Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electron Shuttle in MOF Derived TiO_2/CuO Heterojunction Boosts Light Driven Hydrogen Evolution

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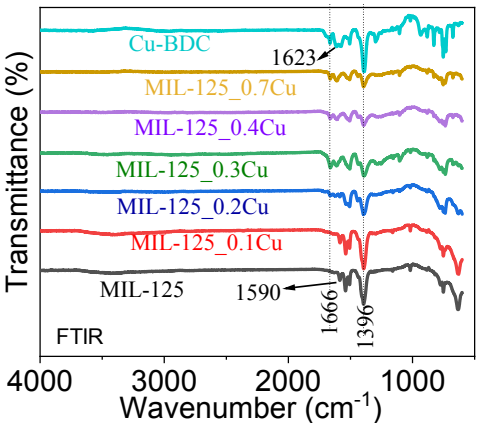

Figure S1. The FTIR spectra of MIL-125, MIL-125_xCu, and Cu-BDC.

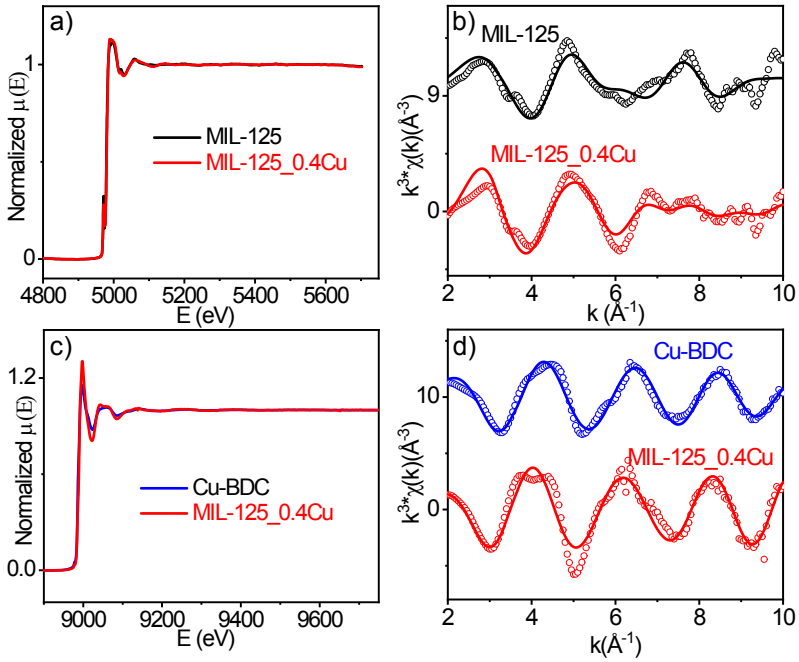

Figure S2. The EXAFS spectra of MIL-125 and MIL-125_0.4Cu at Ti k-edge in energy space (a) and k-space (b). The EXAFS spectra of Cu-BDC and MIL-125_0.4Cu at Cu k-edge in energy space (c) and k-space (d). The solid lines in (b) and (d) are the fitting results.

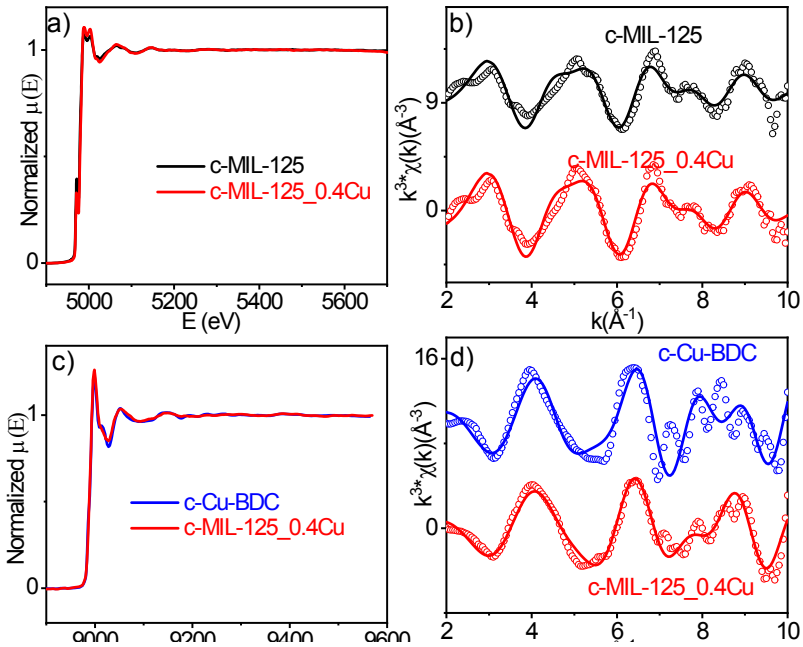

Figure S3. The EXAFS spectra of c-MIL-125 and c-MIL-125_0.4Cu at Ti k-edge in energy space (a) and k-space (b). The EXAFS spectra of c-Cu-BDC and c-MIL-125_0.4Cu at Cu k-edge in energy space (c) and k-space (d). The solid lines in (b) and (d) are the fitting results.

Table S1. The EXAFS fitting parameters for MIL-125 and MIL-125_0.4Cu at Ti k-edge

Sample	Vector	N	σ^2 (Å^2)	R (Å)
MIL-125	Ti-O_1	3.05	0.01	1.82
	Ti-O_2	0.43	0.01	1.96
	Ti-O_3	1	0.01	2.07
	Ti-(O)-Ti	0.86	0.01	2.67
MIL-125_0.4Cu	Ti-O_1	2.5	0.009	1.82
	Ti-O_2	0.75	0.01	1.97
	Ti-O_3	2.14	0.009	2.03
	Ti-(O)-Ti	0.7	0.01	3.04

Table S2. The EXAFS fitting parameters for Cu-BDC and MIL-125_0.4Cu at Cu k-edge

Sample	Vector	N	σ^2 (Å^2)	R (Å)
Cu-BDC	$Cu-O_1$	4	0.006	1.96
	$Cu-O_2$	1	0.0062	2.25
MIL-125_0.4Cu	$Cu-O_1$	4.25	0.0034	1.99
	$Cu-O_2$	1.43	0.001	2.23

Table S3. The EXAFS fitting parameters for c-MIL-125 and c-MIL-125_0.4Cu at Ti k-edge

Sample	Vector	N	σ^2 (Å^2)	R (Å)
c-MIL-125	Ti-O	2.68	0.01	1.94
	Ti-(O)-Ti	1.58	0.01	3.05
c-MIL-125_0.4Cu	Ti-O	3.4	0.01	1.93
	Ti-(O)-Ti	1.65	0.01	3.04

Table S4. The EXAFS fitting parameters for c-Cu-BDC and c-MIL-125_0.4Cu at Cu k-edge

Sample	Vector	N	σ^2 (Å^2)	R (Å)
c-Cu-BDC	Cu-O	4	0.0052	1.94
	Cu-(O)-Cu	2	0.006	2.88
C-MIL-125_0.4Cu	Cu-O	4	0.0059	1.89
	Cu-(O)-Cu	2	0.0087	2.90

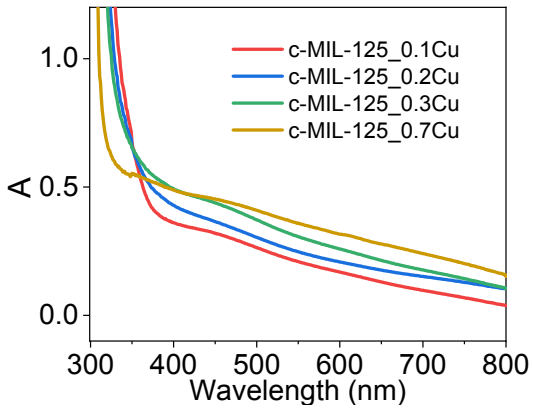

Figure S4. Diffuse reflectance spectra of c-MIL-125_xCu.

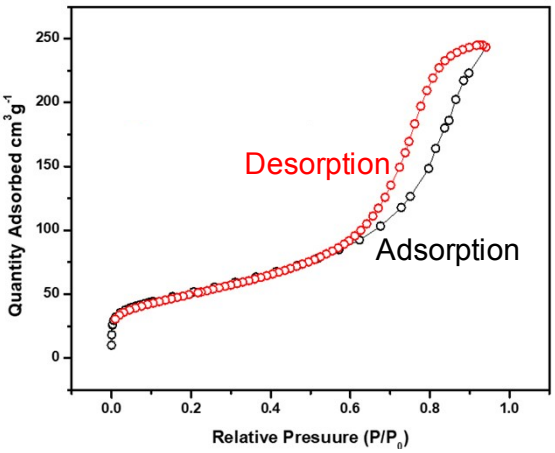

Figure S5. N_2 adsorption/desorption isotherm of c-MIL-125_0.4Cu

Table S5. Surface area and pore structure for samples. [a] Obtained from the N_2 adsorption experiment. [b] Collected from the literature[1-2].

Samples	BET surface area	Pore size	Pore volume
[a]c-MIL-125_0.4Cu	178 m^2/g	8.5 nm	0.38 cm^3/g
[b]MIL-125[1]	1254 m^2/g	0.9 nm	0.52 cm^3/g
[b]c-MIL-125[1]	60 m^2/g	3~5 nm	0.15 cm^3/g
[b]Cu-BDC[2]	507.621 m^2/g	6 nm	0.34 cm^3/g

Table S6. Parameters of HER experiments

Variables	Trials	H_2 (μmol/g)
Control experiment	No $[Ru(bpy)_3]^{2+}$	0
	No TEOA	0
	No catalyst	291
	Conventional TiO_2	105
Current of LED	0.1 A	19036
	0.2 A	19669
Amount of catalyst	0.2mg c-MIL-125_0.4Cu	19036
	0.5mg c-MIL-125_0.4Cu	7348
	1mg c-MIL-125_0.4Cu	6431
TEOA concentration	0.1mL TEOA	16471
	0.2mL TEOA	19036
	0.4mL TEOA	15642

Figure S6. (a) SEM image of c-MIL-125_0.4Cu used for measuring EDX; EDX mapping images of c-MIL-125_0.4Cu for Ti (b) and Cu (c).

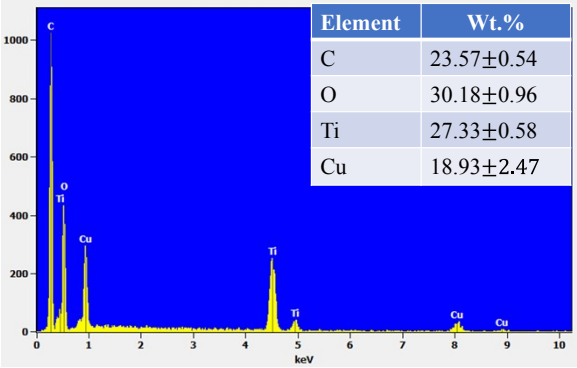

Figure S7. EDX data of c-MIL-125_0.4Cu

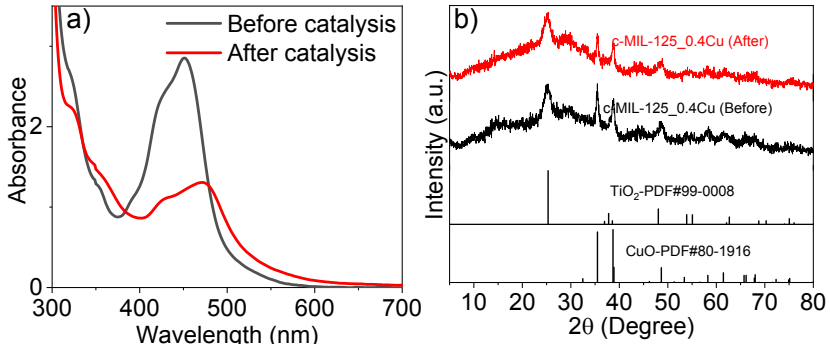

Figure S8. (a) The comparison of UV-Visible absorption spectra of $[Ru(bpy)_3]^{2+}$ before and after photocatalysis. (b) The comparison of XRD patterns of c-MIL-125_0.4Cu before and after photocatalysis.

Table S7. Fitting parameters for TA kinetics of $[Ru(bpy)_3]^{2+}/Al_2O_3$ and $[Ru(bpy)_3]^{2+}$/c-MIL-125 at 500 nm following 450 nm excitation

MOF	τ_1 (ps)	A_1 (%)	τ_2 (ps)	A_2 (%)	τ_3 (ps)	A_3 (%)
$[Ru(bpy)_3]^{2+}$/c-MIL-125	15.4	55.6	620.0	30.9	>>5ns	13.5
$[Ru(bpy)_3]^{2+}/Al_2O_3$	4.34	54.4	697.0	27.7	>>5ns	17.9

Reference

1. Liao, Y.-T.; Huang, Y.-Y.; Chen, H. M.; Komaguchi, K.; Hou, C.-H.; Henzie, J.; Yamauchi, Y.; Ide, Y.; Wu, K. C., Mesoporous TiO2 Embedded with a Uniform Distribution of Cuo Exhibit Enhanced Charge Separation and Photocatalytic Efficiency. *ACS Appl. Mater. Interfaces*, **2017**, *9*, 42425-42429.
2. Zhang, H.-X.; Huang, H.-L.; Li, C.-X.; Meng, H.; Lu, Y.-Z.; Zhong, C.-L.; Liu, D.-H.; Yang, Q.-Y., Adsorption Behavior of Metal–Organic Frameworks for Thiophenic Sulfur from Diesel Oil. *Ind. Eng. Chem. Res.* **2012**, *51*, 12449-12455.