Supporting Information for

Enhanced Photocatalytic Activity of Ag/Ag₃PO₄ Coaxial Hetero-Nanowires

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Experimental Section



Scheme S1. Schematic illustration of the selective growth process of Ag /Ag₃PO₄ core-shell hetero-nanowires.

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, AgNO₃ (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 AgNO₃ 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 ployols and PVP via centrifugation, and dispersed in the aqueous solution containing PVP with a concentration of 200 mM.

2. Synthesis of Ag /Ag₃PO₄ hetero-nanowire

As shown in the above Scheme S1, the as-prepared Ag nanowires were added into silver-ammino $([Ag(NH_3)_2]^+)$ complex aqueous solution (0.2 M) with stirring for 20 min. Then, Na₂HPO₄ aqueous solution (0.15 M) was added, and Ag nanowire/Ag₃PO₄ cube heterostructure have been synthesized. The above samples were diluted with water and stirred strongly for 20 min. Finally, the obtained Ag /Ag₃PO₄ hetero-nanowire 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 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 $\lambda \ge 420$ 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 α 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. The photoluminescence (PL) spectra of the photocatalysts were measured on the Hitachi F-7000 Fluorescence spectrophotometer with an excitation wavelength of 440 nm.

Additional Figures and Discussions



Fig. S1. (A-D) SEM images of Ag/Ag₃PO₄ core-shell hetero-nanowires with different magnifications.



Fig. S2. The band gap of Ag/Ag₃PO₄ core-shell nanowires calculated from the Kubelka-Munk Function.

Results and discussions:

According to Kubelka-Munk Function, the relation between absorption coefficient and band gap energy can be described by the equation

$$(\alpha h\nu)^{1/2} = A(h\nu - Eg)$$

in which α , v, A and Eg are absorption coefficient, light frequency, proportionality constant and band gap, re-spectively. Plot $(\alpha hv)1/2$ vs hv and the bandgap could be evaluated by extrapolating the straight line to the hv axis intercept. As shown in the above figure, the band-gap of Ag/Ag₃PO₄ nanowires is 2.40eV, indicating that the Ag/Ag₃PO₄ core-shell structure possess same band gap with pure Ag₃PO₄ particles. Accordingly, the conduction band potential and valence band potential energy for the composite is 0.45 and 2.85 eV. ^[1,2]

[1] Y. Hou, F. Zuo, Q. Ma, C. Wang, L. Bartels, P. Feng, J. Phys. Chem. C, 2012, 116, 20132.

[2] X. Guo, N. Chen, C. Feng, Y. Yang, B. Zhang, G. Wang, Z. Zhang, Catal Commun, 2013, 38, 26.



Fig. S3. (A, B) SEM images of the products prepared at the PVP concentration of 100 mM, (C, D) SEM images of the products prepared in the absence of PVP.



Fig. S4. The intensity and spectral distribution of the light source employed in the degradation experiments.



Fig. S5. (A-B) SEM images of cubic Ag₃PO₄ crystals with different magnifications.



Fig. S6. (A,B) SEM images of irregular Ag₃PO₄ particles prepared by directly reacting AgNO₃ with Na₂HPO₄.



Fig. S7. The photoluminescence (PL) spectrums of Ag/Ag_3PO_4 core-shell hetero-nanowire, Ag_3PO_4 cubes, Ag_3PO_4 particles.

Results and discussions:

To further investigate the enhanced photocatalytic activity over Ag/Ag₃PO₄ nanowires, their photoluminescence (PL) spectra have been measured to explain the migration, transfer, and recombination processes of the photoinduced electron–hole pairs in this core-shell heterostructure. Fig. S7 shows the PL spectra of Ag/Ag₃PO₄ core-shell hetero-nanowire, Ag₃PO₄ cubes, Ag₃PO₄ particles. Obviously, the pure Ag₃PO₄ cubes and particles have a strong and wide peak in the range of 500-575 nm and a small peak around 660 nm respectively in the PL spectrum. However, in the case of the Ag/Ag₃PO₄ core-shell hetero-nanowires, both the strong peak and small peak have been greatly decreased, which clearly indicate that the photoinduced electron–hole pair can migrate easily between Ag nanowire and Ag₃PO₄ nanoshell and the recombination of Ag/Ag₃PO₄ core-shell hetero-nanowire can serve as an alternate approach to reduce the recombination rate of the photoinduced electron–hole pair and improve the corresponding photocatalytic activity.



Fig. S8 Photoelectric conversion performances of Ag_3PO_4 cubes and Ag_3PO_4 particles in 0.1 M Na₂SO₄ aqueous solutions and under visible light irradiation (λ >420 nm).

Results and discussions:

Except for the photocatalytic performances, the photoelectric conversion properties over Ag/Ag_3PO_4 core-shell nanowires, Ag_3PO_4 cubes, and spherical particles deposited on Tin-doped indium oxide (ITO) glass have been detailedly investigated. As shown in Fig. S8, it can be found that the Ag/Ag_3PO_4 core-shell nanowires exhibit higher photoelectric conversion efficiency than Ag_3PO_4 cubes and commonly spherical Ag_3PO_4 particles, clearly indicating that the formation of Ag/Ag_3PO_4 core-shell nanowires could effectively promote the seperation of photogenerated electron-hole pairs and decreasing their recombination ratio. These results clearly indicating that structure-controlled synthesis of metal/ Ag_3PO_4 hetero-nanomaterials is also very feasible strategy for enhancing their photoelectric performances.