

Supporting Information

The magnetic Fe₃O₄ encapsulated VAN@MIL-101(Fe) with mixed-valence sites and mesoporous as efficient bifunctional water splitting photocatalyst

Yuan Guo,^a Chao Feng,^a Shanshan Qiao,^a Shixin Wang,^a Tingxiang Chen,^a Li Zhang,^a Yansong Zhao,^b Jide

Wang^{*a}

*^aKey Laboratory of Oil & Gas Fine Chemicals Ministry of Education & Xinjiang Uyghur Autonomous
Region, Xinjiang University, Urumqi 830046, Xinjiang, China*

*^bDepartment of Safety, Chemistry and Biomedical Laboratory Sciences, Faculty of Engineering and Science,
Western Norway University of Applied Sciences, Inndalsveien28,5063 Bergen, Norway*

* Corresponding author. E-mail: awangjd@sina.cn

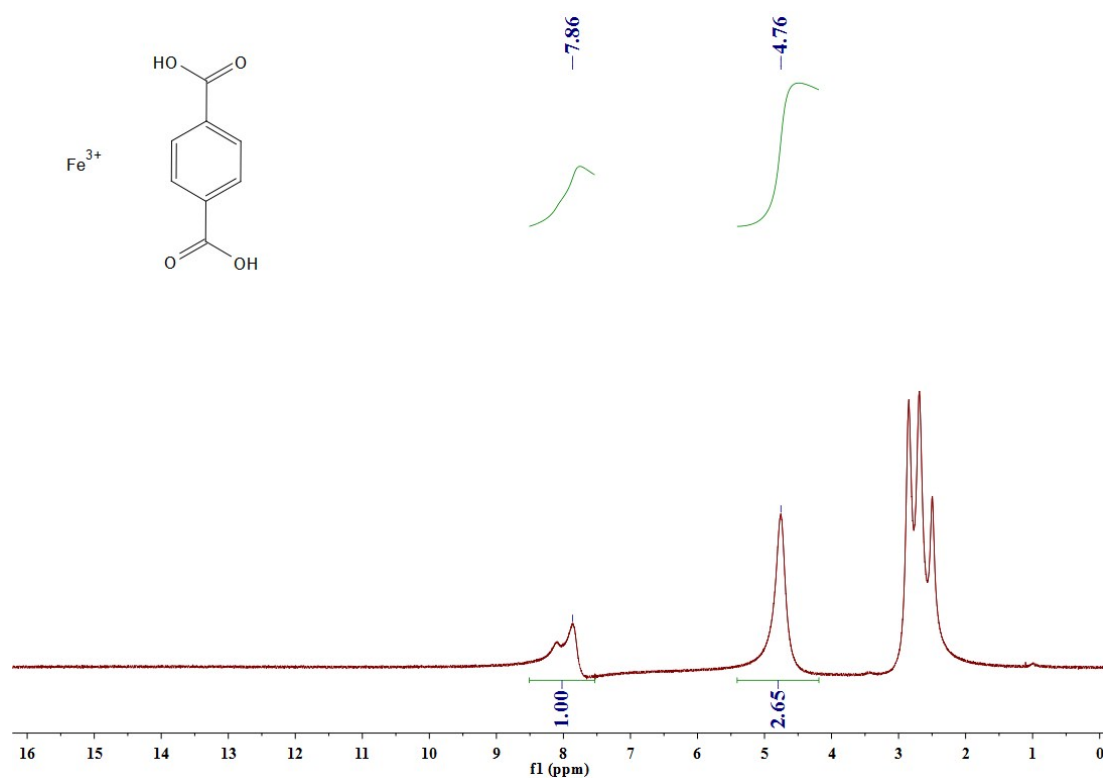


Fig. S1 $^1\text{H-NMR}$ spectra analysis of the dissolved MIL-101-Fe. ($^1\text{H NMR}$ (400 MHz, DMSO) δ 7.86 (s, 1H), 4.76 (s, 3H)).

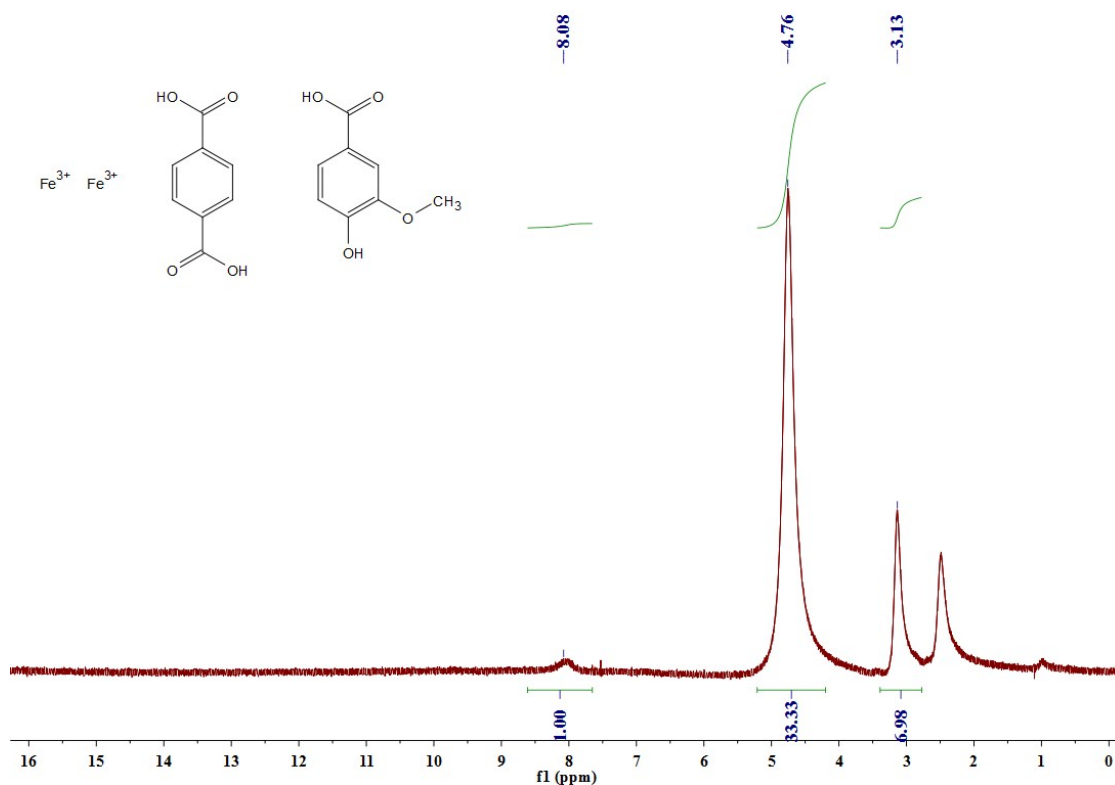


Fig. S2 $^1\text{H-NMR}$ spectra analysis of the dissolved VAN@MIL-101(Fe). ($^1\text{H NMR}$ (400 MHz, DMSO) δ 8.08 (s, 1H), 4.76 (s, 33H), 3.13 (s, 7H)).

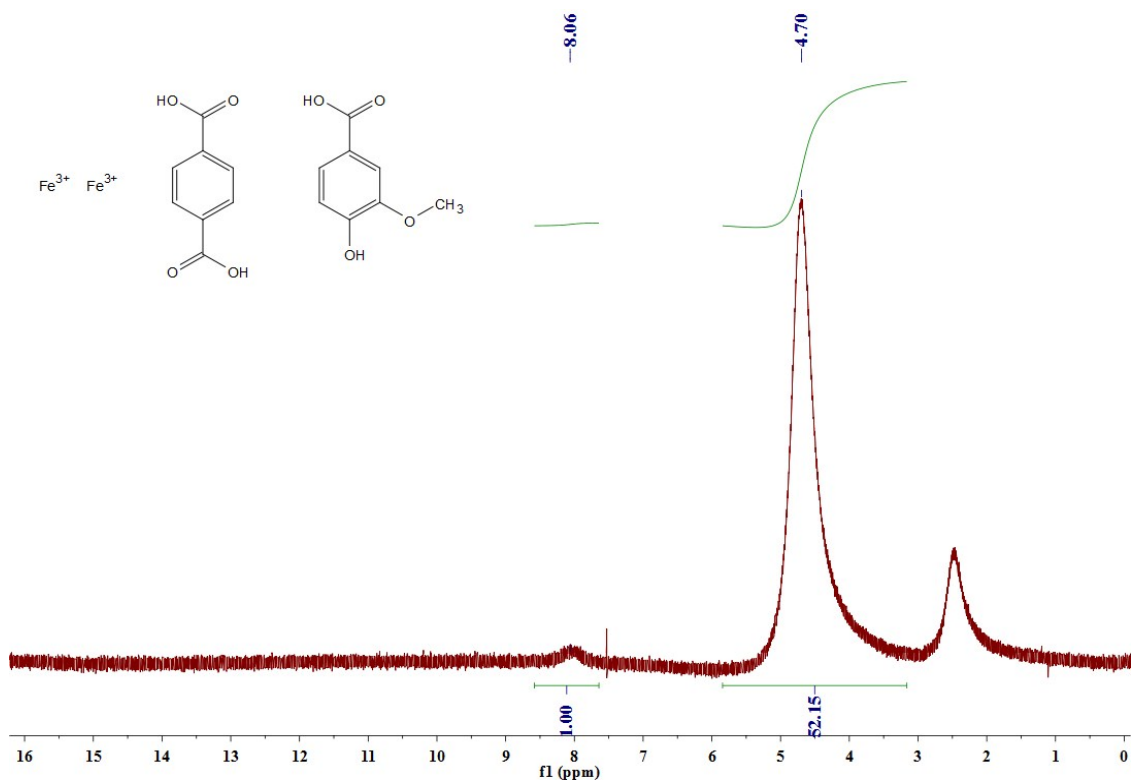


Fig. S3 ^1H -NMR spectra analysis of the dissolved $\text{Fe}_3\text{O}_4/\text{VAN@MIL-101}(\text{Fe})$. (^1H NMR (400 MHz, DMSO) δ 8.06 (s, 1H), 4.70 (s, 52H)).

Table S1. BET surface areas and pore features of hierarchical porous MIL-101(Fe), VAN@MIL-101(Fe) and $\text{Fe}_3\text{O}_4/\text{VAN@MIL-101}(\text{Fe})$.

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	Pore volumes (cm^3/g)		
		$V_{\text{total}}^{\text{b}}$	$V_{\text{micro}}^{\text{c}}$	$V_{\text{meso}}^{\text{d}}$
MIL-101(Fe)	1613	1.370	0.535	0.584
VAN@MIL-101(Fe)	2389	1.576	0.422	0.959
$\text{Fe}_3\text{O}_4/\text{VAN@MIL-101}(\text{Fe})$	869	0.802	0.216	0.593

^a **SBET**: Brunauer–Emmett–Teller (BET) surface area. ^b **Vtotal**: Total pore volume calculated from the nitrogen adsorption data at $P/P_0 = 0.998$. ^c **Vmicro**: Micropore volume obtained by the t-plot method. ^d **Vmeso**: Mesopore volume calculated by the Barrett–Joyner–Halenda (BJH) adsorption method.

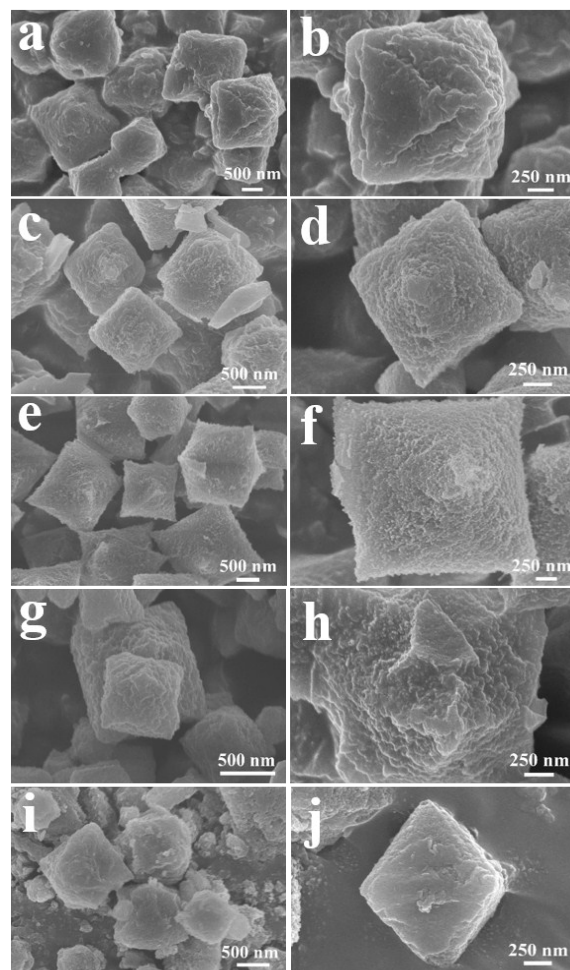


Fig. S4 SEM images of the MIL-101(Fe) regulated by vanillin obtained in DMF at 110 °C for 20h, and the MIL-10(Fe) regulated by vanillin samples prepared with different molar ratios of H₂BDC and vanillin. a.b: n(H₂BDC):n(vanillin)=1:1; c.d: 1:5; e.f: 1:7; g.h: 1:8; i.j: 1:10.

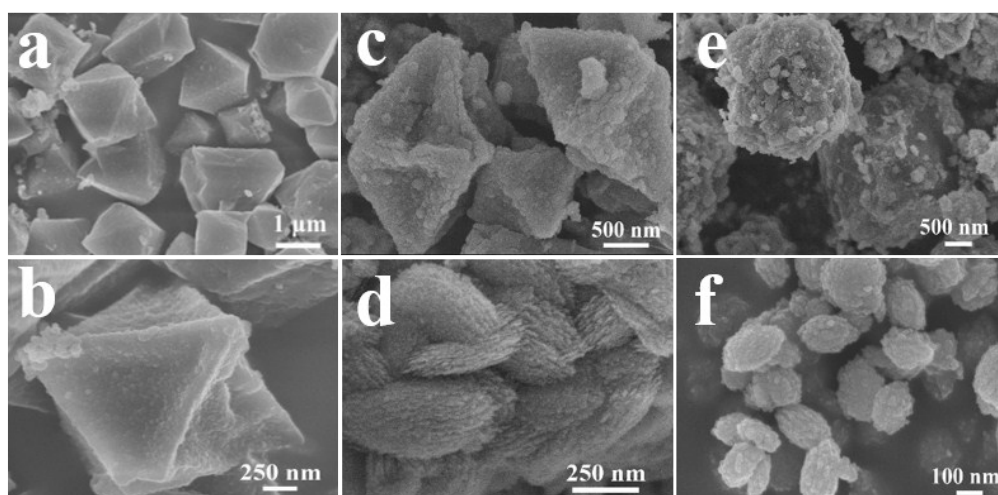


Fig. S5 SEM images of the MIL-101(Fe) regulated by vanillin obtained in DMF at 110 °C for 20 h, and the MIL-101(Fe) regulated by vanillin samples prepared with different molar ratios of FeCl₃·6H₂O and H₂BDC. a.b:n(FeCl₃·6H₂O):n(H₂BDC)=1:2; c,d: 7:1; e: 10:1; f: 20:1.

Table S2. Reference experiments about photocatalytic oxidation of water for catalysts (MIL-101(Fe), VAN@MIL-101(Fe))

and Fe₃O₄/ VAN@MIL-101(Fe)) under different catalytic conditions (1 mg catalyst, 1.0 × 10⁻³ M [Ru(bpy)₃](ClO₄)₂, 20.0 × 10⁻³ M Na₂S₂O₈, 80 × 10⁻³ M sodium borate buffer (initial pH=10.0)).

Catalyst	Electron acceptor	Photosensitizer	Irradiation	OER activity
-	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	Yes	No
MIL-101(Fe)	-	[Ru(bpy) ₃] ²⁺	Yes	No
VAN@MIL-101(Fe)	-	[Ru(bpy) ₃] ²⁺	Yes	No
Fe ₃ O ₄ / VAN@MIL-101(Fe)	-	[Ru(bpy) ₃] ²⁺	Yes	No
MIL-101(Fe)	Na ₂ S ₂ O ₈	-	Yes	No
VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	-	Yes	No
Fe ₃ O ₄ / VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	-	Yes	No
MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	No	No
VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	No	No
Fe ₃ O ₄ / VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	No	No
MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	Yes	Yes
VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	Yes	Yes
Fe ₃ O ₄ / VAN@MIL-101(Fe)	Na ₂ S ₂ O ₈	[Ru(bpy) ₃] ²⁺	Yes	Yes

Table S3. Reference experiments about photocatalytic reduction of water for catalysts (MIL-101(Fe), VAN@MIL-101(Fe) and Fe₃O₄/ VAN@MIL-101(Fe)) under different catalytic conditions (5mg catalysts, 1 mL triethanolamine (TEOA) and 9 mL H₂O, total reaction volume 10 mL).

Catalyst	Reaction system	Irradiation	HER activity
-	10% TEOA+90% H ₂ O	Yes	No
MIL-101(Fe)	100% H ₂ O	Yes	No
VAN@MIL-101(Fe)	100% H ₂ O	Yes	No
Fe ₃ O ₄ / VAN@MIL-101(Fe)	100% H ₂ O	Yes	No
MIL-101(Fe)	10% TEOA+90% H ₂ O	No	No
VAN@MIL-101(Fe)	10% TEOA+90% H ₂ O	No	No
Fe ₃ O ₄ / VAN@MIL-101(Fe)	10% TEOA+90% H ₂ O	No	No
MIL-101(Fe)	10% TEOA+90% H ₂ O	Yes	No
VAN@MIL-101(Fe)	10% TEOA+90% H ₂ O	Yes	Yes
Fe ₃ O ₄ / VAN@MIL-101(Fe)	10% TEOA+90% H ₂ O	Yes	Yes

Table S4. Comparison of the catalytic performance of photocatalytic oxidation of water about different catalysts of other works.

Catalyst	Reaction condition	Evolved oxygen	Ref.
Fe ₃ O ₄ /VAN@MIL-101(Fe)	300 W Xe lamp ($\lambda \geq 420$ nm); 1 mg catalyst; 1.0×10^{-3} M [Ru(bpy) ₃] (ClO ₄) ₂ , 20.0×10^{-3} M Na ₂ S ₂ O ₈ , 80×10^{-3} M sodium borate buffer (initial pH=10.0).	360000 μ mol/g/h	This work
VAN@MIL-101(Fe)	300 W Xe lamp ($\lambda \geq 420$ nm); 1 mg catalyst; 1.0×10^{-3} M [Ru(bpy) ₃] (ClO ₄) ₂ , 20.0×10^{-3} M Na ₂ S ₂ O ₈ , 80×10^{-3} M sodium borate buffer (initial pH=10.0).	269400 μ mol/g/h	This work
MIL-101(Fe)-NH ₂	300 W Xe lamp ($\lambda \geq 420$ nm); 1 mg catalyst; 1.0×10^{-3} M [Ru(bpy) ₃] (ClO ₄) ₂ , 20.0×10^{-3} M Na ₂ S ₂ O ₈ , 80×10^{-3} M sodium borate buffer (initial pH=10.0).	123660 μ mol/g/h	[1]
MIL-101(Fe)	300 W Xe lamp ($\lambda \geq 420$ nm); 1 mg catalyst; 1.0×10^{-3} M [Ru(bpy) ₃] (ClO ₄) ₂ , 20.0×10^{-3} M Na ₂ S ₂ O ₈ , 80×10^{-3} M sodium borate buffer (initial pH=10.0).	219000 μ mol/g/h	[1]
Cu-ZIF-400	Catalyst (0.20 g/L); NaPi buffer solution (pH 7.0, 10.0 mL); Na ₂ S ₂ O ₈ (5.0 mM); [Ru(bpy) ₃]Cl ₂ (1.0 mM); LED lamp, $\lambda = 420$ nm	53.4 μ mol/g/h	[2]
MIL-100(Fe)	Catalyst (15 mg); acetate buffer (100 mM, pH = 4) or deionized water (pH = 6.8); NaIO ₃ (5.0 mM); LED lamp, $\lambda = 420$ nm	6.06 μ mol/g/h	[3]
MIL-100(Fe)@BiVO ₄	Catalyst (15 mg); acetate buffer (100 mM, pH = 4) or deionized water (pH = 6.8); NaIO ₃ (5.0 mM); LED lamp, $\lambda = 420$ nm	333.3 μ mol/g/h	[3]

Red TiO ₂ - RuO ₂ co-catalyst	100 mg TiO ₂ with RuO ₂ modification was dispersed in 100 mL aqueous solution containing 0.85 g AgNO ₃ ; The reaction temperature:10 °C; 300 W Xe lamp ($\lambda = 420$ nm).	81.6 $\mu\text{mol/g/h}$	[4]
Mo doped Bi ₂ WO ₆	0.1 g of photocatalysts; 0.1 M NaOH; 0.02 M Na ₂ S ₂ O ₈ ; 100 mL water; 300 W Xeon lamp, $\lambda > 420$ nm	147.2 $\mu\text{mol/g/h}$	[5]
g-C ₃ N ₄ /BiVO ₄	0.02 g photocatalysts; 0.05 M AgNO ₃ ; 12 mL water; 300 W Xeon lamp, $\lambda > 420$ nm	328 $\mu\text{mol/g/h}$	[6]
0.5% FeOOH NSs/BiVO ₄	0.1 g photocatalyst; 0.85 g of AgNO ₃ ; 270 mL of water; 300 W Xe lamp ($\lambda > 400$ nm).	1130.0 $\mu\text{mol/g/h}$	[7]
Pt@Cu ₂ O/WO ₃	0.300 g photocatalyst; 200 mL of 0.01 M aqueous AgNO ₃ solution; 300 W Xe lamp without cut-off filter	1238.6 $\mu\text{mol/g/h}$	[8]
Co@Co ₃ O ₄	5 mg photocatalysts; 80 mM Na ₂ S ₂ O ₈ ; 10 mL 0.1 M NaOH (pH = 13); 20 mL water; 300 W, Xe lamp, $\lambda > 420$ nm	2278 $\mu\text{mol/g/h}$	[9]
BiO _{2-x} UTNSs	20 mg photocatalysts; 2 mg methyl viologen; 80 mL water; 300 W Xe lamp, AM 1.5 G	2715.4 $\mu\text{mol/g/h}$	[10]

Table S5. Comparison of the catalytic performance of photocatalytic reduction of water about different catalysts of other works.

Catalyst	Reaction condition	Evolved hydrogen	Ref.
Fe ₃ O ₄ /VAN@MIL-101(Fe)	300 W Xe lamp ($\lambda \geq 420$ nm); 5 mg catalysts, 10% TEOA + 90% H ₂ O, total reaction volume 10 mL.	584 $\mu\text{mol/g/h}$	This work

VAN@MIL-101(Fe)	300 W Xe lamp ($\lambda \geq 420$ nm); 5 mg catalysts, 10% TEOA + 90% H ₂ O, total reaction volume 10 mL.	480 $\mu\text{mol/g/h}$	This work
NH ₂ -MIL-125/TiO ₂	50 mg catalysts, 60 mL Na ₂ S ₉ H ₂ O (0.2 M) and Na ₂ SO ₃ (0.3 M); 300W Xe lamp ($\lambda = 420$ nm)	490 $\mu\text{mol/g/h}$	[11]
ZIF-8	Methanol (CH ₃ OH) was used as a sacrificial electron donor; Xe lamp irradiation (AM 1.5 G, 100 mW cm ⁻²).	0.01 $\mu\text{mol/g/h}$	[12]
MoS ₂ @ZIF-8	Methanol (CH ₃ OH) was used as a sacrificial electron donor; Xe lamp irradiation (AM 1.5 G, 100 mW cm ⁻²).	68.4 $\mu\text{mol/g/h}$	[12]
15.0 wt%MOC-16/g-C ₃ N ₄	300 W Xe lamp ($\lambda \geq 420$ nm); 10 mg catalysts, 2 mL TEOA + 18 mL H ₂ O, total reaction volume 20 mL.	515 $\mu\text{mol/g/h}$	[13]
Cu ₂ O/C ₃ N ₄	0.1 g photocatalysts; 180 mL triethanolamine (TEOA); 35 \pm 5°C; 20 mL water; 300 W Xe lamp, $\lambda > 420$ nm	241.3 $\mu\text{mol/g/h}$	[14]
Cu/Cu ₂ O@NC	2 mg of photocatalysts; 50 mL CH ₃ OH (10%); 300 W Xeon lamp, $\lambda > 420$ nm	379.6 $\mu\text{mol/g/h}$	[15]
Au/TiO ₂	20 mg photocatalysts; 80 mL water; 300 W Xe lamp, $\lambda > 420$ nm	120 $\mu\text{mol/g/h}$	[16]
M-Doped La ₂ Ti ₂ O ₇	1 g photocatalysts; 500 mL water; High-pressure Hg lamp (Ace Glass Inc., 450 W)	400 $\mu\text{mol/g/h}$	[17]
Ti ₃ C ₂ T _x /CdS	0.300 g photocatalyst; 80 ml of 10 vol.% lactic acid; 300 W Xe lamp, $\lambda > 420$ nm	473 $\mu\text{mol/g/h}$	[18]
CdS/Cu ₇ S ₄ /g-C ₃ N ₄	dispersed into 100 mL aqueous solution containing 0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃ ; 300 W Xe lamp, $\lambda > 420$ nm	357 $\mu\text{mol/g/h}$	[19]

suspended in the 1000 ml reaction solution; methanol (20%); isopropyl alcohol (30%).

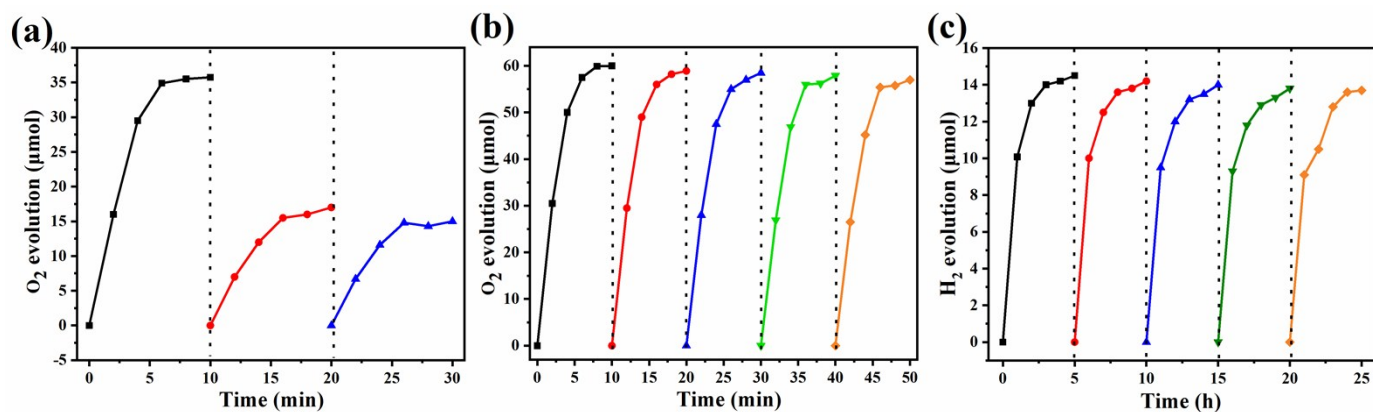


Fig. S6 (a) Recycle study of MIL-101(Fe) in the light-driven water oxidation reaction; (c), (d) Recycle study of Fe₃O₄/VAN@MIL-101(Fe) in the light-driven water oxidation reaction and water reduction reaction, respectively, the reaction system was evacuated after each run.

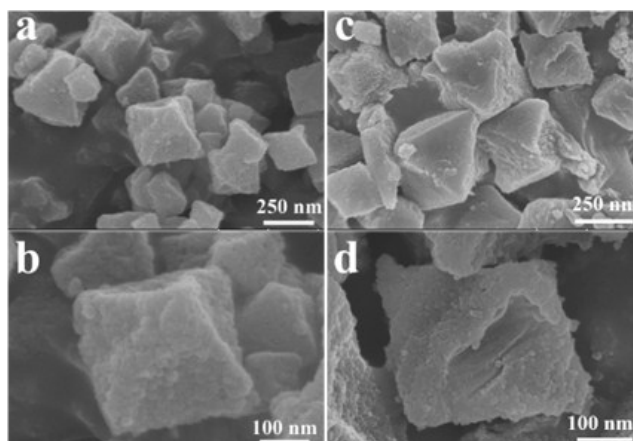


Fig. S7 SEM images of Fe₃O₄/VAN@MIL-101(Fe) recovered after 5 cycles: (a,b) after photocatalytic OER; (c,d) after photocatalytic HER.

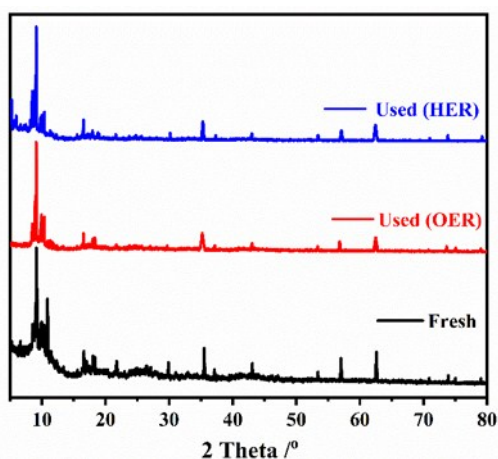


Fig. S8 Comparison of XRD of fresh Fe₃O₄/VAN@MIL-101(Fe) with recycled Fe₃O₄/VAN@MIL-101(Fe) in OER and HER after 5 cycles.

References

1. L. Chi, Q. Xu, X. Liang, J. Wang and X. Su, *Small* (Weinheim an der Bergstrasse, Germany), 2016, **12**.
2. Y. Zhang, X. Zhou, F. Zhang, T. Tian, Y. Ding and H. Gao, *J. Catal.*, 2017, **352**, 246-255.
3. Q. Han, Y. Dong, C. Xu, Q. Hu, C. Dong, X. Liang and Y. Ding, *ACS Appl. Mater. Inter.*, 2020, **12**, 10410-10419.
4. X. Hong, J. Tan, H. Zhu, N. Feng, Y. Yang, J. T. S. Irvine, L. Wang, G. Liu and H.-M. Cheng, *Chem–Eur. J.*, 2019, **25**, 1787-1794.
5. Y. Hu, A. Etogo, R. Liu, J. Ren, L. Qi, C. Zheng, J. Ning and Y. Zhong, *J. Mater. Chem. A*, 2016, **4**.
6. H. J. Kong, D. H. Won, J. Kim and S. Woo, *Chem. Mater.*, 2016, **28**.
7. G. Ge, M. Liu, C. Liu, W. Zhou, D. Wang, L. Liu and J. Ye, *J. Mater. Chem. A*, 2019, **7**, 9222-9229.
8. H. Gong, Y. Zhang, Y. Cao, M. Luo, Z. Feng, W. Yang, K. Liu, H. Cao and H. Yan, *Appl. Catal. B-Environ.*, 2018, **237**.
9. D. Wang, J. Guo, D. Hu, Q. Xu, L. Zhang and J. Wang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 8300-8307.
10. B. Sun, Y. Qian, Z. Liang, Y. Guo, Y. Xue, J. Tian and H. Cui, *Sol. Energ. Mat. Sol. C.*, 2019, **195**, 309-317.
11. R. Bibi, H. Huang, M. Kalulu, Q. Shen, L. Wei, O. Oderinde, N. Li and J. Zhou, *ACS Sustain. Chem. Eng.*, 2018, **6**, 8856–8867.
12. R. Ren, H. Zhao, X. Sui, X. Guo, X. Huang, Y. Wang, Q. Dong and J. Chen, *Catalysts*, 2019, **9**, 89-98.
13. Y. Wang, L. Liu, D. Wu, J. Guo, J. Shi, J. Liu and C. Su, *Chin. J. Catal.*, 2019, **40**, 1198-1204.
14. J. Chen, S. Shen, P. Guo, M. Wang, P. Wu, X. Wang and L. Guo, *Appl. Catal. B-Environ.*, 2014, **152-153**, 335-341.
15. L. Lu, X. Xu, J. Yan, F. N. Shi and Y. Huo, *Dalton T.*, 2018, **47**, 2031-2038.
16. O. Rosseler, M. V. Shankar, M. K.-L. Du, L. Schmidlin, N. Keller and V. Keller, *J. Catal.*, 2010, **269**, 179-190.
17. D. Hwang, H. Kim, J. S. Lee, J. Kim, W. Li and S. Oh, *J. Phys. Chem. B*, 2005, **109**, 2093-2102.
18. Y. Yang, D. Zhang and Q. Xiang, *Nanoscale*, 2019, **11**.
19. J. Chu, X. Han, Z. Yu, Y. Du and P. Xu, *ACS Appl. Mater. Inter.*, 2018, **10**.
20. D. Saadetnejad and R. Yildirim, *Int. J. Hydrogen Energ.*, 2018, **43**, 1116-1122.