

## Electronic Supplementary Information

### Ultrastable nitrogen-doped carbon encapsulating molybdenum phosphide nanoparticles as a highly efficient electrocatalyst for hydrogen generation

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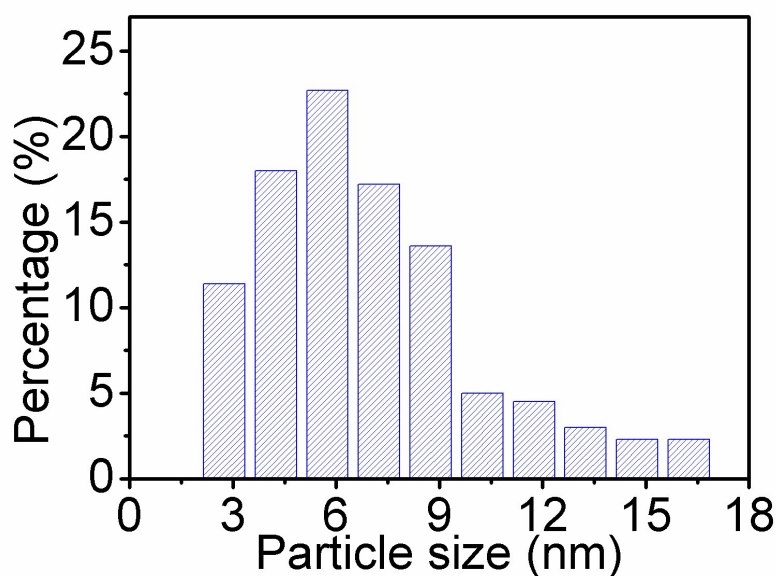
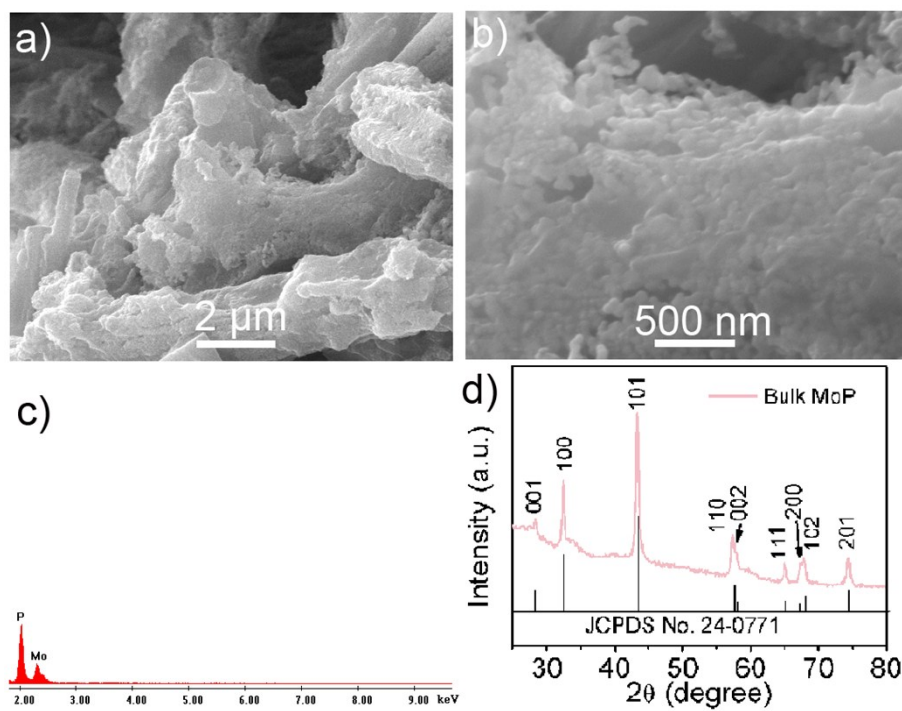
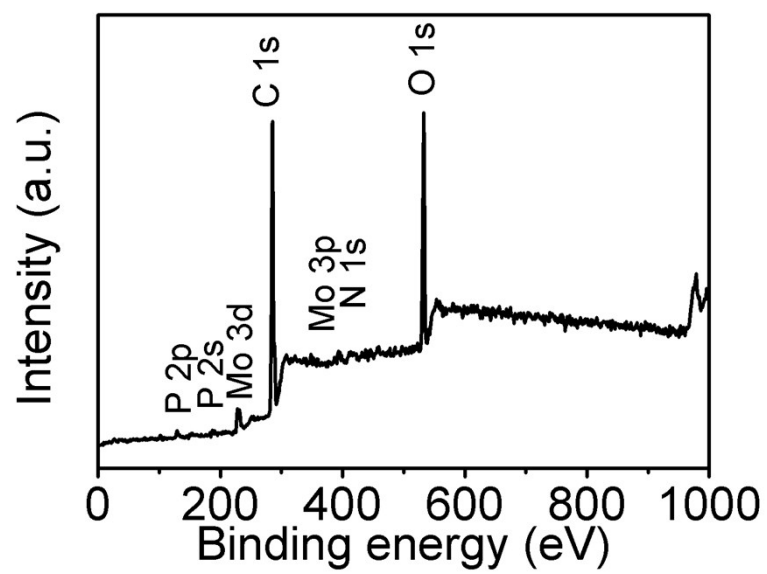


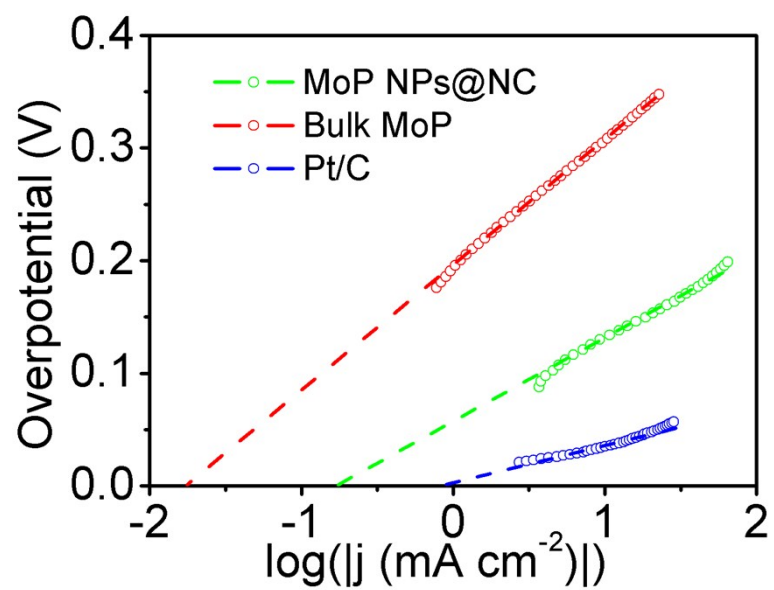
Fig. S1. Particle size distribution histograms of MoP NPs@NC.



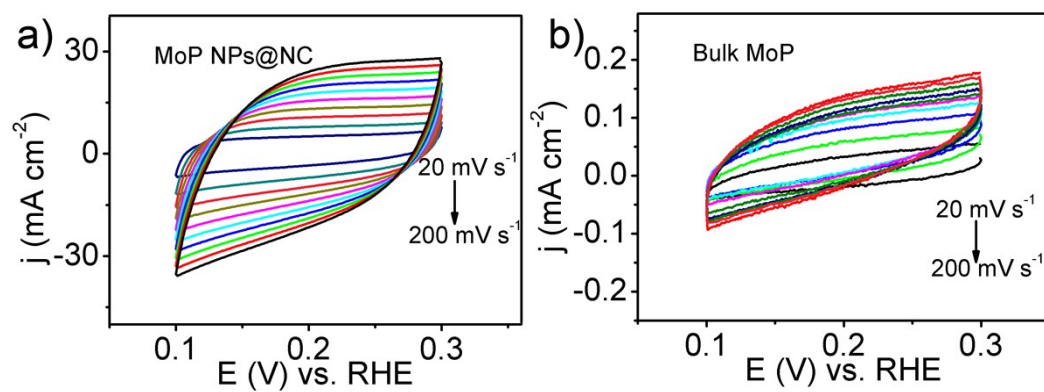
**Fig. S2.** (a) Low- and (b) high-magnification SEM images of bulk MoP. (c) EDX spectrum and (d) XRD pattern for bulk MoP.



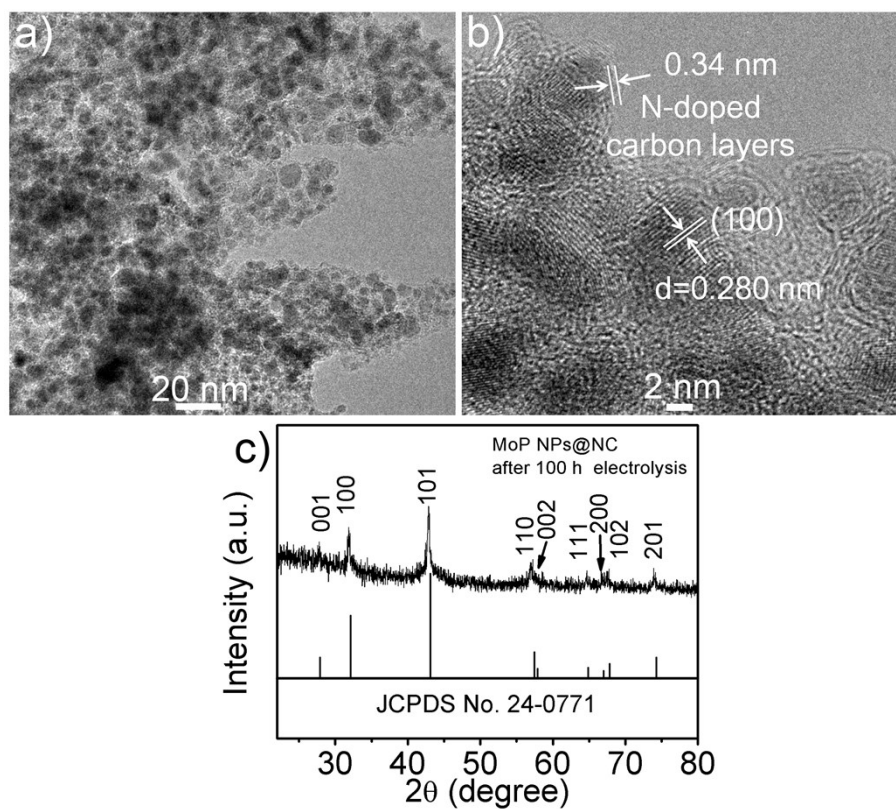
**Fig. S3.** The survey spectrum of the MoP NPs@NC.



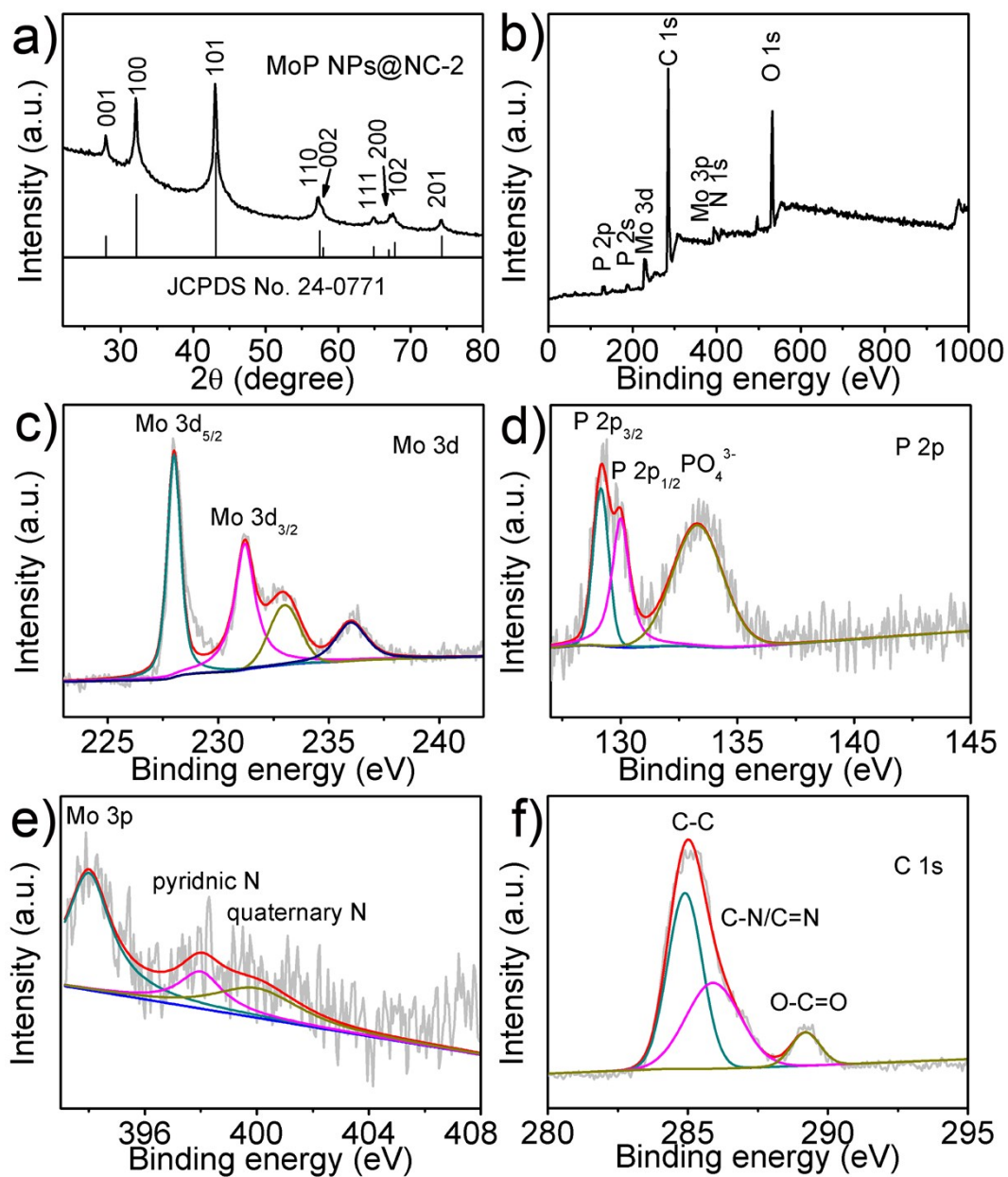
**Fig. S4.** Calculation of exchange current density of MoP NPs@NC, bulk MoP and Pt/C by applying extrapolation method to the Tafel plot.



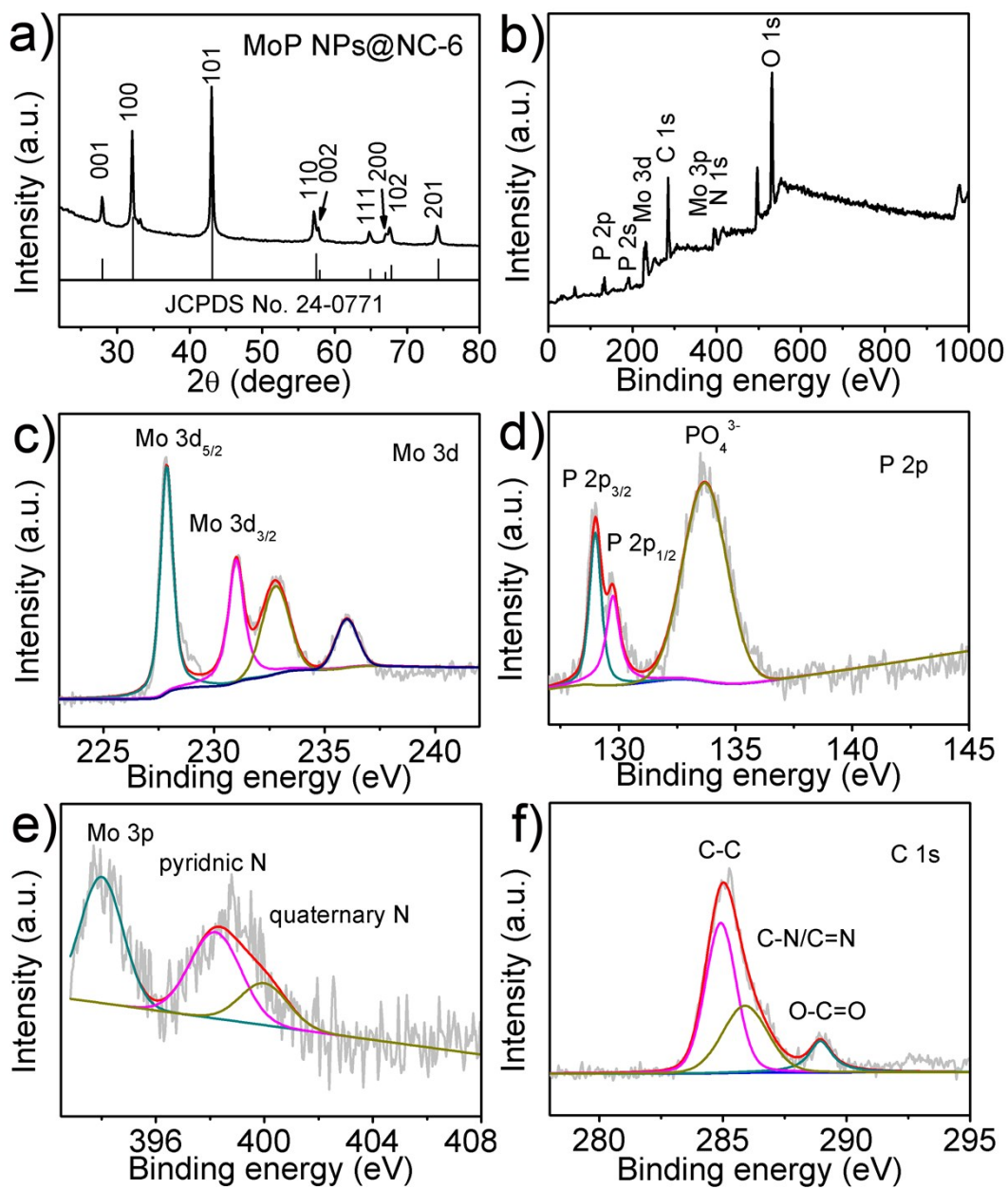
**Fig. S5.** CVs for (a) MoP NPs@NC and (b) bulk MoP.



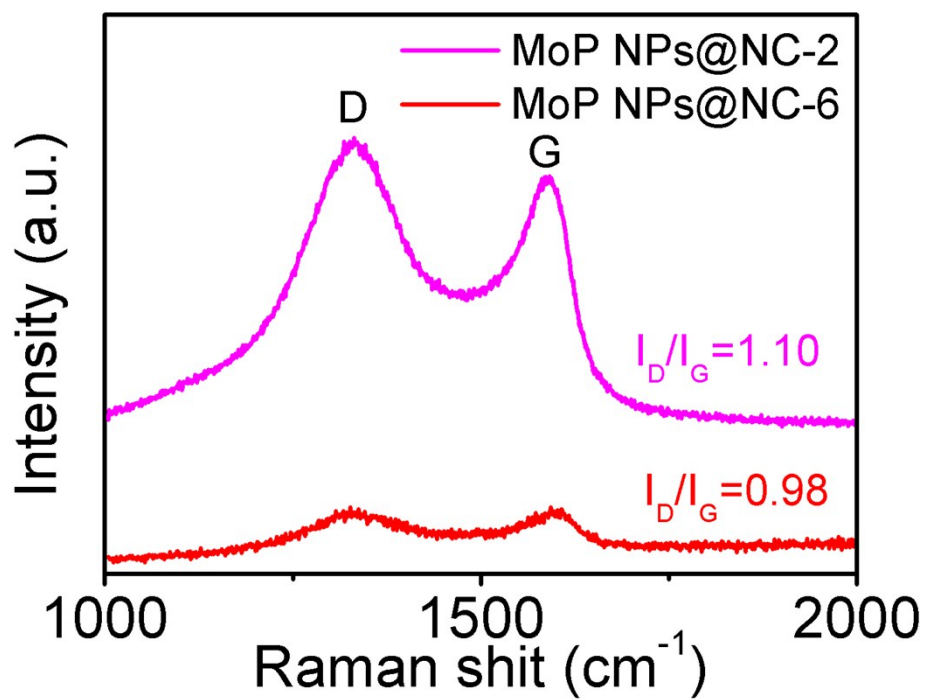
**Fig. S6.** (a and b) TEM images and (c) XRD pattern of MoP NPs@NC after long-term stability test.



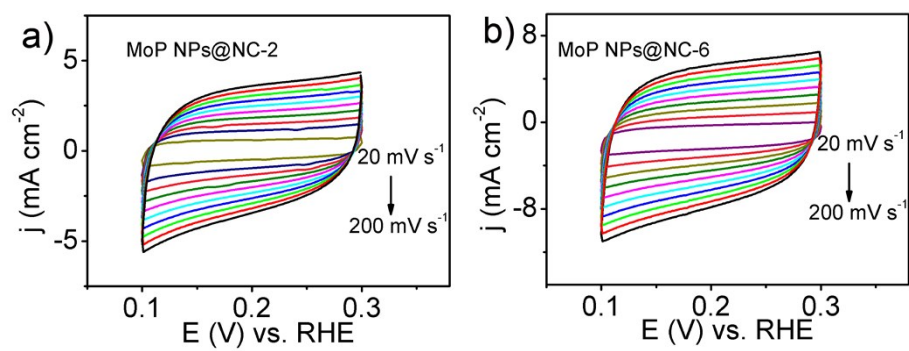
**Fig. S7.** (a) XRD pattern of MoP NPs@NC-2. (b) The survey XPS spectra of the MoP NPs@NC-2. (c-f) The high-resolution XPS spectra of the MoP NPs@NC-2.



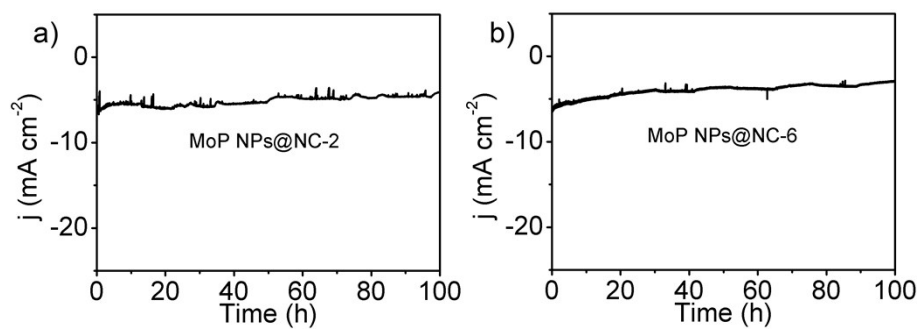
**Fig. S8.** (a) XRD pattern of MoP NPs@NC-6. (b) The survey XPS spectra of the MoP NPs@NC-6. (c-f) The high-resolution XPS spectra of the MoP NPs@NC-6.



**Fig. S9.** Raman spectrum for MoP NPs@NC-2 and MoP NPs@NC-6.



**Fig. S10.** CVs for (a) MoP NPs@NC-2 and (b) MoP NPs@NC-6.



**Fig. S11.** Time-dependent current density curves for (a) MoP NPs@NC-2 and (b) MoP NPs@NC-6.

**Table S1.** Comparison of the electrocatalytic activity of MoP NPs@NC with other Mo-based HER catalysts recently reported for acidic solutions.

| Catalyst                                    | Current density<br>( $j$ , mA cm <sup>-2</sup> ) | $\eta$ at the corresponding<br>$j$ (mV) | Ref.      |
|---------------------------------------------|--------------------------------------------------|-----------------------------------------|-----------|
|                                             | 10                                               | 115                                     |           |
| MoP NPs@NC                                  | 30                                               | 147                                     | This work |
|                                             | 100                                              | 193                                     |           |
| MoP                                         | 10                                               | 246                                     | 2         |
| MoP/CF                                      | 10                                               | 200                                     | 3         |
| MoP nanoparticle                            | 30                                               | 180                                     | 4         |
| MoP interconnected<br>network nanoparticles | 10                                               | 125                                     | 5         |
| amorphous MoP                               | 10                                               | 90                                      | 6         |
| 3D MoP                                      | 10                                               | 105                                     | 7         |
| MoS <sub>2(1-x)</sub> P <sub>x</sub>        | 10                                               | 150                                     | 8         |
| MoP/CC                                      | 10                                               | 124                                     | 9         |
| MoP <sub>2</sub> /Mo                        | 10                                               | 143                                     | 10        |
| MoS <sub>2</sub> /Mo foil                   | 18.6                                             | 300                                     | 11        |
| MoS <sub>2</sub> /Mo                        | 10                                               | 168                                     | 12        |
| amorphous MoS <sub>x</sub>                  | 10                                               | 200                                     | 13        |
| MoS <sub>x</sub> /graphene/CC               | 100                                              | ~225                                    | 14        |
| PPy/MoS <sub>x</sub> /GCE                   | 50                                               | 60                                      | 15        |
| MoN                                         | 70                                               | 300                                     | 16        |
| Mo <sub>2</sub> C@NC                        | 10                                               | 124                                     | 17        |
| $\beta$ -Mo <sub>2</sub> C                  | 10                                               | 172                                     | 18        |

**Table S2.** Comparison of the electrocatalytic activity of MoP NPs@NC with other non-noble metal HER catalysts recently reported for neutral solutions.

| Catalyst                    | Current density<br>( $j$ , mA cm <sup>-2</sup> ) | Overpotential at the<br>corresponding $j$ (mV) | Ref.      |
|-----------------------------|--------------------------------------------------|------------------------------------------------|-----------|
| MoP NPs@NC                  | 2                                                | 80                                             | This work |
|                             | 10                                               | 136                                            |           |
| MoP/CF                      | 1                                                | ~300                                           | 3         |
| MoP/CC                      | 10                                               | 187                                            | 9         |
| MoP <sub>2</sub> NPs/Mo     | 10                                               | 211                                            | 10        |
| MoS <sub>2</sub> /Mo        | 2                                                | 172                                            | 12        |
| Mo <sub>2</sub> C@NC        | 10                                               | 156                                            | 17        |
| WP NAs/CC                   | 2                                                | 95                                             | 19        |
| CoP/CC                      | 2                                                | 65                                             | 20        |
| Co-NRCNTs                   | 2                                                | 380                                            | 21        |
| FeP/Ti                      | 10                                               | 102                                            | 22        |
| bulk Mo <sub>2</sub> C      | 1                                                | 200                                            | 23        |
| bulk Mo <sub>2</sub> B      | 1                                                | 250                                            | 23        |
| H <sub>2</sub> -CoCat/FTO   | 2                                                | 385                                            | 24        |
| Co-S/FTO                    | 2                                                | 83                                             | 25        |
| CuMoS <sub>4</sub> crystals | 2                                                | 210                                            | 26        |

**Table S3.** Comparison of the electrocatalytic activity of MoP NPs@NC with other non-noble metal HER catalysts recently reported for alkaline solutions.

| Catalyst                        | Current density<br>( $j$ , mA cm <sup>-2</sup> ) | Overpotential at the<br>corresponding $j$<br>(mV) | Ref.      |
|---------------------------------|--------------------------------------------------|---------------------------------------------------|-----------|
| MoP NPs@NC                      | 10                                               | 80                                                | This work |
| MoP/CC                          | 10                                               | 80                                                | 9         |
| MoP <sub>2</sub> NPs/Mo         | 10                                               | 194                                               | 10        |
| MoS <sub>2</sub> /Mo            | 2                                                | 172                                               | 12        |
| Mo <sub>2</sub> C@NC            | 10                                               | 60                                                | 17        |
| $\beta$ -Mo <sub>2</sub> C      | 10                                               | 112                                               | 18        |
| WP NAs/CC                       | 10                                               | 150                                               | 19        |
| CoP/CC                          | 10                                               | 209                                               | 20        |
| Co-NRCNTs                       | 10                                               | 370                                               | 21        |
| bulk Mo <sub>2</sub> B          | 1                                                | 250                                               | 23        |
| Ni                              | 10                                               | 400                                               | 23        |
| Co-S/FTO                        | 1                                                | 480                                               | 25        |
| Ni <sub>2</sub> P nanoparticles | 20                                               | 250                                               | 27        |
| Ni wire                         | 10                                               | 350                                               | 28        |
| Ni-Mo alloy/Ti foil             | 10                                               | 80                                                | 28        |

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