Supporting Information for

Selective growth of Ag_3PO_4 submicro-cube on Ag nanowire to fabricate necklace-like heterostructure for photocatalytic applications

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Experimental Section

Scheme S1. Schematic illustration of the selective growth process of Ag Nanowire/Ag_3PO_4 cube necklace-like heterostructures.

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≈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 water for several times to remove excess ployols and PVP via centrifugation, and dried at room temperature.

2. Synthesis of Ag nanowire/Ag_3PO_4 cube heterostructures

As shown in the above Scheme S1, the as-prepared Ag nanowires were added into silver-ammino ([Ag(NH_3)_2]^+) complex aqueous solution (0.15 M) with stirring for 20 min. Then, Na_2HPO_4 aqueous solution (0.15 M) was added, and Ag nanowire/Ag_3PO_4 cube heterostructure have been synthesized. The above samples were diluted with water and stirred strongly for 20 min. Finally, the obtained Ag nanowire/Ag_3PO_4 samples were dried at room temperature.

3. Photocatalytic Reactions
In all catalytic activity of experiments, the samples (0.2 g) were put into a solution of MO or 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-2500PC, 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 and Discussions

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 Ag nanowire/Ag₃PO₄ cube necklace-like heterostructure with low magnifications.
Fig. S3. (A-D) SEM images of cubic Ag₃PO₄ submicro-crystals with different magnifications.
Fig. S4 The ultraviolet–visible diffusive absorption spectrum of metallic Ag nanowires.
Results and discussion

Note that [Ag(NH$_3$)$_2$]$^+$ complex play a crucial role for the successfully epitaxial growth of Ag$_3$PO$_4$ submicro-cubes on Ag nanowires to fabricate necklace-like heterostructure. As shown in Fig. S5, when [Ag(NH$_3$)$_2$]$^+$ complex was replaced by AgNO$_3$ or CH$_3$COOAg, no any Ag/Ag$_3$PO$_4$ heterostructures have been formed and only the mixtures of Ag$_3$PO$_4$ crystals and Ag nanowires have been obtained. On the basis of above results, we consider that when Ag nanowires were added into [Ag(NH$_3$)$_2$]$^+$ complex solution, the external silver atoms of Ag nanowires could react with the free NH$_3$ molecule to form NH$_3$Ag$_n$ (n=1,2) complexes,[1] which may be favorable for the succedent epitaxial growth of Ag$_3$PO$_4$ crystals. Furthermore, as the Na$_2$HPO$_4$ aqueous solution was added, [Ag(NH$_3$)$_2$]$^+$ complex has been gradually decomposed by H$^+$ ions and released Ag$^+$ ions to react with PO$_4^{3-}$ ions and form Ag$_3$PO$_4$ crystals. As a result, the release rates of Ag$^+$ ions might be satisfied for the epitaxial growth of Ag$_3$PO$_4$ on the Ag nanowires, and Ag nanowires/Ag$_3$PO$_4$ cubes heterostructures have been fabricated. In contrast, in the presence of AgNO$_3$ or CH$_3$COOAg precursor, the external silver atoms of Ag nanowires cannot be effectively activated by the NO$_3^-$ and CH$_3$COO$^-$ ions as a result of their high chemcial stabilities. On the other hand, the free Ag$^+$ ions present in this reaction system in considerable concentrations, and the growth process of Ag$_3$PO$_4$ crystals is spontaneous and uncontrollable, which leads to the rapid nucleation and growth of Ag$_3$PO$_4$ crystals, resulting in a mixture of Ag nanowires and Ag$_3$PO$_4$.

References

Results and discussion

During the synthesis process of Ag nanowire/Ag$_3$PO$_4$ cube heterostructures, the [Ag(NH$_3$)$_2$]$^+$ complex has been gradually decomposed by H$^+$ ions from Na$_2$HPO$_4$ and release Ag$^+$ ions for the epitaxial growth of Ag$_3$PO$_4$ crystals on Ag nanowires. As a result, it is important to know the effect of release rates of Ag$^+$ ions on the Ag$_3$PO$_4$ crystal growth and formation process of Ag/Ag$_3$PO$_4$ heterostructures. Thereby, the morphology changes of Ag/Ag$_3$PO$_4$ products prepared with NaH$_2$PO$_4$ and H$_3$PO$_4$ have been studied. As shown in Fig. S6A,B, when NaH$_2$PO$_4$ was used, only some Ag$_3$PO$_4$ nanoparticles have been formed on Ag nanowires. Furthermore, when Na$_2$HPO$_4$ was replaced with H$_3$PO$_4$, no any Ag$_3$PO$_4$ crystals with cubic morphology have been formed and only a mixture of irregular Ag$_3$PO$_4$ particles and Ag nanowires has been prepared (shown in Fig. S6C,D). Based on the above results, we consider that the rapid release of Ag$^+$ ions from [Ag(NH$_3$)$_2$]$^+$ complex due to the more H$^+$ ions contained in NaH$_2$PO$_4$ and H$_3$PO$_4$ may be disadvantage for the selective epitaxial growth of Ag$_3$PO$_4$ nanocubes on the Ag nanowires.
Results and discussion

The morphology of Ag$_3$PO$_4$ crystals in the necklace-like heterostructure can be easily tuned through adjusting the aging time of the [Ag(NH$_3$)$_2$]$^+$ complex. As shown in Fig. S7A,B, when [Ag(NH$_3$)$_2$]$^+$ complex solution has been aged at room temperature for 1 h, the as-prepared Ag$_3$PO$_4$ crystals formed on the Ag nanowires possess irregularly cubic morphology with multiple facets. Further increasing the aging time up to 2 h, the formed Ag$_3$PO$_4$ transformed into regular tetrahedron structure. However, when the aging time has been prolonged to 6 h, the obtained Ag$_3$PO$_4$ products with irregularly spherical morphologies have been formed on the Ag nanowires and no any cubes has been observed. Herein, we consider that with increasing the aging time, the ratios between NH$_3$ to Ag in [Ag(NH$_3$)$_2$]$^+$ complex has been gradually decreased as a result of high volatility of NH$_3$, and the growth rate of Ag$_3$PO$_4$ crystals has been accelerated. Thereby, the growth rates of various planes in Ag$_3$PO$_4$ crystals have been changed, resulting in the morphology transformations of Ag$_3$PO$_4$ crystals. Furthermore, when the ratios between NH$_3$ to Ag in [Ag(NH$_3$)$_2$]$^+$ complex have been further decreased, the growth process of Ag$_3$PO$_4$ crystals is spontaneous and uncontrollable, which leads to the rapid nucleation and same growth rates of various planes of Ag$_3$PO$_4$ crystals, resulting in an irregularly spherical morphology.
Results and discussion

Furthermore, this selective epitaxial growth process can also be used to prepare other semiconductor/Ag nanowire heterostructures. As shown in Fig. S8A,B, when Na₂HPO₄ was replaced by NaBr to react with [Ag(NH₃)₂]⁺ complex in this synthesis system, AgBr nanoparticles with flexuous nanostructures have been formed, but no necklace-like heterostructures has been synthesized. Moreover, when Na₂WO₄ was used in this process, Ag₂WO₄/Ag branched heterostructure have been formed. More specifically, the generation rates of AgX were strongly dependent on the [Ag(NH₃)₂]⁺ complex precursor, which can be served as a general and facile synthesis process for the fabrication of semiconductor/metal hetero-photocatalysts with novel morphology and structure.
Fig. S9. The intensity and spectral distribution of the light source employed in the degradation experiments.
Results and discussion

The typical necklace-like Ag nanowire/Ag₃PO₄ cube photocatalysts (shown in Fig. 1) were recycled and reused for five cycles, and their photocatalytic performances have been shown in the Fig. S10. It can be found that the as-prepared necklace-like hetero-structure maintains a high photocatalytic activity for the degradation of both MO and RhB dyes during all these five cycles. More specifically, the degradation time of MO dye is usually in the range of 7-8 min, and the degradation of RhB dye generally needs 2-3 min. Furthermore, these demonstrations clearly reveal that the necklace-like hetero-structure could serve as a stable and efficient visible-light photocatalyst.

Furthermore, the SEM images of the Ag nanowire/Ag₃PO₄ cube photocatalyst after five cycles have been shown in the Fig. S11. It can be clearly seen that except for the slight truncation of sharp corners and edges on Ag₃PO₄ cubes, the used photocatalyst generally kept their original necklace-like hetero-structure, indicating that the as-prepared hetero-photocatalyst possesses relatively high physical stabilities.