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Electronic Supplementary Information

Activating photocatalytic hydrogen evolution by constructing Ni-based organical layers and tailoring its crystal facets

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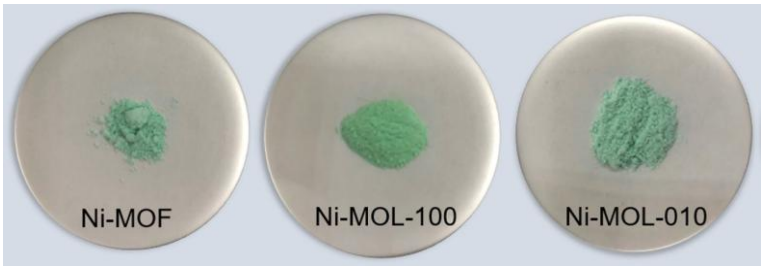

Figure S1. The samples of bulky Ni-MOF, Ni-MOL-100 and Ni-MOL-010 from left to right, respectively.

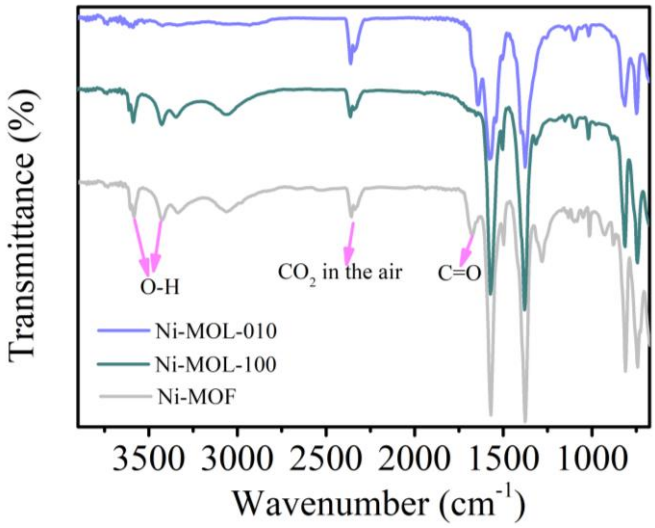

Figure S2. Fourier Transform infrared spectroscopy (FT-IR) spectra of bulky Ni-MOF, Ni-MOL-100 and Ni-MOL-010, respectively.

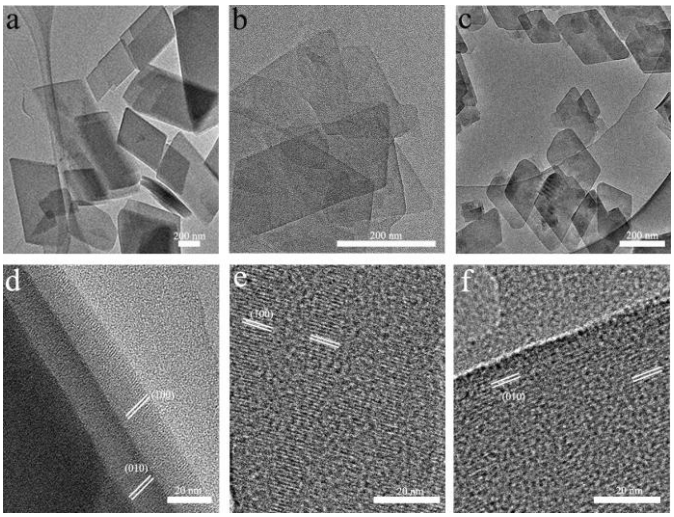

Figure S3. TEM images of (a) bulky Ni-MOF, (b) Ni-MOL-100 and (c) Ni-MOL-010, respectively. HRTEM images of (d) bulky Ni-MOF, (e) Ni-MOL-100 and (f) Ni-MOL-010.

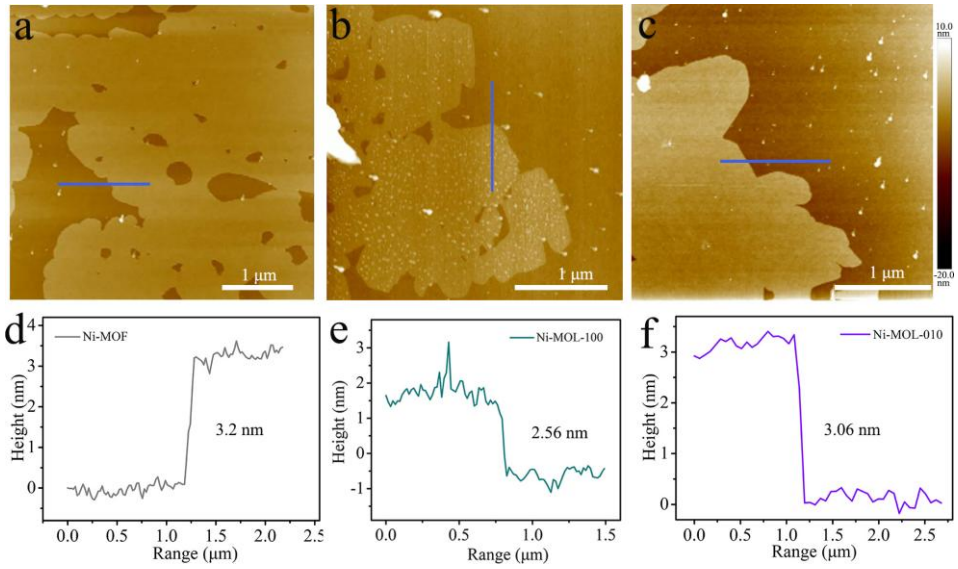

Figure S4. AFM results of (a) bulky Ni-MOF, (b) Ni-MOL-100 and (c)Ni-MOL-010. The one on the far right is the ruler bar of the AFM. The thickness of (d) bulky Ni-MOF, (e) Ni-MOL-100 and (f) Ni-MOL-010.

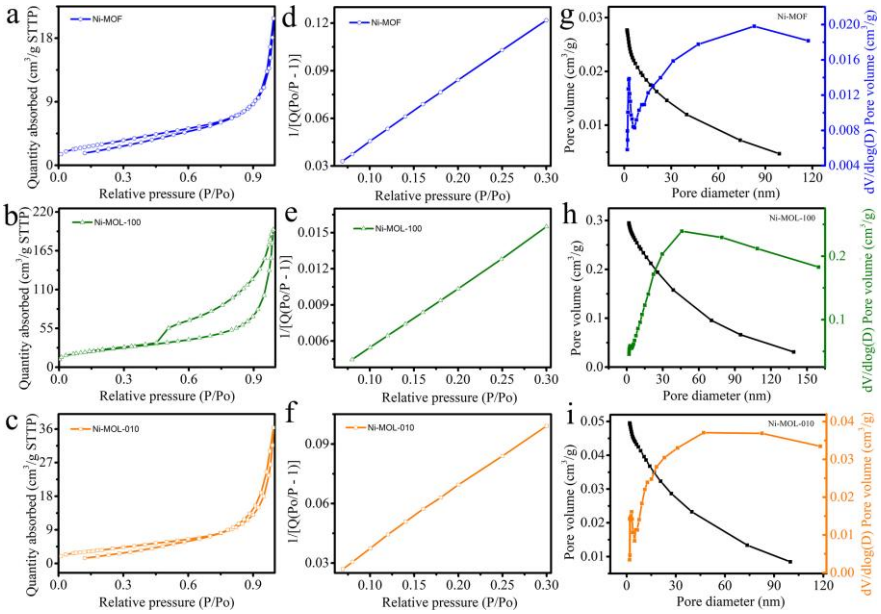

Figure S5. Plots of the linear region for the Brunauer-Emmett-Teller (BET) of (a) bulky Ni-MOF, (b) Ni-MOL-100 and (c) Ni-MOL-010. Nitrogen adsorption-desorption isotherms of (d) bulky Ni-MOF, (e) Ni-MOL-100 and (f) Ni-MOL-010. Corresponding non-local density functional theory (NLDFT) pore size distributions (PSD) of (g) bulky Ni-MOF, (h) Ni-MOL-100 and (i) Ni-MOL-010.

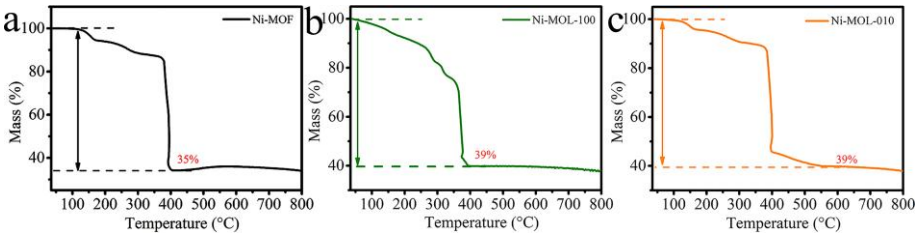

Figure S6. Thermal gravimetric analysis (TGA) curves of (a) bulky Ni-MOF, (b) Ni-MOL-100 and (c) Ni-MOL-010 under air atmosphere, respectively.

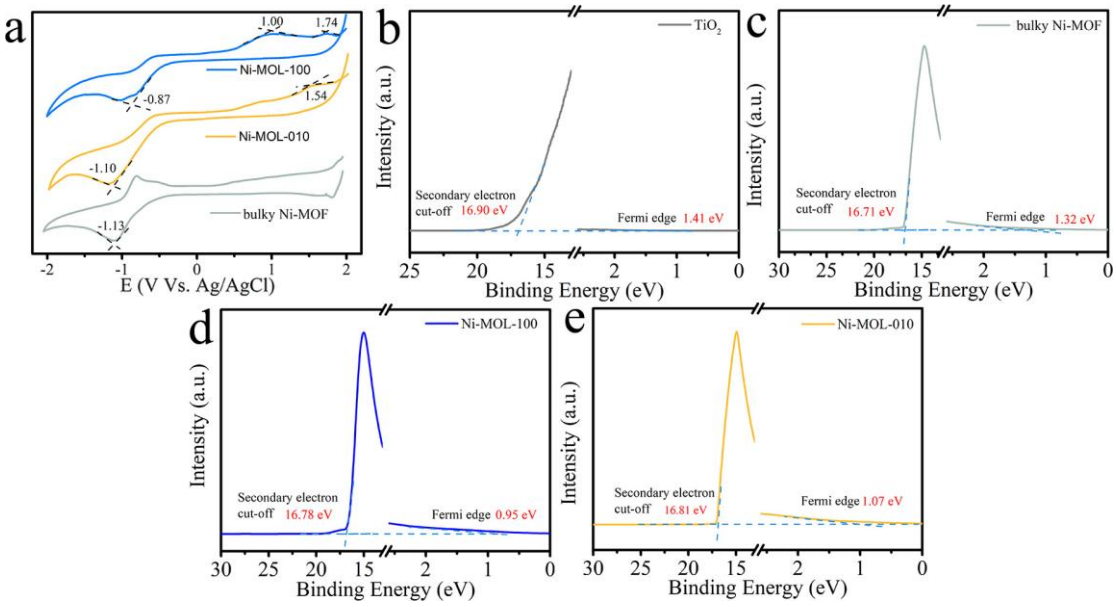

Figure S7. (a) Cyclic voltammetry (CV) reduction and oxidation curves of Ni-MOL-100, Ni-MOL-010 and bulky Ni-MOF, respectively. Ultraviolet photoelectron spectroscopy (UPS) spectra showing the Fermi levels of the (b) TiO_2, (c) bulky Ni-MOF, (d) Ni-MOL-100 and (e) Ni-MOL-010, respectively.

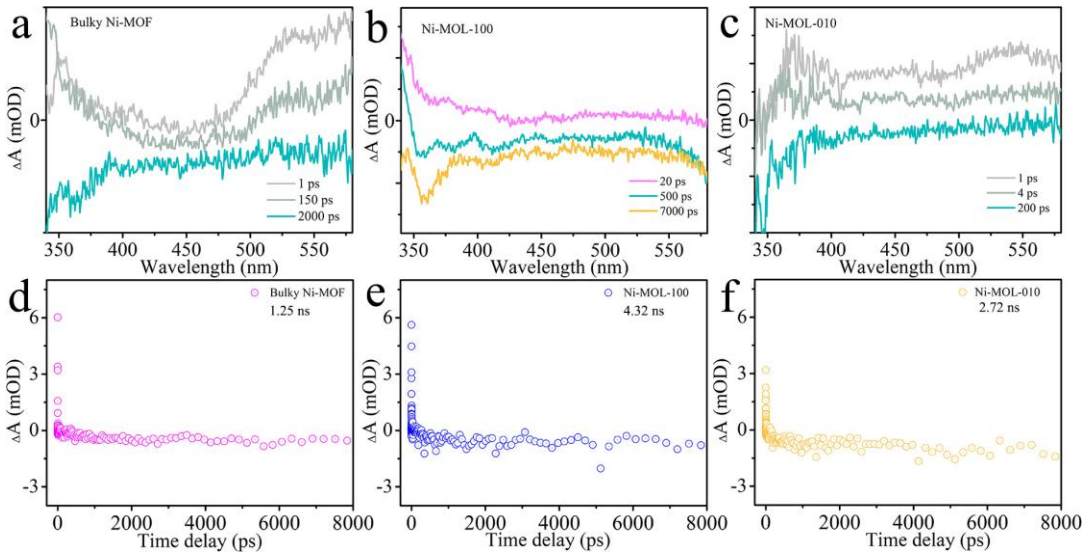

Figure S8. Transient absorption spectra of (a) bulky Ni-MOF, (b) Ni-MOL-100, and (c) Ni-MOL-010, respectively. Transient absorption decay profiles of (d) bulky Ni-MOF, (e) Ni-MOL-100 and (f) Ni-MOL-010, respectively.

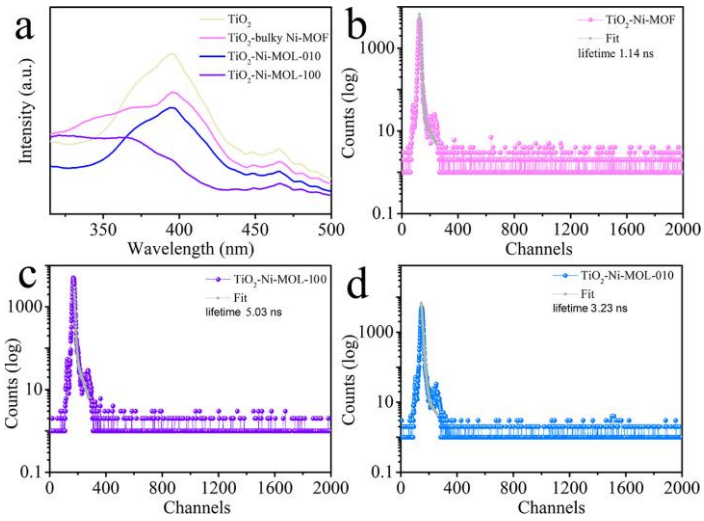

Figure S9. The fluorescence of (a) TiO_2, mixed TiO_2-bulky Ni-MOF, mixed TiO_2-Ni-MOL-100 and mixed TiO_2-Ni-MOL-010, respectively. Fluorescence decay profiles of (b) mixed TiO_2-bulky Ni-MOF, (c) mixed TiO_2-Ni-MOL-100 and (d) mixed TiO_2-Ni-MOL-010, respectively.

Figure S10. The photograph of the reactor setup for hydrogen evolution experiments. Left is under off light; right is under irradiation by 300 W Xenon light (AM 1.5G) under stirring. The photos show excellent dispersibility of Ni-MOLs in water/MeOH mixture.

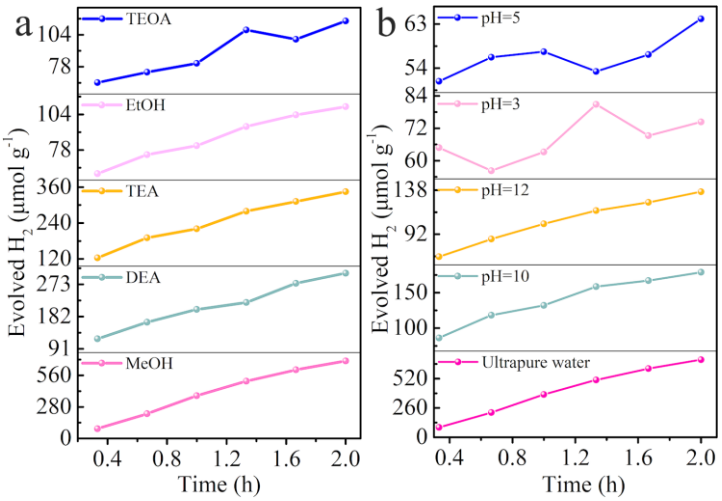

Figure S11. (a) Hydrogen evolution arrays using 30 mg TiO_2 and 5 wt% of Ni-MOL-100 with different sacrificial agents (diethylamine-DEA; triethylamine-TEA; triethanolamine-TEOA). (b) Hydrogen evolution arrays using 30 mg TiO_2 and 5 wt% of Ni-MOL-100 with different pH values.

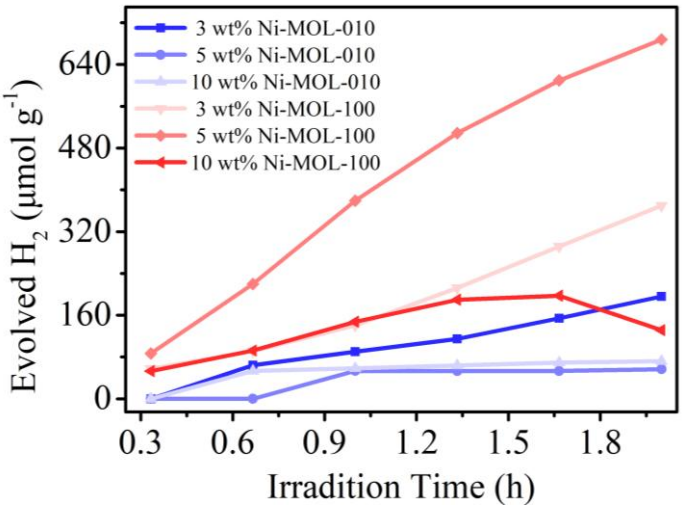

Figure S12. The hydrogen evolution arrays in 80 mL H_2O and 20 mL MeOH mixture using 30 mg TiO_2 and different x wt% of cocatalysts (Ni-MOL-100 and Ni-MOL-010) (x = 3, 5, 10).

Table S1. Comparison of recent reports on MOF-based photocatalysts.

Evolved H_2	Light source	Sacrificial agent	μmol g^{-1} h^{-1}	Reference
TiO_2-Ni-MOL-100	AM 1.5G	MeOH	343.6	This work
TiO_2-Ni-MOL-010	AM 1.5G	MeOH	25.6	This work
TiO_2-Ni-MOF	AM 1.5G	MeOH	0	This work
NH_2-MIL-125-Ti	>380	TEOA	17	1
NH_2-MIL-125-Ti	>420	TEOA	0	2
RuN_3/ZIF-67	>405	TEOA	4.85	3
CdS/MCM-41	>420	TEOA	55.5	4
NH_2-UiO-66(Zr)	>420	Na_2S	0	5
Pt/NH_2-UiO-66(Zr)	>380	TEOA	50.26	6
NH_2-MIL-125(Ti)(T110)	>400	TEOA	60.8	7

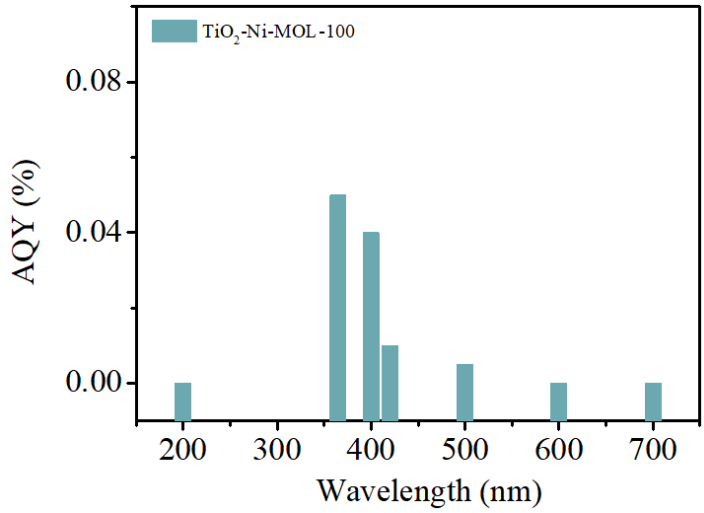

Figure S13. Wavelength-dependent AQY of photocatalytic hydrogen evolution by mixed TiO_2 with Ni-MOL-100.

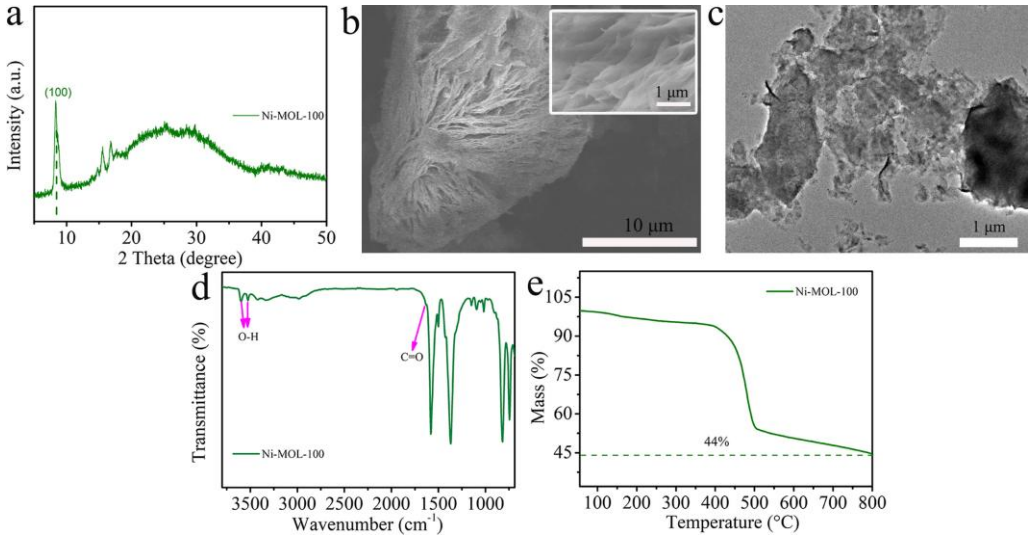

Figure S14. (a) PXRD, (b) SEM images, (c) TEM image, (d) FT-IR spectrum, and (e) TGA curve of Ni-MOL-100 as-synthesized after photocatalytic hydrogen evolution.

Table. S2. The Bader charge and free energy of H atom adsorbing on different Ni sites of cocatalysts.

	Bader charge	**ΔGH***
TiO_2-Ni-MOL-100	1.406	-0.1512
TiO_2-Ni-MOL-100-2	1.220	0.2568
TiO_2-Ni-MOL-010	0.9781	1.207

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