

**Enhancement of Photoredox Catalytic Properties of
Porphyrinic Metal-organic Frameworks Based on Titanium
Incorporation by Post-synthetic Modification**

Junhui He,^a Yajun Zhang,^a Juan He,^b Xiaoliang Zeng,^a Xiandeng Hou,^{ab}
and Zhou Long^{*a}

^a*Analytical & Testing Center, Sichuan University, Chengdu 610064, China;*

^b*Department of Chemistry, Sichuan University, Chengdu 610064, China.*

Supporting Information

* To whom correspondence should be addressed. E-mail: longzhou@scu.edu.cn
Telephone: +86-137-3084-2563

Chemicals and Materials.

All chemicals were at least AR grade and used without further treatment. 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_6TCPP) was purchased from Chensoon (Shanghai, China). $ZrOCl_2$, $TiCp_2Cl_2$, TiO_2 (5-10 nm in particle size) and ZrO_2 , (200-400 nm in particle size) were purchased from Aladdin Reagents Co. Ltd. (Shanghai, China). N, N-Dimethylformamide (DMF), methanol, ethanol, acetic acid, formic acid, hydrofluoric acid (HF), terephthalic acid, $FeCl_3 \cdot 6H_2O$, $Cr(NO_3)_3$, tetrabutyl titanate, and other chemicals or standards were obtained from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). All chemicals and materials were kept at 4 °C in the dark until use. Ultrapure water (18.25 M Ω ·cm) used for all experiments was obtained from a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China).

Instrument and Measurement

The exchange rate was evaluated by using an ARCOS FHS12 inductively coupled plasma-optical emission spectrometer (ICP-OES) (SPECTRO, Germany). The solid sample was dissolved in a 5 mL mixture of HNO_3 and HCl (v:v, 7:3) and heated at 200 °C for 1 h. H_2SO_4 and 1 g $(NH_4)_2SO_4$ was added and the mixture was heated until clear before further filtration or dilution for measurement.

The powder X-ray diffraction (PXRD) patterns were carried out with an EMPYREAN (Panalytical Inc., Netherlands) with a Cu sealed tube. For the thermal stability test, 5-10 mg of PCN-224 or PCN-224(Zr/Ti) crystals were heated using a DSC1 thermogravimetric analyzer (Mettler Toledo, Switzerland) from 30 °C to 600 °C at a rate of 5 °C min^{-1} under N_2 flow of 50 $ml\ min^{-1}$. The morphology of the samples was characterized by field emission scanning electron microscope (SEM) (Hitachi, Japan), and the elemental mapping was accomplished by the energy dispersive X-ray spectroscopy (EDS) coupled to the SEM. The X-ray photoelectron spectra (XPS) were collected with an AXIS Ultra DLD 800 X (Kratos, UK). The FT-IR spectra were collected with a Nicolet IS10 FT-IR spectrometer (Thermo Inc., USA) using KBr pellets.

The photoluminescence (PL) lifetime measurement was performed on an Fluorolog-3 spectrofluorometer (Horiba, Japan) with a spectra laser (371 nm, Horiba Scientific) as the excitation source and a picosecond photon detection module (PPD-850, Horiba Scientific) as the detector. The PL intensity was measured by using an F-7000 spectrofluorometer (Hitachi, Japan) with the excitation at 420 nm. The UV-visible diffuse reflectance spectra (UV-DRS) were collected with a UV-3600 spectrometer (Shimadzu, Japan), with $BaSO_4$ as the reflectance standard. The Mott-Schottky curves were obtained from an Autolab PGSTAT12 potentiostat/galvanostat (Metrohm, Switzerland) in a three-electrode cell. A $Ag/AgCl$ electrode (3 M of KCl) was used as the reference electrode and a Pt plate was used as the counter electrode, with a solution of 0.1 M Na_2SO_4 as the electrolyte. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass, with a slurry of sample in ethanol dipped on the surface. Electrochemical impedance spectra (EIS) were obtained using an CHI-660

electrochemical workstation (Chinstruments, China) in a three-electrode system with 0.5 M Na₂SO₄ as the electrolyte. The electron paramagnetic resonance (EPR) spectra of the generated radicals spin-trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) or 2,2,6,6-tetramethylpiperidine (TEMP), were collected at room temperature by using a BRUKER spectrometer (EXM, Germany).

Experiment

The MB or TC removal and degradation was evaluated by $100(1-C/C_0)\%$ and $100(1-C/C_e)\%$, respectively, where C_0 is the initial concentration, C_e is the concentration at the ad/desorption equilibrium and C is the instant concentration of MB determined by UV-vis. A 500W iodine tungsten lamp with 420 nm cut-off filter was served as the light source.

For the degradation of MB, 2 mg catalyst was dispersed in 20 mL of MB (5 mg/L) in water, which was kept under stirring in the dark for 60 min to reach the ad/desorption equilibrium. The mixture was then exposed to a visible light source under stirring for MB degradation. Since the beginning, 0.5 mL of the homogeneous mixture was collected every 10 min, with the supernatant obtained after centrifugation and analyzed instantly by UV-vis at 572 nm. For the degradation of TC, 8 mg catalysts were dispersed in 20 mL TC solution (10 mg/L), followed by stirring in the dark for 60 min to reach the equilibrium of adsorption-desorption. The mixture was then exposed to visible light under continues. Since the beginning, 0.5 mL of the homogeneous mixture was collected every 10 min, with the supernatant obtained after centrifugation and analyzed instantly by UV-vis at 267 nm.

For the photo-reduction of Se(VI), 2.5 mg catalyst was dispersed in 5 mL mixture (1 : 4, v : v) of formic acid and water to form a homogeneous suspension. Then the suspension was pumped into a quartz pipe which included in a UV lamp (Philips 15 W/T8, ex at 254 nm). Upon UV irradiation, reductive radicals generated from the formic acid could scavenge the strongly oxidizing holes at the valence band of the photocatalyst, with Se(VI) reduced to H₂Se and CO₂ produced. The generated volatile Se species were subsequently determined by atomic spectrometry (optimal conditions listed in Table S1).

Synthesis of PCN-224: 312.5 mg ZrOCl₂ and 62.5 mg H₆TCPP were dissolved in the mixture of 125 mL DMF and 62.5 mL acetic acid and kept under ultrasound for 30 min. The obtained mixture was kept at 65 °C for 72 h and then cooled down to room temperature. The collected dark purple crystals (PCN-224) by centrifugation were thoroughly washed with DMF and ethanol, and then dried at 80 °C under vacuum.

Synthesis of PCN-224(Zr/Ti): TiCp₂Cl₂ (375 mg, 1.5 mmol equiv based on Ti) and the PCN-224 crystals (415 mg, 1.5 mmol equiv based on the organic linkers) were mixed in 60 mL DMF. The obtained mixture was kept at 120 °C for different periods of time and then cooled down to room temperature. The obtained crystals, PCN-224(Zr/Ti), were collected by centrifugation and thoroughly washed with DMF (3 x 20mL) and ethanol (3 x 20mL), and then dried at 80 °C under vacuum for 24 h.

Synthesis of UiO-66: 65 mg ZrOCl₂·8H₂O and 34 mg terephthalic acid were

dissolved in 10 mL DMF and kept under ultrasound for 30 minutes, followed by drop-wise addition of 0.5 mL HCl. The mixture was sealed in a 15 mL Teflon-lined pressure vessel for 24 h at 120 °C and then cooled down to room temperature. The product of white crystals (UiO-66) were collected by centrifugation and thoroughly washed with DMF (3 x 20 mL) and ethanol (3 x 20 mL), and then dried at 80 °C under vacuum for 24 h. The PXRD pattern of the obtained UiO-66 was compared with the simulated in Figure S15.

Synthesis of MIL-53(Fe): 108 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 664 mg terephthalic acid were dissolved in 40 mL DMF, stirred for 10 min and then transferred into the microwave reactor, with the temperature risen up to 100 °C within 1 min and then kept for 1 h. After cooled down to room temperature, the product of MIL-53(Fe) was collected by centrifugation and thoroughly washed with DMF (3 x 20 mL) and ethanol (3 x 20 mL), and then dried at 80 °C under vacuum for 24 h. The PXRD pattern of the obtained MIL-53(Fe) was compared with the simulated in Figure S16.

Synthesis of MIL-101(Cr): 800 mg $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HF (48 wt %, 2 mmol), 330 mg terephthalic acid were mixed in 10 mL water and kept under ultrasound for 30 min. The mixture was sealed in a 15 mL Teflon-lined pressure vessel at 220 °C for 8 h and cooled down to room temperature. The product of MIL-101(Cr) was collected by centrifugation and thoroughly washed with DMF (3 x 20 mL) and ethanol (3 x 20 mL), and then dried at 80 °C under vacuum for 24 h. The PXRD pattern of the obtained MIL-101(Cr) was compared with the simulated in Figure S17.

Synthesis of MIL-125(Ti): 498 mg terephthalic acid was dissolved in the mixture of 9 mL DMF and 1 mL methanol, and stirred for 10 min. 0.75 mmol tetrabutyl titanate was then added in and stirred for another 10 min. The obtained mixture was kept in the microwave reactor at the temperature of 150 °C for 5 h before cooled down to room temperature. The product of white crystals, MIL-125(Ti), were collected by centrifugation and thoroughly washed with DMF (3 x 20 mL) and ethanol (3 x 20 mL), and then dried at 80 °C under vacuum for 24 h. The PXRD pattern of the obtained MIL-125(Ti) was compared with the simulated in Figure S18.

Tables

Table S1 the optimal parameters of AFS measurement

PMT voltage	-310 V
HLC current	90 mA
Auxiliary current	45 mA
Argon flow rate	320mL.min-1
Hydrogen flow rate	80 mL.min-1
Irradiation time	25 s

Table S2 PL lifetime of PCN-224, the mixture of PCN-224 and TiCp₂Cl₂ and PCN-224(Zr/Ti).

Sample	$\bar{\tau} / ns^a$	τ_i / ns^b	f_i	$\chi^2 R$
PCN-224	0.29	0.19 ± 0.005	0.77	1.46
		0.61 ± 0.006	0.23	
PCN-224+TiCp ₂ Cl ₂	0.27	0.18 ± 0.006	0.76	1.27
		0.57 ± 0.005	0.24	
PCN-224(Zr/Ti)	0.18	0.13 ± 0.002	0.90	1.48
		0.61 ± 0.008	0.10	

a: The PL decay was fitted to the second order exponential decay.

b: The retrieved lifetime was calculated with the standard deviation as error.

The average PL lifetime was calculated using the equation:

$$\bar{\tau} = \sum f_i \tau_i = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3$$

where τ_i is the lifetime and f_i is the contribution factor of τ_i to τ , which were collected from the PL lifetime measurements after proper fitting.

Figures

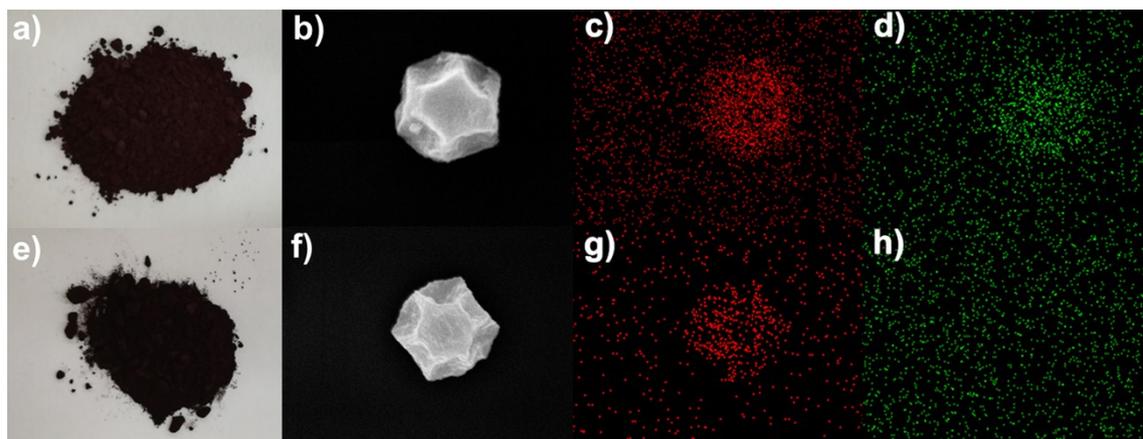


Figure S1 Photograph of the prepared crystals of PCN-224(Zr/Ti) (a) and PCN-224 (e); SEM image of PCN-224(Zr/Ti) (b) and PCN-224 (f); energy-dispersed X-ray mapping image of Zr obtained from PCN-224 (Zr/Ti) (c) and PCN-224 (g); energy-dispersed X-ray mapping image of Ti obtained from PCN-224 (Zr/Ti) (d) and PCN-224 (h).

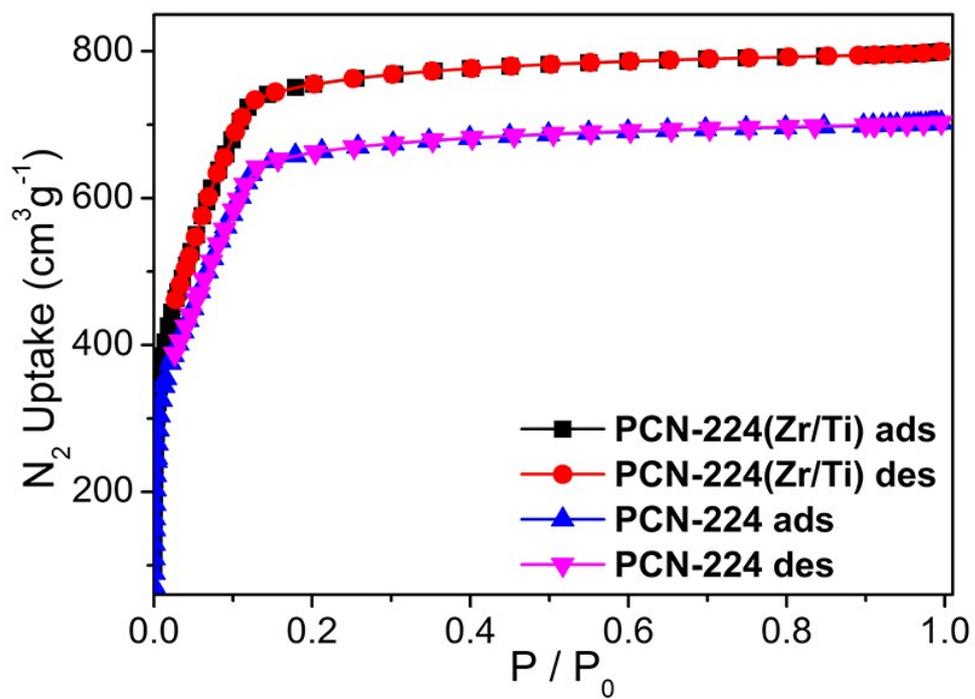


Figure S2 N₂ adsorption/desorption isotherms of PCN-224 and PCN-224(Zr/Ti).

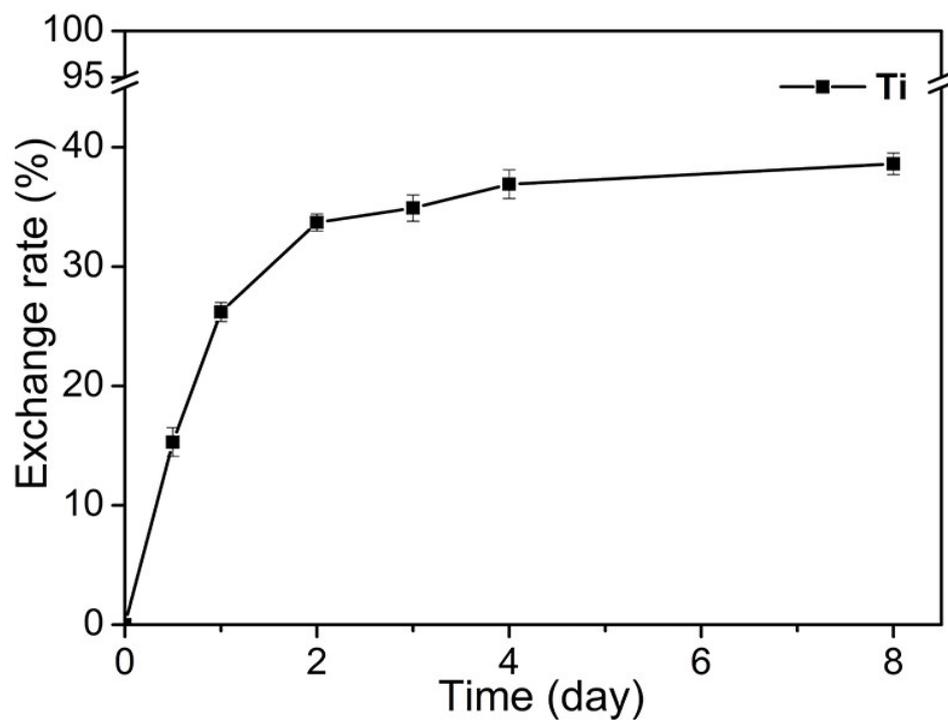


Figure S3 Percentage of Zr substituted by the introduced Ti after the reaction between PCN-224 and TiCp_2Cl_2 at 120 °C for different periods of time (12 h, 1 d, 2 d, 3 d, 4 d and 8 d), determined by ICP-OES.

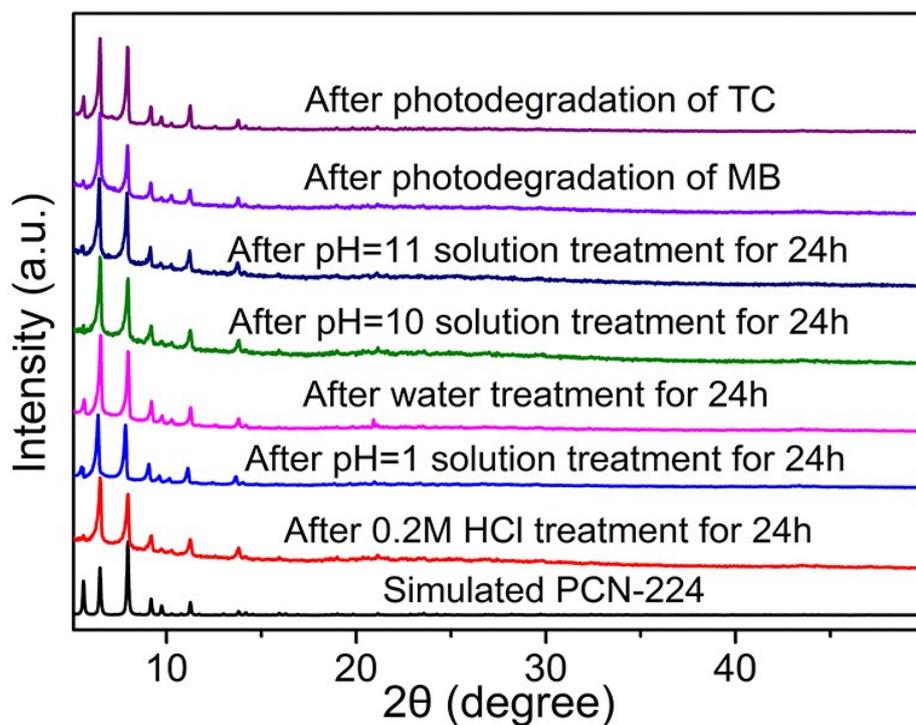


Figure S4 XRD patterns of PCN-224 (Zr/Ti) crystals after treated in acidic/neutral/basic environment or collected after being used as photocatalysts for the degradation of MB and TC (for 3 cycles), compared to the simulated pattern of PCN-224.

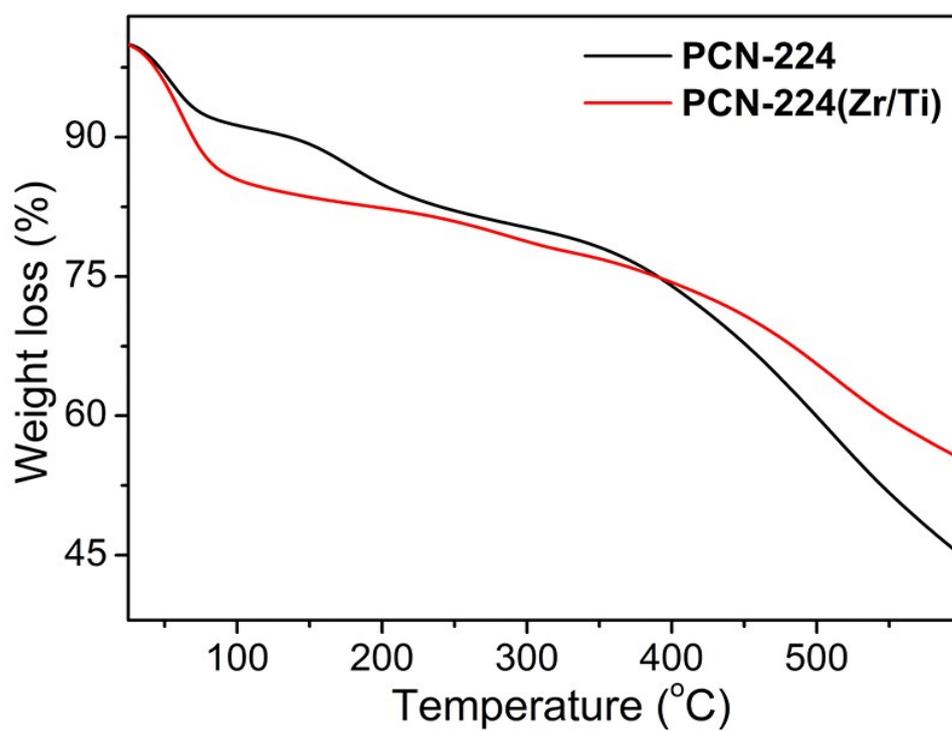


Figure S5 TGA curve obtained from the crystals of PCN-224 and PCN-224(Zr/Ti).

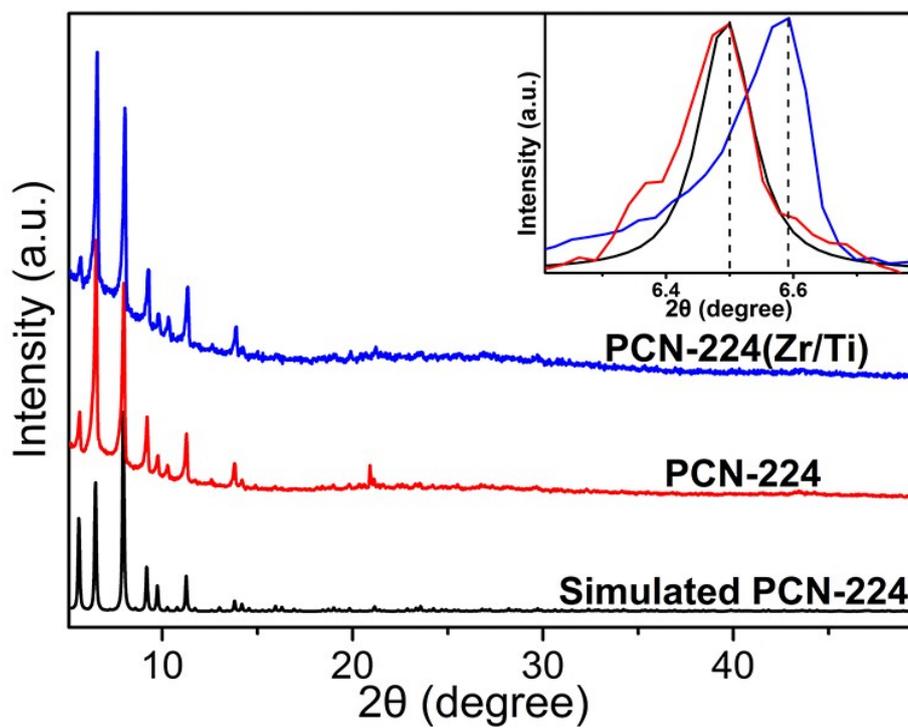


Figure S6 PXRD patterns (inset: partially magnified) of the simulated PCN-224, synthesized PCN-224 and prepared PCN-224(Zr/Ti).

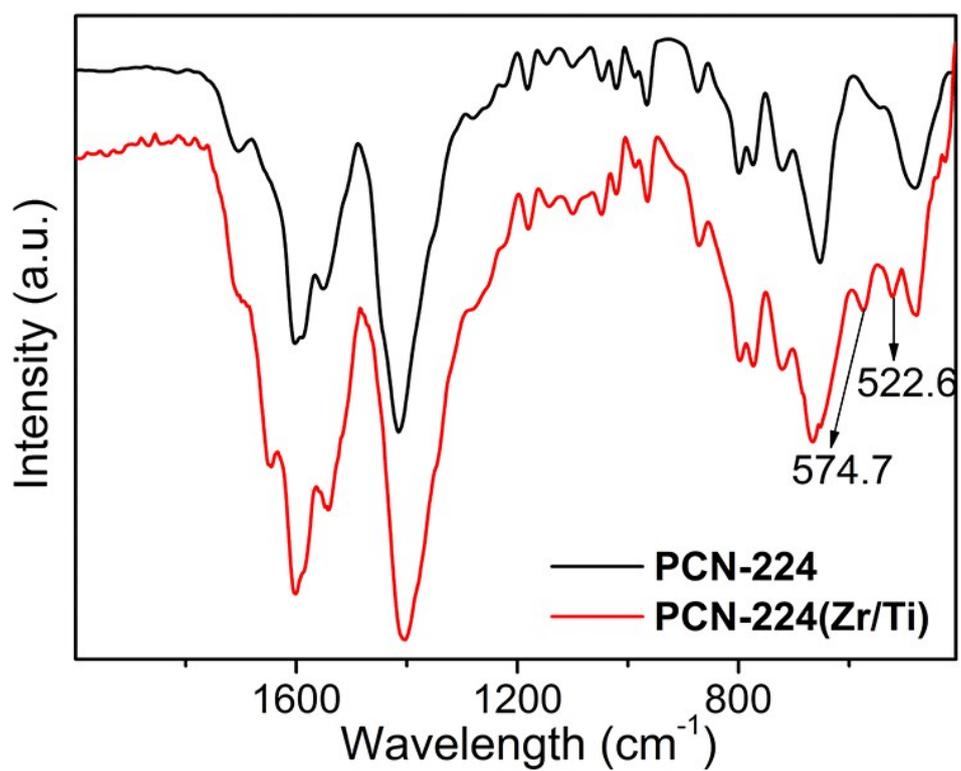


Figure S7 FT-IR spectra of PCN-224 and PCN-224(Zr/Ti) for comparison.

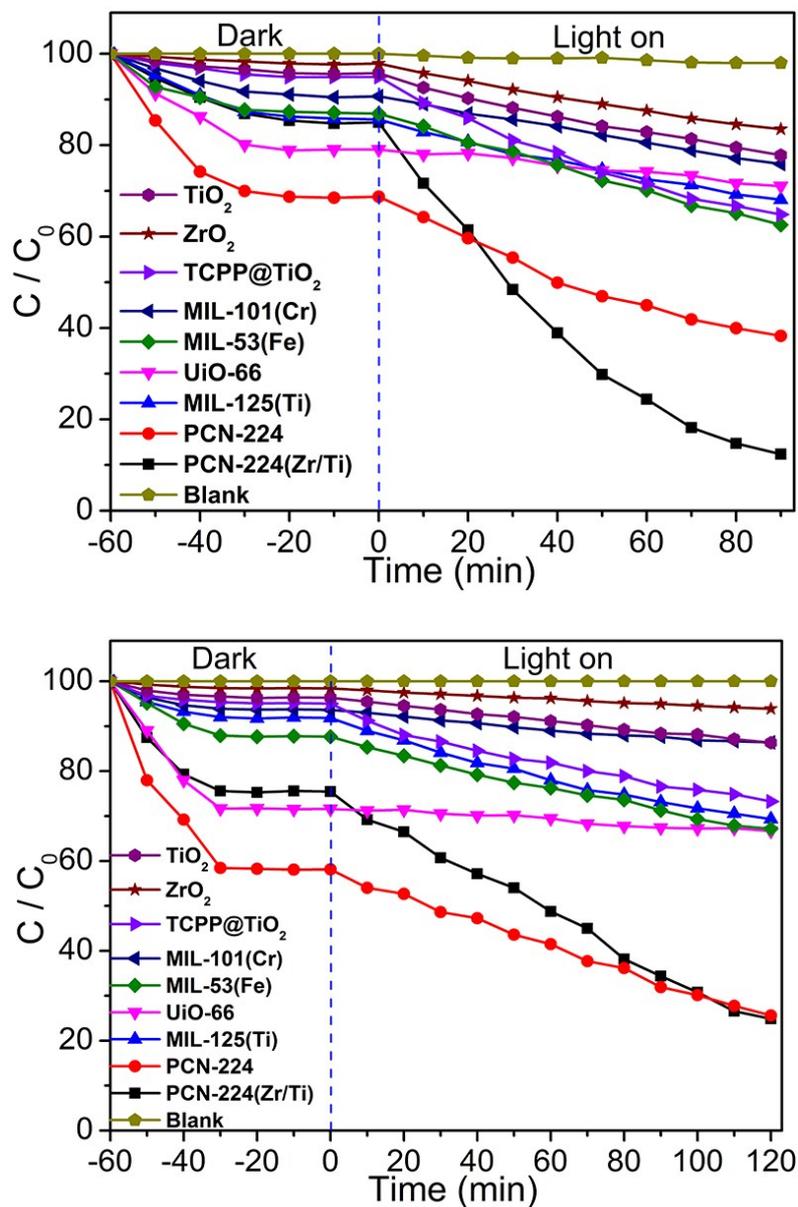


Figure S8 Concentration ratio of MB (top) and TC (bottom) evolved before the ad/desorption equilibrium and during the subsequent photodegradation process by using various photocatalysts, which was calculated by the instant concentration over the initial one, determined by UV-vis.

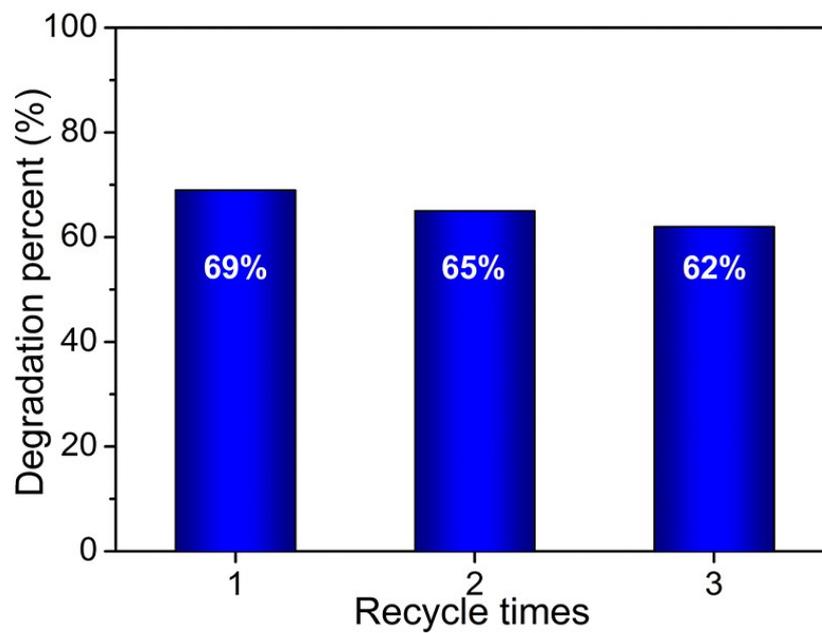
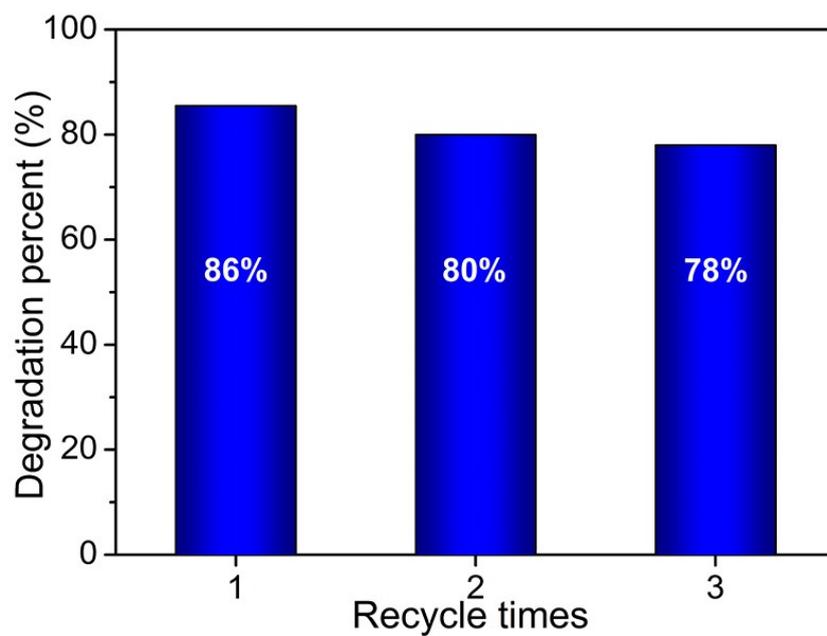


Figure S9 Degradation percentage of MB (top) and TC (bottom) by using the PCN-224(Zr/Ti) as the photocatalysts for each of the three cycles.

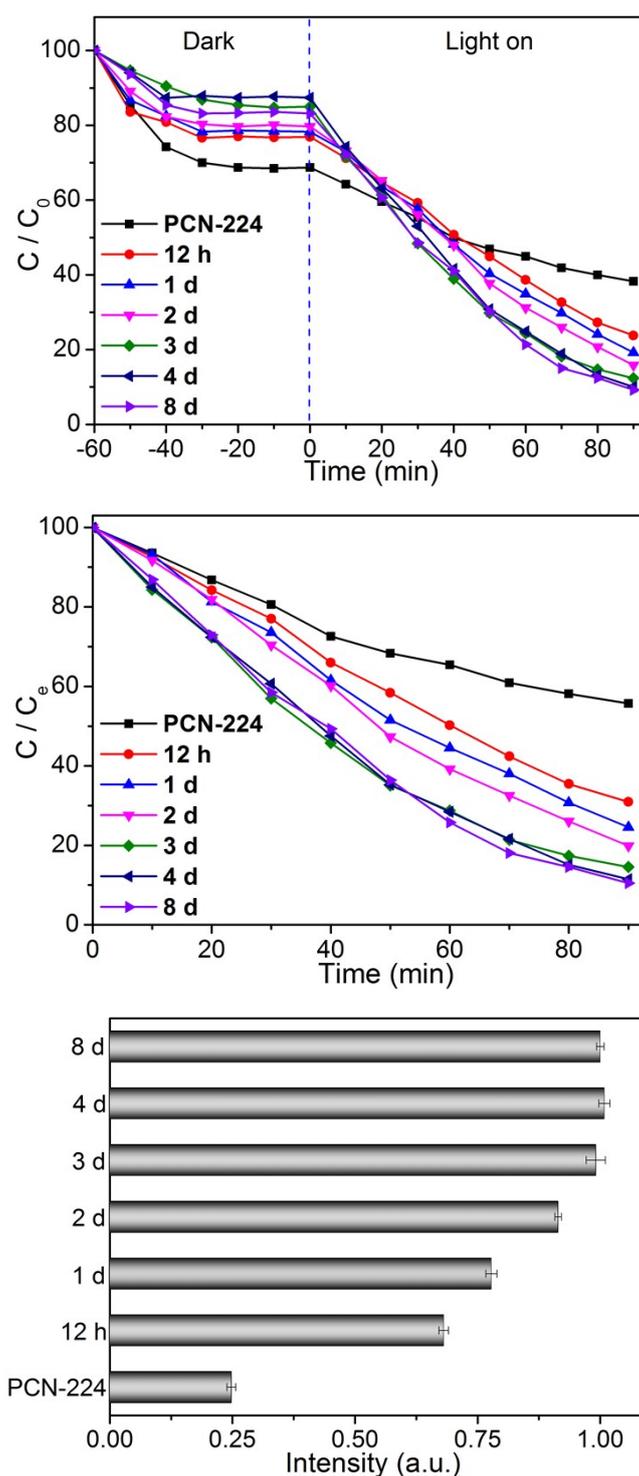


Figure S10 Concentration ratio of MB evolved during the photodegradation process with (top) and without (middle) the process before reaching the ad/desorption equilibrium in the dark, which was calculated by the instant concentration over the initial one determined by UV-vis, and AFS signal intensity of SeH_2 generated via the photoreduction of Se(VI) (bottom), by using the photocatalysts of PCN-224 or PCN-224(Zr/Ti) obtained from the reaction between PCN-224 and TiCp_2Cl_2 at $120\text{ }^\circ\text{C}$ for different periods of time.

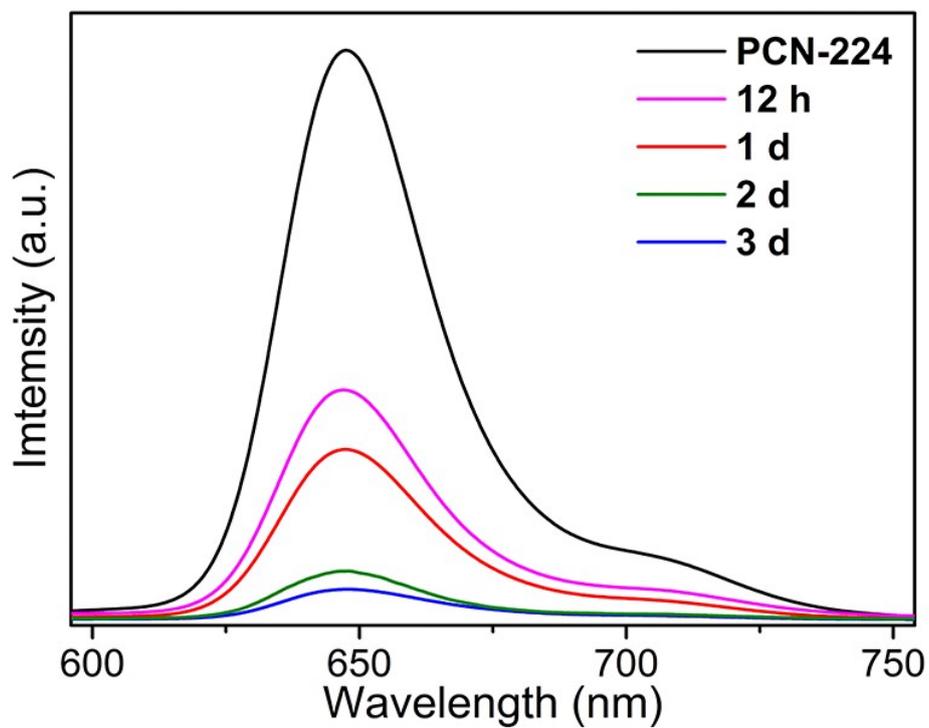


Figure S11 PL spectra of the prepared PCN-224 and PCN-224(Zr/Ti) obtained after the reaction at 120 °C between PCN-224 and TiCp_2Cl_2 at 120 °C for different periods of time.

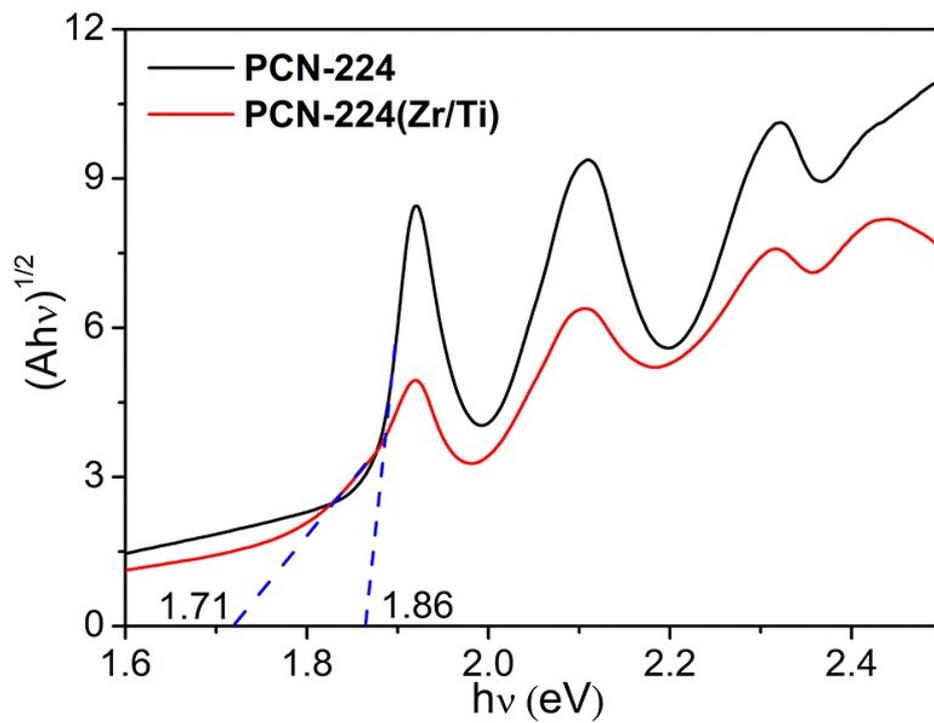


Figure S12 Diffuse reflectance UV-vis spectra of PCN-224 and PCN-224(Zr/Ti).

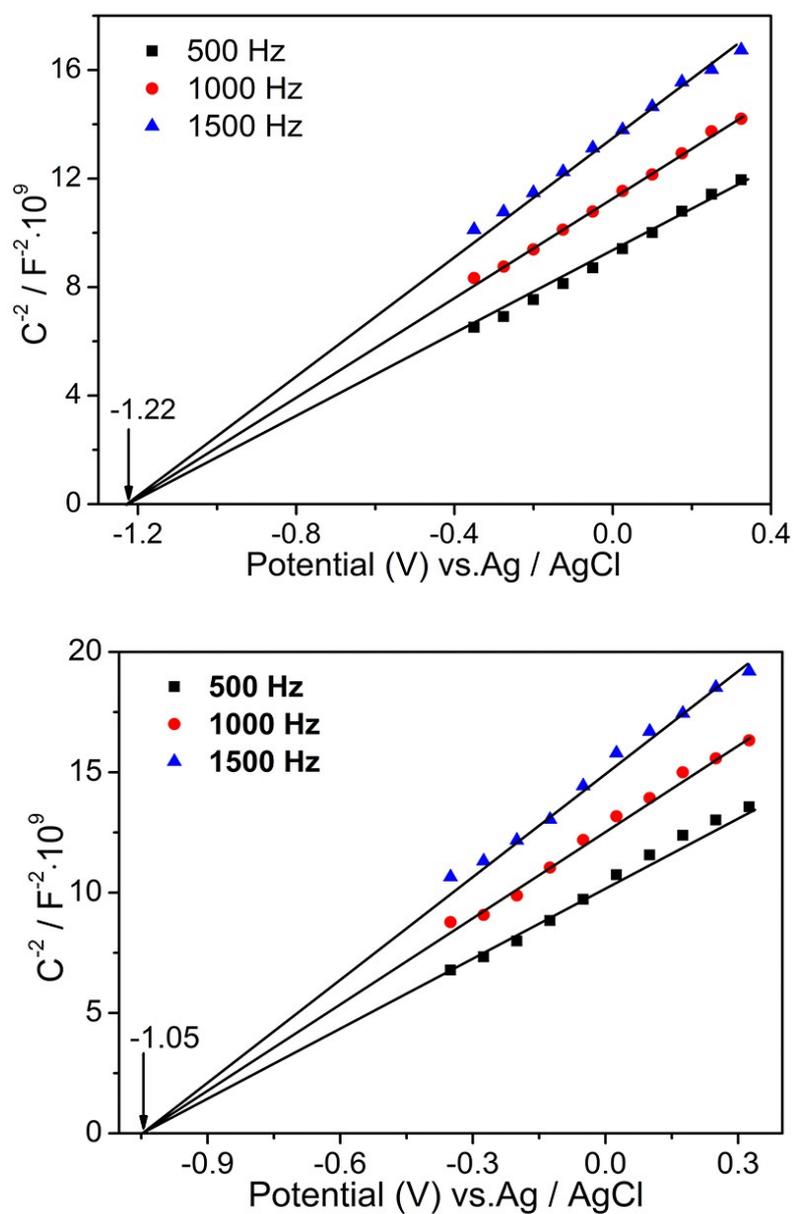


Figure S13 Mott-Schottky plot of PCN-224 (top) and PCN-224 (Zr/Ti) (bottom).

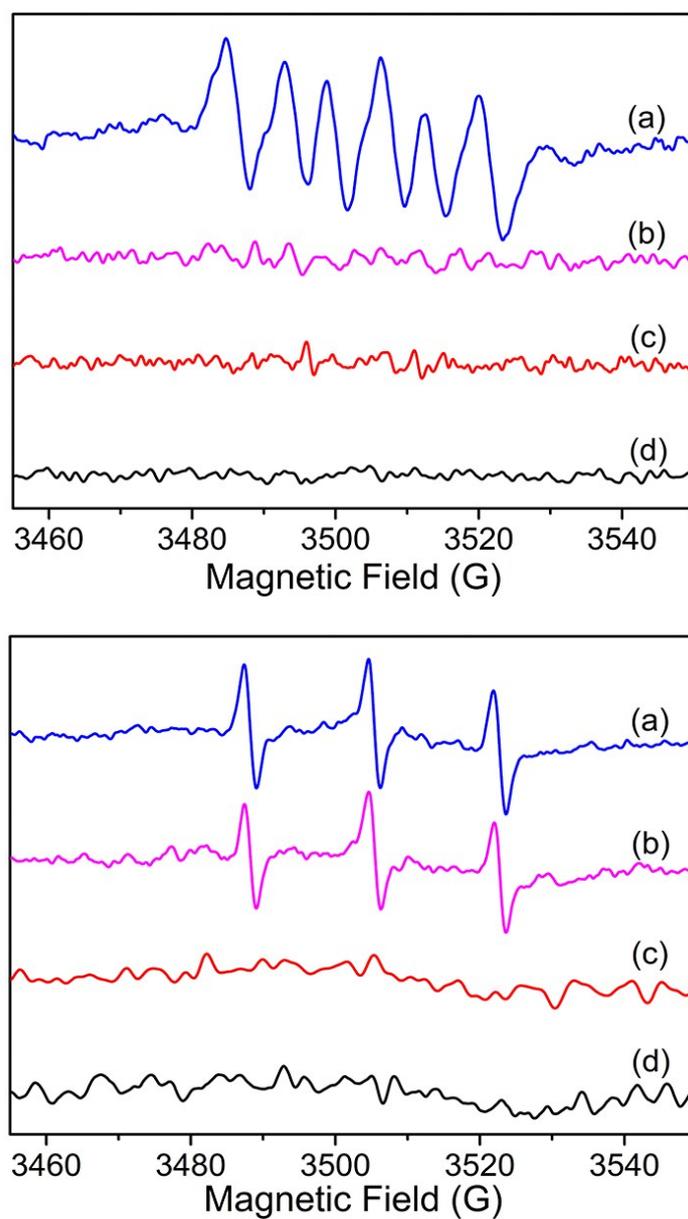


Figure S14 EPR spectra obtained from PCN-224(Zr/Ti) (a) and PCN-224 (b) under the irradiation of visible light by using DMPO (top) and TEMP (bottom) as the spin-trapping agent; EPR spectra obtained from PCN-224(Zr/Ti) (c) and PCN-224 (d) in the dark by using DMPO (top) and TEMP (bottom) as the spin-trapping agent.

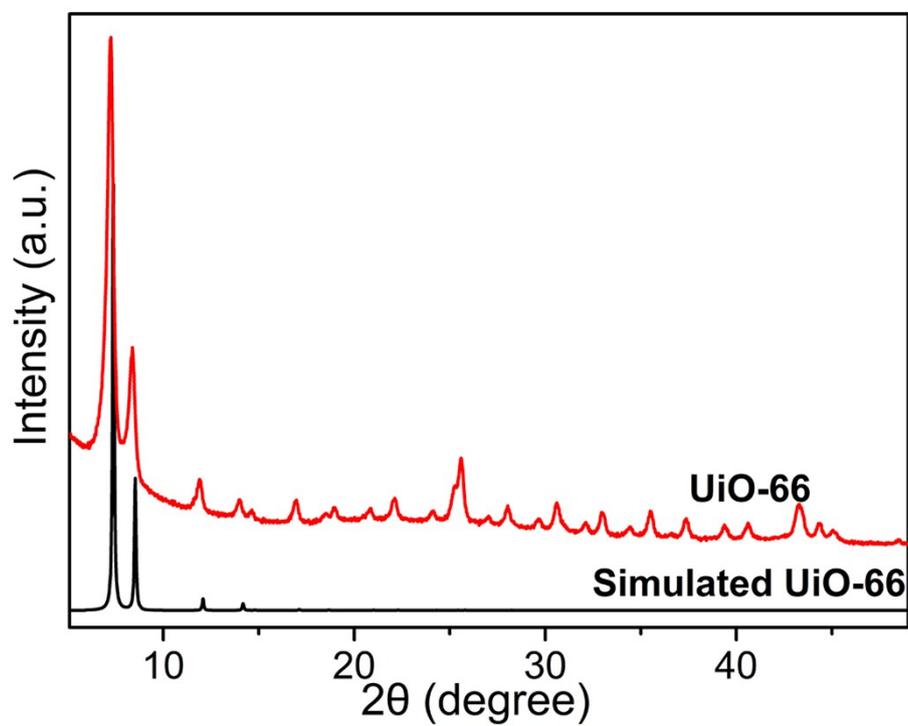


Figure S15 PXRD pattern of the synthesized UiO-66 crystals (red) and the simulated (black).

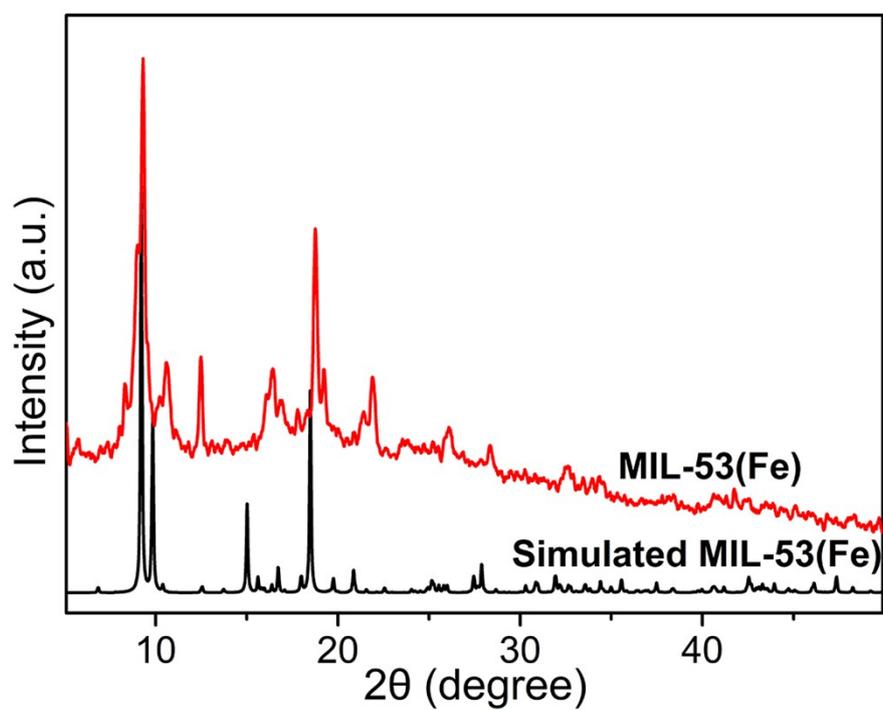


Figure S16 PXRD pattern of the synthesized MIL-53(Fe) crystals (red) and the simulated (black).

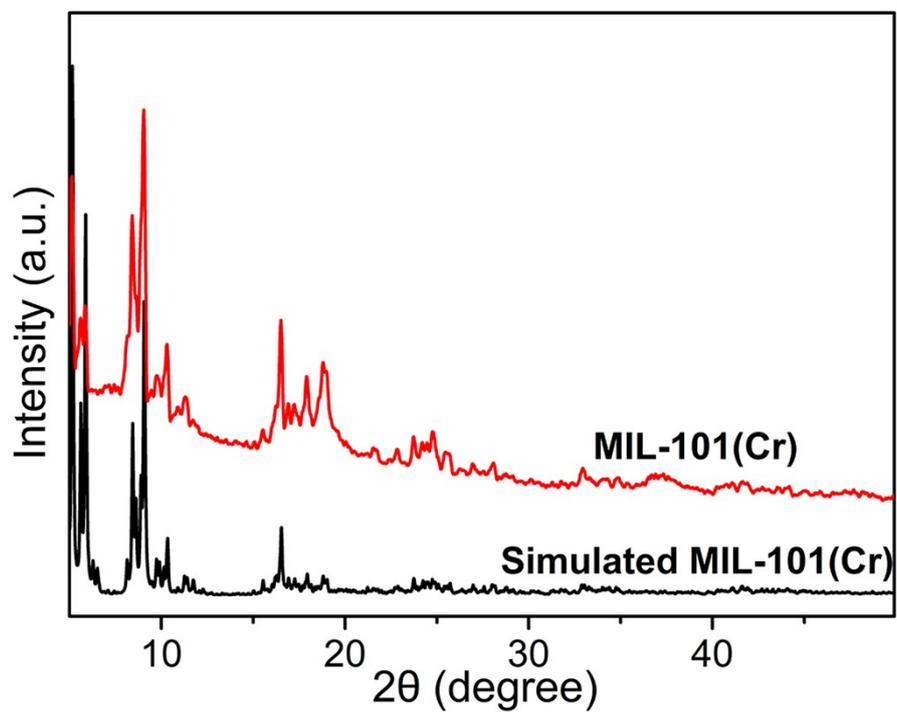


Figure S17 PXRD pattern of the synthesized MIL-101(Cr) crystals (red) and the simulated (black).

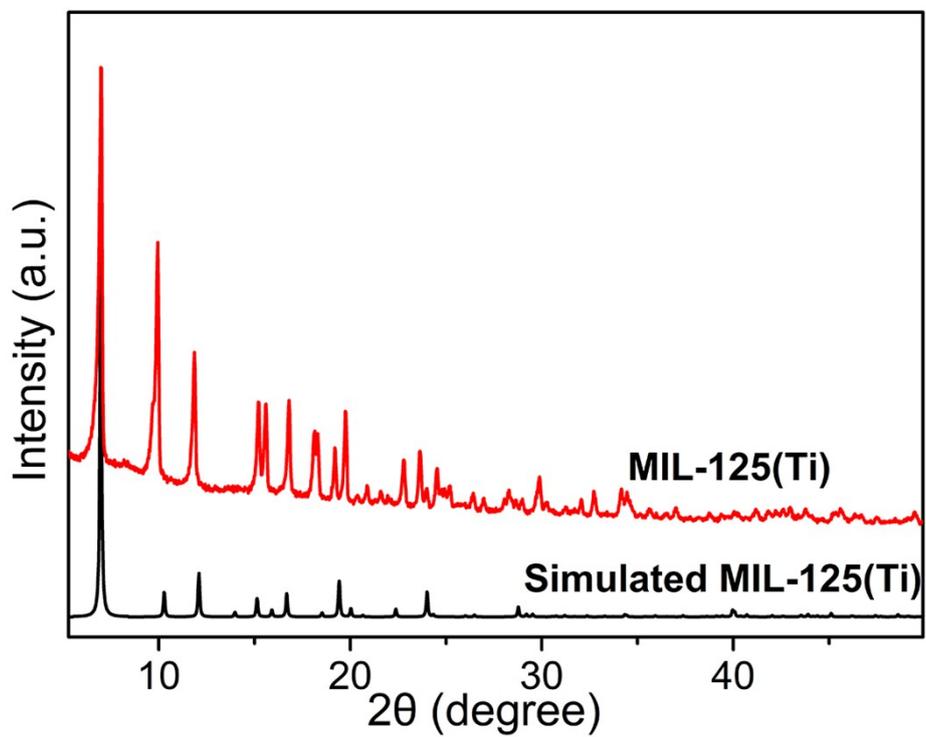


Figure S18 PXRD pattern of the synthesized MIL-125(Ti) crystals (red) and the simulated (black).