Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Facile synthesis and shape evolution of well-defined phosphotungstic acid potassium nanocrystals for highly efficient visible-light-driven photocatalyst

Xinran Li, Huaiguo Xue and Huan Pang*

College of Chemistry and Chemical Engineering
Yangzhou University Yangzhou, Jiangsu 225002 (China)
E-mail: huanpangchem@hotmail.com; panghuan@yzu.edu.cn

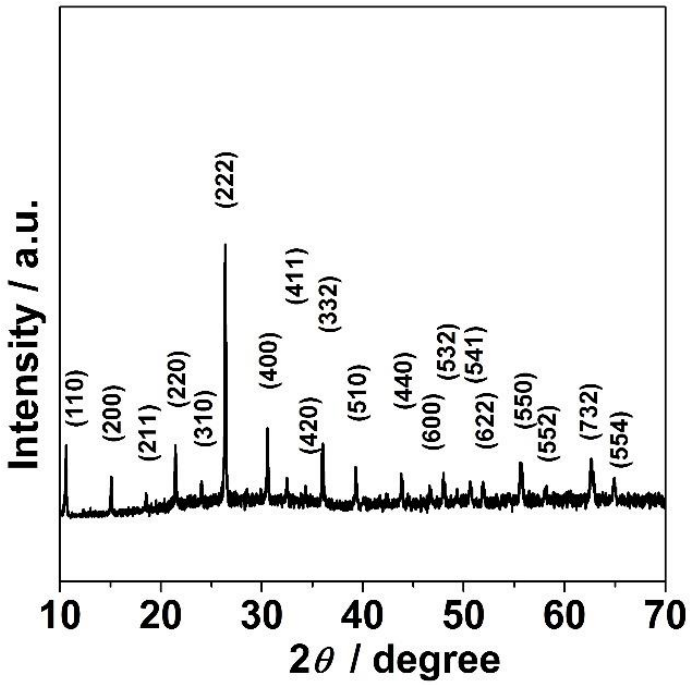

Figure S1. XRD patterns of as-prepared samples obtained from hydrothermal condition of 150 mg KCl and 300 mg phosphotungstic acid at 140 ^{o}C for 12 h.

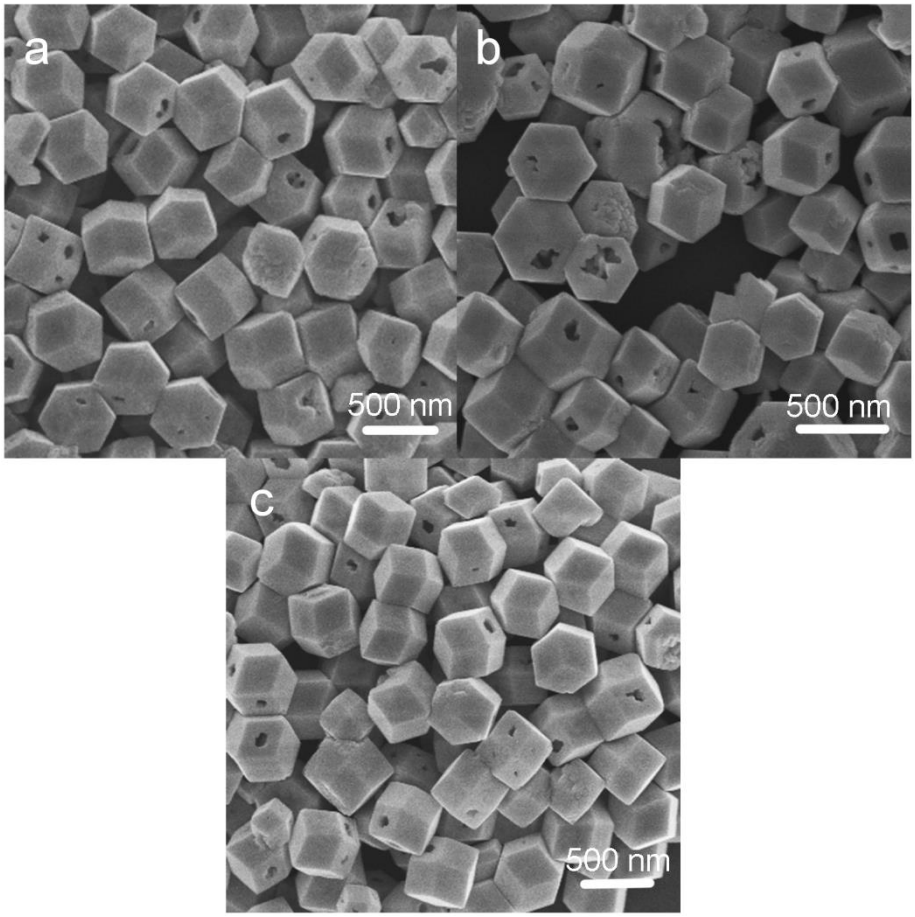

Figure S2. SEM images of samples obtained from hydrothermal conditions: a) 80 mg KCl and 200 mg phosphotungstic acid at 140 ^{o}C for 12 h, b) 300 mg KCl and 500 mg phosphotungstic acid at 140 ^{o}C for 12 h, and c) As-prepared sample-S1.

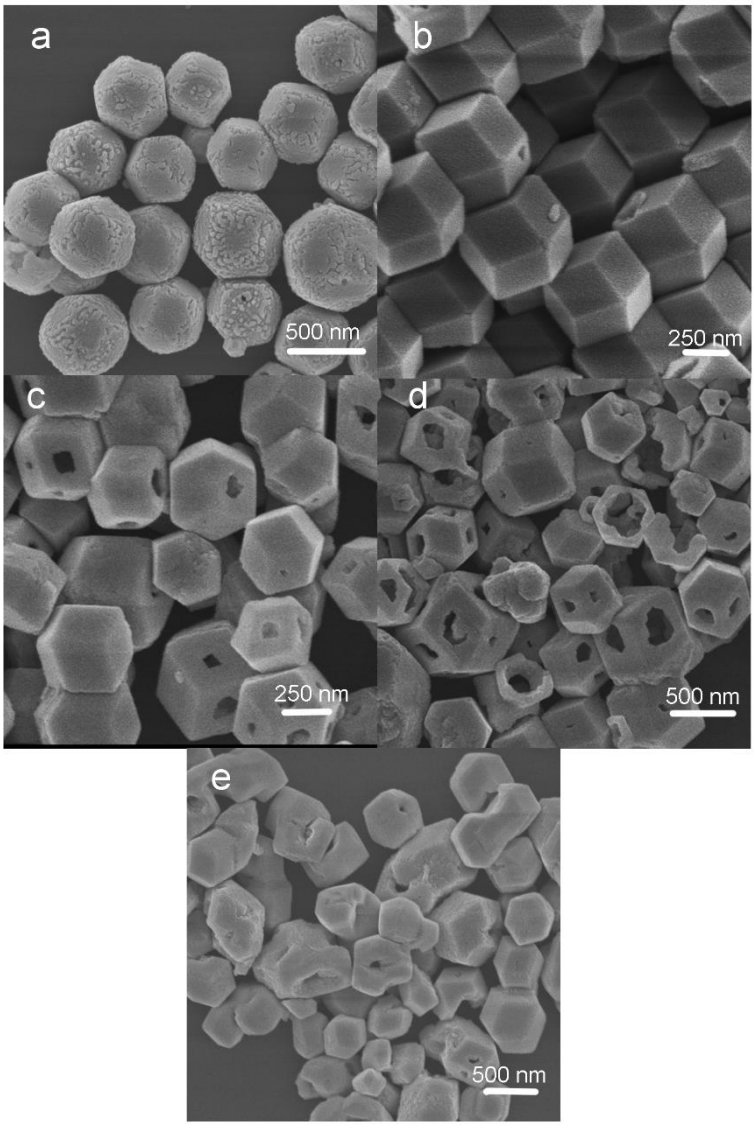

Figure S3. SEM images of as-prepared samples obtained from hydrothermal condition of 150 mg KCl and 300 mg phosphotungstic acid at different temperatures for 12 h: a) 100 ^{o}C, b) 120 ^{o}C-S2, c) 140 ^{o}C-S1, d) 160 ^{o}C, and e) 200 ^{o}C.

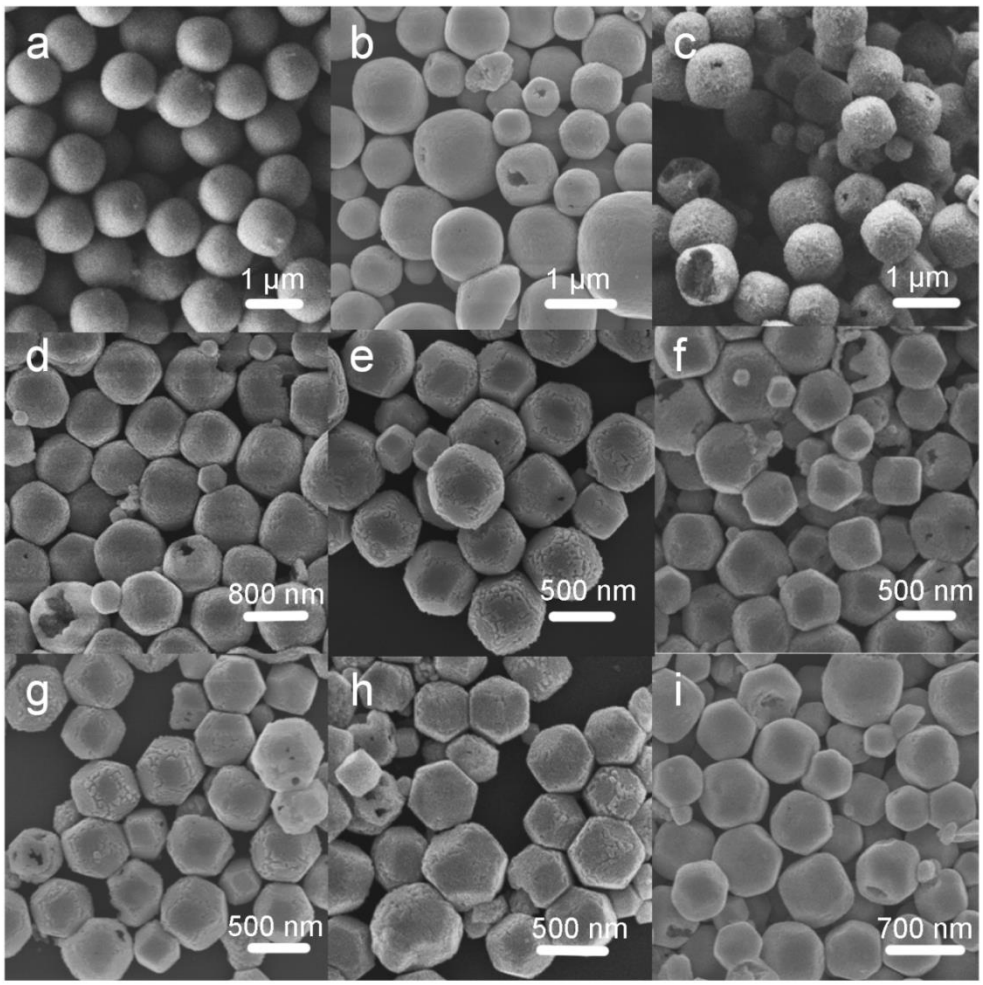

Figure S4. SEM images of as-prepared samples obtained from hydrothermal condition of 150 mg KCl and 300 mg phosphotungstic acid at 100 ^{o}C for different times: a) 1 h-S3, b) 3 h, c) 6 h-S4, d) 9 h, e) 12 h, f) 15 h, g) 18 h, h) 21 h, and i) 24 h.

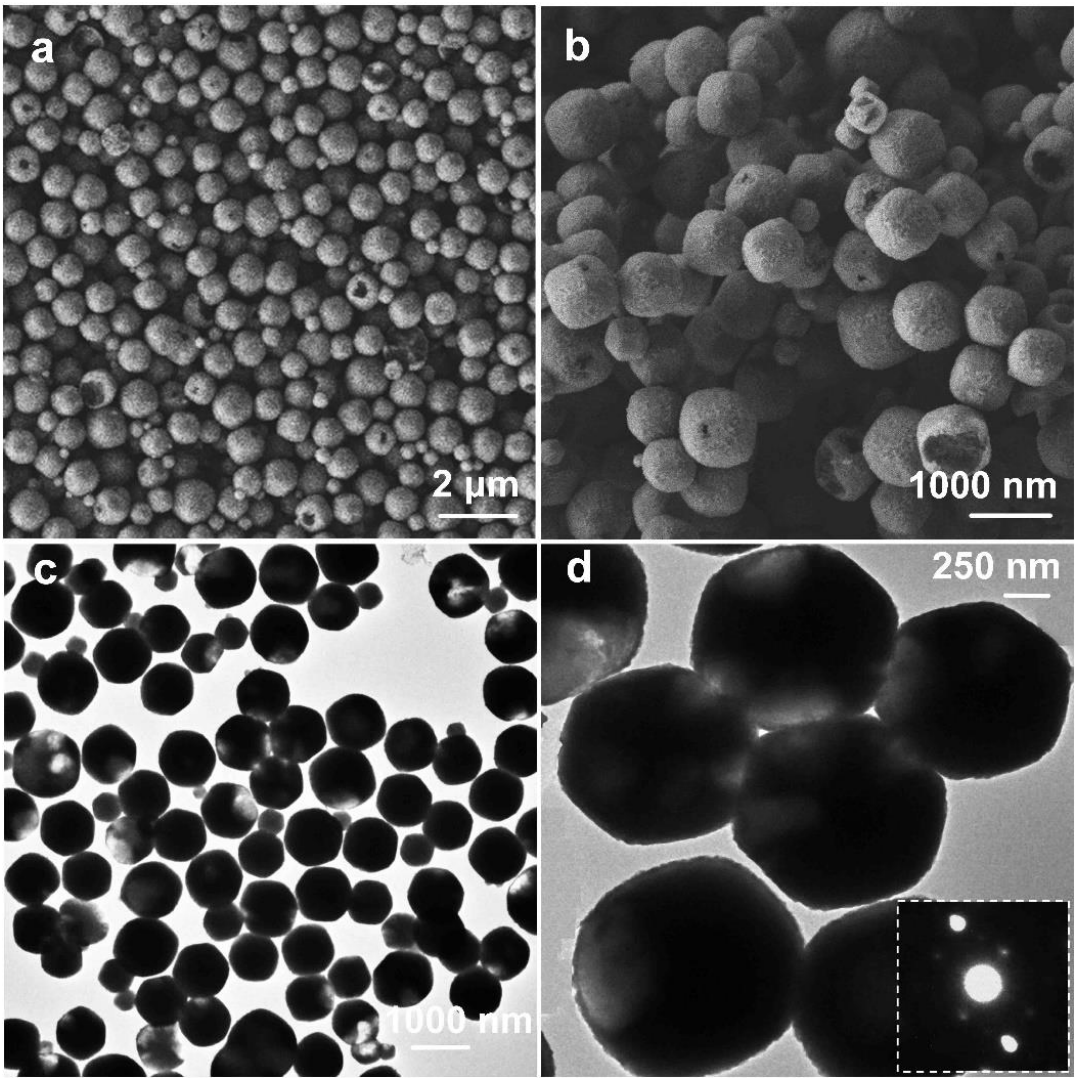

Figure S5. Samples (Denoted by **S4**) obtained from hydrothermal condition of 150 mg KCl and 300 mg phosphotungstic acid at 100 ^{o}C for 6 h: a, b) SEM images, and c, d) TEM images. Inset of d-SAED patterns.

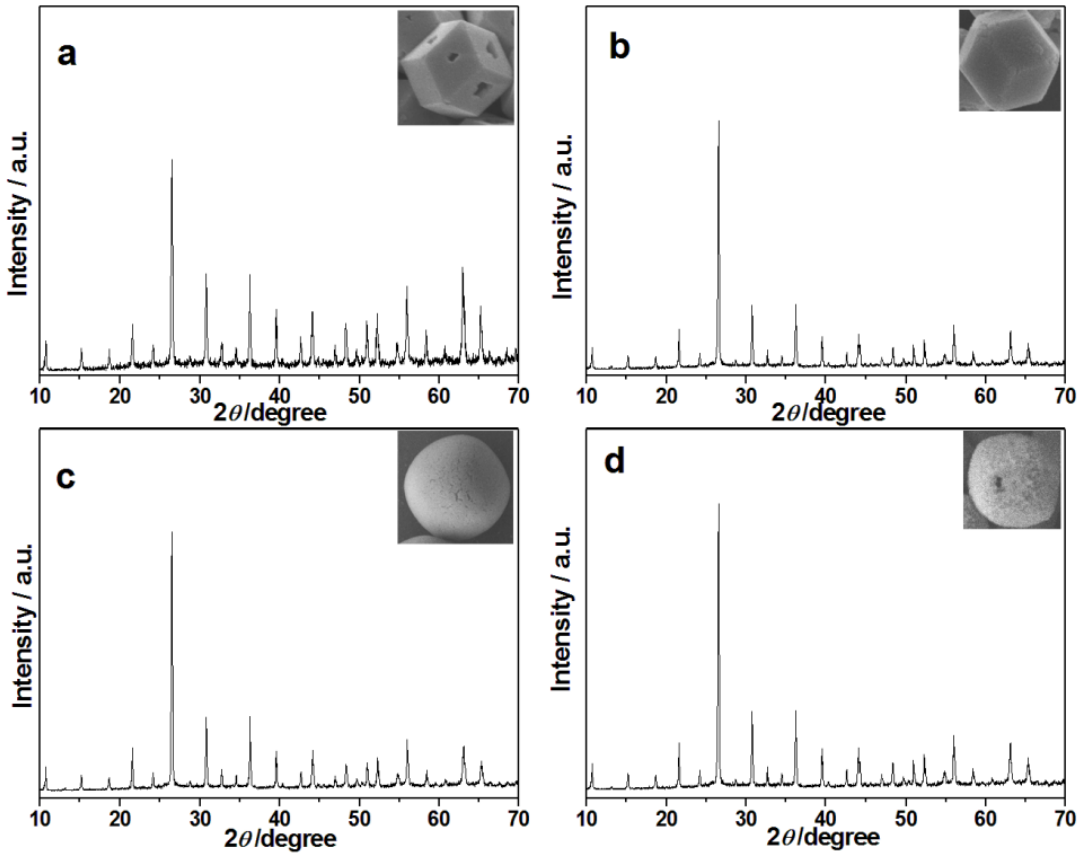

Figure S6. XRD patterns of as-prepared samples, a) S1, b) S2, c) S3, and d) S4.

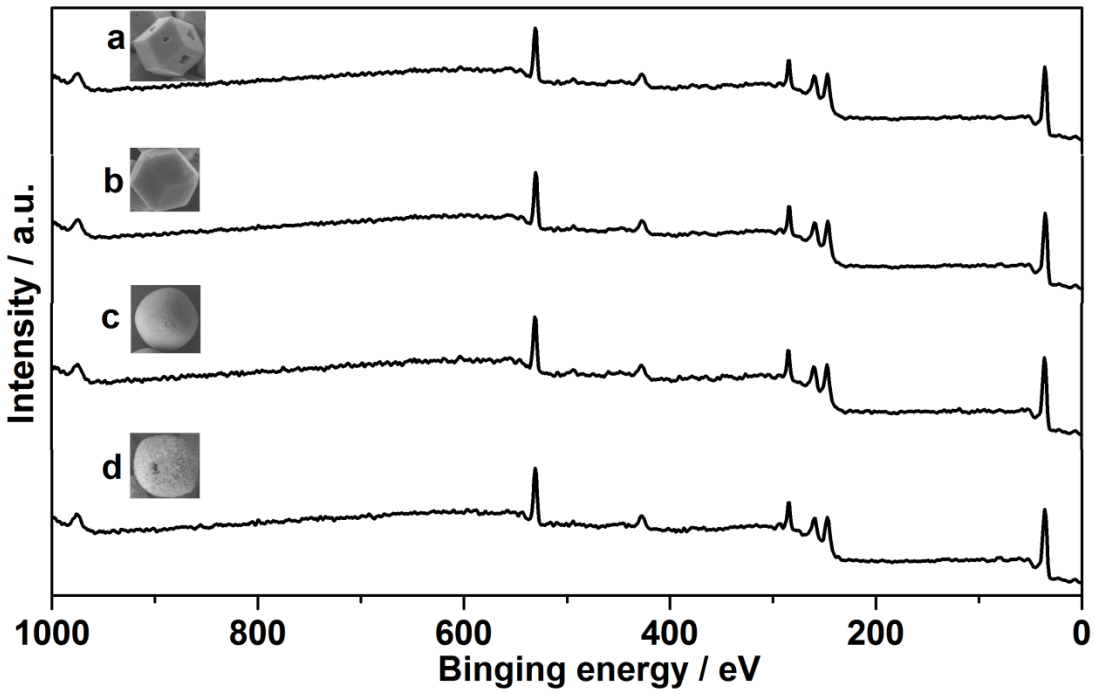

Figure S7. XPS spectra of the as-obtained products: a) S1, b) S2, c) S3, and d) S4.

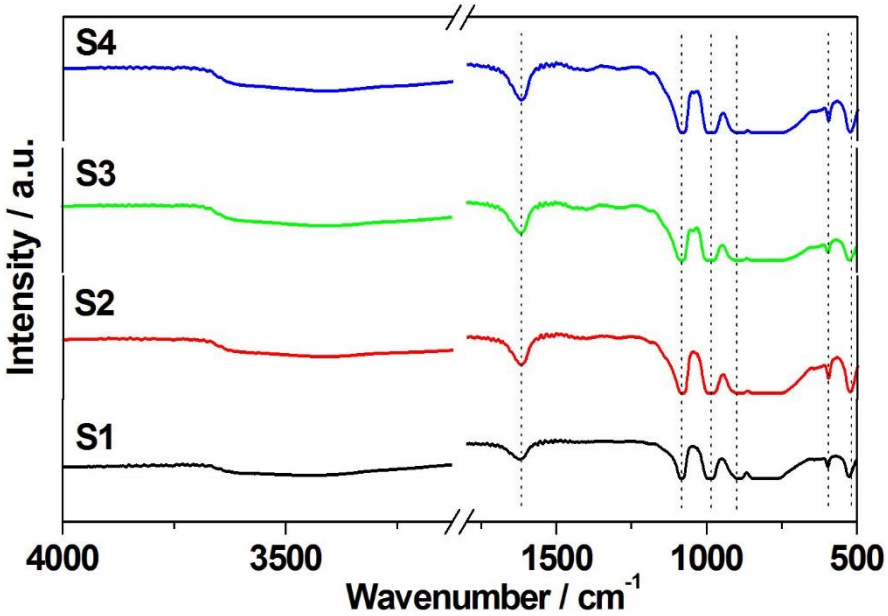

Figure S8. Infrared spectra of as-prepared samples 1083 cm^{-1} for ν_{as} vibration of PO_4 (the central tetrahedral PO_4 bonds in the ions), 988 cm^{-1} for the ν_{as} vibration of $W{=}O_t$ (terminal oxygen linked to a lone tungsten atom), 891 cm^{-1} for ν_{as} of $W\text{-}O_b\text{-}W$ (O_b denotes the oxygen atom between two different W_3O_{13} groups), and 800 cm^{-1} for the ν_{as} of $W\text{-}O_a\text{-}W$ (O_a is the oxygen in the same W_3O_{13}), respectively. The peaks appearing at 594 and 527 cm^{-1} are assigned to the vibration of δ(O-P-O) and ν_s(W-O-W), respectively.[1]

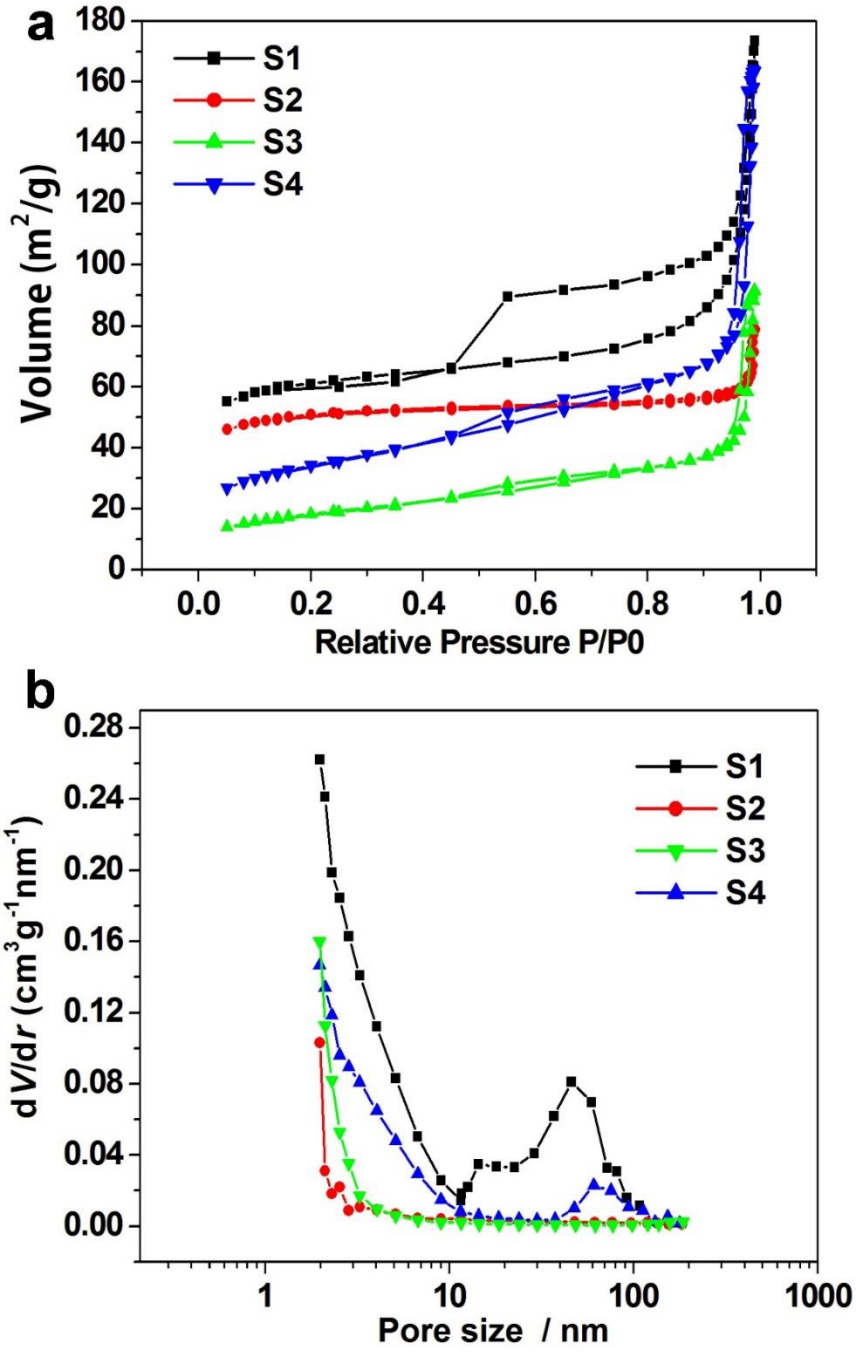

Figure S9. a) N_2 adsorption-desorption isotherms of as-prepared samples (S1, S2, S3 and S4), and b) the pore-size distribution curves**.**

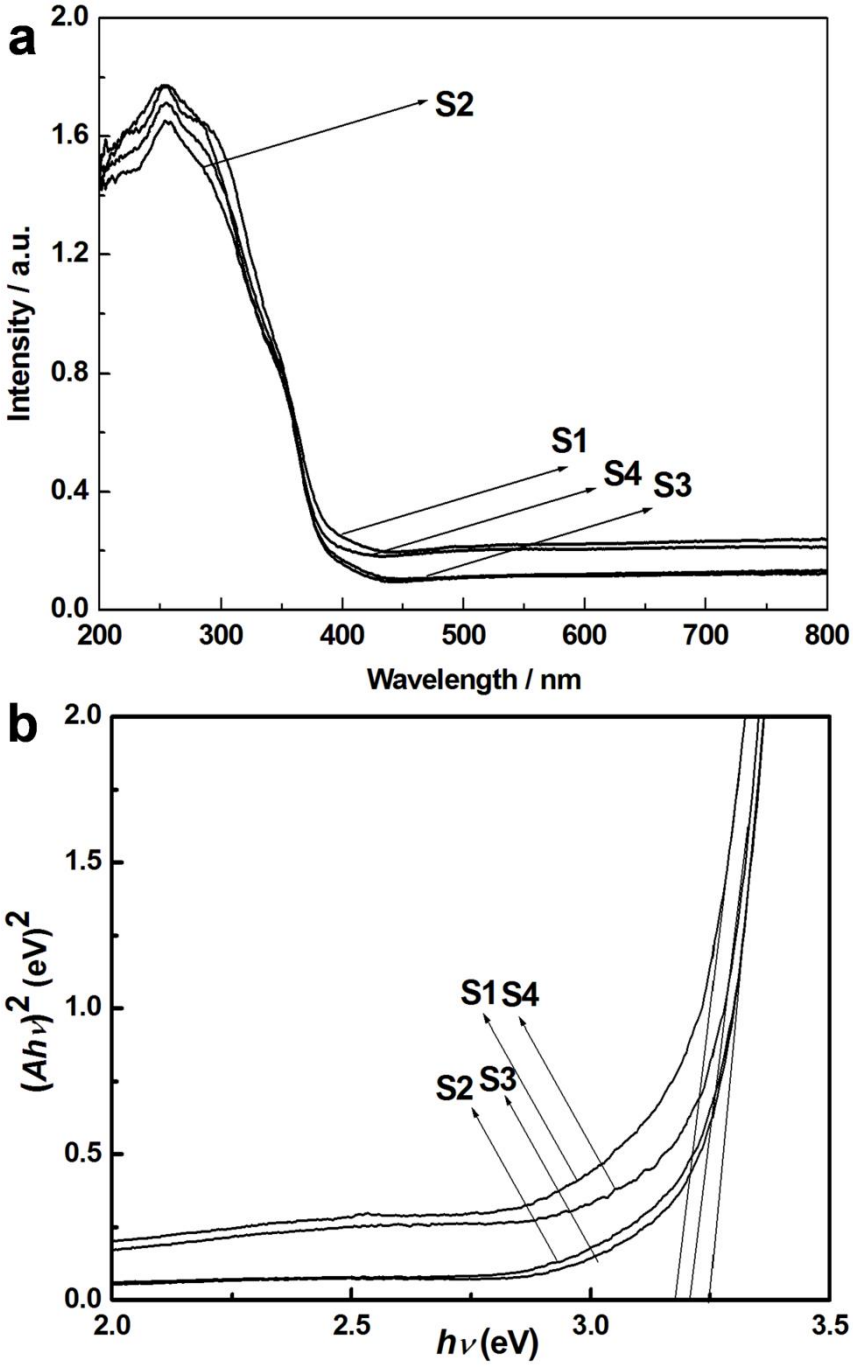

Figure S10. a) UV-vis diffuse reflectance spectra of the as-prepared samples, b) Plots of $(Ahv)^2$ versus hv for the samples.

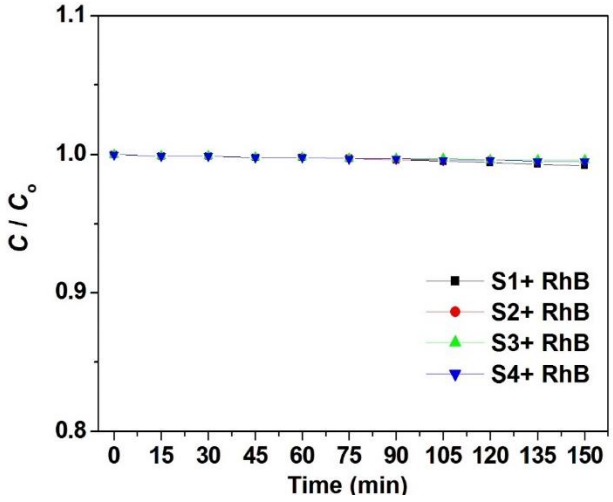

Figure S11. A plot of the photodegradation extent of RhB molecular on the bases of irradiation time for as-prepared samples and RhB (Without any H_2O_2, other conditions are the same as Figure 5).

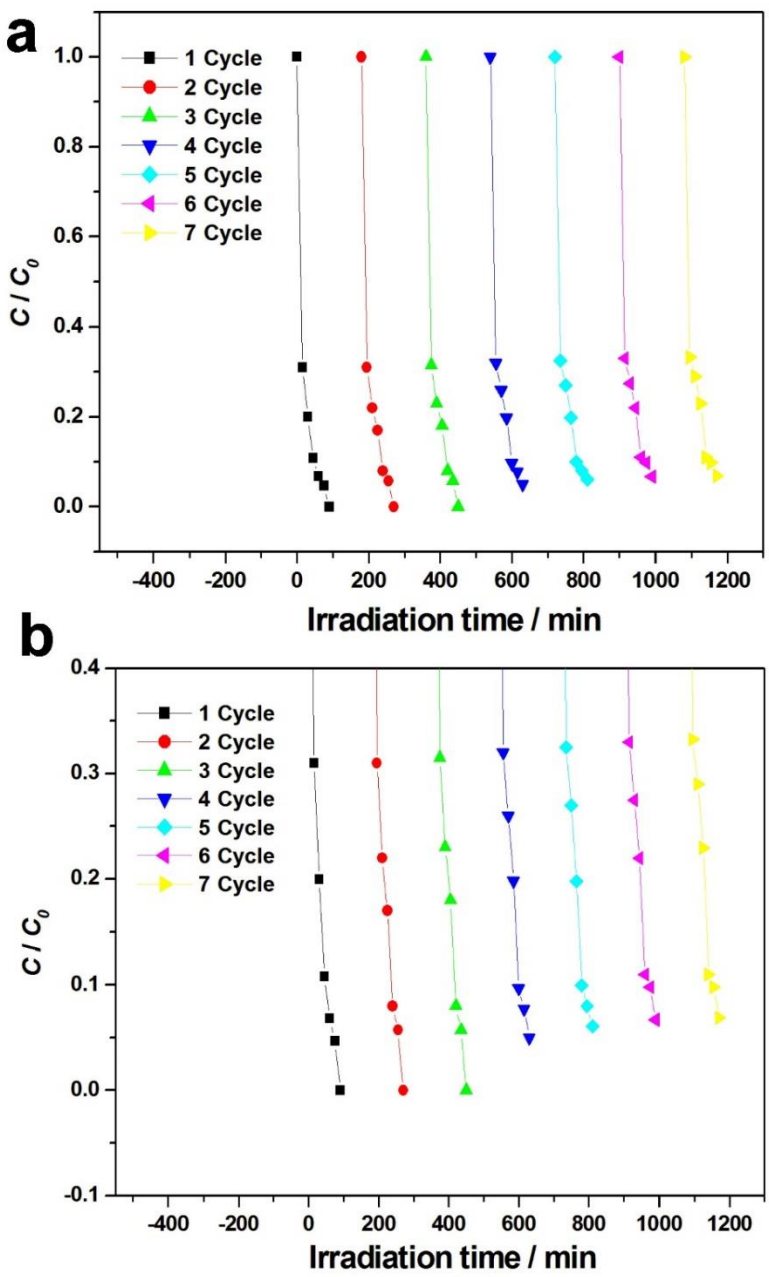

Figure S12. Catalyst-S1 recycle in repetitive degradation of RhB=2 × 10^{-5} M, H_2O_2=2 × 10^{-3} M; S1=0.5 g L^{-1}, pH=2.1.

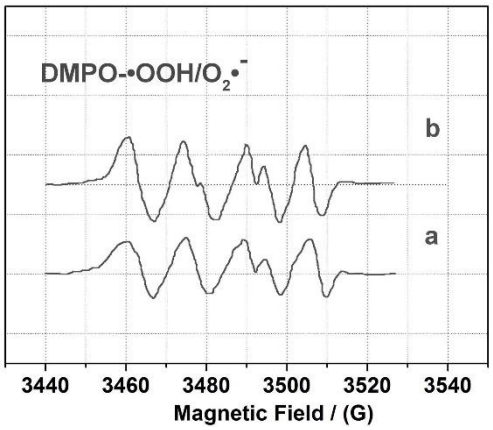

Figure S13. ESR signals of the DMPO-•OOH/O_2•$^-$ adducts for S1 (1 g L^{-1})-H_2O_2 (2 × 10^{-2} mol L^{-1})-RhB (2 × 10^{-5} mol L^{-1}) with different visible light irradiation time: a) 100 s, and b) 300 s.

Photocatalyst	Efficiency / %	Degradation Time / h	Reference
Ag_3PO_4/TiO_2	99	0.75	2
Fe_3O_4-SiO_2-TiO_2/GO	80	2.0	3
PZT coupled with TiO_2	100	4.0	4
Cu_2ZnSnS_4-Pt	100	4.0	5
α-Fe_2O_3 nanocrystals	100	3.0	6
α-Fe_2O_3 hollow microplatelets	80	3.0	7
S1-$K_3PW_{12}O_{40}\cdot nH_2O$	**100**	**1.5**	**This work**

Table S1. Comparison of degradation efficiencies of different materials during the RhB photodegradation driven by visible light reported in previous references.

References

1. N. Essayem, A. Holmqvist, P. Y. Gayraud, J. C. Vedrine and Y. Ben Taarit, *J. Catal.*, 2001, **197**, 273.
2. W. Yao, B. Zhang, C. Huang, C. Ma, X. Song and Q. Xu, *J. Mater. Chem.*, 2012, **22**, 4050.
3. F. Chen, F. Yan, Q. Chen, Y. Wang, L. Han, Z. Chen and S. Fang, *Dalton Trans.*, 2014, **43**, 13537.
4. Q. Wu, D. Li, L. Wu, J. Wang, X. Fu and X. Wang, *J. Mater. Chem.*, 2006, **16**, 1116.
5. X. Yu, A. Shavel, X. Q. An, Z. Luo, M. Ibanez and A. Cabot, *J. Am. Chem. Soc.*, 2014, **136**, 9236.
6. X. Zhou, J. Lan, G. Liu, K. Deng, Y. Yang, G. Nie, J. Yu and L. Zhi, *Angew. Chem. Int. Ed.*, 2012, **124**, 182.
7. H. Liang, W. Chen, X. Jiang, X. Xu, B. Xu and Z. Wang, *J. Mater. Chem. A*, 2014, **2**, 4340.