# Microwave-induced Fast Incorporation of Titanium in UiO-66 Metal-organic Frameworks for Enhanced Photocatalytic Properties

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# Supporting Information

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## Experimental Section

All the chemicals are AR grade or higher. Ultrapure water (18.25 MΩ·cm) used for all experiments was produced with a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China). Zirconium chloride ($ZrCl_4$), tetrabutyl titanate, titanocene dichloride ($TiCp_2Cl_2$), benzene-1,4-dicarboxylic acid (BDC), aluminum chloride hexahydrate ($AlCl_3$ $6H_2O$), ferric chloride hexahydrate ($FeCl_3$ $6H_2O$), titanium dioxide ($TiO_2$ 5-10 nm in particle size), and zirconium dioxide ($ZrO_2$, 200-400 nm in particle size) were purchased from Aladdin Reagents Co. Ltd. (Shanghai, China). N, N-Dimethylformamide (DMF), formic acid, methanol and ethanol were obtained from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Sodium selenate was obtained from Xiya Chemical Industry Co. Ltd. (Shandong, China). All chemicals and standards were kept at 4 $^{o}$C in the dark until use.

**Synthesis of UiO-66.** 1.5 mmol $ZrCl_4$ were dissolved in the mixture of 50 mL DMF and 10 mL concentrated HCl with the aid of ultrasound for 20 minutes. Benzene-1,4-dicarboxylic acid (BDC) and 100 mL DMF were added in and the mixture was put under ultrasound for another 20 min. The obtained mixture was kept in the microwave reactor at the temperature of 120 $^{o}$C for 1 h, and then cooled down to room temperature. The product of white crystals (UiO-66) was collected and thoroughly rinsed with DMF and ethanol, and then dried at 80 $^{o}$C under vacuum.

**Synthesis of UiO-66(Zr/Ti)-S.** $TiCp_2Cl_2$ (375 mg, 1.5 mmol) and the prepared UiO-66 crystals (415 mg, 1.5 mmol equiv based on the organic linkers) were thoroughly mixed in 60 mL DMF. The obtained mixture was kept at 120 $^{o}$C for different periods of time before cooled down to room temperature. The obtained white crystals were rinsed with DMF and then ethanol for three times, respectively (20 mL DMF/ethanol for each time), and dried at 80 $^{o}$C under vacuum.

**Synthesis of MIL-125(Ti).** 3 mmol BDC were 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 $^{o}$C for 5 h before cooled down to room temperature. The obtained white crystals were rinsed with DMF and then ethanol for three times, respectively (20 mL DMF/ethanol for each time), dried at 80 $^{o}$C under vacuum, and characterized with powder X-ray diffraction PXRD (Fig. S11).

**Synthesis of CAU-1.** 1 mmol $AlCl_3$ $6H_2O$ and 0.3 mmol BDC were dissolved in 3.2 mL methanol, stirred for 10 min and then transferred into the microwave reactor, with the temperature risen up to 145 $^{o}$C within 1 min and then kept for 2 min before cooled down to room temperature. The whole suspension was then cooled down to room temperature. The obtained white crystals were rinsed with DMF and then ethanol for three times, respectively (20 mL DMF/ethanol for each time), dried at 80 $^{o}$C under vacuum, and characterized with PXRD (Fig. S12).

**Synthesis of MIL-53(Fe).** 0.4 mmol $FeCl_3$ $6H_2O$ and 4 mmol BDC were dissolved in 40 mL DMF, stirred for 10 min and then transferred into the microwave reactor, with the temperature risen up to 100 $^{o}$C within 1 min and then kept for 1 h. The whole suspension was then cooled down to room temperature. The obtained white crystals were rinsed with DMF and then ethanol for three times, respectively (20 mL DMF/ethanol for each time), dried at 80 $^{o}$C under vacuum, and characterized with PXRD (Fig. S13).

## Characterization

The exchanging extent was evaluated by inductively coupled plasma-optical emission spectrometry (ICP-OES) with an ARCOS FHS12 (SPECTRO Analytical Instruments Inc., Germany). Before the analysis with ICP-OES, each kind of solid sample was dissolved in a 5-mL mixture of $HNO_3$ and HCl (v/v=7:3) and heated at 200 $^oC$ for 1 h. $H_2SO_4$ and 1 g $(NH_4)_2SO_4$ was added in and the mixture was heated until turned clear. The PXRD patterns were collected by an EMPYREAN (Panalytical Inc., Netherlands) with a $Cu_{\kappa a}$ radiation; 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); the fluorescence measurements were performed with a Hitachi F-7000 spectrofluorometer using a 300 nm optical filter, with the excitation at 254 nm; the UV-visible diffuse reflectance spectra (UV-DRS) were collected for the dry-pressed disk samples with a UV-3600 spectrometer (Shimazu, Japen), with $BaSO_4$ used as the reflectance standard.

The product of the photocatalytic process was analyzed by atomic fluorescence spectrometry (AFS) with an AFS-9700 spectrometer (Bejing Haiguang Instrument Inc., China), as well as gas chromatography-mass spectrometry (GC-MS) with a GCMS-QP2010 plus (Shimadzu, Japen). For GC-MS analysis, a Rtx-5 MS capillary column (30 m in length with the inner diameter of 0.25 mm and the inner coating of 0.25 mm) was used, with the injection volume of 1 mL. The temperature of the injection port was 150 $^oC$. The oven temperature was kept at 35 $^oC$ for 1 min and then risen up to 100 $^oC$ with a rate of 5 $^oC$ $min^{-1}$. The flow rate of the carrier gas (He) was 5.0 mL $min^{-1}$, and the voltage of the electron impact ion source was set at 70 eV.

The fluorescence lifetime measurements were performed on an Fluorolog-3 spectrofuorometer (Horiba Jobin Yvon) with a spectra LED (280 nm, S-280, Horiba Scientific) as the excitation source and a picosecond photo detection module (PPD-850, Horiba Scientific) as the detector, and the average 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 $\tau_i$ is the lifetime and $f_i$ is the contribution factor of $\tau_i$ to $\tau$ , which were collected from the fluorescence lifetime measurements after proper fitting. The data were fitted with the third order exponential decay.

The Mott-Schottky curves were obtained by using an Autolab PGSTAT12 potentiosta/galvanostat (Metrohm, Switzerland) in a three-electrode cell. A Pt plate was used as the counter electrode and a Ag/AgCl electrode (3M KCl) was used as the reference 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 mixture containing sample and ethanol dipped on the surface.

Table. S1 The optimal parameters of AFS

| | |
|---|---|
| PMT voltage / V | -310 |
| HLC current / mA | 90 |
| Auxiliary current / mA | 45 |
| Argon flow rate / mL·min$^{-1}$ | 300 |
| Hydrogen flow rate / mL·min$^{-1}$ | 50 |
| Irradiation time / s | 20 |

Table. S2 Fluorescence lifetime of UiO-66, UiO-66(Zr/Ti)-M and the mixture of UiO-66 and $TiCp_2Cl_2$.

| Sample | $\bar{\tau}$ /μs$^{a}$ | $\tau_i$ /μs$^{b}$ | $f_i$ | $\chi_R^2$ |
|---|---|---|---|---|
| UiO-66 | 8.58 | 14.33±0.43 | 0.31 | 1.21 |
| | | 71.74±1.45 | 0.03 | |
| | | 3.11±0.05 | 0.66 | |
| UiO-66+$TiCp_2Cl_2$ | 8.60 | 14.12±0.20 | 0.32 | 1.20 |
| | | 76.45±1.45 | 0.03 | |
| | | 3.10±0.10 | 0.65 | |
| UiO-66(Zr/Ti)-M | 7.80 | 9.84±0.73 | 0.40 | 1.13 |
| | | 39.63±1.24 | 0.07 | |
| | | 2.25±0.10 | 0.53 | |

a: The fluorescence decay was fitted to tri-exponential.

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

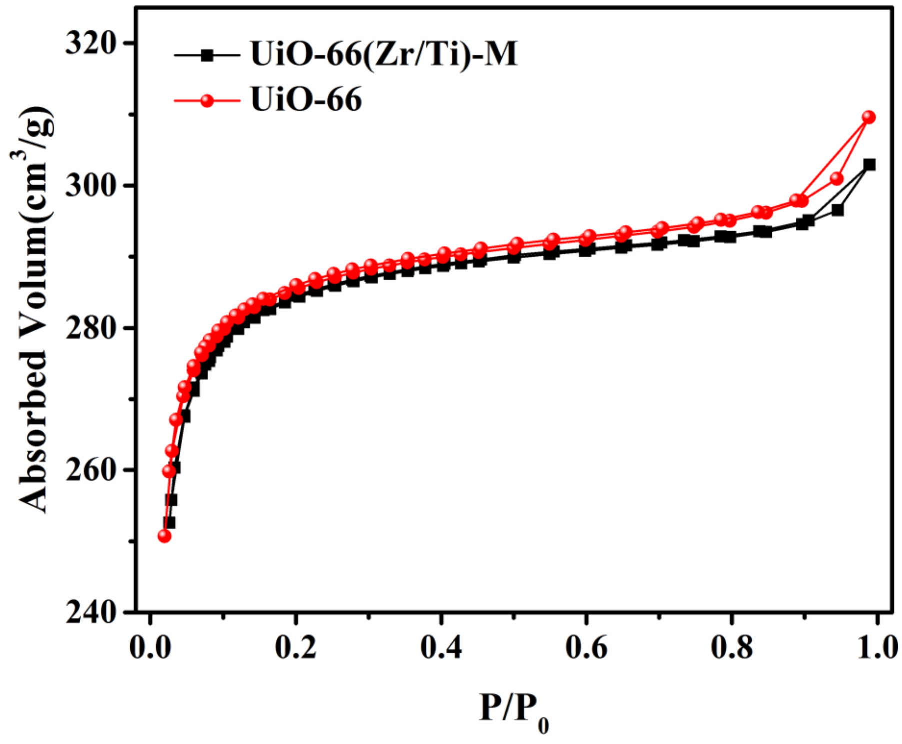

Fig. S1 $N_2$ adsorption/desorption isotherms of pure UiO-66 and UiO-66(Zr/Ti)-M.

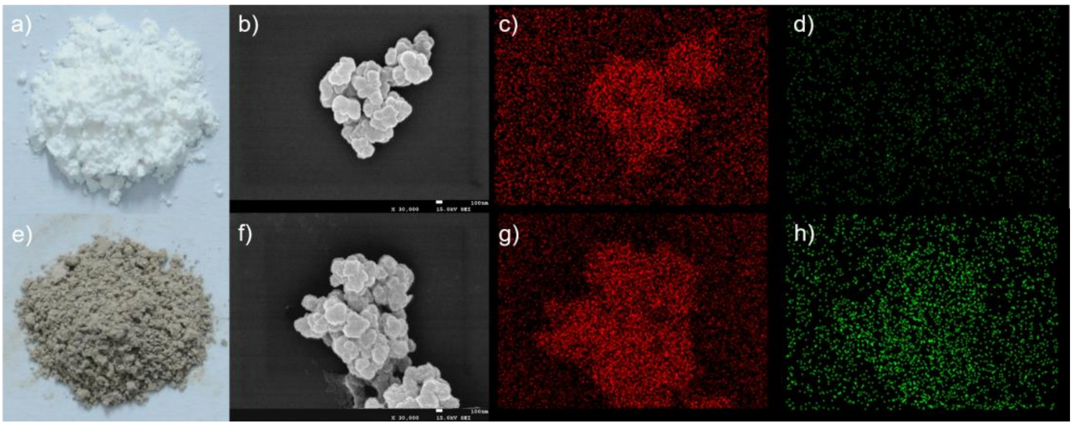

Fig. S2 Photograph of prepared UiO-66 (a) and UiO-66(Zr/Ti)-M (e); scanning electron microscope image of the crystals of UiO-66 (b) and UiO-66(Zr/Ti)-M (f); energy-dispersed X-ray mapping image of Zr obtained from the crystals of UiO-66 (c) and UiO-66(Zr/Ti)-M (g); energy-dispersed X-ray mapping image of Ti obtained from the crystals of UiO-66 (d) and UiO-66(Zr/Ti)-M (h). The UiO-66(Zr/Ti)-M were obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h.

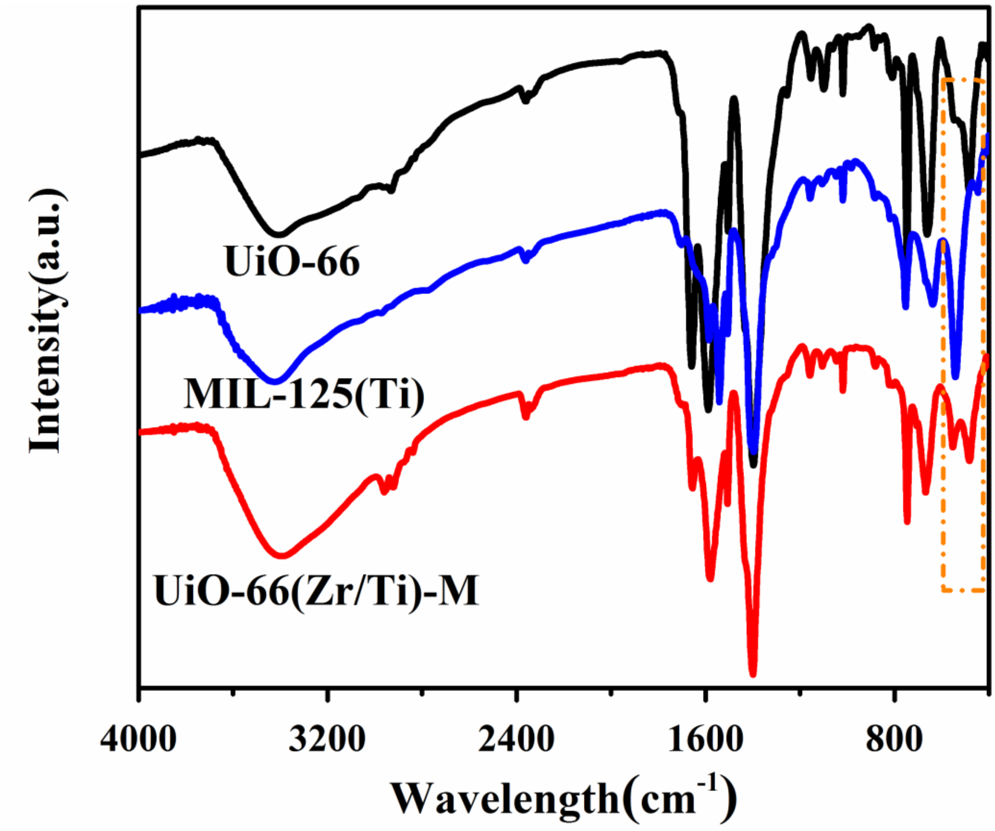

Fig. S3 FT-IR spectra of UiO-66, MIL-125(Ti) and UiO-66(Zr/Ti)-M (obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h).

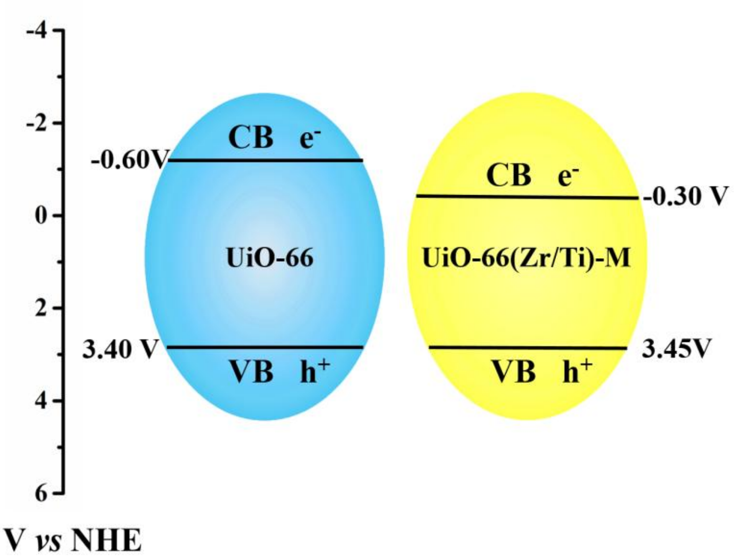

Fig. S4 Energy band structure of UiO-66 and UiO-66(Zr/Ti)-M prepared by the microwave-assisted reaction between UiO-66 and TiCp2Cl2 for 4 h.

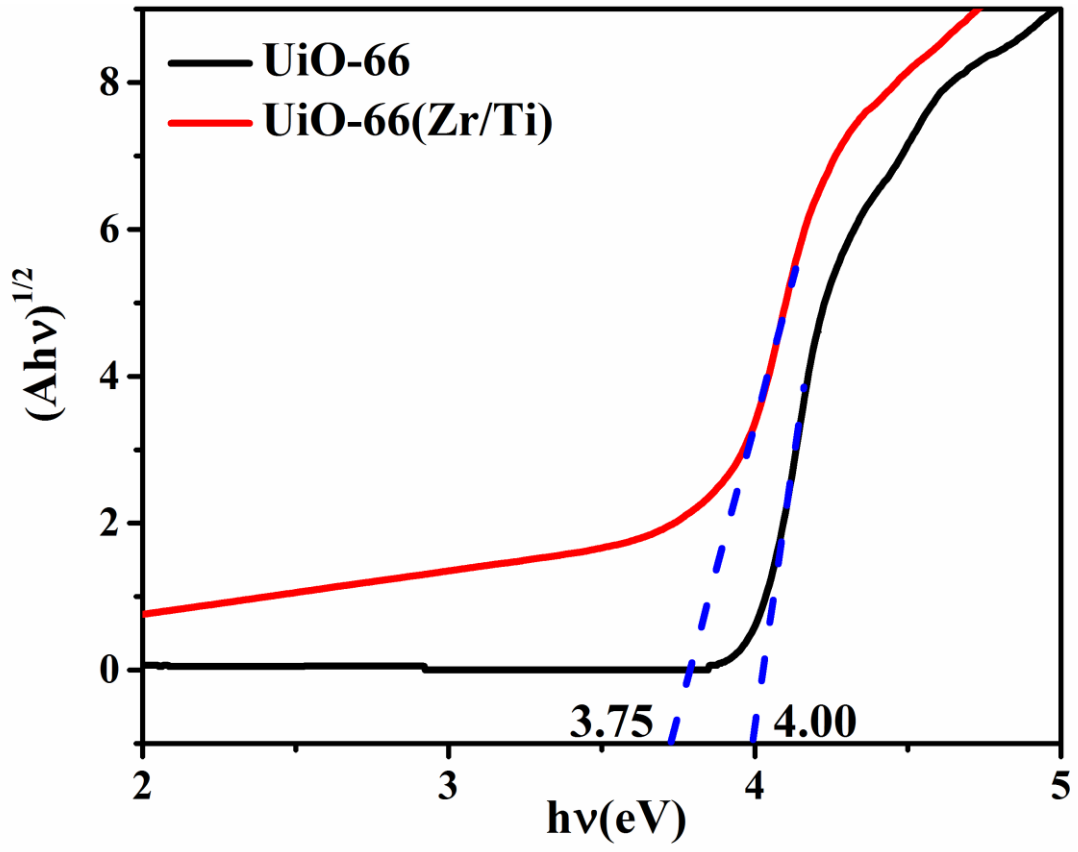

Fig. S5 Diffuse reflectance UV-Vis spectra of UiO-66 and UiO-66(Zr/Ti)-M (obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h).

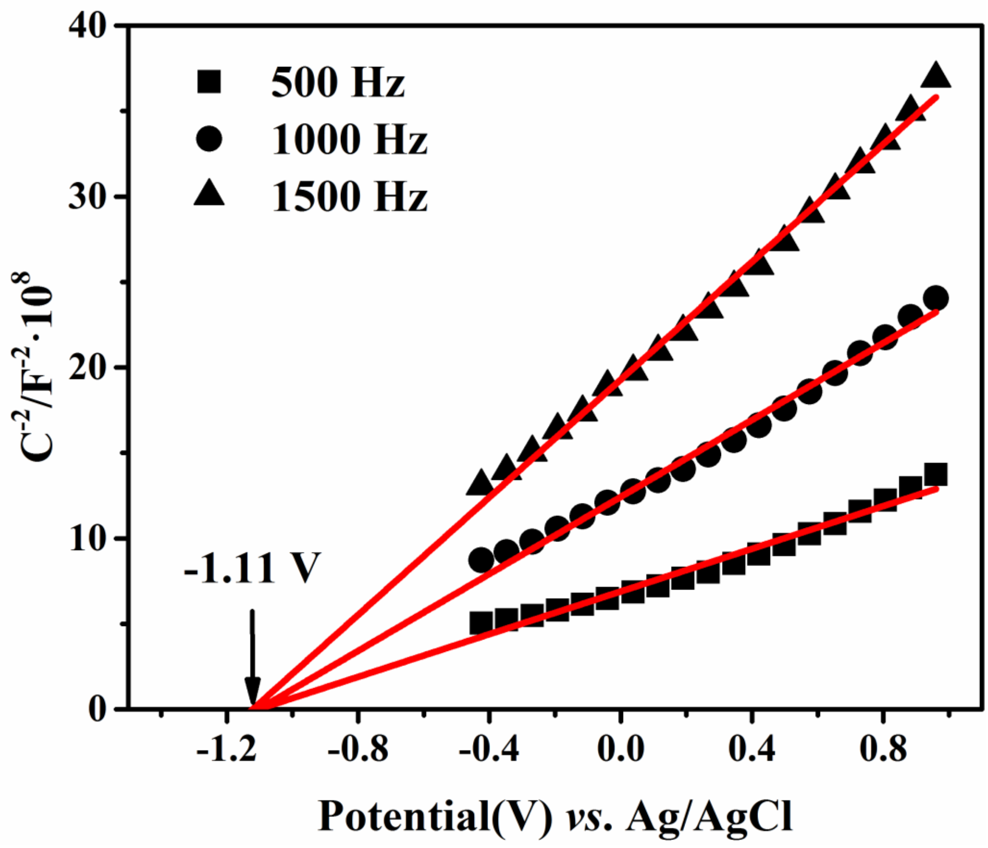

Fig. S6 Mott-Schottky plot of UiO-66

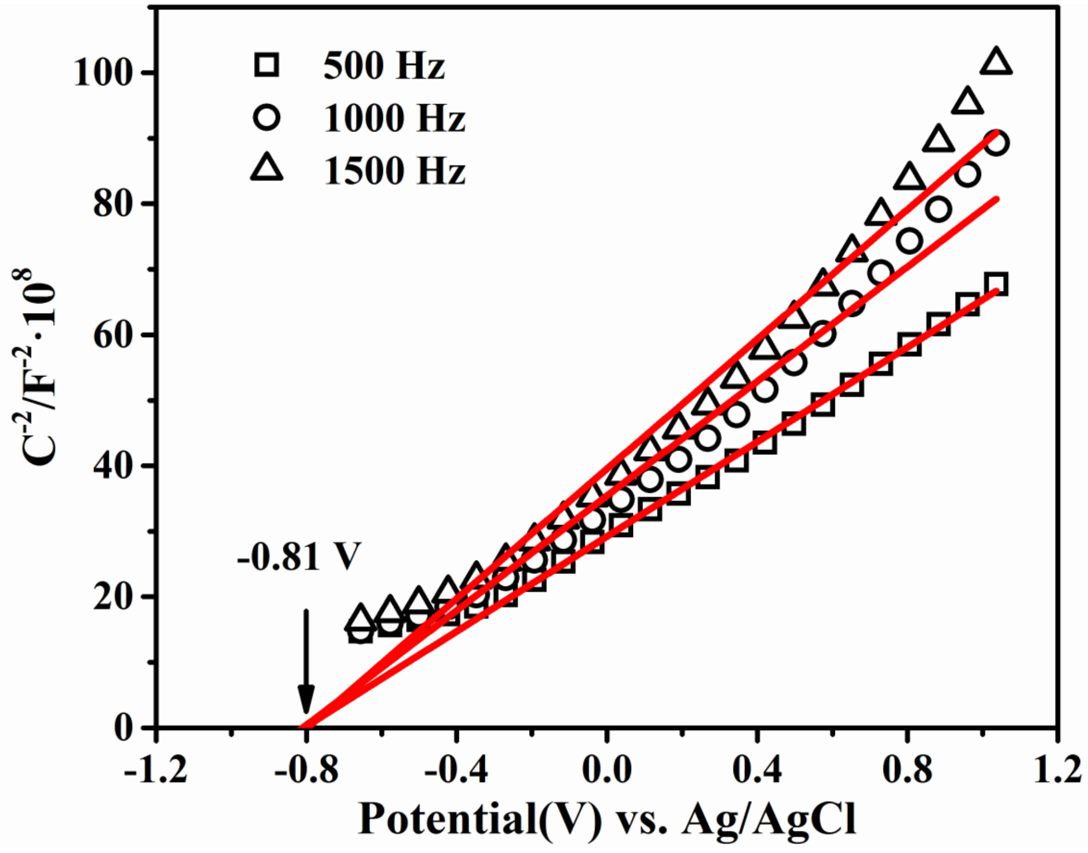

Fig. S7 Mott-Schottky plot of UiO-66(Zr/Ti)-M (obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h).

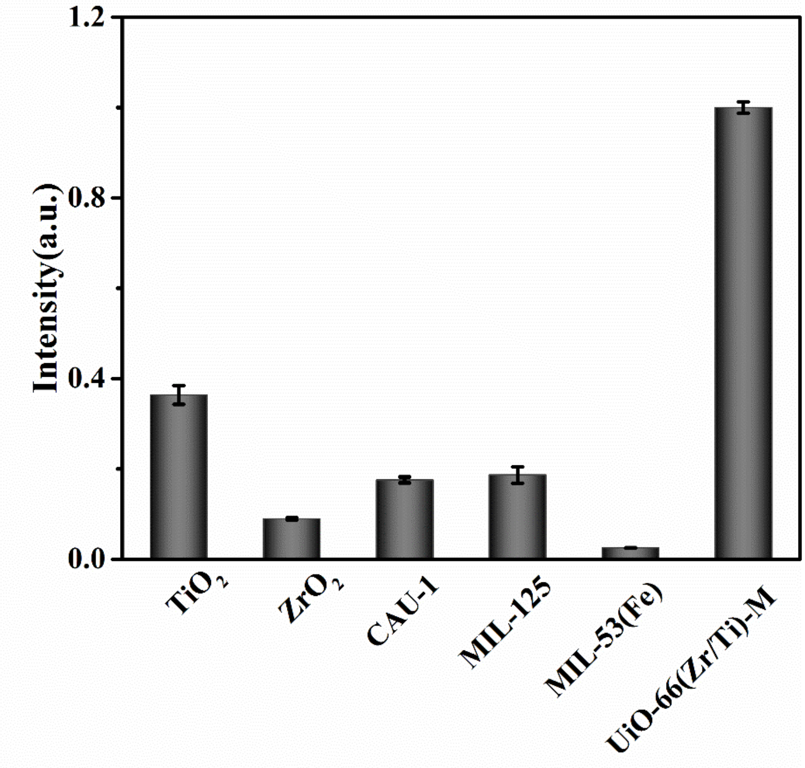

Fig. S8 AFS intensity of Se obtained from the reduction of Se(VI) (200 ppb) *via* PCVG (in 20% HCOOH, v/v) using $TiO_2$, $ZrO_2$, and various MOFs (all 0.5 mg/mL) as the photocatalyst.

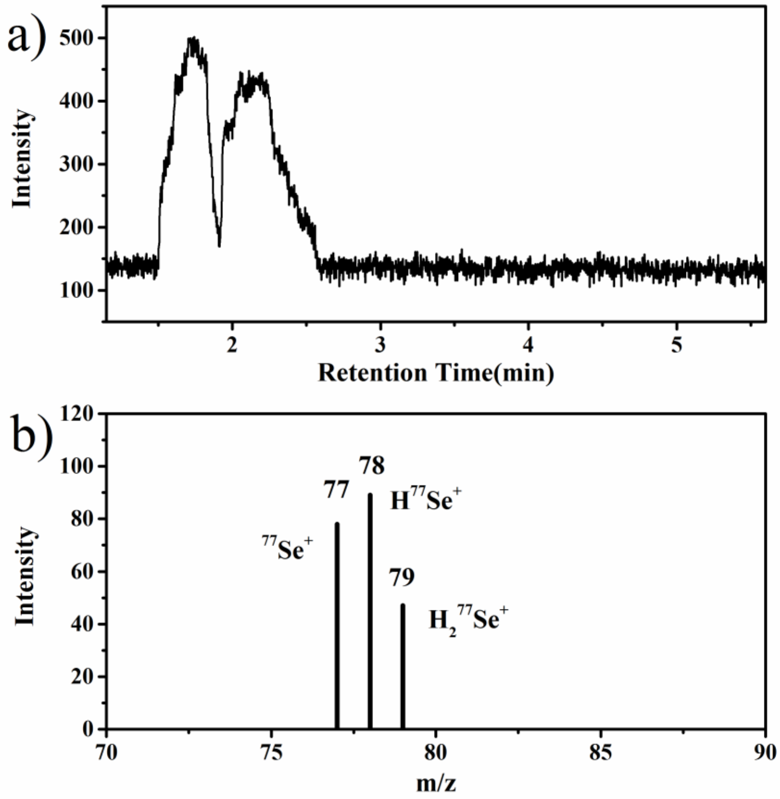

Fig. S9 The products obtained from the PCVG process (in 20% HCOOH, v/v) of Se (VI) using UiO-66(Zr/Ti)-M obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h as a photocatalyst, analyzed with GC-MS: a) the ion chromatogram of $^{77}Se^+$, b) the mass spectra extracted from the total ion chromatographic peak.

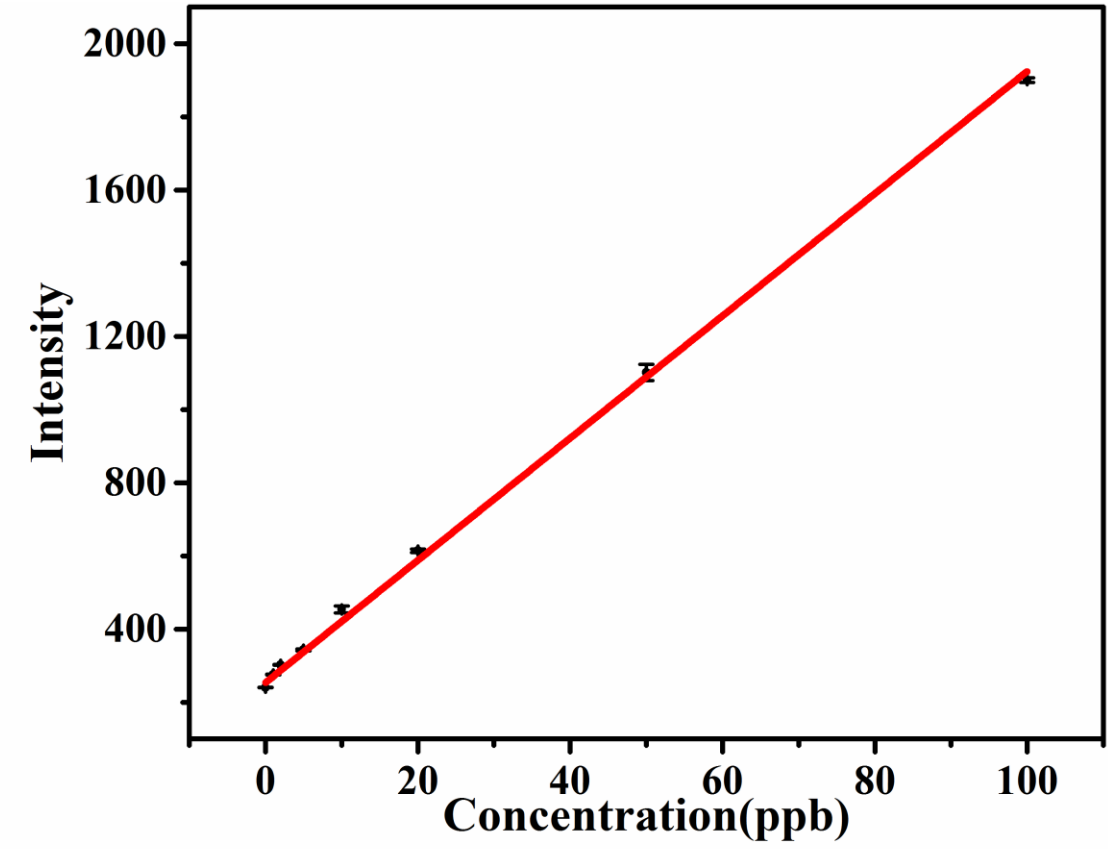

Fig. S10 Calibration curve: intensity of AFS signals after PCVG process of Se (VI) (in 20% HCOOH, v/v, using UiO-66(Zr/Ti)-M obtained from the reaction between UiO-66 and $TiCp_2Cl_2$ for 4 h as a photocatalyst) *versus* the concentration of Se (VI). $r^2$: 0.992, and LOD (3σ): 0.01 ppb.

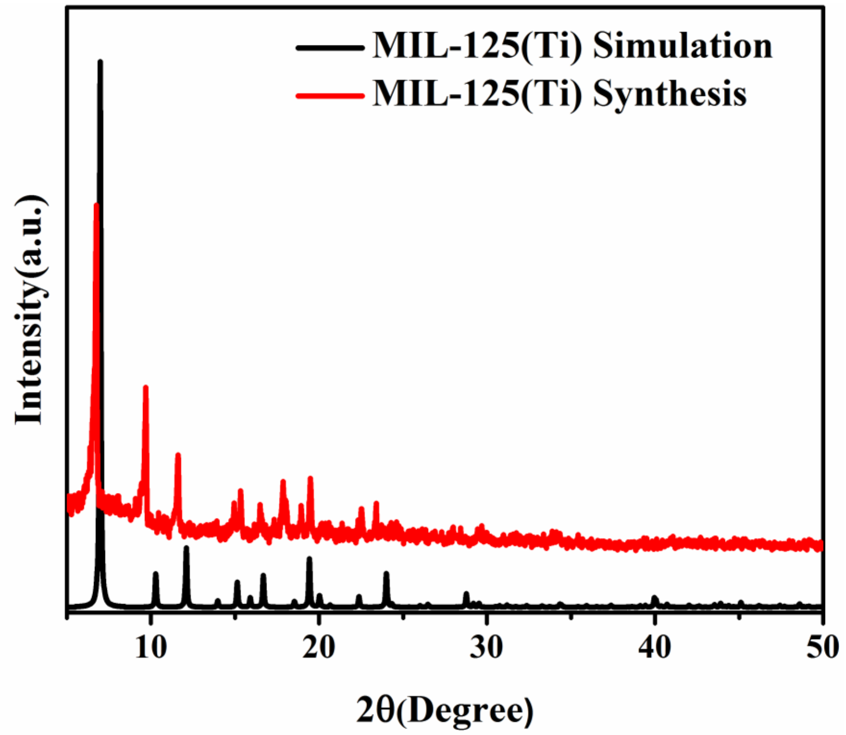

Fig. S11 PXRD patterns of the simulated MIL-125(Ti) and the synthesized MIL-125(Ti) particles.

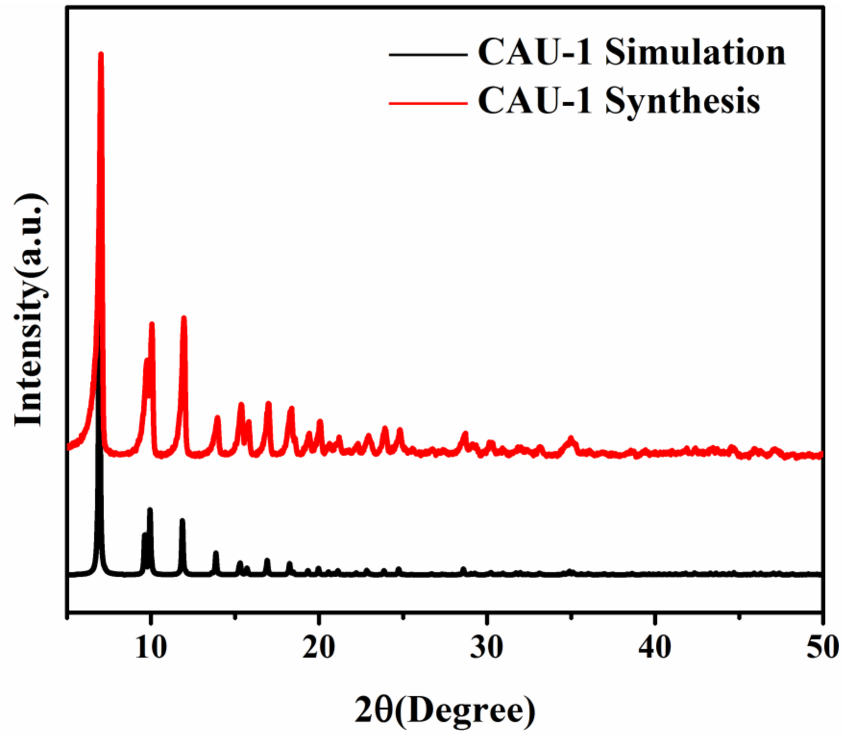

Fig. S12 PXRD patterns of the simulated CAU-1 and the synthesized CAU-1 particles.

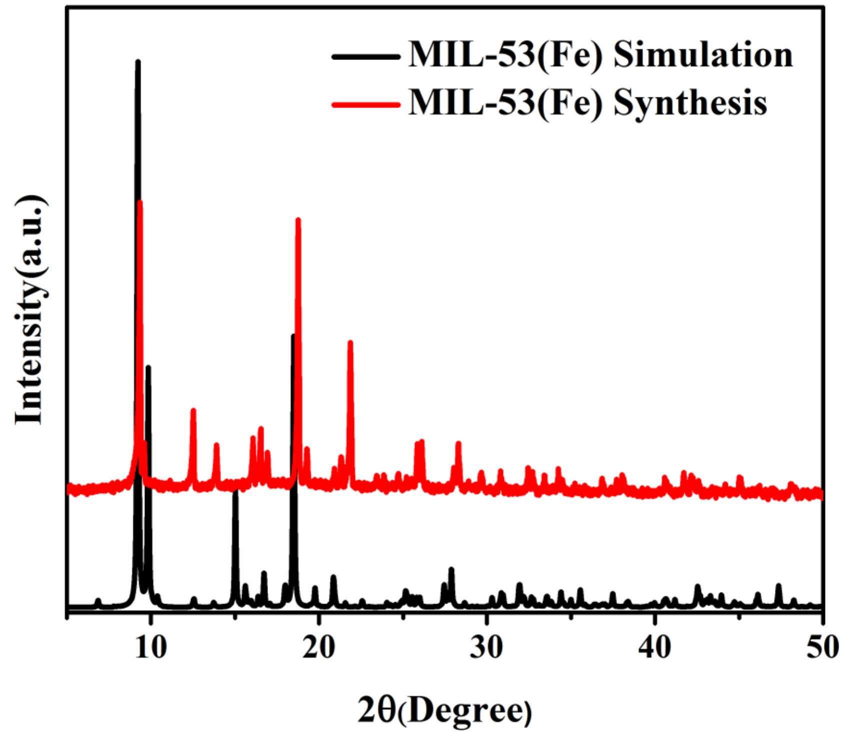

Fig. S13 PXRD patterns of the simulated MIL-53(Fe) and the synthesized MIL-53(Fe) particles.