Supporting Information

for

Pt/POMs/TiO_2 composite nanofibers with enhanced visible-light photocatalytic performance for environmental remediation

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2.1 Chemicals and materials

All chemicals were purchased from Aladdin Chemical Co., Ltd., China. They were used without any further purification.

2.2 Preparation of PMo_{12}/TiO_2 nanofiber composites

Typically, 0.7 g of Polyvinylpyrrolidone (PVP, Mw ≈1,300,000) was dissolved in 15 mL of ethyl alcohol with vigorous stirring for 3 h to form a clear solution. 0.2 mL of acetic acid and 0.4 mL of tetrabutyl titanate (TBT) were added with stirring. Then calculated amount of $H_3PMo_{12}O_{40}$ (20 mol% relative to TBT) was added into the above solution, and it was stirred to form settled solution. The mixed solution was put into a 20 mL plastic syringe for electrospinning. A 15 kV electrical potential was applied with an electrode distance of 15 cm, and an aluminum foil was used as collector. The solution was ejected at a rate of 0.5 $mL\cdot h^{-1}$ controlled with a syringe pump. The obtained nanofibers were calcined at 450°C for 5 h with a heating rate of 2°C min^{-1} in air. Similarly, the pure TiO_2 nanofibers without PMo_{12} were also prepared. **2.3 Characterization**

X-Ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus using filtered Cu Kα radiation (λ= 1.54056 Å). The morphologies of as-obtained photocatalysts were characterized with a JEOL JSM 4800F SEM coupled with an energy-dispersive X-ray (EDX) spectrometer. TEM (transmission electron microscopy) and HRTEM images were measured on a JEM-2100F microscope operated at 200 kV. The UV-vis diffuse reflectance spectra (DRS) were collected on a Shimadzu UV-2600 UV-vis spectrophotometer. X-ray photoelectron spectrum (XPS) analyses were performed on an ESCALABMKII spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. The BET specific surface areas were measured on a Micrometrics ASAP-2020 Automatic specific surface area and porous physical adsorption analyzer. The photoluminescence (PL) spectra were performed at room temperature on a Hitachi F-4600 spectrophotometer with an excitation wavelength 380 nm. IR spectra were recorded on an Alpha Centaurt FTIR spectrophotometer as KBr pellets in the range of 600–4000 cm^{-1} at room temperature.

2.4 Photoelectrochemical measurements

The photocurrent measurements were carried out on a CHI660E Electrochemical Workstation (Shanghai Chenhua Instrument Corp., China) with a conventional three-electrode configuration in a quartz cell. A Pt foil and Hg/Hg_2Cl_2 electrode were served as the counter electrode and reference electrode, respectively. A 300 W Xe lamp (CEL-HXF300, AULIGHT) was used as the light source. A 0.5 M Na_2SO_4 aqueous solution was applied as the electrolyte. Typically, the working electrodes were prepared as follows: 50 mg of the as-prepared photocatalysts were dispersed into 5 mL ethanol with sonication for 30 min to make a slurry. Next, 0.5 mL of the solution was uniformly dropped onto a 1×4 cm^2 FTO glass substrate. The working electrode prepared with the sample has an active area of *ca.* $3cm^2$. Finally, the prepared electrodes were dried at 60 ^oC for 3h to obtain the working electrodes.

2.5 Electrochemical impedance spectroscopy (EIS) measurements

The EIS measurements was conducted using a Model CS350 electrochemistry station (Wuhan CorrTest Instrument Corporation) in 0.1 M KCl solution containing 5 mM $Fe(CN)_6^{3-/4-}$ with a frequency range from 0.01 Hz to 10 kHz at 0.2 V. The EIS data were recorded using a conventional three-electrode system, where samples on FTO glass with an active area of ca. 1.0 cm^2 were prepared as the working electrode, a Pt wire as counter electrode and Ag/AgCl as a reference electrode, respectively.

2.6 Photocatalytic degradation of MO and TC

The photocatalytic activity of as-prepared photocatalysts were evaluated *via* the photodegradation of MO and TC applying a glass vessel with a water-cooling jacket as reactor and a 300 W xenon-lamp (CEL-HXF300, AULIGHT) with a 420 nm cut-off filter as illuminant. The irradiation distance between the mixture solution and the lamp was about 15 cm. Typically, 20 mg of $Pt/PMo_{12}/TiO_2$ composites were dispersed into 20 mL of MO (20 ppm) aqueous solution (pH=1) or 20 mL of tetracycline solution (40 ppm). Before light irradiation, the mixture solution was stirred in darkness for a period of time to obtain the saturated absorption of MO/TC molecules onto the catalysts, then above solution was illuminated under visible-light irradiation. About 1 mL of the suspension was withdrawn at given irradiation time intervals, centrifuged subsequently, and measured at the maximum absorption wavelength of 506 nm for MO and 357 nm for TC by a Shimadzu UV-2600 UV-vis spectrophotometer.

2.7 Photocatalytic reduction of Cr(VI)

Typically, 20 mg of photocatalyst was added into an aqueous solution containing 20 mL of $K_2Cr_2O_7$ solution (160 ppm) and 20 mL isopropanol. Similarly, the suspensions were stirred in the dark for 0.5 h to obtain absorption-desorption equilibrium between the $K_2Cr_2O_7$ and the catalyst surface prior to irradiation. Then above mixture was stirred and exposed to the visible-light irradiation. every 10 min, about 2 mL of suspension was taken out, centrifuged, and measured at a maximum absorption wavelength of 365 nm.

2.8 Active species trapping experiment

To detect the active species in the photocatalytic process of MO and TC, triethanolamine (TEOA), isopropanol (IPA) and 4-hydroxy-TEMPO were employed as hole (h^+) scavenger, hydroxyl radical ($\cdot OH$) scavenger and superoxide radical ($\cdot O_2^-$) scavenger, respectively. Typically, 20 mg of $Pt/PMo_{12}/TiO_2$ photocatalyst with different scavengers were dispersed into 20 mL of 20 ppm MO aqueous solution or 20 mL of tetracycline solution (40 ppm), and the following processes were similar to the MO/TC photodegradation process.

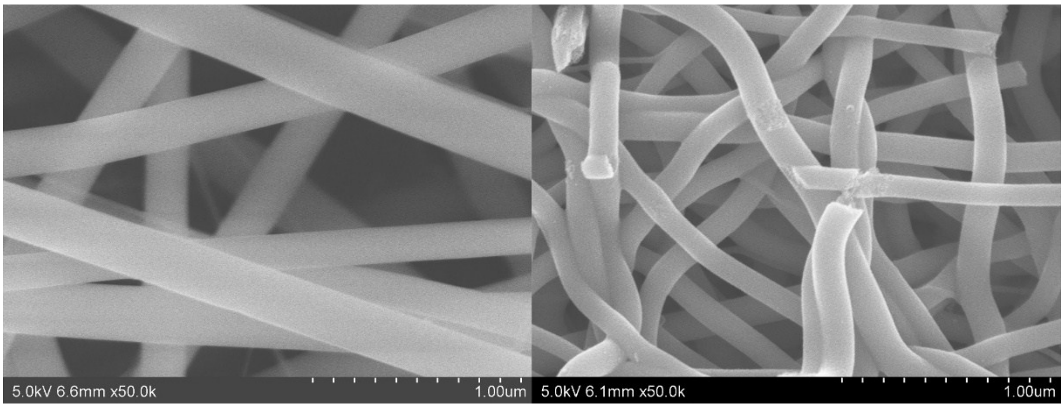


Fig. S1 The SEM images of as-prepared $PVP/PMo_{12}/TiO_2$ nanofibers (20 mol% Mo/Ti) before calcination (a) and after calcination at 450 °C(b).

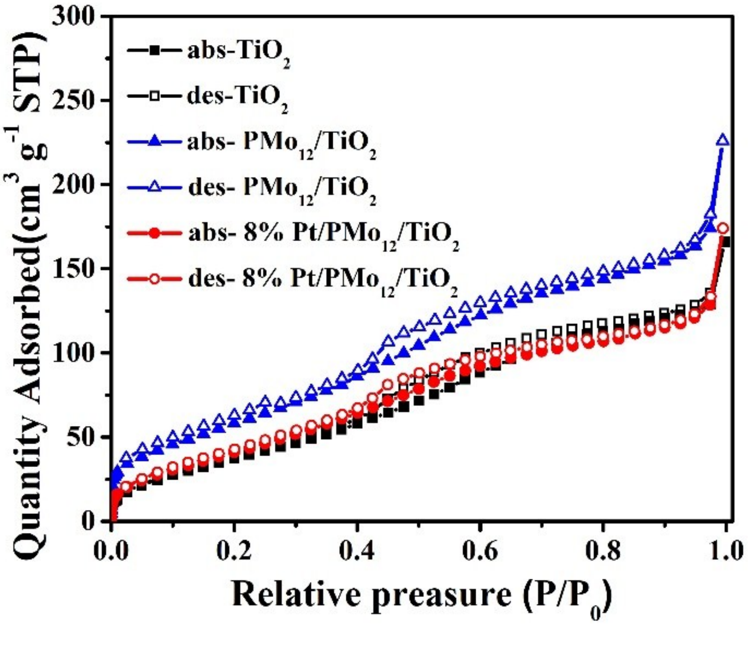


Fig. S2 Nitrogen adsorption−desorption isotherms of TiO_2, PMo_{12}/TiO_2 and $8\%Pt/PMo_{12}/TiO_2$ samples. The BET surface areas of TiO_2, PMo_{12}/TiO_2 and $8\%Pt/PMo_{12}/TiO_2$ are 158.692, 225.863 and 189.854 $m^2 \cdot g^{-1}$, respectively.

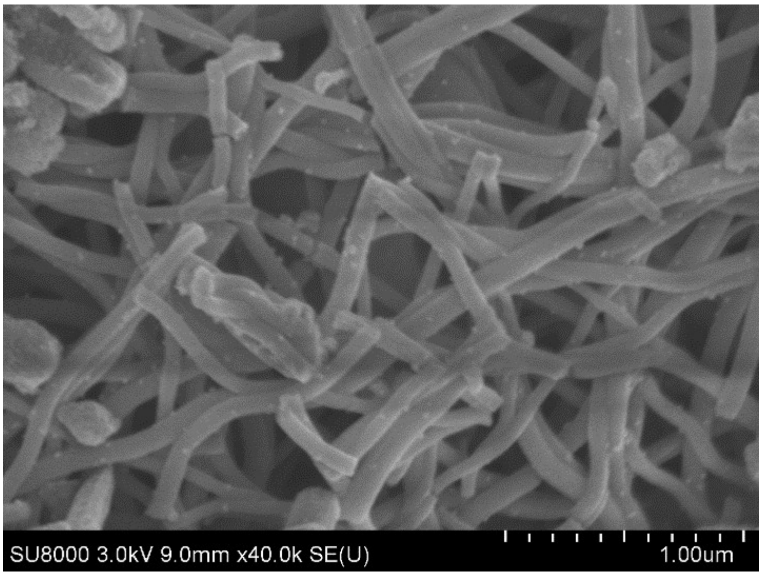


Fig. S3 The SEM images of 8%Pt/PMo_{12}/TiO_2 composite nanofibers.

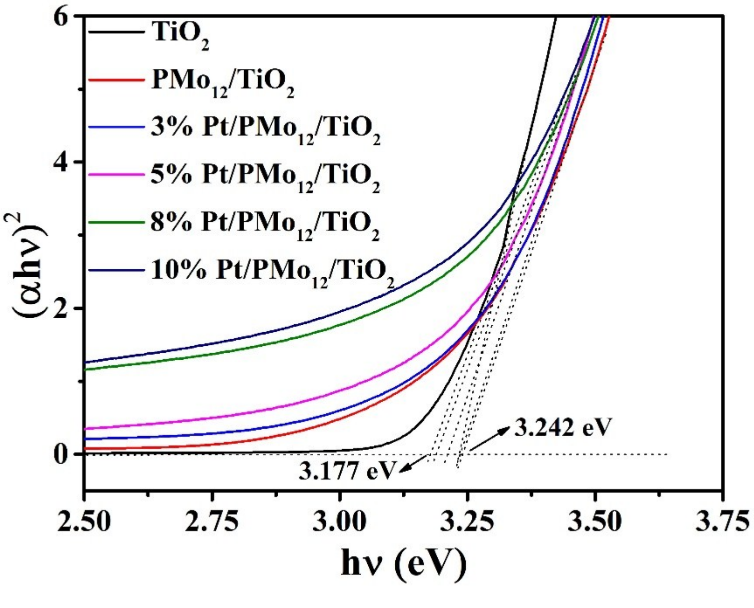


Fig. S4 Calculated band gap energy by the plot of $(\alpha h\nu)^2$ *vs* $h\nu$ for different samples.

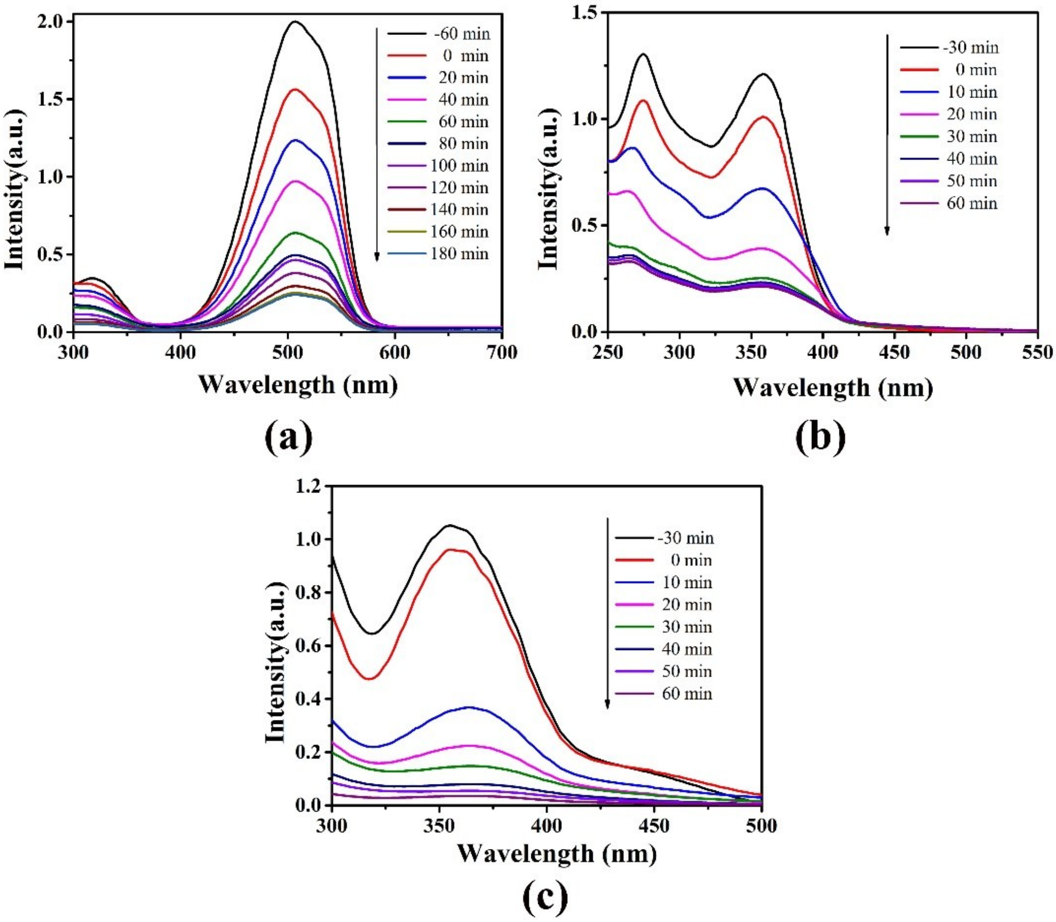


Fig. S5 The profiles of photocatalytic degradation MO(a); TC(b); photoreduction of Cr(VI) (c) by 8%Pt/PMo_{12}/TiO_2 under visible-light irradiation ($\lambda > 420$ nm).

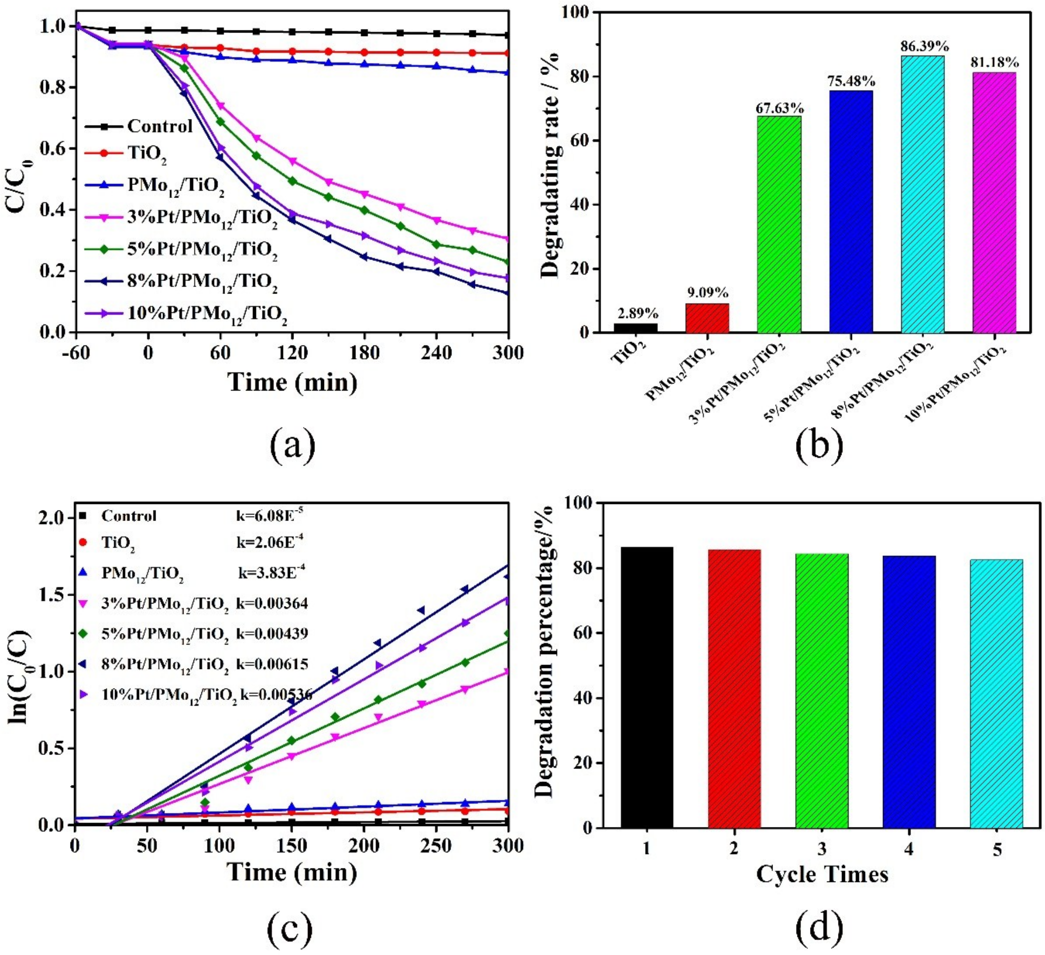


Fig. S6 (a) The profiles of photodegradation of Bisphenol A using different photocatalysts under visible-light irradiation (λ > 420 nm). (b) The degradation rate of Bisphenol A for different photocatalysts within 300 min.(c) The corresponding reaction rate constant *k* of removal of Bisphenol A.(d) Cycle runs in the photocatalytic degradation of Bisphenol A using 8%Pt/PMo_{12}/TiO_2. The experiment conditions: 50 mg of different photocatalyst and 20 mL of Bisphenol A solution (10 ppm) was used in photocatalysis process. The maximum absorption wavelength of Bisphenol A is about 276 nm.

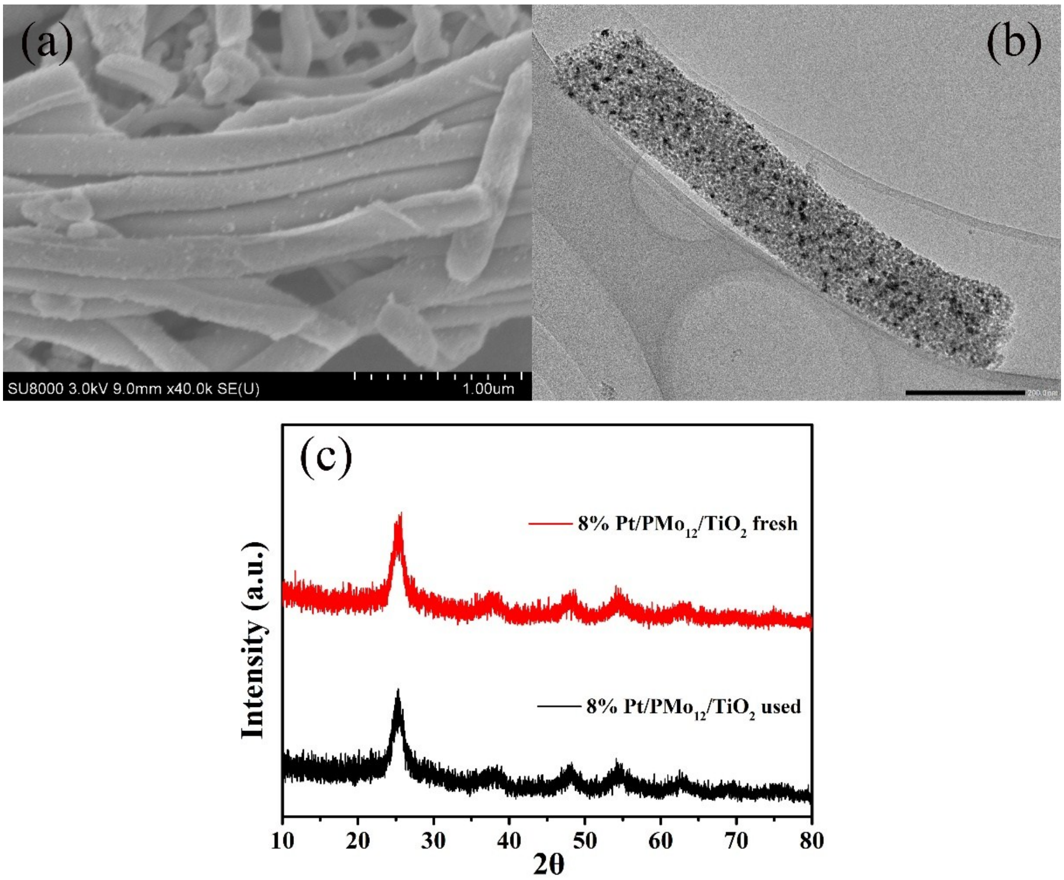


Fig. S7 The SEM, TEM and XRD data of 8%Pt/PMo_{12}/TiO_2 sample after the degradation process.

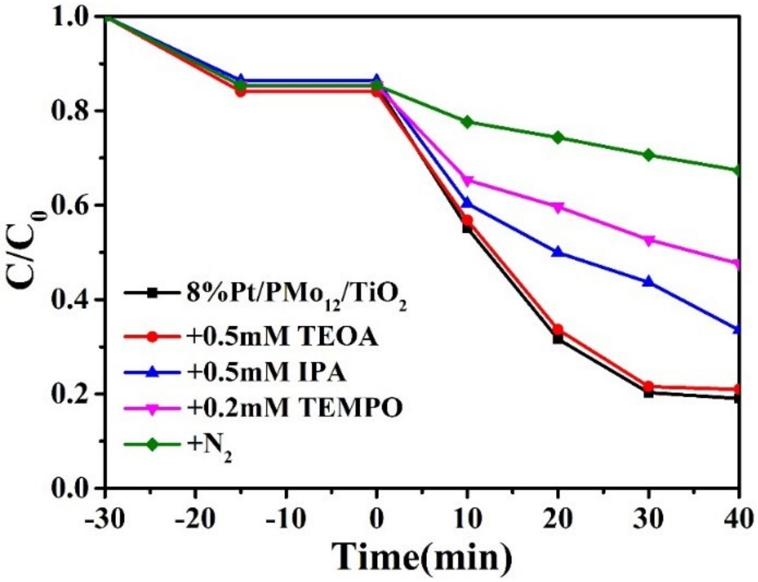
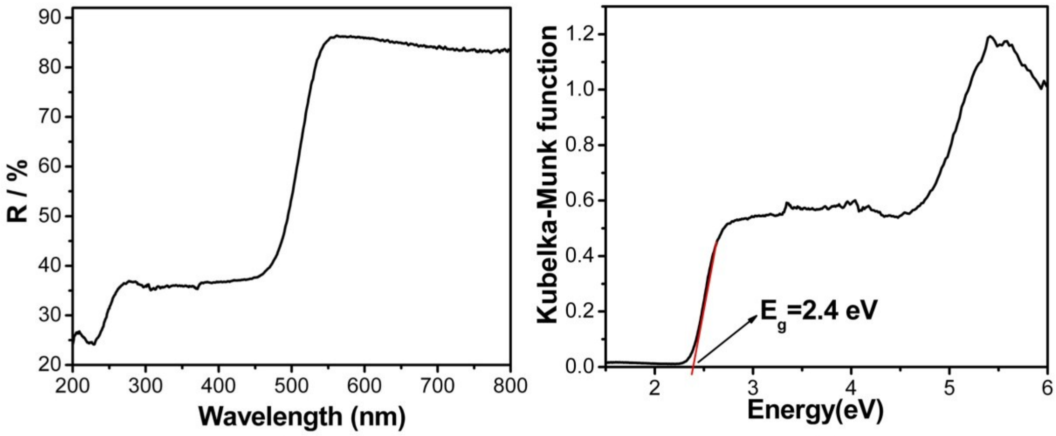


Fig. S8 The effects of various scavengers and N_2 on the photocatalytic degradation of TC for 8%Pt/PMo_{12}/TiO_2.

The HOMO and LOMO calculation of $H_3PMo_{12}O_{40}$



(a) (b)

Fig. S9 (a) UV-vis diffuse reflection spectrum and (b) plot of K-M function against energy *E* of $H_3PMo_{12}O_{40}$.

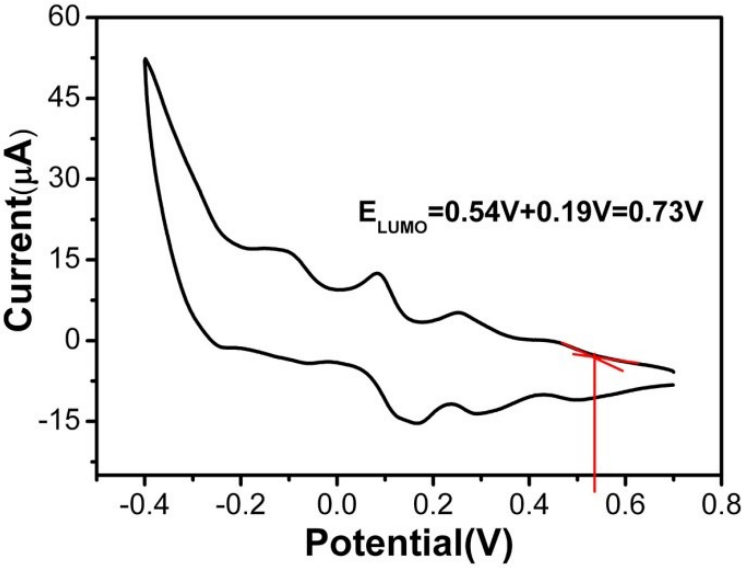


Fig. S10 The cyclic voltammograms of $H_3PMo_{12}O_{40}$. Cyclic voltammograms were recorded on a CHI660E Electrochemical Workstation, using glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl reference electrode. Electrolyte is 0.1M Na_2SO_4/H_2SO_4 aqueous solution (pH=1.5), the concentration of $H_3PMo_{12}O_{40}$ is 1 mmol/L).

The LUMO and HOMO values of PMo_{12} are obtained *via* cyclic voltammetry and UV-vis diffuse reflectance spectra methods. The band gap E_g of PMo_{12} was estimated to be 2.4 eV from the K-M function (**Fig. S9**), and the LUMO of PMo_{12} is about 0.73 V according to result of cyclic voltammetry (**Fig. S10**). Thus, the HOMO of PMo_{12} is calculated to be 3.13 V ($E_{(HOMO)}=E_{(LUMO)}+E_g$).

Table S1 The photodegradation activity comparison of 8%Pt/PMo_{12}/TiO_2 with PMo_{12}/TiO_2/Ag-5.41.[1]

Sample	Pollutant	MO	TC	Cr
8%Pt/PMo_{12}/TiO_2	Time	180 min	40 min	60 min
	Removal	88.06%	80.95%	96.43%
PMo_{12}/TiO_2/Ag-5.41	Time	120 min	60 min	60 min
	Removal	100%	80%	79.10%

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Table S2 he comparison of TC degradation activity of Pt/PMo_{12}/TiO_2 with previous literatures

Photocatalyst	Concentration ($mg\ L^{-1}$)	Dosage ($g\ L^{-1}$)	Time (min)	Removal (%)	Light source	Reference
2.5% Ag/$AgIn_5S_8$	10	0. 3	120	95.3	300 W Xe lamp; $\lambda > 400$ nm	1
10% Ag@AgI/V_I-BOI	20	0.3	60	86.40	300 W Xe lamp; $\lambda > 420$ nm	2
N-TiO_2 /rGO	10	1.0	60	98	300 W Xe lamp; $\lambda > 400$ nm	3
N-CNT/mpg-C_3N_4	20	1.0	240	67.1	300 W Xe lamp; $\lambda \geq 400$ nm	4

CQDs/g-C_3N_4	10	0.5	240	78.6	250 W Xe lamp; $\lambda > 420$ nm	5
GQDs/mpg-C_3N_4	20	1.0	120	65	300 W Xe lamp; $\lambda \geq 400$ nm	6
h-BN/g-C_3N_4	10	1.0	60	79.7	300 W Xe lamp; $\lambda \geq 400$ nm	7
Ag10-CN-Na_2SO_4	10	0.5	60	70	350 W Xe lamp; $\lambda > 420$ nm	8
10 wt% g-C_3N_4/BOC	20	0.5	360	90	1000WXe lamp; $800 > \lambda > 290$	9
TiO_2-Ag@TiO_2	20	0.1	120	75	300 W Xe lamp; $\lambda > 420$ nm	10
Bi_2WO_6/$CuBi_2O_4$	15	0.5	60	94	300 W Xe lamp; $\lambda > 400$ nm	11
Co_3O_4@CoO/g-C_3N_4	10	0.6	120	97	500 W Xe lamp	12
CuO/ZnO n (Cu/Zn) =0.1	40	0.3	60	88.5	300 W Xe lamp; $780 \geq \lambda \geq 400$	13
Bi_2WO_6/BiOBr W/Br= 1:2	10	0.2	150	93	300 W Xe lamp; $\lambda \geq 420$ nm	14
8%Pt/PMo_{12}/TiO_2	**40**	**1.0**	**40**	**80.95**	**300 W Xe lamp; $\lambda \geq 420$ nm**	**This work**

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Table S3 he comparison of Cr(VI) reduction activity of $Pt/PMo_{12}/TiO_2$ with previous literatures

Photocatalyst	**Concentration (mg L^{-1})**	**Dosage (g L^{-1})**	**Time (min)**	**Removal (%)**	**Light source**	**Reference**
$Cu_2In_2ZnS_5$ /Gd_2O_2S:Tb 1wt.%	80	1.0	210	93	300W Xe lamp(λ>400 nm)	1
			180	92	300W Xe lamp(λ>800 nm)	
			60	91	A 500 W mercury lamp	
ZIF-8@CuPd 5wt%	20	0.2	60	89.2	Solar light simulator	2
5% DE-Bi_2S_3	160	1.0	240	70.2	300W Xe lamp(λ>400 nm)	3
1%PANI/$MgIn_2S_4$	50	1.0	50	97	300W Xe lamp(λ>420 nm)	4
TiO_2 -WO_3(2.5%)	100	1.0	120	90	UV-illumination (300 W)	5
$MoSe_2$/CdSe	150	1.0	80	95	780 nm >λ>400 nm	6
SnS_2/SnO_2 TOS-C_4	50	1.0	30	100	λ> 420 nm	7
15-PPy/SnS_2	50	1.0	120	100	300W Xe lamp	8
Ag/Bi_4O_7 /CNNS-40	50	0.3	60	98	300 W Xe lamp; 420 nm< λ < 780 nm	9
MoS_2NF	10	0.25	180	72.77	500W Xe lamp; λ>420 nm	10
Ag/BiOCl	10	1.0	180	65	500 W tungsten light lamp; (λ> 400 nm)	11
Bi_2O_3	40	0.8	120	70	500 W Xe lamp	12

					(λ> 400 nm)	
8%Pt/PMo_{12}/ TiO_2	**80**	**0.5**	**60**	**96.43**	**300 W Xe lamp; λ ≥ 420 nm**	**This work**

Reference:

(1) X.J. Liu, B.B. Liu, L. Li, Z.H. Zhuge, P.B. Chen, C. Li, Y.Y. Gong, L.Y. Niu, J.Y. Liu, L. Lei, C.Q. Sun, *Appl. Catal. B: Environ.*, 2019, **15**, 82-90.

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