standard potential of the AgBr/Ag pair (0.007V) than that of Ag₃PO₄/Ag pair (0.451V) may enhance the replacement rate between Ag and O₂²⁻ and result in a product with irregular structures rather than a wire-like structure.