Supporting Information

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

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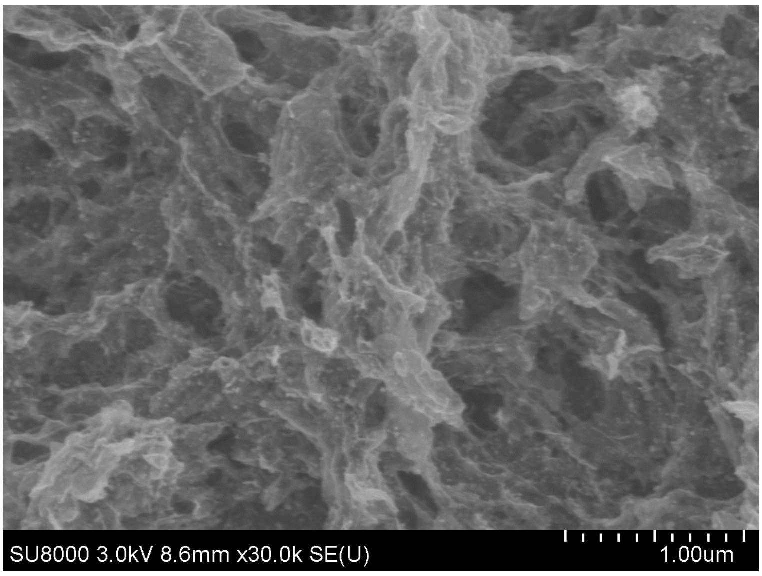
1. HER property of Fe_3C/NGr

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,[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,[2] carbides,[3] nitrides[4] and borides[3a] containing Mo, Ni and/or Co exhibit excellent HER activity. In this study, the category of Fe_3C/NGr catalytic materials is also expanded to HER. The Fe_3C-based HER activity was unprecedentedly evaluated.

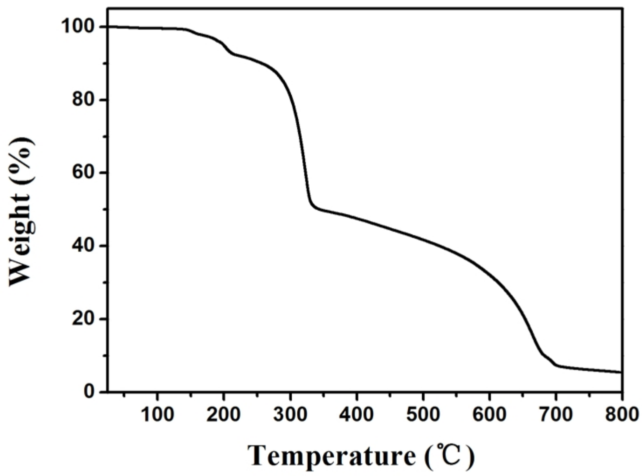
The favorable HER catalytic performance of Fe_3C/NGr was occasionally discovered. With the same loading of 0.57 mg cm^{-2} on the GCE, Fe_3C/NGr-1, Fe_3C/NGr-0.5, Fe_3C/NGr-0.25, NGr and commercial Pt/C display different HER activities in 0.5 M H_2SO_4 solution. As shown in Figure S3, all the Fe_3C/NGr catalysts possess much lower onset overpotentials (η) than the pure NGr. With increasing Fe_3C content in the Fe_3C/NGr samples, the onset η for HER reduces, suggesting that the Fe_3C nanoparticles are the active substances for HER. The Fe_3C/NGr-1 displays a η 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_3C/NGr-1 catalyst exhibits an extremely large cathodic current density of 8 mA cm^{-2} at η= 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_3C loading amount is, the larger the Tafel slope becomes. Compared to the other non-precious metal catalysts in previous reports, the Fe_3C/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_3C/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_3C/NGr-1 catalyst during long-term cycling. All of the above results demonstrate that the Fe_3C/NGr-1 sample possesses excellent HER activity and excellent stability with prospective in replacing precious metal-based HER catalysts.

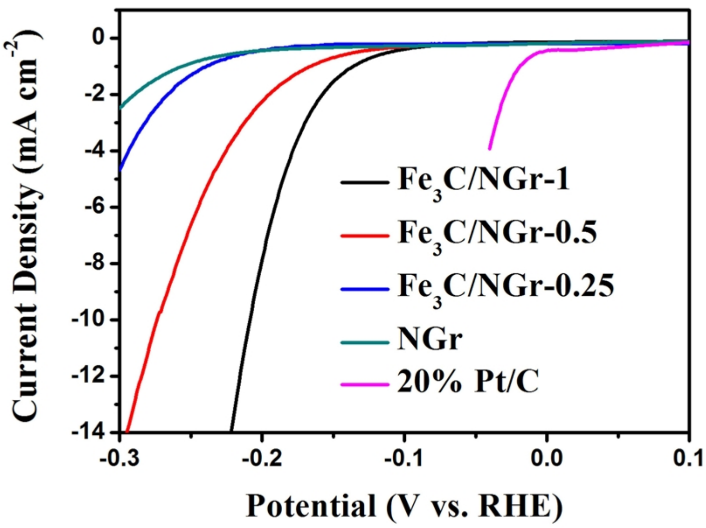
2. **Figure S1** SEM image of Fe_3C/NGr.



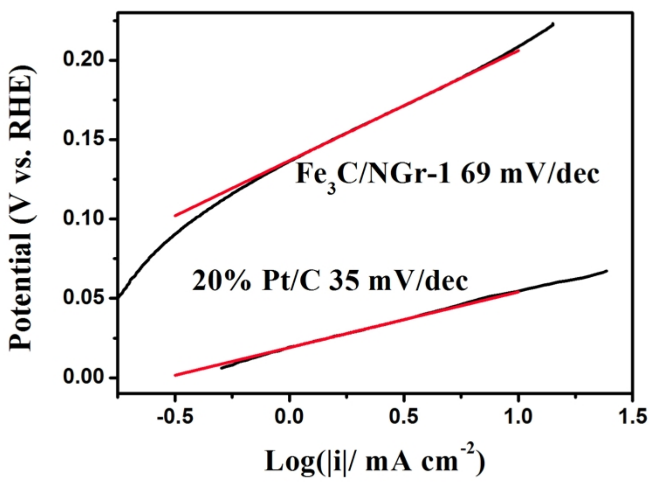
3. **Figure S2** TGA curve of the Fe_3C/NGr precursors measured from 25 to 800°C in nitrogen atmosphere with a heating rate of 10°C min^{-1}.



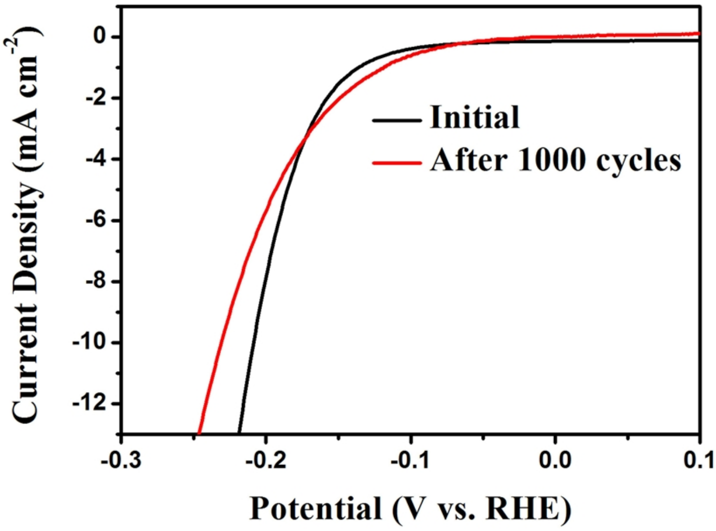
4. **Figure S3** Polarization curves of various Fe_3C/NGr samples and the commercial Pt/C catalyst.



5. **Figure S4** Tafel plots of Fe_3C/NGr-1 and commercial Pt/C catalyst.



6. **Figure S5** Comparative polarization curves of the initial cycle and the 1000 cycle for Fe_3C/NGr-1.



7. **Table S1** The compared properties of various Fe_3C-based materials for ORR

	Fe_3C/NGr	N-Fe/Fe_3C@C	Ar-800	Fe_3C/C-800
onset potient [V vs. RHE]	+1.07	+0.84	+0.91	+1.05
half-wave potient [V vs. RHE]	+0.89	+0.79	+0.74	+0.83
n	3.9-4.0	3.98	3.7-3.85	3.8-4
durability[a]	89.5%	–	74.2%	81%
reference[b]	this work	[6a]	[6b]	[6c]

[a] The durability measured by chronoamperometry for 10 000 s

[b] the sequence of reference brings into correspondence with main paper

8. References

1 J. Greeley, T. F. Jaramillo, J. Bonde, I. B. Chorkendorff, J. K. Norskov, *Nat. Mater.* 2006, **5**, 909-913.

2 (a) D. Voiry, H. Yamaguchi, J. W. Li, R. Silva, D. C. B. Alves, T. Fujita, M. W. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nat. Mater.* 2013, **12**, 850-855; (b) D. Merki, X. L. Hu, *Energ Environ. Sci.* 2011, **4**, 3878-3888.

3 (a) H. Vrubel, X. L. Hu, *Angew. Chem. Int. Ed.* 2012, **51**, 12703-12706; (b) W. F. Chen, C. H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, R. R. Adzic, *Energ Environ. Sci.* 2013, **6**, 943-951.

4 W. F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. M. Zhu, R. R. Adzic, *Angew. Chem. Int. Ed.* 2012, **51**, 6131-6135.