Supporting information

Facile synthesis, characterization, mechanism and enhanced visible-light photocatalytic activity of SiW_{12}/α-Fe_2O_3 nanocomposite

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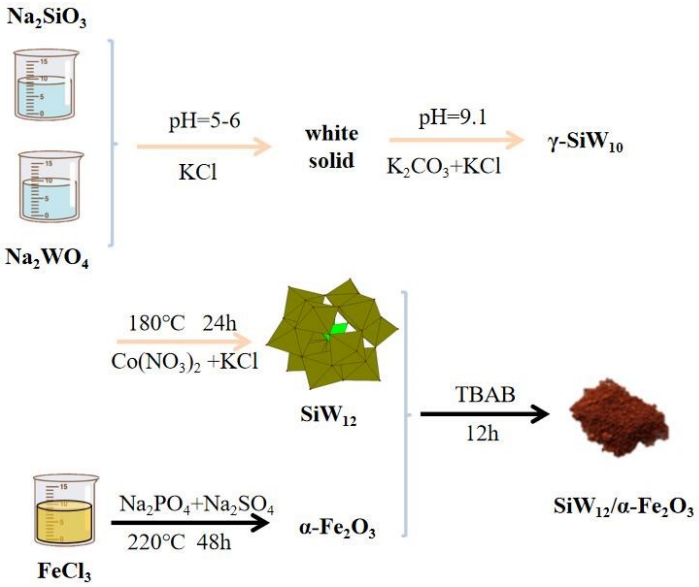
Experimental

All of the chemicals used are analytic grade without any further purification.

Synthesis of Samples



Scheme S1： the preparation process of SiW_{12}/α-Fe_2O_3 nanocomposite

Synthesis of 3D open-framework structure SiW_{12} precursor [1-3]

5.00 mmol Na_2SiO_3 was dissolved in 10 mL deionized water (recorded as liquid A). 55 mmol Na_2WO_4 was dissolved in 30 mL deionized water (recorded as liquid B). When solution B is completely dissolved, a certain concentration of HCl is added to adjust the pH value to 5-6, and then liquid A was added. The mixture solution was proceed for 100min under vigorous stirred. Then a certain amount of KCl was added and white precipitation was separated by centrifugation.

The filtered white product was dissolved in 85 ml water, the insoluble substance was filtered out, the pH was adjusted to 9.1 by 2M K_2CO_3, and kept it unchanged for 16 minutes. Then KCl (0.27mmol) was added, the white solid was separated for 10 minutes, and the white powder was obtained by drying.

0.75g γ-SiW_{10} powder were dissolved in 10 mL 0.5M potassium chloride solution. 4M nitric acid was add under full stirring and adjust the pH to 1. Cobalt nitrate 2mmol was added after the precursor was dissolved, and the reaction was carried out in 180 degree Teflon-lined autoclave for 24 hours, then he reaction solution was transferred to a beaker. The golden rod-like crystal is produced after about one week.

Synthesis of α-Fe_2O_3 nanorings [4]

$FeCl_3$ (2.67 mmol), NaH_2PO_4 (0.015 mmol) and Na_2SO_4 (0.045 mmol) were dissolved in 80 ml deionized water in turn, respectively. The solution was fully stirred 40min and then transferred to the reactor of Teflon-lined autoclave. The reaction lasted for 48 hours at 220 ^{0}C. The red product was obtained and washed by water and alcohol repeatedly.

Reference:

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Characterization

The structure and composition of the samples are characterized by FT-IR (Affinity-1 of Shimadzu), X-ray powder diffraction (XRD) collected on Shimadzu powder diffractometer with Cu Ka radiation, (λ=0.15405nm). XPS the UV-vis diffffused reflectance spectra were recorded on UV-2550, Shimadzu, Japan. The morphologies of the samples are observed by Scanning electron microscopy (SEM) ZEISS SUPRA55, and the EIS test using Princeton electrochemical workstation. Three-electrode system was used in the test. The mixed solution was 75 mL 0.05 mol/L potassium ferricyanide and 75 mL 0.1 mol/L potassium chloride. Cyclic voltammetry also uses the above test conditions.

Photocatalytic activity

100mL 10mg / L MB was transferred into the photocatalytic reactor as the initial solution, and the pH value was adjusted by HCl. The amount of photocatalyst is 0.1g. The photocatalyst is adsorbed by dark light for 30 min before photocatalysis, and then the xenon lamp is turned on for photocatalysis (illumination: 18.085 mW/cm^2). Take samples every 10 minutes, 9 times in total. The photocatalysis experiment of different mineralization degree is basically the same as this, only adding different concentration of sodium chloride into the initial solution.

Three different masking agents were used to mask the active components, isopropanol to mask the photogenerated holes, triethanolamine to mask the hydroxyl radicals, and benzoquinone to mask the superoxide radicals. The dosage of isopropanol and triethanolamine is 1ml. The dosage of p-benzoquinone was 0.05g.

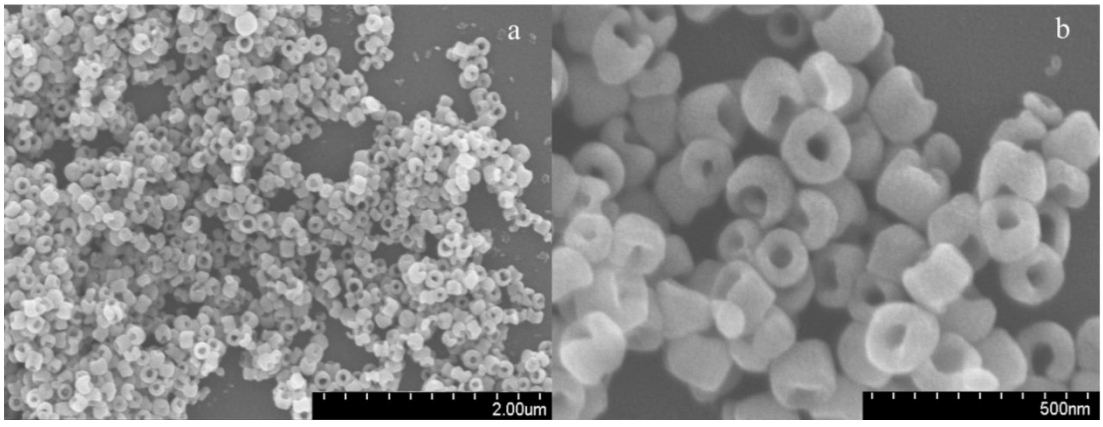


Fig.S1 SEM images of α-Fe_2O_3 nanoring

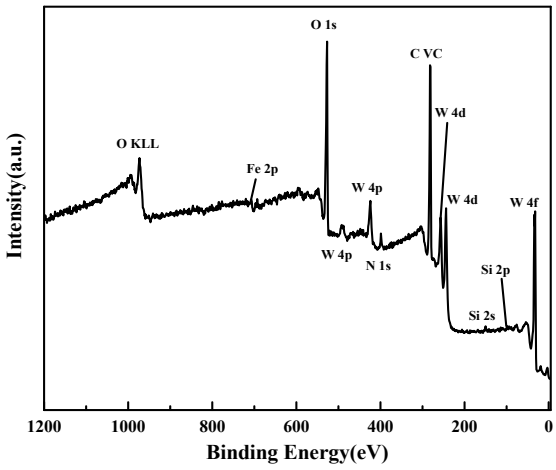


Fig.S2 The full survey spectrum of the SiW_{12}/α-Fe_2O_3 composite

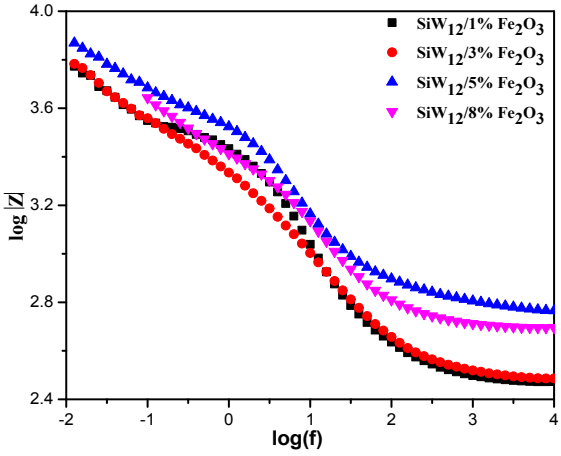


Fig.S3 The Bode plots of composites with different amount of Fe_2O_3

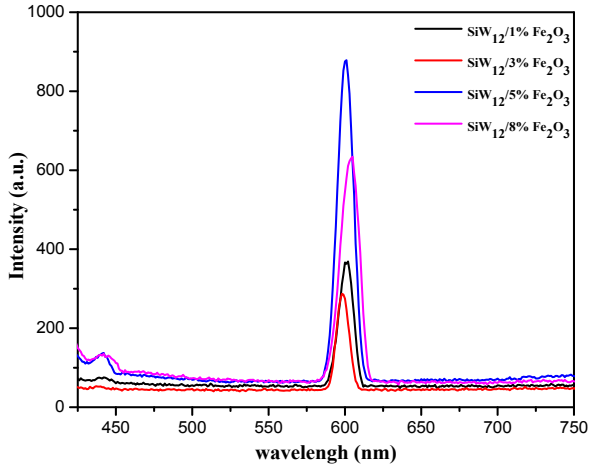


Fig.S4 The PL spectra of composites with different amount of Fe_2O_3

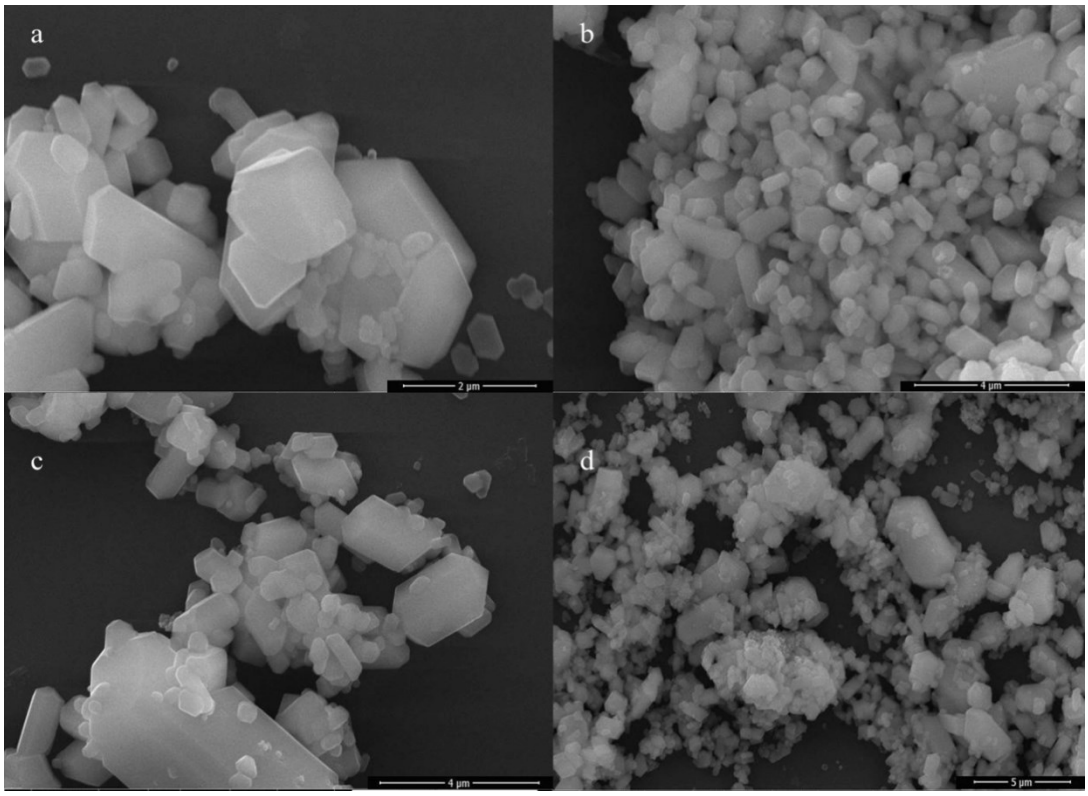


Fig.S5 SEM images of SiW_{12}/α-$Fe_2O_3$with different ratio (a)SiW_{12}/1%α-Fe_2O_3,TBAB 10ml. (b)SiW_{12}/3%α-Fe_2O_3,TBAB 10ml. (c)SiW_{12}/5%α-Fe_2O_3,TBAB 10ml. (d)SiW_{12}/8%α-Fe_2O_3, TBAB 10ml

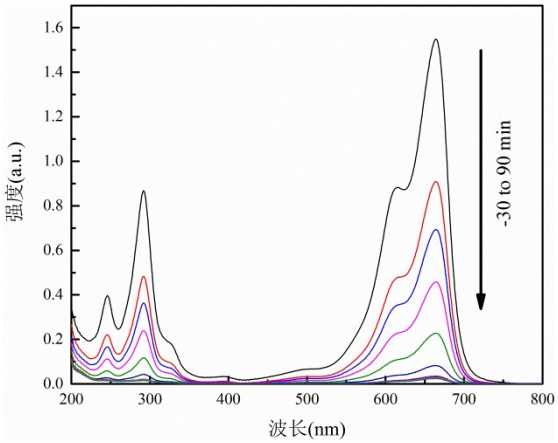


Fig.S6 The profiles of photocatalytic performance of SiW_{12}/3%α-Fe_2O_3

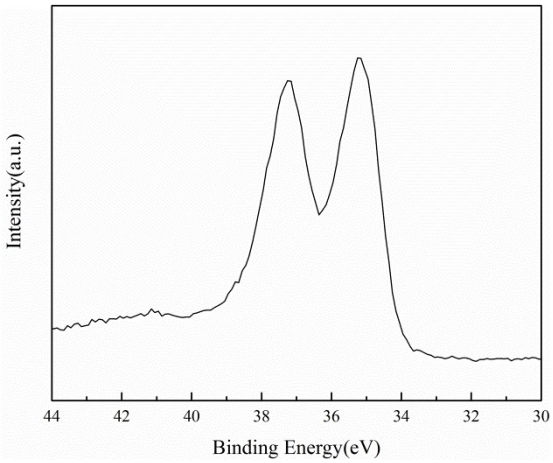
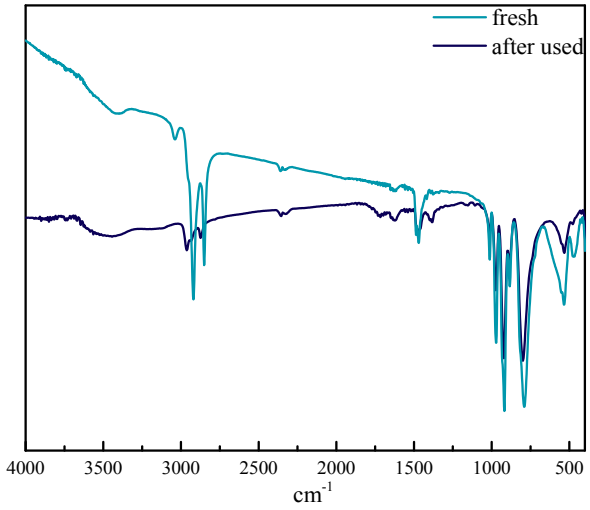


Fig.S7 XPS spectrum for W of the composite after the photocatalytic degradation



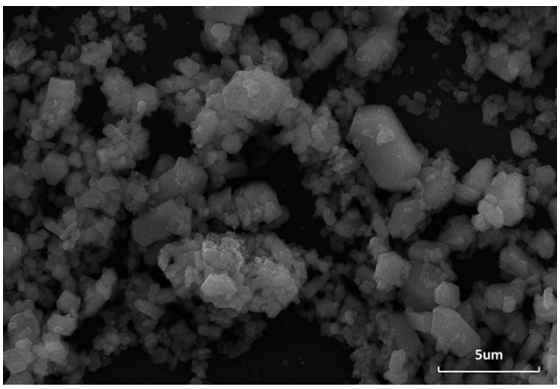


Fig. S8 The IR spectra and SEM image of the SiW_{12}/3%α-Fe_2O_3 composite after photocatalytic degradation

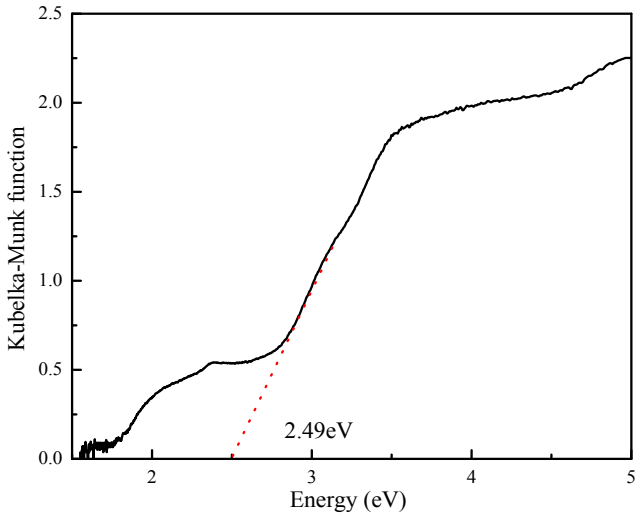


Fig S9 K-M function against energy E of SiW_{12} polyoxometalate

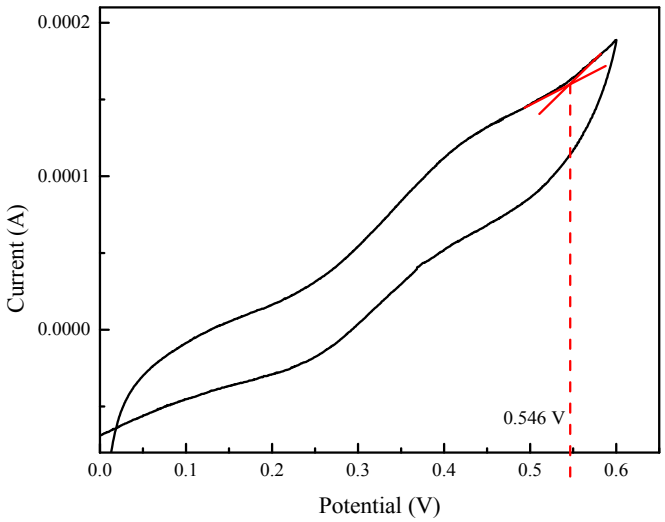


Fig S10 The cyclic voltammograms of SiW_{12} polyoxometalate

The LUMO and HOMO positions are determined by CV test and UV-vis diffuse reflectance spectra methods. The band gap Eg of SiW_{12} polyoxoanion was estimated to be 2.49 eV from the K-M function (Fig. S10), and the LUMO of SiW_{12} polyoxoanion is about 0.79V (E_{LUMO} =0.241 V+0.546 V) according to result of cyclic voltammetry (Fig. S11). Thus, the HOMO of SiW_{12} polyoxoanion is calculated to be 3.28 V (E_{HOMO} =E_{LUMO} +Eg).

Table S1 The comparison of MB degradation activity of SiW_{12}/3%α-Fe_2O_3 with literature.

Photocatalyst	Concentration ($mg \cdot L^{-1}$)	Dosage ($g \cdot L^{-1}$)	Time (min)	Remove (%)	Light Source	Reference
Fe_2O_3	10	0.5	120	73	200W Xe lamp λ>420 nm	1
K_8/EuW_{10}	2	0. 25	2880	91	200W Xe lamp λ400-700 nm	2
TiO_2	4	1	50	70	9W UVP lamp λ=360-400 nm	3
TiO_2	13.5	0.2	60	78	100W UV lamp λ=365nm	4
CdS@ZIF-8	10	1	120	72	500W Osram UV λ>420 nm	5
$FeWO_4$@$ZnWO_4$/ZnO	10	1	240	76	100W Osram UV lamp λ>420 nm	6
Mg-Doped ZnO	3.4	1.2	10	83.3	Simulated sunlight	7
$[Cu_8L_8[Mo_{12}O_{46}(AsPh)_4]_2]\cdot H_2O$	3.4	0.35	180	70	100W Xe lamp λ>420 nm	8
$[Cu_4(L_3)_4Mo_6O_{18}(O_3AsPh)_2]$	16.9	0.35	120	97	125W UV	9
$[Ag_{10}(pyttz\text{-}Ⅱ)_6(trz)_2(H_2O)_6][HP_2W_{18}O_{62}]_2\cdot 8H_2O$	3.4	0.5	120	74	125W UV	10
Fe_2O_3/TiO_2	25	25	180	94	300W Osram UV λ>420 nm	11
SnO_2/Fe_2O_3	10	1	240	98.4	125W Hg lamp	12
SiW_{12}/3%α-Fe_2O_3	10	0.1	90	97.8	18.085 mW/cm^2 Xe lamp λ>420 nm	This work

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