Electronic Supplementary Information


Hongyu Mou,[a]# Jinfang Wang,[a]# Dongkun Yu,[a]# Deliang Zhang,[b]# Fu Lu,[c] Lei Chen,[b] Debao Wang,[b] and Tiancheng Mu*[a]

[a] Department of Chemistry, Renmin University of China, No 59 Zhongguancun Street, Beijing 100872, China. E-mail: tcmu@ruc.edu.cn
[b] Shandong Key Laboratory of Biochemical Analysis, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.
[c] College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

# These authors contributed equally to this work.
Table of the contents

1. Experiment Section

2. Supplementary Figures and Discussion

3. Supplementary Tables

4. References
1. Experiment Section

Materials.

NiCl$_2$·6H$_2$O, CuCl$_2$·2H$_2$O, FeCl$_2$·6H$_2$O, CoCl$_2$·6H$_2$O, KOH, NaH$_2$PO$_2$·H$_2$O, malonic acid, oxalic acid, succinic acid, and glutaric acid were purchased from Macklin, Pt/C (20 wt %) and IrO$_2$ were purchased from Alfa Aesar, and all other chemical materials were purchased from Sigma-Aldrich without further purification.

Preparation of Ni$_2$P@graphene composites.

The Ni$_2$P@graphene composites were prepared by a solution processing, followed by pyrolytic of deep eutectic solvents yield Ni$_2$P@graphene composites. The detailed steps are as follows: First, 0.01 mol NiCl$_2$·6H$_2$O and 0.07 mol malonic acid were mixed well and placed in an oil bath at 90 °C, and stirred to form DES. Subsequently, the resulting DES was placed at the center of a tube furnace, and 2.0 g of NaH$_2$PO$_2$·H$_2$O was placed at the upstream side and near to DES. After it was flushed with N$_2$ gas, the center of the furnace was elevated to the reaction temperature of 400 °C with a ramping rate of 5 °C min$^{-1}$ and kept at 400 °C for 4 h to convert the DES to Ni$_2$P@graphene. As the furnace cooled, the Ni$_2$P@graphene composites were obtained. By changing the amount of malonic acid used to regulate the loading of graphene, the amount of malonic acid in the experiment were 0.03 mol, 0.05 mol, 0.07 mol, and 0.09 mol for the preparation of DES-1, DES-2, DES-3, and DES-4, the corresponding phosphating and pyrolysis products are labeled as Ni$_2$P@G-1, Ni$_2$P@G-2, Ni$_2$P@G-3, and Ni$_2$P@G-4 respectively. In addition, Ni$_2$P@graphene composites were prepared by changing the carbon precursor (oxalic acid, succinic acid, or glutaric acid).

Preparation of phosphide@graphene composites.

The phosphide@graphene composites were prepared by a solution processing, followed by pyrolytic of deep eutectic solvents yield phosphide@graphene composites. The detailed steps are as follows: First, 0.01 mol CuCl$_2$·2H$_2$O, FeCl$_2$·6H$_2$O, or CoCl$_2$·6H$_2$O, and 0.07 mol malonic acid were mixed well and placed in an oil bath at 70-120 °C, and stirred to form a uniform liquid. The resulting liquid and NaH$_2$PO$_2$·H$_2$O were heated in a tube furnace under nitrogen atmosphere at 400 °C and held for 4 hours. As the furnace cooled, the metal phosphide@graphene composites were obtained.
**Electrochemical measurements.**

HER polarization curve tests were conducted on a 3000 potentiostat/galvanostat with a three-electrode electrochemical cell. Graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl filled) as the reference electrode. A carbon cloth electrode with an area of 1×1 cm² used as the working electrode. Typically, 20 mg catalyst was suspended in 0.5 mL deionized water, 0.45 mL ethanol with 50 μL Nafion solution (5 wt.%) to form homogeneous ink assisted by ultrasound. Then 180 μL of the ink was spread onto the surface of carbon cloth by a micropipette and dried under room temperature. The final loading for all catalysts and 20 % commercial Pt/C electrocatalys on work electrode is 2.4 mg/cm². Experiments were conducted in an 1.0 M KOH electrolyte at room temperature. The potential range was from 2.0 to -1.5 V (vs. Ag/AgCl) and the scan rate was 3 mV·s⁻¹. Cyclic voltammetry (CV) was carried out to calculate the capacitance ($C_{dl}$). The obtained $C_{dl}$ can be converted into an electrochemically active surface area (ECSA) using the formula: \[\text{ECSA} = \frac{C_{dl}}{C_s},\] where the specific capacitance value (Cs) was 40 μF·cm⁻².[1] All the polarization curves were recorded with a 90% iR compensation. As for the Faradaic efficiency measurements, gas chromatography (Agilent 6820, Ar carrier, molecule sieve 5A column, TCD detector) was used to determine the experimentally evolved amount of H₂ and O₂. Faraday law to calculate the theoretical amount of H₂ and O₂ expected based on a chronoamperometry.

**Characterization.**

Solution ¹H NMR experiments were performed on a Bruker DMX 300 NMR spectrometer (300 MHz) with d6-dimethyl sulfoxide as the standard. The chemical shift data were later processed by the MestReNova Program. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments-Waters LLC, USA) system at a heating rate of 10 °C·min⁻¹. XRD patterns were collected using a Rigaku D/max-2500 diffractometer. AFM was taken on a Bruker Multimode 8 instrument under the AC mode (tapping mode). Sample morphologies were characterized using a Hitachi SU8010 field emission scanning electron microscope (FESEM) and JEOL-2100F TEM. X-ray photoelectron spectroscopic (XPS) analysis was performed by an ESCALAB MK X-ray photoelectron spectrometer. The spectra were calibrated using the C1s (284.8 eV). We fit peaks by means of XPS-peak-differenating analysis software called “XPSPEAK4.0”. FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer.
and the sample was prepared by the KBr pellet method. Specific surface areas and pore size
distribution were analyzed on Micromeritics ASAP 2020 N₂ adsorption analyzer using the BET
(Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Halenda) methods, respectively.

**Density functional theory (DFT) calculation.**

The DFT calculations were conducted using the Dmol3 code[2] with DN basis to express the wave
function of valence electrons and DFT Semi-core Pseudopotals (DSPPs) to describe the interactions of
valence electrons and ionic cores. The functional of generalized gradient approximation (GGA) with
Perdew, Burke, and Ernzerhof (PBE)[3] was used throughout to describe the electron-electron exchange
and correlation interactions. For the sampling of Brillouin-zone integrals, a (1 × 1 × 1) k-point grid was
used, and meanwhile, global Orbital cutoff 4.5 Å was employed as the maximum value from all the
cutoffs specific to each element in this system. The convergence tolerance of an energy of 10⁻⁵ Ha was
taken, and the relaxation of the unit cell, including the atoms, was performed by Geometry Optimization.
The atom positions were relaxed until the remaining force acting on the atoms was less than 4 × 10⁻⁴ Ha
Å⁻¹.

**Turn-over frequency analysis.**

The total number of hydrogen turnovers was calculated from the current density according to:

\[
\# H_2 = \left( \frac{1 \text{ C} \cdot \text{s}^{-1}}{1000 \text{ m}^2} \right) \left( \frac{1 \text{ mol} \cdot \text{e}^-}{96485.3 \text{ C}} \right) \left( \frac{1 \text{ mol} H_2}{2 \text{ mol e}^-} \right) \left( \frac{6.022 \times 10^{23} \text{ H}_2 \text{ molecules}}{1 \text{ mol H}_2} \right)
\]

\[
= 3.12 \times 10^{15} \frac{H_2}{\text{ cm}^2} \frac{\text{ mA}}{\text{ cm}^2} \frac{\text{ per}}{\text{ mA}} \text{ cm}^2
\]

The active sites per real surface area is calculated from the following formula:

\[
\text{The hexagonal unit cell has a molar volume of } \text{Ni}_2\text{P:}
\]

\[
V_m = \frac{M}{\rho} = \frac{148.37 \text{ g} \cdot \text{mol}^{-1}}{7.351 \text{ g} \cdot \text{cm}^{-3}} = 20.184 \frac{\text{ cm}^3}{\text{ mol} \cdot \text{Ni}_2\text{P}}
\]

Each formula unit contains 3 atoms of Ni and P.

The average surface occupancy thus becomes:
Number of active sites (Ni₂P) = \( \left( \frac{3 \text{ atoms / formula unit}}{20.184 \text{ cm}^3/\text{mol Ni}_2\text{P}} \right)^{2/3} \times \frac{2.0 \times 10^{16}}{6.022 \times 10^{23} \text{ mol}^{-1}} \) atoms/cm²

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

\[
\text{TOF} = \frac{(3.12 \times 10^{15} \frac{\text{H}_2}{\text{s/cm}^2} \text{ per mA/cm}^2) \times |j|}{\# \text{ active sites} \times A_{ECSA}}
\]
2. Supplementary Figures and Discussion

![DSC spectra of DES-3](image1)

**Figure S1.** Differential Scanning Calorimeter (DSC) spectra of DES-3.

![FT-IR spectra](image2)

**Figure S2.** FT-IR spectra of DES-3, NiCl₂·6H₂O, and malonic acid.

In order to characterize the mixture solvents, differential scanning calorimetry (DSC) and infrared (IR) spectrum were carried out. It can be confirmed from the DSC curves that DES \( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} : \text{malonic acid} = 1:7 \) starts to melt at 79.6 °C, and the melting point of other DESs with different molar ratio are listed in Table S1. As can be seen that with the molar ratio of malonic acid increases, the melting point of DES first decreases and then increases, the detail melting point as shown in Table S1. This eutectic temperature is lower than the melting point of malonic acid (135 °C) and NiCl₂·6H₂O (140 °C) (Figure S1). In addition, infrared (IR) spectroscopy confirms the interaction between the components that compose DES (Figure S2). Before the formation of DES, in NiCl₂·6H₂O, hydroxyl group of water interacted with chloride, whose vibration mode was O-H···Cl. The O-H corresponded to peak around 3428.5 cm⁻¹. After the formation of DES, chloride and carboxyl group of malonic acid formed a new vibration mode, O-H···Cl. This weakens the original vibration mode. And, as a result, the above peak moves toward low wave numbers. Similarly, in pure malonic acid, the stretching vibration peak of the
The carbonyl group is 1718.0 cm\(^{-1}\), and after forming DES, the peak shifts to 1702.3 cm\(^{-1}\). This is because Ni coordinates with carbonyl oxygen. The above interactions are beneficial for the formation of DESs. DSC demonstrated the formation of DES; the interactions between hydrogen bond donors and acceptors verified the intrinsic cause of the formation of DESs.

**Figure S3.** Raman spectra of Ni\(_2\)P and Ni\(_2\)P@graphene.

**Figure S4.** XPS studies of the catalysts for (a) Ni 2p, (b) P 2p, and (d) C 1S.
X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the surface electronic state and composition of Ni$_2$P/G. The presence of elements C, Ni, and P has been supported by the survey scan spectrum (Fig. S4). For the C 1s XPS spectrum of the nanohybrid, signals including the aromatic linked carbon (C=C, 284.6 eV), the C in oxygen single-bonded carbon bonds (C-O, 285.7 eV), and the carboxylate carbon (O=C=O, 288.4 eV) can be observed (Fig. S4c), indicating that there are oxygen-containing functional groups on the graphene shell. These functional groups are highly active for anchoring Ni-P species during the synthesis process, thus greatly enhancing the structural stability of the nanohybrids. Fig. S4b shows the high resolution spectrum of Ni 2p, the peak of the binding energy of 852.9 eV (Ni 2p$_{3/2}$) is consistent with the Ni$^{2+}$ of Ni$_2$P. The binding energy of 873.7 and 856.1 eV and the corresponding two satellite peaks are attributed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ in the nickel oxide produced by the surface oxidation of Ni$_2$P. The corresponding P 2p edge confirmed the presence of P$^\delta$ at 129 eV.

Figure S5. SEM images of Ni$_2$P@G prepared at different pyrolysis temperatures, a) 300 °C, b) 500 °C.
Figure S6. SEM and the corresponding elemental mapping of Ni$_2$P@G-3.

Figure S7. TEM image of Ni$_2$P@G-3. Inset: particle size distribution of the samples.

Figure S8. HRTEM images of Ni$_2$P@G-3 composites.
**Figure S9.** $\text{N}_2$ adsorption-desorption isotherms of Ni$_2$P@graphene and the corresponding pore-size distribution plots (insert image).

**Figure S10.** LSV curves of Ni$_2$P@G prepared at different pyrolysis temperatures.

**Figure S11.** LSV curves of Ni$_2$P@G prepared at different pyrolysis times.
Figure S12. LSV curves of Ni$_2$P@G with different molar ratios of NiCl$_2$·6H$_2$O and malonic acid.

Figure S13. Cyclic voltammetry of Ni$_2$P@G-3 0.10-0.2 V (vs. RHE) at different scan rate.

Figure S14. SEM images of Ni$_2$P@G-3 after stability experiments.

Figure S15. Elemental mapping of Ni$_2$P@G-3 after stability experiments.
Figure S16. XRD patterns of initial and after stability experiments of Ni$_2$P@G-3, and carbon cloth.

Figure S17. TEM images of Ni$_2$P@G prepared at different graphene precursors. (a) oxalic acid, b) malonic acid, c) succinic acid, and d) glutaric acid.

It can be seen from TEM images that graphene encapsulated Ni$_2$P composites can be prepared with different carboxylic acid precursors.

Figure S18. Raman spectra of Ni$_2$P@G-1, Ni$_2$P@G-2, Ni$_2$P@G-3, and Ni$_2$P@G-1.

According to the Raman spectra, the intensity ratio of 1D/1G of graphene ranged from 0.627 to 0.648, this indicated that the graphene in Ni$_2$P@G prepared by NiCl$_2$·6H$_2$O and malonic acid with different molar ratio had the same defects and degree of graphitization.
Figure S19. LSV curves of products obtained from different carboxylic acid precursors.

Figure S20. TEM images of a) copper phosphide@G, c) iron phosphide@G, and e) cobalt phosphides; HRTEM images of b) copper phosphide@G, d) iron phosphide@G, and f) cobalt phosphides.

The TEM and HRTEM images of the synthesis of different metal phosphatides by malonic acid and metal chloride are shown in Figure S19. As can be seen from TEM and HRTEM images, the synthesized metal phosphatides are all coated with graphite.

Figure S21. LSV curves of different phosphatides.
Figure S22. (a) OER linear sweeping voltammetry curves of Ni$_2$P@G-3, Ni$_2$P, G, IrO$_2$, and CC electrodes. Corresponding (b) Tafel plots. (c) Nyquist plots (at $\eta = 300$ mV). (d) Stability of Ni$_2$P@G-3 with an initial polarization curve and after 2000 cycles (the inset image shows chronoamperometric curve).

Figure S23. Comparison of voltage between Ni$_2$P@G and other state-of-the-art non-precious metal dual-function catalysts at 10 mA·cm$^{-2}$ current density.$^{[10-19]}$
3. Supplementary Tables

**Table S1.** The freezing point of DES-1, DES-2, DES-3, and DES-4.

<table>
<thead>
<tr>
<th></th>
<th>DES-1</th>
<th>DES-2</th>
<th>DES-3</th>
<th>DES-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting point (°C)</td>
<td>76.2</td>
<td>54.8</td>
<td>54.6</td>
<td>59.4</td>
</tr>
</tbody>
</table>

**Table S2.** Compare the HER performance of Ni$_2$P@G with other reported non-precious HER electrocatalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P@G</td>
<td>103</td>
<td>56.5</td>
<td>1M KOH</td>
<td>this work</td>
</tr>
<tr>
<td>Zn-Co-S</td>
<td>176</td>
<td>86.3</td>
<td>1M KOH</td>
<td>20</td>
</tr>
<tr>
<td>NiO</td>
<td>110</td>
<td>100</td>
<td>1M KOH</td>
<td>21</td>
</tr>
<tr>
<td>MoSe$_2$-CoSe$_2$</td>
<td>237</td>
<td>89</td>
<td>1M KOH</td>
<td>22</td>
</tr>
<tr>
<td>Mo$_2$N-Mo$_3$C</td>
<td>154</td>
<td>68</td>
<td>1M KOH</td>
<td>23</td>
</tr>
<tr>
<td>Fe$<em>{1.8}$Mo$</em>{4.1}$O$_7$-MoO$_2$</td>
<td>197</td>
<td>79</td>
<td>1M KOH</td>
<td>24</td>
</tr>
<tr>
<td>Cu-Ni$_3$S$_2$</td>
<td>128</td>
<td>76.2</td>
<td>1M KOH</td>
<td>25</td>
</tr>
<tr>
<td>Co$<em>9$Mo$</em>{30}$@N-carbon</td>
<td>218</td>
<td>73.5</td>
<td>1M KOH</td>
<td>26</td>
</tr>
<tr>
<td>C, N doped carbon</td>
<td>380</td>
<td>76.9</td>
<td>1M KOH</td>
<td>27</td>
</tr>
<tr>
<td>1T-MoSe$_2$</td>
<td>152</td>
<td>52</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>28</td>
</tr>
<tr>
<td>carbon nanotubes-MoSe$_2$</td>
<td>170</td>
<td>67</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>29</td>
</tr>
<tr>
<td>Fe$<em>{4.1}$Ni$</em>{9.8}$S$_8$</td>
<td>146</td>
<td>--</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>30</td>
</tr>
<tr>
<td>Fe-MoS$_2$</td>
<td>104</td>
<td>59</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>31</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>229</td>
<td>100.7</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>32</td>
</tr>
<tr>
<td>Monolayer MoS$_2$</td>
<td>385</td>
<td>109</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>33</td>
</tr>
<tr>
<td>N@MoPC$_4$</td>
<td>108</td>
<td>69.4</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>34</td>
</tr>
</tbody>
</table>
Table S3. Compare the OER performance of Ni$_2$P@G with other reported non-precious OER electrocatalysts in KOH electrolyte.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P@G</td>
<td>$\eta_{10}=275$</td>
<td>56.2</td>
<td>this work</td>
</tr>
<tr>
<td>NiCo@NiCoO$_2$</td>
<td>$\eta_{10}=366$</td>
<td>83.97</td>
<td>35</td>
</tr>
<tr>
<td>CeO$_2$-embedded NiO</td>
<td>382</td>
<td>118.7</td>
<td>36</td>
</tr>
<tr>
<td>Co$<em>{0.70}$Fe$</em>{0.29}$WO$_4$</td>
<td>327</td>
<td>53</td>
<td>37</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>307</td>
<td>56</td>
<td>38</td>
</tr>
<tr>
<td>Co$_2$S$_8$@carbon</td>
<td>302</td>
<td>67</td>
<td>39</td>
</tr>
<tr>
<td>CoOOH</td>
<td>266</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>CoO$_x$</td>
<td>306</td>
<td>67</td>
<td>41</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>370</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td>N-CoFe LDHs</td>
<td>281</td>
<td>40.03</td>
<td>43</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Co$</em>{1.4}$P</td>
<td>300</td>
<td>80</td>
<td>44</td>
</tr>
<tr>
<td>Ni$<em>{0.13}$Co$</em>{0.87}$S$_{1.097}$</td>
<td>316</td>
<td>54.72</td>
<td>45</td>
</tr>
<tr>
<td>NiCoP</td>
<td>297</td>
<td>57.35</td>
<td>46</td>
</tr>
<tr>
<td>Ni-Fe LDH</td>
<td>280</td>
<td>49.4</td>
<td>47</td>
</tr>
<tr>
<td>NiPS$_3$</td>
<td>301</td>
<td>43</td>
<td>48</td>
</tr>
<tr>
<td>SnCoFe-Ar</td>
<td>300</td>
<td>42.3</td>
<td>49</td>
</tr>
</tbody>
</table>
4. References


