Electronic Supplementary Information (ESI)

Metal Organic Frameworks CAU-1 as New Photocatalyst for Photochemical Vapor Generation for Analytical Atomic Spectrometry

JiaJia, ZhouLong, Chengbin Zheng, Xi Wu and Xiandeng Hou*

1. Chemicals

All the chemicals are AR grade. Ultrapure water (18.25 MΩ·cm) was produced with a purification water system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China). Tetrabutyl titanate, aluminum chloride hexahydride, zinc chloride, ferric chloride hexahydride, terephthalic acid (BDC) and 2-anmio terephthalic acid (BDC-NH_2) were purchased from Aladdin Reagents Co.Ltd.(Shanghai, China). N, N-Dimethylformamide (DMF), formic acid and ethanol were obtained from Kelong Chemical Reagent Co. Ltd. (Chengdu, China); standard aqueous Se(VI) was obtained from National Institute of Metrology China (Beijing, China). All chemicals and standards were kept at 4 ^{o}C in the dark until use.

2. Instrumentation

The microwave reactor (Master) was purchased from Sineo Microwave Chemistry Technology Co. Ltd. (Shanghai, China). The powder X-ray diffraction (PXRD) patterns were obtained with a X'Pert Pro MPD (Philips, Netherlands) using Cu_{ka} radiation. The GC/MS data were obtained with a GCMS-QP2010 plus (Shimadzu, Japan). The atomic fluorescence data were obtained with an AFS-2202 (Beijing Haiguang Instrument Co., Beijing, China). The optimal parameters for the PCVG-AFS system were summarized in Table S1.

Table. S1 The optimum parameters of AFS

AFS parameters	
PMT voltage	-310 V
HCL current	80 mA
Auxiliary current	40 mA
Excitation wavelength	196.0 nm
Argon flow rate	400 mL/min
Hydrogen flow rate	100 mL/min

3. Some Experimental Data

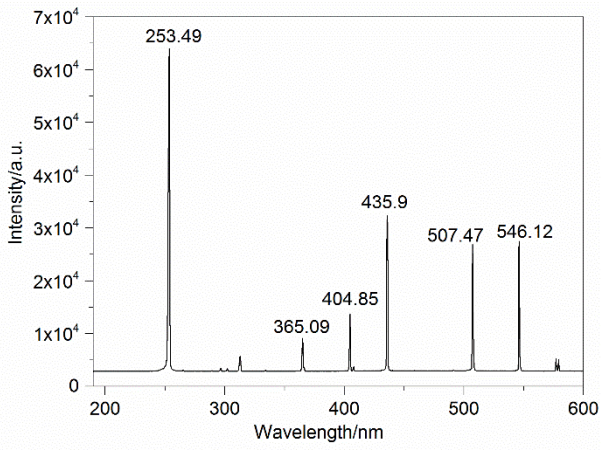

Fig. S1 The UV lamp emission spectra

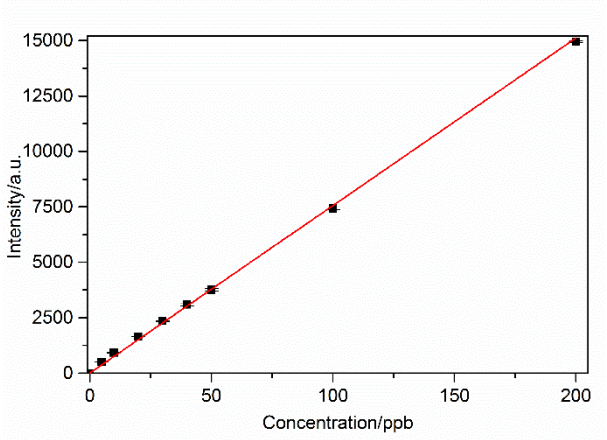

Fig. S2 Calibration curve: AFS intensities versus Se(VI) concentrations. r^2: 0.993, and LOD (3σ): 0.04 ppb

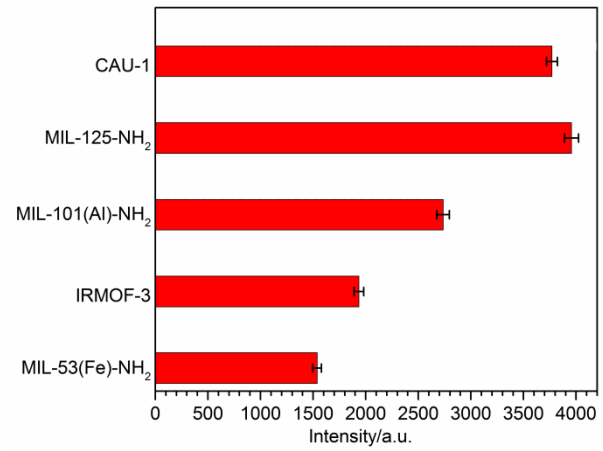

Fig. S3 AFS intensity obtained from various MOFs as a photocatalyst (50 mg) for the PCVG (using 10% of HCOOH, v/v) of Se(VI) (50 ppb).

4. Synthesis and Characterization

CAU-1:

232 mg of $AlCl_3 \cdot 6H_2O$ and 58 mg of BDC-NH_2were dissolved in 3.2 mL of methanol, and then stirred for 10 min and transferred into the microwave reactor, with the temperature risen up to 145 ^oC in 1 min and held for 2 mins. The whole suspension was then cooled down to room temperature. The obtained light yellow crystalswere washed with ethanol and then dried at 120 ^oC in vacuum.

MIL-125-NH_2:

0.6 mmol of tetrabutyl titanate and 1.2 mmol of BDC-NH_2 were dissolved in mixture of 5 mL DMF and 5 mL methanol, stirring for 10 min and transferred into the microwave reactor, with the temperature risen up to 150 ^oC in 1 min and held for1 hour. The whole suspension was then cooled down to room temperature. The obtained yellow crystals were washed with ethanol, dried at 120 ^oC in vacuum, and characterized with PXRD (Fig. S4).

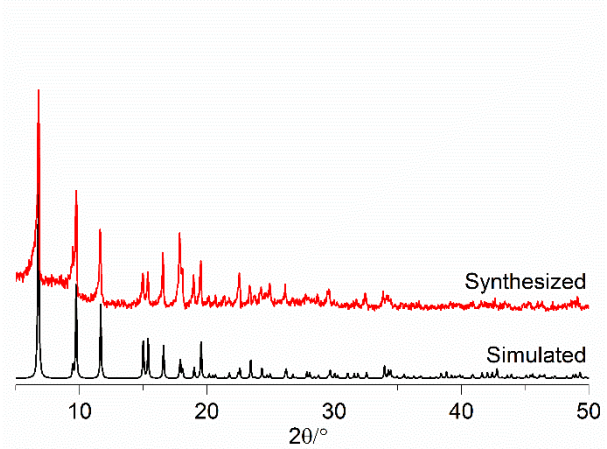

Fig. S4 PXRD patterns of MIL-125-NH_2.

MIL-101(Al)-NH_2:

510 mg of $AlCl_3 \cdot 6H_2O$ and 560 mg of BDC-NH_2 were dissolved in 30 mL of DMF, stirred for 10 min and then transferred into the microwave reactor, with the temperature risen up to 130 ^oC in 1 min and held for 1 hour. The whole suspension was then cooled down to room temperature.The obtained light yellow crystals were washed with ethanol, dried at 120 ^oC in vacuum, and then characterized with PXRD (Fig. S5).

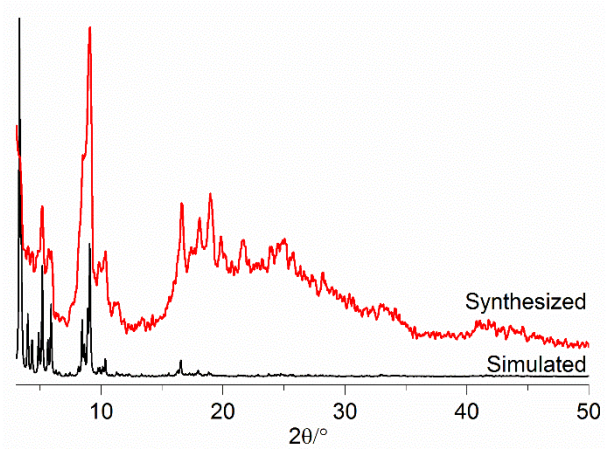

Fig. S5 PXRD patterns of MIL-101(Al)-NH_2

IRMOF-3:

170 mg of $ZnCl_2$•$6H_2O$ and 51 mg of BDC-NH_2 were dissolved in 15 mL of DMF, stirred for 10 min. The obtained light yellow crystals were washed with ethanol, dried at 120 °C in vacuum, and then characterized with PXRD (Fig. S6).

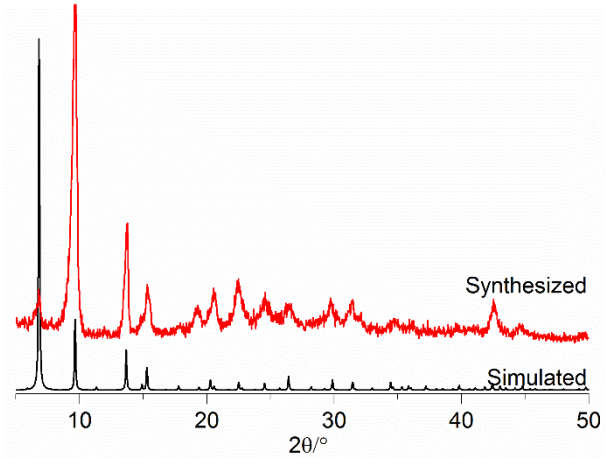

Fig. S6 PXRD patterns of IRMOF-3

MIL-53(Fe)-NH_2:

1.0812 g of $FeCl_3$•$6H_2O$ and 0.3327 g of BDC were dissolved in 40 mL of DMF, stirred for 10 min and then transferred into the microwave reactor, with the temperature risen up to 100 °C in 1 min and held for 1 hour. The whole suspension was then cooled down to room temperature. The obtained red-brown crystalswere washed with ethanol, dried at 120 °C in vacuum, and then characterized with PXRD (Fig. S7).

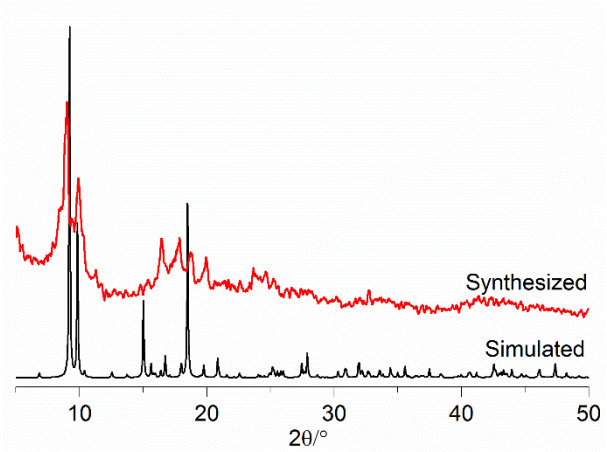

Fig. S7 PXRD patterns of MIL-53(Fe)-NH_2