Assembly of Ag₃PO₄ Nanoparticles on Two-dimensional Ag₂S Sheets

as Visible-Light-Driven Photocatalysts

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Fig. S1. FTIR of ZnS (en), Ag₂S sheets, and AA0.31

The FTIR of ZnS (en) template exhibits bands corresponding to ethylene diamine molecules. The typical peaks located at 1597 cm⁻¹, 1354 cm⁻¹ and 636 cm⁻¹ are related to the NH₂ scissors, CH₂ wag and NH₂ rock^{1,2}, respectively, and the peak at 440 cm⁻¹ is assigned to the Zn–S bond, which reveals that the as-prepared precursor is an inorganic–organic hybrid. During the latter process of preparing Ag₂S sheets,

some functional groups are weakened or removed. For AA0.31, the appearance of the peak at 1660 cm⁻¹ indicates the existence of residual NH_2 group. The peak at 555

cm⁻¹ is ascribed to the O—P–O bending vibration, and the other two peaks at 873 and 1017 cm⁻¹ are due to the symmetric and asymmetric stretching vibrations of P–O–P rings³. The appearance of characteristic peaks of phosphate anion further verifies the formation of Ag_3PO_4 on the surface of Ag_2S sheets induced by the residual NH₂ group.

Reference

Z. X.Deng, C.Wang, X. M.Sun and Y. D. Li, *Inorg Chem* 2002, **41**, 869-873.
Z. X.Deng, L. B.Li and Y. D. Li, *Inorg Chem* 2003, **42**, 2331-2341.
Y. M.He, L. H. Zhang, B. T. Teng and M. H. Fan, *Environmental science & technology* 2015, **49**, 649-656.



Fig.S2. SEM image of pure Ag₃PO₄ sample.



Fig. S3. UV–vis diffuse reflectance spectra of pure Ag_3PO_4 .



Fig. S4. FESEM image of $Ag_3PO_4@Ag_2S$ sample.



Fig. S5. Photocatalytic degradation curve of RhB solution over $Ag_3PO_4@Ag_2S$ sample (about 80% dye is decomposed after 60-min photocatalysis reaction).



Fig. S6. Photocatalytic degradation curve of RhB solution over mechanically mixed sample



Fig.S7. Photocatalytic degradation curve of RhB solution over Ag₃PO₄@Ag₂S sample without the presence of en. The sample was prepared according to the ref.31.



Fig.S8.Photocatalytic degradation curve of phenol solution over AW0.01.



Fig S9. Recyclability of the pure Ag₃PO₄ in four successive photocatalytic experiments.

For the stability of pure Ag_3PO_4 , in the first two cycles, the degradation time of the dyes is longer than 20min; however, Ag will be formed after third cycle. Therefore the degradation time of the third and fourth time are shortened for the surface plasmon resonance (SPR) of Ag nanoparticles. However, excessive Ag will result in the failure of the performance of Ag_3PO_4 . At last, a layer of Ag particles gradually cover on the surface of Ag_3PO_4 and prevent Ag_3PO_4 from absorbing light. The Ag layers also can inhibit the contanct of holes from Ag_3PO_4 with the dyes. Excessive Ag nanoparticles on Ag_3PO_4 probably result in the recombination of photogenerated electron-hole pairs and hinder the contact of dye molecules with Ag_3PO_4 . Therefore, the performance will be deteriorated. Please see the reference (W.G. Wang, B.Cheng, J.G. Yu et al, Chem. Asian J. 2012, 7, 1902 – 1908).



Fig. S10. XRD pattern of the used AA031 sample after the first photocatalytic test.

In order to elucidate the photocatalytic mechanism of the Ag_3PO_4/Ag_2S photocatalyst, AA0.31 sample before and after 1 cycle have been characterized by EDS, and the results are listed in Table 1. We can find that the atom content of Ag is increased for the used AA 0.31, compared to that of original sample and it is higher than the sum of the duple of S and triple P, implying the formation of metallic Ag.

	Element content (at %)			
catalyst	Ag	Р	0	S
AA0.31	29.77	8.9	59.88	1.45
AA0.31 after 1 cycle	33.32	8.89	56.23	1.554

Table 1: EDS results of AA0.31 before and after 1 cycle