

Electronic Supplementary Information (ESI)

**Three-dimensional supramolecular phosphomolybdate architecture derived Mo
based electrocatalytic system for overall water splitting**

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Catalytic reduction of 4-nitrophenol and RhB

In a typical reaction, freshly prepared NaBH₄ was added in 4-nitrophenol solution. During this process, color of this solution changes from pale yellow to bright yellow. Then, catalyst (2 mg) was added to this solution with stirring. At a given time interval, a certain amount of solution was withdrawn and recorded immediately with UV-vis spectrometer. Apparent rate constant (k_{app}) was obtained from first-order rate model with the decay of absorption at 400 nm (Eq. 1). Based on Lambert-Beer law, $c/c_0 = I/I_0$, the equation can be converted to $\ln(I/I_0) = -k_{app}t$ at last.

$$\ln(c/c_0) = -k_{app}t \text{ (Eq. 1)}$$

To study the kinetic process of this reduction reaction, a set of apparent rate constants were obtained with constant NaBH₄ concentration (0.02 mol·L⁻¹) while varying concentration of 4-nitrophenol. The concentrations of 4-nitrophenol were 2×10^{-3} , 4.0×10^{-3} , 6×10^{-3} , 8×10^{-3} , 1×10^{-2} and 1.2×10^{-2} mol·L⁻¹. Based on above data, the curve of k_{app} versus concentration of 4-nitrophenol was drawn. Langmuir-Hinshelwood model (Eq. 2) was employed to fit these curve. In this equation, K_{4-NP} and K_{NaBH_4} are the adsorption constants of 4-nitrophenol and NaBH₄; k represents the surface rate constant; S is the surface area; n and m are the Freundlich exponents. For 4-nitrophenol and NaBH₄, these values are 0.6 and 1.0 respectively.

$$k_{app} = k \times S \times K_{4NP}^n [4NP]^{n-1} (K_{BH_4} [BH_4^-])^m / \{1 + (K_{4NP} [4NP])^n + (K_{BH_4} [BH_4^-])^m\}^2$$

(Eq. 2)

For RhB, at first, catalyst (2 mg) was added to its solution (1.0 mL, 10 mg·L⁻¹) with stirring. Then freshly prepared NaBH₄ (2.0 mL, 0.02 mol·L⁻¹) was added. At a given time interval, a certain amount of solution was withdrawn and recorded immediately with UV-vis spectrometer. The apparent rate constant was calculated based on the

decay of absorption at 553 nm.

Table S1 The element contents of **MoO₂@NC** and **Mo₂C@NC** photocatalysts.

	MoO₂@NC	Mo₂C@NC(A)	Mo₂C@NC(B)
Mo(%)	8.2	8.4	8.5
O(%)	16.4	2.1	1.8
C (%)	69.9	84.3	84.6
N (%)	5.5	5.2	5.1
N-Mo	46.5	25.5	30.2
Pyridinic-N	43.2	29.6	40.1
Pyrrolic-N	10.3	12.8	29.7
Graphitic-N	0	32.1	0

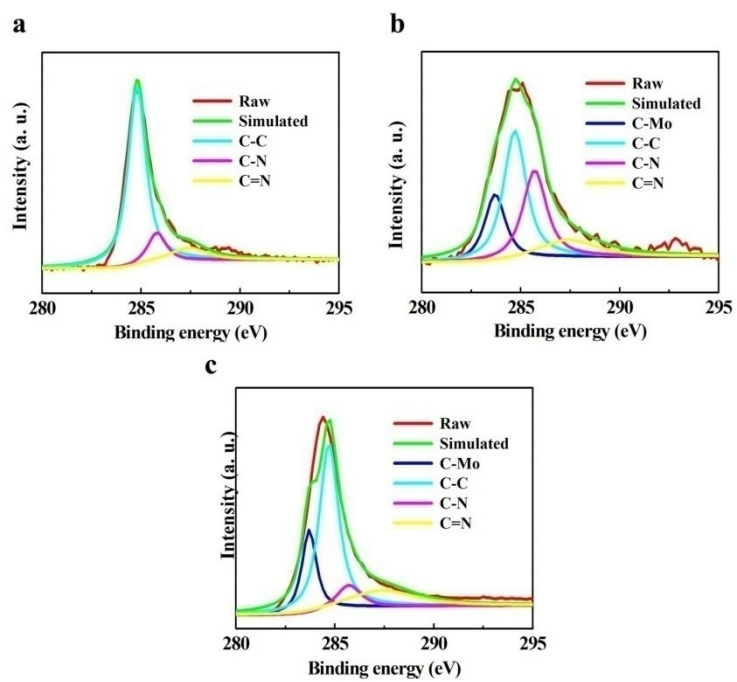


Fig. S1 High resolution C1s XPS of (a) $\text{MoO}_2@\text{NC}$; (b) $\text{Mo}_2\text{C}@\text{NC(A)}$; (c) $\text{Mo}_2\text{C}@\text{NC(B)}$.

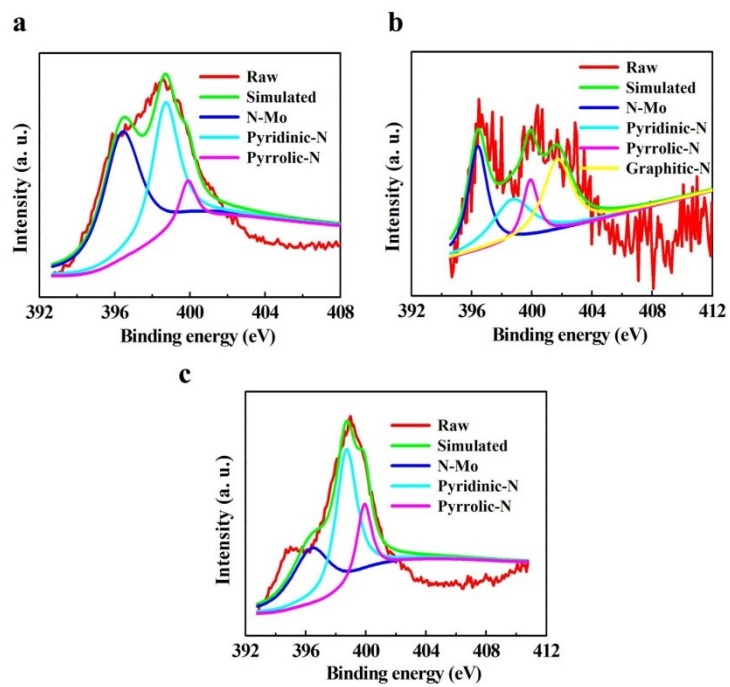


Fig. S2 High resolution N1s XPS of (a) $\text{MoO}_2@\text{NC}$; (b) $\text{Mo}_2\text{C}@\text{NC(A)}$; (c) $\text{Mo}_2\text{C}@\text{NC(B)}$.

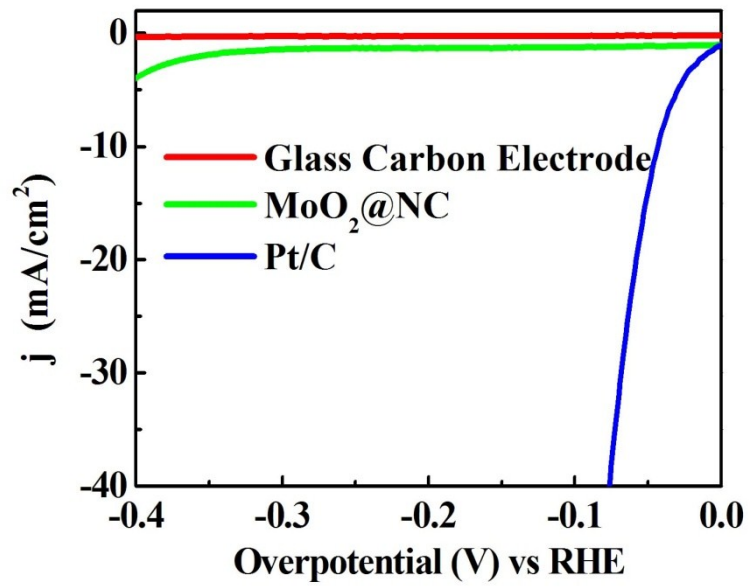


Fig. S3 Polarization curves of Pt/C, glass carbon electrode and **MoO₂@NC** in 1.0 M KOH.

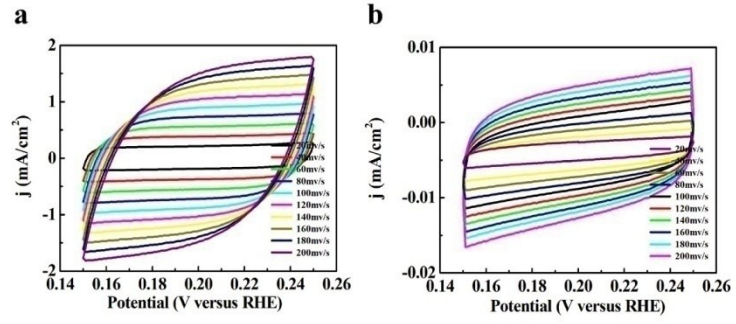


Fig. S4 CV curves in the potential range without redox current peaks of (a) $\text{Mo}_2\text{C@NC(A)}$ in 1.0 M KOH; (b) $\text{Mo}_2\text{C@NC(B)}$ in 1.0 M KOH.

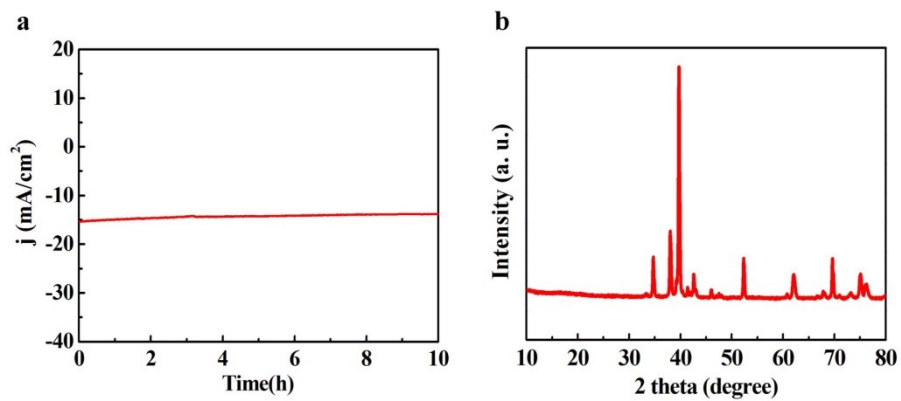


Fig. S5 (a) Time dependence current density of **Mo₂C@NC(A)** for 10 h in 0.5 M H₂SO₄;
(b) recycled PXRD of **Mo₂C@NC(A)** after 10 h.