SUPPORTING INFORMATION

Three-in-One: Achieving Robust and Effective Hydrogen-Evolving Hybrid Materials by Integrating Polyoxometalate, Photo-responsive Metal-Organic Framework, and in-situ Generated Pt nanoparticles

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Table of content

1. Figure S1-S16

1. Figure S1-S17

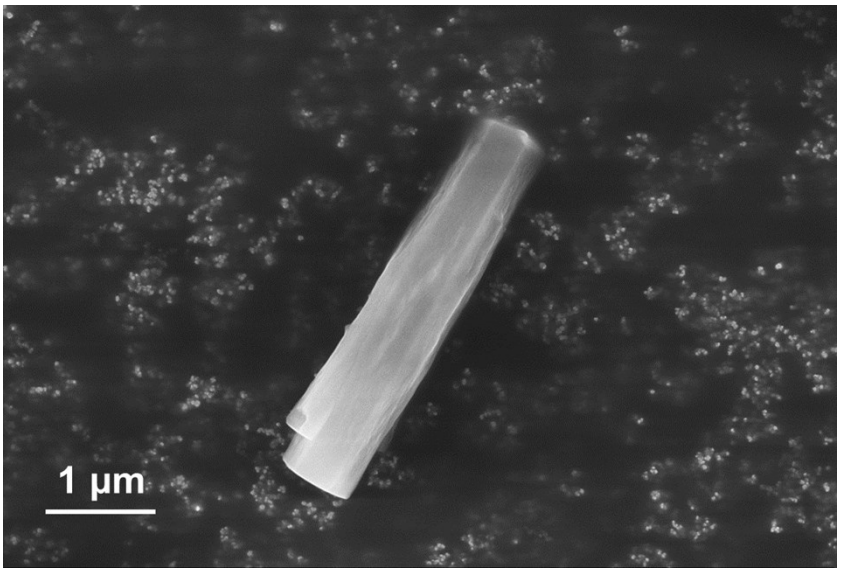


Figure S1. SEM image of NU-1000.

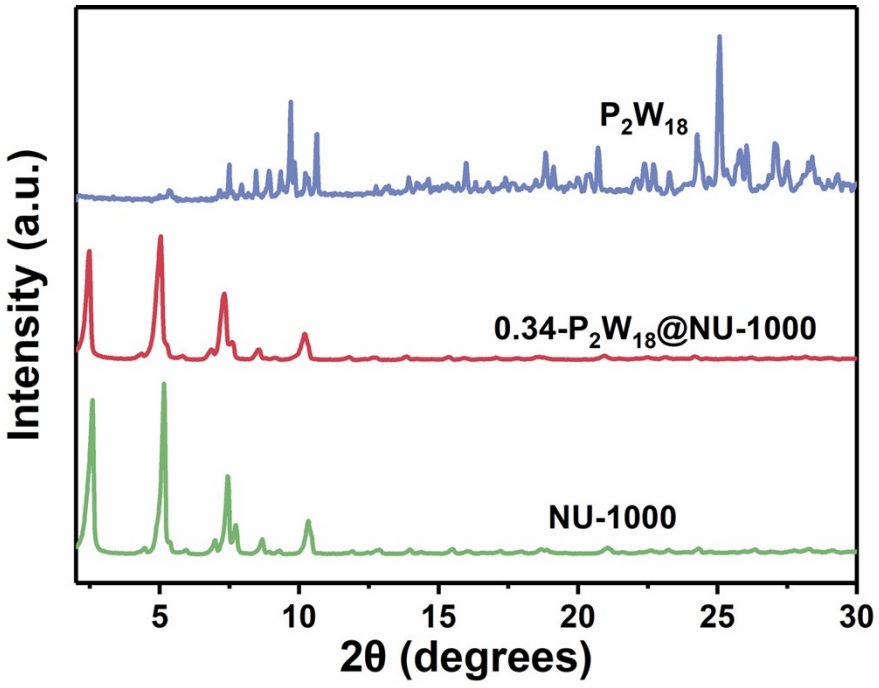


Figure S2. PXRD patterns of $\mathbf{P_2W_{18}}$, 0.34-$\mathbf{P_2W_{18}}$@NU-1000 and NU-1000.

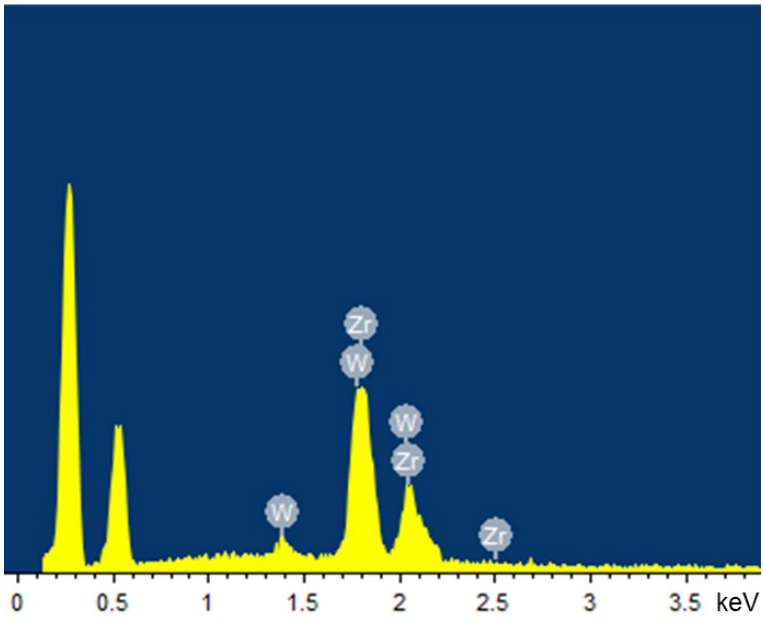


Figure S3. EDS elemental analysis of 0.34-$\mathbf{P_2W_{18}}$@NU-1000.

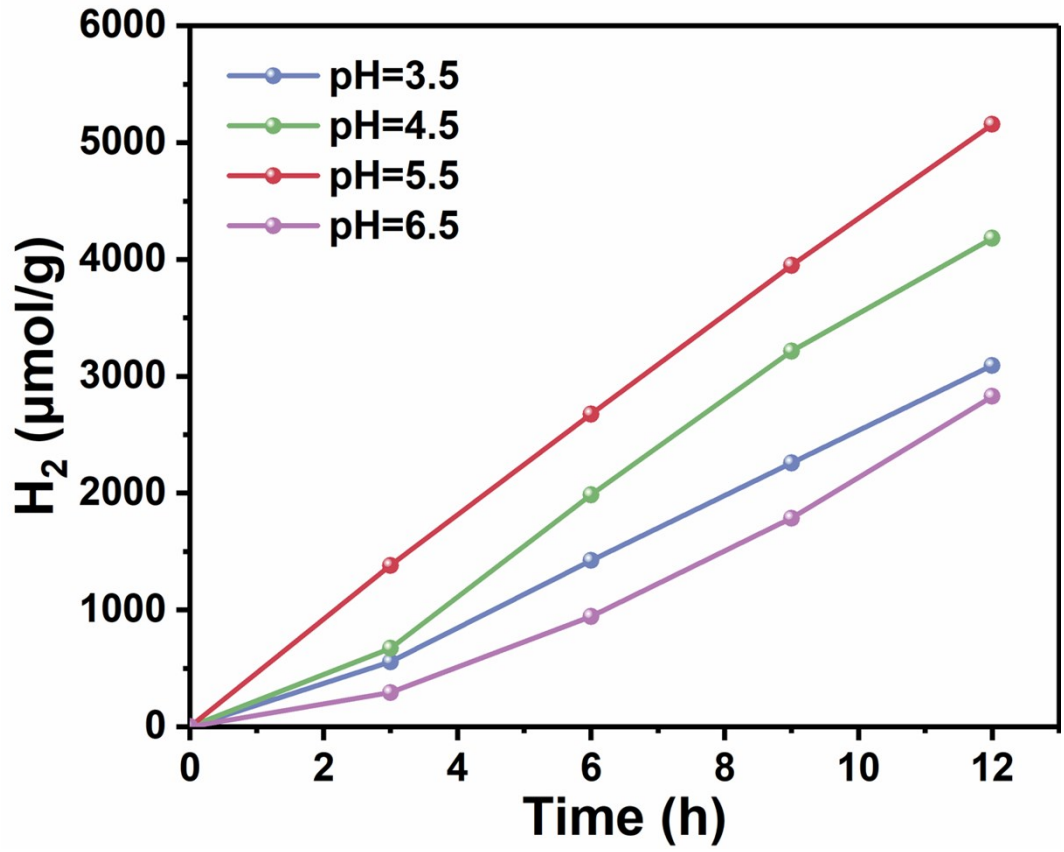


Figure S4. Photocatalytic hydrogen evolution at different pH values. Conditions: 10 mg of 0.34-$\mathbf{P_2W_{18}}$@NU-1000, 1 wt% Pt, 20 mL of 1 M AA aqueous, 300 W Xe-lamp.

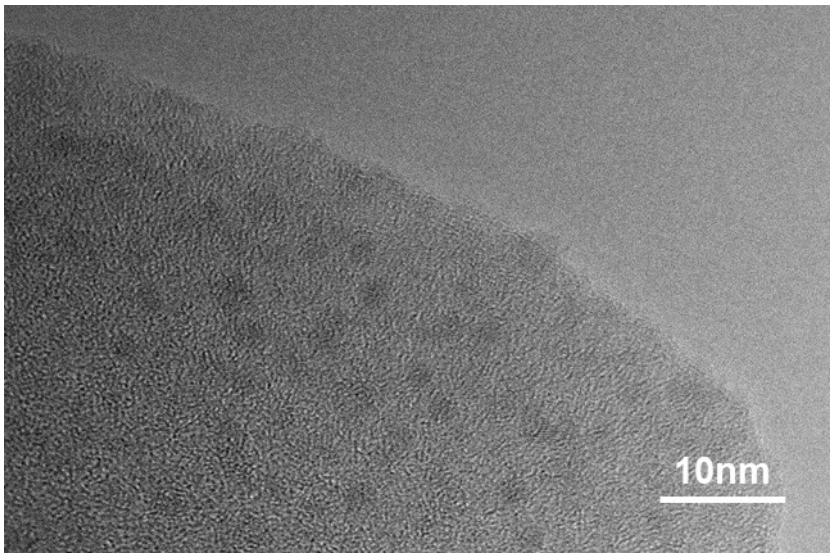


Figure S5. High resolution TEM image of NU-1000-Pt.

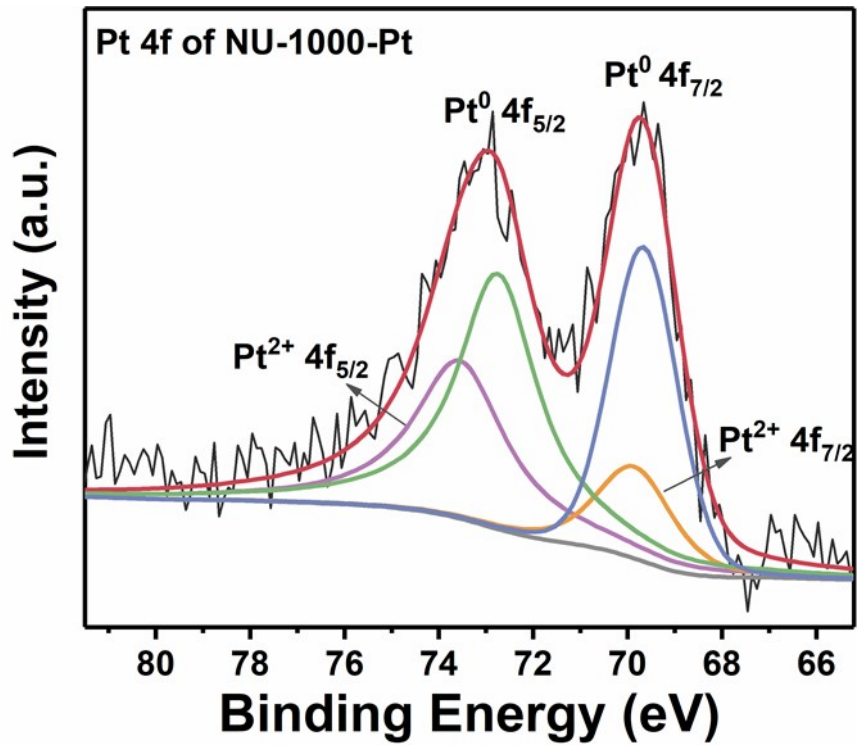


Figure S6. High resolution XPS spectra of Pt 4f in NU-1000-Pt.

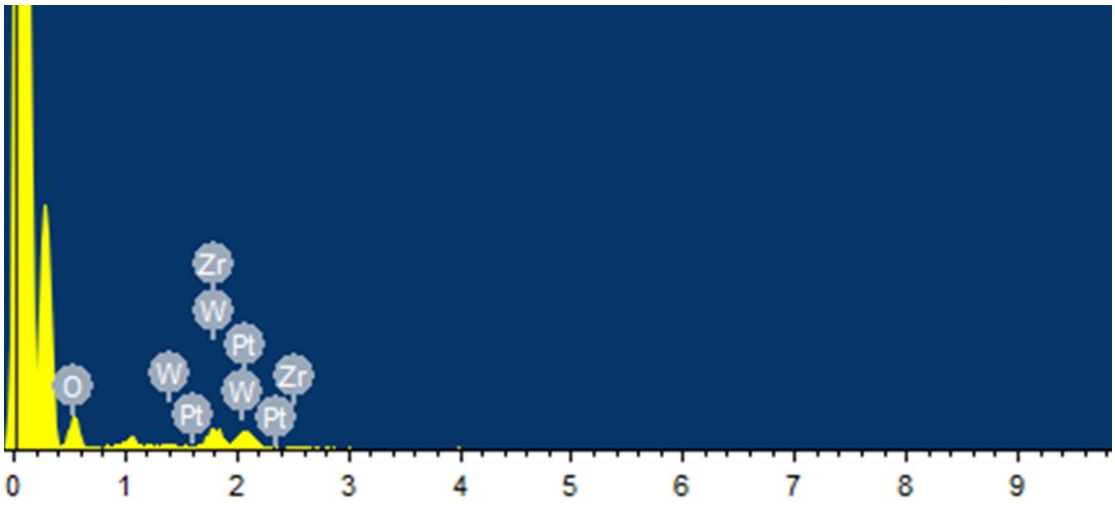


Figure S7. EDS elemental analysis of 0.34-$\mathbf{P_2W_{18}}$@NU-1000-Pt.

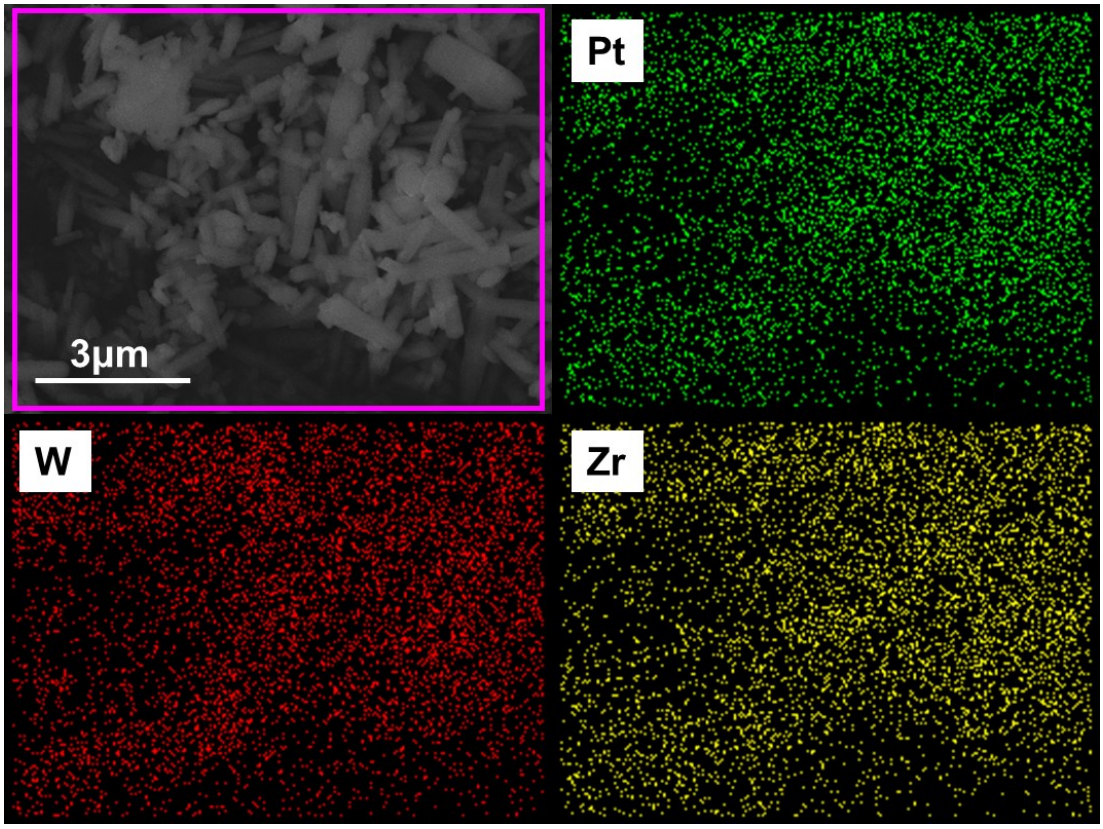


Figure S8. The corresponding elemental mapping images of 0.34-$\mathbf{P_2W_{18}}$@NU-1000-Pt.

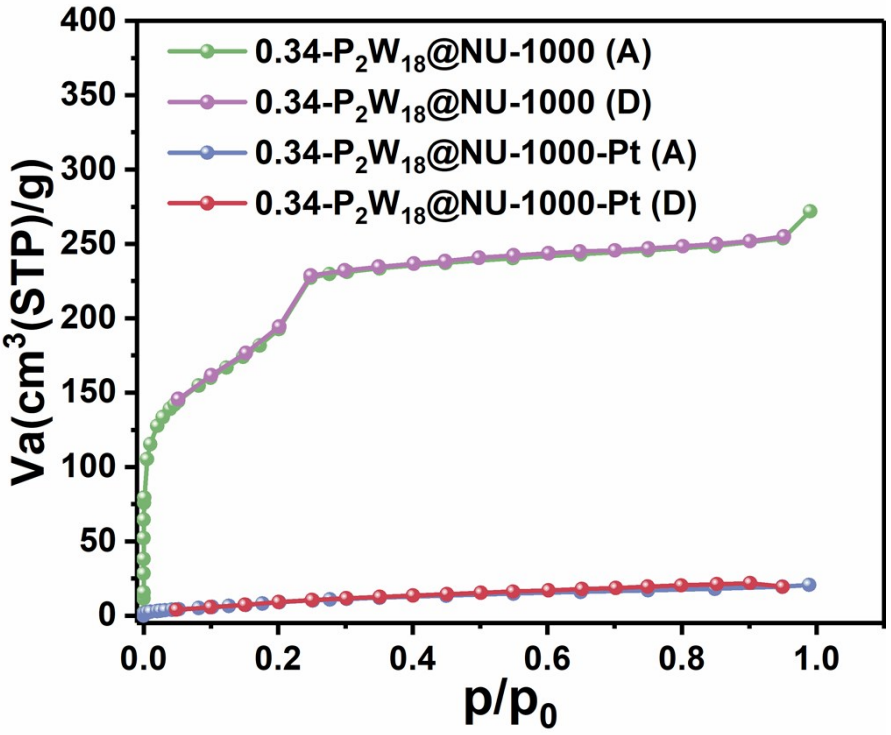


Figure S9. The comparison of low temperature N_2 adsorption-desorption isotherms of 0.34-**P_2W_{18}**@NU-1000 before and after photocatalysis.

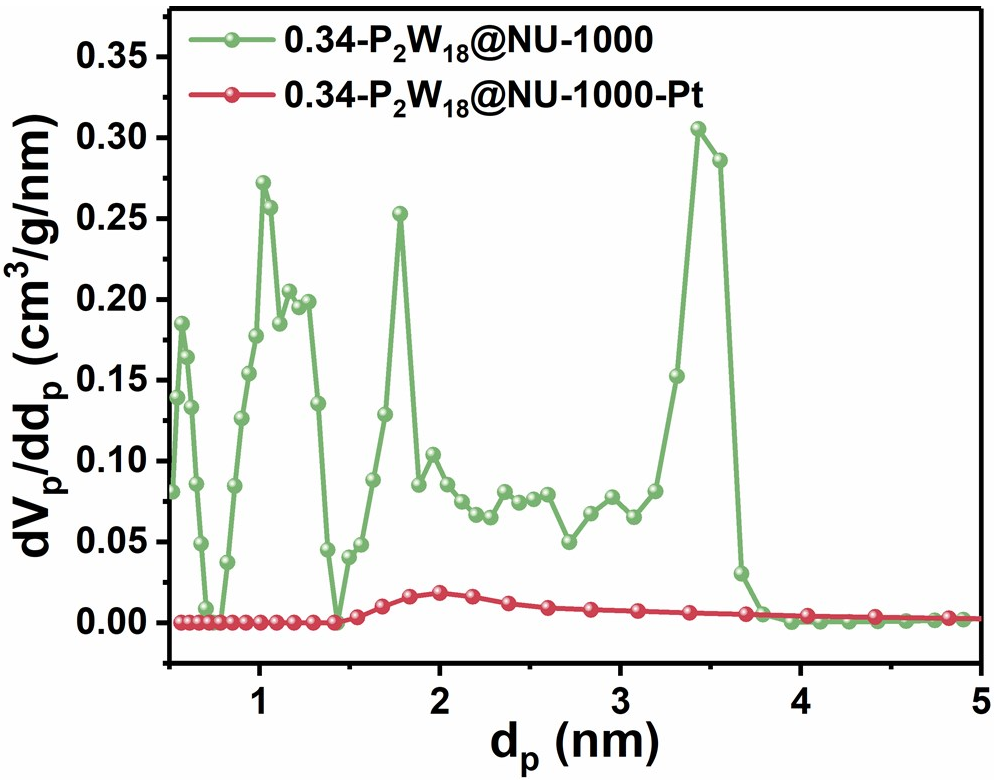


Figure S10. The comparison of the pore distribution curves of 0.34-**P_2W_{18}**@NU-1000 before and after photocatalysis

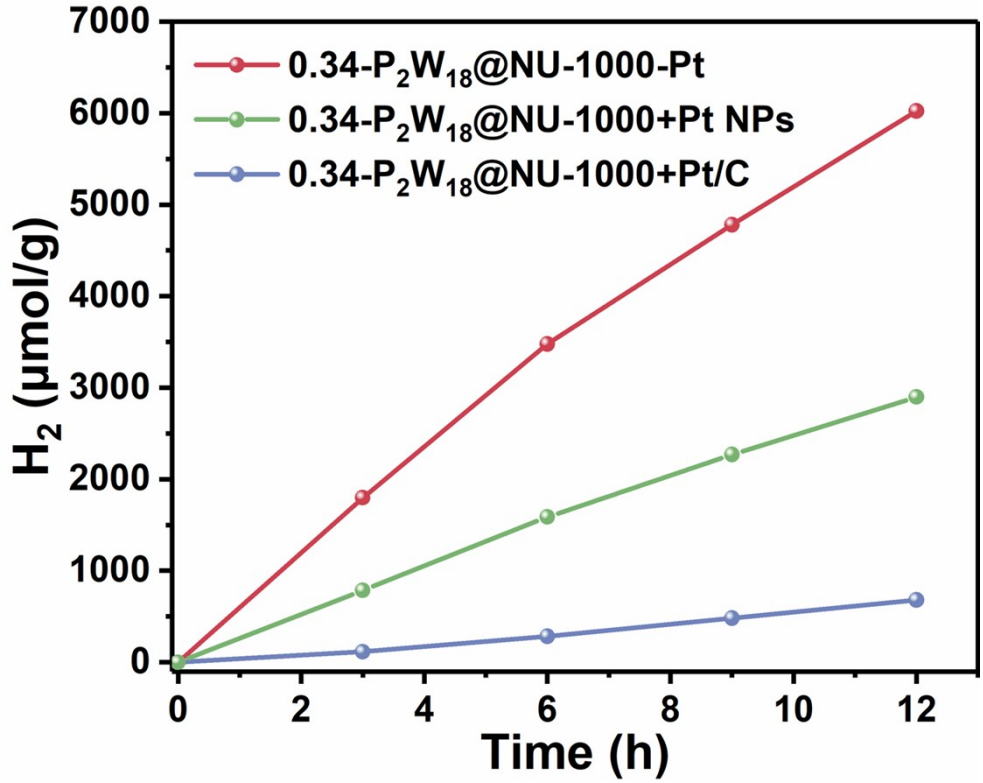


Figure S11. Photocatalytic hydrogen evolution of 0.34-$\mathbf{P_2W_{18}}$@NU-1000 with different types of Pt sources which contain equal amount of Pt species.

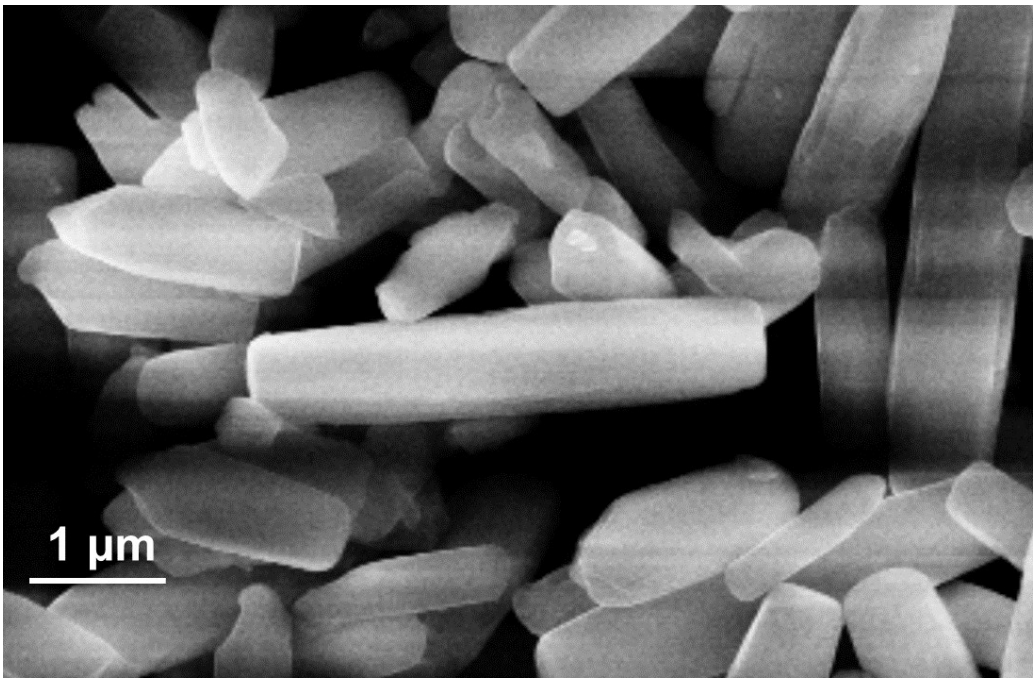


Figure S12. SEM image of 0.34-$\mathbf{P_2W_{18}}$@NU-1000 after photocatalytic hydrogen evolution for 12 h.

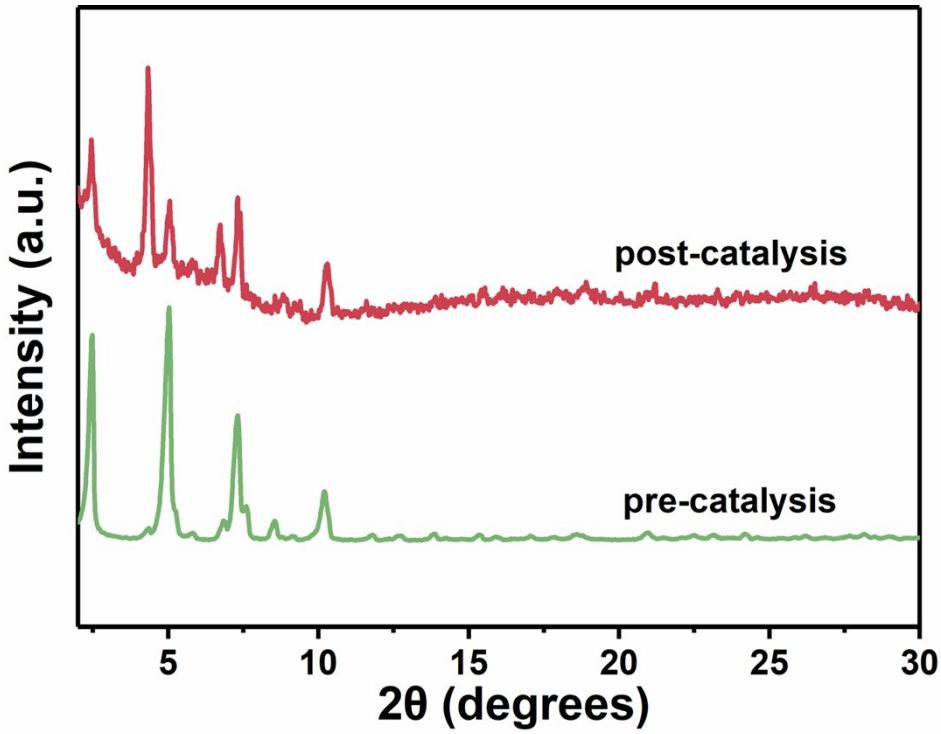


Figure S13. PXRD patterns of 0.34-$\mathbf{P_2W_{18}}$@NU-1000 before and after photocatalytic reaction for 12 h.

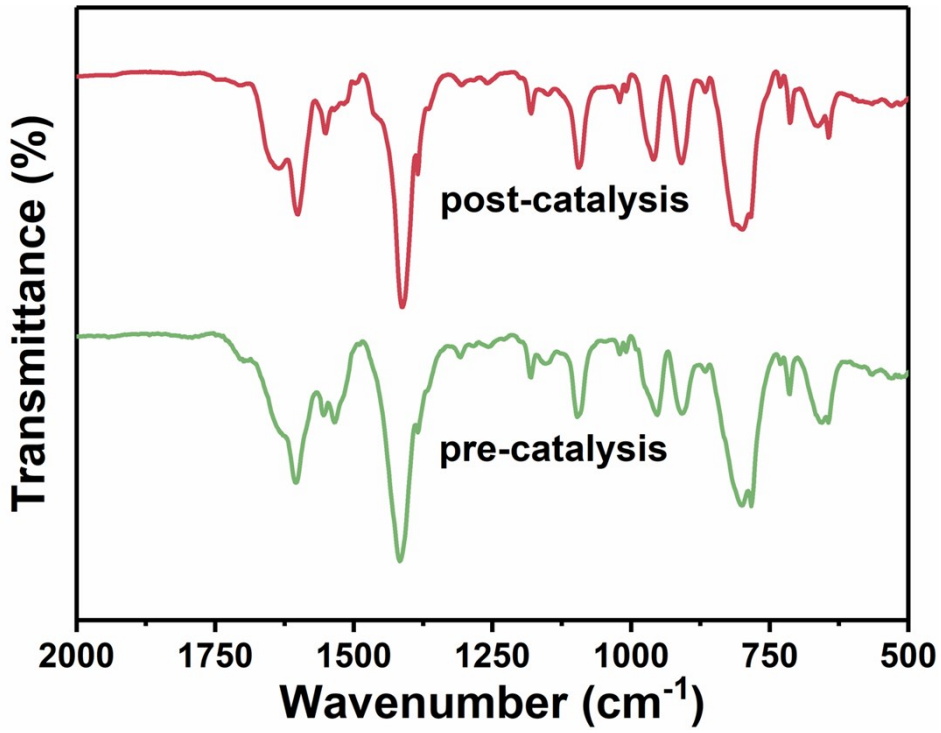


Figure S14. FT-IR spectra of 0.34-$\mathbf{P_2W_{18}}$@NU-1000 before and after photocatalysis for 12 h.

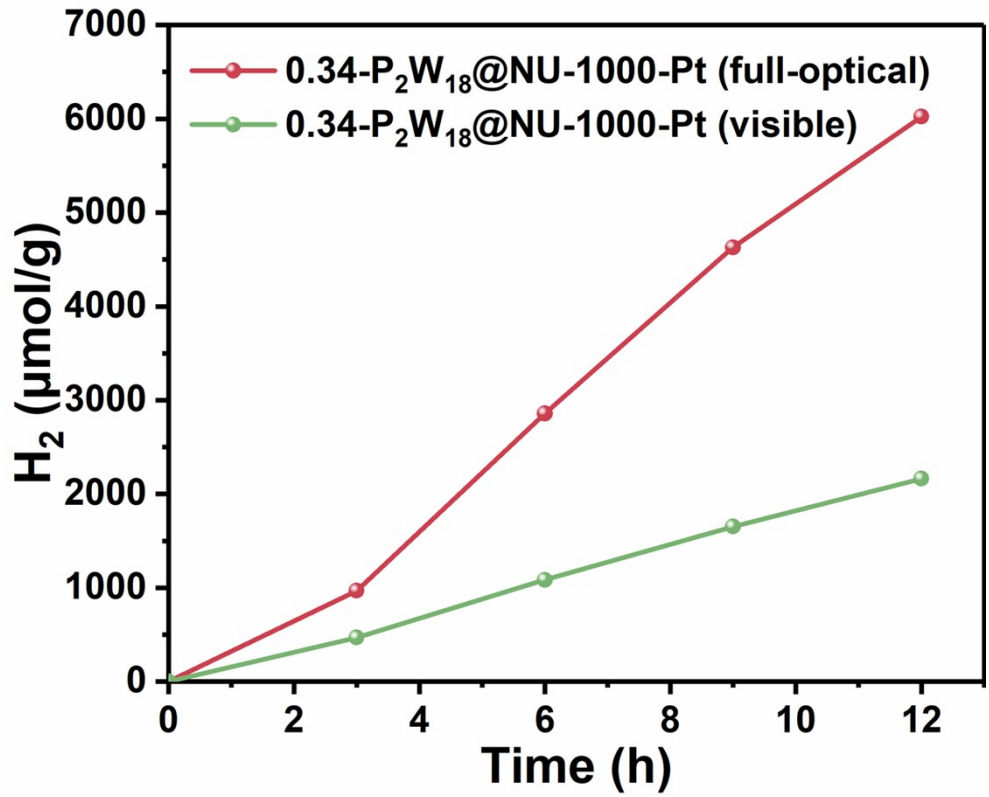


Figure S15. Photocatalytic hydrogen under different light sources. Reaction conditions: 10 mg of 0.34-$\mathbf{P_2W_{18}}$@NU-1000, 0.25 wt% Pt, pH=5.5, 20 mL of 1 M AA aqueous, 300 W Xe-lamp.

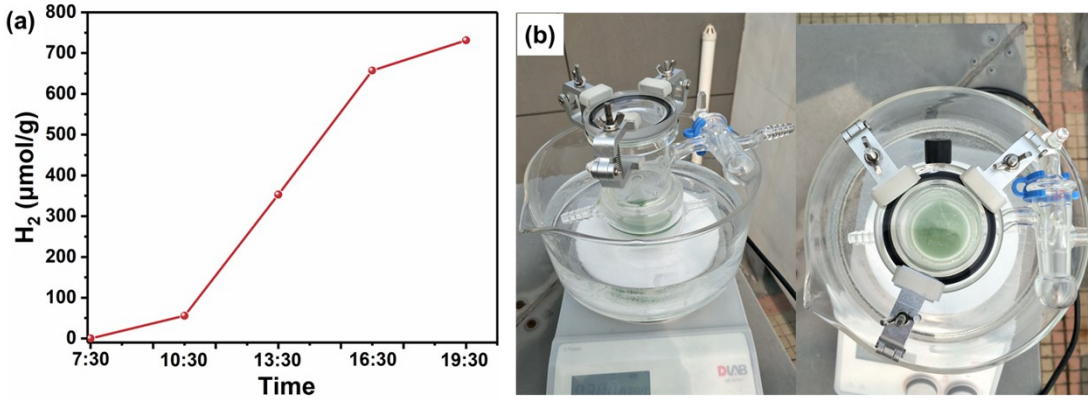
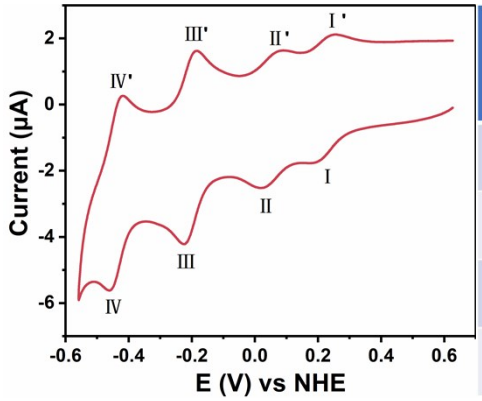


Figure S16. (a) Photocatalytic hydrogen evolution of 0.34-$\mathbf{P_2W_{18}}$@NU-1000 under Natural Sunlight. Weather conditions (obtained from the website of China National Meteorological Observatory *http://www.weather.com.cn*): Beijing, China; N 39°43'29'', E 116°9'51"; ASL 130 m; July 15th, 2019; 34 ℃/24 ℃, Cloudy; Visibility: 4 km; UV intensity level (at noon): 7. Experiment conditions: 10 mg 0.34-$\mathbf{P_2W_{18}}$@NU-1000 catalyst, 0.25 wt% Pt, 20 ml of 1 M AA aqueous at pH 5.5. (b) Photos of equipment for photocatalytic hydrogen evolution under Natural Sunlight.



Peak	E (V)	Peak	E (V)	Formal Potential (V)
Ⅰ	0.195	Ⅰ'	0.250	0.223
Ⅱ	0.022	Ⅱ'	0.080	0.102
Ⅲ	-0.230	Ⅲ'	-0.180	-0.205
Ⅳ	-0.460	Ⅳ'	-0.420	-0.440

Figure S17. Left: Cyclic voltammogram of $\mathbf{P_2W_{18}}$ (10^{-4} M) in 0.1 M H_2SO_4 aqueous solution using glassy carbon working electrode, saturated calomel electrode (SCE) reference electrode, and Pt wire auxiliary electrode; Right: the corresponding peak potentials and calculated formal potentials for different redox couples. Scan rate: 50 mV/s. The measured potential was expressed by converting to normal hydrogen electrode (NHE).

2. Table S1-S2

Table S1. Comparison of different photocatalytic systems for hydrogen production using POM@MOF composites. TON is defined as n (1/2 H_2)/ n (catalyst).

Catalyst	Photosensitizer	Solvent	Time	TON	Ref.
$\mathbf{P_2W_{18}}$@NU-1000-Pt	——	H_2O	120 h	5464	This work
PNPMOF	——	H_2O	6 h	64	[1]
$\mathbf{Ni_4P_2W_{18}}$@MOF-1	——	H_2O/MeOH	72 h	1476	[2]
$\mathbf{P_2W_{15}V_3}$@MIL-101	$[Ru(bpy)_3]^{2+}$	DMF/ H_2O /CH_3CN	8 h	56	[3]
WD-POM@SMOF-1	$[Ru(bpy)_3]^{2+}$	H_2O/MeOH	12 h	392	[4]
$\mathbf{P_2W_{18}}$@UiO	——	DMF/CH_3CN	14 h	307	[5]

Table S2. PL decay (at 505 nm) lifetimes of NU-1000, 0.34-$\mathbf{P_2W_{18}}$@NU-1000 samples upon excitation at 365 nm, the PL decays were corrected by IRF.

Compounds	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
NU-1000	0.76	3.89	15.17
0.34-$\mathbf{P_2W_{18}}$@NU-1000	0.53	3.01	13.23

3. Apparent quantum yield calculation

$$n_{photons}=\frac{Pt\lambda}{hcN_A}=7.136\times10^{-3}\ \text{mol} \quad (1)$$

$$\phi=\frac{2\times n_{H2}}{n_{photons}}=1.69\% \quad (2)$$

Where P is the illumination power ($P=EA_R$, $E=2.6\ mW/cm^2$), A_R is the irradiation area (πR^2, R=2.1 cm), t is the illumination time (s, in our cases t =43200 s), equivalent wavelength λ=549 nm for full optical Xe-lamp, h is the Planck constant, c is the velocity of light and N_A is Avogadro's number.

4. References

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5. Z. M. Zhang, T. Zhang, C. Wang, Z. Lin, L. S. Long and W. Lin, *J. Am. Chem. Soc.*, 2015, **137**, 3197-3200.