Electronic Supplementary Information

In Situ Preparation of MOF-derived Magnetic Carbonaceous Catalyst for Visible-Light-Driven Hydrogen Evolution

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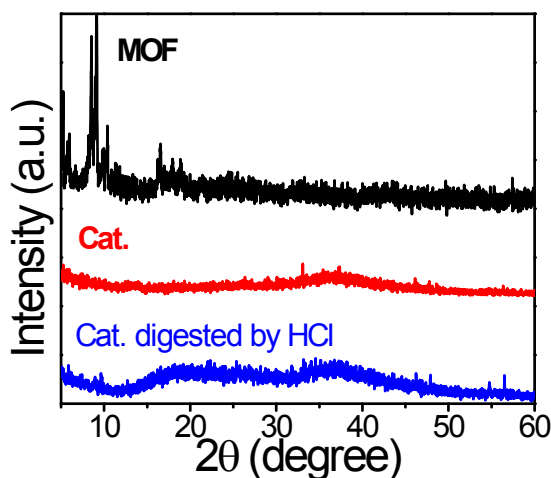**The XRD patterns of MIL-101(Fe), Cat. and Cat. digested by HCl**

Figure S1. The XRD patterns of MIL-101(Fe), Cat. and Cat. decomposed. The diffraction peaks of MIL-101(Fe) are consistent with the literature,[1] reflecting a crystalline structure. For the catalyst however XRD peaks corresponding to crystalline phases of carbon or Fe phase can not be clearly identified. XRD patterns of Cat. decomposed implied amorphous carbon.

Quantum Efficiency (QE) calculation procedures

The quantum yield for H_2 generation was calculated using the following equation (1):[2]

$$Q \; E(100\%) = \frac{n \times N(H_2)}{N(p \; ho \; t \;)n} \times 100$$

eq. (1)

where the electron factor n of the reaction ($2H^+ + 2e^- \rightarrow H_2$) is 2, and $N(H_2)$ is the number of produced H_2 molecules. Hydrogen production was calculated from the amount of H_2 produced from the first 6 h of light irradiation. N(photons) is the number of absorbed photons during the H_2 evolution and are calculated by the following equation (2):

$$N(p \; ho \; t \;)n = t \times S \times Q$$

eq. (2)

where t is irradiation time (s), S is the effective light irradiation area (m^2), and Q is the photon

flux of the incident light (number of photons m^{-2} s^{-1}). Q was measured using a radiometer (FZ-A, Opto-electronic Instrument of Beijing Normal University, light spectrum, 400−1000 nm). The average QE for the catalyst was calculated with uncertainties based on the multiple measurements. The spectral distribution of the white-light LED source is shown in Figure S2, which ranges the whole visible region from 400 to 750 nm without any filter.
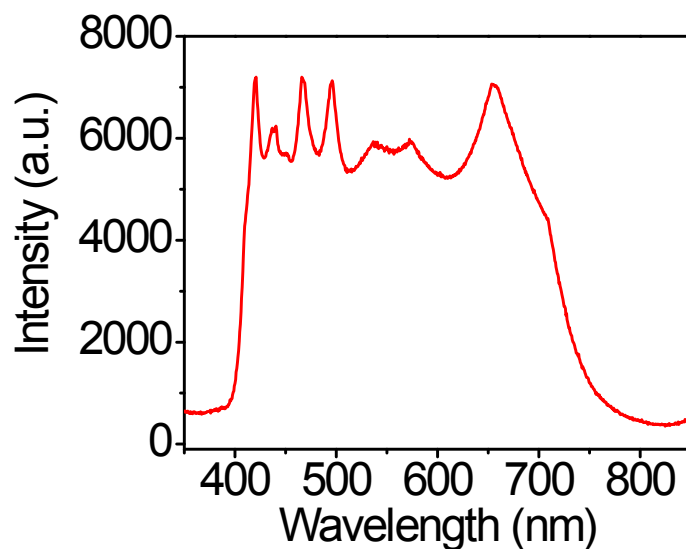

Figure S2 The spectral distribution of white-light LED source without any filter.
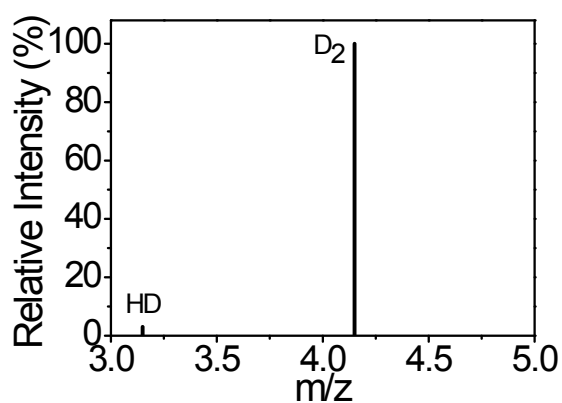
Deuteration experiments

Figure S3 The Mass Spectrum of the produced gas mixture when water was replaced by deuterium oxide in the photocatalysis.
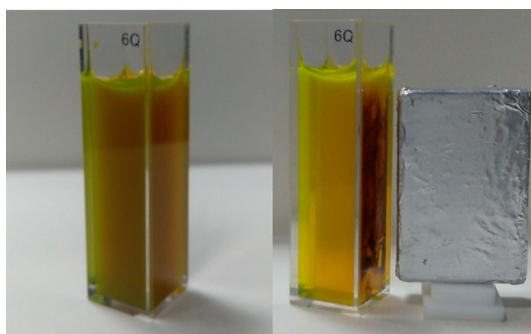
Figure S4 The catalyst exhibited magnetic behaviors and can be conveniently recycled by an external magnet. The right picture clearly showed an external magnet attracted the catalyst in the solution (left) to the one wall of the cuvette.

Synthesis, characterization and photoactivities of MIL-53(Fe)

Based on previous literatures,[3] MIL-53(Fe) was prepared by dissolving 0.270 g (1 mmol) of $FeCl_3 \cdot 6H_2O$ and 0.166 g (1 mmol) of BDC in 5 mL of DMF. The mixture was then introduced into a 50 mL Teflon-lined microwave vessel and sealed. The reaction was then rapidly heated to 150 °C at 300 W, and was held at this temperature for 30 minutes. After cooling to room temperature, the particles were isolated by centrifuging, and were washed with DMF and ethanol.
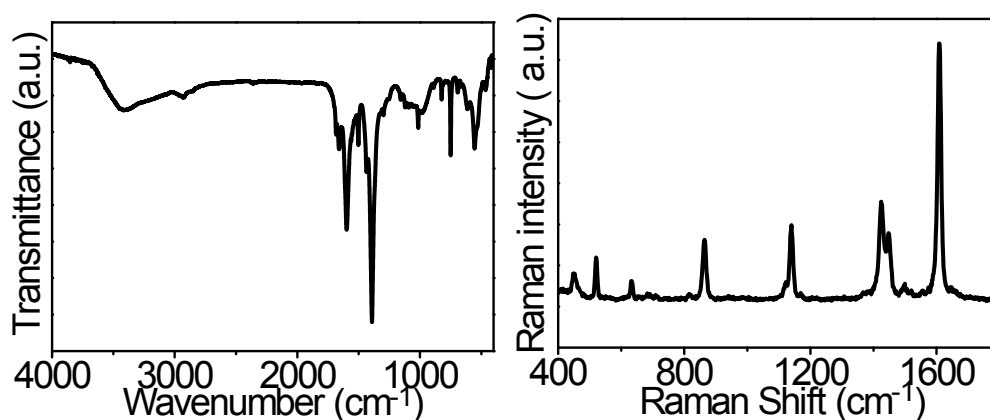

Figure S5 The FTIR (left) and Raman spectra (Raman) of the as-prepared MIL-53(Fe). The characteristic bands are consistent with those reported in literatures, [3] indicating a successful synthesis.

By use of MIL-53(Fe) as the precursor, a catalyst with a higher carbon content (weight ratio of 4.5%) than that of MIL-101(Fe)-derived catalyst was obtained. The H_2 evolution

efficiency of this as-prepared catalyst was ~48 μmol gas produced within 5 h using 5 mg MOFs precursors, decreasing to less than half of that from MIL-101(Fe) derived catalyst under identical conditions.

Fitting methods for laser photolysis experiments

Transient decay measurements at a single wavelength detected by PMT detectors were used to extract lifetime components of relevant samples. Each probe wavelength can be fitted by a sum of up to four exponentials with a least-squares-fitting program. The exponential growth or decay process can be expressed in mathematical terms as the following equation (3):

$$I(t) = c_0 + c_1 e^{-\frac{t}{\tau_1}} + c_2 e^{-\frac{t}{\tau_2}} + c_3 e^{-\frac{t}{\tau_3}} + c_4 e^{-\frac{t}{\tau_4}}$$

eq. (3)

where $I(t)$ is the decay model reflecting the response of the sample to an infinitely short excitation, and c_0 is the background, c_1, c_2, c_3, c_4 the pre-exponential factors reflecting the weight of corresponding characteristic lifetime components of τ_1, τ_2, τ_3 and τ_4, respectively. Positive pre-exponential factors indicate decay processes whereas negative values are characteristic for growth processes.

Table S1 Tabulated fitting results of lifetime components for the above samples. The percentage numbers in parentheses indicate the corresponding weight ratio of extracted lifetime components and those rise times are specified.

Sample	403 nm τ (EY$^{-\bullet}$)	460 nm τ (EY$^{+\bullet}$)	560 nm τ (^{3}EY*)
EY			132 μs(100%)
EY+Cat.		18 μs (rise, 52%)	31μs (100%)
		248 μs (48%)	
EY+TEA	12 μs (rise, 53%)		32 μs (100%)
	Long, > 6 ms (47%)		
EY+Cat.+TEA	19 μs (rise, 57%)	Long , (> ms)	26μs (100%)
	long , > ms(43%)		

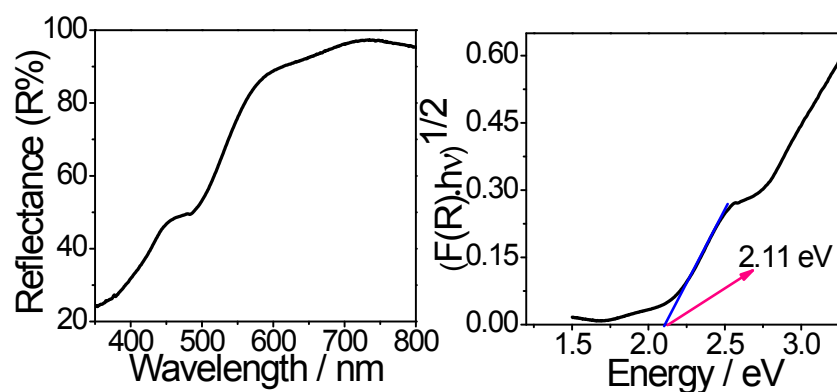**Band gap determination of MIL-101 (Fe)**

Figure S6 The UV/VIS diffuse reflectance spectra (left) and corresponding Tauc plot (right) of MIL-101 (Fe).

References

1.   Maksimchuk, N. V.; Kovalenko, K. A.; Fedin, V. P.; Kholdeeva, O. A., *Chem. Commun.* **2012,** *48* (54), 6812-6814.

2.   (a) Yu, S.; Kim, Y. H.; Lee, S. Y.; Song, H. D.; Yi, J., *Angew. Chem., Int. Ed.* **2014,** *53* (42), 11203-7; (b) Min, S.; Lu, G., *J. Phys. Chem. C* **2012,** *116* (37), 19644-19652; (c) Das, A.; Han, Z.; Haghighi, M. G.; Eisenberg, R., *Proc. Natl. Acad. Sci. U.S.A.* **2013,** *110* (42), 16716–16723.

3.   (a) Gordon, J.; Kazemian, H.; Rohani, S., *Microporous Mesoporous Mater.* **2012,** *162*, 36-43; (b) Zhang, Y.; Li, G.; Lu, H.; Lv, Q.; Sun, Z., *Rsc Adv.* **2014,** *4* (15), 7594.