Electronic Supplementary Material (ESI) for New Journal of Chemistry.

α-MoC_{1-x} Nanorods as Efficient Hydrogen Evolution Reaction Electrocatalyst

Punian Yin, [a, †] Huizhu Cai, [a, †] Xiao Zhang, [a] Bingbing Chen, [a] Yang Liu, [a] Rui Gao, **[b, c, d] Chuan Shi, *[a]

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.*

[b] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Post Office Box 165, Taiyuan, Shanxi 030001, China*

[c] *Beijing Advanced Innovation Center for Materials Genome Engineering, Beijing, China.*

[d] *School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, China.*

[†] These authors contributed equally to this work.

* Corresponding author.
E-mail addresses: chuanshi@dlut.edu.cn (Chuan Shi)
** Corresponding author.
E-mail addresses: gaorui@imu.edu.cn (Rui Gao).

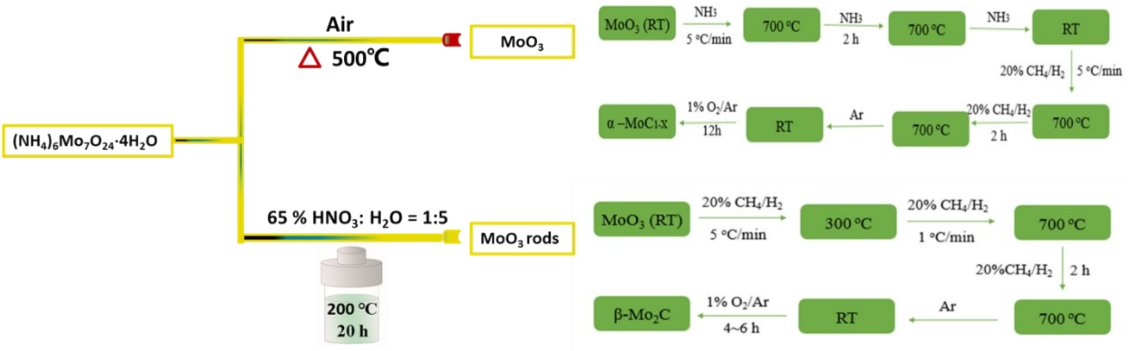

Figure S1 Schematic explanation of the synthetic procedure of the molybdenum carbide-based catalysts.

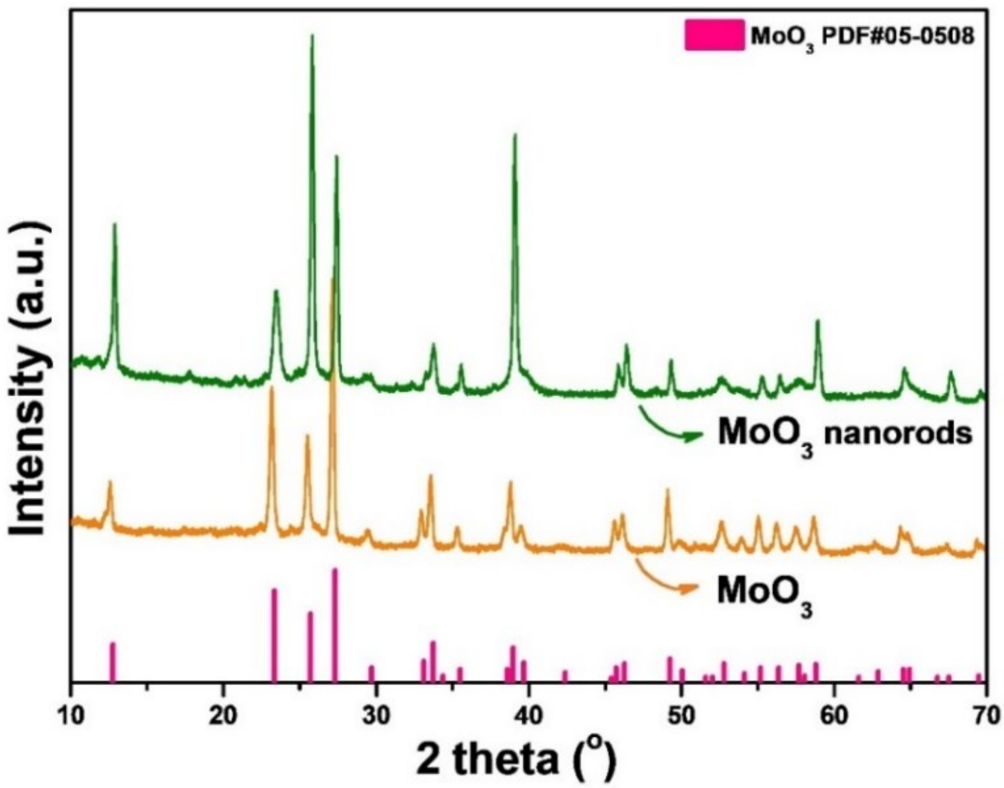

Figure S2 XRD patterns of MoO_3 and MoO_3 nanorods.

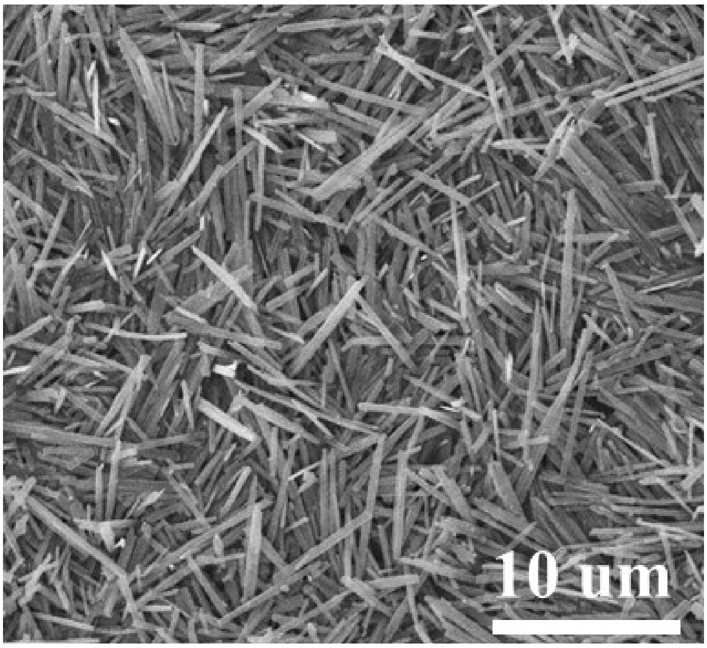

Figure S3 Scanning electron microscopy (SEM) images of MoO_3 nanorods.

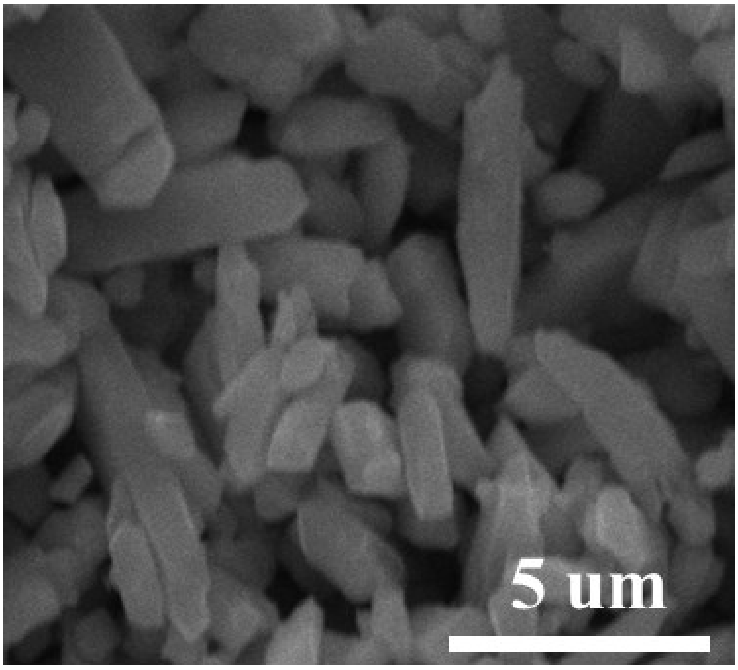

Figure S4 Scanning electron microscopy (SEM) images of MoO_3.

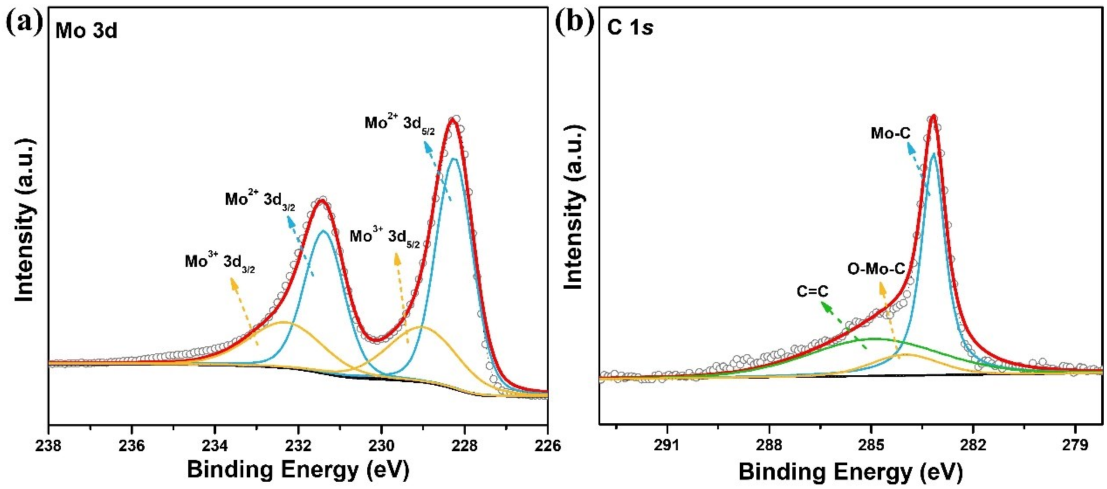

Figure S5 XPS spectra for Mo 3d (a), C 1s (b) of α-MoC_{1-x} nanorods catalyst.

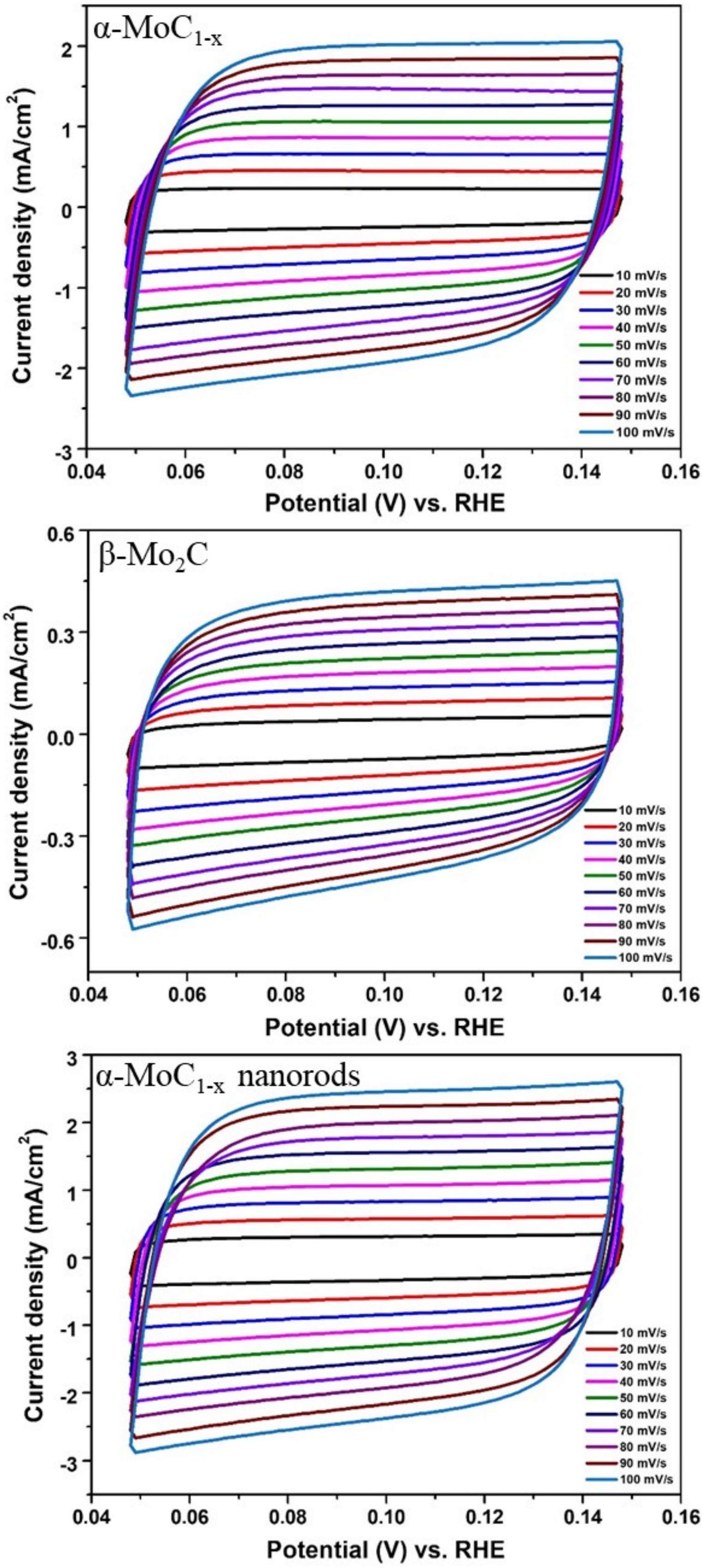

Figure S6 Cyclic voltammograms of α-MoC_{1-x}, β-Mo_2C and α-MoC_{1-x} nanorods with various scan rates in 0.5 M H_2SO_4.

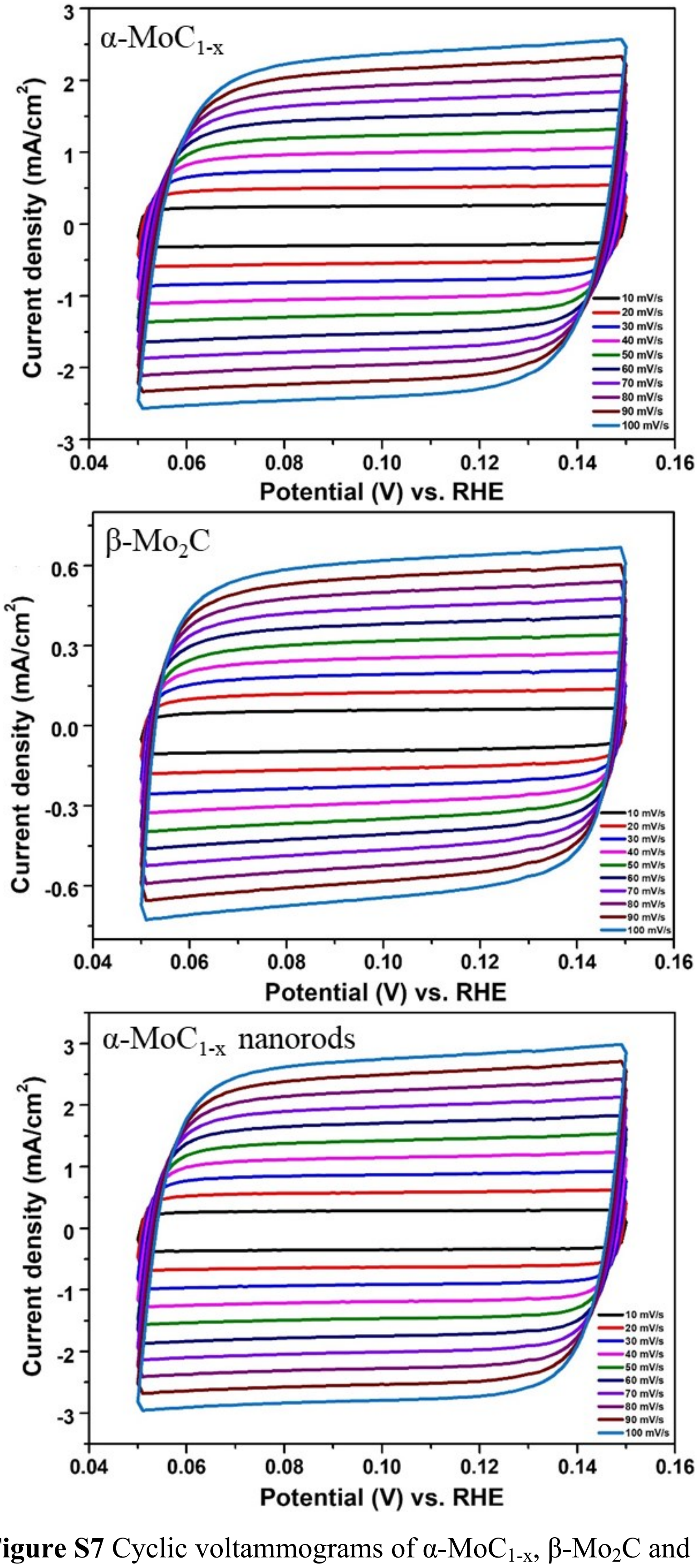

Figure S7 Cyclic voltammograms of α-MoC_{1-x}, β-Mo_2C and α-MoC_{1-x} nanorods with various scan rates in 1.0 M KOH.

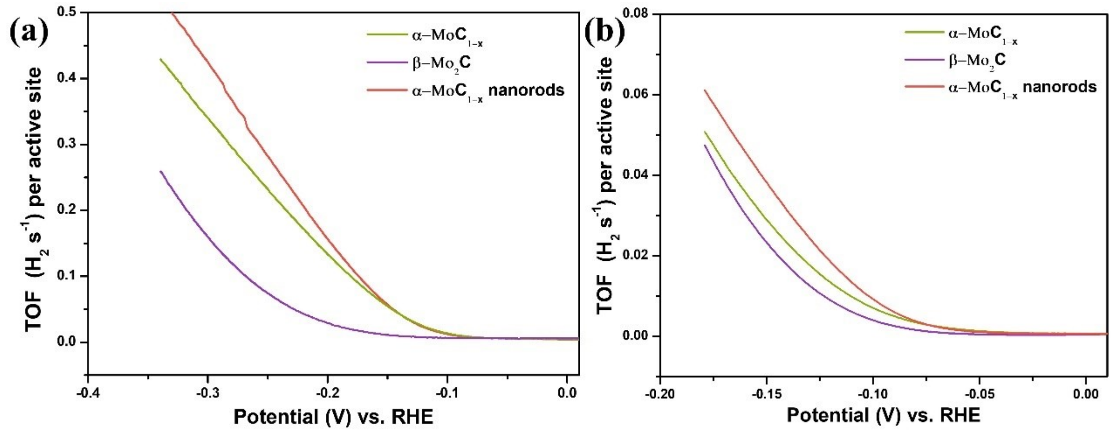

Figure S8 The TOF values of α-MoC_{1-x}, β-Mo_2C and α-MoC_{1-x} nanorods catalysts in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH solution.

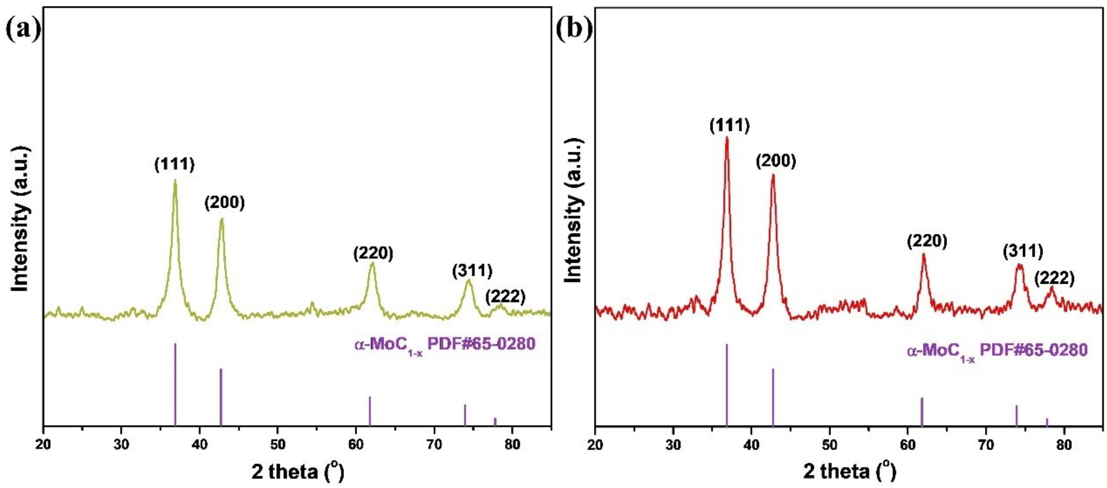

Figure S9 The XRD patterns of α-MoC_{1-x} nanorods catalyst after stability tests for HER in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH solution.

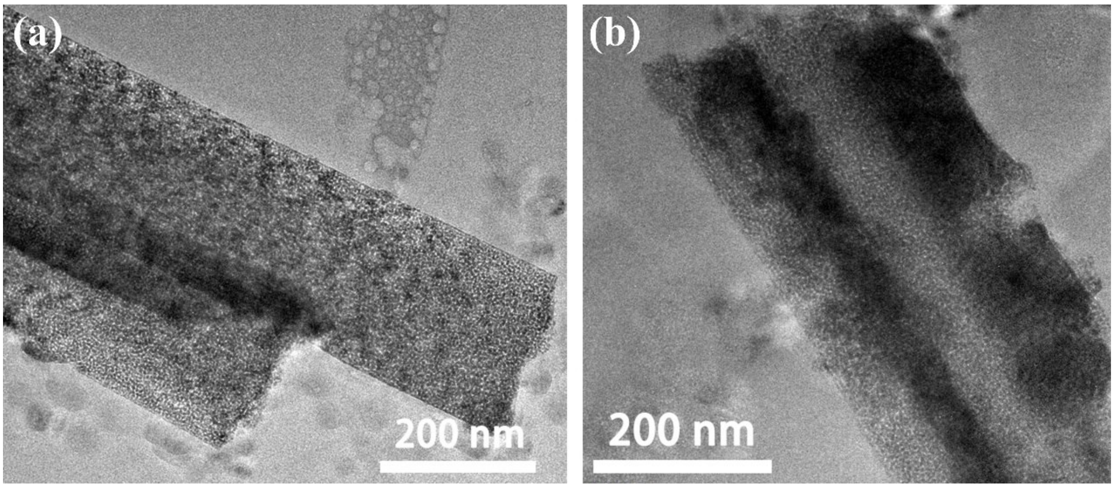

Figure S10 The TEM images of α-MoC_{1-x} nanorods catalyst after stability tests for HER in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH solution.

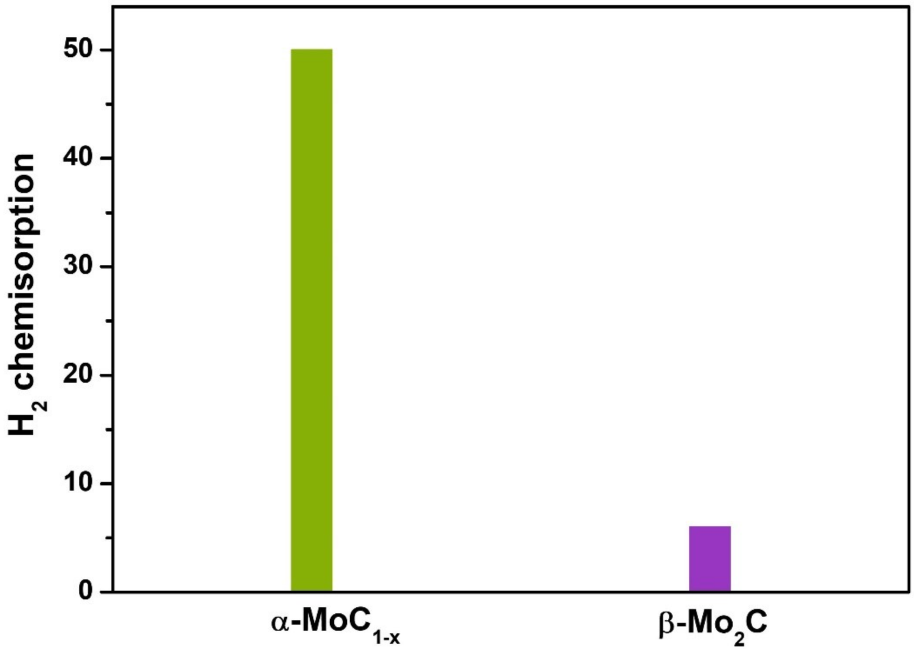

Figure S11 H_2-Chemisorption profiles of α-MoC_{1-x} and β-Mo_2C.

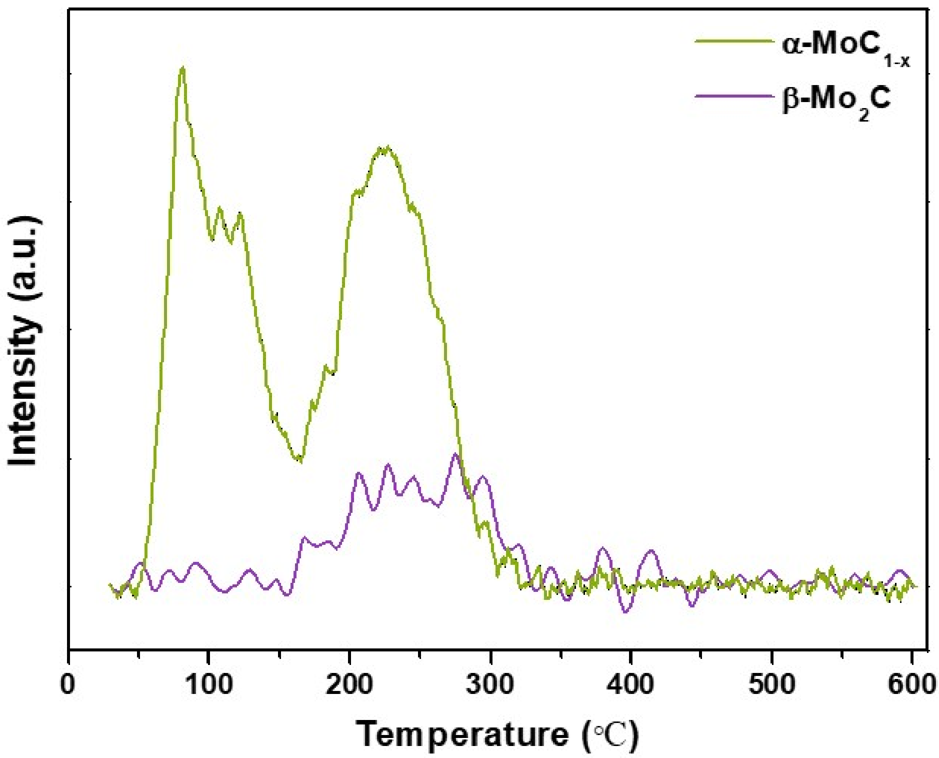

Figure S12 H_2-TPD profiles of α-MoC_{1-x} and β-Mo_2C.

Table S1 Summary of representative α-MoC_{1-x} -based HER catalysts in 0.5 M H_2SO_4.

Catalysts	j (mA/cm^2)	η (mV)	Tafel slope	Ref
Mo_xC-0.4	10	48	155	[1]
MoC@C	10	63.6	120	[2]
α-MoC_{1-x}/β-Mo_2C	10	78	242	[3]
α-MoC_{1-x}-MoP/C	10	57	173	[4]
α-MoC_{1-x} nanorods	10	60	127	This work

Table S2 ICP results of α-MoC_{1-x} nanorods before and after durability tests

	Fresh sample	Used sample in 0.5 M H_2SO_4	Used sample in 1.0 M KOH
Mo content (wt. %)	46.7	44.9	45.8

Calculated Electrochemically Active Surface Area

$$A_{ECSA} = \frac{\text{electrochemical capacitance}}{40\ \mu F\ cm^{-2}\ \text{per}\ cm^{2}_{ECSA}}$$

Turnover Frequency Calculations

The turnover frequency can be calculated by the following formula:

$$TOF = \frac{\text{no. of total hydrogen turnovers/ } cm^2 \text{ of geometric area}}{\text{no. of active sites/ } cm^2 \text{ of geometric area}}$$

The total number of hydrogen turnovers per current density can be calculated by the formula:

$$\text{No. of } H_2 = \left(\text{per}\frac{mA}{cm^2}\right)\left(\frac{1\ C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ \text{mol of e}}{96485.3\ C}\right)\left(\frac{1\ \text{mol of } H_2}{2\ \text{mol of e}}\right)\left(\frac{6.022 \times 10^{23} H_2 \text{ molecules}}{1\ \text{mol of } H_2}\right)$$

$$= 3.12 \times 10^{15}\frac{H_2\ s^{-1}}{cm^2}\text{per}\frac{mA}{cm^2}$$

Active sites per real surface area:

For α-MoC_{1-x}

$$\text{active sites} = \left(\frac{8\ \text{atoms/unit cell}}{77.8\ Å^3\text{/unit cell}}\right)^{\frac{2}{3}} = 2.19 \times 10^{15}\ \text{atoms}\ cm^{-2}_{real}$$

For β-Mo_2C

$$\text{active sites} = \left(\frac{2\ \text{atoms/unit cell}}{37.2\ Å^3\text{/unit cell}}\right)^{\frac{2}{3}} = 1.42 \times 10^{15}\ \text{atoms}\ cm^{-2}_{real}$$

Finally, plot of current density can be converted into a TOF plot according to:

$$TOF = \frac{\left(3.12 \times 10^{15}\frac{H_2\ s^{-1}}{cm^2}\ \text{per}\frac{mA}{cm^2}\right) \times |j|}{(\text{active sites per real surface area}) \times A_{ECSA}}$$

References

[1] X. Zhang, J. Wang, T. Guo, T. Liu, Z. Wu, L. Cavallo, Z. Cao, D. Wang, Structure and phase regulation in MoxC (α-MoC_{1-x}/β-Mo_2C) to enhance hydrogen evolution, *Appl. Catal. B: Environ.* 247 (2019) 78-85.

[2] C. Lv, Z. Huang, Q. Yang, G. Wei, Z. Chen, M.G. Humphrey, C. Zhang, Ultrafast synthesis of molybdenum carbide nanoparticles for efficient hydrogen generation, *J. Mater. Chem. A* 5 (2017) 22805-22812.

[3] T. Liu, X. Zhang, T. Guo, Z. Wu, D. Wang, Boosted hydrogen evolution from α-MoC_{1-x}-MoP/C heterostructures, *Electrochim. Acta* 334 (2020) 135624.

[4] Z. Chen, T. Guo, Z. Wu, D. Wang, Boron triggers the phase transformation of MoxC (alpha-MoC_{1-x}/beta-Mo_2C) for enhanced hydrogen production, *Nanotechnology*, 31 (2019) 105707.