Electronic Supplementary Information

Microporous mixed-metal (Na/Cu) mixed-ligand (flexible/rigid) metal–organic framework for photocatalytic H_2 generation

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Section S1 Photocatalytic Activity of Typical MOFs for H_2 Production

Table S1 Photocatalytic activity of some typical MOF-based and MOF-derived catalysts for H_2 production.

Entry	MOFs	Metal Node	Additional Loaded Catalysts	Light Source	Photocatalytic Activity
1	**Na/Cu–MOF (this work)**	**Na/Cu**	**No**	**visible light**	**4650 μmol·g^{-1}·h^{-1}**
2	Al-PMOF[1]	Al	Pt	visible light	200 μmol·g^{-1}·h^{-1}
3	MOF-253-Pt[2]	Al	Pt	visible light	100–200 μmol·g^{-1}·h^{-1}
4	CdS/MIL-101[3]	Cr	Pt	visible light	14.1 mmol·g_{CdS}^{-1}·h^{-1}
5	Pt/NH_2-MIL-101[4]	Cr	Pt	visible light	110 mol_{H2}·mol_{cat}^{-1}
6	Pt@UiO-66[5]	Zr	Pt	visible light	116 μmol·g^{-1}·h^{-1}
7	UiO-66-[FeFe](dcbdt)$(CO)_6$[6]	Zr	[FeFe](bdt)$(CO)_6$	LED	3.5 μmol/5 mg
8	Pt@MOF[7]	Zr	Pt	visible light	3400–7000 mol/48 h
9	POM@UiO[8]	Zr	$[P_2W_{18}O_{62}]^{6-}$	visible light	699 μmol·h^{-1}·g^{-1}
10	Ru–Pt@UIO-67[9]	Zr	Pt(dcbpy)Cl_2 + $[Ru(dcbpy)(bpy)_2]^{2+}$	LED	0.55 μmol/(1.47 mmol Pt complex and 0.42 mmol Ru complex)
11	Pt/Ti-MOF-NH_2[10]	Ti	Pt	visible light	3.67 μmol/10 mg·h^{-1}
12	Pt@CdS/UiO-66[11]	Zr	Pt	visible light	47 μmol·mg^{-1}·h^{-1}
13	Calix-3/Pt@UiO-66-NH_2[12]	Zr	Pt, Calix-3	visible light	1528 μmol·g^{-1}·h^{-1}
14	ErB + Pt@UiO-66[13]	Zr	Pt	visible	4.6 μmol/10

				light	$mg \cdot h^{-1}$
15	CdS + RGO@UiO-66[14]	Zr	RGO	visible light	105 μmol/50 $mg \cdot h^{-1}$
16	g-C_3N_4@UiO-66[15]	Zr	Pt	visible light	14.11 μmol/10 $mg \cdot h^{-1}$
17	[FeFe]@ZrPF[16]	Zr	[Fe_2S_2]	visible light	3.5 μmol/2 μM
18	Pt@UiO-66-NH_2[17]	Zr	Pt	UV light	2.8 mL for 3 h 45 mg
19	Pt/Ti-MOF-NH_2[18]	Ti	Pt	visible light	15.5 μmol/10 mg
20	Co@NH_2-MIL-125[19]	Ti	Co-dioxime-diimine	visible light	TOF of 0.8 h^{-1} for 65 h
21	$[Ru_2(p\text{-}BDC)_2]_n$[20]	Ru	MV^{2+}	visible light	TON of 8.16 h^{-1}
22	$[Ni_2(PymS)_4]_n$[21]	Ni	No	LED	6 $\mu mol \cdot mg^{-1}$
23	Ni@MOF-5[22]	Zn	Eosin Y, Ni	visible light	30.22 $\mu mol \cdot g^{-1} \cdot h^{-1}$
24	rGO–PDI-Co[23]	Co	rGO	visible light	225 $\mu mol \cdot g^{-1} \cdot h^{-1}$
25	$[Cu^{II}(RSH)(H_2O)]_n$[24]	Cu	No	visible light	7.88 $mmol \cdot g^{-1} \cdot h^{-1}$
26	$\{[Cu^{I}Cu^{II}_2(DCTP)_2]NO_3 \cdot 1.5DMF\}_n$[25]	Cu	Pt	visible light	32 $\mu mol \cdot g^{-1} \cdot h^{-1}$
27	Cu-I-bpy[26]	Cu	No	UV light	7.09 $mmol \cdot g^{-1} \cdot h^{-1}$
28	Ni_4P_2@MOF[27]	Zr	$[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$	visible light	TON of 1476 for 72 h
29	ZZULI–1[28]	Cu	$[W_{12}O_{40}]^{8-}$ + $[W_6O_{19}]^{2-}$	visible light	6.61 $mmol \cdot g^{-1} \cdot h^{-1}$
30	CdS@NU-1000[29]	Zr	Pt	visible light	1870 $\mu mol \cdot g^{-1} \cdot h^{-1}$
31	Al-TCPP-0.1Pt[30]	Al	Pt	visible light	129 $\mu mol \cdot g^{-1} \cdot h^{-1}$

Section S2 Characterization of Na/Cu–MOF

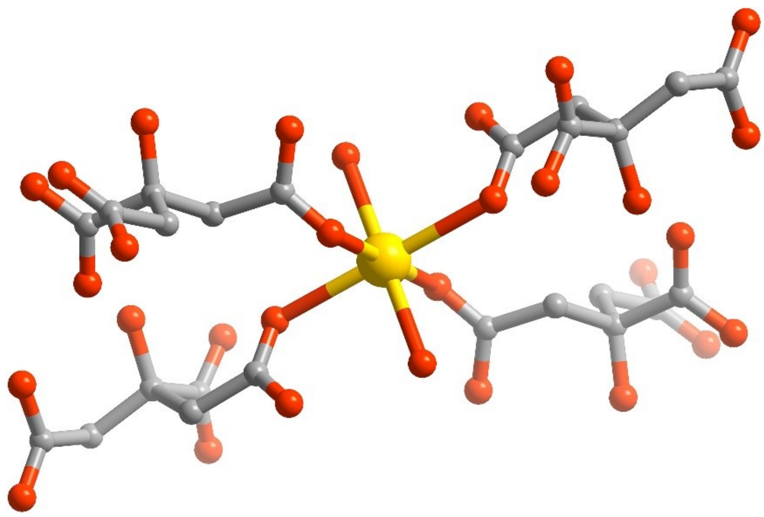

Fig. S1 The coordinate environment of Na(I) ions in **Na/Cu–MOF**.

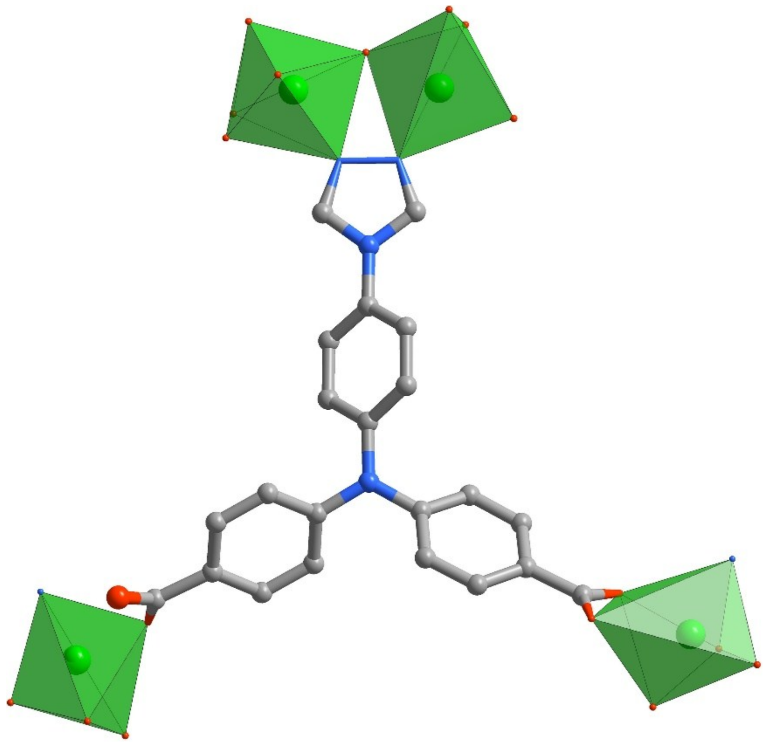

Fig. S2 The coordinate environment of L_1 ligands in **Na/Cu–MOF**.

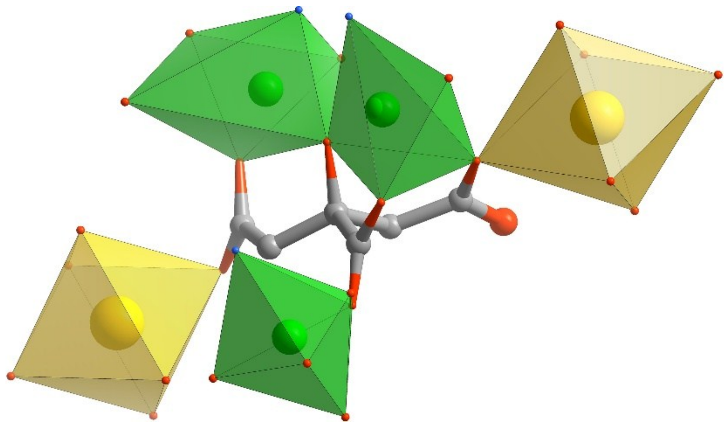

Fig. S3 The coordinate environment of L_2 ligands in **Na/Cu–MOF**.

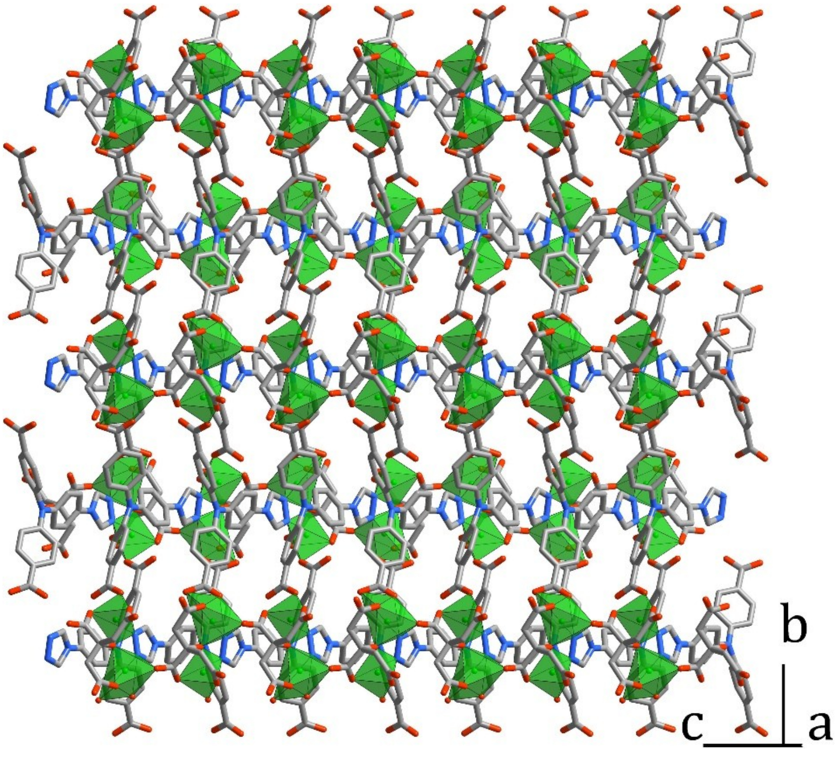

Fig. S4 The 2D bilayer grids of **Na/Cu–MOF**, which are connected by L_1 and L_2 ligands as well as binuclear $\{Cu_2\}$ units.

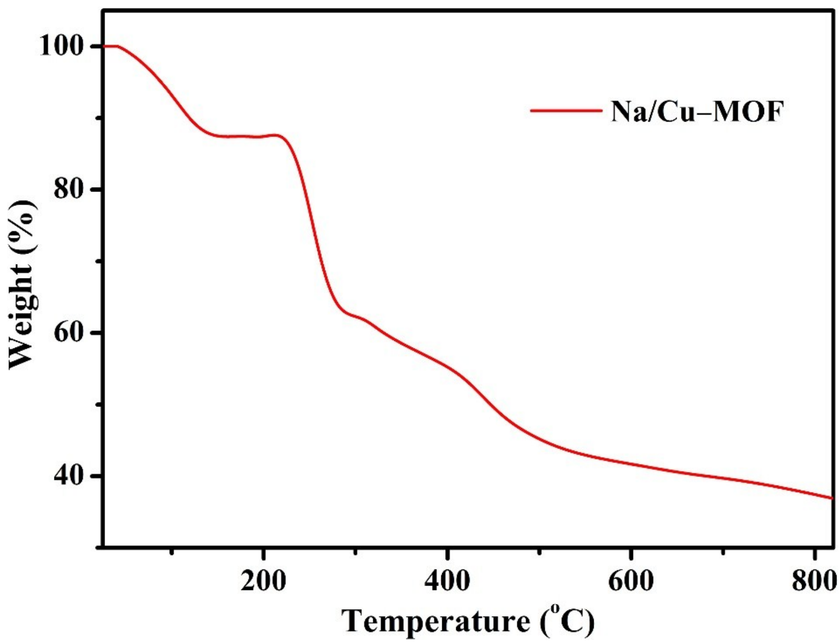

Fig. S5 The TGA curve of **Na/Cu–MOF** under flowing nitrogen atmosphere.

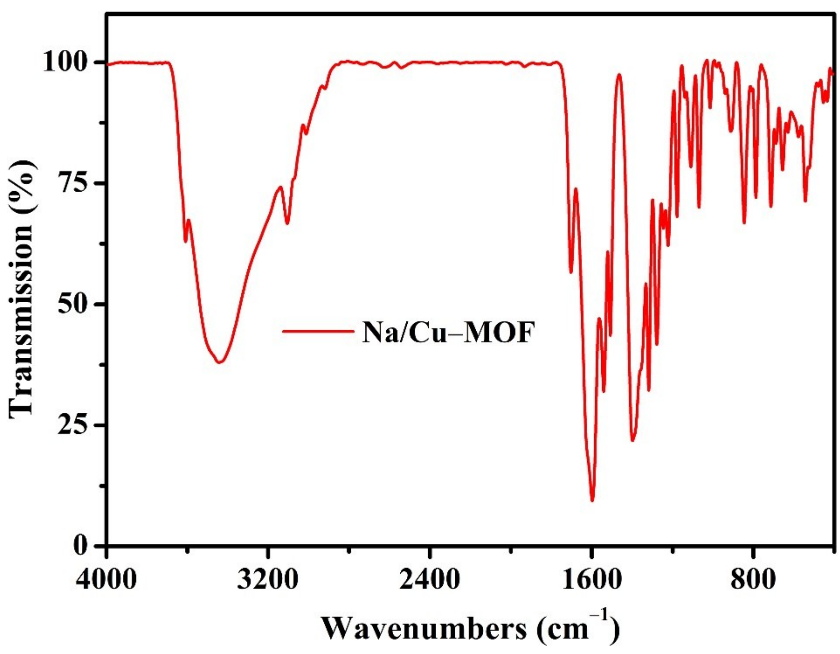

Fig. S6 The IR spectrum of **Na/Cu–MOF**.

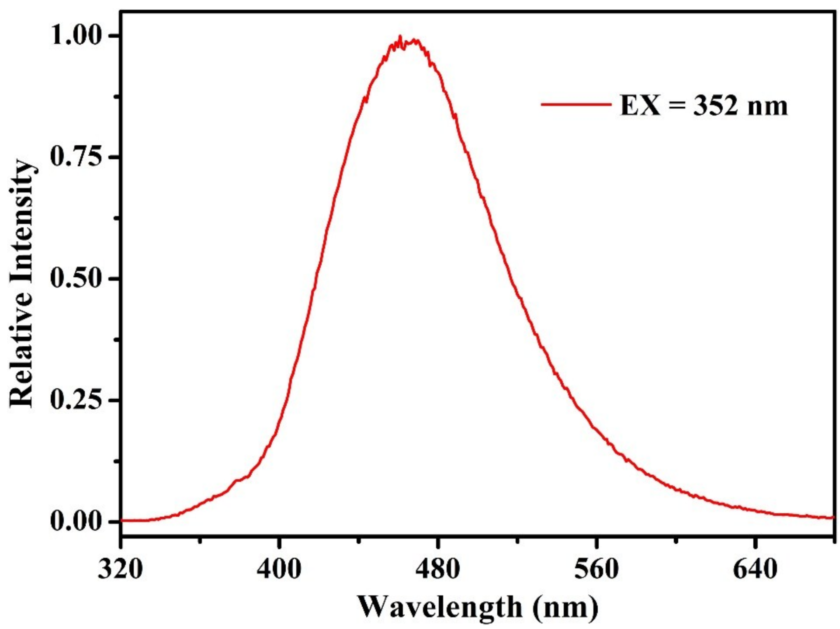

Fig. S7 The emission spectrum of **Na/Cu–MOF** (EX = 352 nm).

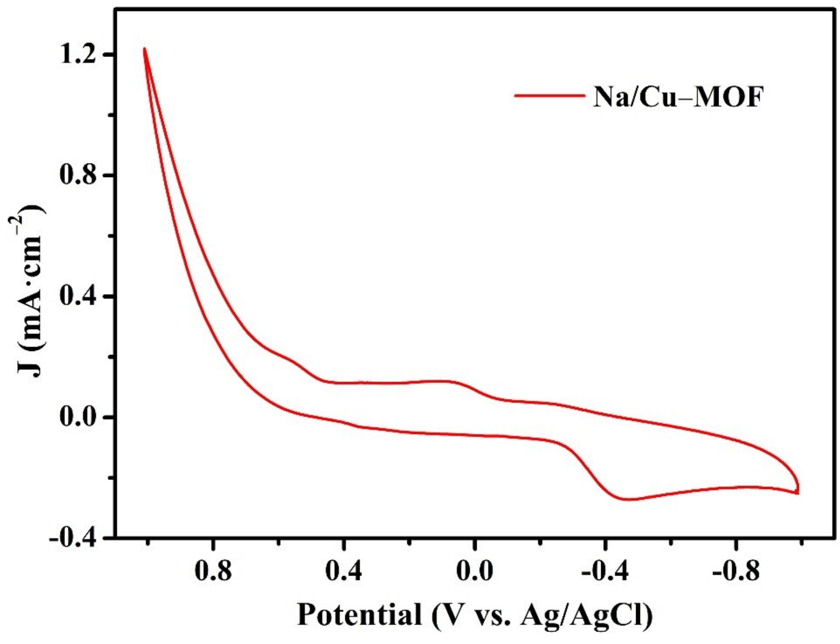

Fig. S8 The cyclic voltammogram of **Na/Cu–MOF** in KOH aqueous solutions at pH = 13.0. Conditions: platinum counter electrode, carbon paste working electrode, and Ag/AgCl reference electrode.

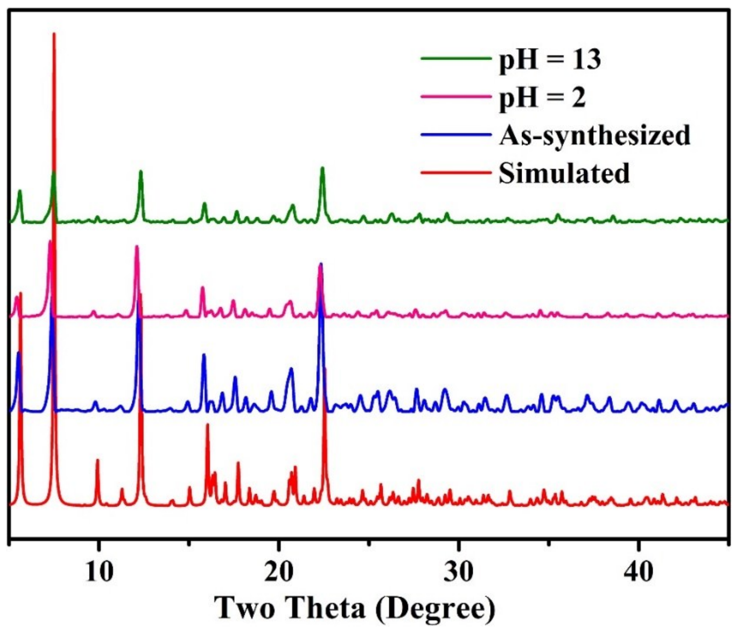

Fig. S9 PXRD patterns of **Na/Cu–MOF** after immersing in HCl/KOH aqueous solutions of different pH for 12 hours.

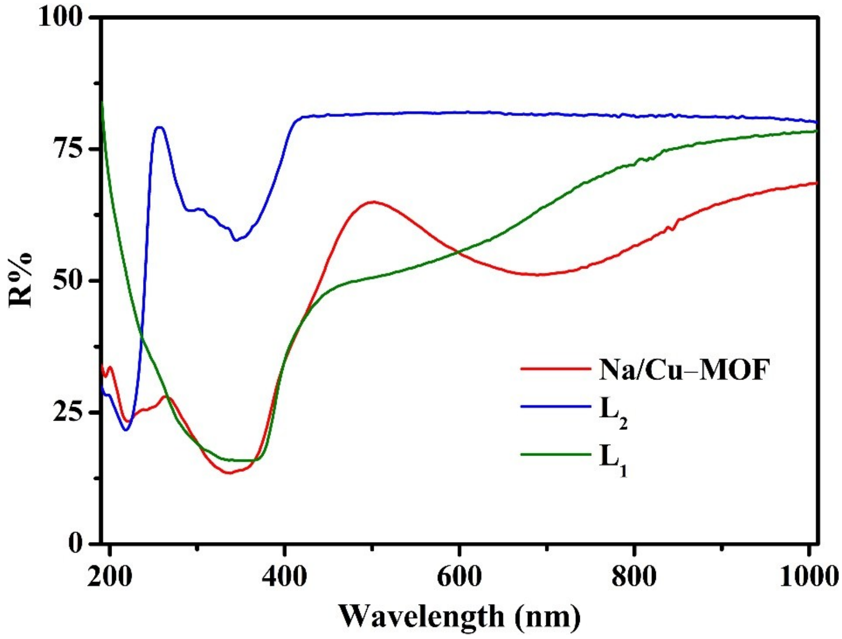

Fig. S10 The diffuse reflectance spectra of **Na/Cu–MOF**, L_1 and L_2.

Section S3 Characterization of Cu–MOF

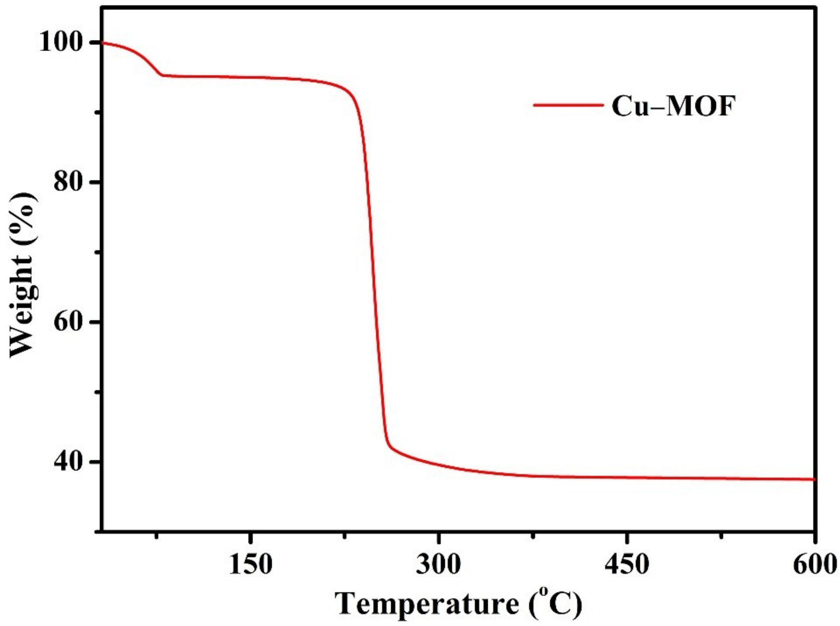

Fig. S11 The TGA curve of **Cu–MOF** under flowing nitrogen atmosphere.

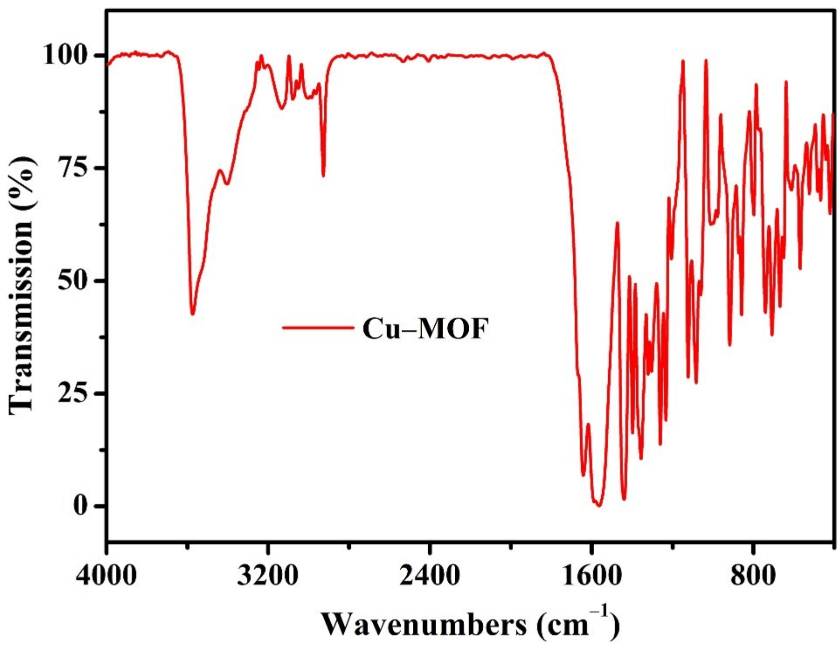

Fig. S12 The IR spectrum of **Cu–MOF**.

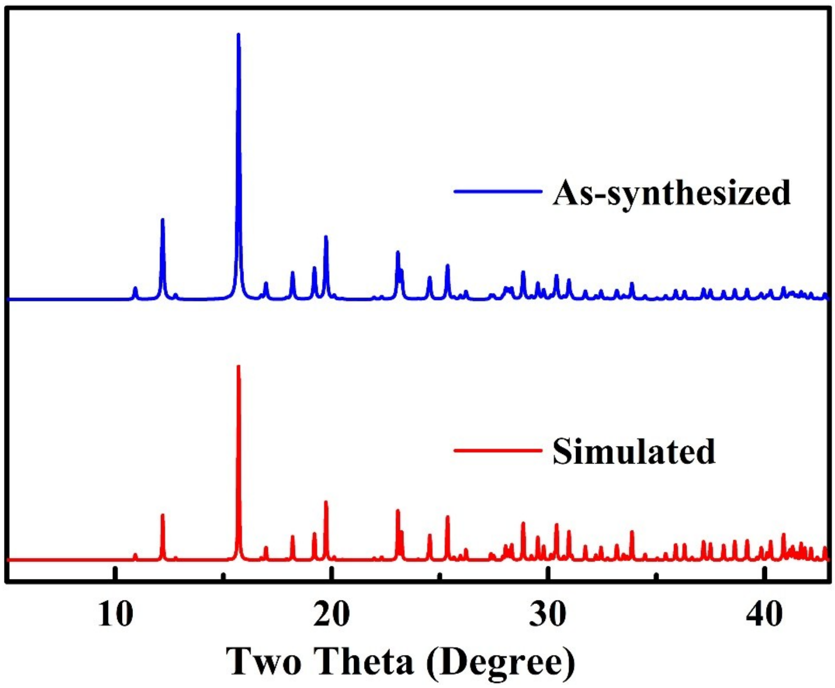

Fig. S13 The PXRD patterns of **Cu–MOF**.

Section S4 Photocatalytic Experiments

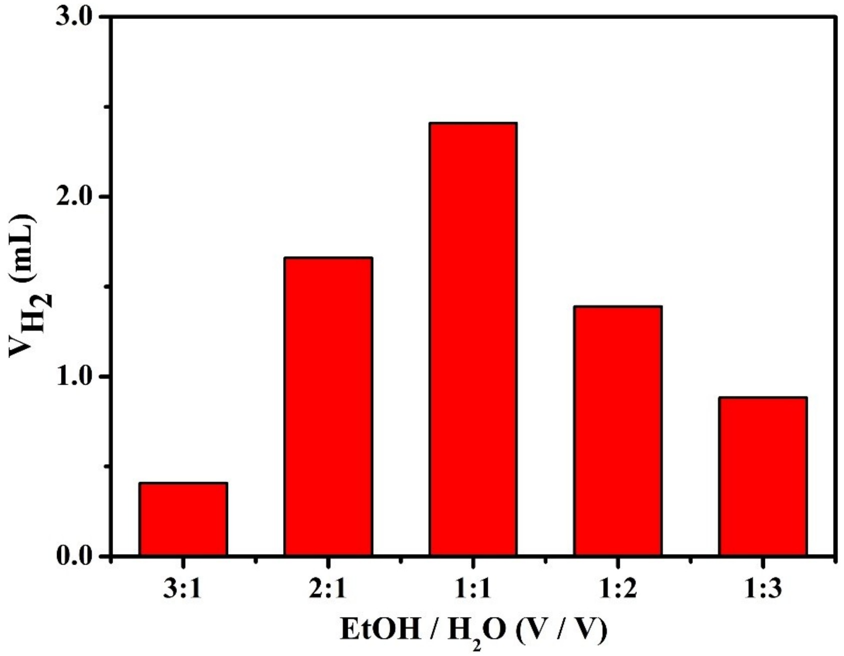

Fig. S14 Photocatalytic H_2 generation with various volume ratio of EtOH/H_2O.

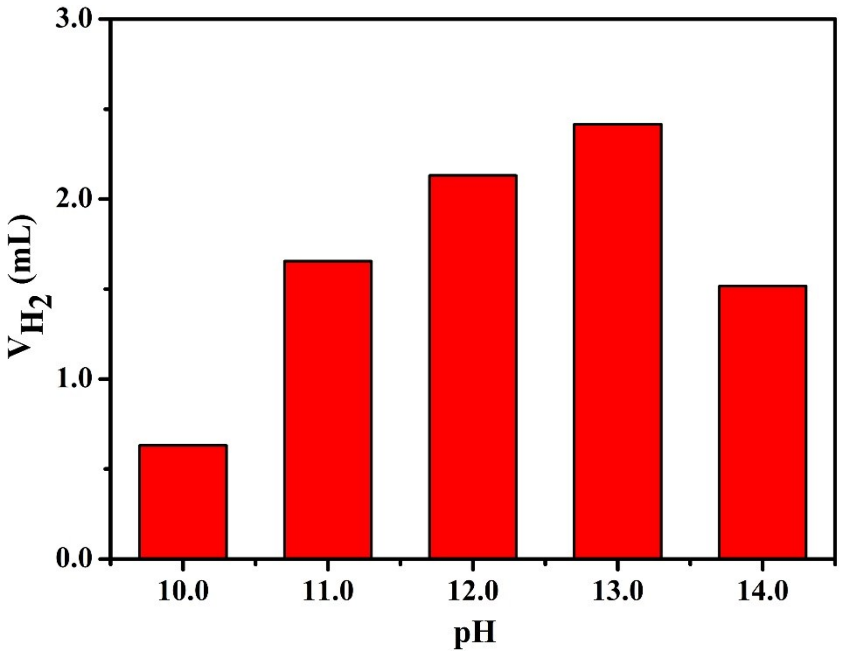

Fig. S15 Photocatalytic H_2 generation at different pH values.

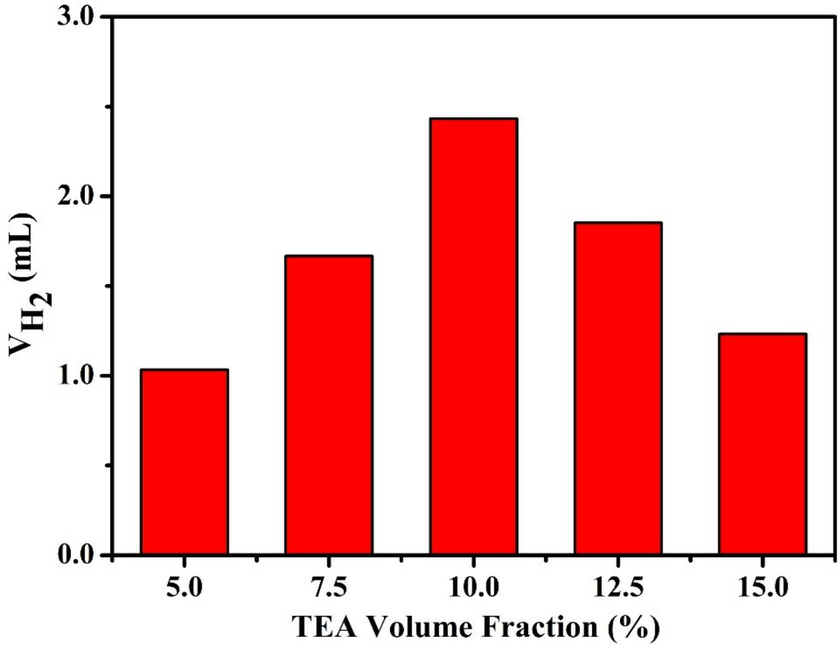

Fig. S16 Photocatalytic H_2 generation with various TEA concentrations.

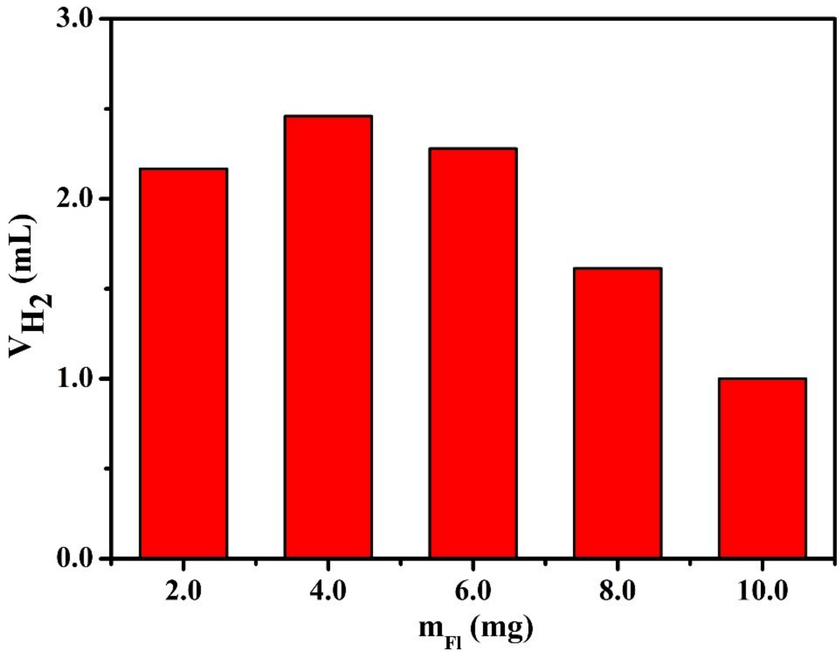

Fig. S17 Photocatalytic H_2 generation with various mass of fluorescein.

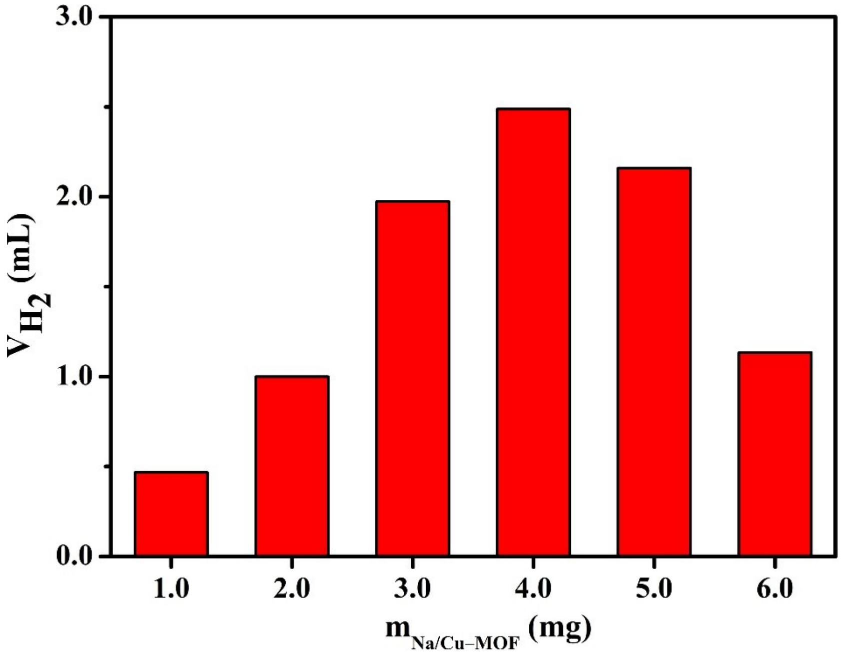

Fig. S18 Photocatalytic H_2 generation with various mass of **Na/Cu–MOF**.

Section S5 References

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