Support Information

Controlled Synthesis of Peony-Shaped Photocatalyst Grains of Ag₃PO₄/Zn₃(PO₄)₂ by Coprecipitation and Recrystallization Technology



Fig.1S. a) high - magnification TEM images of flower-shaped $Ag_3PO_4/Zn_3(PO_4)_2$ composite. b) TEM image taken from the edge of the composite.



Fig.2S. EDX analysis of as-synthesized sample.



Fig.3S. XRD patterns of samples extracted from the solution for preparing peony-shaped $Ag_3PO_4/Zn_3(PO_4)_2$ composite at different reaction times. The peaks labeled with asterisk are assigned to orthorhombic $Zn_3(PO_4)_2$ and the other peaks can be indexed to cubic Ag_3PO_4 crystals. The sample separated from solution at 2 min shows a weak XRD pattern. It can be deduced to be AgAc crystals based on the reaction phenomenon. It also shows a band-like structure similar to the commercial AgAc (Fig.4S).



Fig.4S. The SEM image of sample separated from the solution at 2 min.



Fig.5S. The photos of the 20 ml of $0.15M \text{ Zn}(NO_3)_2$ solution was mixed with 20 ml of $0.1M \text{ KH}_2\text{PO}_4$ solution to obtain pure $\text{Zn}_3(\text{PO}_4)_2$ precipitate, then 20 ml of $0.2M \text{ AgNO}_3$ solution was added . After reacting for 2h, the white precipitate did not change its color, which indicates that after $\text{Zn}_3(\text{PO}_4)_2$ crystallizes, it is difficult to transform to Ag_3PO_4 by ion-exchange process even in the Ag^+ saturated solution.



Fig.6S. The color change of the Ag₃PO₄/Zn₃(PO₄)₂ precipitates at different time



Fig.7S.a) UV-Vis diffusive absorption spectrum of pure Ag_3PO_4 samples fabricated with 0.2M AgNO₃ solution (20ml) and 0.1M KH₂PO₄ (20ml). b) The calculation results of the bandgap of $Zn_3(PO_4)_2$ based on the $(\alpha hv)^2$ -hv curve.



Fig.8S. Room temperature photoluminescence spectra of a) pure $Zn_3(PO_4)_2$ and peony-shaped $Ag_3PO_4/Zn_3(PO_4)_2$ composite and b) pure Ag_3PO_4 .



Fig.9S . Photocatalytic curves of RhB solution over peony- shaped $Ag_3PO_4/Zn_3(PO_4)_2$ with the presence of different quenchers.

The calculation of the band gap (Eg) of $Zn_3(PO_4)_2$:

According to the plot of $(ahv)^{2/n}$ versus energy, the band gap (E_g) of $Zn_3(PO_4)_2$ has been calculated to be 3.2 eV, respectively. The band structure of $Zn_3(PO_4)_2$ can be estimated according to the equations:

$$E_{\rm C} = -(\chi(\mathbf{A})^a \cdot \chi(\mathbf{B})^b \cdot \chi(\mathbf{C})^c)^{1/(a+b+c)} + \frac{1}{2}E_{\rm g} + E_{\rm 0}$$
$$E_{\rm V} = E_{\rm C} + E_{\rm g}$$

where E_{VB} is the valence band edge potential, χ is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, and E_0 is the energy of free electrons on the hydrogen scale (about 4.5 eV vs NHE). χ value of $Zn_3(PO_4)_2$ is determined to be 6.16 eV. E_g of $Zn_3(PO_4)_2$ is calculated to be 4.5eV, therefore , the E_{CB} and E_{VB} of $Zn_3(PO_4)_2$ are 0.59 and 5.09 eV, respectively.