Supporting Information

A silicotungstate-based copper-viologen hybrid photocatalytic compound for efficient degradation of organic dyes under visible light

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1. General methods and materials

All of the reagents were purchased from commercial channels and used without further purification. The ligand PBPY was synthesized according to a reported method [S1] All water used during the catalyst syntheses and photocatalytic measurements was distilled water. The Powder X-ray diffraction (PXRD) were collected on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation 2θ range from 5° to 50°. UV-Vis diffuse reflectance spectra (DRS) were carried out on a HITACHIU-3010 spectrometer, and used a $BaSO_4$ plate as a standard reference. Thermogravimetric analysis (TGA) curves were recorded on a TA Instrument Q600 SDT thermogravimetric analyser in N_2 at a heating rate of 10 °C min^{-1}. UV-Vis diffuse reflectance spectra of MB solution were performed on a HITACHI U-3900H spectrometer. The C, H and N elemental analyses (EA) were performed on a Vario EL III elemental analyzer. High resolution imaging of the wet ball-milled sample was conducted on a Hitachi SU8220 cold field emission scanning electron microscope (FESEM). Tungsten content of the reference sample was determined by inductively coupled plasma optical emission spectroscopy (Thermo Scientific iCAP 7400 duo). During the ball-milling process, around 300 mg of the compound powder and 10 mL anhydrous alcohol were placed inside a 100 mL stainless steel jar alongside ten 5 mm stainless steel milling balls at room temperature and sealed properly, this combination was then subjected to 2 h milling in a grinder mill at 400 rpm.

1.1 Catalysts preparation

$[Cu_2(PBPY)_2][SiW_{12}O_{40}]$ (**1**) : A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.031 g, 0.13 mmol), N-(3-pyridyl)-4,4'-bipyridinium chloride (0.054 g, 0.20mmol), $H_4SiW_{12}O_{40} \cdot xH_2O$ (0.300 g, 0.10 mmol), NaOH (0.008 g, 0.20 mmol) and H_2O (10 mL) was stirred for 30 min in air, and then sealed in a 25mLTeflon-lined steel bomb, which was heated at 160 °C for 48 h and then cooled to room temperature at a rate of 5 $°C \cdot h^{-1}$. Finally, brownish black block crystals were collected by filtration, washed with distilled water for 3 times and then dried at room temperature for 12 h (0.120 g, 53.21 % based on Cu). Elemental Anal. Calc. (%): C 10.39, H 0.70, N 2.42; found: C 10.44, H 0.75, N 2.49.

Reference sample $[PBPY]_4[SiW_{12}O_{40}]$: A mixture of 10 mL N- (3- pyridyl)-4,4'-bipyridinium chloride (0. 43 g, 1.6 mmol) aqueous solution and 10mL $H_4SiW_{12}O_{40}$ (1.44 g, 0.5 mmol) aqueous solution was stirred in a 100 mL flask for 30 min in air, then white crystalline powders of $[PBPY]_4[SiW_{12}O_{40}]$ was obtained by centrifugation at 3000 rpm for 10 min, washed with distilled water for 3 times and then dried at room temperature for 24 h. (0.96 g, 63.16 % based on PBPY). Elemental Anal. Calc. (%): C 18.91, H 1.27, N 4.41; found: C 19.21, H 1.36, N 4.15. ICP-OES(W): Calc. (57.88%), found (58.0%).

1.2 X-ray single crystal diffraction

Crystallographic data for **1** were measured on a Rigaku R-AXIS SPIDER CCD diffractometer using graphite monochromatized Mo/*Kα* radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-square technique on F^2 with SHELXL-97.

Crystal data for **1**.

Empirical formula	$C_{30}H_{24}Cu_2N_6O_{40}SiW_{12}$	
Formula weight	3469.92 g /mol	
Crystal system	Triclinic	
Space group	*P -1*	
Unit cell dimensions	a = 11.710(2) Å	α = 95.65(3)°
	b = 11.890(2) Å	β = 114.28(3)°
	c = 12.710(3) Å	γ = 111.22(3)°
Volume	1438.7(5) Å^3	
Crystal density (calculated)	4.005 g/cm^3	
F (000)	1526	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2σ (I)]	[a]R1 = 0.0992, [b]wR2 = 0.2369	
R indices (all data)	R1 = 0.1169, wR2 = 0.2560	

[a]$R_1 = \sum || F_o| - |F_c|| / \sum |F_o|$. [b]$wR_2 = [\sum [w (F2\ o - F2\ c)^2] / \sum [w (F2\ o)^2]]^{1/2}$.

1.3 Photocatalytic measurements

The photodegradation experiment was performed in a 250 mL beaker upon different light source. A 300W xenon lamp (PLS-SXE 300C, Beijing Perfect Light Co., Ltd), with a 420 nm filter are used as full spectrum and visible light sources, respectively. Typically, 50 mg of sample powder after ball milling was dispersed into 100 mL of 100 mL of MB (methylene blue), RhB (Rhodamine B), CV (crystal violet) aqueous solution ($c = 10\ mg \cdot L^{-1}$), respectively. The distance between the solution and the light source was about 10 cm. Prior to photo irradiation, the suspensions were magnetically stirred in the dark for 30 min to attain the adsorption/desorption equilibrium between the dye and the surface of the catalyst under ambient conditions. At varied irradiation time intervals, 3 mL suspension was collected and analyzed by UV-Vis spectroscopic measurements

1.4 Photocurrent measurements

Electrochemical measurements were carried out with a typical three-electrode system using an electrochemical workstation (AUTOLAB PGSTAT 100, Metrohm), in which an Ag/AgCl electrode was used as reference electrode, platinum plate electrode as the counter electrode respectively, and 0.5 M Na_2SO_4 aqueous solution as the supporting electrolyte. To prepare the working photoelectrode, a suspension consist of 40 mg as-prepared photocatalyst, 336 μL 5 wt.% Nafion™ solution (Du Pont) and 1664 μL absolute ethanol were dispersed by ultrasonic vibration for 30 min first, and then cleaned FTO glass substrate thoroughly. Then 40 μL as-prepared suspension was dip-coated onto the FTO glass substrate with a covered area of 1 cm^2 and dried under ambient conditions, this procedure was repeated 3 times to get an optimization uniform film. The lamp used as visible and full-spectrum light source were the same as the photocatalytic degradation process.

2. Additional Data and Figures

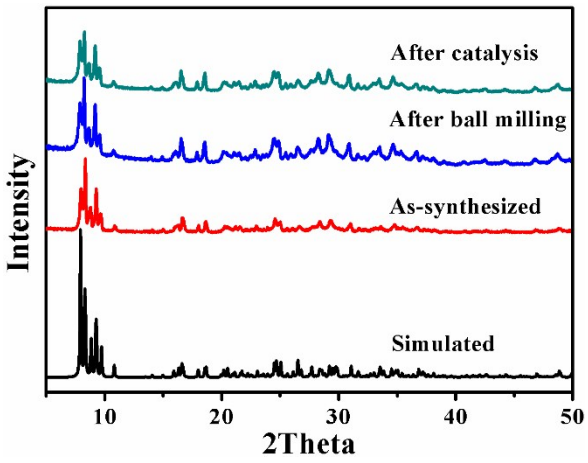

Fig. S1. Powder X-ray diffraction patterns of **1**.

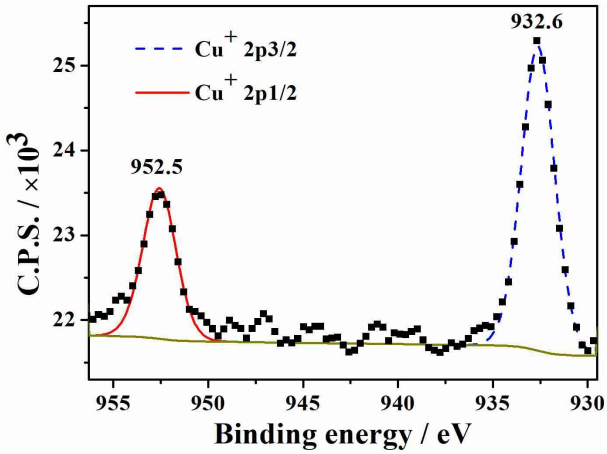

Fig. S2. The high resolution XPS spectrum of Cu 2p for **1**.

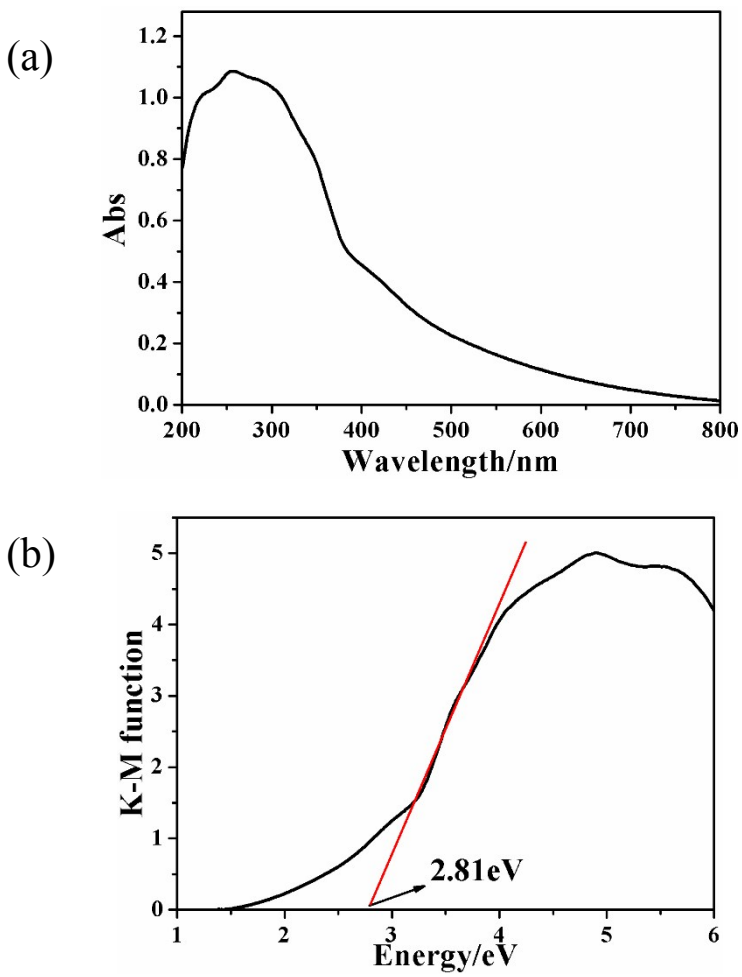

Fig. S3. (a) UV−vis absorption spectrum and (b) optical band gap energy of $[PBPY]_4[SiW_{12}O_{40}]$ (The reference compound).

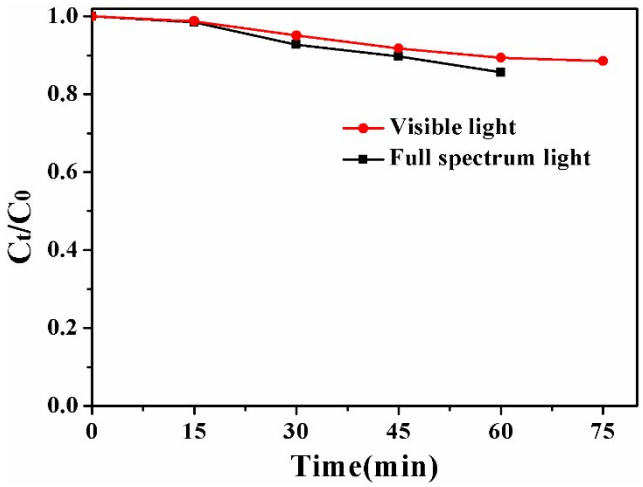

Fig. S4. Degeneration rates of MB (blank reaction without catalyst) with visible (red line) and full spectrum light (black line) irradiation. Initial concentrations: MB (10 mg/L, pH= 6.3).

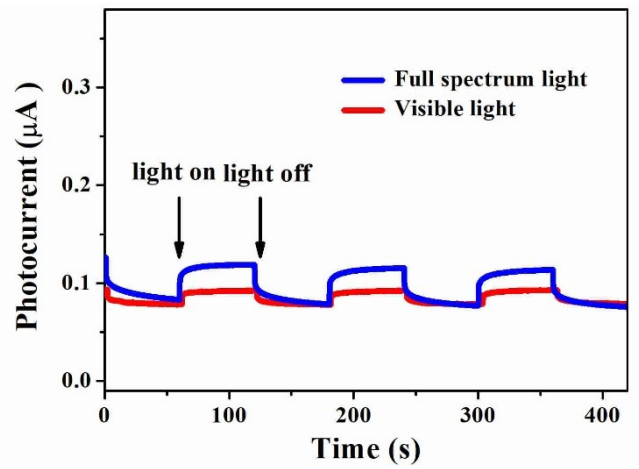

Fig. S5. The photocurrent responses (0.37 V bias) of $[PBPY]_4[SiW_{12}O_{40}]$ in 0.5 M Na_2SO_4 electrolyte under visible light (red) and full spectrum light (blue) respectively.

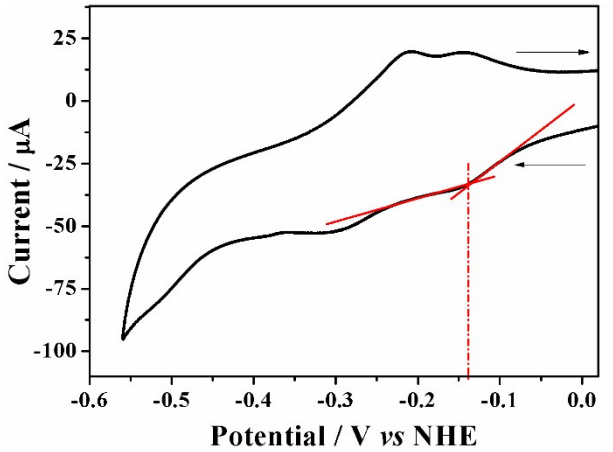

Fig. S6. The CV curve of compound **1**. CV measured in a pH 4.5 medium (0.5 M CH_3COONa/CH_3COOH) containing 0.1M Na_2SO_4. The scan rate was 20 $mV \cdot s^{-1}$. Working, reference, and counter electrodes are carbon paste electrode modified with compound **1** (3 mm diameter disk), Ag/AgCl, and Pt, respectively.

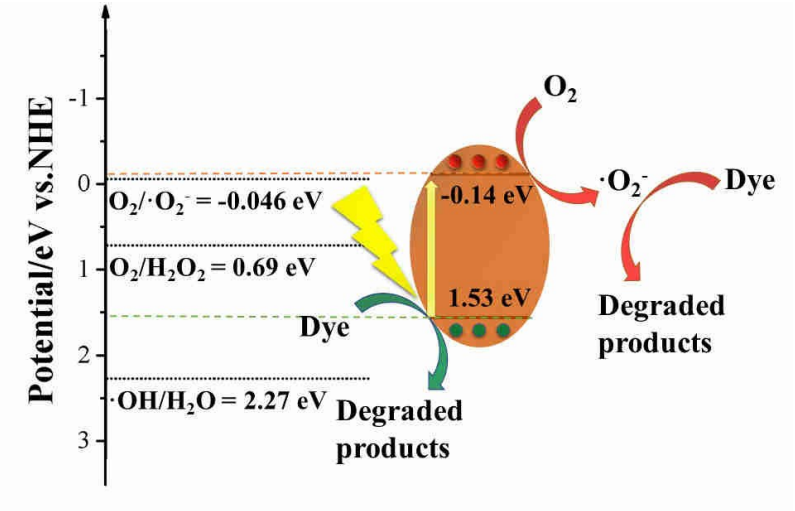

Fig. S7. Schematic illustration of photocatalytic mechanism of the photodegradation reaction with compound **1** as catalyst.

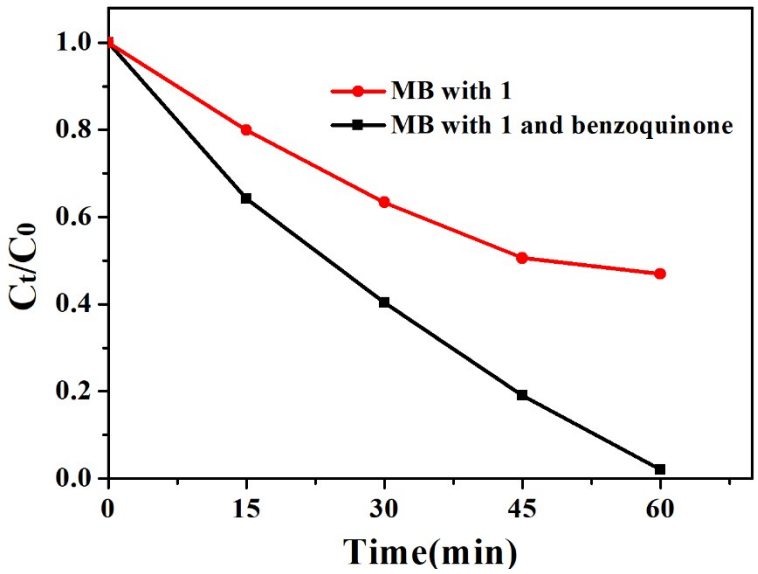

Fig. S8. Degeneration rates of MB under full spectrum light irradiation with compound **1** and compound **1** in the presence of benzoquinone as catalyst.

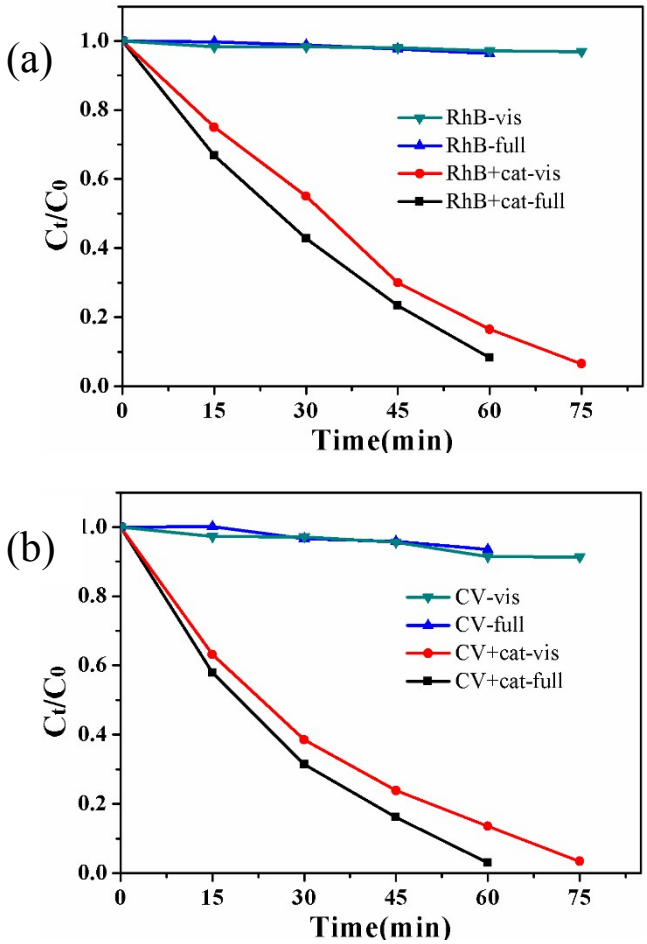

Fig. S9. Degeneration rates of (a) RhB and (b) CV with full spectrum and visible light irradiation. Initial concentrations: RhB (10 mg/L, pH= 6.8), CV (10 mg/L, pH= 6.6), cat. **1** (0.05 g).

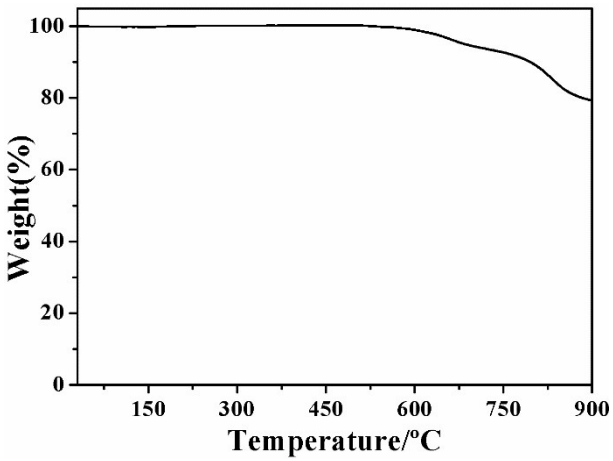

Fig. S10. TG Thermal gravimetric curve of compound **1**.

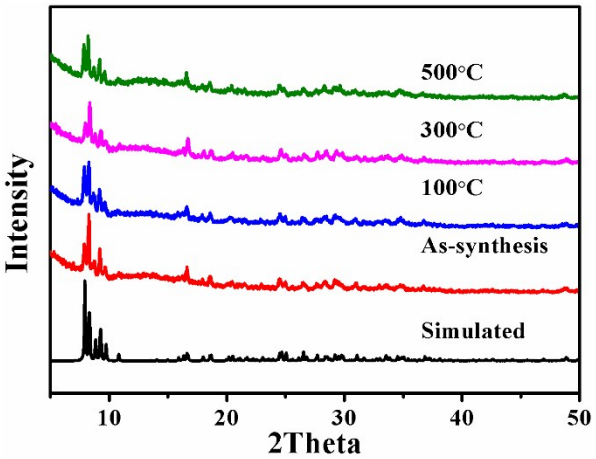

Fig. S11. Powder XRD patterns of **1** calcined at different temperatures.

Table S1

Photocatalytic capacity of various compounds toward MB.

Photocatalyst	Amount of catalyst (mg)	Time (min)	Degradation efficiency (%)	Irradiation	Ref.
$[Cu^{I}_{2}Cu^{II}(BBPTZ)_{6}][SiW_{12}O_{40}]\cdot 12H_{2}O$	50	90	97.5	Hg lamp	S2
$[Cu_{2}(2,2'\text{-tmbpt})_{2}(SiW_{12}O_{40})]\cdot 9H_{2}O$	30	120	41	125W Hg lamp	S3
$Cu_{2}(2,3'\text{-tmbpt})_{2}(SiW_{12}O4_{0})]\cdot 6H_{2}O$	30	120	54	125W Hg lamp	S3
$[Cu_{2}(2,4'\text{-tmbpt})_{2}(SiW_{12}O_{40})(H_{2}O)_{2]}\cdot 6.5H_{2}O$	30	120	58	125W Hg lamp	S3
$[Cu_{2}(4,4'\text{-tmbpt})_{2}(SiW_{12}O_{40})(H_{2}O)_{4}]\cdot 13.5H_{2}O$	30	120	74	125W Hg lamp	S3
$[H_{2}L][CuL][SiW_{12}O_{40}]\cdot 2H_{2}O$	50	90	89.5	125W Hg lamp	S4
$[Cu(L)(H_{2}O)]_{2}[SiW_{12}O_{40}]$	100	160	18.5	Xe lamp	S5
$[Cu_{4}(1,4\text{-ttb})_{4}(SiW_{12}O_{40})(H_{2}O)_{8}]\cdot 4H_{2}O$	15	180	82	Hg lamp	S6
$[Cu_{2}(btx)_{2}(C_{2}O_{4})][H_{2}SiW_{12}O_{40}]\cdot 12H_{2}O$	-	60	78.1	Visible light	S7

Table S2

Cycling runs in the degradation of MB solution (100 ml of 10 $mg \cdot L^{-1}$)

Photocatalyst	Compound **1**	
cycles	Full spectrum (60min)	Visible light (75min)
1	97.98%	96.74%
2	97.98%	96.02%
3	97.92%	95.93%
4	97.85%	95.91%
5	97.79%	95.71%
Photocatalyst	$[PBPY]_4[PW_{12}O_{40}]$ (reference sample)	
cycles	Full spectrum (60min)	Visible light (75min)
1	35.93%	26.93%
2	35.19%	27.05%
3	36.20%	26.74%
4	33.85%	26.42%
5	36.65%	26.53%
Photocatalyst	Without catalyst	
cycles	Full spectrum (60min)	Visible light (75min)
1	14.39%	11.46%
2	14.40%	11.45%
3	14.42%	11.47%
4	14.38%	11.45%
5	14.38%	11.42%

References

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