Supporting Information

Introduction of Mediator for Enhancing Photocatalytic Performance via Post-Synthetic Metal Exchange in Metal-Organic Frameworks (MOFs)

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1. Experimental Section

Materials 2-aminoterephthalic acid (H_2ATA) was purchased from Alfa Aesar Co. $ZrCl_4$ and $TiCl_4$ were purchased from Aladdin Co. Anhydrous *N,N*- dimethylformamide (DMF) was purchased from Sigma Aldrich Co. Anhydrous dichloroethane was purchase from J&K Scientific Ltd. All the reagents were used as received without further purification.

Synthesis of NH_2-Uio-66(Zr) NH_2-Uio-66(Zr) was prepared following a previous reported procedure with slight modifications. $ZrCl_4$ (0.240g, 1.029 mmol) and 2-aminoterephthalic acid (H_2ATA) (0.1860g, 1.029 mmol) were dissolved in anhydrous *N,N*- dimethylformamide (DMF) (60ml) at room temperature. De-ionized water (0.19ml) was dropped to the mixture. The thus-obtained mixture was stirred at room temperature for 10 minutes and was transferred to a 100 ml Teflon liner and heated at 120°C for 24 hours. After hydrothermal treatment, the resultant suspension was washed with DMF and methanol respectively, extracted by Soxhlet extractor with methanol and vacuum dried to obtain the product.

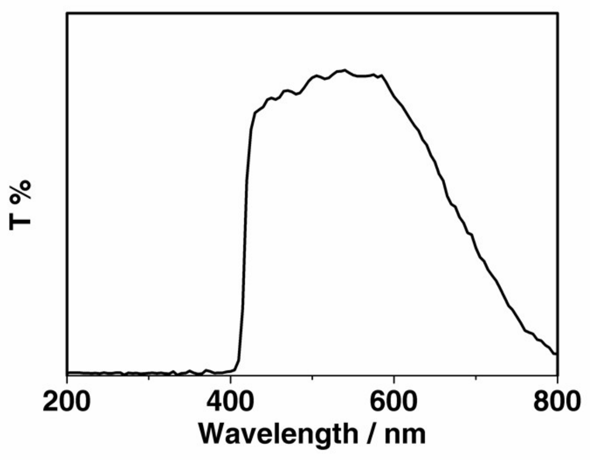
Synthesis of $TiCl_4(THF)_2$ $TiCl_4(THF)_2$ was synthesized according to the previous reported procedure with slight modifications. $TiCl_4$ (2.9 ml, 26.4 mmol) was dissolved in anhydrous dichloroethane (50 ml) in a 250mL round-bottomed flask under inert conditions. Anhydrous tetrahydrofuran (THF) (8.6 ml, 105.8 mmol) was added to the above solution at 0 °C to form a yellow solution. Anhydrous n-hexane (100 ml), which was dried by sodium, was used to precipitate yellow powder. The resultant powder was filtered and washed with n-hexane (2 × 50 mL) and dried for 3 hours over a Schlenk line. The resulted yellow $TiCl_4(THF)_2$ was used immediately for post-synthetic exchange.

Post-synthetic exchange of NH_2-UiO-66(Zr) with $TiCl_4(THF)_2$ The post-synthetic exchange of NH_2-UiO-66 with $Ti(OC_4H_9)_4$ was carried out according to the previous reported procedure with some modifications. NH_2-UiO-66(Zr) (0.28g) was dispersed in anhydrous DMF (7ml). $TiCl_4(THF)_2$ (0.34 g) was added to the above suspension under inner condition. The mixture was incubated at 100°C and 120°C for specific time, respectively. The solids were separated from the solvent via centrifugation, and washed with fresh DMF and methanol. The solids were dried at 40°C in a vacuum for 24 hours to get Ti exchanged NH_2-Uio-66(Zr) (denoted as NH_2-Uio-66(Zr/Ti)).

Characterizations X-ray diffraction (XRD) patterns were collected on a D8 Advance

X-ray diffractometer (Bruker, Germany) with Cu Kα radiation. UV-visible diffuse reflectance spectra (UV-DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA). $BaSO_4$ was used as a reflectance standard in the UV-visible diffuse reflectance experiment. BET surface area and the CO_2 adsorption were carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). For BET surface area analyses, the samples were degassed in vacuum at 200 °C for 12h and then measured at 77 K. CO_2 adsorption isotherms were measured at 0 °C after degassed in vacuum at 200 °C for 15h. The exchange extent was monitored by Inductively Coupled Optical Emission Spectrometer (ICP-OES) on Optima 8000 (PerkinElmer). Before ICP-OES experiment, the solid sample was digested in mixture of HNO_3 and milli-Q water and the exchanged Zr moiety in the solution was collected from the first residual solution. The X-ray absorption fine structure (XAFS) spectra were collected in Shanghai Synchrotron Radiation Facility (SSRF) with a Si (111) double-crystal monochromator in transmission mode. The source of BL14W1 is a 38-pole wiggler device with maximum magnetic field 1.2 T and magnet period 80 mm. The storage ring was operated at 3.5 GeV with injection currents of 100 mA.

Photocatalytic reaction The photocatalytic reaction was performed in a sealed system pre-saturated with CO_2 atmosphere in the presence of TEOA as a sacrificial agent under visible-light irradiations. The photocatalyst (50 mg) suspended in a mixture of MeCN and TEOA (60 mL, v/v=5:1) were degassed and saturated with CO_2 before the photocatalytic reaction. The reaction was performed under the irradiation of a 300 W Xe lamp with a UV-cut filter to remove all wavelengths less than 420 nm and an IR-cut filter to remove all wavelengths larger than 800 nm (as shown in the following figure). The $HCOO^-$ formed was detected by IC (881 Compact IC pro, Metrosep) with Metrosep A supp 5 250/4.0 column. The column temperature was maintained at 303 K. A mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ was used as the eluent.



The UV/Vis spectrum of a UV-cut and an IR-cut filter.

2. Computational Section

Optimizations of the Structures The projector-augmented wave (PAW) formalism of density functional theory (DFT) was used as implemented in the Vienna ab initio simulations package (VASP),[1-4] and the Perdew-Burke-Ernzerhof (PBE) type exchange-correlation was adopted.[5] In the geometrical optimizations, an energy cutoff of 400 eV and a 5 × 5 × 5 Monkhorst-Pack k-point grid were employed. For NH_2-Uio-66(Zr), it was constructed from Uio-66(Zr) with cubic phase (Fm-3m), and the unit cell contains 126 atoms with a formula of $Zr_6O_{32}N_6C_{48}H_{34}$. For the Ti-doped NH_2-Uio-66(Zr), one Zr atom in the unit cell was replaced by one Ti atom. During the structural optimizations, the cell shape and the positions of all atoms were allowed to be relaxed, and the force convergence threshold was set to 0.03 eV/Å.

Electronic Structures The calculated density of states (DOSs) of NH_2-Uio-66(Zr) are shown in Fig. S6. In the figures, the Fermi level is set to zero. It is noted that there are three kinds of oxygen atoms in the system, including the oxygen of bridging hydroxo group, the bridging oxygens linked to two Zr atoms, and the oxygens belonged to the carboxylic group of ATA, respectively. From the Fig. S7d, it is clear that the valence band near the Fermi level is mainly derived from the 2p lone pair of nitrogen atom, while the conduction band is dominated by the π* states of the ligand ATA.

Table S1 The amount of Ti moiety in the NH_2-Uio-66(Zr/Ti) and the exchanged Zr moiety in the solution.

Sample	Ti(IV) content in catalysts / atomic %	Exchanged Zr(IV) content in solution / atomic %
NH_2-Uio-66(Zr)	0	0
NH_2-Uio-66(Zr/Ti)-100-4	34.2	29.3
NH_2-Uio-66(Zr/Ti)-120-4	53.4	46.5

Table S2 EXAFS fit parameters for the prepared samples.

path	CN[a]	R (Å)[b]	σ^2 (Å^2)[c]	R_{factor} (%)[d]
Fit of pristine NH_2-Uio-66(Zr) (K range is 3.01-13.77, R range is 1.1-3.8)				
Zr-$O_{\mu3}$	2.17	2.06	0.0055	0.07
Zr-O	6.51	2.27	0.0085	
Zr-Zr	4.064	3.52	0.0054	
Fit of NH_2-Uio-66(Zr/Ti)-120-16 (K range: 3.23-12.17, R range: 1.3-4.9)				
Ti-$O_{\mu3}$	2.16	1.93	0.0044	2.4
TI-O	6.49	2.26	0.0093	
TI-Zr	3.42	3.29	0.010	

[a] Coordination number; [b] Bond length; [c] Debye-Waller factor; [d] The goodness-of-fit index.

Fig. S1 The SEM images of prepared samples: (a) pure NH_2-Uio-66(Zr); (b) NH_2-Uio-66(Zr/Ti)-120-16

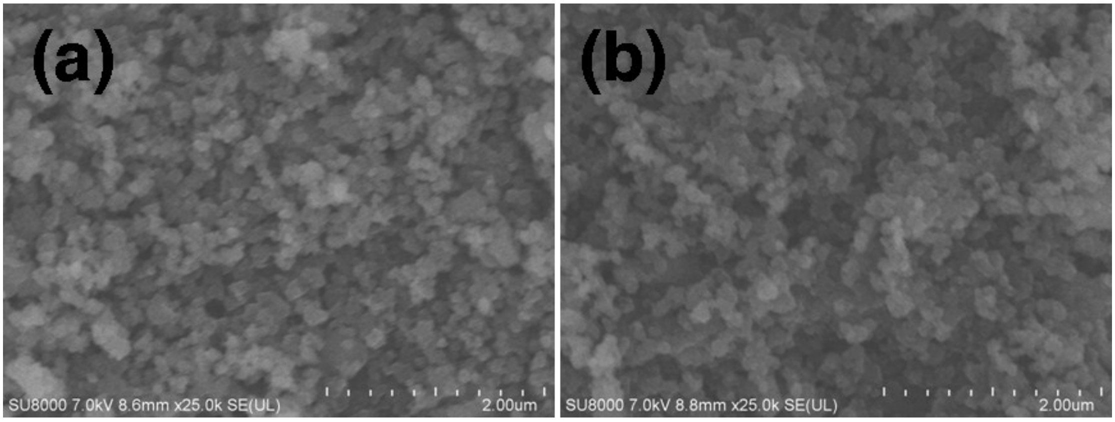


Fig. S2 N_2 adsorption/desorption isotherms (77 K) of the prepared samples.

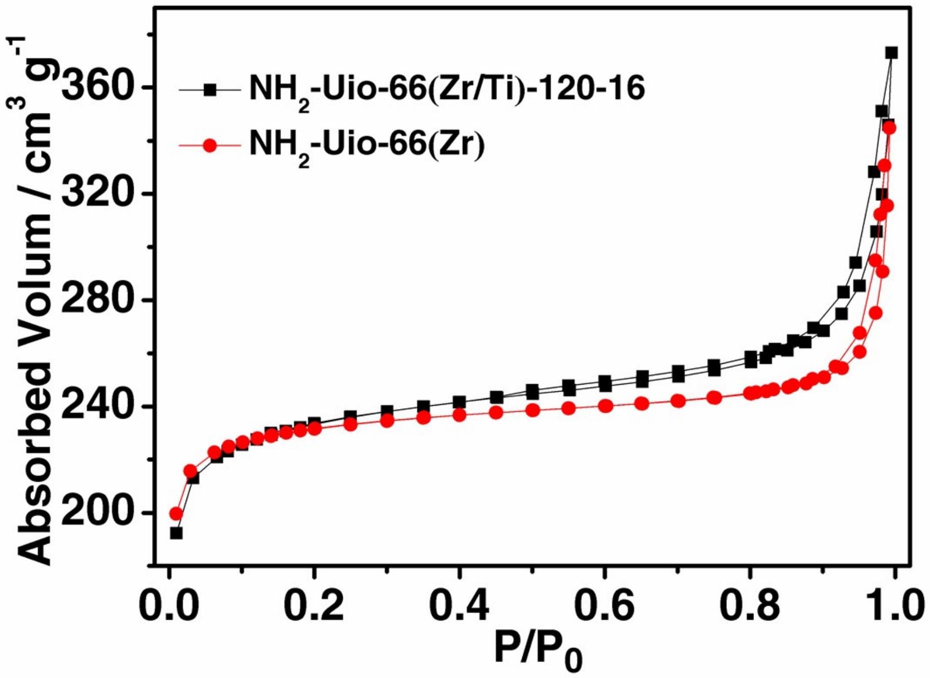


Fig. S3 The UV/Vis spectra of the prepared samples.

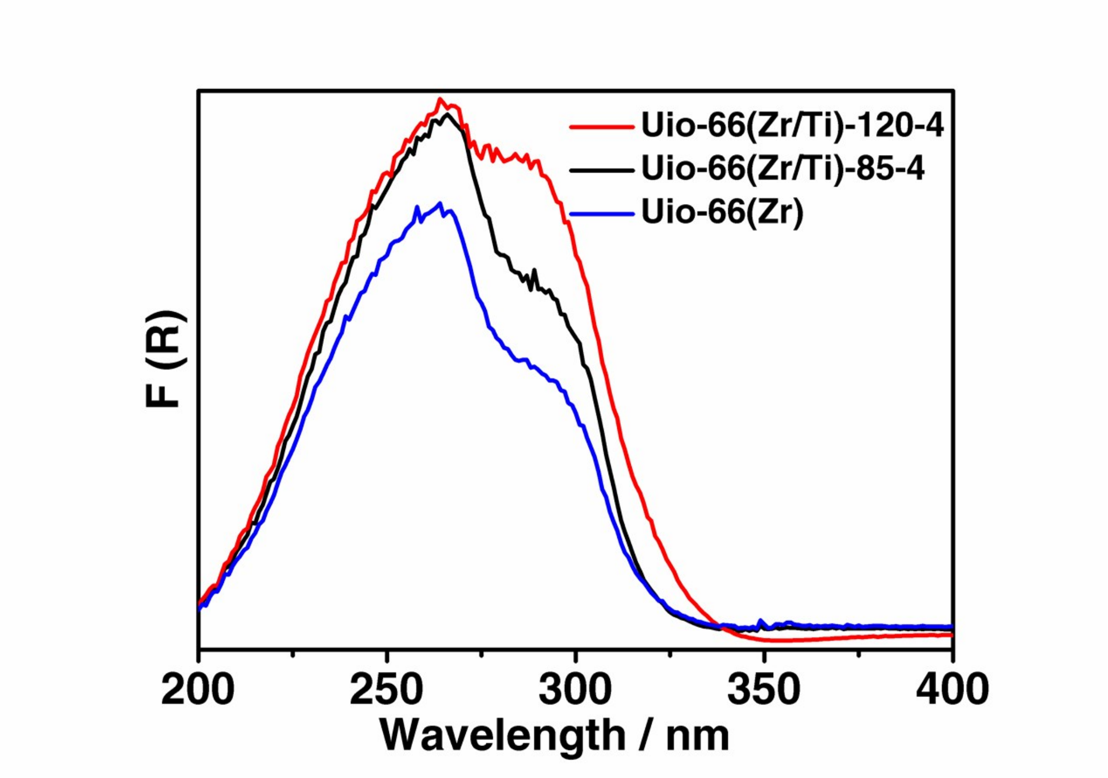


Fig. S4 Comparison between the experimental and best fit k^3-weighted χ(R) of (a) pristine NH_2-Uio-66(Zr); (b) NH_2-Uio-66(Zr/Ti)-120-16.

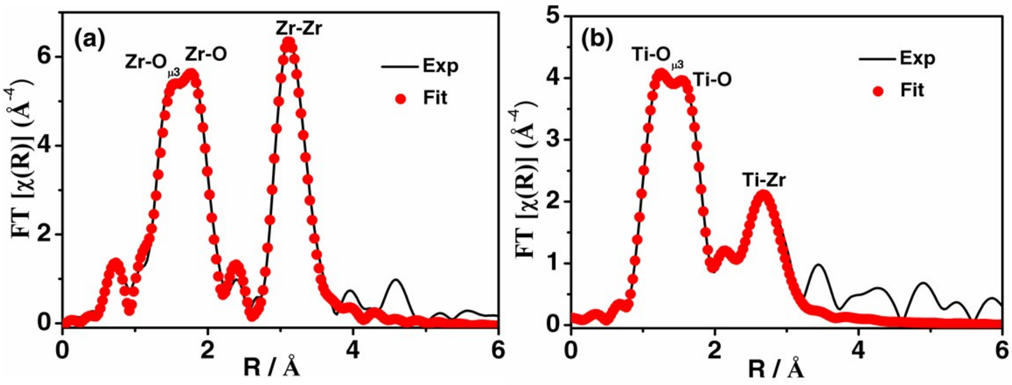
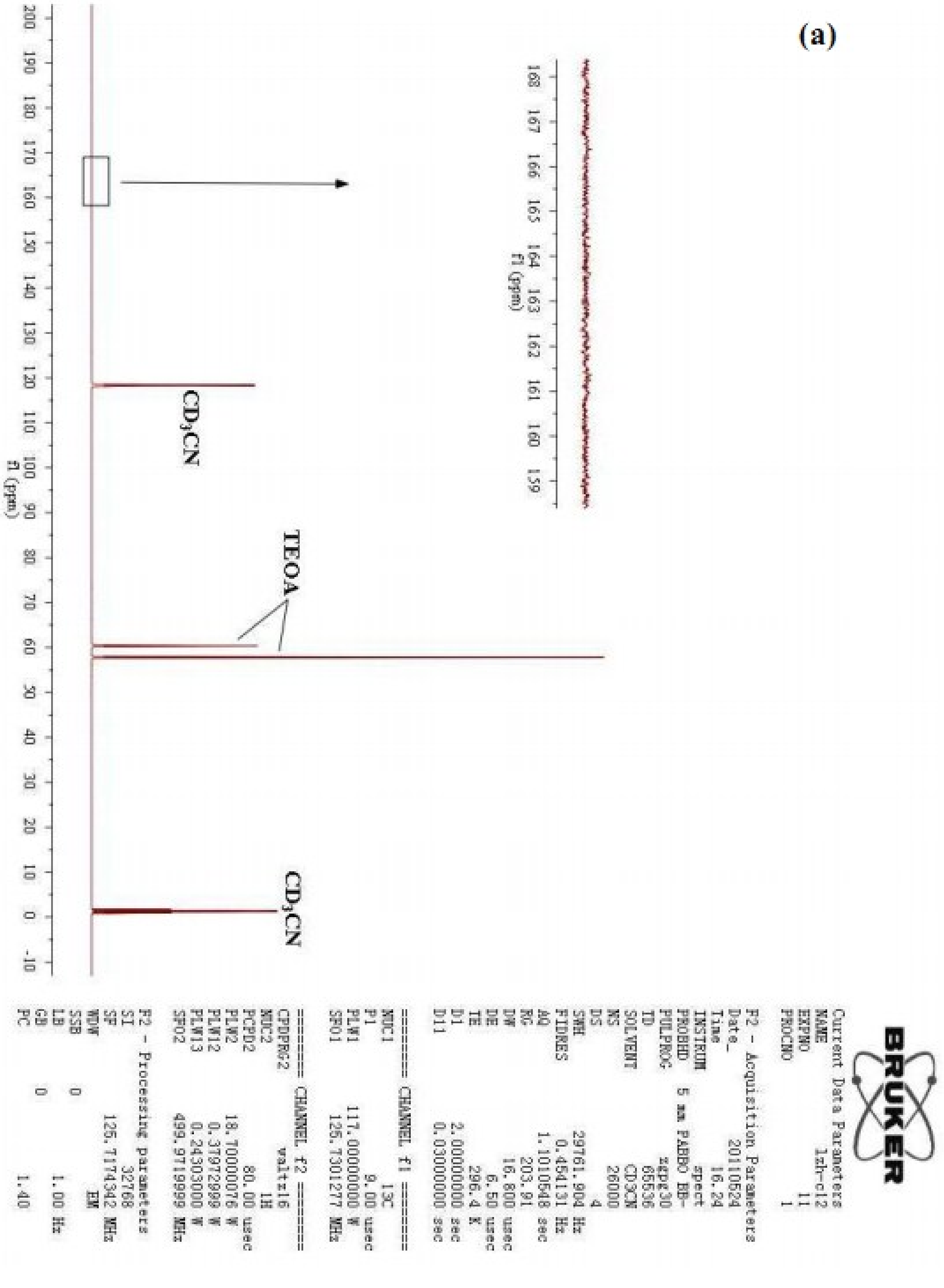


Fig. S5 The ^{13}C NMR spectra for the product obtained under the following reaction conditions in a NMR tube (a) 5 mg NH$_2$-MIL-125(Ti), 5 ml CD$_3$CN/TEOA (5:1 v/v), ^{12}CO$_2$, 10h; (b) 5 mg NH$_2$-MIL-125(Ti), 5ml CD$_3$CN/TEOA (5:1 v/v), ^{13}CO$_2$, 10h. [1]



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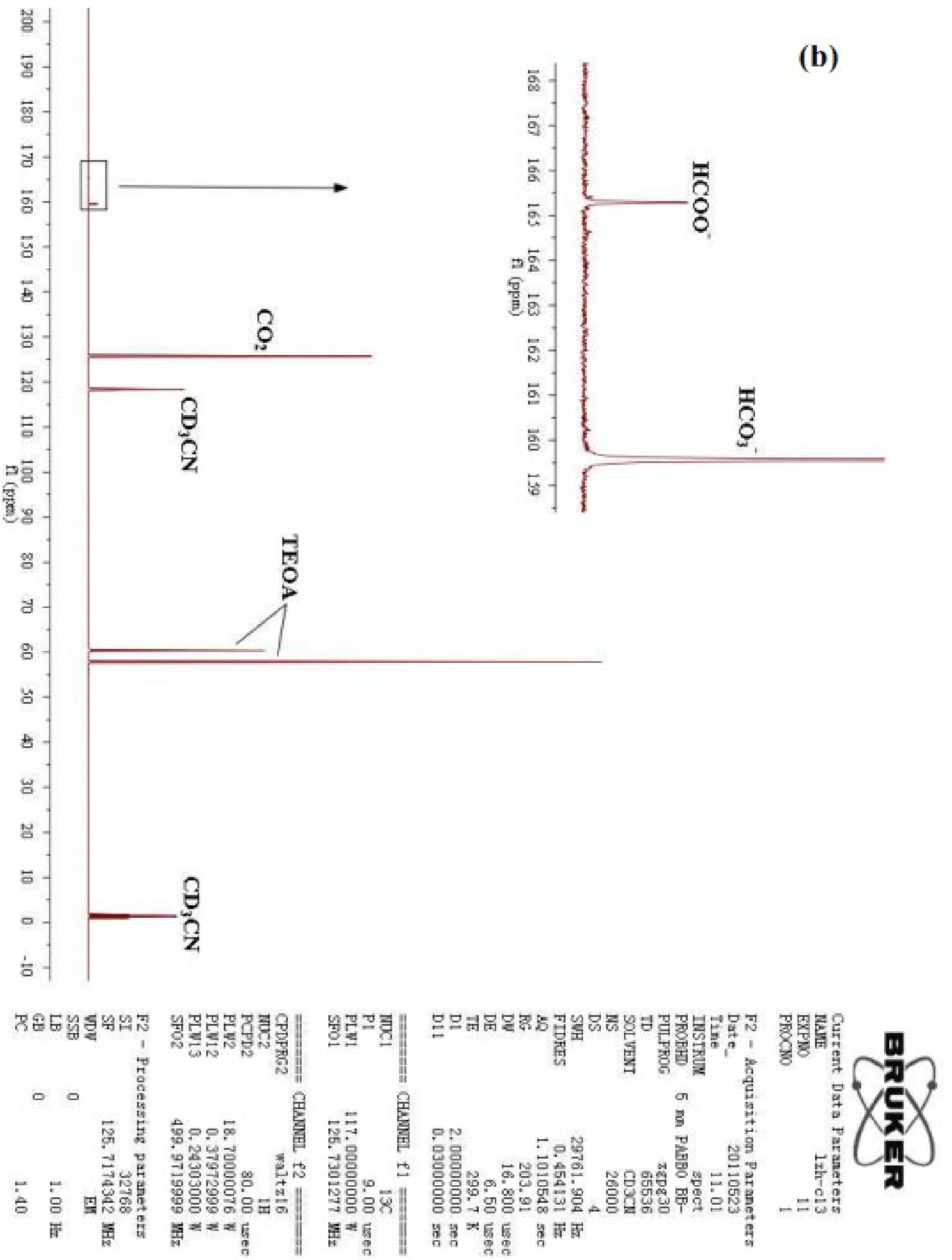

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[1] Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 3364-3367.

Fig. S6 (a) XRD patterns of fresh and used NH_2-Uio-66(Zr/Ti)-120-16; (b) N_2 adsorption/desorption isotherms (77 K) of fresh and used NH_2-Uio-66(Zr/Ti)-120-16.

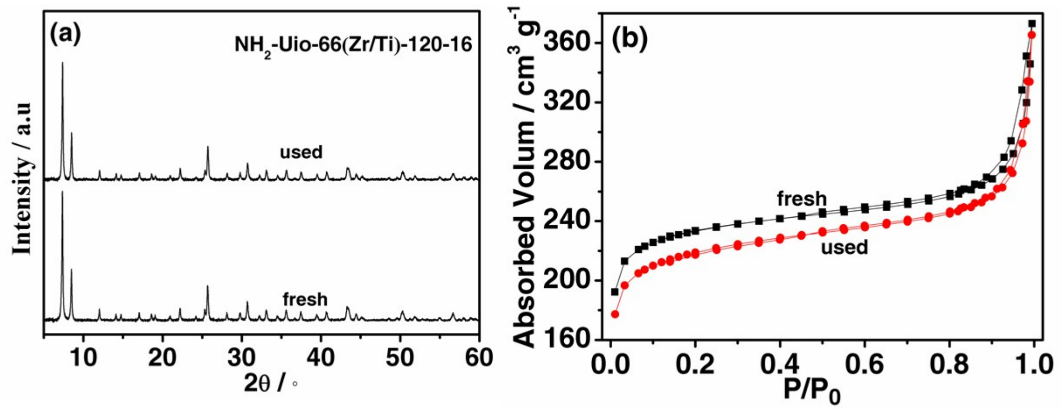

Fig. S7 CO_2 adsorption isotherms (1 atm, 273 K) of the prepared samples.

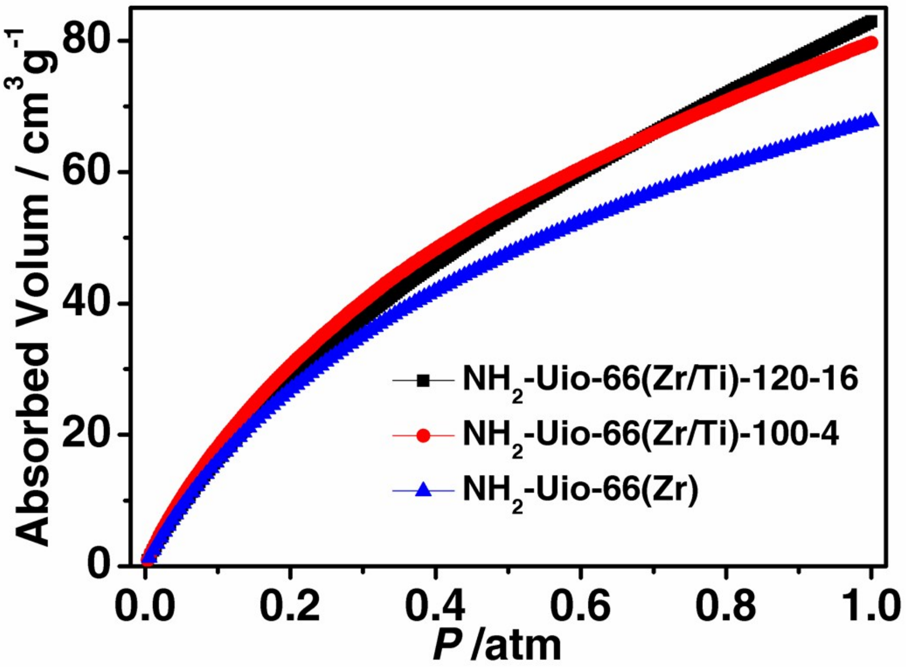

Fig. S8 Some atomic partial DOSs of NH_2-Uio-66(Zr).

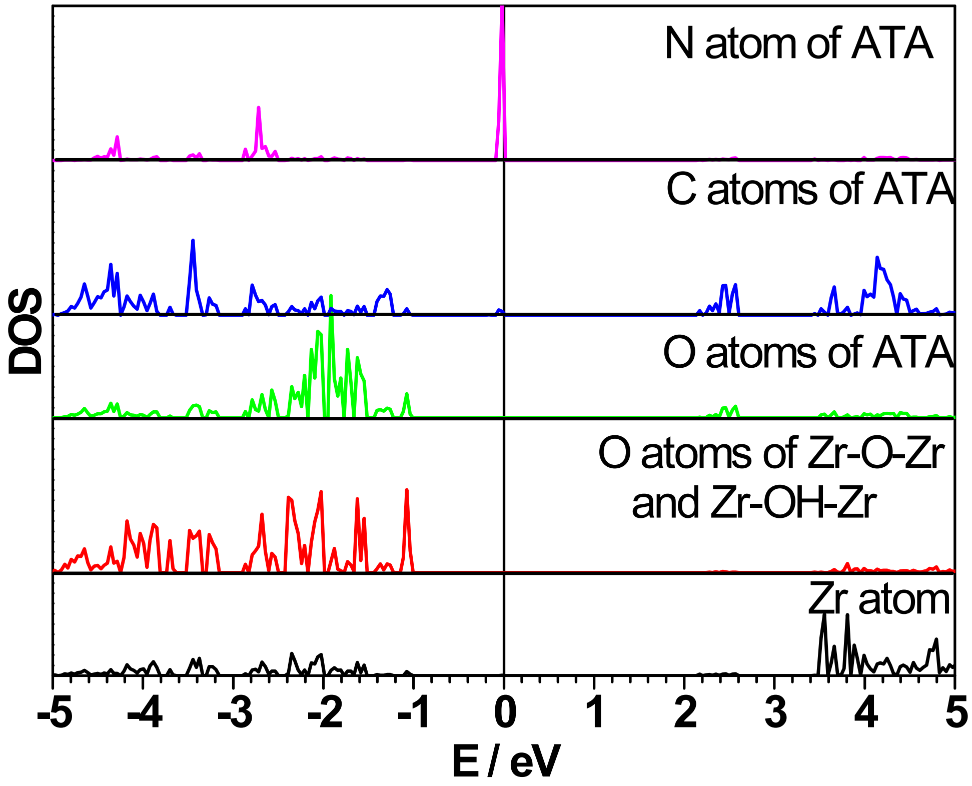

Fig. S9 The ESR spectra taken at different time after irradiations was switched off over (a) NH_2-Uio-66(Zr); (b) NH_2-Uio-66(Zr/Ti) (inset shows the expansion of the selected region). The samples were dispersed in a mixture of CH_3CN and TEOA for ESR study and ESR spectra were collected at 250K in Ar.

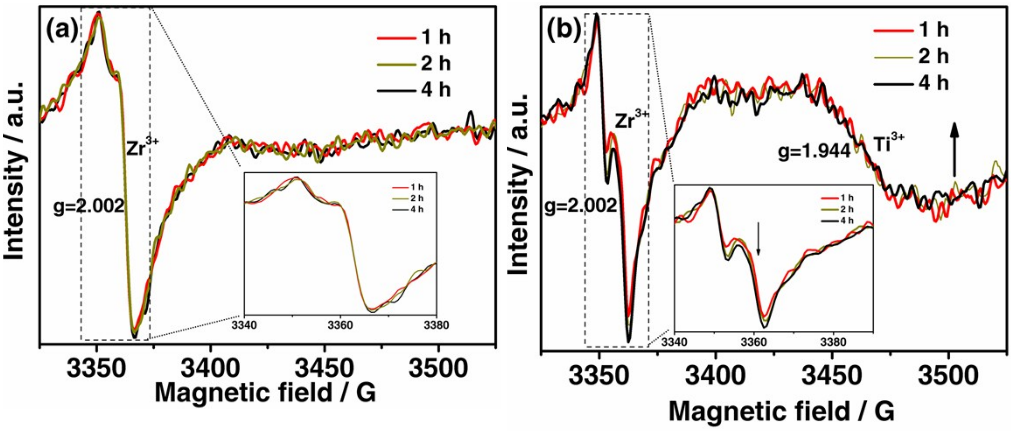

Fig. S10 Photographs of NH_2-Uio-66(Zr/Ti) in N_2 and CO_2 under visible light irradiation