Supporting Information

One-step Pyrolytic Synthesis of Small Iron Carbide Nanoparticles/3D Porous Nitrogen-riched Graphene for Efficient Electrocatalysis

Hao Huang, Xun Feng, Cuicui Du, Siyuan Wu and Wenbo Song

1. HER property of Fe$_3$C/NGr.
2. Figure S1: SEM image of Fe$_3$C/NGr.
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1. HER property of Fe$_3$C/NGr

Electrocatalytic hydrogen evolution reaction (HER) also holds tremendous promise as an efficient and clean solution to face the energy crisis. Unfortunately, as same as ORR, the current HER catalysts also incorporate noble metals,\textsuperscript{1} whose high-cost limits the application of renewable H$_2$ production. During the past few years, in-depth study on developing novel HER catalysts has been made, and transition metal sulfides,\textsuperscript{2} carbides,\textsuperscript{3} nitrides\textsuperscript{4} and borides\textsuperscript{3a} containing Mo, Ni and/or Co exhibit excellent HER activity. In this study, the category of Fe$_3$C/NGr catalytic materials is also expanded to HER. The Fe$_3$C-based HER activity was unprecedentedly evaluated.

The favorable HER catalytic performance of Fe$_3$C/NGr was occasionally discovered. With the same loading of 0.57 mg cm$^{-2}$ on the GCE, Fe$_3$C/NGr-1, Fe$_3$C/NGr-0.5, Fe$_3$C/NGr-0.25, NGr and commercial Pt/C display different HER activities in 0.5 M H$_2$SO$_4$ solution. As shown in Figure S3, all the Fe$_3$C/NGr catalysts possess much lower onset overpotentials ($\eta$) than the pure NGr. With increasing Fe$_3$C content in the Fe$_3$C/NGr samples, the onset $\eta$ for HER reduces, suggesting that the Fe$_3$C nanoparticles are the active substances for HER. The Fe$_3$C/NGr-1 displays a $\eta$ value as low as 100 mV, manifesting a superior HER activity. The cathodic current density of a catalytic material is another important criterion for HER activity. The Fe$_3$C/NGr-1 catalyst exhibits an extremely large cathodic current density of 8 mA cm$^{-2}$ at $\eta= 200$ mV, which is 20 times of the pure NGr. It is also much larger than the other two samples with similar constituents. Tafel slope is an inherent property of an electrocatalyst that is determined by the rate-limiting step of HER. Figure S4 depicts that the lower the Fe$_3$C loading amount is, the larger the Tafel slope becomes. Compared to the other
non-precious metal catalysts in previous reports, the Fe$_3$C/NGr-1 shows a relatively low Tafel slope (69 mV decade$^{-1}$). Due to a remarkably enhanced HER rate at a moderate increase of the overpotential, the small Tafel slope of the Fe$_3$C/NGr-1 sample will be beneficial to practical application.

Besides the HER activity, stability is another significant aspect of a catalyst. To probe the durability of the catalyst, a continuous CV scanning (between -0.2 and +0.4 V vs. RHE) was conducted at 50 mV s$^{-1}$ in an acidic environment, after which, the HER activity was compared with its initial behavior. A minor difference between the as-measured curve at the initial cycle and the ultimate cycle (after 1 000 continuous cycles) was observed in Figure S5, suggesting an admissive durability of the Fe$_3$C/NGr-1 catalyst during long-term cycling. All of the above results demonstrate that the Fe$_3$C/NGr-1 sample possesses excellent HER activity and excellent stability with prospective in replacing precious metal-based HER catalysts.
2. **Figure S1** SEM image of Fe$_3$C/NGr.

3. **Figure S2** TGA curve of the Fe$_3$C/NGr precursors measured from 25 to 800°C in nitrogen atmosphere with a heating rate of 10°C min$^{-1}$. 
4. **Figure S3** Polarization curves of various Fe₃C/NGr samples and the commercial Pt/C catalyst.

![Polarization curves of various Fe₃C/NGr samples and the commercial Pt/C catalyst.](image)

5. **Figure S4** Tafel plots of Fe₃C/NGr-1 and commercial Pt/C catalyst.

![Tafel plots of Fe₃C/NGr-1 and commercial Pt/C catalyst.](image)
6. **Figure S5** Comparative polarization curves of the initial cycle and the 1000 cycle for Fe₃C/NGr-1.

![Comparative polarization curves](image)

7. **Table S1** The compared properties of various Fe₃C-based materials for ORR

<table>
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<tr>
<th></th>
<th>Fe₃C/NGr</th>
<th>N-Fe/Fe₃C@C</th>
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<tr>
<td>onset potential</td>
<td>+1.07</td>
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<td>durability$^a$</td>
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<td>[6b]</td>
<td>[6c]</td>
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$^a$ The durability measured by chronoamperometry for 10 000 s

$^b$ the sequence of reference brings into correspondence with main paper
8. References


