

Electronic Supplementary Information:

## Biomass-Derived Electrocatalytic Composites for Hydrogen Evolution

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**Table S1** Compositions and BET surface area. The proportions of raw materials used for synthesis and the BET surface area of the final products including the Mo<sub>0.1</sub>Soy, Mo<sub>0.25</sub>Soy, Mo<sub>1</sub>Soy and Mo<sub>1</sub>Soy/RGO catalysts as well as the commercial bulk Mo<sub>2</sub>C powder.

Sample	AMo:Soy (g:g) <sup>a</sup>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
bulk Mo <sub>2</sub> C	--	0.9
Mo <sub>0.1</sub> Soy	1:10	12.3
Mo <sub>0.25</sub> Soy	1:4	7.6
Mo <sub>1</sub> Soy	1:1	5.2
<b>AMo:Soy:RGO (g:g:g)<sup>b</sup></b>		
Mo <sub>1</sub> Soy/RGO	1:1:1	254.2

<sup>a</sup> the weight ratio of raw ammonium molybdate (AMo) to dry soybean powder (Soy). <sup>b</sup> the proportion among raw ammonium molybdate, dry soybean powder, and reduced graphene oxide powder (RGO).

The specific surface areas of the samples were determined using the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2020 instrument.

**Table S2** The results of the linear combination fitting of the Mo-K edge EXAFS spectra of the Mo<sub>1</sub>Soy catalyst in Fig. 3c.

sample	R-factor <sup>a</sup>	Mo <sub>2</sub> C		Mo <sub>2</sub> N	
		weight	error	weight	error
Mo <sub>1</sub> Soy	0.06407	0.568533	0.012888	0.431467	0.02853

<sup>a</sup> The measure of absolute deviation of the fit from the experimental data.

**Table S3** Comparison of the overpotentials ( $\eta_{10}$ ) for driving 10 mA cm<sup>-2</sup> and the mass activity of reported non-precious HER catalysts in acidic media.

Catalysts	$\eta_{10}$ (mV) <sup>a</sup>	$j@ \eta=150\text{mV}$ (mA cm <sup>-2</sup> ) <sup>a</sup>	Loading (mg cm <sup>-2</sup> )	Mass activity@ $\eta=150\text{mV}$ (mA mg <sup>-1</sup> )
Mo <sub>1</sub> Soy	177	3.5	1.4	2.5
Mo <sub>1</sub> Soy/RGO	109	31.6	0.47	67.2
Mo <sub>2</sub> C in ref 33	210	1	1.4	0.7
Mo <sub>2</sub> C/CNT in ref 34	152	9.8	2	4.9
CuMoS <sub>4</sub> in ref 23	310	0.5	0.0416	12.0
Co-promoted MoS <sub>3</sub> in ref 27	180	2	0.0366	54.6
double-gyroid MoS <sub>2</sub> in ref 30	230	1	0.06	16.7
MoS <sub>2</sub> /RGO in ref 39	160	8.0	1	8.0
MoS <sub>3</sub> /CNT in ref 26	250	0.50	0.021	23.8
WS <sub>2</sub> nanosheets in ref 22	150	9	0.285	31.6

<sup>a</sup> The reported overpotentials and current densities were collected under different conditions.

**Table S4** Overpotential ( $\eta$ ), charge-transfer resistance ( $R_{ct}$ ), Tafel slope ( $b_R$ ) and exchange current density ( $j_{0,R}$ ) collected in a H<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution for various Mo<sub>2</sub>C-based catalysts.

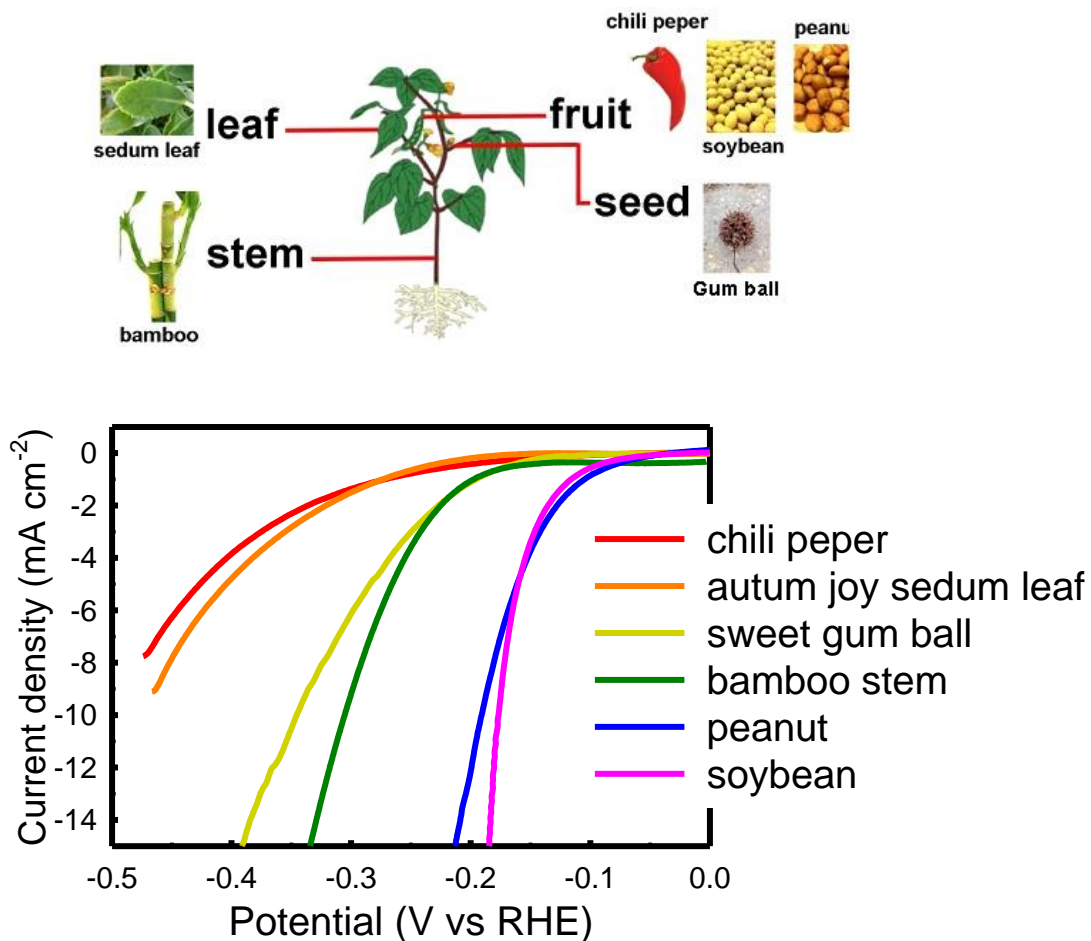
Sample	Mo <sub>2</sub> C Loading (mg cm <sup>-2</sup> )	$\eta_{10,i}$ (mV) <sup>a</sup>	$\eta_{10,f}$ (mV) <sup>b</sup>	$R_{ct}$ @ $\eta=100$ mV ( $\Omega$ )	$b_R$ (mV dec <sup>-1</sup> ) <sup>c</sup>	$j_{0,R}$ (mA cm <sup>-2</sup> ) <sup>d</sup>
Mo <sub>1</sub> Soy/RGO	0.47	109	117	9.0	62.7	$3.7 \times 10^{-2}$
Mo <sub>1</sub> Soy	1.4	177	184	31.7	66.4	$1.3 \times 10^{-2}$
Mo <sub>2</sub> C/C	2.0	226	390	36.1	59.4	$8.1 \times 10^{-3}$
bulk Mo <sub>2</sub> C	2.0	311	>500	1600	87.6	$6.9 \times 10^{-4}$

<sup>a</sup> Initial overpotential at 10 mA cm<sup>-2</sup> of cathodic current ( $j_{cat}$ ). <sup>b</sup> Overpotential at 10 mA cm<sup>-2</sup> after potential sweeps for 3000 cycles between -0.3 and +0.63 V vs RHE. <sup>c</sup> Slopes obtained from the plot of overpotential versus  $\log(R_{ct}^{-1})$  in Fig. 7. <sup>d</sup> Exchange current density calculated by the charge-transfer resistance at zero overpotential.

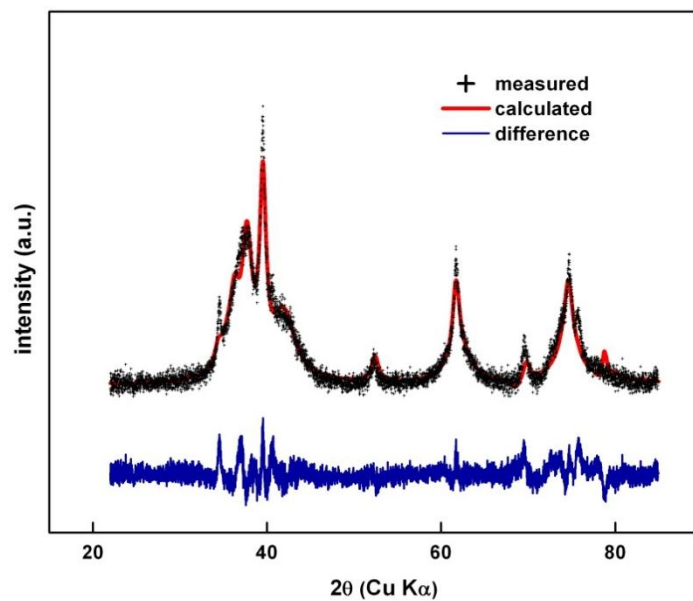
At sufficiently small  $\eta$  (mass transfer resistance  $\ll$  charge transfer resistance), the exchange current density,  $j_{0,R}$ , can be determined via the equation:

$$R_{ct} = \frac{RT}{nFj_{0,R}}$$

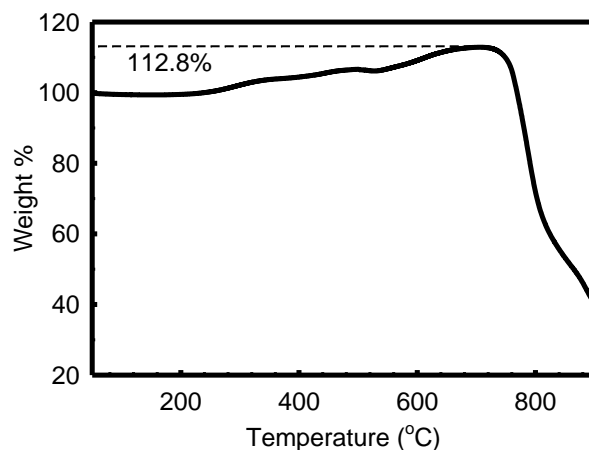
where  $R_{ct}$  is the charge transfer resistance at zero overpotential,  $n$  represents the number of electrons exchanged,  $F$  (96485 C mol<sup>-1</sup>) the Faraday constant, and  $R$  (8.314 J mol<sup>-1</sup>K<sup>-1</sup>) the gas constant.



**Fig. S1** Raw materials and their HER activity. The polarization curves of different biomass-derived catalysts collected in hydrogen-purged 0.1 M HClO<sub>4</sub> solution (scan rate 2 mV s<sup>-1</sup>). The catalysts were made by annealing ammonium molybdate with different biomass sources including ground chili pepper, sedum leaf, sweet gum ball, bamboo stem, peanut and soybean at 800°C under Ar for 2 h.

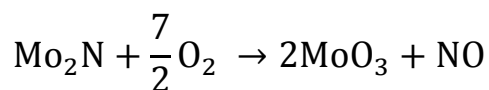
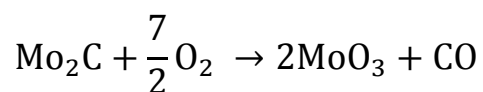


**Fig. S2** XRD spectra and the Rietveld refined spectra based on two phases (not including amorphous carbon phase), with orthorhombic  $\text{Mo}_2\text{C}$  and cubic  $\text{Mo}_2\text{N}$ . The refinement showed that the ratio of  $\beta\text{-Mo}_2\text{C}$  to  $\gamma\text{-Mo}_2\text{N}$  is 0.546 to 0.454.



**Fig. S3** TGA thermograms of the Mo<sub>1</sub>Soy catalyst in oxygen from 50 to 900 °C.

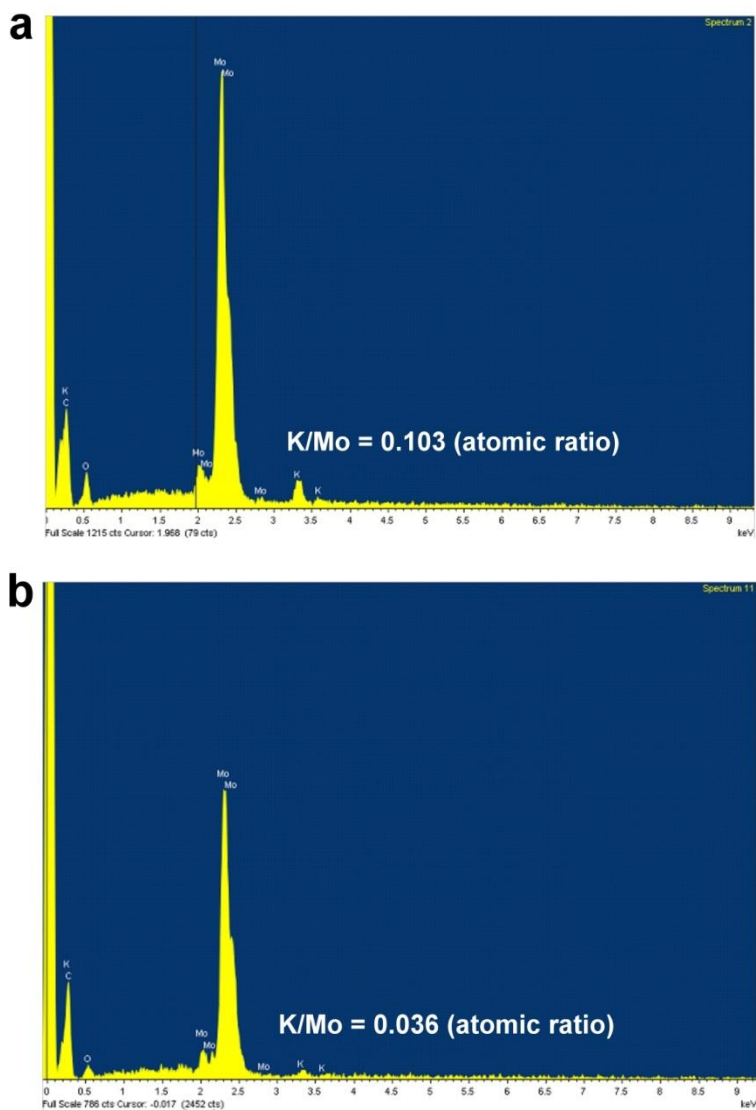
Thermogravimetric measurements and differential thermal analysis were performed with a Perkin Elmer Diamond thermogravimetric/ differential thermal analyzer. The sample was placed in an alumina sample holder. Measurements in pure oxygen with a flow rate of 100 ml min<sup>-1</sup> were carried out over a temperature range of 50–900 °C at a heating rate of 20 °C min<sup>-1</sup>. The Mo<sub>2</sub>C and Mo<sub>2</sub>N particles in the Mo<sub>1</sub>Soy sample are oxidized and transformed to MoO<sub>3</sub> in this condition.



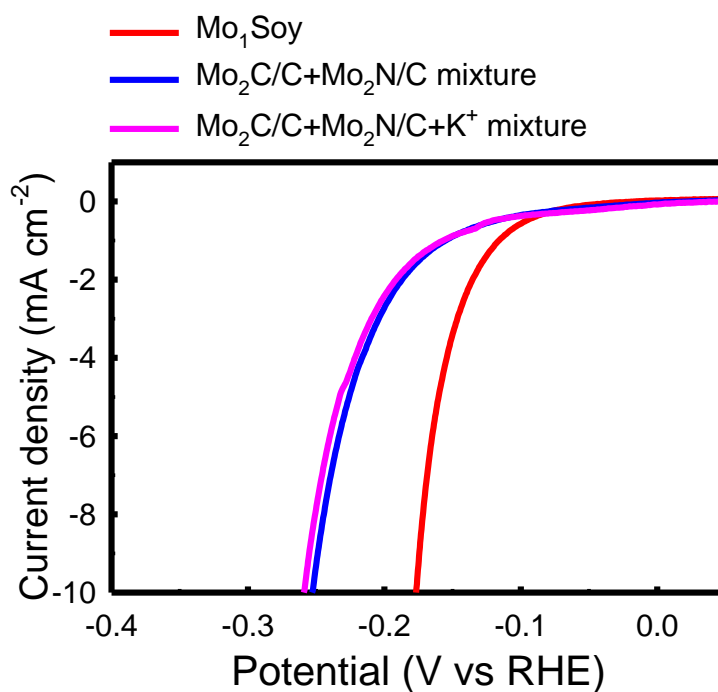
$$\frac{W_{\text{MoO}_3} + W_{\text{C}}}{W_{\text{Mo}_2\text{C}} + W_{\text{Mo}_2\text{N}} + W_{\text{C}}} = 1.128$$

$$\frac{(W_{\text{Mo}_2\text{N}} + W_{\text{Mo}_2\text{C}})}{W_{\text{Mo}_2\text{C}} + W_{\text{Mo}_2\text{N}} + W_{\text{C}}} \times 100\% = 31.6\%$$

Thus, the weight percent of the active β-Mo<sub>2</sub>C phase in Mo<sub>1</sub>Soy is 17.4 wt%. The weight percent of the active β-Mo<sub>2</sub>C phase in Mo<sub>1</sub>Soy/RGO was determined with the same method as 11.6 wt%.

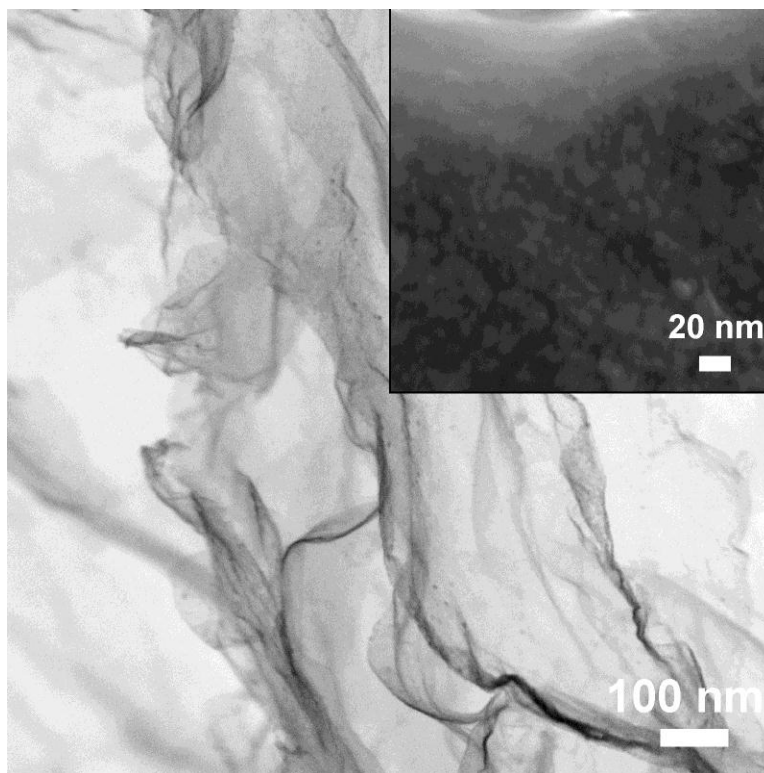


**Fig. S4** The EDX spectra of **a**, Mo<sub>1</sub>Soy and **b**, Mo<sub>1</sub>Soy/RGO catalysts showing the presence of a trace amount of potassium. The atomic ratio of K to Mo is included.

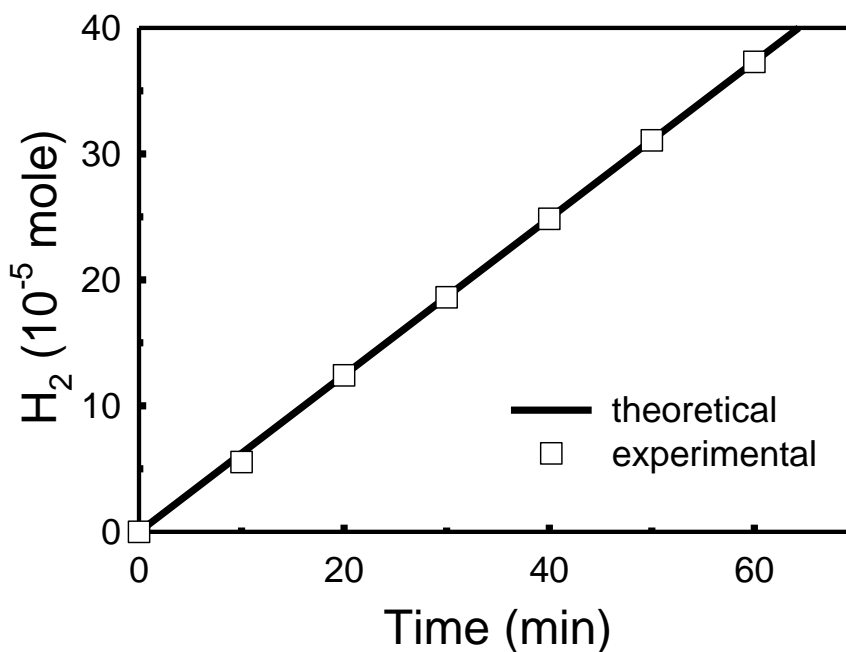


**Fig. S5** The HER polarization curves of the Mo<sub>1</sub>Soy catalyst (1.4 mg Mo<sub>2</sub>C cm<sup>-2</sup>), the mixture of the Mo<sub>2</sub>C/C and Mo<sub>2</sub>N/C (weight ratio Mo<sub>2</sub>C:Mo<sub>2</sub>N = 55:45) with a Mo<sub>2</sub>C loading of 1.4 mg cm<sup>-2</sup>, and the mixture of Mo<sub>2</sub>C/C, Mo<sub>2</sub>N/C and KNO<sub>3</sub> (weight ratio Mo<sub>2</sub>C:Mo<sub>2</sub>N:KNO<sub>3</sub> = 55:45:10.1; molar ratio K/Mo = 0.103) with a Mo<sub>2</sub>C loading of 1.4 mg cm<sup>-2</sup>. The curves were collected in a H<sub>2</sub>-purged 0.1M HClO<sub>4</sub> solution (scan rate = 2 mVs<sup>-1</sup>).



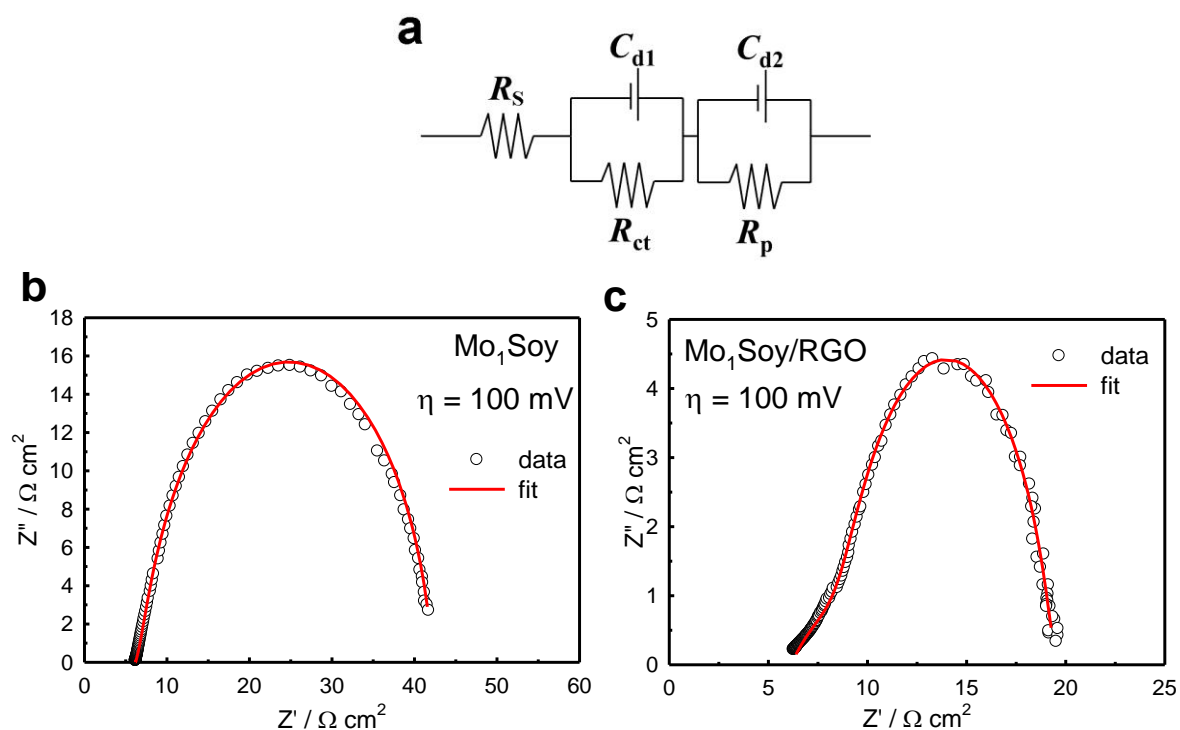


**Fig. S6** The negative SEM image of the RGO-supported Mo<sub>1</sub>Soy catalyst. The inset SEM picture shows that the nanocatalysts are well distributed on a single layer RGO.



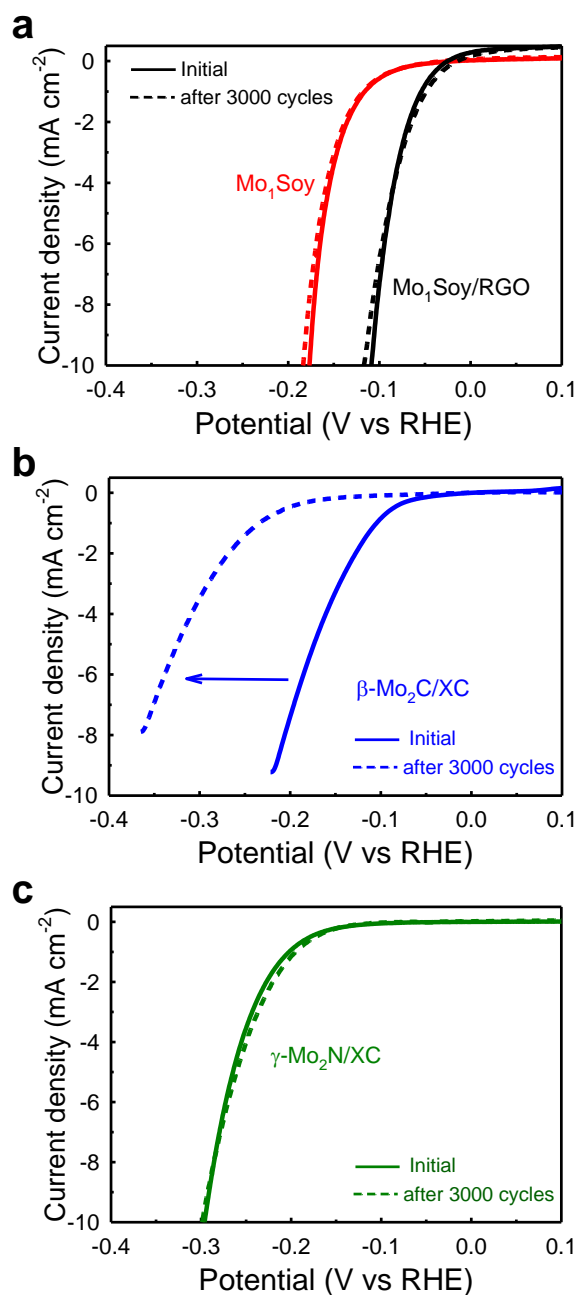
**Fig. S7** The faradic efficiency for HER under chronopotentiometry at a cathodic current of  $10 \text{ mA cm}^{-2}$ . The calculated quantity of hydrogen (—) and the experimentally collected hydrogen ( $\square$ ) are compared.

The Faradic yield of HER on the  $\text{Mo}_1\text{Soy/RGO}$  catalyst was estimated by comparing the amount of produced hydrogen during chronopotentiometry at a cathodic current of  $10 \text{ mA cm}^{-2}$  with the calculated hydrogen amount, as shown in Fig. S7. The Faradic yield at the first 10 min was 89.1% and then increased to 99.9% at around 20 min. This phenomenon is similar to the HER activation process reported in ref. 33.



**Fig. S8** (a) The two-time-constant model, where  $R_s$  is the series resistance,  $R_{ct}$  denotes the charge transfer resistance,  $R_p$  related to is the porosity the electrode surface, and the double layer capacitance is represented by the elements  $C_{d1}$  and  $C_{d2}$ . The Nyquist plots of experimental and simulated data for (b) the  $\text{Mo}_1\text{Soy}$  and (c) the  $\text{Mo}_1\text{Soy/RGO}$  catalysts simulated by the two-time-constant model.

A two-time-constant model was used to describe the response of the HER on the  $\text{Mo}_1\text{Soy}$  and  $\text{Mo}_1\text{Soy/RGO}$  electrodes. The model consists of a series resistance,  $R_s$ , in series with two parallel branches; one is related to the charge-transfer process ( $C_{d1}$ - $R_{ct}$ ); another is related to the surface porosity ( $C_{d2}$ - $R_p$ ). The porosity resistance  $R_p$  of  $\text{Mo}_1\text{Soy/RGO}$  and  $\text{Mo}_1\text{Soy}$  obtained by fitting the experimental data is 4.52 and 4.48  $\Omega$ , respectively. However, at  $\eta = 100\text{mV}$  the charge transfer resistance  $R_{ct}$  (31.7  $\Omega$ ) of the  $\text{Mo}_1\text{Soy}$  is much higher than  $R_{ct}$  of the  $\text{Mo}_1\text{Soy/RGO}$  catalyst (9.0  $\Omega$ ). Thus,  $R_{ct}$  dominates the reaction.



**Fig. S9** HER polarization curves of (a) the Mo<sub>1</sub>Soy and Mo<sub>1</sub>Soy/RGO catalysts, (b) the Mo<sub>2</sub>C/C and (c) the Mo<sub>2</sub>N/C nanoparticles before and after potential sweeps (-0.3 ~ +0.63 V vs RHE) for 3000 cycles in 0.1 M HClO<sub>4</sub> solutions (scan rate 2 mV s<sup>-1</sup>).