In Situ Synthesis of MoP Nanoflakes Intercalated N-Doped Graphene Nanobelts from MoO₃–Amine Hybrid for High-Efficient Hydrogen Evolution Reaction

Chao Huang, Chaoran Pi, Xuming Zhang,* Kang Ding, Ping Qin, Jijiang Fu, Xiang Peng, Biao Gao, Paul K. Chu, and Kaifu Huo*

Molybdenum phosphide (MoP) is a promising non-noble-metal electrocatalyst in the hydrogen evolution reaction (HER), but practical implementation is impeded by the sluggish HER kinetics and poor chemical stability. Herein, a novel high-efficiency HER electrocatalyst comprising MoP nanoflakes intercalated nitrogen-doped graphene nanobelts (MoP/NG), which are synthesized by one-step thermal phosphiding organic–inorganic hybrid dodecylamine (DDA) inserted MoO₃ nanobelts, is reported. The intercalated DDA molecules are in situ carbonized into the NG layer and the sandwiched MoO₃ layer is converted into MoP nanoflakes which are intercalated between the NG layers forming the alternatingly stacked MoP/NG hybrid nanobelts. The MoP nanoflakes provide abundant edge sites and the sandwiched MoP/NG hybrid enables rapid ion/electron transport thus yielding excellent electrochemical activity and stability for HER. The MoP/NG shows a low overpotential of 94 mV at 10 mA cm⁻², small Tafel slope of 50.1 mV dec⁻¹, and excellent electrochemical stability with 99.5% retention for over 22 h.

1. Introduction

Hydrogen is a clean, abundant, and renewable energy source and may substitute nonrenewable fossil fuels such as coal and petroleum in the future.[1,2] Electro catalysts play a vital role in electrochemical water splitting in large-scale hydrogen production and although noble Pt and its alloy are the best hydrogen evolution reaction (HER) electrocatalysts,[3] the scarcity and high cost impede wide application.[4] Hence, tremendous efforts have been devoted to developing alternative non-noble-metal electrocatalysts for efficient hydrogen production.[5,6]

Transition metal phosphides (TMPs) such as molybdenum phosphide (MoP) are promising HER electrocatalysts due to the low cost, abundance, and high catalytic activities under both acidic and alkaline conditions.[7,8] The negatively charged P atoms in TMPs could trap positively charged protons during HER leading to high HER activity.[1,9] Previous studies have disclosed that larger P content improves the HER activity of TMPs.[1,9] Nevertheless, if the P content is too high, electron delocalization of metals is restricted resulting in large electrochemical polarization and sluggish HER kinetics as a result of the lower conductivity.[10] To overcome this hurdle, conductive carbon materials such as porous carbon, graphite, and carbon nanotubes have been introduced to construct MoP/carbon nanocomposites to improve the electron conductivity.[11] For example, Ojha et al.[12] reported that MoP nanoparticles assembled on reduced graphene oxide exhibited a low overpotential of 162 mV at a current density of 10 mA cm⁻². Besides the conductivity, the HER activity is associated with the amount of active sites of the electrocatalysts since hydrogen production via water splitting occurs on the surface of the catalysts. To this point, 2D MoP nanosheets or nanoflakes are desirable to improve to HER activity due to the increased numbers of surface sites compared to nanoparticles. If the unilamellar MoP nanosheets or nanoflakes and graphene are alternately stacked to form MoP/graphene heterostructure at the molecular scale, the enhanced electrocatalytic properties of MoP could be achieved because of the synergistic utilization of these 2D materials via the high-quality heterointerfaces. However, to the best of our knowledge, such highly ordered or superlattice-like structures with MoP/graphene hybrid for HER have not been reported.

Herein, we propose a facile strategy to produce alternately stacked MoP nanoflakes and nitrogen-doped graphene layers

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(MoP/NG) via a one-step process involving phosphidizing dodecylamine (DDA, CH$_3$(CH$_2$)$_{11}$NH$_2$) inserted MoO$_3$ nanobelts, which demonstrate high-efficiency electrocatalytic activity for HER. The intercalated DDA molecules are in situ carbonized into the NG layer and the sandwiched MoO$_3$ layer is converted into island-like MoP nanoflakes which are intercalated into the carbonized NG interlayers forming the alternately stacked MoP/NG hybrid.[15] The layer-by-layer MoP/NG hybrid possesses several advantages boosting the superior electrocatalytic performance. First, the thin MoP nanoflakes are separated and stabilized between the NG layers and the alternately stacked structure inhibits restacking and aggregation of MoP nanoflakes even at a high MoP content of 92 wt%, thus producing abundant electroactive sites for HER. Second, the superlattice-like structure of MoP/NG leads to more accessible active sites and promote ion migration. Third, the NG layers improve the overall conductivity enabling fast electron transfer and the smaller charge transfer resistance. Fourth, the alternately stacked structure of MoP/NG hybrid prevents oxidation of MoP nanoflakes thereby providing good structural and electrochemical durability. Fifth, the high-quality heterointerfaces of MoP and NG layer result in strong chemical interactions via P=C bonding and so enhanced HER activity is achieved on account of the partial negative charge on P atoms.[12] Owing to these unique advantages, the MoP/NG delivers excellent HER performance with a small overpotential of 94 mV at 10 mA cm$^{-2}$, small Tafel slope of 50.1 mV dec$^{-1}$, and excellent durability with 99.5% current retention for over 22 h. Even at 70 °C, the MoP/NG hybrids retain the high electrochemical stability. Our promising results offer prospective insights into the design and synthesis of efficient non-noble-metal electrocatalysts via constructing the alternately stacked structure using layered materials as precursors, such as MoO$_3$, HNB$_3$O$_8$, V$_2$O$_5$ and MoS$_2$.

2. Results and Discussion

Figure 1 shows the synthetic process of the lamellar MoP/NG hybrid nanobelts. The scanning electron microscopy (SEM) images reveal that the MoO$_3$ nanobelts with a diameter of 300 nm and length of ten micrometers are hydrothermally produced as described previously[16] (Figure S1a,b, Supporting Information). MoO$_3$ nanobelts were separated and stabilized between the NG layers in the MoP/NG hybrid nanobelts. For comparison, MoP nanobelts are also prepared by thermal processing of MoO$_3$ nanobelts using NaH$_2$PO$_2$ as the phosphorus source. The interlayered DDA molecules are in situ carbonized into the NG layer and the sandwiched MoO$_3$ layer is converted into MoP nanoflakes forming the MoP/NG hybrid nanobelts comprising alternating stacked MoP nanoflakes and NG layers as schematically illustrated in Figure 1c.

Figure S4 (Supporting Information) depicts the XRD pattern of MoO$_3$/DDA after annealing at different temperature. At 700 °C, all the XRD peaks (Figure 2a) at 27.95°, 32.17°, 43.15°, 57.48°, 64.93°, 67.03°, 67.86°, 74.33°, and 85.67° could be attributed to (001), (100), (110), (111), (200), (102), (201), and (112) planes of hexagonal MoP phase (JCPDS No. 24-0771) and no other peaks could be identified,[5] suggesting complete conversion from MoO$_3$ to MoP. No carbon peaks can be observed due to the poor crystallinity and unstacked interlayers of NG.[21] The Raman scattering spectrum (Figure S5, Supporting Information) shows typical peaks at 1360 and 1590 cm$^{-1}$ corresponding to the D and G bands of graphene, respectively, indicating that the interlayer DDA is carbonized to NG nanobelts at 700 °C.[22] The SEM image of the MoP/NG hybrid in Figure 2b reveals that the MoP/NG nanobelts have a width of 300 nm and length up to 10 µm similar to the MoO$_3$/DDA nanobelts (Figure S1c,d, Supporting Information). The high-resolution SEM image (Figure 2c) indicates that the surface of MoP/NG is coarse with many small nanoflakes embedded into the nanobelts. The high-resolution transmission electron microscopy (HRTEM) image (Figure 2d) discloses that the MoP nanoflakes are anchored on NG and the lattice fringes of 0.336 and 0.213 nm correspond to the (001) and (101) planes of MoP.[23] The elemental maps of MoP/NG (Figure 2e) show that Mo, P, C, and N are homogeneously distributed throughout the nanobelts further corroborating the formation of MoP/NG hybrid nanobelts. For comparison, MoP nanobelts are also prepared by thermal processing of MoO$_3$ nanobelts but without DDA intercalation. Different from the hybrid MoP/NG nanobelts, the SEM images in Figure S6 (Supporting Information) reveal the MoP nanobelts have obvious mesopores (5–10 nm) due to the volume shrinkage.[24–26] To confirm the alternately stacked MoP/NG hybrid structure, we remove the thin MoP
nanoflakes layer between the NG layers by immersing the MoP/NG hybrid nanobelts in the 0.5 M KOH solution at 50 °C. The TEM images (Figure S7a,b, Supporting Information) show thin NG nanobelts are produced and NG is amorphous. Energy-dispersive X-ray spectroscopy (EDS) confirms that the nanobelts have no Mo and P (Figure S7c, Supporting Information). The thickness of the NG is about 3.26 nm by atomic force microscopy (AFM), which is larger than a single-layer graphene due to the restacking of in situ isolated NG after removing MoP in 0.5 M KOH. Since the NG nanobelts have a similar width as the MoP/NG nanobelts, it can be concluded that the nanobelts originate from the intercalated NG layers. The NG content in the MoP/NG nanobelts is determined by thermogravimetry (TG) as shown in Figure S8 (Supporting Information). The amount of NG in MoP/NG is about 8 wt% and the Brunauer–Emmett–Teller (BET) areas (Figure S9, Supporting Information) of the MoP and MoP/NG nanobelts are measured to be 31.4 and 48.5 m² g⁻¹, respectively. The larger BET surface area of MoP/NG is attributed to the thin MoP nanoflakes and lamellared structure of the MoP/NG nanobelts.

X-ray photoelectron spectroscopy (XPS) is conducted to determine the composition and chemical states of the MoP/NG nanobelts. The high-resolution spectra of Mo 3d, P 2p, and C1s are exhibited as shown in Figure 3a–c. Two peaks at the low binding energy (228.2/231.2 eV) are assigned to Mo⁺⁺ in MoP. The two doublets at 235.5 eV/233.4 eV (MoO₂ 3d₅/₂/3d₃/₂) and 231.9 eV/228.8 eV (MoO₃ 3d₅/₂/3d₃/₂) in Figure 3a can be assigned to high-oxidation-state Mo (MoO₃ and MoO₂).[11,15] The peaks of P 2p at 129.4 and 130.4 eV are attributed to low-valence P in MoP[27] and those at higher binding energy (green line in Figure 3b) are attributed to PO₄³⁻ or P₂O₅ due to oxidation.[8,28] Compared to MoP nanobelts, the peaks of Mo–O and P–O bonds acquired from MoP/NG hybrid are weaker, suggesting the NG inhibits oxidation of MoP, which is favorable to maintaining the high activity of MoP during the HER process. In the MoP/NG, the P–C bond can be identified suggesting strong interfacial interaction between MoP and NG and it is also reflected by the C1s profile (Figure 3c).[12,29,30] The C signal in the MoP stems from adsorbed gaseous hydrocarbon molecules during XPS analysis, while the C–N and C–P signals arise from the NG layer and interfacial C–P in MoP/NG. The interfacial interaction of C–P enhances proton adsorption, electron transfer, and structural stability of the MoP/NG electrode bonding well for the HER activity.[31] The N 1s XPS of MoP/NG is shown in Figure S10 (Supporting Information), indicating the formation of NG.

The HER activities of MoP/NG nanobelts and MoP nanobelts with an active mass of 0.28 mg cm⁻² are evaluated by linear sweep voltammetry (LSV) at a scanning rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ using a three-electrode configuration. All the potentials in polarization curves are iR corrected (Figure S11, Supporting Information) and the polarization curves of the hybrid MoP/NG nanobelts and MoP nanobelts are shown in Figure 4a. For comparison, the polarization curves of commercial 20% Pt/C, NG, and bare glassy carbon electrode (GCE) acquired under the same measurement conductions are also provided. The overpotential of Pt/C (46 mV) at a current density of 10 mA cm⁻² is measured as reference, which is similar to the previous report (45 mV).[32–36] The MoP nanobelts show a high overpotential of 170 mV at a current density of 10 mA cm⁻², whereas the MoP/NG nanobelts exhibit a small overpotential of 94 mV at 10 mA cm⁻² in acid media (Figure 4a) as well as an overpotential of 153 mV at 10 mA cm⁻² in basic solution (Figure S12, Supporting Information). Moreover, the MoP/NG nanobelts at 10 mA cm⁻² are lower than that of previously reported MoP based electrocatalysts (Table S1, Supporting Information) such as MoP NA/CC (124 mV at 10 mA cm⁻²),[15] MoP/N, P dual-doped carbon (116 mV at 10 mA cm⁻²),[13] reduced graphene oxide and MoP composites (105 mV at 10 mA cm⁻²),[33] cluster-like MoP (119 mV at 10 mA cm⁻²),[11] and hierarchical core–shell MoS₂@MoP (108 mV at 10 mA cm⁻²).[34] The corresponding Tafel slopes of MoP, MoP/NG, and commercial
is 50.1 mV dec$^{-1}$ and smaller than that of the bare MoP nanobelts (86.1 mV dec$^{-1}$) and many other phosphide electrocatalysts such as MoP nanoparticles (54 mV dec$^{-1}$), MoP NA/CC (58 mV dec$^{-1}$), MoP/rGO (111 mV dec$^{-1}$), and Mo$_2$C@C (60 mV dec$^{-1}$), suggesting the superior HER kinetics. The improved HER activity of MoP/NG stems from enriched redox sites of 2D MoP nanoflakes, more electronegative P atoms flourishing the electrochemical activity, and the sandwiched structure favoring the transfer of protons and electrons.

Electrochemical impedance spectroscopy (EIS) is employed to determine the charge transfer resistance (Figure 4c) and the equivalent circuit is presented in Figure S13 (Supporting Information). The MoP/NG nanobelts have a resistance of 13.8 $\Omega$ cm$^2$ (Table S2, Supporting Information) that is smaller than that of the MoP nanobelts (238.5 $\Omega$ cm$^2$), implying efficient electron transport and favorable HER kinetics at the MoP/NG interfaces.

The stability is also critical to durable performance. The long-term stability of MoP/NG is evaluated by CV at 200 mV s$^{-1}$. The polarization curves (Figure 4d) show slight deterioration at the cathodic current after 10 000 cycles and chronoamperometry (Figure S14, Supporting Information) shows that the cathodic current is maintained for over 22 h with 99.5% retention at a current density of 10 mA cm$^{-2}$ confirming the high stability of MoP/NG in acidic media. On the other hand, the polarization curves of MoP (Figure S15, Supporting Information) indicate poor stability with obvious degradation from $-0.26$ to $-0.34$ V at a current density of 40 mA cm$^{-2}$. To further evaluate the structural and chemical stability, the XPS spectra of MoP/NG and MoP after 22h duration are shown in Figures S16 and S17 (Supporting Information). The amount of Mo$-_p$P bond in MoP/NG has no obvious changes after 22 h duration, however, the Mo$-_p$P content decreases and P$-_O$ content increases in MoP nanobelt after 22 h due to the surface oxidation of MoP, suggesting the enhanced oxidation resistance due to the protection of the inserted NG layer in the MoP/NG hybrid. The double-layer capacitance ($C_{dl}$) at the solid–liquid interface is proportional to the effective electrochemical surface.

As shown in Figure 4e,f, $C_{dl}$ of the MoP/NG hybrid nanobelts is 9.10 mF cm$^{-2}$, which is 35 times larger than that of the MoP nanobelts (0.26 mF cm$^{-2}$) (Figure S18, Supporting Information), indicating more exposed active sites on MoP/NG consistent with the enhanced catalytic activity.

We investigate the HER activity of the alternately stacked MoP/NG nanobelts at different temperature from 25 to 70 $^\circ$C. As shown in Figure S19 (Supporting Information), the polarization curves and corresponding Tafel slopes of the MoP/NG hybrid nanobelts reveal satisfactory HER activity even at 70 $^\circ$C, further indicating that the superior HER kinetics stems from the increased active sites and enhanced conductivity of the sandwiched structure.

3. Conclusion

In summary, a high-efficient HER electrocatalyst composed of alternately stacked MoP/NG lamellar nanobelts is prepared by one-step thermal phosphide of DDA intercalated MoO$_3$ nanobelts. The in situ formed MoP nanoflakes are confined between carbonized NG layers. The 2D MoP nanoflakes provide abundant edge sites to improve the HER activity, while the NG layer
acts as the conductive layer for fast electron transport and also against agglomeration and corrosion of MoP during HER. The alternately stacked MoP and NG layers have strong chemical interactions via P–C bonding causing a partial negative charge on P and attracting protons to the electrocatalyst surface to enhance the HER activity. The MoP/NG hybrid nanobelts have a small overpotential of 94 mV at a current density of 10 mA cm\(^{-2}\), small Tafel slope of 50.1 mV dec\(^{-1}\), small charge transfer resistance (13.8 \(\Omega \text{ cm}\(^{2}\) ), and excellent cycling stability. The results not only reveal an attractive electrocatalyst with excellent HER activity, but also offer prospective insights into the design and synthesis of efficient non-noble-metal electrocatalysts.

4. Experimental Section

Synthesis of Hybrid MoP/NG Nanobelts: All the chemicals were purchased from Sigma and used without purification. The MoO\(_3\) nanobelts were synthesized by hydrothermal reaction as previous report\(^{[16,40]}\). The DDA (\(\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\)) was used to thrust into the interlamination of two neighboring layers of MoO\(_3\). First, 0.2 g of MoO\(_3\) and 0.066 g of \(\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\) (DDA) were dissolved in 30 mL alcohol under stirring for 5 min and transferred to a 50 mL Teflon-lined stainless steel autoclave heated at 100 °C for 24 h. The white product (MoO\(_3\)/DDA) was obtained after washing with ethanol several times and dried at 80 °C in vacuum overnight. Then, the MoO\(_3\)/DDA nanobelts were placed at the downstream side of sodium hypophosphite (\(\text{NaH}_2\text{PO}_2\)) in the furnace tube and the distance between them was about 20 cm. After being kept at 700 °C for 2 h in Ar, the hybrid MoP/NG nanobelts were collected when the furnace was naturally cooled down to room temperature. The pure MoP nanobelts were obtained via the similar method without adding DDA molecule.

Materials Characterization: The morphology, structure, and composition of the samples were determined by XRD using the Cu K\(\alpha\) radiation (\(\lambda = 1.5418 \text{ Å}\)) (Philips X’ Pert Pro), field-emission scanning electron microscopy (FESEM, FEI nanoSEM 450), TEM (FEI Titan 60-300 Cs), and XPS (ESCALB MK-II). Raman scattering spectroscopy was conducted using a 514.5 nm argon laser as the excitation source.
Electrochemical Measurements: The commercial 20% Pt/C catalyst was purchased from Sigma-Aldrich. The electrochemical measurements were carried out on a three-electrode system (CHI 760e, Shanghai CHI Company, China) in 0.5 M H₂SO₄ solution with a carbon sheet (1 cm × 1 cm) as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and modified GCE as the working electrode. All the potentials were referenced to the reversible hydrogen electrode (RHE) according to the equation: E_{RHE} = E_{SCE} + 0.0591 × pH.¹ The SCE also calibrated referenced to the RHE is shown in Figure S20 (Supporting Information). It was present in the hydrogen-saturated electrolyte with a Pt wire as the working electrode. Hence, a value of 0.23 V was added in an overpotential of RHE. In order to prepare the working electrode, 12 mg of samples were dissolved in 3 mL of deionized water under sonication for 30 min and 5 μL of solution was loaded onto the GCE with a diameter of 3 mm at a loading density about 0.28 mg cm⁻². After drying in air, 5 μL of diluted Nafton (0.5% Nafton-water-ethanol solution) covered the GCE to fix the electrocatalyst. LSV was acquired by CHI760e at a scanning rate of 5 mV s⁻¹. The EIS was tested at overpotential of 100 mV in a frequency range between 100 kHz and 0.1 Hz with an AC perturbation of 5 mV.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
electrocatalysts, hydrogen evolution reaction, layer-by-layer structure, molybdenum phosphides, sandwiched nanobelts

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Supporting Information

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Figure S1. SEM images of pristine MoO$_3$ nanobelts (a-b) and MoO$_3$/DDA hybrid nanobelts (c-d).
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Figure S8. TG curves of mesoporous MoP nanobelts and MoP/NG nanobelts.
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Figure S13. Electrical equivalent circuit used to simulate the Nyquist plots in Figure 4c, where $R_s$ is the electrolyte resistance, $R_{ct}$ is the charge-transfer resistance, and $C_{dl}$ represents the double-layer capacitance.\textsuperscript{[1-3]}
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Figure S20. CV of SCE calibrated with respect to RHE at a scanning rate of 1 mV s$^{-1}$. The inset is the enlarged CV curve. The average of the two potentials at which the current crosses zero is taken to be the thermodynamic potential of the hydrogen electrode reaction.$^{[4]}$
Table S1. Performance comparison of MoP/NG with other precious-metal-free HER electrocatalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>media</th>
<th>10 mA cm(^{-2}) (mV)</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>Ref.</th>
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<tr>
<td>MoP/NG nanobelts</td>
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<td>0.5 M H(_2)SO(_4)</td>
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<td>50.1</td>
<td>This work</td>
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<td>153</td>
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<td>This work</td>
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<td>MoP/N,P dual-doped carbon</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>116</td>
<td>51</td>
<td>[5]</td>
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<tr>
<td>MoSe(_2)/rGO</td>
<td>0.16</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>~120</td>
<td>69</td>
<td>[6]</td>
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<tr>
<td>MoP NA/CC</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>124</td>
<td>58</td>
<td>[7]</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>125</td>
<td>54</td>
<td>[8]</td>
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<td>MoC-Mo(_2)C HNWs</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>126</td>
<td>43</td>
<td>[9]</td>
</tr>
<tr>
<td>Porous Mo(_2)C</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>142</td>
<td>53</td>
<td>[10]</td>
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<td>0.5 M H(_2)SO(_4)</td>
<td>152</td>
<td>88</td>
<td>[11]</td>
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<tr>
<td>MoP/rGO</td>
<td>1.6</td>
<td>1 M KOH</td>
<td>162</td>
<td>57</td>
<td>[11]</td>
</tr>
<tr>
<td>Material</td>
<td>Initial MOs</td>
<td>0.5 M H2SO4</td>
<td>Current Efficiency (%)</td>
<td>Reference</td>
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<td>Mo2C/GCSs</td>
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<td>MoP</td>
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<td>c-Mo2C</td>
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<td>γ-Mo2N</td>
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<td>108</td>
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<tr>
<td>MA-MoS2</td>
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<td>104</td>
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<tr>
<td>Mo2C/CNT</td>
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<td>--</td>
<td>55.2</td>
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<tr>
<td>Mo2C</td>
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<td>--</td>
<td>87.6</td>
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Table S2. Fitted parameters of the electrocatalysts at an overpotential of 100 mV according to the equivalent circuit in Figure S13.

<table>
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<tr>
<th>Electrocatalysts</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
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<td>MoP/NG</td>
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<td>13.8</td>
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<tr>
<td>MoP</td>
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<td>238.5</td>
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<tr>
<td>Pt/C</td>
<td>0.52</td>
<td>2.8</td>
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References


