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Supporting Information for

Facile synthesis of tetrahedral Ag_3PO_4 submicro-crystals with enhanced photocatalytic properties

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Experimental Section

1. Synthesis of tetrahedral Ag_3PO_4 submicro-crystals

In a typical tetrahedral Ag_3PO_4 submicro-crystals synthesis, the silver foils (4×4 cm) was placed in aqueous solution containing the PVP (0.3 M) and NaH_2PO_4 (0.2 M). 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. The tetrahedral Ag_3PO_4 submicro-crystals for photocatalytic experiments were removed from the Ag_3PO_4/Ag foils by brief sonication treatment.

2. Photocatalytic Reactions

In all catalytic activity of experiments, the samples (0.2 g) were put into a solution of RhB or MO 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 or MO 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.

3. 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 Kα 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.

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Additional Figures

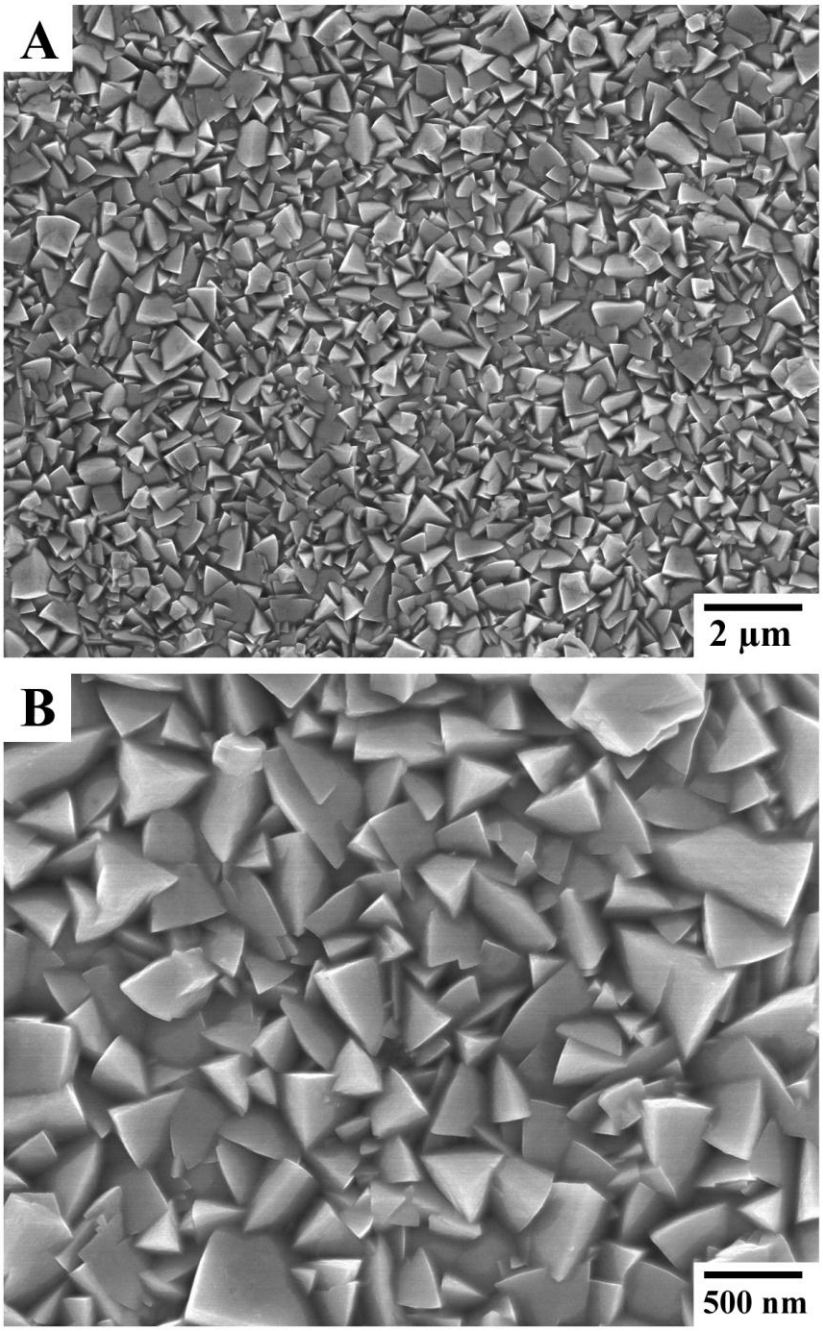

Fig. S1. (A,B) SEM images of tetrahedral Ag_3PO_4 submicro-crystals with different magnifications.

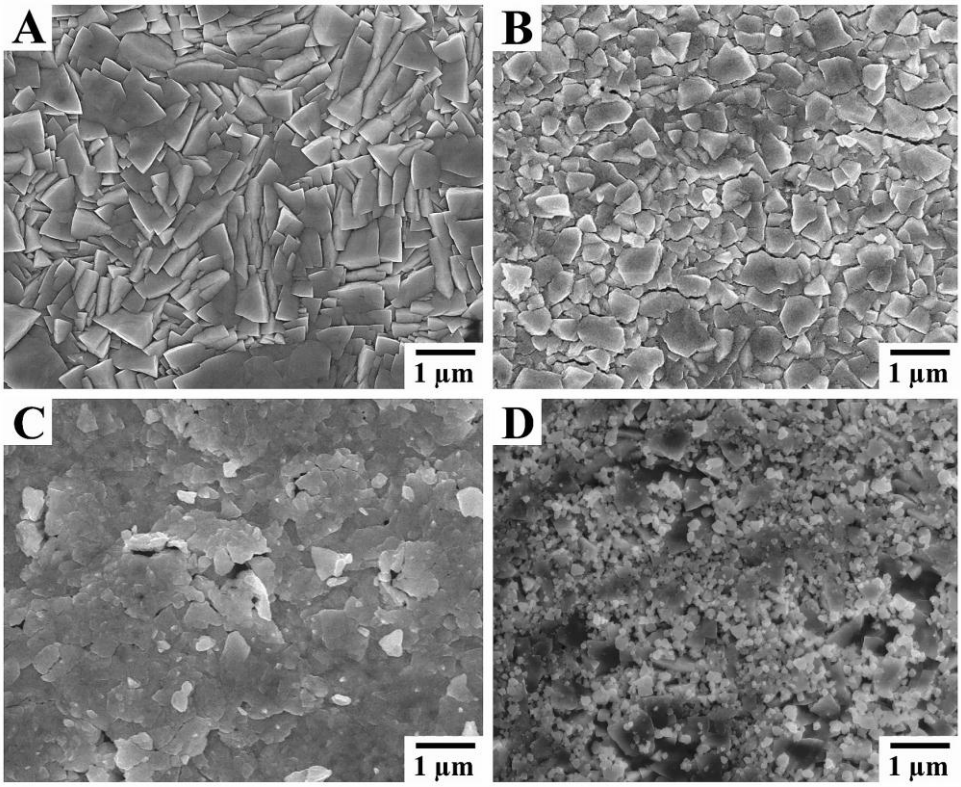

Fig. S2. (A,B) SEM images of the Ag_3PO_4 products synthesized by adjusting the PVP concentrations.

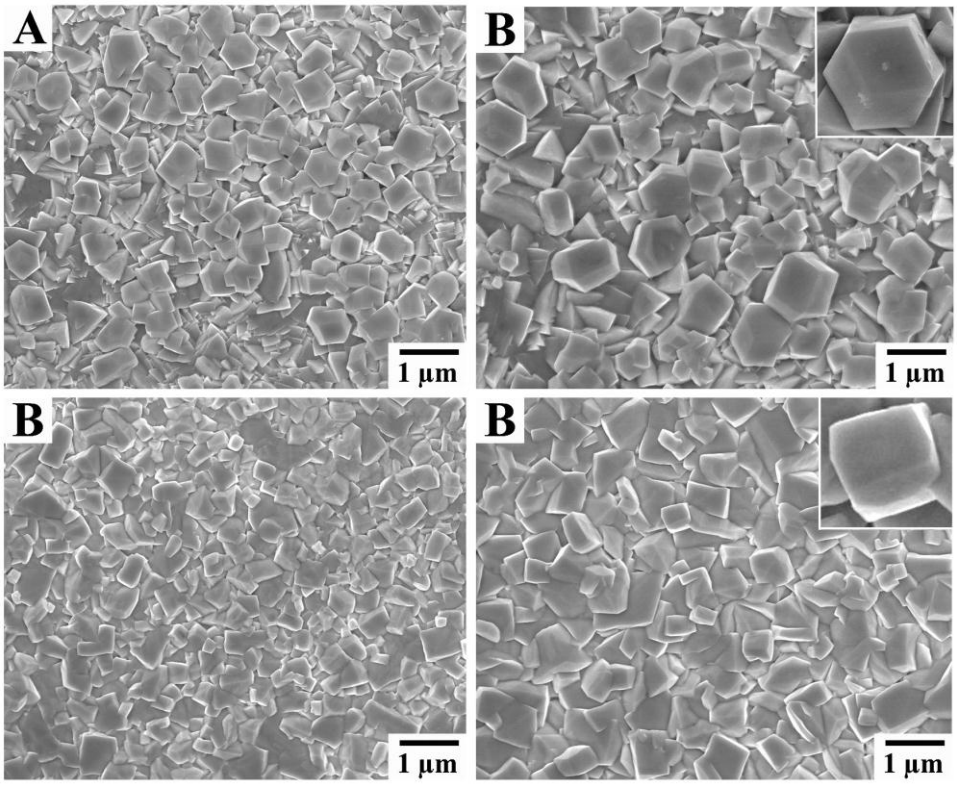

Fig. S3. SEM images of Ag_3PO_4 products prepared with the help of (A,B) CH_3COONa and (C,D) NH_3,.

Results and discussion

The morphology and structure of as-prepared Ag_3PO_4 could be further tailored by introducing additional structure inducing agents during the oxidation growth process. As shown in Fig. S3A,B, when small amount of CH_3COONa was introduced into this reaction system, irregular rhombic dodecahedral crystals have been formed. Moreover, it should be noted that their uniformity of the obtained Ag_3PO_4 crystals were much lower than that of the tetrahedral Ag_3PO_4 structures. Furthermore, in the presence of NH_3 solution, irregular Ag_3PO_4 cubic crystals with large dimensions have been synthesized. Thereby, we consider that the small amount of CH_3COONa or NH_3 solution could change the oxidation growth process of Ag_3PO_4 crystals and induce their morphological transition from tetrahedral structure to rhombic dodecahedral or cubic structure.

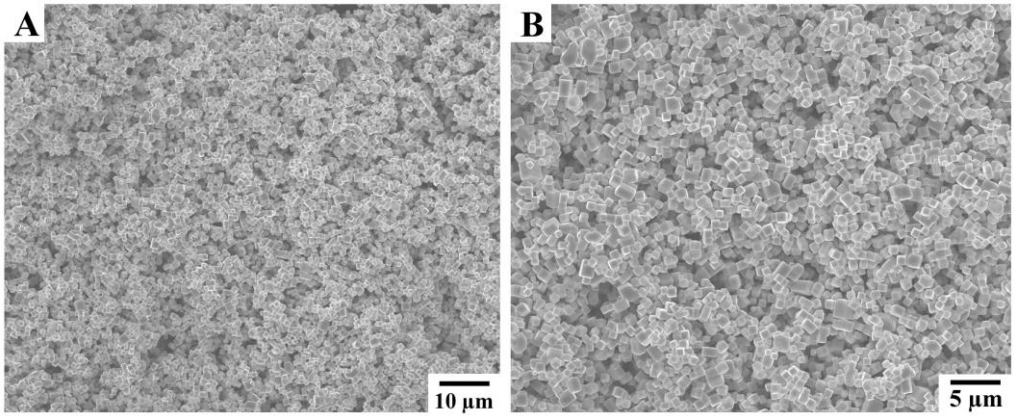

Fig. S4. (A,B) SEM images of cubic Ag_3PO_4 submicro-crystals with different magnifications.

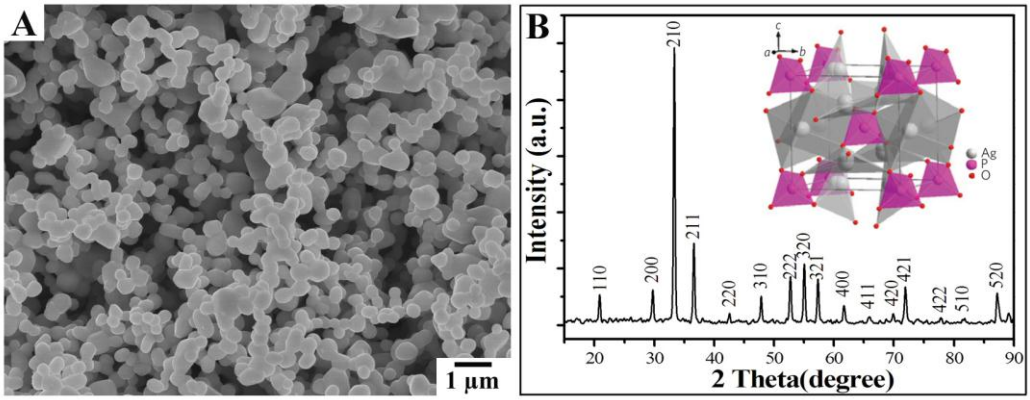

Fig. S5. (A) SEM images of irregular Ag_3PO_4 particles prepared by directly reacting $AgNO_3$ with Na_2HPO_4, (B) XRD pattern of irregular Ag_3PO_4 particles.

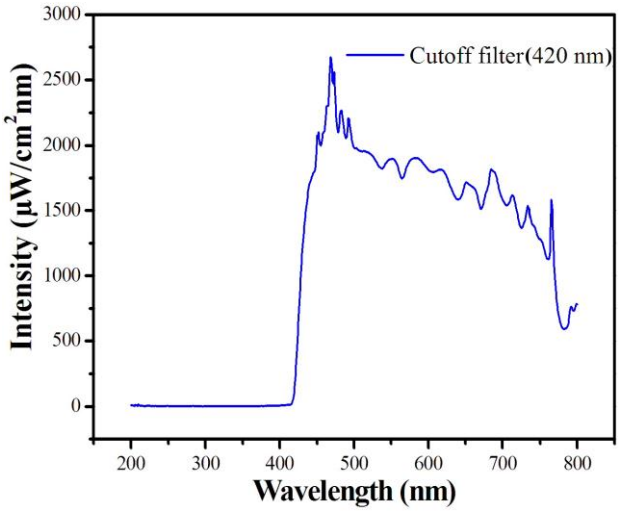

Fig. S6. The intensity and wavelength distribution of the irradiation light employed in the organic decomposition experiments. Integral intensities were measured under the actual experimental conditions.

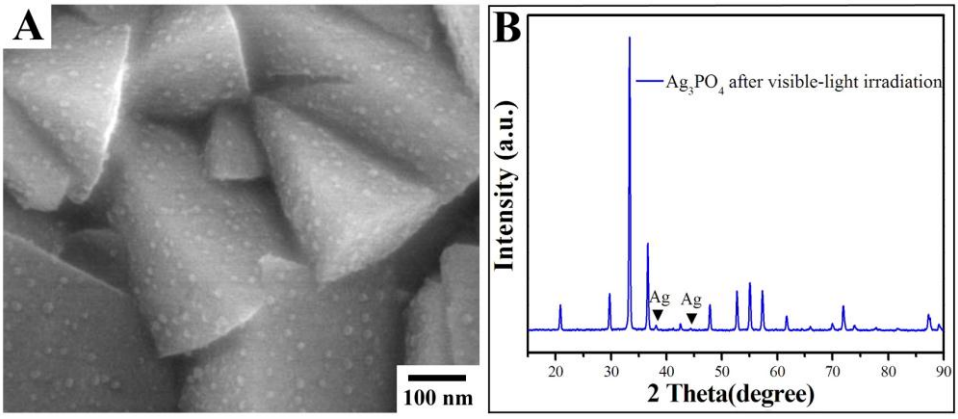

Fig. S7 (A) SEM images of the Ag_3PO_4 crystals after visible-light illumination; (B) their XRD pattern.

Results and discussion

In order to further confirm the fact of enriched Ag^+ cations in Ag_3PO_4 {111} planes could be partly reduced by the photogenerated electrons, the tetrahedral Ag_3PO_4 submicro-crystals were illuminated by visible light for 10 min. Fig. S7A show the typical SEM images of the products after visible-light illumination. It can be seen that large quantities of metallic Ag nanocrystals with highly uniform dimensions about 10-20 nm have deposited on the surfaces of Ag_3PO_4 crystals. Additionally, the crystalline structure of the Ag/Ag_3PO_4 heterocrystals has been further studied and shown in Fig. S7B. It can be clearly seen that small diffraction peaks of metallic Ag have been evidently observed, indicating that the Ag^+ cations in Ag_3PO_4 {111} planes could readily proceed.