

Metal (metal=Fe, Co), N codoped nanoporous carbon for efficient electrochemical oxygen reduction

Xiaojuan Wang,^a He Fu,^a Wei Li,^a Jie Zheng,^{*a} and Xingguo Li^{*a}

^a *Beijing National Laboratory for Molecular Sciences (BNLMS), (The State Key Laboratory of Rare Earth Materials Chemistry and Applications), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.*

Pore size distributions calculation methods:

We carried out a calculation model – N₂ at 77K on carbon (slit/cylinder pores, QSDFT adsorption), which is integrated in the commercial software package ASIQwin from Quantachrome to analyze pore size distributions of our systems. Quenched state density functional theory (QSDFT), which is a multicomponent DFT, complements non-local density functional theory (NLDFT) and Grand Canonical Monte Carlo Simulation (GCMC) methods, and allows for a major improvement of the accuracy of DFT pore size distribution analyses of disordered carbon materials from low-temperature nitrogen adsorption isotherms. It is suitable to the calculation of pore size distributions from ca. 0.5 nm up to ca. 40 nm. In contrast to the previous NLDFT models that assumed flat, structureless, graphitic pore walls, the QSDFT method takes the effects of surface roughness and heterogeneity into account explicitly. The detailed QSDFT method is seen in Quantachrome's instructions.

Characterization of the samples

Composition analysis of the samples

Table S1 The composition (in wt%) and the BET surface area (S_{BET}) of the nC-based ORR catalyst samples.

Sample	N	C	H	Metal	S_{BET} (m ² g ⁻¹)
nC	0.12	88.79	0.3	-	694.7
N-nC	4.85	81.77	1.53	-	1006.0
Fe-nC	0.17	89.83	1.38	1.0	720.7
N-Fe-nC	2.47	81.45	1.83	2.0	870.8
Co-nC	0.13	90.55	1.18	2.0	676.4
N-Co-nC	2.75	88.83	0.82	5.6	845.1

Structural characterization

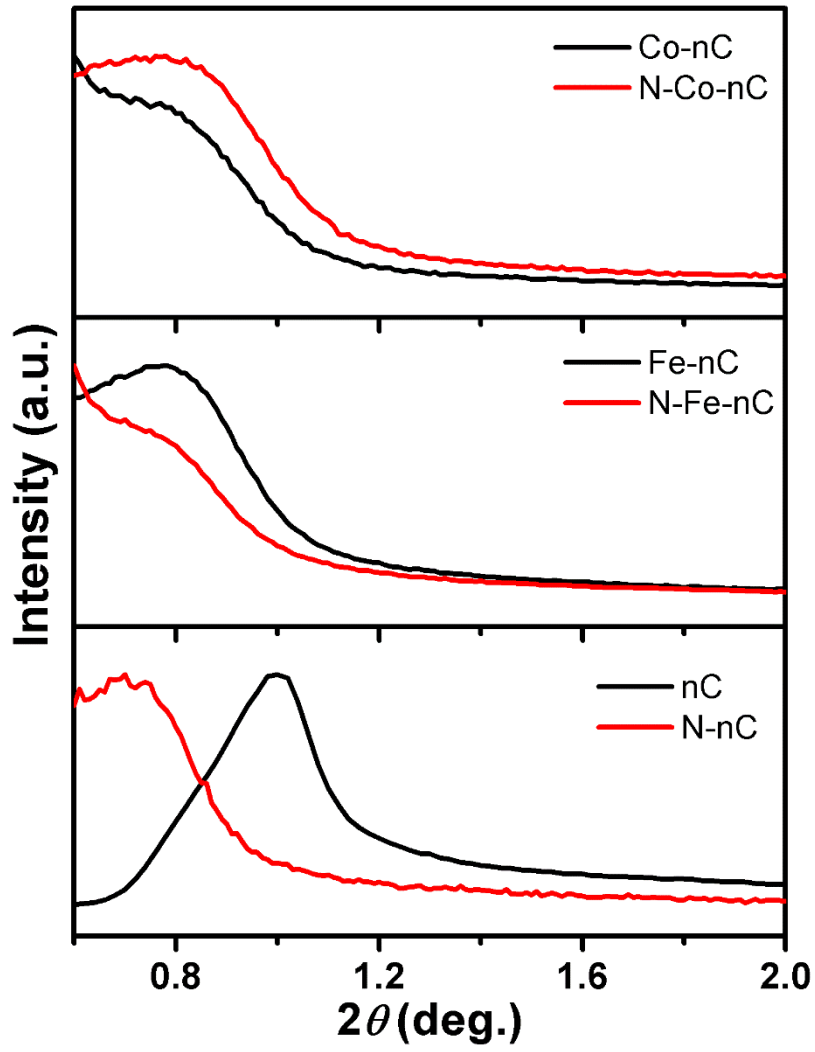


Figure S1. Small angle X-ray diffraction patterns of the modified nanoporous carbon materials.

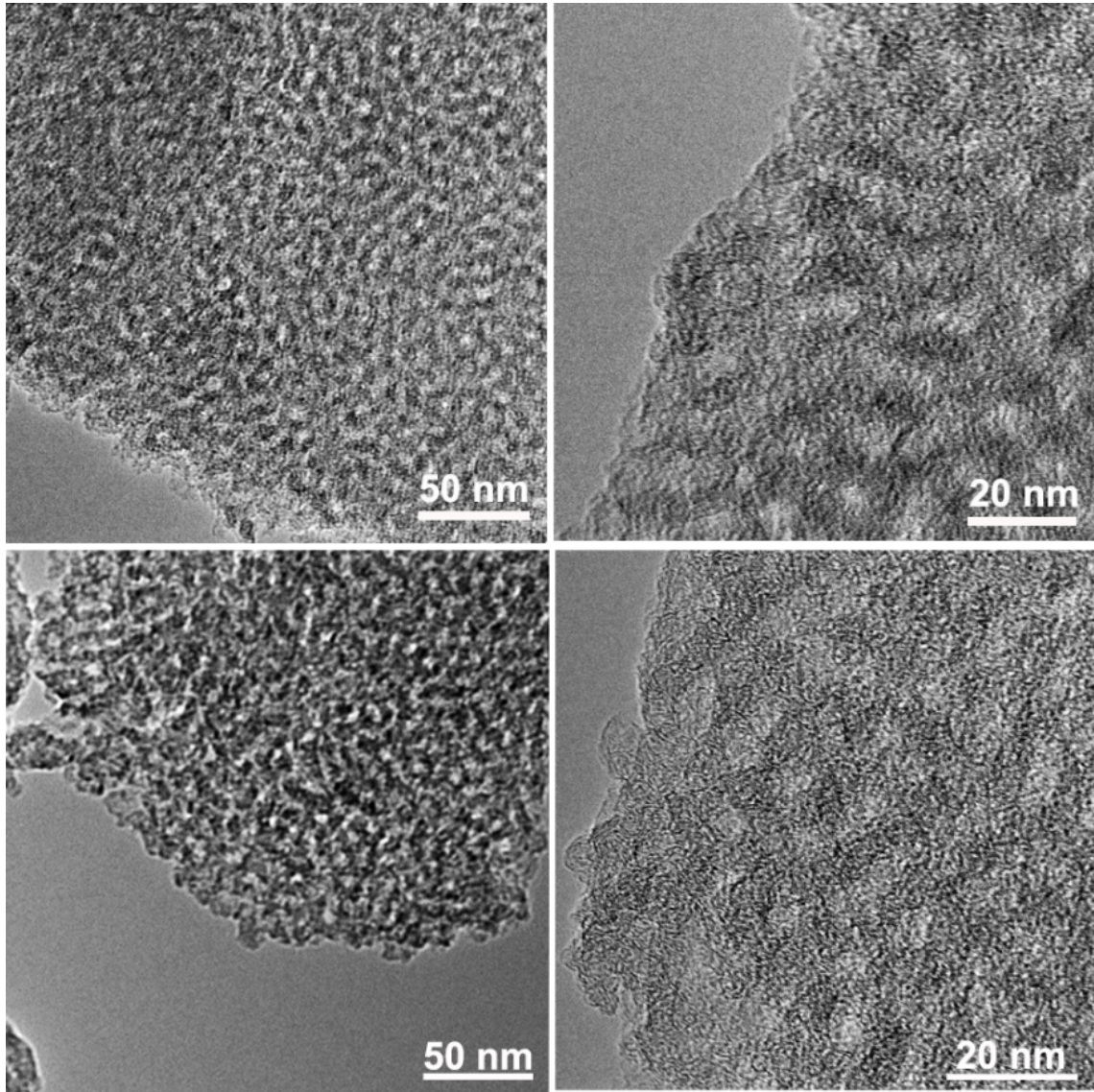


Figure S2. Additional TEM images of nC (a,b) and N-nC (c,d).

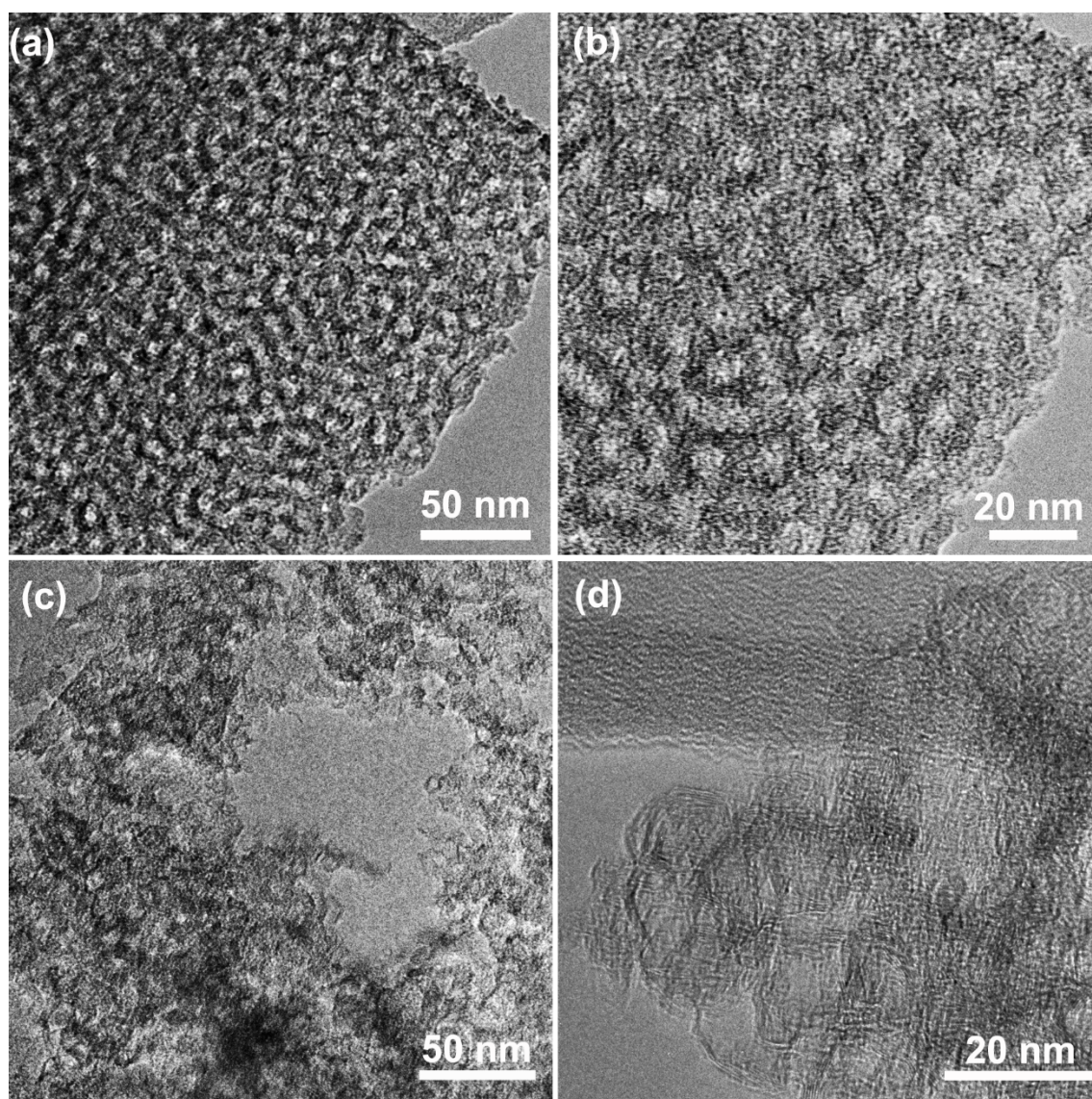


Figure S3. Additional TEM images of Fe-nC (a,b) and N-Fe-nC (c,d).

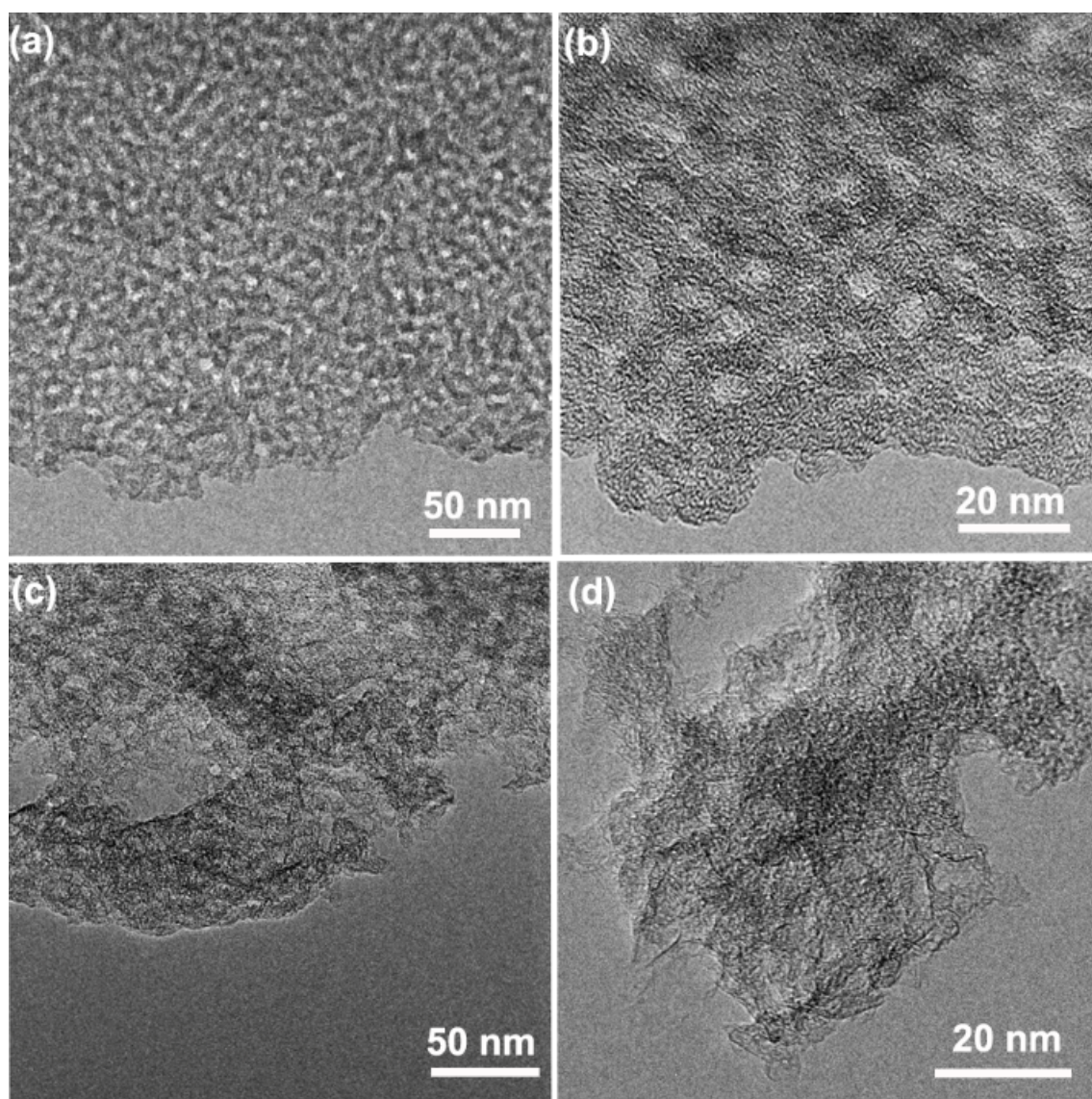


Figure S4. Additional TEM images of Co-nC (a,b) and N-Co-nC (c,d)

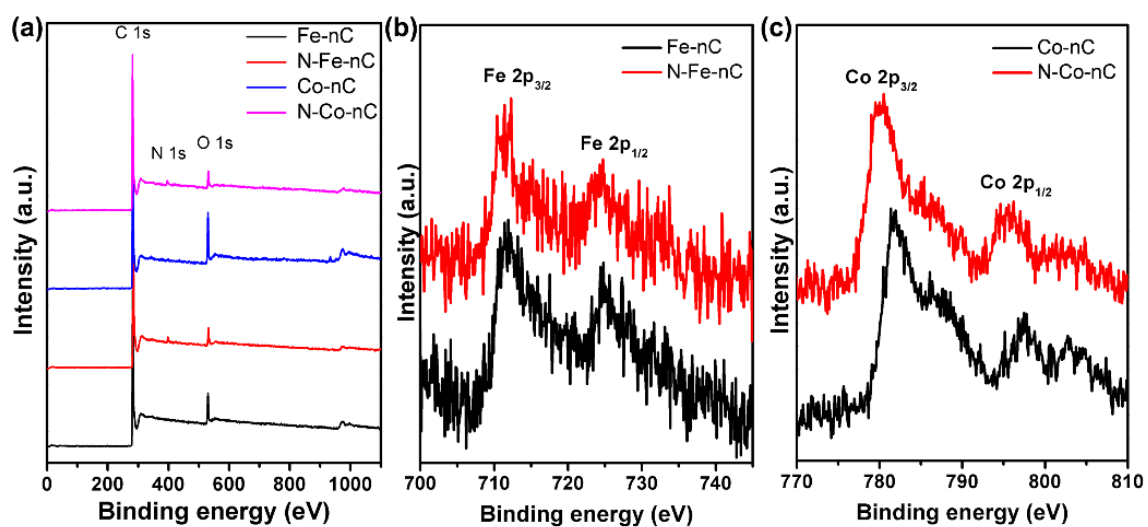


Figure S5. XPS survey scan of Fe-nC, N-Fe-nC, Co-nC and N-Co-nC (a); High resolution XPS spectrum of Fe 2p for Fe-nC and N-Fe-nC (b) and Co 2p for Co-nC and N-Co-nC (c). For high

resolution spectrum, eighty sweeps are carried out for Co 2p, Fe 2p. In the survey scan curves, there is few signals about iron and cobalt.

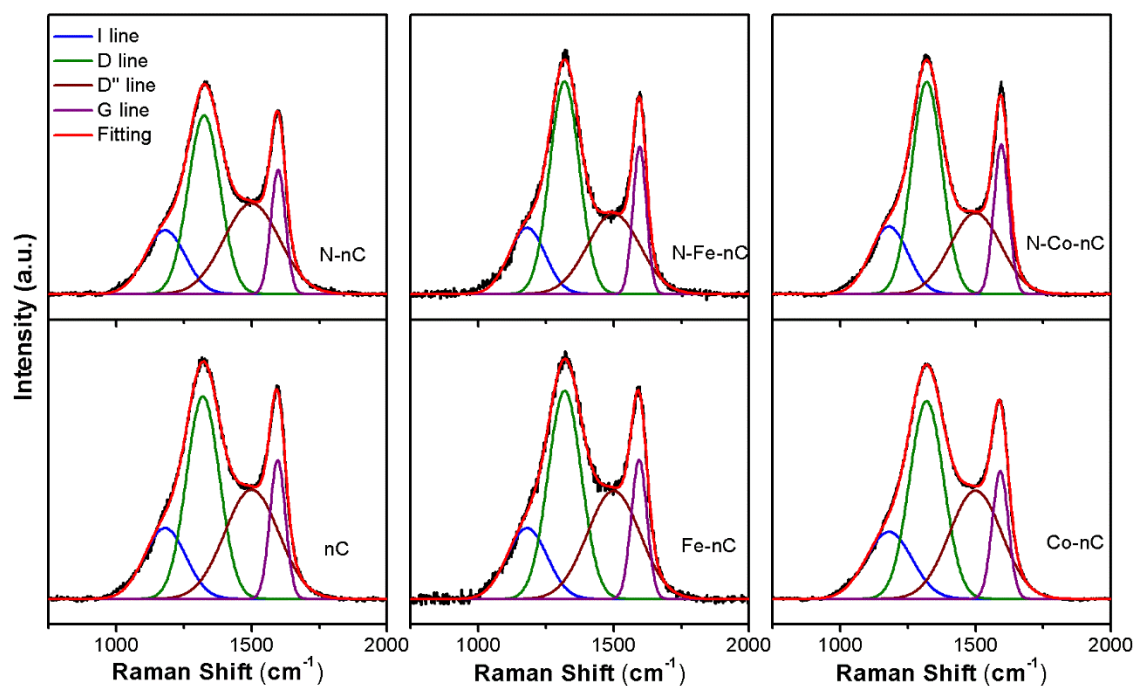


Figure S6. Raman spectra of the samples. The spectra are deconvoluted into four components following the approach by Sharifi et al¹ and Nitze et al²: the I band at 1180 cm^{-1} , the D band at 1340 cm^{-1} , the D'' band at 1500 cm^{-1} and the G band at 1590 cm^{-1} .

Electrochemical characterization

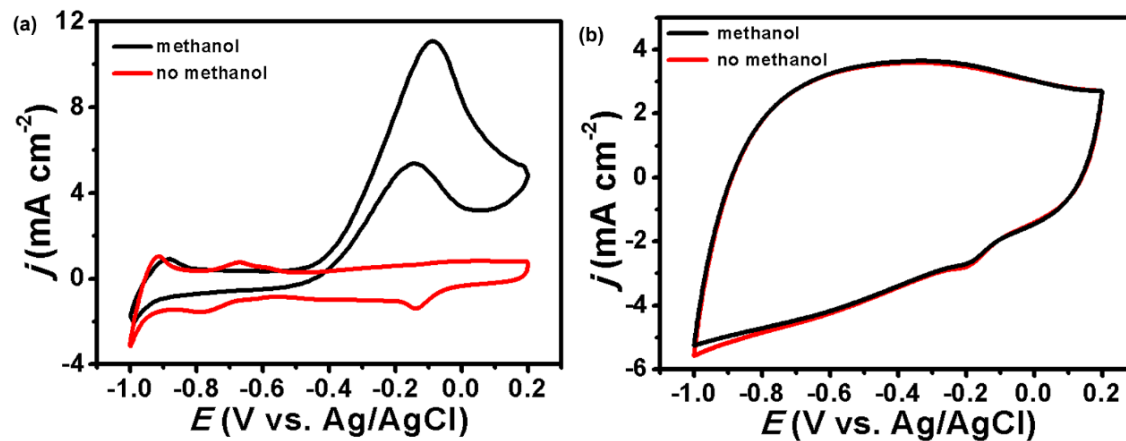


Figure S7 Cyclic voltammograms of Pt/C (a) and N-Fe-nC (b) in O_2 saturated 0.1 M aqueous KOH electrolyte solution and O_2 saturated 0.1 M KOH containing 1 M methanol at a scan rate of 50 mV s^{-1} .

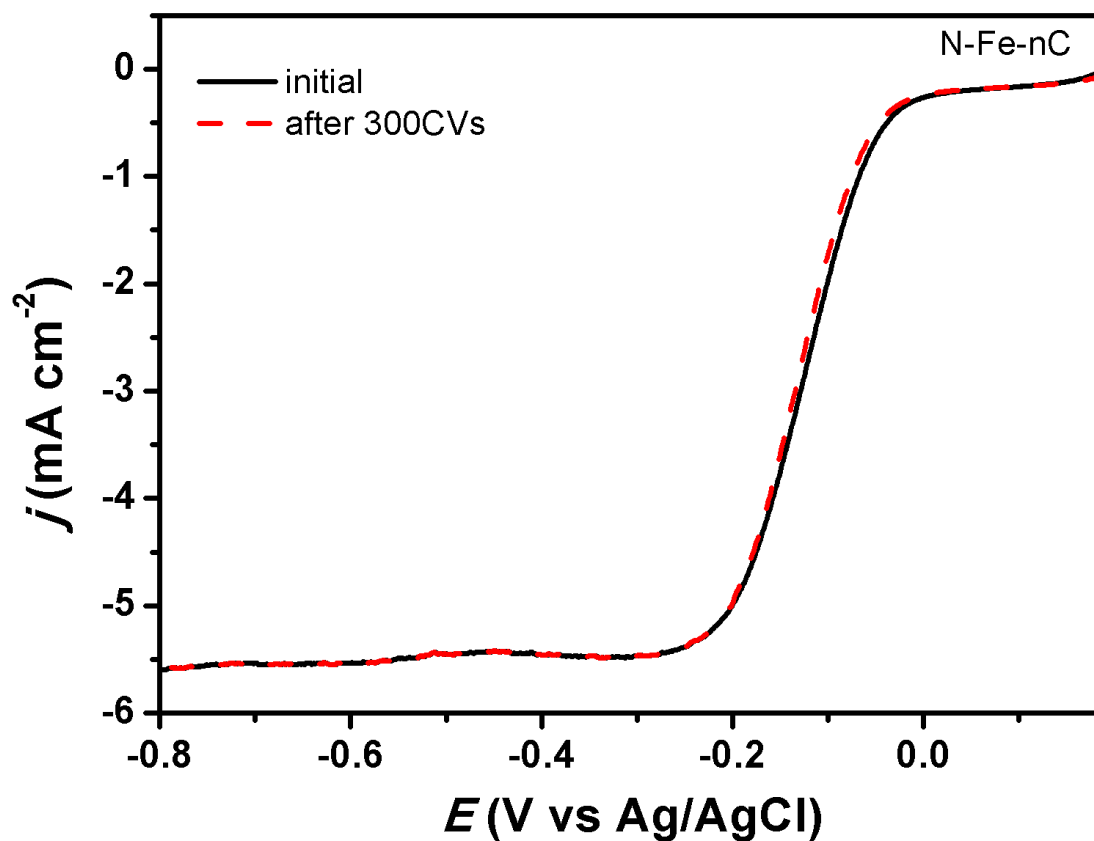


Figure S8. Characterization of the durability of the N-Fe-nC catalyst. RRDE polarization curves of the N-Fe-nC catalyst before and after 300 potential cycles in O₂-saturated 0.1 M KOH. Potential cycling was carried out between 0.2 and -1.0 V (versus Ag/AgCl) at 50 mV s⁻¹.

References

1. Sharifi, T.; Nitze, F.; Barzegar, H. R.; Tai, C.-W.; Mazurkiewicz, M.; Malolepszy, A.; Stobinski, L.; Wagberg, T. *Carbon* **2012**, *50* (10), 3535-3541.
2. Nitze, F.; Andersson, B. M.; Wagberg, T. *Physica Status Solidi B-Basic Solid State Physics* **2009**, *246* (11-12), 2440-2443.