

## Enhanced photocatalytic activity of B<sub>12</sub>-based catalyst co-photosensitized by TiO<sub>2</sub> and Ru(II) towards dechlorination

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### Experimental

#### Preparation of B<sub>12</sub>-TiO<sub>2</sub>

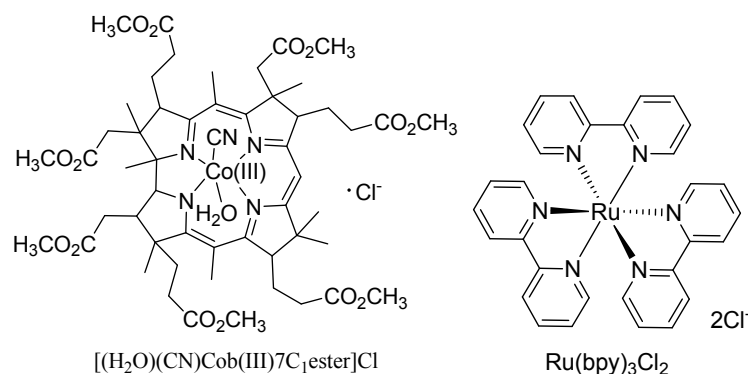
[(CN)(H<sub>2</sub>O)Cob(III)7COOH]Cl (2.5 mg, 2.4 × 10<sup>-3</sup> mmol) was added to 5 mL methanol dispersion of mesoporous anatase TiO<sub>2</sub> microspheres (30 mg) and the mixture was stirred at room temperature for 4 h. Then the hybrid B<sub>12</sub>-TiO<sub>2</sub> was obtained after centrifugation and washed with methanol for three times.

The Co content of B<sub>12</sub>-TiO<sub>2</sub> was 6.9 × 10<sup>-5</sup> mol·g<sup>-1</sup>, which was determined through detecting the absorbance change of the characteristic peak of [(CN)(H<sub>2</sub>O)Cob(III)7COOH]Cl at 523 nm in the supernatant by UV-vis spectra.

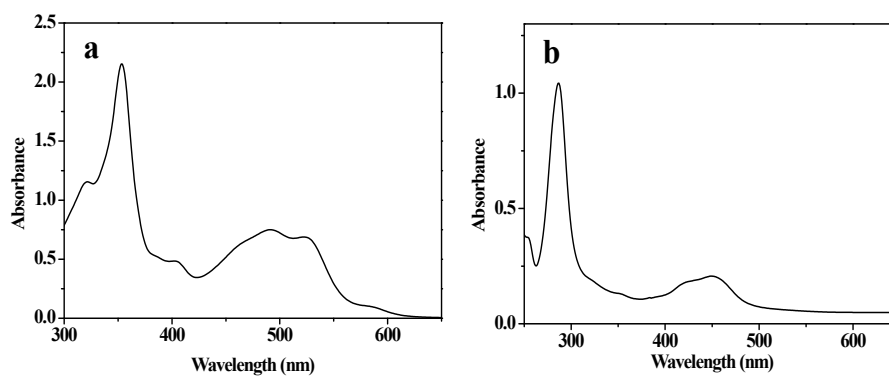
#### Preparation of Ru(II)-TiO<sub>2</sub>

Ru(dcb)(bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (5 mg, 5.8 mmol) was added to 5 mL methanol dispersion of mesoporous anatase TiO<sub>2</sub> microspheres (30 mg) and the mixture was stirred at room temperature for 4 h. Then the hybrid Ru(II)-TiO<sub>2</sub> was obtained after centrifugation and washed with methanol for three times.

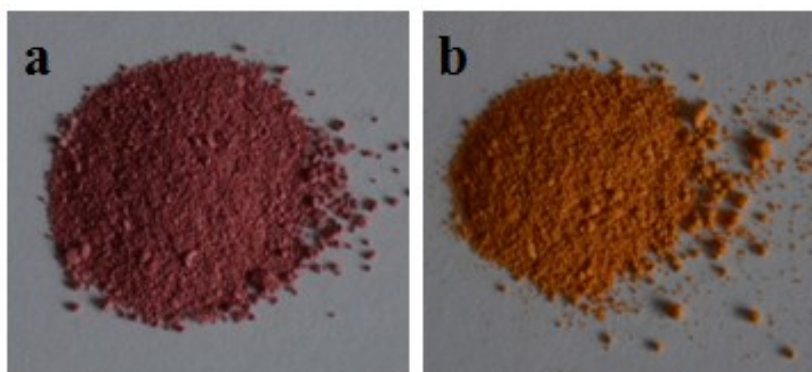
The Ru content of Ru(II)-TiO<sub>2</sub> was 1.75 × 10<sup>-4</sup> mol·g<sup>-1</sup>, which was determined through detecting the absorbance change of the characteristic peak of Ru(dcb)(bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> at 480 nm in the supernatant by UV-vis spectra.



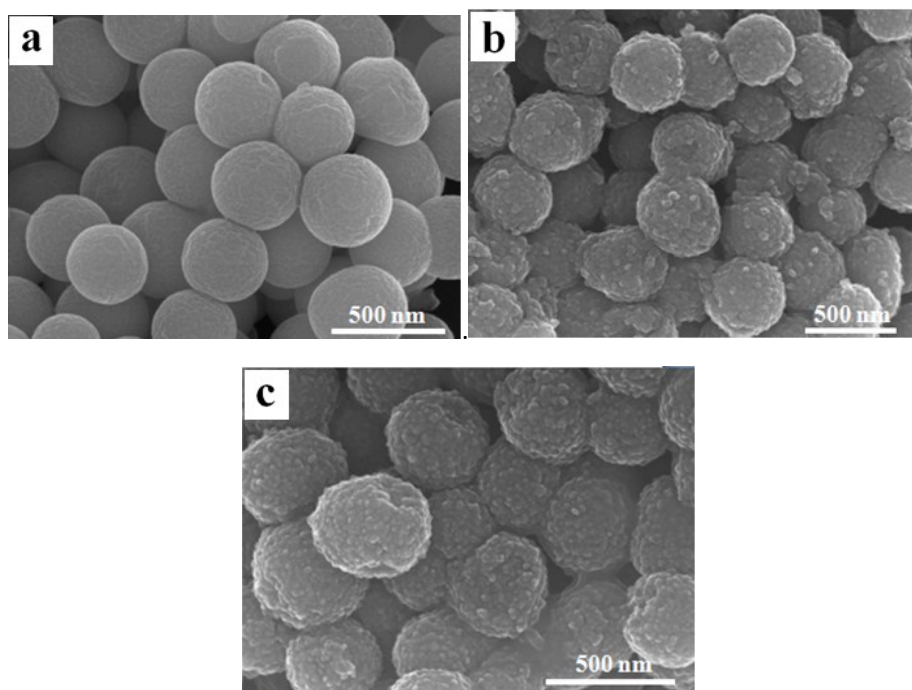
**Fig. S1** Structures of  $[(\text{CN})(\text{H}_2\text{O})\text{Cob}(\text{III})7\text{C}_1\text{ester}]\text{Cl}$  and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ .



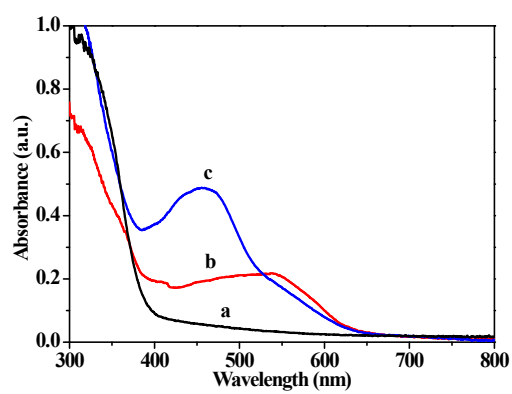
**Fig. S2** UV-vis spectra of  $\text{Cob}(\text{III})7\text{C}_1\text{ester}$  (a) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (b) in methanol.



**Fig. S3** Photographs of  $\text{B}_{12}\text{-TiO}_2$  (a) and  $\text{Ru}(\text{II})\text{-TiO}_2$  (b).



**Fig. S4** SEM images of titanium glycolate (a),  $\text{B}_{12}\text{-TiO}_2$  (b) and  $\text{Ru}(\text{II})\text{-TiO}_2$  (c).



**Fig. S5** Diffuse reflectance UV-vis spectra of TiO<sub>2</sub> (a), B<sub>12</sub>-TiO<sub>2</sub> (b) and Ru(II)-TiO<sub>2</sub> (c).