Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Polyoxometalates-tuning photocatalytic performance of g-C_3N_4 under visible light

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Experimental Section

Chemicals and materials

Melamine($C_3H_6N_6$, AR grade, MW=126.12g mol^{-1}), $H_4SiW_{12}O_{40}\cdot 26H_2O$(AR grade, MW= 2878.17 g mol^{-1}), $H_3PW_{12}O_{40}\cdot xH_2O$(AR grade, MW= 2880.05 g mol^{-1}),$H_3PMo_{12}O_{40}\cdot xH_2O$(AR grade, MW=1825.25 g mol^{-1}),methanol(CH_4O, AR grade, MW=32.04 g mol^{-1}), methyl orange($C_{14}H_{14}N_3NaO_3S$, AR grade, MW=323.77 g mol^{-1}) were purchased from Aladdin Chemistry Co. Ltd. All chemicals were used without further purification. Double distilled water was used in the catalyst preparation and subsequent catalytic tests.

Synthesis of g-C_3N_4

The graphitic-carbon nitride (g-C_3N_4) samples were prepared by directly calcining melamine in air. Typically, 20 g of melamine powder was put into a alumina crucible with a cover, then heated at a rate of 5 °Cmin^{-1} to reach a temperature of 550°C and keep this temperature for 3h in air. After the sample was cooled naturally to room temperature, the resulting powder was grinded in the agate mortar and used in subsequent studies.

Preparation of POM/C_3N_4 hetero-nanostructured photocatalysts

In a typical procedure, 0.5g of C_3N_4 power was added into 20mL methanol and then the centrifugal tube was placed in an ultrasonic bath for 10 hours to completely disperse the C_3N_4. The desired amount of $H_4SiW_{12}O_{40}\cdot 26H_2O$ (0.005g, 0.01g, 0.05g, 0.1g and 0.15g), $H_3PW_{12}O_{40}\cdot xH_2O$ (0.05g) and $H_3PMo_{12}O_{40}\cdot xH_2O$ (0.05g) was dissolved in 10mL methanol. The above POM solution was successively added into the acidified C_3N_4 suspension. After stirring for 2 hours, the suspension was centrifuged at 10000 rpm followed by a thorough washing with methanol to remove the excess POM anions. After the solid dried at 70℃ for 10 hours, the dry simple was put into an alumina crucible with a cover and heated at a rate of 2 $℃min^{-1}$ to 200℃ and calcined 4 hours. The final products are named as SiW_{12}/C_3N_4-1, SiW_{12}/C_3N_4-2, SiW_{12}/C_3N_4-3, SiW_{12}/C_3N_4-4, $SiW_{12}/$ C_3N_4-5, PW12/C_3N_4 and PMo_{12}/C_3N_4, respectively (the mass of POM were 0.005g, 0.01g, 0.05g, 0.1g, 0.15g, 0.05g and 0.05g, respectively).

Characterization

X-ray diffraction (XRD) patterns of samples were scanned on the Bruker AXS D8 Focus using filtered Cu-Kα radiation (λ= 1.54056 Å). The FTIR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on an Alpha Centaur FT/IR spectrometer. UV−vis diffuse reflectance spectra (DRS) of the samples were collected on a UV-2600 UVvis spectrophotometer (Shimadzu), with an integrating sphere, and BaSO4 was used as the reference. A JEOL JSM 4800F SEM coupled with an energy-dispersive X-ray (EDX) spectrometer was used to characterize sample morphology. High-resolution TEM (transmission electron microscopy) images were obtained via an FEI Tecnai G2 operated at 200 kV. XPS were carried out on an ESCALABMKII spectrometer with an Al-Ka (1486.6 eV) achromatic X-ray source. The PL spectra were recorded on a VarianCary Eclipse500 fluorescence spectrophotometer. The excitation wavelength was 250 nm.

Photocatalytic activity

The photocatalytic activities of the as-prepared samples were evaluated by degradation of methyl orange (MO) solution using a 300 W Xe lamp(Peking ceaulight, CEL-HXF300) with a 400 nm cut-off filter as the light source and a self-made glass vessel with a water-cooling jacket as reactor. The irradiation distance between the lamp and the mixture solution was 15 cm. Fifty milligrams of photocatalyst were dispersed in 50 mL 20 ppm of MO solution (pH =2). Prior to irradiation, the suspensions were magnetically stirred for an hour in the dark to ensure that the adsorption–desorption equilibrium between the organic molecules and the catalyst surface was reached. At given time intervals, 2.0 mL of the reaction solution was taken, centrifuged, and measured on a XinMao UV-vis spectrometer UV-7502 at a maximum absorption wavelength of 506 nm. The SiW_{12}/C_3N_4-3 (20 mg) powder loaded with 1.0 wt% Pt (H_2PtCl_6), triethanolamine (TEOA) (30 mL) and deionized water (90 mL) was added into flask. The resulting mixture was ultrasonicated 30 min to obtain a well-dispersed photocatalyst suspension. After complete removal of air, the suspension was irradiated under a 300 W Xe light source.

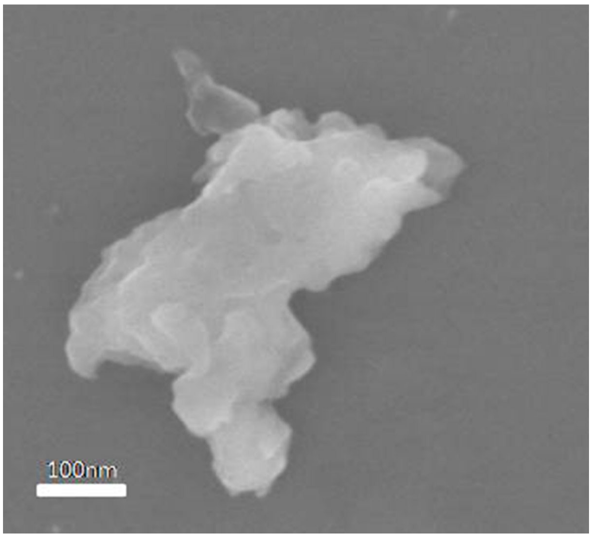


Fig S1. The SEM image of SiW_{12}/C_3N_4-3.

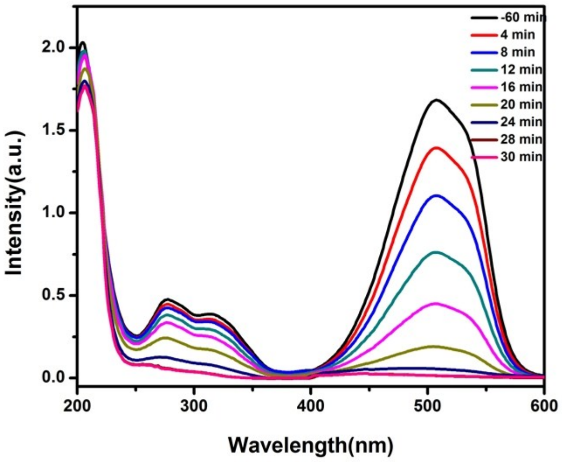


Fig.S2. UV-Vis spectral changes during the photodegradation of MO mediated by SiW_{12}/C_3N_4-3 under visible light irradiation.

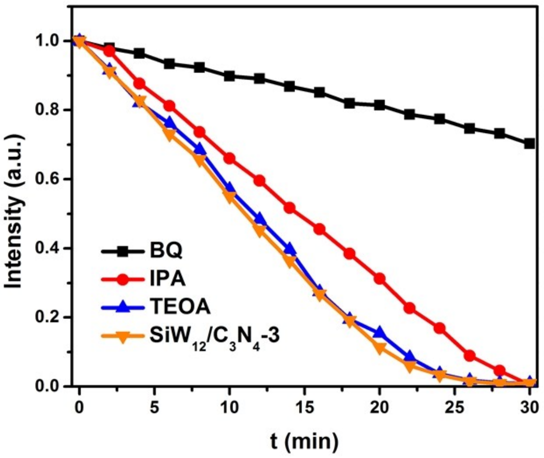


Fig.S3 Photocatalytic degradation of MO over SiW_{12}/C_3N_4-3, photocatalyst alone and with the addition of IPA or BQ and TEOA.

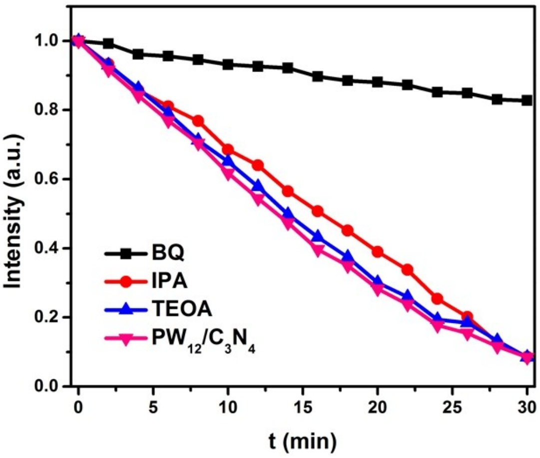


Fig.S4 Photocatalytic degradation of MO over PW_{12}/C_3N_4 photocatalyst alone and with the addition of IPA or BQ and TEOA.

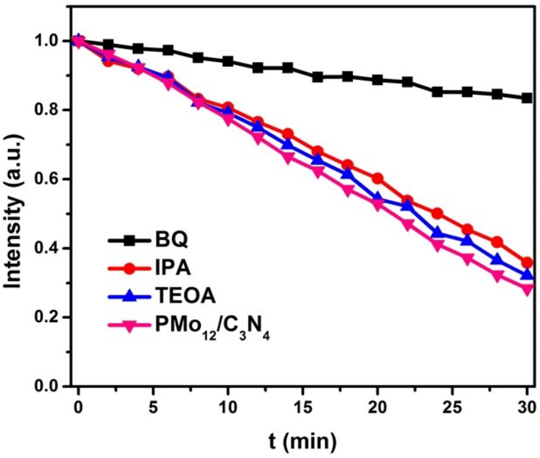


Fig.S5 Photocatalytic degradation of MO over PMo_{12}/C_3N_4 photocatalyst alone and with the addition of IPA or BQ and TEOA.

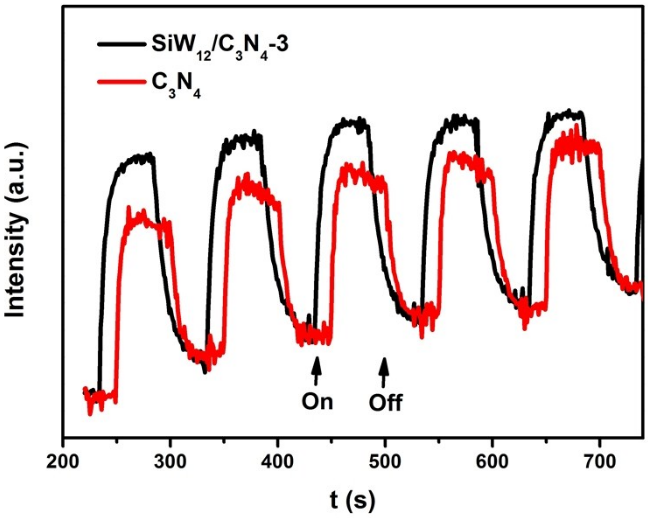


Fig.S6. Photocurrent response test of SiW_{12}/C_3N_4-3 and C_3N_4.

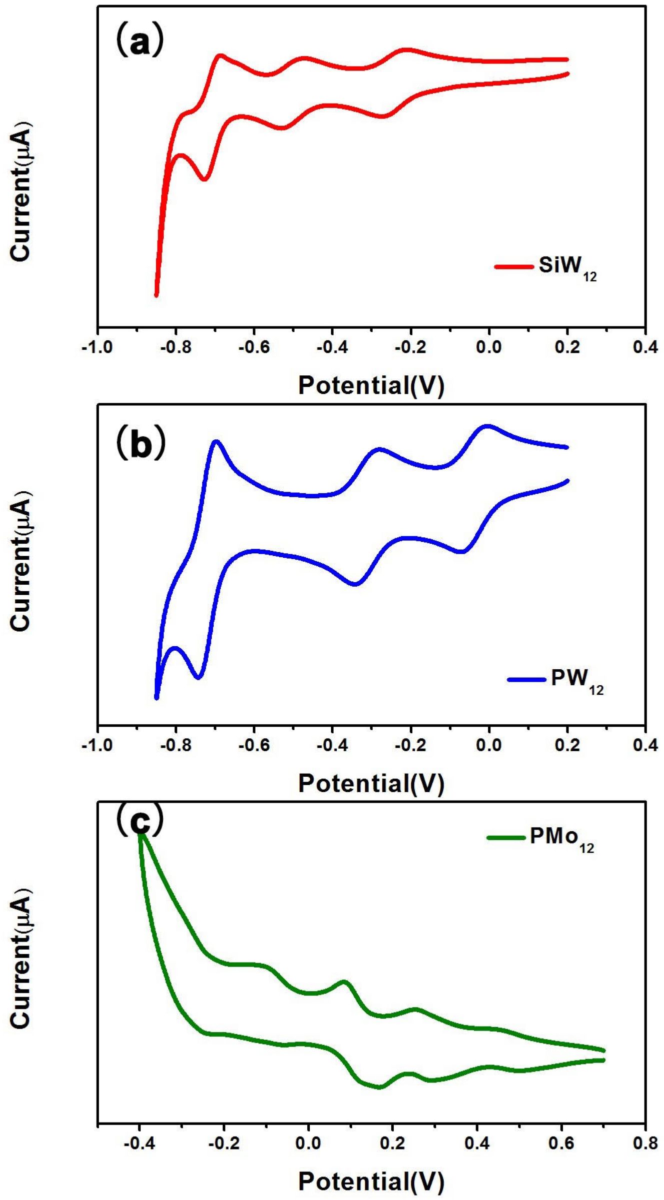
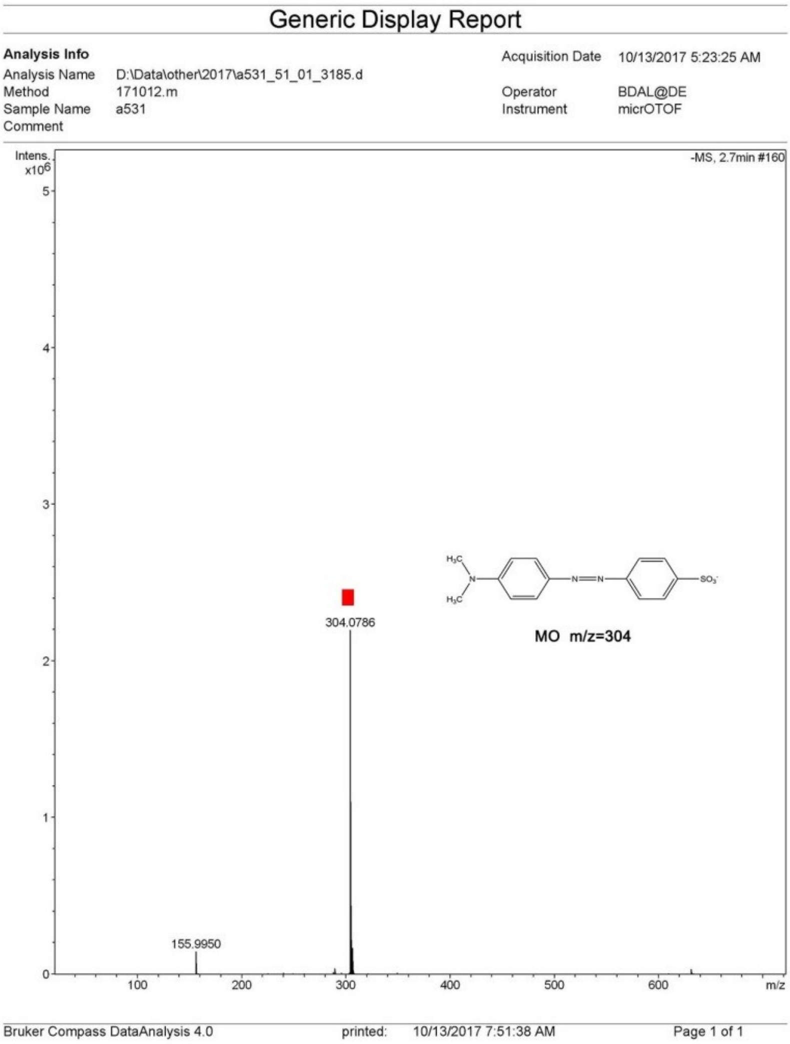


Fig.S7. The CV curves of Keggin POMs (a) SiW_{12}, (b) PW_{12} and (c) PMo_{12}. Cyclic voltammograms were recorded on a CHI660E Electrochemical Workstation, using glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl reference electrode. Electrolyte is 0.1M Na_2SO_4/H_2SO_4 aqueous solution (pH=1.5), the concentration of POM is 1 mmol/L.



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Instrument micrOTOF

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Fig. S8. The HPLC/MS image of MO without light irradiation. HPLC/MS identified intermediate products yielded during the process of visible-light photocatalytic degradation of MO. C_{18} column, UV detector (λ= 227nm), and acetonitrile/water (60/40, v/v) was used as a mobile phase at a flow rate of 1.0 mL/min.

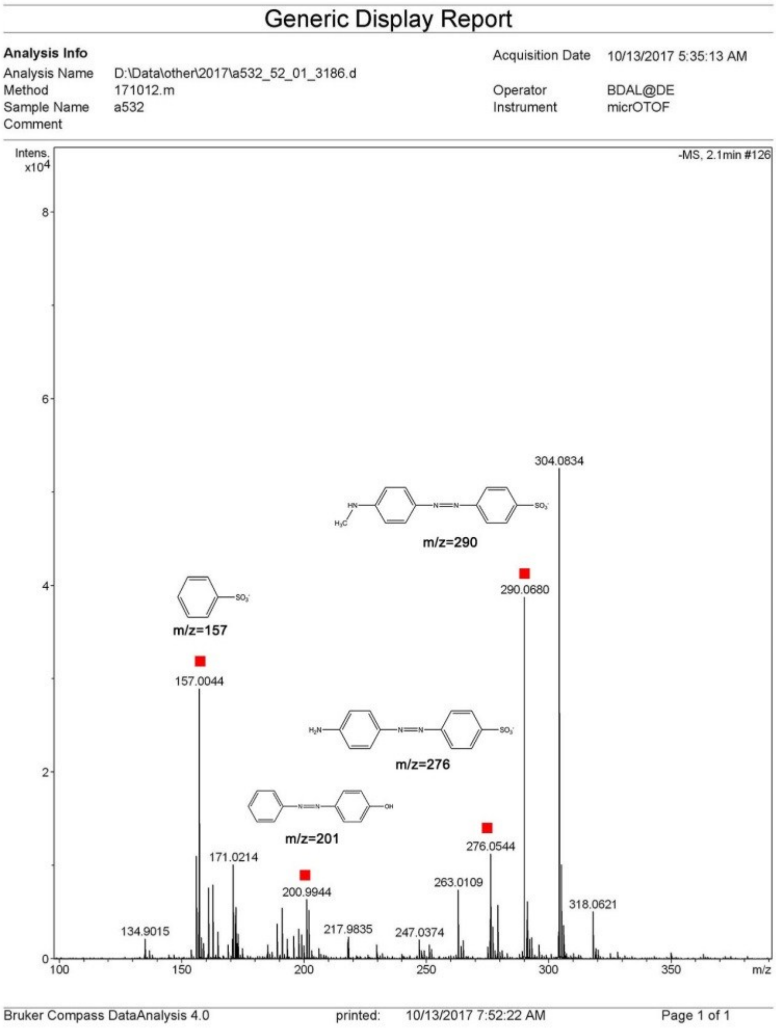

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Fig. S9. The main intermediate products generated during the process of photocatalytic degradation of MO using $SiW_{12}/g\text{-}C_3N_4$ as catalysts after 15 min visible light irradiation.

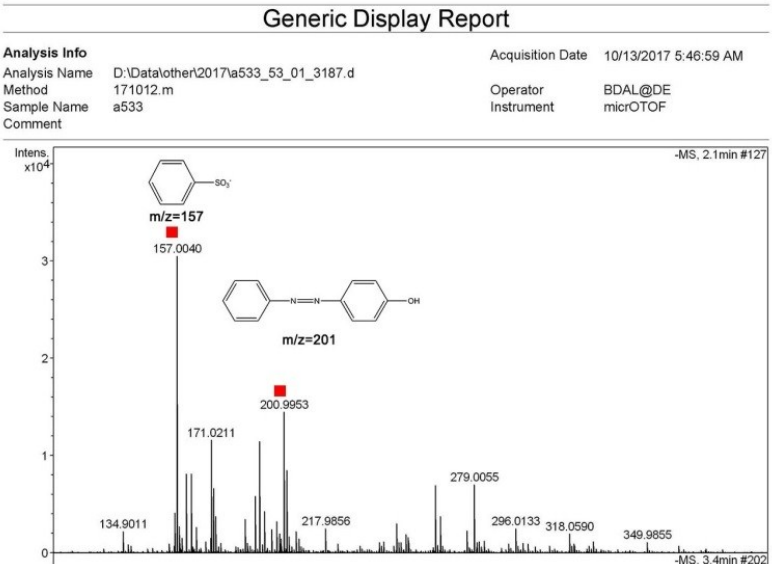

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Fig. S10. The main intermediate products generated during the course of photocatalytic degradation of MO over $SiW_{12}/g\text{-}C_3N_4$ after 30 min visible light irradiation.

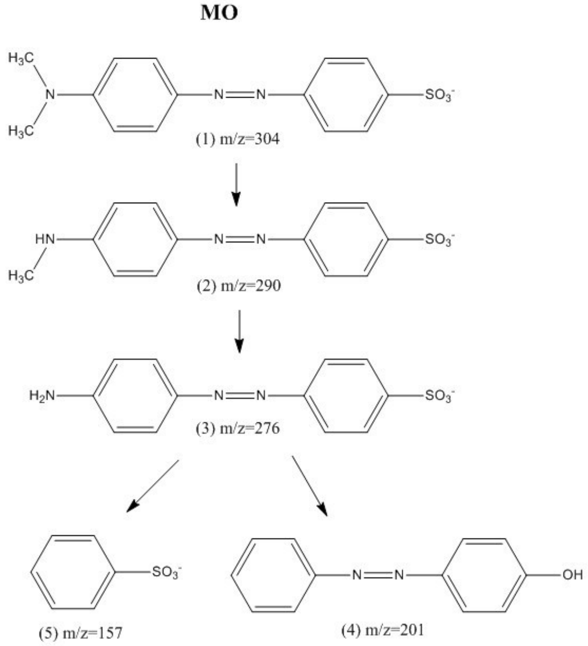


Fig. S11. Proposed degradation pathway of aqueous MO in the visible-light irradiating $SiW_{12}/g\text{-}C_3N_4$ system.

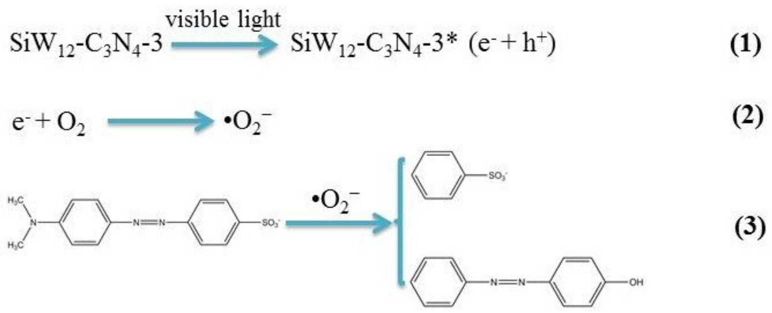
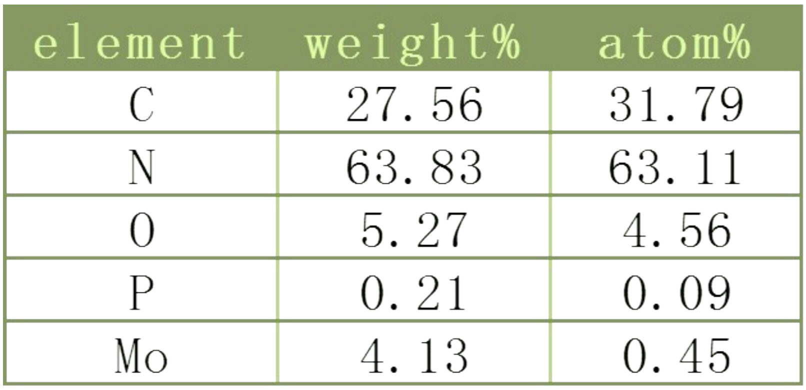


Fig. S12. Proposed degradation process and product.

element	weight%	atom%
C	29.61	34.36
N	62.12	61.79
O	3.97	3.46
P	0.16	0.08
W	4.14	0.31

Fig. S13. EDX spectrum of PW_{12}/C_3N_4.



element	weight%	atom%
C	27.56	31.79
N	63.83	63.11
O	5.27	4.56
P	0.21	0.09
Mo	4.13	0.45

Fig. S14. EDX spectrum of PMo_{12}/C_3N_4.