Supporting information

A water-insouble and visible-light induced polyoxometalate-based photocatalyst

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Physical Measurements.

Infrared (IR) spectra were recorded in the range 400–4000 cm^{-1} on a Perkin Elmer Spectrum using KBr pellets. X-ray powder diffraction (XRPD) was performed with a Rigaku DMAX 2500 diffractometer. Crystallite shapes were observed using transmission electron microscopy (TEM) (Jcol, 1200EX, Japan).The absorbency of the solution was analyzed by a Lambda35 spectrophotometer (Perkin–Elmer, USA). The BET areas of CuPW were calculated from nitrogen adsorption data determined at 77.5 K using an ASAP 2020 surface analyzer, and the pretreatment temperature was 180°C.

X-Ray crystallography (see ref. 9)

Structural measurements for complex **CuPW** was performed on a Mercury CCD (2x2 bin mode) diffractometer with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) at 20 ^{o}C. Empirical from equivalents were made from ψ- scan data using the program SHELXTL 97 at the data reduction stage along with the correction for Lorentz and polarization effects. The structure analysis was performed by using the Crystal Structure crystallographic program package. The structures of **CuPW** was solved by the direct methods (Wingx32, SIR- 92), and successive Fourier difference syntheses. The final structures were examined with the program PLATON and no additional symmetry element was detected. All non-hydrogen atoms were refined with anisotropic thermal parameters. Idealized positions of H atoms belonging to water molecules were located from Fourier difference maps and refined isotropically. The O-H distance between solvent oxygen atoms and hydrogen atoms were restrained in the normal range. The highest peaks 5.144 and the deepest hole -5.366 locate close to W4 with distance 1.31 Å and to W16 with distance 0.66 Å, respectively, and may be ascribed to the ghosts of the two heavy atoms. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html. Crystal parameters and other experimental details of the data collection for complex **CuPW** are summarized in Table S1. CCDC reference number **721722**.

Table S1. Crystal data and structure refinements for complex **CuPW**.

Complex	**CuPW**
Empirical formula	$C_{72}H_{58}Cu_6N_{12}O_{76}P_4W_{18}$
Formula weight	6121.72
Temperature (K)	293(2) K
Wavelength (Å)	0.71073 A
Crystal system	triclinic
Space group	P-1
a (Å)	14.368(3)
b (Å)	16.605(4)
c (Å)	26.351(7)
α(°)	80.594(10)
β (°)	80.948(9)
γ(°)	67.301(8)
Volume (Å^3)	5691(2)
Z	2
F(000)	5496
Crystal description	Prism
Crystal colour	Blue
Calculated density (mg/cm^3)	3.574
Crystal size (mm)	0.20 x 0.15 x 0.08
θ range for data collection (°)	2.04 to 27.39
Limiting indices	-18<=h<=18
	-21<=k<=20
	-34<=l<=34
Data/restraints/parameters	25265 / 10 / 1723
R(int) /R(sigma)	0.0505/0.0791
Goodness-of-fir on F^2	1.046
Final R Indices [I&lt2σ(I)]	R1 = 0.0672, wR2 = 0.0712
Indices(all data)	R1 = 0.1573, wR2 = 0.1630
Largest diff. peak and hole	5.144 and -5.366 e. Å^{-3}

[a] $R1=\sum\|F0\|-\|Fc\|/\sum|F0|$. [b] $wR2=\{\sum[w(F0^2-Fc^2)^2]/\sum[w(F0^2)^2]\}^{1/2}$

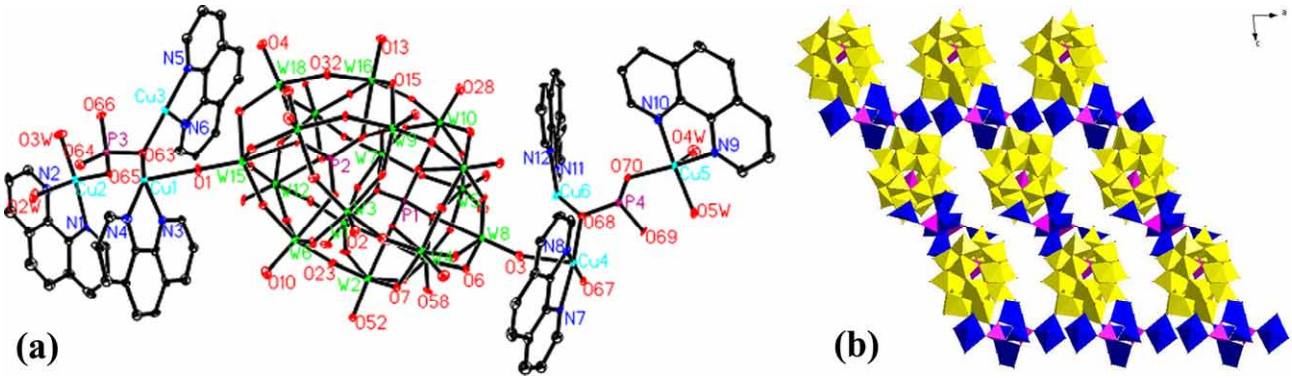

Figure S1. (a) Drawing of the asymmetric unit of photocatalyst single crystal. (b) View of the 2D layer constructed from Wells-Dawson type anions and hexacopper phosphate cations in the photocatalyst (see ref. 9).

Ref. 9. H. X. Yang, S. P. Guo, J. Tao, J. X. Lin, R. Cao, Cryst. Growth Des. 2009, 9, 4735.

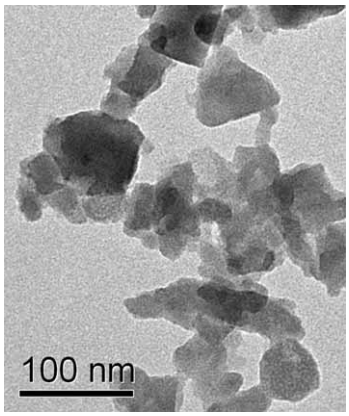

Figure S2. TEM image of the CuPW photocatalyst.

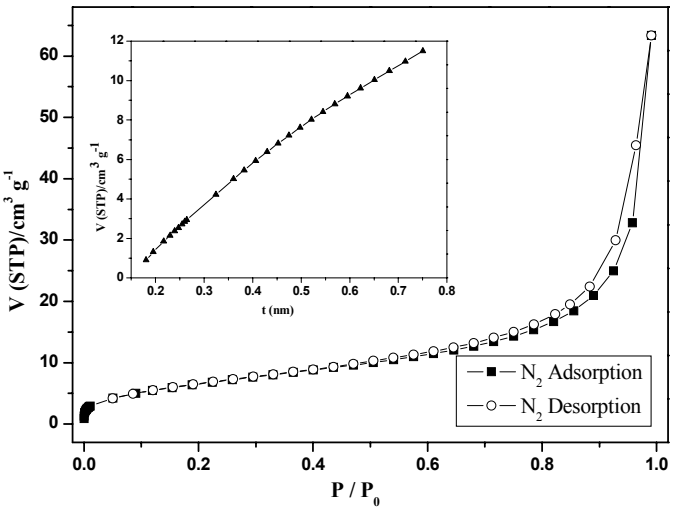

Figure S3. Gas sorption isotherms of **CuPW** photocatalyst for N_2 at 77K. Inset shows *V*-*t* curve of **CuPW** established using the *t* values determined on nonporous material.

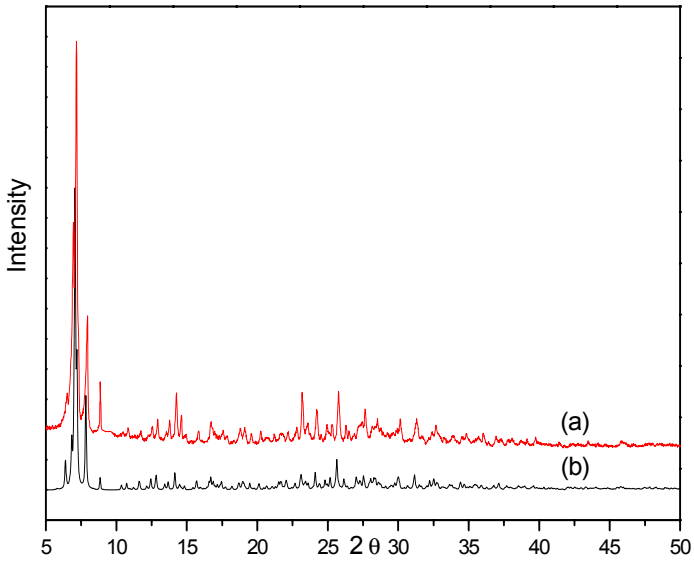

Figure S4. (a) Simulated XPRD patterns of the photocatalyst single crystal. (b) Experimental XPRD patterns of the photocatalyst powders.

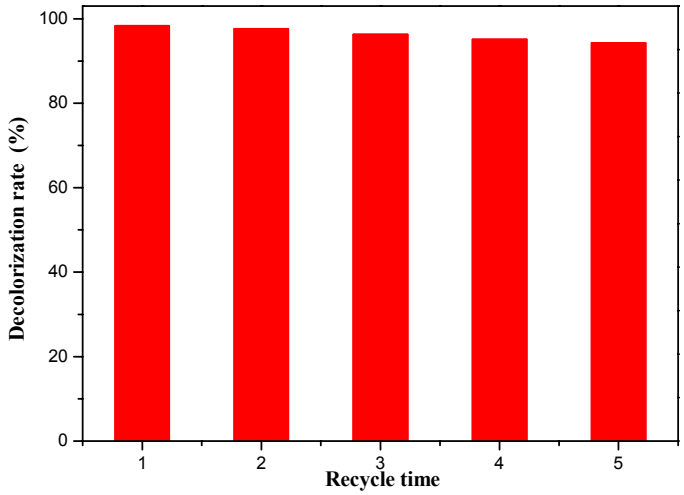

Figure S5. Effect of recycle time on the decolorization rate of methyl orange solution. Photocatalyst **CuPW,** 0.5g/l; MO concentration, 15 mg/l; H_2O_2, 1.5 mmol/l ; irradiation time; 3 hours.

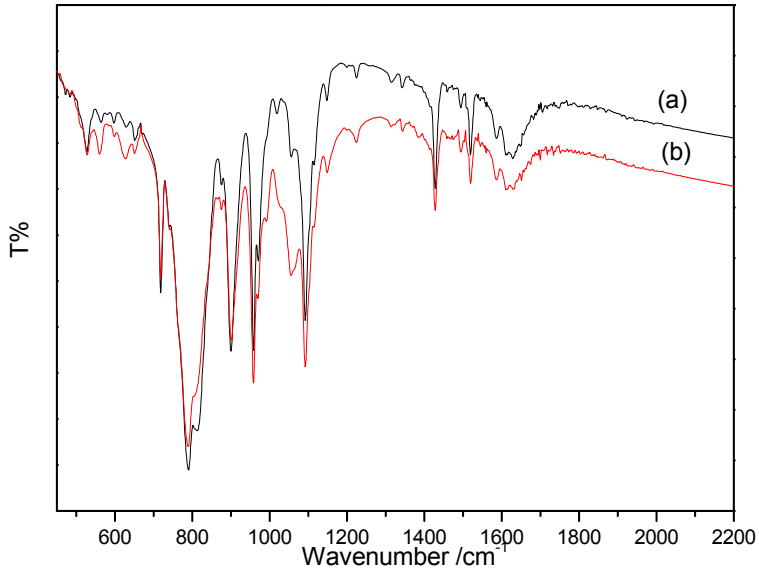

Figure S6. The IR curves of the photocatalyst before (a) and after (b) photocatalysis degradation for 5 cycles.