SUPPORTING INFORMATION

Size-matching encapsulation of high-nuclearity Ni-containing polyoxometalate into light-responsive MOF for robust photogeneration of hydrogen

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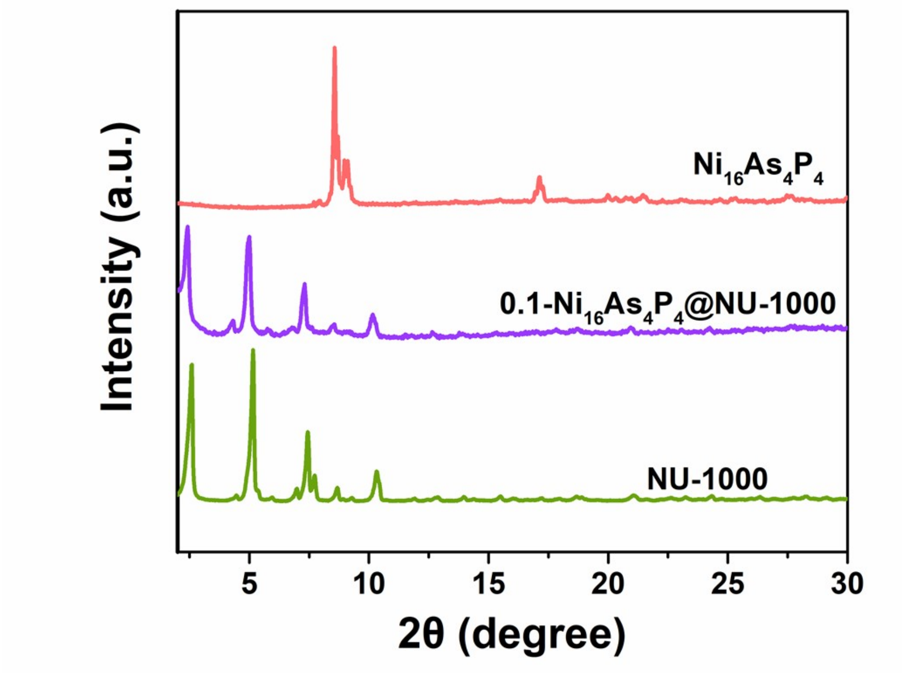

Fig. S1 PXRD patterns of $\mathbf{Ni_{16}As_4P_4}$, 0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000 and NU-1000.

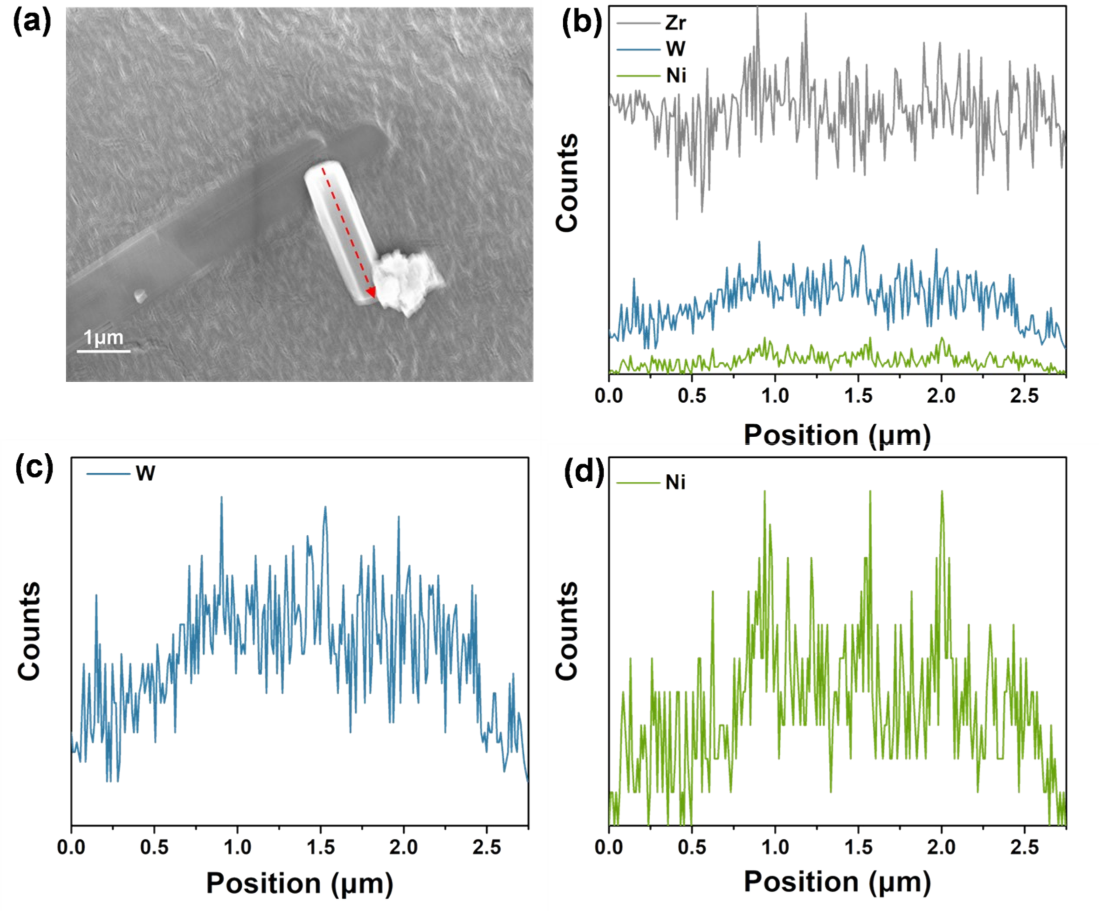

Fig. S2 (a) Scanning electron microscopy (SEM) micrograph and (b) linear energy dispersive X-ray (EDS) spectrum of different elements of the 0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000 sample collected along the red dash line shown in Figure S2a, (c, d) enlarged linear EDS signals of W and Ni elements.

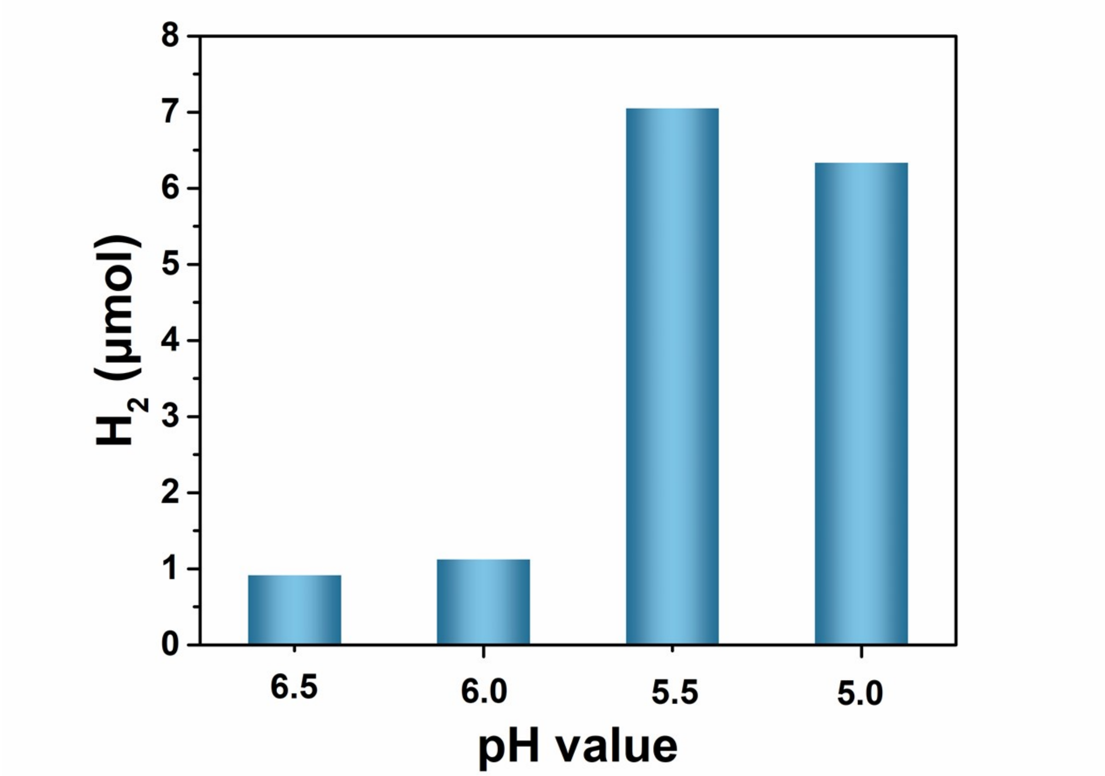

Fig. S3 Photocatalytic hydrogen evolution of 1.0-**$Ni_{16}As_4P_4$**@NU-1000 at different pH values. Conditions: 2 mg of 1.0-**$Ni_{16}As_4P_4$**@NU-1000, 20 mL of 1 M AA aqueous solution, 300 W Xe-lamp, reaction time of 6 h.

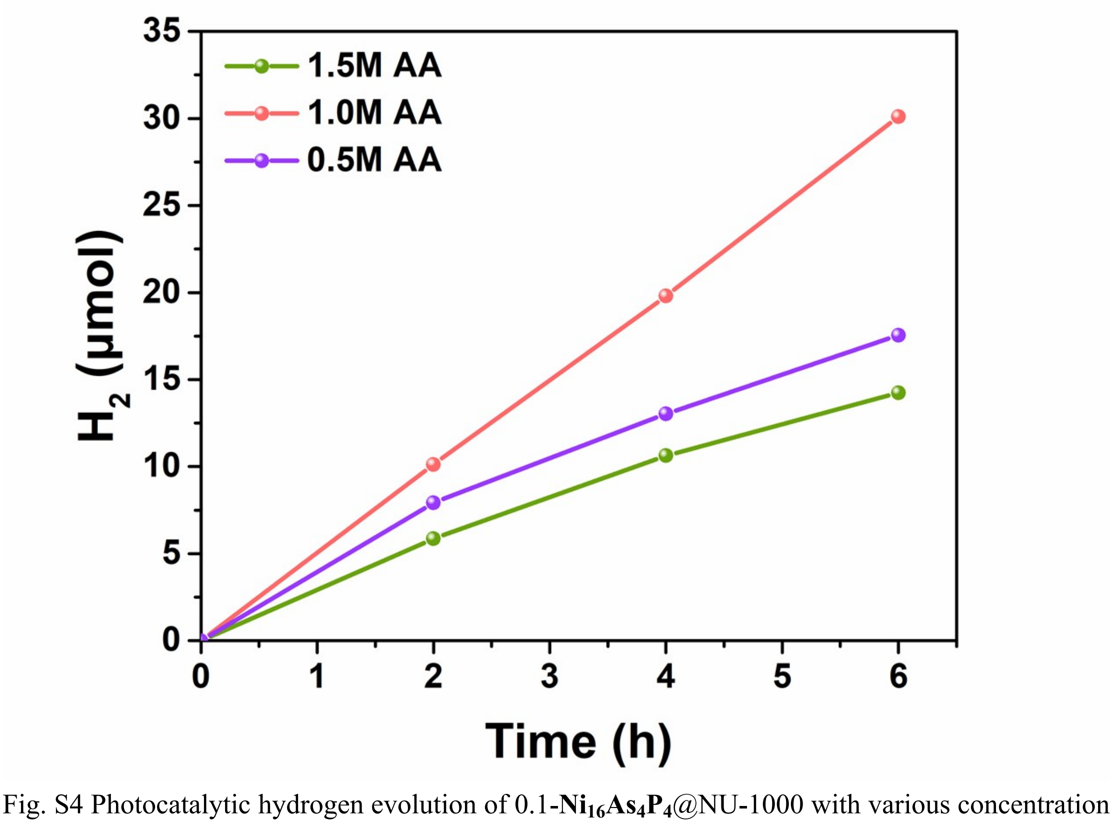

Fig. S4 Photocatalytic hydrogen evolution of 0.1-**$Ni_{16}As_4P_4$**@NU-1000 with various concentration of AA. Conditions: 0.1-**$Ni_{16}As_4P_4$**@NU-1000, 20 mL of AA aqueous solution at pH 5.5, 300 W Xe-lamp.

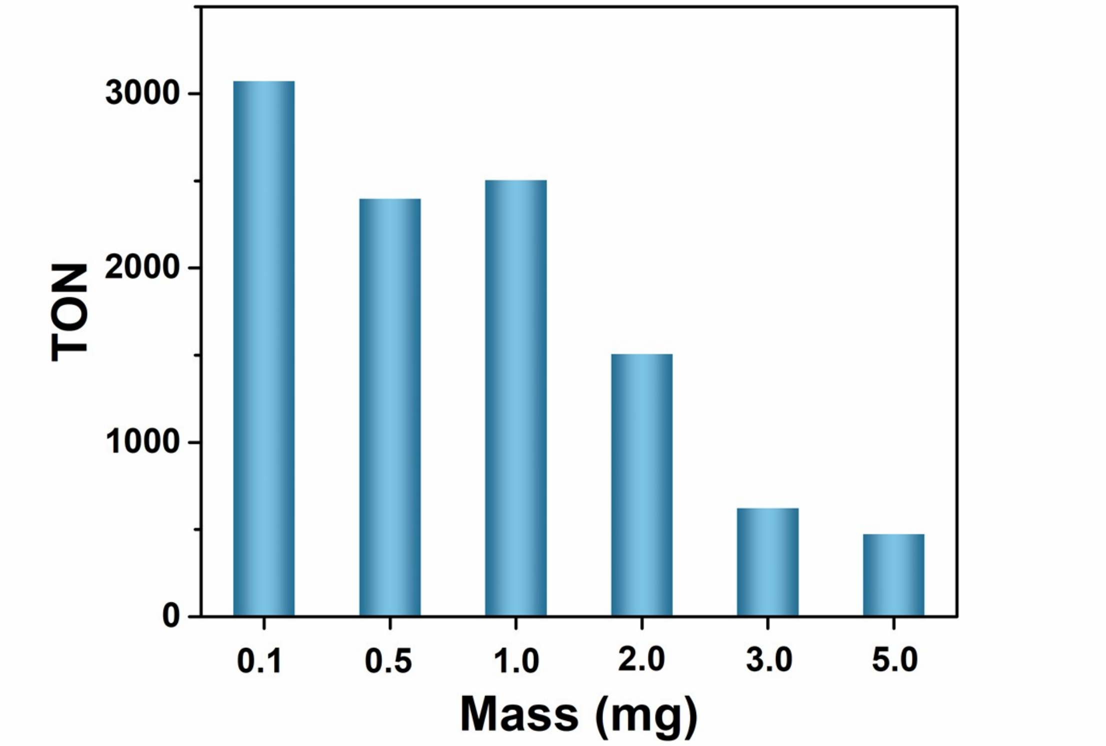

Fig. S5 Photocatalytic hydrogen evolution with the different usage amount of 0.1-**$Ni_{16}As_4P_4$**@NU-1000 during photocatalysis. Conditions: 0.1-**$Ni_{16}As_4P_4$**@NU-1000, 20 mL of 1 M AA aqueous solution at pH 5.5, 300 W Xe-lamp, reaction time of 6 h.

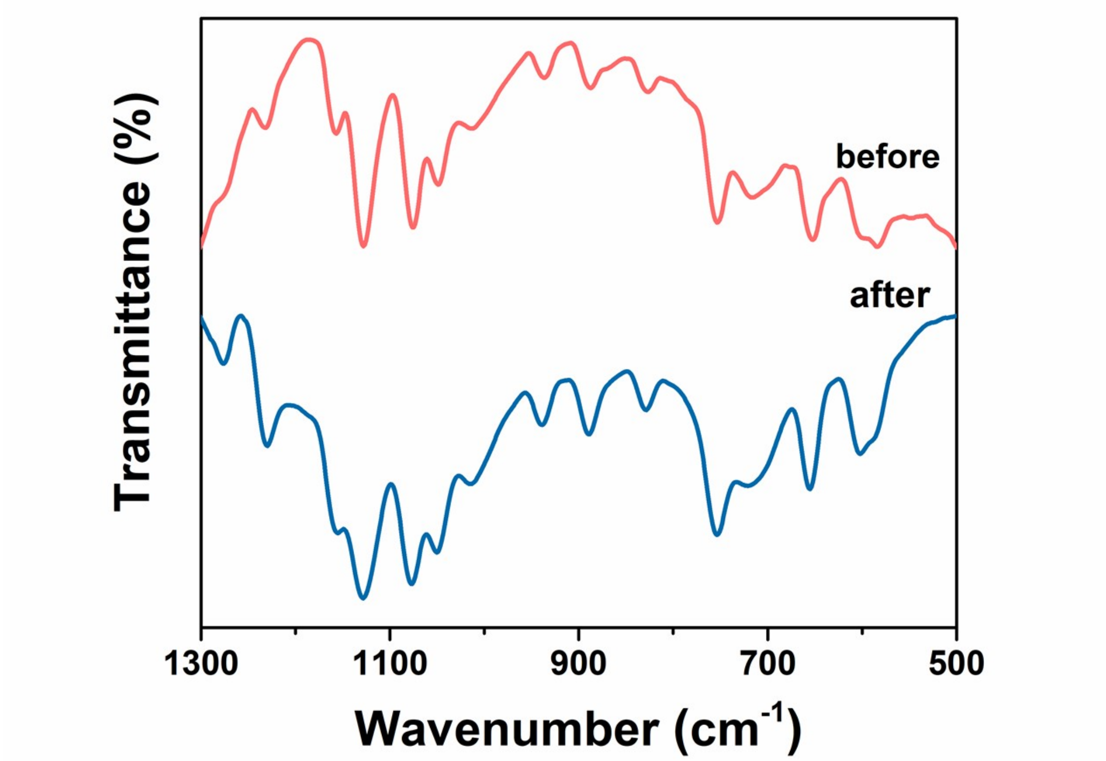

Fig. S6 FT-IR spectra of 0.1- **$Ni_{16}As_4P_4$** @NU-1000 before and after photocatalysis for 6 h.

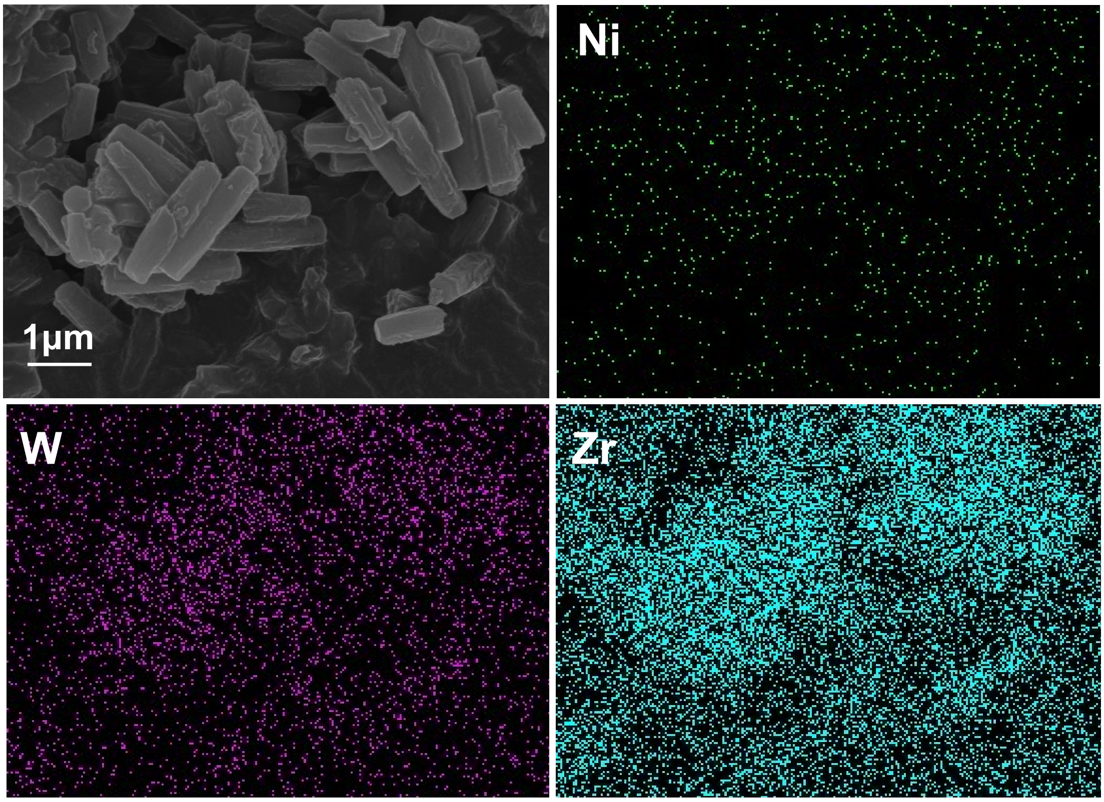

Fig. S7 EDS mapping images of 0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000 after photocatalytic hydrogen evolution for 6 h.

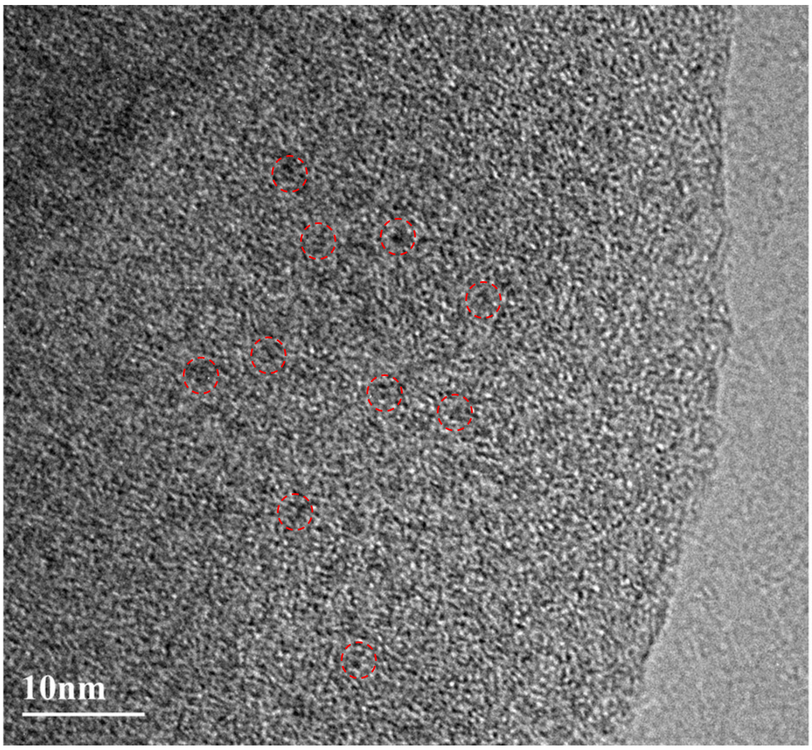

Fig. S8 High resolution-TEM image of 0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000 after photocatalysis for 6 h.

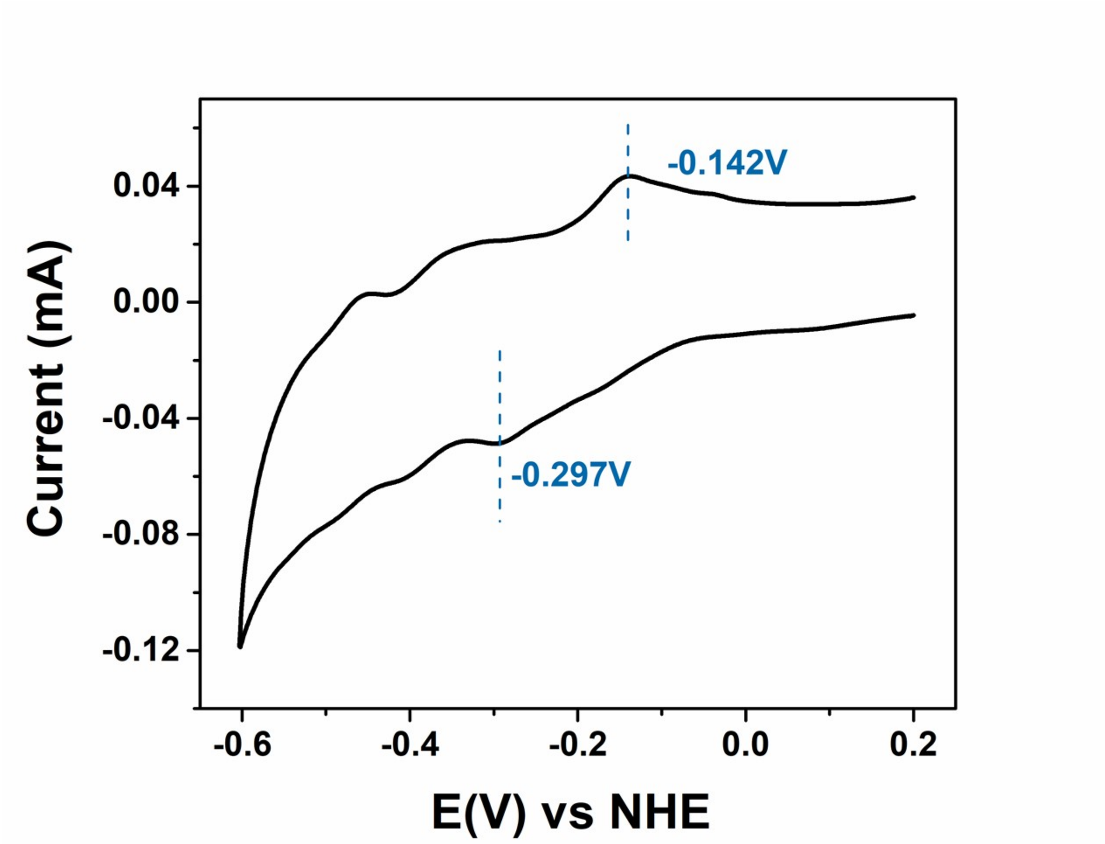

Fig. S9 Cyclic voltammetry curve of **$Ni_{16}As_4P_4$** in 0.1M H_2SO_4 aqueous solution with a three-electrode cell comprising of a glassy carbon working electrode, a Pt wire auxiliary electrode, and a saturated Ag/AgCl reference electrode. LUMO potential of **$Ni_{16}As_4P_4$** was calculated according to the following equation: E (LUMO) $=E_{1/2}= (E_{pc}+E_{pa})/2$

2. Table S1-S2

Table S1. Comparison of different POM@MOF composites as catalysts for photocatalytic H_2 evolution reaction.

Catalysts	Photosensitizer	Sacrificial reagent	TON	Time	Ref.
$\mathbf{P_2W_{15}V_3}$@MIL-101	$[Ru(bpy)_3]^{2+}$	TEOA	70	8h	[1]
$\mathbf{Ni_4P_2}$@MOF-1	Covalently-linked $[Ru(bpy)_3]^{2+}$ moiety	methanol	1476	72h	[2]
$\mathbf{P_2W_{18}}$@UiO	Covalently-linked $[Ru(bpy)_3]^{2+}$ moiety	TEOA	79	14h	[3]
$\mathbf{PW_{12}}$-Pt@NH_2-MIL-53	MIL-53 framework	AA	66	6h	[4]
WD-POM@SMOF-1	$[Ru(bpy)_3]^{2+}$ units	TEOA	392	12h	[5]
$\mathbf{Ni_3P_2W_{16}}$@NU-1000	NU-1000 framework	AA	2714	12h	[6]
$\mathbf{P_2W_{18}}$@NU-1000-Pt	NU-1000 framework	AA	5464	120h	[7]
$\mathbf{Ni_{16}As_4P_4}$@NU-1000	NU-1000 framework	AA	28600	120h	This work

Table S2. Luminescence decay lifetimes of NU-1000, 0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000 samples upon excitation at 365 nm.

Samples	**τ_1(ns)**	**τ_2(ns)**	**τ_3(ns)**
NU-1000	0.75	3.92	16.53
0.1-$\mathbf{Ni_{16}As_4P_4}$@NU-1000	0.48	2.36	13.21

3. Apparent quantum yield calculation

$$n_{photons} = \frac{Pt\lambda}{hcNA} = 3.568\times10^{-3}\ \text{mol}$$

$$AQY(\%) = \frac{2 \times n_{H2}}{n_{photons}} \times 100\% = 1.715\%$$

Where P is the illumination power (P=EA_R, E=2.6 mW/cm^2), A_R is the irradiation area (πR^2, R=2.1cm), t is the illumination time (s, in our cases t =21600 s), equivalent wavelength λ=549 nm for full optical Xe-lamp, h is the Planck constant, c is the velocity of light and NA is Avogadro's number. The illumination time (t = 21600 s) and hydrogen generation amount are based on data recorded in 6-hour timescale.

4. References

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