

## Supporting Information

### **Design and synthesis of Porous Channel-rich Carbon Nanofibers for Self-standing Oxygen Reduction Reaction and Hydrogen Evolution Reaction Bifunctional Catalysts in Alkaline Medium**

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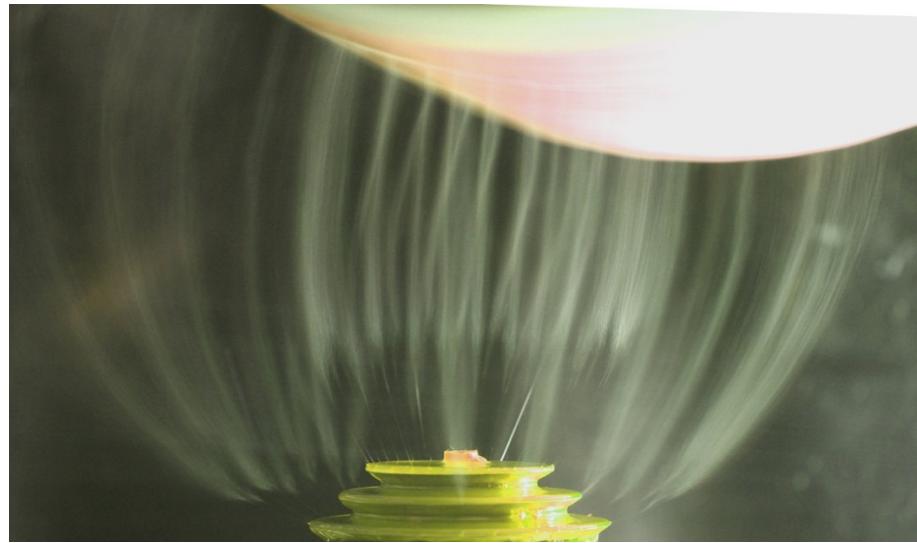


Fig. S1. Scalable preparation of Fe-rich nanofiber films by self-designed free-surface electrospinning setup.

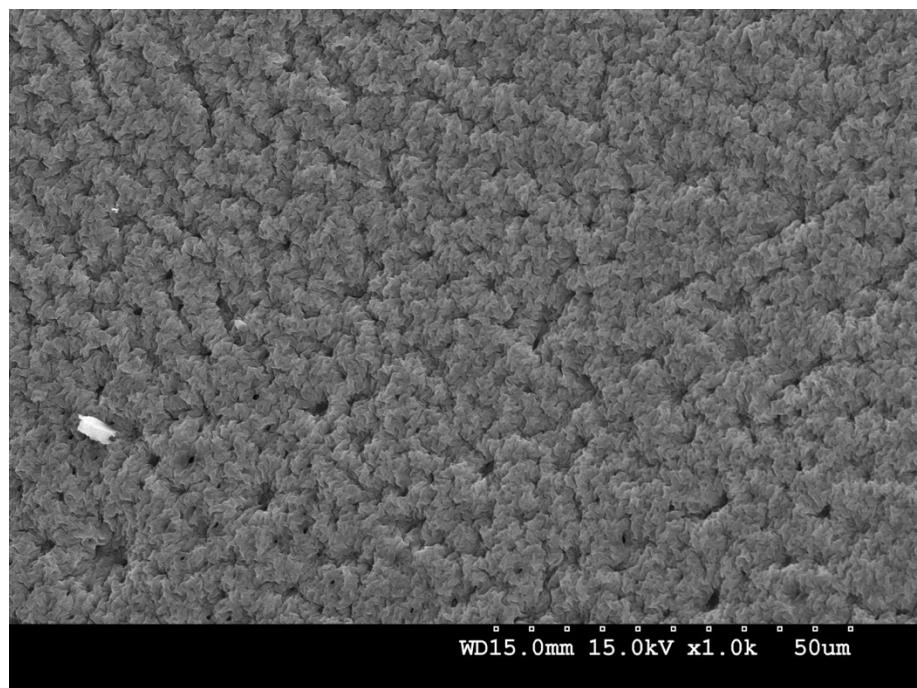


Fig. S2. SEM of the 800 °C carbonized PAN/CA mixed polymers. Abundant pores and defects are formed in the pyrolyzed carbon.

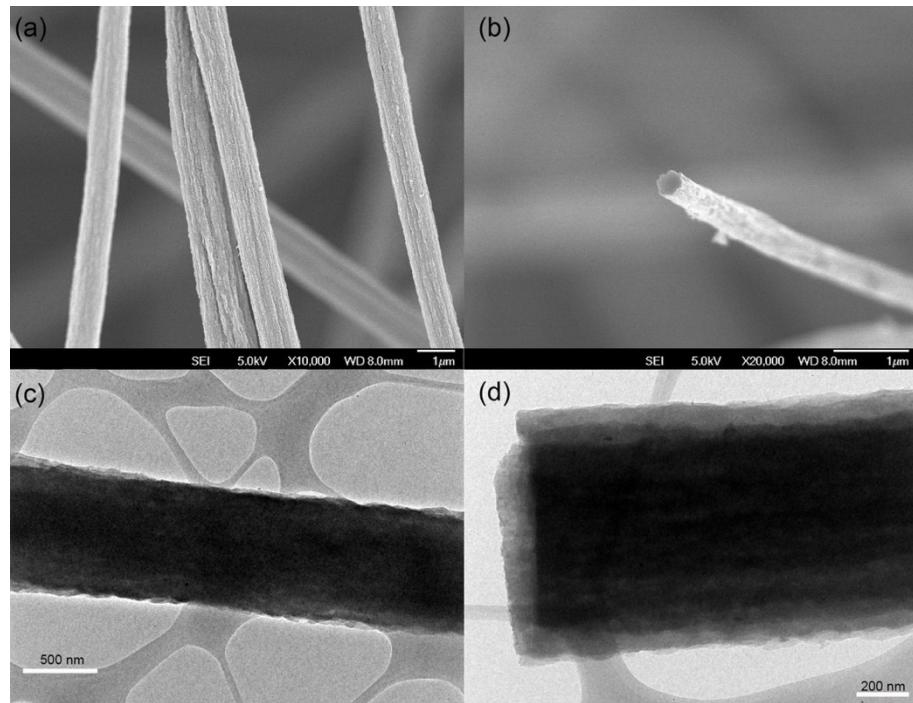


Fig. S3 The morphology of 1:0.2 PAN/CA carbon fiber. (a-b) SEM; (c-d) TEM.

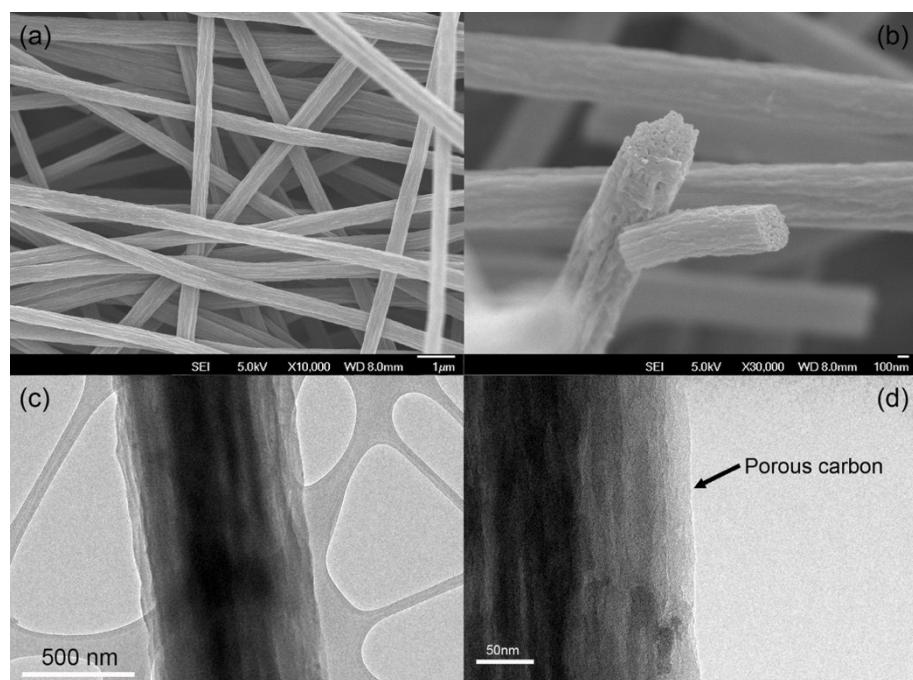


Fig. S4 The morphology of 1:0.5 PAN/CA carbon fiber. (a-b) SEM; (c-d) TEM.

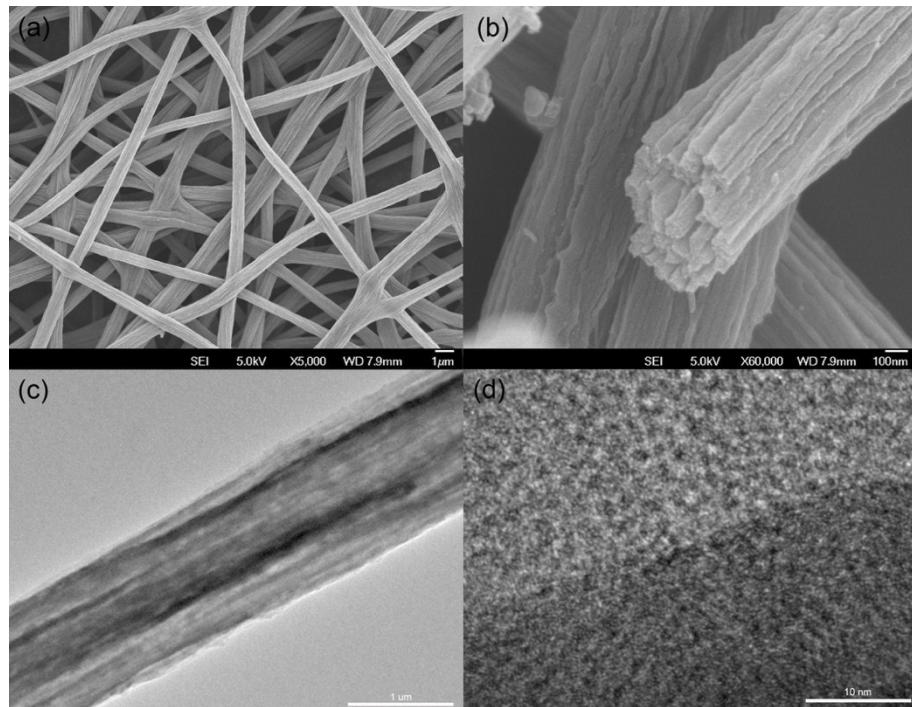


Fig. S5 The morphology of 1:1 PAN/CA carbon fiber. (a-b) SEM; (c-d) TEM.

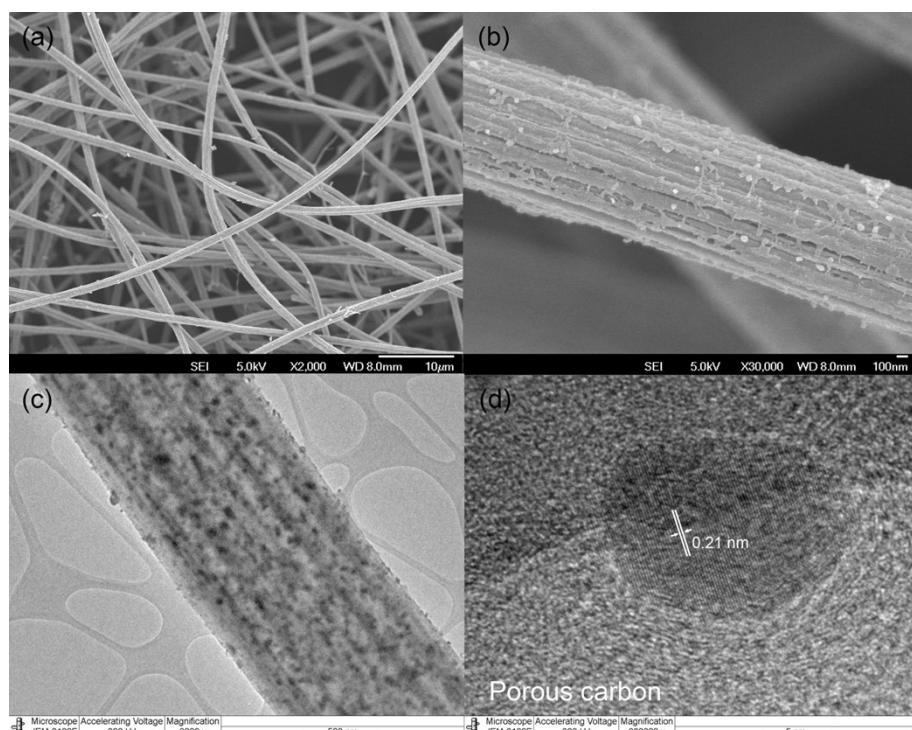


Fig. S6 The morphology of 1:1 PAN/CA-based Fe-CACNFs. (a-b) SEM; (c-d) TEM.

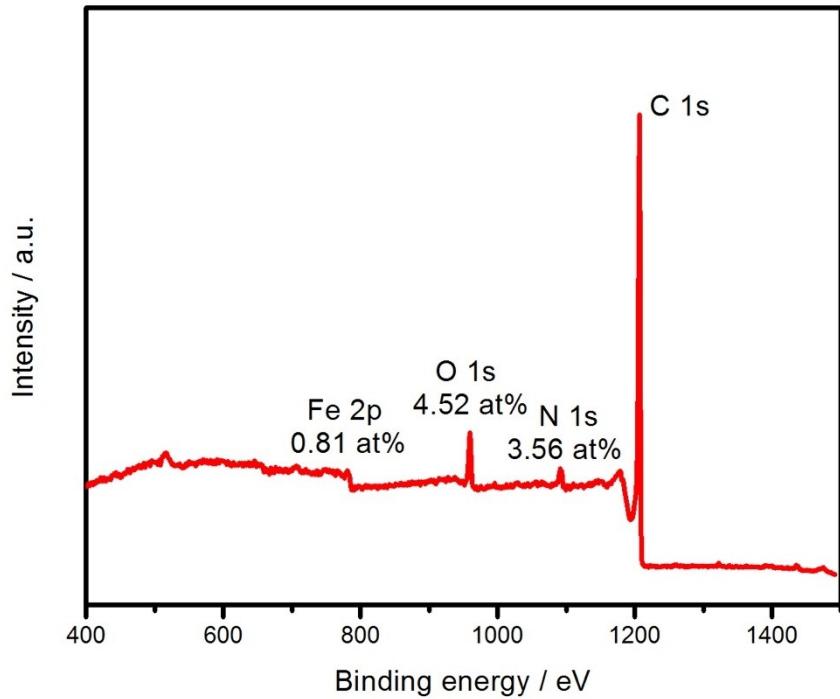


Fig. S7 The XPS survey spectra of Fe-CACNF.

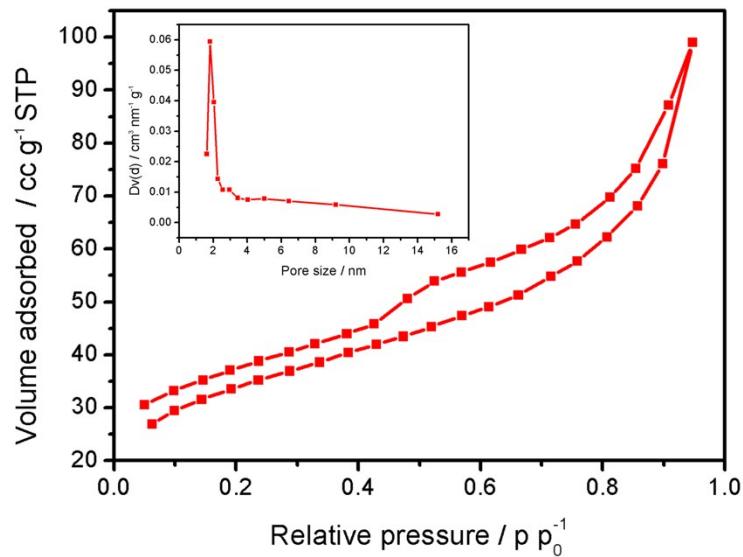


Fig. S8 The  $N_2$  adsorption-desorption isotherms and pore distribution of Fe-CACNFs.

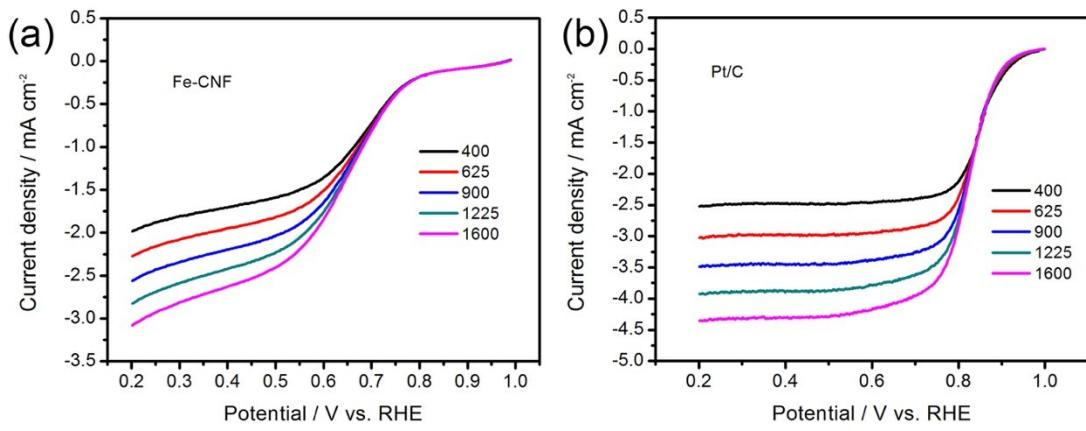


Fig. S9 The LSVs of Fe-CNF and Pt/ C at different rotating speed.

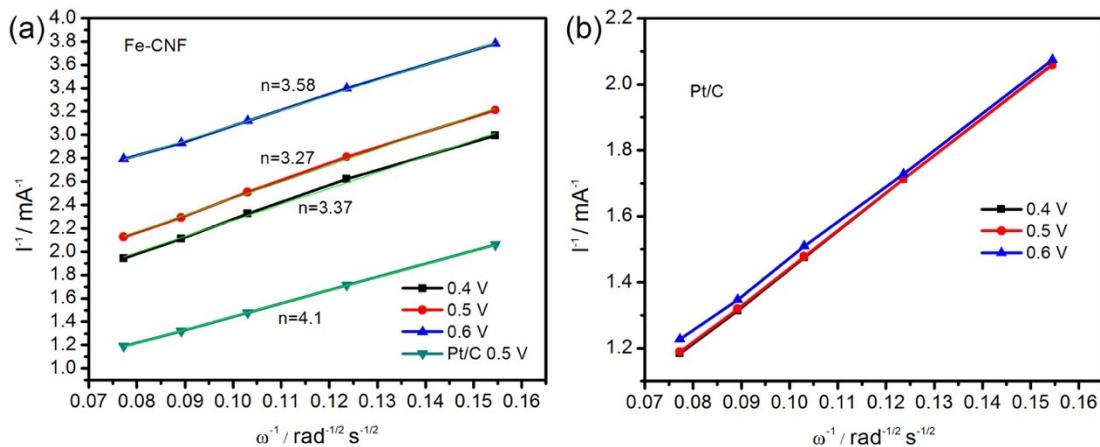


Fig. S10 The K-L plots of Fe-CNF and Pt/C.

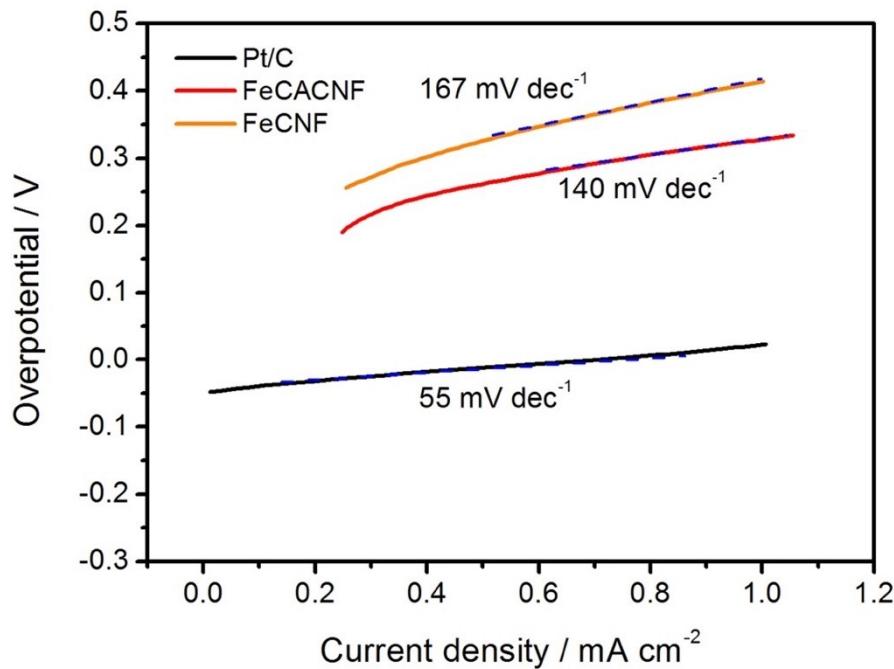


Fig. S11 HER Tafel plots of Fe-CNF, Fe-CACNF and Pt/C in 1 M KOH.

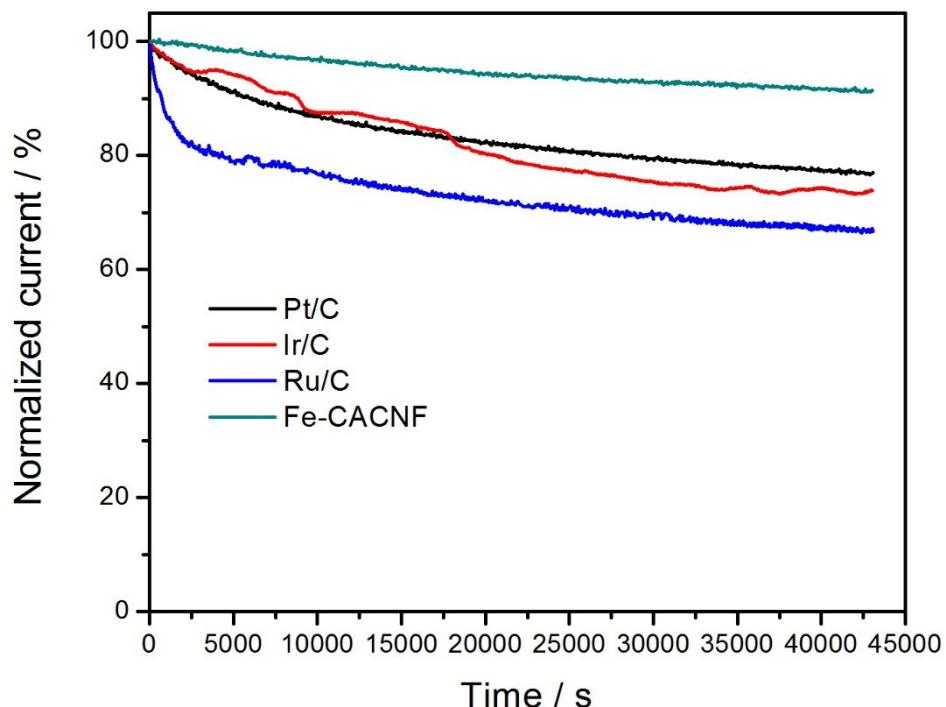


Figure S12 ORR stability of Pt/C, Ir/C, Ru/C and Fe-CACNF for 12 h.

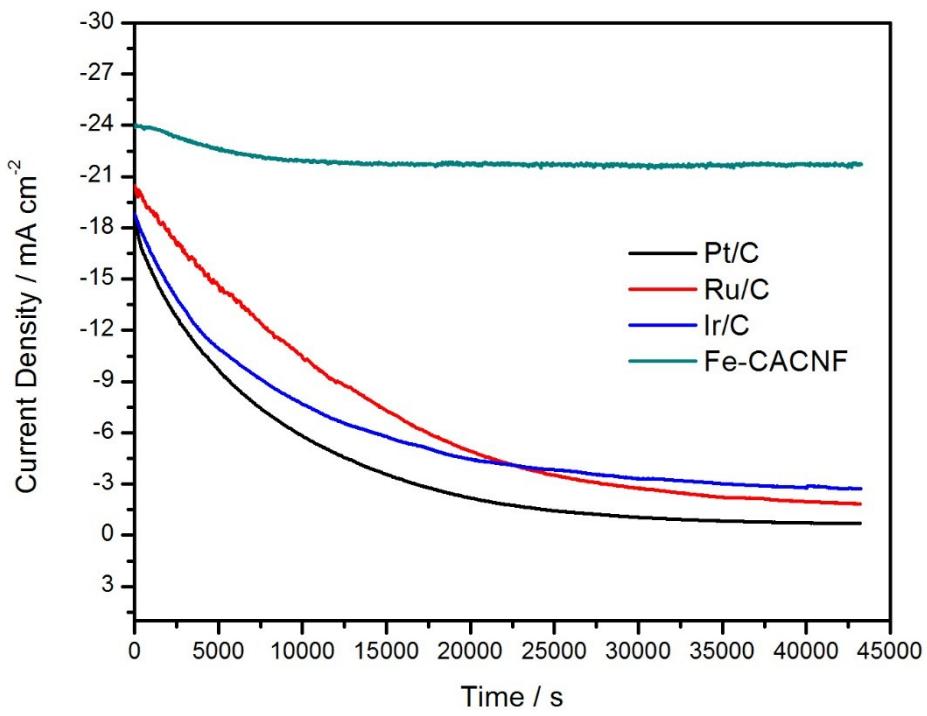


Figure S13 HER stability of Pt/C, Ir/C, Ru/C and Fe-CACNF for 12 h.

Table S1 The comparison of the ORR activities for Fe-CACNF with some recently reported ORR catalysts.

Catalyst	$E_{onset}$ / V	$E_{half-wave}$ / V	electrolyte	Ref.
Fe-CACNF	0.96	0.83	0.1M KOH	This work
Nanoporous carbon nanofiber films	0.97	0.82	0.1M KOH	1
Co <sub>4</sub> N carbon fibers network and carbon cloth	-	0.80	0.1M KOH	2
P-doped g-C <sub>3</sub> N <sub>4</sub> grown on carbon-fiber paper	0.94	0.67	0.1M KOH	3
Ni <sub>3</sub> Fe-N doped carbon sheets	0.90	0.78 (@-3 mA / cm <sup>2</sup> )	0.1M KOH	4
Fe/N-CNTs	0.96	0.81	0.1M KOH	5
Fe @ N-C	~0.95	0.83	0.1M KOH	6
Co@ Co <sub>3</sub> O <sub>4</sub> /NC-1	-	0.80	0.1M KOH	7
CoO/N-graphene	~0.90	0.81	1M KOH	8
Co-N-C HHMTs	0.92	0.82	0.1M KOH	9
NixCoyO <sub>4</sub> /Co-NG	-	0.80	0.1M KOH	10

Table S2 The comparison of the HER activities for Fe-CACNF with some electrocatalytic activities of the recently reported carbon-based HER catalysts.

Catalyst	Overpotential (mV) vs RHE @ 10 mA cm <sup>-2</sup>	electrolyte	Ref.
Fe-CACNF	330@10 mA/cm <sup>2</sup> 440@80 mA/cm <sup>2</sup>	1M KOH	This work
Ni <sub>3</sub> S <sub>2</sub> /MWCNTs	480	1M KOH	11
Co/N-doped CNTs	370	1M KOH	12
Fe@N-C	330	1M KOH	13
o-CoSe <sub>2</sub> /CC	270@10 mA/cm <sup>2</sup> 450@65 mA/cm <sup>2</sup>	1M KOH	14
FeCo@NCNTs-NH	~ 280	0.1M H <sub>2</sub> SO <sub>4</sub>	15
N, S-doped graphitic sheets	310	0.1M KOH	16
N, P Co-doped carbon network	470	0.1M KOH	17
Porous N-rich carbon/Co	300	1M KOH	18

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