

Enable Coal with High Electrocatalytic Activity for Oxygen Reduction Reaction via Nitrogen Doping

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It is of a great challenge to develop high efficient nonprecious electrocatalysts to replace Pt-based catalysts for oxygen reduction reaction (ORR). This study introduces a cost-effective and environmentally friendly ORR electrocatalyst based on nitrogen doped coal (NOC) via a pre-oxidization of raw coal followed by a urea assisted annealing process. The obtained materials show great electrocatalytic activity with the onset potential, half-wave potential, and diffusion-limited current density comparable to those of a commercial Pt/C catalyst. In addition, it follows a four-electron pathway and has relatively low peroxide yield. Finally, it exhibits a good stability and strong tolerance to methanol poisoning. The demonstrated high performance makes NOC a promising catalyst for applications in metal air batteries and alkaline fuel cells.

Surface morphology and microstructures of the raw coal (RC), OC, and the as-prepared NOC were first explored by scanning electron microscopy (SEM). As shown in Fig. 1a, after the ball milling, the raw coal exhibits an irregular surface as a bulk material. After oxidization, surface morphology of OC does not change much (Fig. 1b). After further pyrolysis, the resulting NOC exhibits highly porous microstructures (Fig. 1c-d), which can be attributed to the release of volatile matter in the coal during the high temperature thermal treatment. The energy-dispersive X-ray spectroscopy (EDS) elemental analysis was further performed on the area shown in Fig. 1d. As shown in Fig. 1e, besides the main element C, NOC also contains N, O, Si, Ca, Fe, Mg, Al, Si, S, and Ti. It should be noted that incorporation of these elements including Fe, Al, N, Si and S has been proved as an efficient way to boost the catalytic activity of the carbon based catalysts. Meanwhile, a detailed EDS spectrum corresponding to Fig. 1d shows

that N elements are uniformly distributed among the NOC matrix (Fig. 1f). High resolution transmission electron microscopy (HRTEM) was further performed to explore the structure.

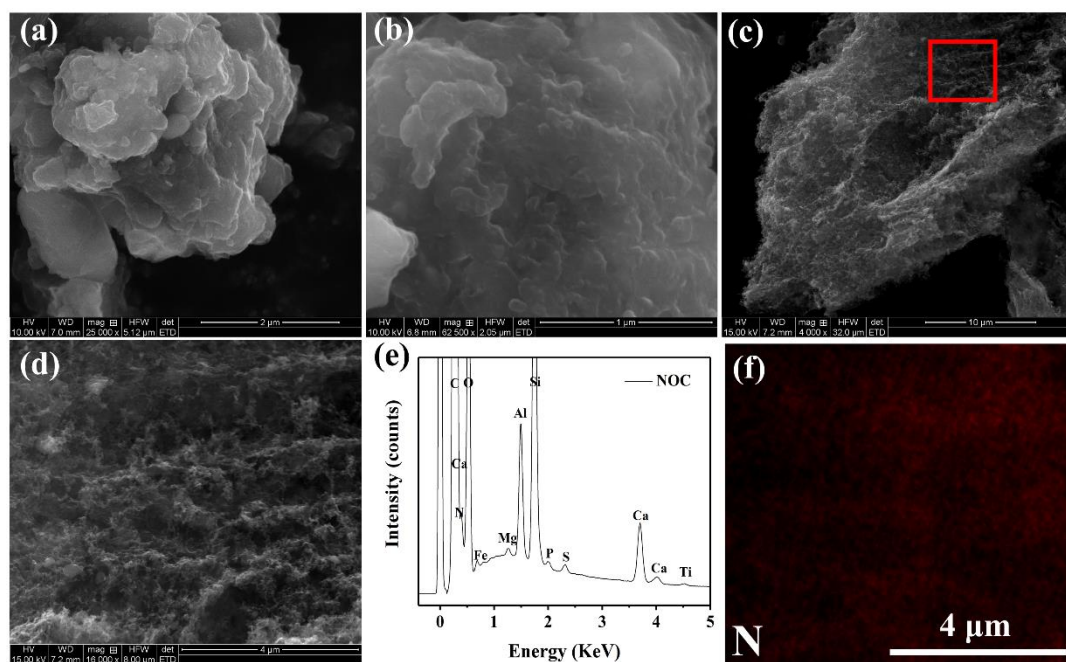


Figure 1. (a) SEM image of raw coal. (b) SEM image of oxidized coal. (c) SEM image of nitrogen doped oxidized coal (NOC). (d) Magnified SEM image of the selected area indicated in (c). (e) EDS spectra and (f) corresponding N elemental mapping of the area in Fig. 1d.

Electrocatalytic activity of the NOC was first assessed by the cyclic voltammetry (CV) in O_2 -saturated or N_2 -saturated alkaline solutions. As shown in the Fig. 2a, there is a prominent cathodic peak corresponding to O_2/OH^- in an O_2 saturated electrolyte within the potentials ranging from -0.05 to 1.5 V. This reduction peak vanished in the N_2 -saturated electrolyte, indicating a high ORR activity of NOC²⁸. Linear sweep voltammetry (LSV) measurement was further conducted to assess the activity of NOC at a scan rate of 10 mV/s (Fig. 2b). As a comparison, RC, NRC, and commercial 20 wt% Pt/C were evaluated under the same condition. Common descriptors for evaluating electrocatalysts toward ORR are the onset potential (E_{onset}) and half-wave potential ($E_{1/2}$). The onset potential is defined as the potential corresponding to a current density of -0.1 mA/cm²²⁹. A higher E_{onset} suggests a higher catalytic activity. E_{onset} of RC is

~0.752 V and it increases a little after directly nitrogen doping without oxidization. Whereas, NOC has a much more positive E_{onset} of 0.945 V, which is very close to that of Pt/C (0.966 V). NOC shows a high $E_{1/2}$ which corresponds to the potential at which half of the peak current is observed of 0.755 V. It is slightly smaller than that of the Pt/C (0.831 V), further verifying its superior activity. It also indicates that introduction of the peroxidation step can significantly improve the ORR activity. The high ORR activity of NOC is also reflected on its high diffusion-limited current density of 5.1 mA/cm² at 0.2 V (vs. RHE). It is almost the same to that of 5.2 mA/cm² for Pt/C and superior to many of the reported nonprecious catalysts. Fig. 2c reveals a small Tafel slope of 90 mV/dec delivered by the NOC, suggesting its good kinetic activity.

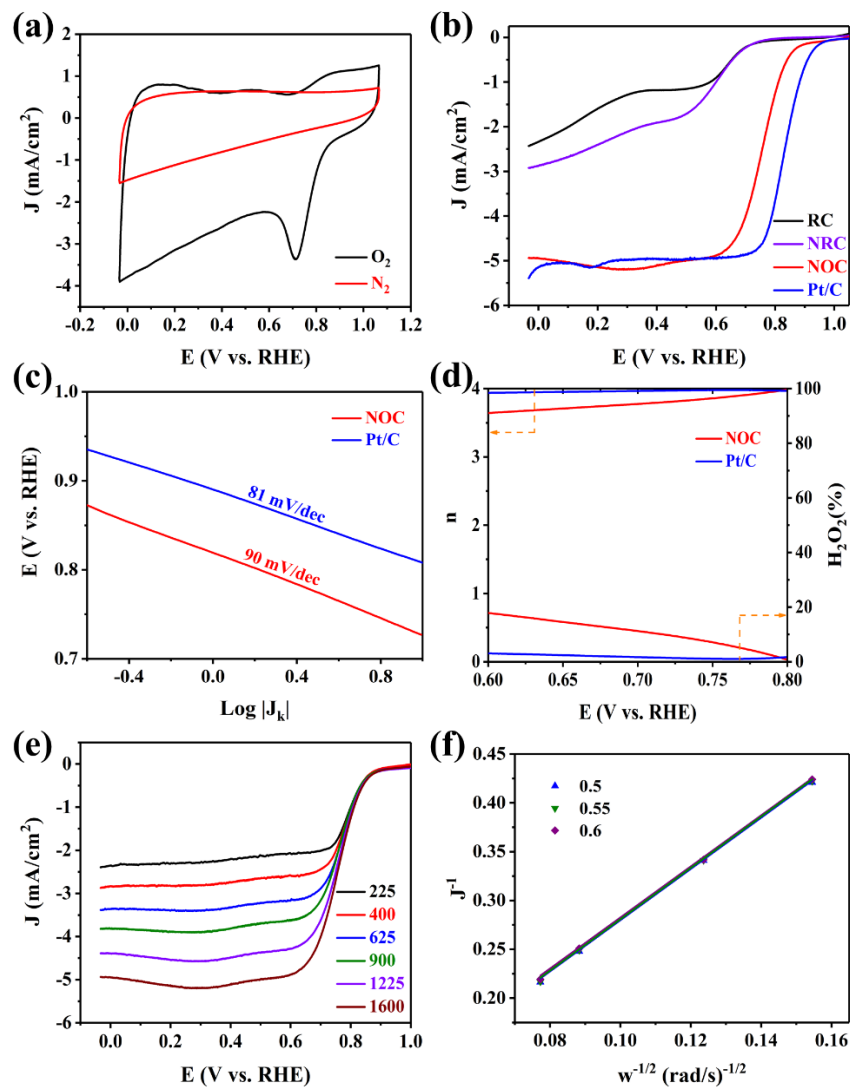


Figure 2. (a) Cyclic voltammetry curves of NOC in O₂-saturated or N₂-saturated 0.1 M

KOH electrolytes. (b) Linear sweep voltammetry (LSV) curves of RC, NRC, NOC and Pt/C at 1600 rpm. (c) Tafel slope (d) electron transfer number (n) and H_2O_2 yield of NOC and Pt/C. (e) LSV curves, and (f) Koutecky-Levich plots of NOC at different rotation speeds.

The electron transfer kinetics and the pathway of ORR can be further clarified by evaluating the electron transfer number (n) per O_2 molecule and the yield of peroxide molecule (H_2O_2 %) (Fig. 2d). The measured n of NOC at 0.7 V is 3.77, implying that it follows a four-electron pathway in a potential range of 0.6 V to 0.8 V. The LSV curves of NOC at different rotating speeds (225~1600 rpm) are plotted in the Fig. 2e. As expected, the E_{onset} remains constant, while the cathodic current density increases with the increase of the rotation speeds, which is due to the enhanced mass transport. Fig. 2f is the corresponding Koutecky-Lecich (K-L) plot under different applied potentials. The good linearity of the K-L plot indicates the first-order reaction kinetics. The fitted lines measured under different potentials are almost parallel, suggesting consistent n values. The calculated n is 3.7 agrees well with the result shown in Fig. 2d, further demonstrating the four-electron pathway.