

Supporting information

PtFe Nanoparticles Supported on Electroactive Au-PANI Core@Shell Nanoparticles for High Performance Bifunctional Electrocatalysis

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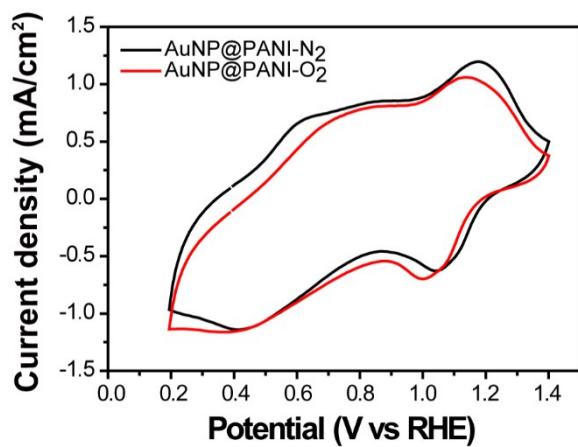


Fig. S1 Cyclic voltammograms (CVs) of AuNP@PANI in a N₂ and O₂-saturated 0.1 M HClO₄ solution.

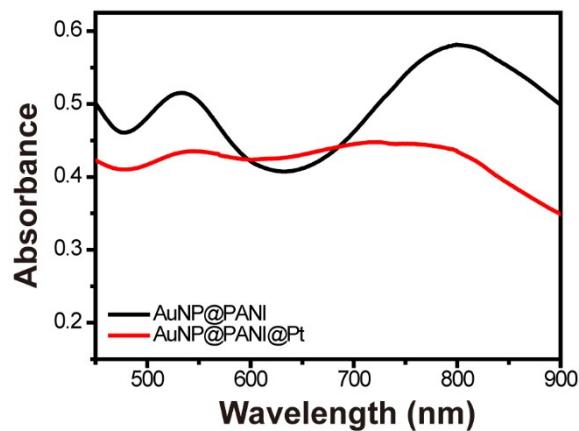


Fig. S2 UV-Vis spectra of AuNP@PANI (black curve) and AuNP@PANI@Pt (red curve) nanostructures with aniline/Pt molar ratio of 1:1.

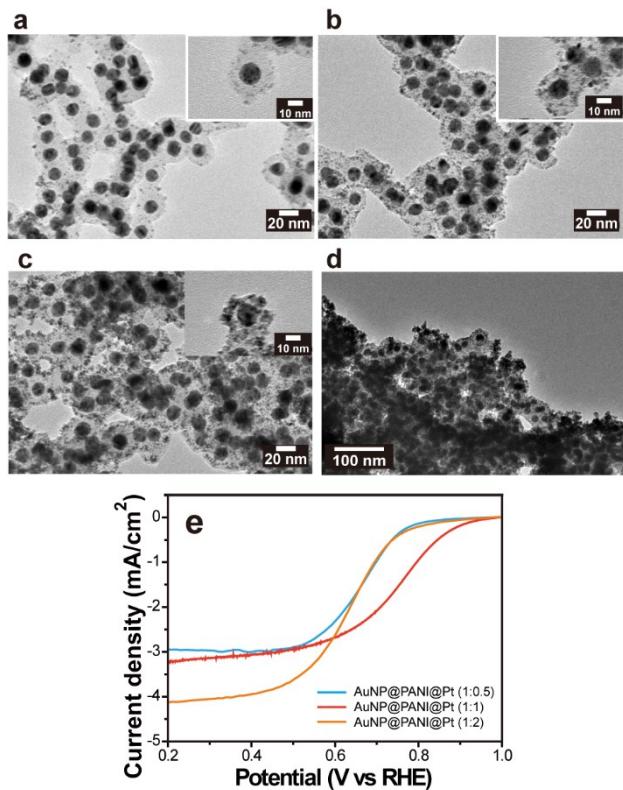


Fig. S3 TEM images of AuNP@PANI@Pt nanostructures synthesized at different molar ratio of aniline and platinum precursor: (a) 1:0.2, (b) 1:0.5, (c) 1:1 and (d) 1:2. (f) LSVs of AuNP@PANI@Pt nanostructures. LSVs were recorded in O_2 -saturated 0.1 M HClO_4 at 1600 rpm and at a scan rate of 5 mVs^{-1} .

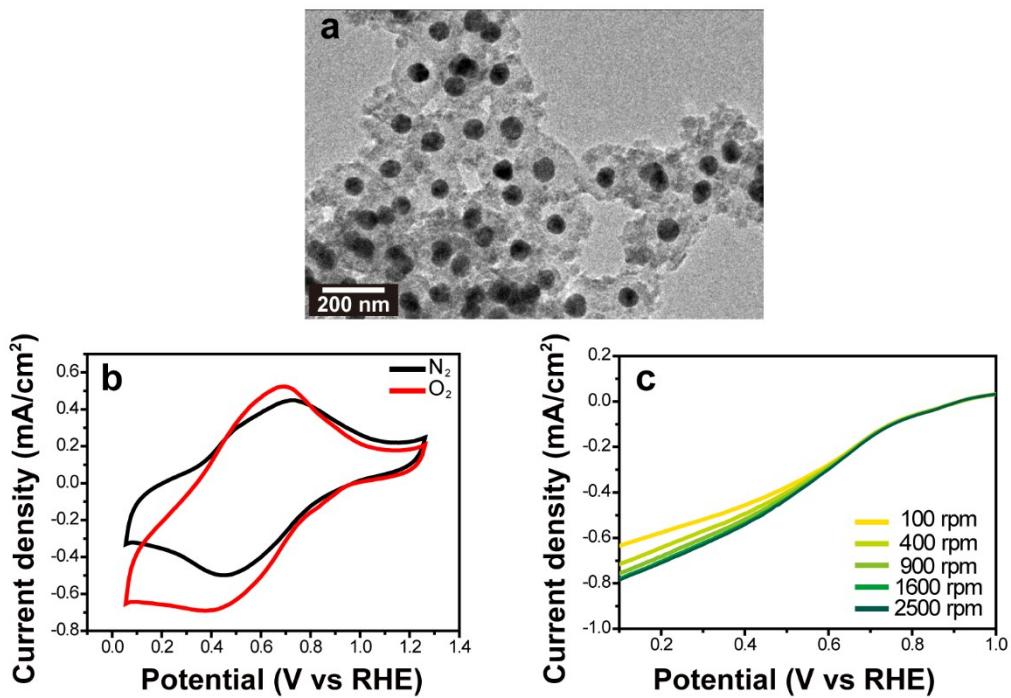


Fig. S4 TEM Image of AuNP@PANI@Fe (a); the cyclic voltammograms of AuNP@PANI@Fe (b) in a N₂ and O₂-saturated 0.1 M HClO₄ solution; linear sweep voltammograms of AuNP@PANI@Fe (c) in oxygen-saturated 0.1 M HClO₄ at various rates (100, 400, 900, 1 600 and 2 500 rpm) and potential scan rate 5 mVs⁻¹.

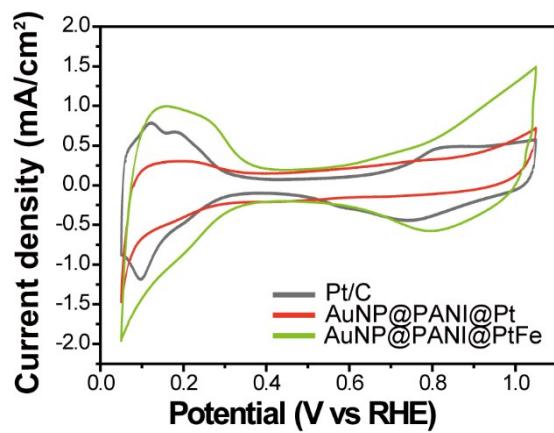


Fig. S5 Cyclic voltammograms of AuNP@PANI@Pt and AuNP@PANI@PtFe in a N₂-saturated 0.1 M HClO₄ solution at a scan rate of 20 mVs⁻¹.

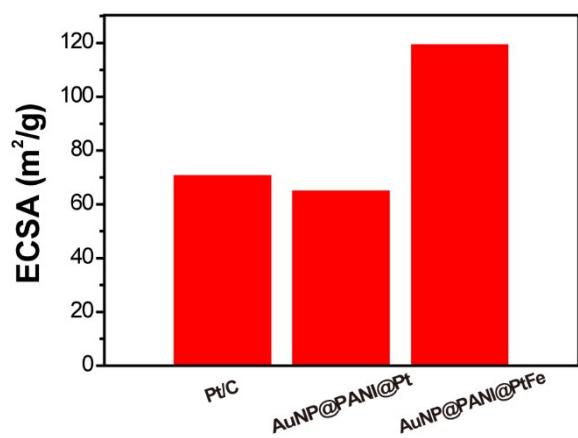


Fig. S6 Electrochemical surface areas (ECSA) determined after activity testing for electrochemical characteristics of voltammetrically AuNP@PANI@Pt and AuNP@PANI@PtFe.

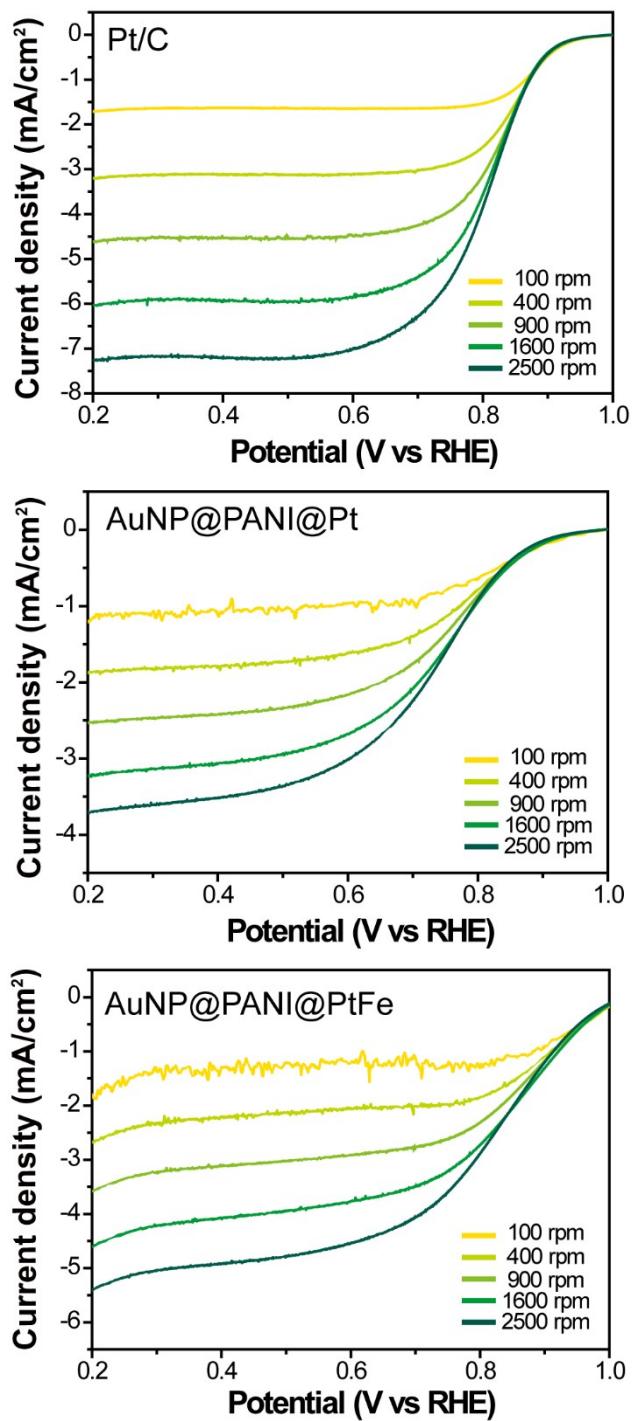


Fig. S7 LSVs of AuNP@PANI@Pt and AuNP@PANI@PtFe measured in O_2 -saturated 0.1 M HClO_4 solution. The scan rate was 5 mVs^{-1} and the different rotation speed.

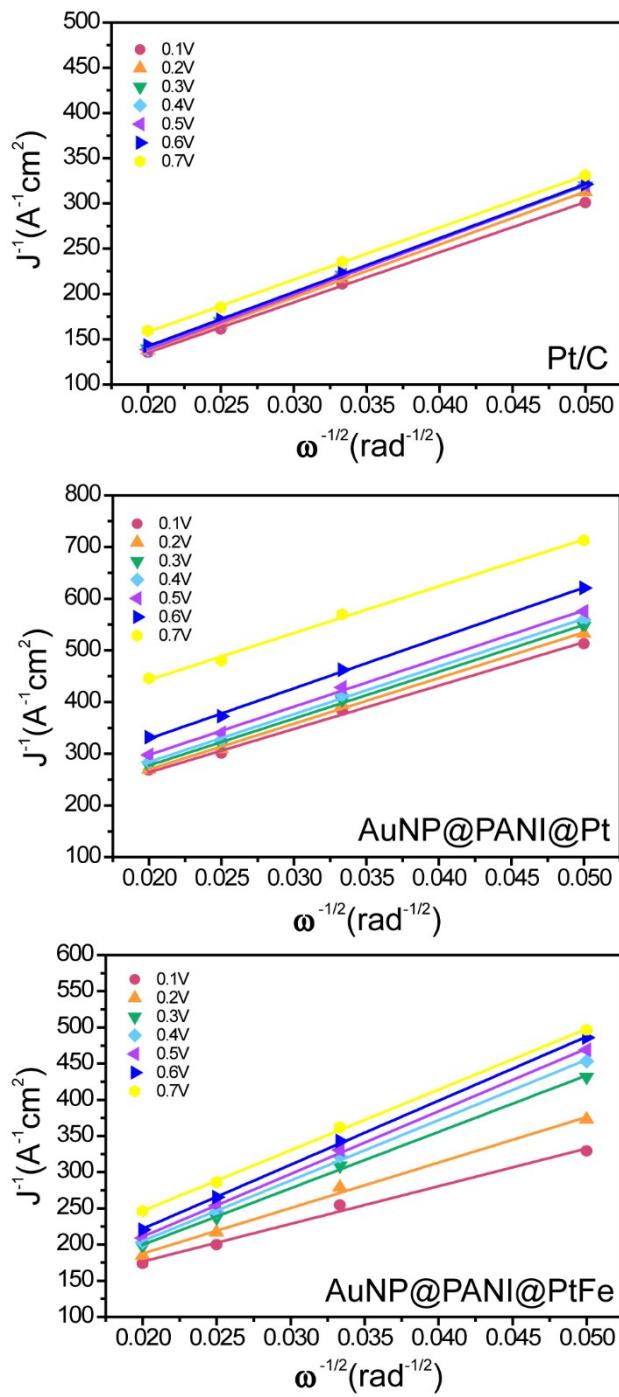


Fig. S8 Koutecky-Levich plots derived from the data in LSVs at different potential.

Sample \ Potential	0.1V	0.2V	0.3V	0.4V	0.5V	0.6V	0.7V
Pt/C	3.77	3.57	3.48	3.42	3.44	3.5	3.63
AuNP@PANI@Pt	2.49	2.37	2.31	2.26	2.24	2.15	2.31
AuNP@PANI@PtFe	4.02	3.33	2.68	2.5	2.41	2.36	2.49

Table S1. Electron transfer number determined from fit lines of the Koutecky-Levich plots derived at different potential.

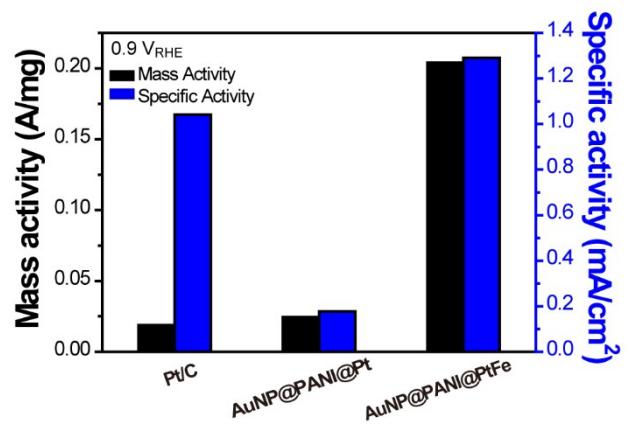


Fig. S9 The mass and specific activities for ORR performance at 0.90 V versus RHE obtained using AuNP@PANI@Pt and AuNP@PANI@PtFe.

Sample	Mass Activity (A/mg)	Specific Activity (mA/cm ²)	Ref.
AuNP@PANI@PtFe	0.21	1.29	This work
FePt₃/C	0.30	1.38	<i>Nano Lett.</i> , 2011 , 11, 919-926 [1]
PtFe Nanoparticles	0.27	0.54	<i>J. Phys. Chem. C</i> 2015 , 119, 3971-3978 [2]
PtFe@Pt/CNT	0.25	-	<i>RSC Adv.</i> , 2015 , 5, 66471-66475 [3]
fcc-PtFe/C	0.60	0.75	<i>J. Am. Chem. Soc.</i> , 2015 , 137, 15478-15485 [4]
fct-PtFe/C	1.50	2.25	<i>J. Am. Chem. Soc.</i> 2015 , 137, 15478-15485 [4]
PtFe/C	0.25		<i>Energy Environ. Sci.</i> , 2016 , 9, 2623-2632 [5]

Table S2. Summary of the reported ORR performance for PtFe catalysts at 0.90 V versus RHE in acidic media (0.1 M HClO₄).

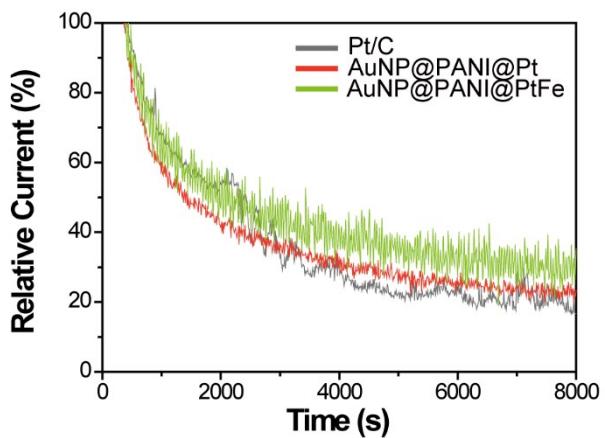


Fig. S10 The durability test of the catalysts by chronoamperometric measurement at 0.7 V for 8000 s.

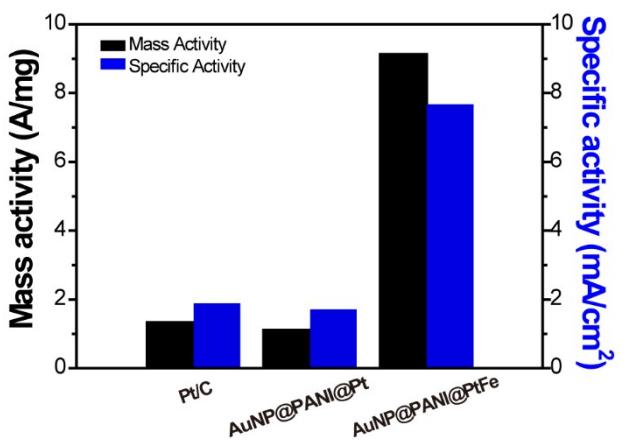


Fig. S11 The mass activity and specific activity of MOR performance for AuNP@PANI@Pt and AuNP@PANI@PtFe at 0.8 V versus RHE.

Sample	Mass Activity (A/mg)	Specific Activity (mA/cm ²)	j _f /j _b	Ref.
AuNP@PANI@PtFe	9.13 (@0.8 V vs RHE and @0.5 V vs SCE)	7.66	1.10	This work
PtFe/C	0.24 (@0.5V vs SCE)	1.30	-	<i>Electrochimica Acta</i> 2014 , 139, 61-68 ^[6]
PtFe@Pt	0.82 (@0.5 V vs SCE)	-	-	<i>Chem. Commun.</i> , 2015 , 51, 3215-3218 ^[7]
PtFe	0.55 (@0.65 V vs SCE)	2.03	1.01	<i>J. Mater. Chem. A</i> , 2015 , 3, 1182-1187 ^[8]
PtRuFe	1.14 (@0.65 V vs SCE)	1.74	1.41	<i>J. Mater. Chem. A</i> , 2015 , 3, 1182-1187 ^[8]
PtFe NCs	0.57 (@0.65 V vs SCE)	1.04	1.09	<i>Chem. Commun.</i> , 2016 , 52, 3903-3906 ^[9]
PtFeAu NCs	1.32 (@0.65 V vs SCE)	3.01	1.52	<i>Chem. Commun.</i> , 2016 , 52, 3903-3906 ^[9]
PtFe/CNT	-	-	1.14	<i>Fuel</i> 2016 , 182, 1-7 ^[10]

Table S3. Summary of the reported MOR performance for diverse PtFe catalysts.

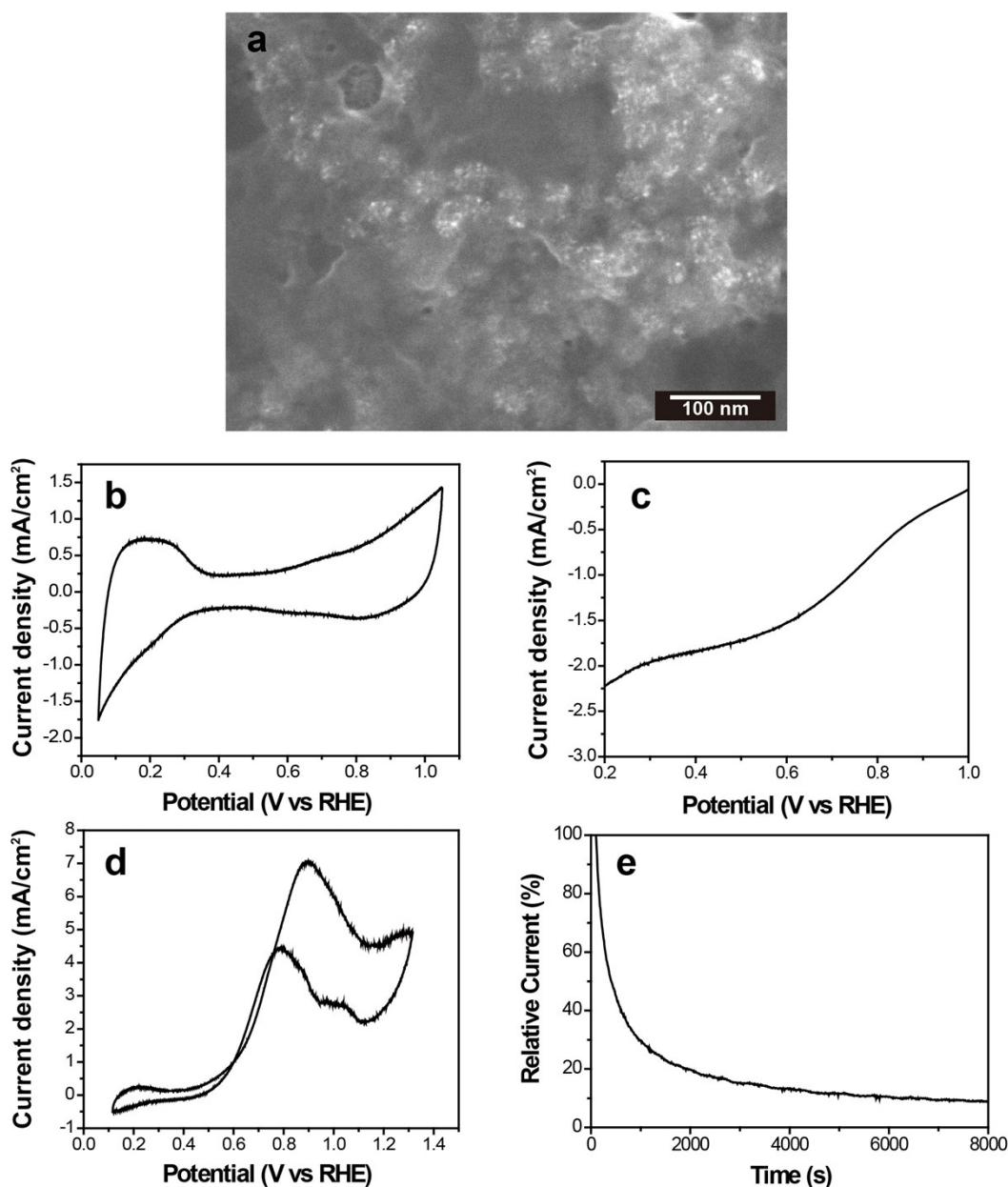


Fig. S12 SEM Image of PANI@PtFe catalyst (a); the CV of PANI@PtFe (b) in a N₂ saturated 0.1 M HClO₄ solution; LSV of PANI@PtFe catalyst (C) in O₂-saturated 0.1M HClO₄ at 1600 rpm and potential scan rate 5 mVs⁻¹; CV of PANI@PtFe (d) in 0.1 M HClO₄ + 0.1 M methanol at scan rate 20 mVs⁻¹; durability test of the PANI@PtFe by CA measurement (e) at 0.7 V for 8000 s.

References

- [1] C. Wang, D. van der Vliet, K. L. More, N. J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A. P. Paulikas, G. Karapetrov, D. Strmcnik, N. M. Markovic, V. R. Stamenkovic, *Nano Lett.*, **2011**, *11*, 919-926.
- [2] B. Han, C. E. Carlton, J. Suntivich, Z. Xu, Y. Shao-Horn, *J. Phys. Chem. C*, **2015**, *119*, 3971-3978.
- [3] H. Liu, M. Dou, F. Wang, J. Liu, J. Ji, Z. Li, *RSC Adv.*, **2015**, *5*, 66471-66475.

- [4] D. Y. Chung, S. W. Jun, G. Yoon, S. G. Kwon, D. Y. Shin, P. Seo, J. M. Yoo, H. Shin, Y.-H. Chung, H. Kim, B. S. Mun, K.-S. Lee, N.-S. Lee, S. J. Yoo, D.-H. Lim, K. Kang, Y.-E. Sung, T. Hyeon, *J. Am. Chem. Soc.*, **2015**, *137*, 15478-15485.
- [5] X. X. Du, Y. He, X. X. Wang, J. N. Wang, *Energy Environ. Sci.*, **2016**, *9*, 2623-2632.
- [6] Q. Lv, Y. Xiao, M. Yin, J. Ge, W. Xing, C. Liu, *Electrochim. Acta*, **2014**, *139*, 61-68.
- [7] J. Zhu, M. Xiao, K. Li, C. Liu, W. Xing, *Chem. Commun.*, **2015**, *51*, 3215-3218.
- [8] Z. Cai, Y. Kuang, X. Qi, P. Wang, Y. Zhang, Z. Zhang, X. Sun, *J. Mater. Chem. A*, **2015**, *3*, 1182-1187.
- [9] Z. Cai, Z. Lu, Y. Bi, Y. Li, Y. Kuang, X. Sun, *Chem. Commun.*, **2016**, *52*, 3903-3906.
- [10] J. R. Rodriguez, S. Fuentes-Moyado, T. A. Zepeda, J. N. Díaz de León, J. Cruz-Reyes, M. T. Oropeza-Guzman, G. Berhault, G. Alonso-Núñez, *Fuel*, **2016**, *182*, 1-7.