Synthesis of graphitized hierarchical porous carbon supported transition-metal for electrochemical conversion

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Preparation of Ni/NC for TPD

The Ni/NC material was prepared using the same procedure with ho-Ni/NC just tuning the pyrolysis temperature to 700 °C. We choose this temperature for ensuring the carbon supported with metal atoms was obtained.

Preparation of hi-Ni/NC with different shell thickness

hi-Ni/NC(0.3) and hi-Ni/NC(0.4) samples were synthesized using the same method with hi-Ni/NC except that the amount of CaCO3 template to 0.3 g and 0.4 g, respectively.

Measurement of electrochemical performance:

A platinum wire and Ag/AgCl electrode were counter and reference electrode, respectively. The catalyst-coated rotating ring-disk electrode (RRDE) were used as the working electrode. The catalytic ink was obtained by dispersing the catalysts (3 mg) in EtOH (120 μL) and 5 wt % Nafion solution (30 μL). Then the ink (7 μL) dropped cast on the RRDE electrode to form a thin film. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) of prepared catalysts were conducted in O_2-saturated 0.1 M KOH （0.1 M $HClO_4$） solution. The kinetic process was obtained from Koutecky-Levich equation:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{1/2}}+\frac{1}{J_K} \qquad (1)$$

$$B=0.62nFC_0{D_0}^{2/3}V^{-1/6} \qquad (2)$$

where ω is the angular velocity of the disk. J, J_k and J_L present the measured, kinetic and limiting diffusion current densities, respectively. n is the electron transfer number. F is the Faraday constant (96485 C mol^{-1}). C_0 is the O_2 concentration (1.2×10^{-6} $mol\cdot cm^{-3}$). D_0 is the diffusion coefficient (1.9×10^{-5} $cm^2\cdot s^{-1}$), and V is the kinematic viscosity (0.01 $cm^2\cdot s^{-1}$) in the 0.1 M KOH solution.

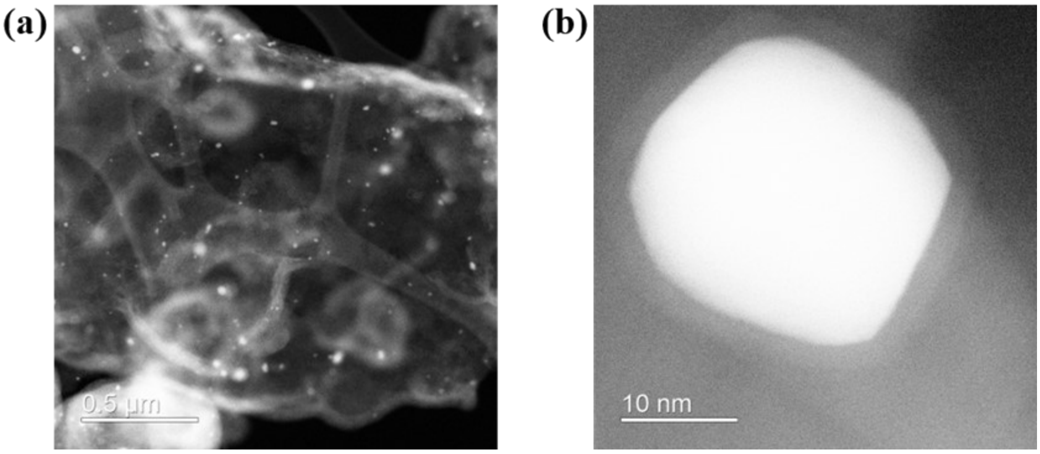

Fig. S1 The HAADF-TEM images of hi-Ni/NC at low (a) and high (b) magnifications.

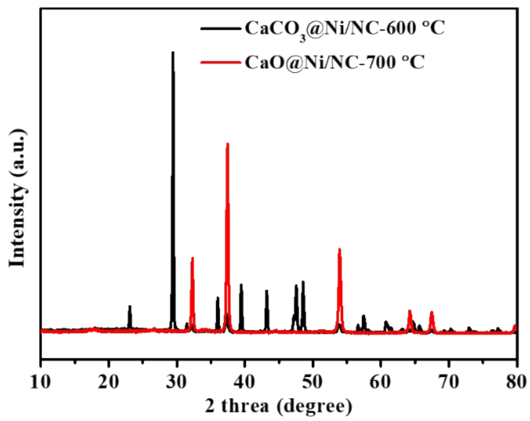

Fig. S2 The XRD patterns of $CaCO_3$@Ni/NC-600°C and CaO@Ni/NC-700°C.

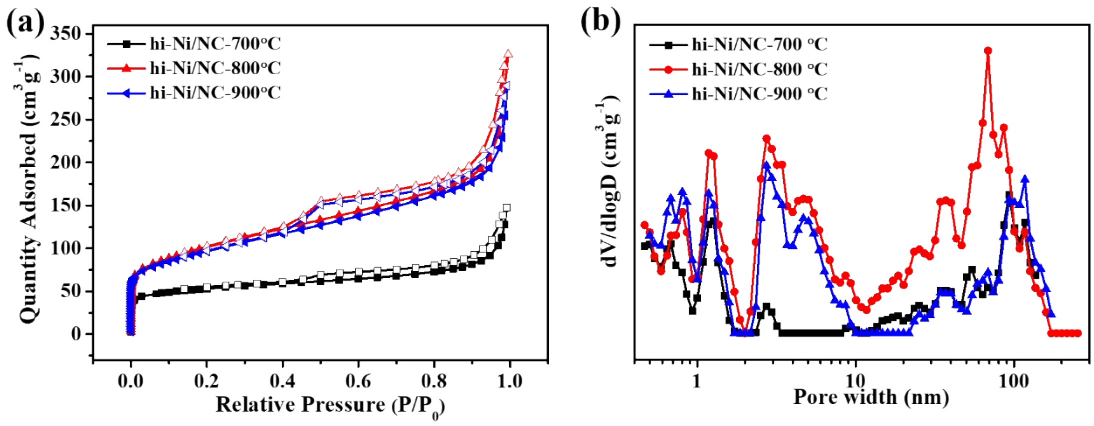

Fig. S3 The N_2 adsorption-desorption isotherms (a) and the pore size distribution (b) of hi-Ni/NC-700°C, hi-Ni/NC-800°C and hi-Ni/NC-900°C.

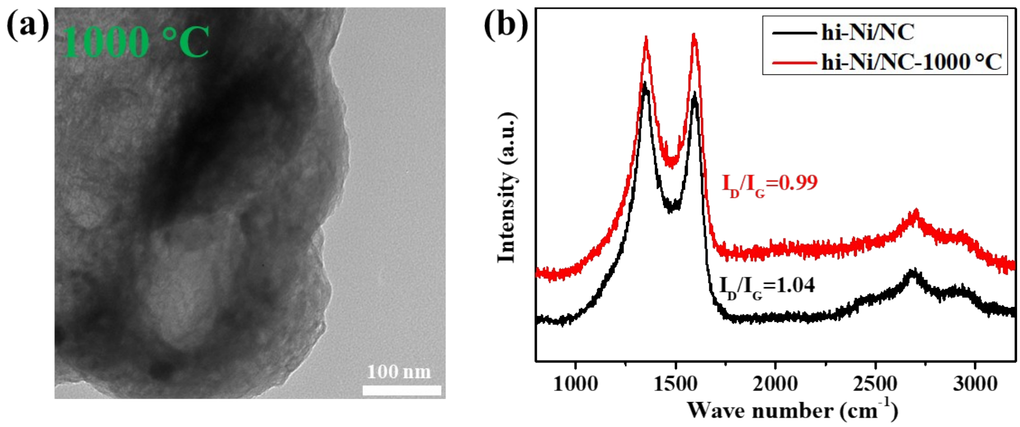

Fig. S4 (a) The TEM image hi-Ni/NC-1000 °C; (b) Raman spectra of hi-Ni/NC and hi-Ni/NC-1000 °C

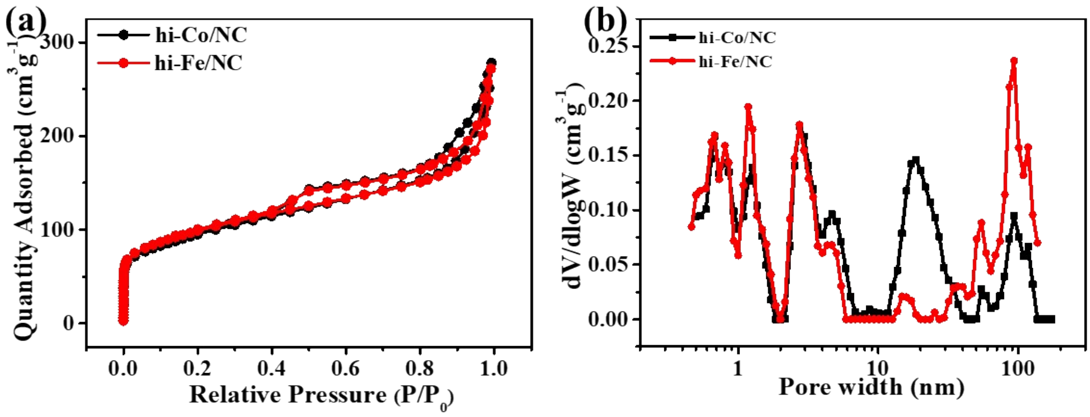

Fig. S5 The N_2 adsorption-desorption isotherms (a) and the pore size distribution (b) of hi-Co/NC, hi-Fe/NC.

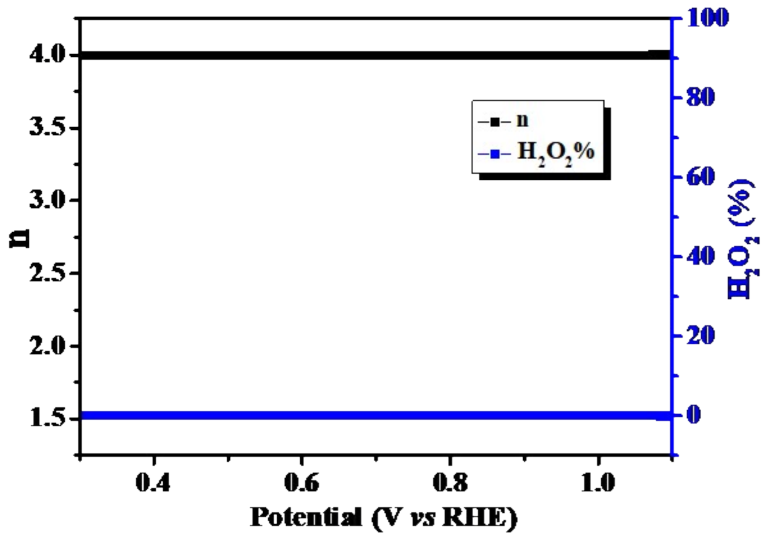

Fig. S6. The electron transfer number and H_2O_2% of hi-Fe/NC.

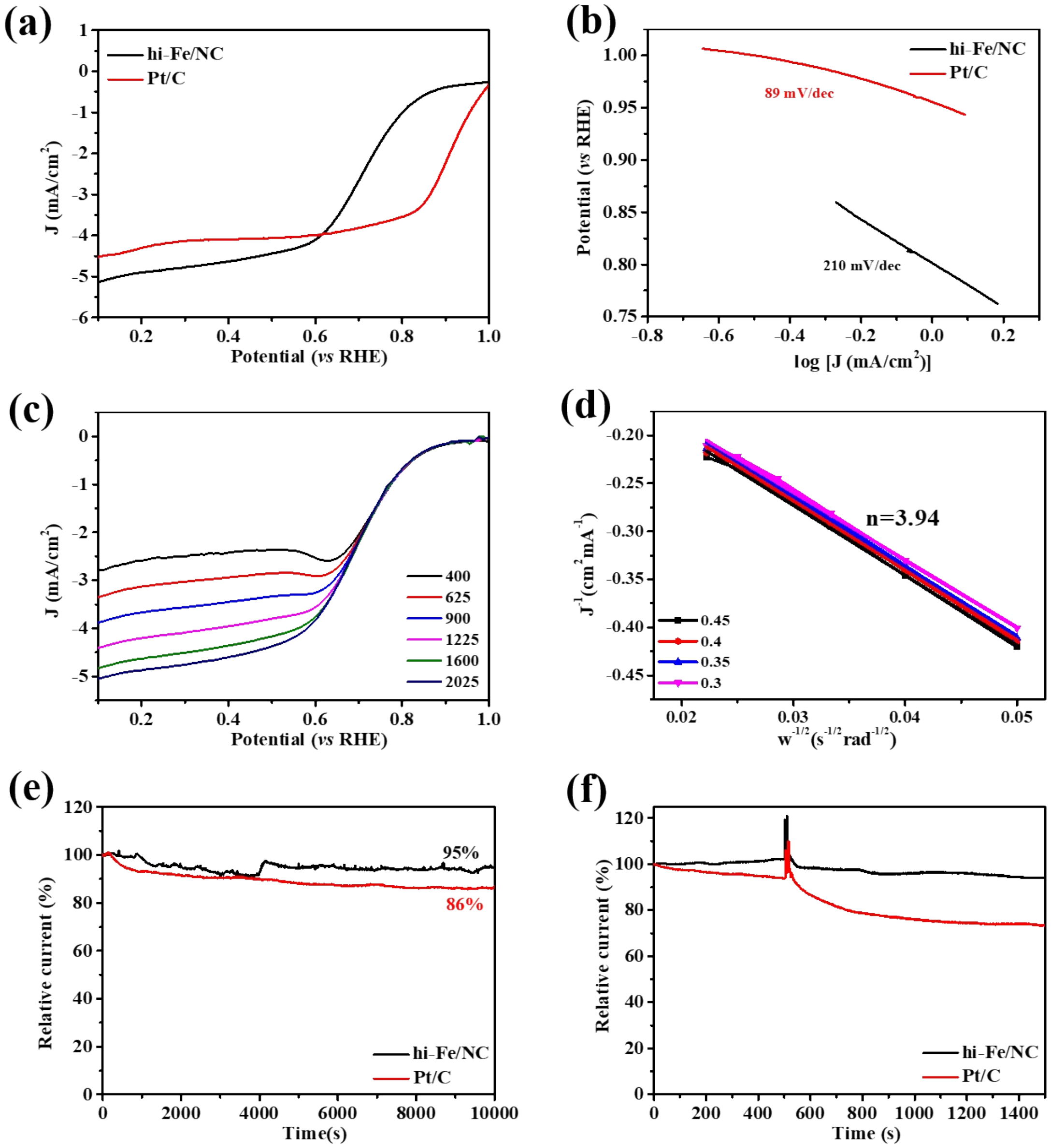

Fig. S7 The LSV curves of hi-Fe/NC and Pt/C in 0.1 M $HClO_4$ solution at the rotation rate of 1600 rpm (a); the Tafel plots (b); the LSV curves at the different rotation rates from 400 rpm to 2025 rpm (c); the electron transfer number (d); the i-t curves (e); and the methanol tolerance (f) of hi-Fe/NC.

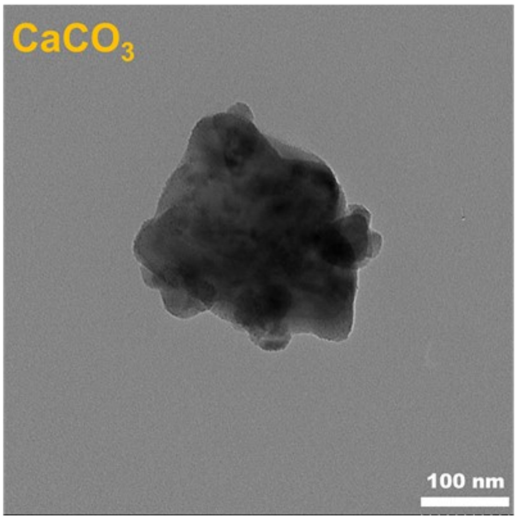

Fig. S8 The TEM image of CaCO3 template.

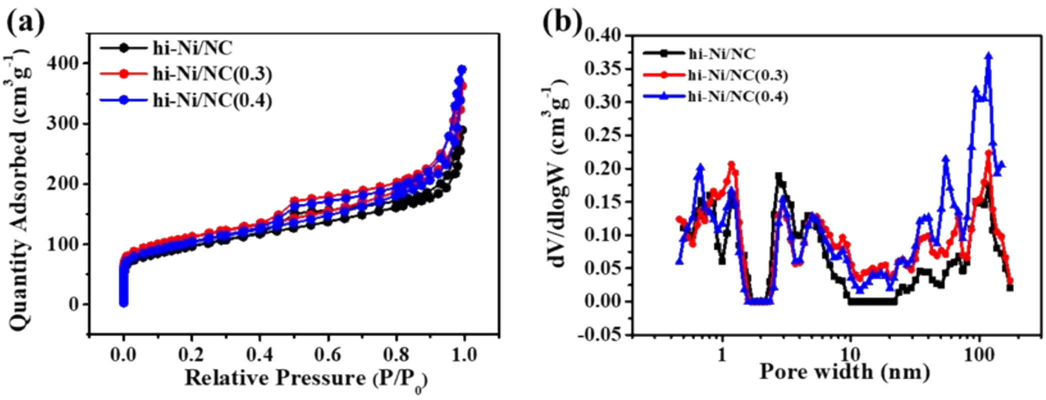

Fig. S9 The N_2 adsorption-desorption isotherms (a) and the pore size distribution (b) of hi-Ni/NC with different shell thickness.

As can be seen from Fig. S9, the N_2 adsorption-desorption isotherms and the pore size plots on three samples are almost same. No obvious relationship between the mesopore size and shell thickness of hi-Ni/NC

Table S1. Physico-chemical properties of the hierarchical porous carbons.

	Surface Area (m^2/g)	Micropore Area (m^2/g)	Mesopore Area (m^2/g)	Pore Volume (m^3/g)
hi-NC	132.7	105.2	44.9	0.18
hi-Ni /NC-1	249.5	201.9	129.1	0.29
hi-Ni /NC-2	281.8	229.5	171.1	0.35
hi-Ni/NC-3 (hi-Ni/NC)	340.4	251.0	220.3	0.44
hi-Ni/NC-700℃	194.4	151.4	68.4	0.22
hi-Ni/NC-800℃	343.3	235.5	231.8	0.5
ho-Ni/NC	291.1	255.3	49.0	0.25

Table S2. The Ni amount of the hierarchical porous carbon.

	hi-NC	hi-NC-1	hi-NC-2	hi-NC-3
Ni wt%	0 wt%	0.68 wt%	0.75 wt%	1.0 wt%

Table S3. Comparison of the ORR activities of the obtained hi-Fe/NC with previously reported Fe-based catalysts.

Catalyst	Electrolyte	$E_{1/2}$ (V vs. RHE)	Reference
FeSA-N-C	0.1 M KOH	0.891	*Angew. Chem. Int. Ed.* 2018, 57, 8525.
Fe-SAs/NSC	0.1 M KOH	0.87	*J. Am. Chem. Soc.* 2019, 141, 20118.
AC@f-FeCoNC900	0.1 M KOH	0.89	*Energy Environ. Sci.* 2019, 12, 1317.
Fe-N-C HNSs	0.1 M KOH	0.87	*Adv. Mater.* 2019, 31, 1806312.
Fe-N-C/FeN	0.1 M KOH	0.81	*Nano-Micro Lett*. 2020, 12, 163.
Fe-N-C/N-OMC	0.1 M KOH	0.93	*Appl. Catal. B-Environ.* 2020, 280, 119411.
meso-Fe-N-C	0.1 M KOH	0.846	*ACS Catal.* 2021, 11, 74-81.
Fe-N-C SA/HCF	0.1 M KOH	0.802	*Small.* 2020, 16, 1905920.
hi-Fe/NC	0.1 M KOH	0.93	[This work]