

## Supporting Information:

### A Novel 3D Inorganic Heteropoly Blue as Visible-Light Responsive Photocatalyst

*Bao-Li Fei,<sup>\*a,b</sup> Wen Li,<sup>a</sup> Jinag-Hong Wang,<sup>a</sup> Qing-Bo Liu,<sup>c</sup> Jiang-Ying Long,<sup>c</sup>  
Yang-Guang Li,<sup>d</sup> Kui-Zhan Shao,<sup>d</sup> Zhong-Min Su,<sup>\*d</sup> Wei-Yin Sun<sup>\*b</sup>*

#### Contents

1. XPS spectra of W 4f level of **1**. (**Fig. S1**)
2. IR spectra of compound **1**. (**Fig. S2**)
3. The experimental (top) and simulated (bottom) X-ray powder diffraction (XRPD) patterns of **1**. (**Fig. S3**)
4. The temporal absorption spectrum changes of RhB under visible light irradiation in the aerated aqueous solution corresponding to different conditions. (**Fig. S4**)
5. Plotted degradation of RhB ( $2 \times 10^{-5}$  mol L<sup>-1</sup>) in the presence of **1** (0.3784 g L<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub> ( $2 \times 10^{-3}$  mol L<sup>-1</sup>) under visible irradiation purged with a) nothing b) O<sub>2</sub> (air), c) N<sub>2</sub>. pH = 2.5. (**Fig. S5**)
6. Plotted degradation of RhB ( $2 \times 10^{-5}$  mol L<sup>-1</sup>) in the presence of **1** (0.3784 g L<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub> ( $2 \times 10^{-3}$  mol L<sup>-1</sup>) under visible irradiation with a) no stirring, b) intensely and continuously stirring. pH = 2.5. (**Fig. S6**)
7. The configuration of Rhodamine-B. (**Fig. S7**)
8. The experimental (top) X-ray powder diffraction (XRPD) patterns of original **1** and after photocatalytic reactions (bottom).

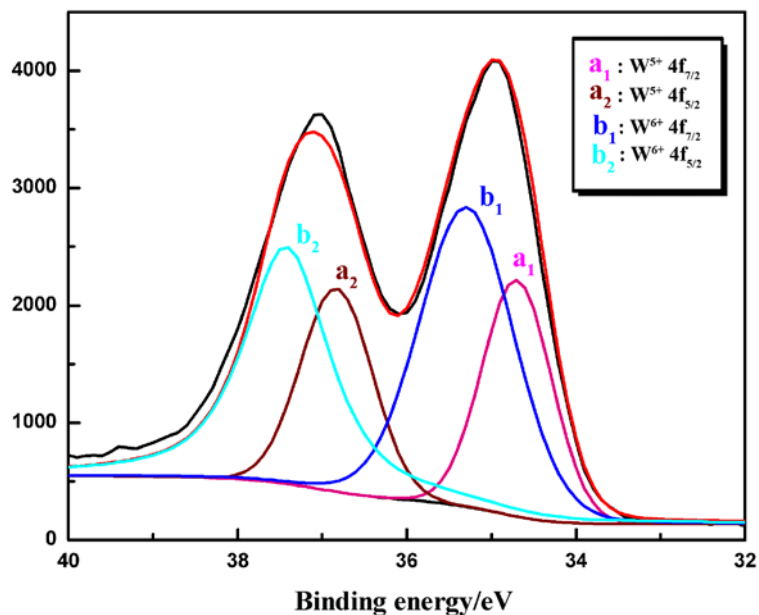


Fig. S1. XPS spectra of W 4f level of **1**. The XPS of **1** shows four partially overlapped peaks, and the fit of curve provides with positions of these four peaks at 34.70, 35.30, 36.83 and 37.42 eV attributing to  $W^V 4f_{7/2}$ ,  $W^{VI} 4f_{7/2}$ ,  $W^V 4f_{5/2}$  and  $W^{VI} 4f_{5/2}$ , respectively. The ratio of the peak area for  $W^V$  to  $W^{VI}$  is ca. 4:8.

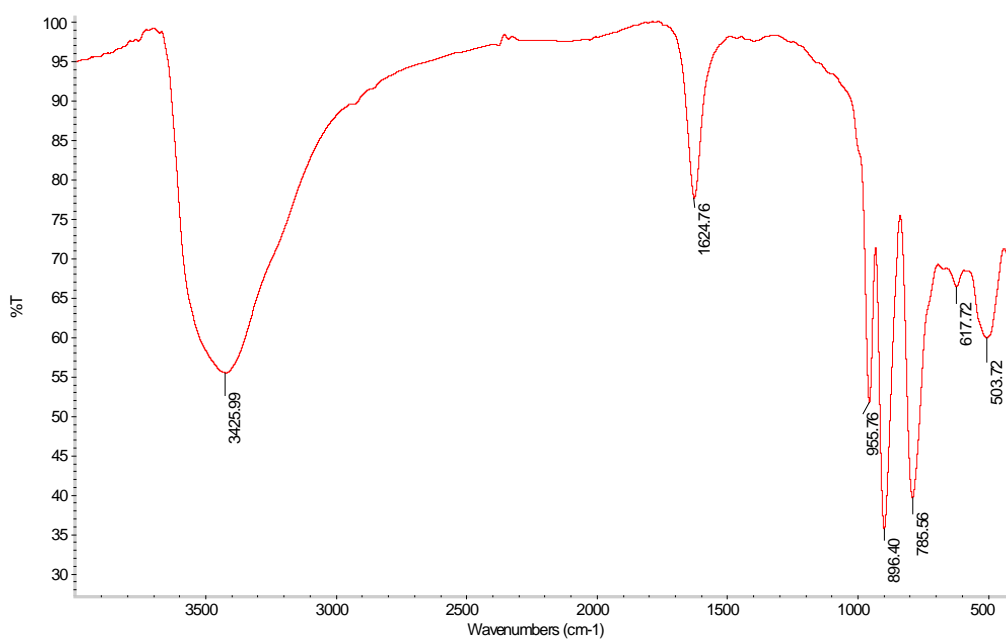


Fig. S2. IR spectra of compound **1**.

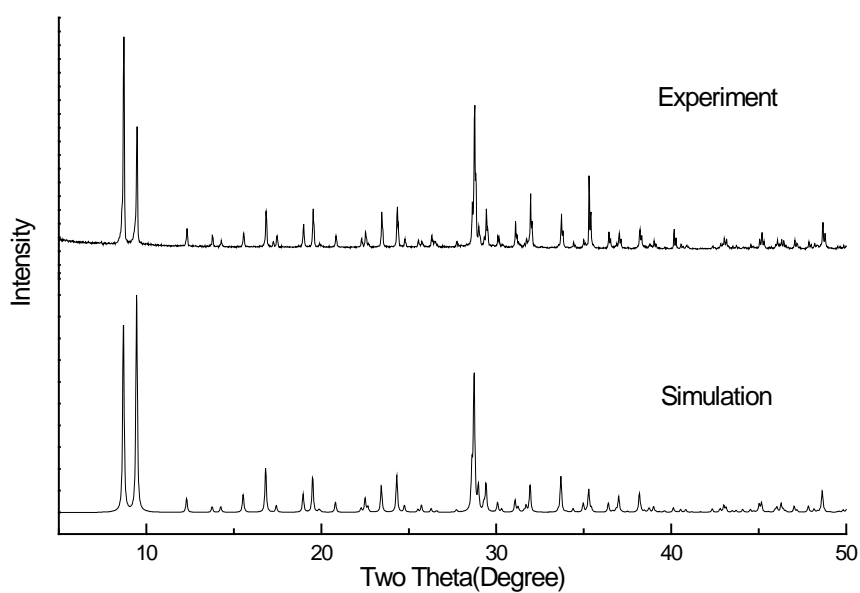


Fig. S3. The experimental (top) and simulated (bottom) X-ray powder diffraction (XRPD) patterns of **1**, showing the bulk product is in good agreement with the calculated pattern based on the result of single-crystal X-ray diffraction.

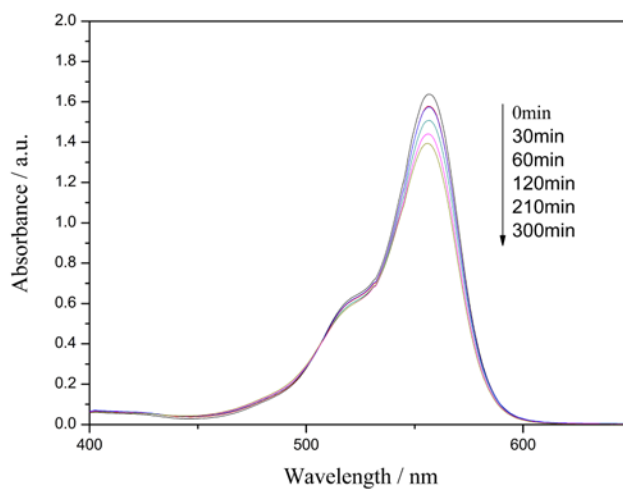


Fig. S4. a) The temporal absorption spectrum changes of RhB under visible light irradiation in the aerated aqueous solution, corresponding to trace a in Fig. 4. Initial concentrations: RhB,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ; pH = 2.5.

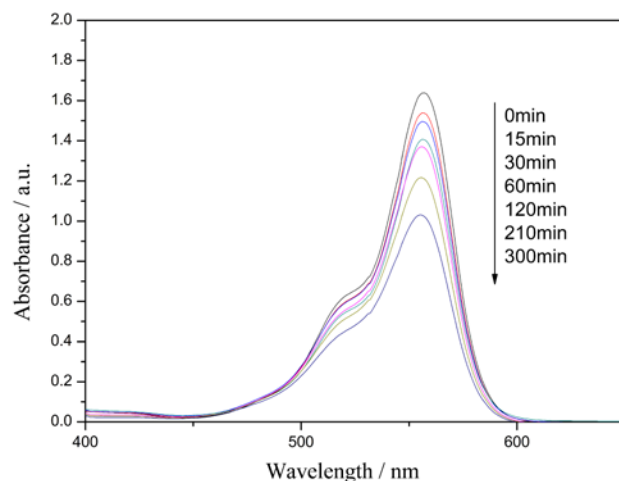


Fig. S4. b) The temporal absorption spectrum changes of RhB under visible light irradiation in the aerated aqueous solution, corresponding to trace b in Fig. 4. Initial concentrations: RhB,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ;  $\text{H}_2\text{O}_2$ ,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; pH = 2.5.

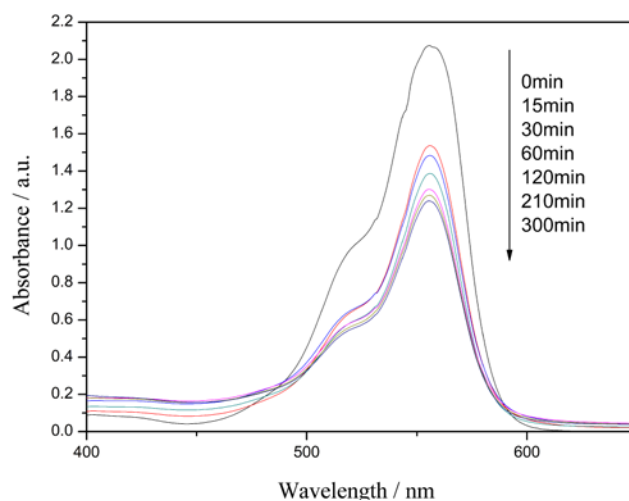


Fig. S4. c) The temporal absorption spectrum changes of RhB over compound **1** in the absence of any irradiation in the aerated aqueous solution, corresponding to trace c in Fig. 4. Initial concentrations: RhB,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ; **1**,  $0.3784 \text{ g L}^{-1}$ ; pH = 2.5.

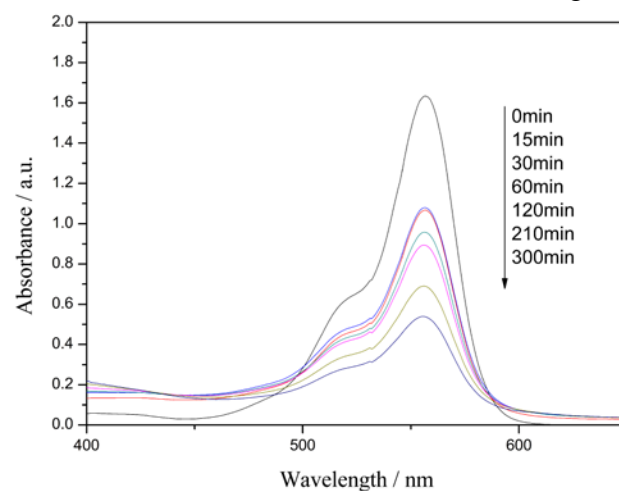


Fig. S4. d) The temporal absorption spectrum changes of RhB under visible light

irradiation in the aerated aqueous solution, corresponding to trace d in Fig. 4. Initial concentrations: RhB,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ; **1**,  $0.3784 \text{ g L}^{-1}$ ; pH = 2.5.

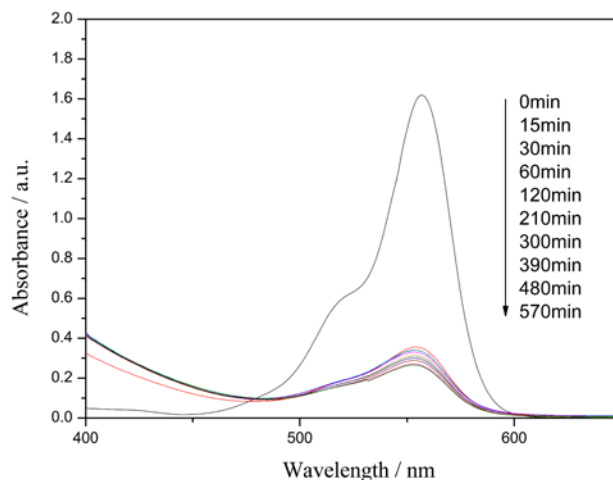


Fig. S4. e) The temporal absorption spectrum changes of RhB in the absence of any irradiation in the aerated aqueous solution, corresponding to trace e in Fig. 4. Initial concentrations: RhB,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ; **1**,  $0.3784 \text{ g L}^{-1}$ ;  $\text{H}_2\text{O}_2$ ,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; pH = 2.5.

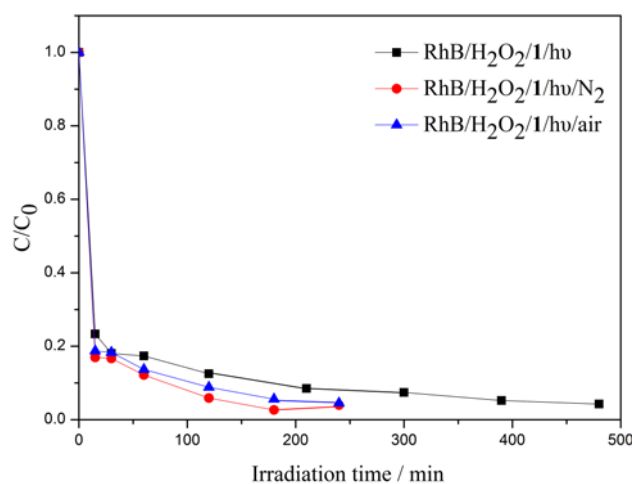


Fig. S5. Plotted degradation of RhB ( $2 \times 10^{-5} \text{ mol L}^{-1}$ ) in the presence of **1** ( $0.3784 \text{ g L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ) under visible irradiation purged with a) nothing, b)  $\text{O}_2$  (air), c)  $\text{N}_2$ . pH = 2.5.

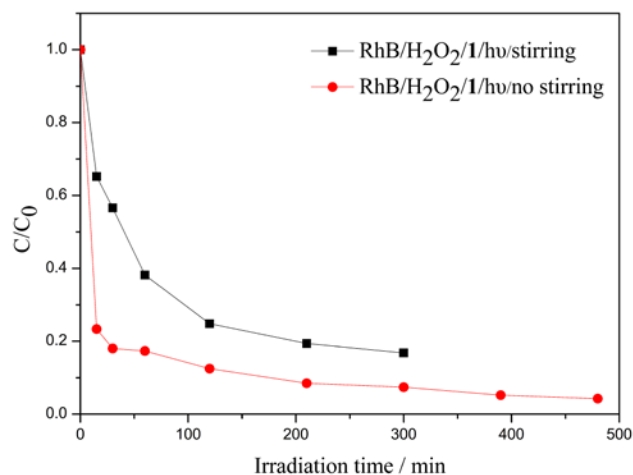


Fig. S6. Plotted degradation of RhB ( $2 \times 10^{-5} \text{ mol L}^{-1}$ ) in the presence of **1** ( $0.3784 \text{ g L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ) under visible irradiation with a) no stirring, b) with intensely and continuously stirring. pH = 2.5.

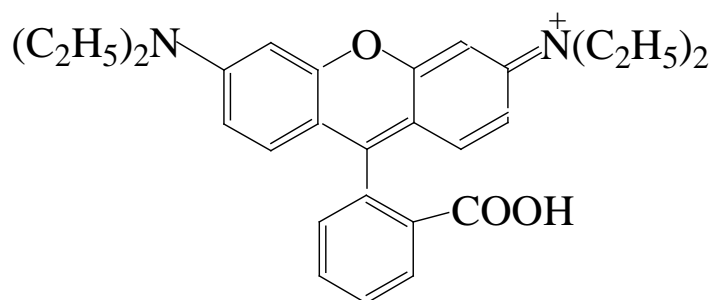


Fig. S7. The configuration of Rhodamine-B.

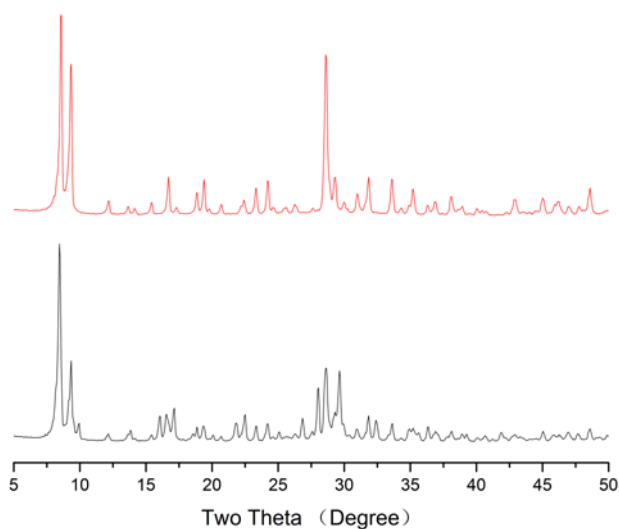


Fig. S8. The experimental (top) X-ray powder diffraction (XRPD) patterns of original **1** and after photocatalytic reactions (bottom).