Supporting Information

Synergistic Incorporation of Hybrid Heterobimetal-Nitrogen Atoms into Carbon Structures for Superior Oxygen Electroreduction Performances

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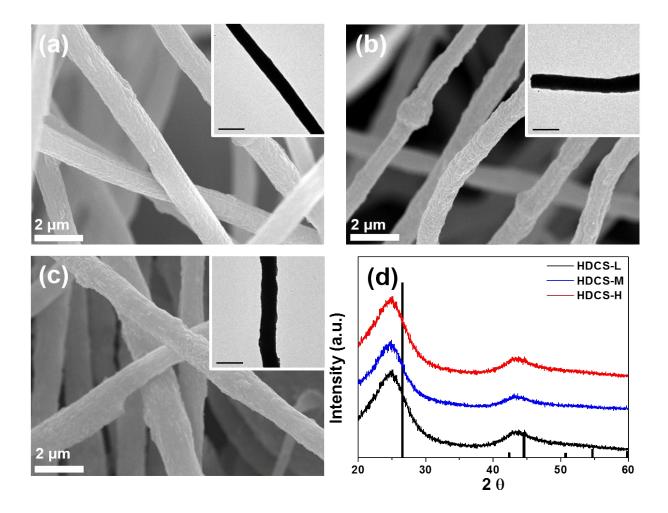


Fig. S1. SEM images of (a) electrospun HDCS-L, (b) HDCS-M, and (c) HDCS-H. The insert indicates corresponding TEM images and all scale bars are $2\mu m$. (d) XRD patterns of the as-prepared HDCSs in comparison with XRD reference data of carbon (JCPDS No. 89-8487, black bar).

To further identify the morphology of the as-prepared HDCSs, we performed TEM analysis. As shown in the insert of Fig. S1(a-c). All as-prepared HDCSs consist of an 1-D structure and diameter of approximately $0.8 \sim 1.2 \mu m$, which is in good agreement with the SEM data. Furthermore, to confirm doping effects of the transition metal element on the carbon structure, the XRD patterns of as-prepared HDCSs are compared with XRD reference data of carbon. In particular, as indicated in Fig. S1(d), the peaks of the as-prepared HDCSs were slightly shifted towards lower diffraction angles, resulting from the increase in inter-spacing distances of carbon structure due to the presence of the incorporated hybrid dopants, which is good agreement in previously reported results.^{R1-3}

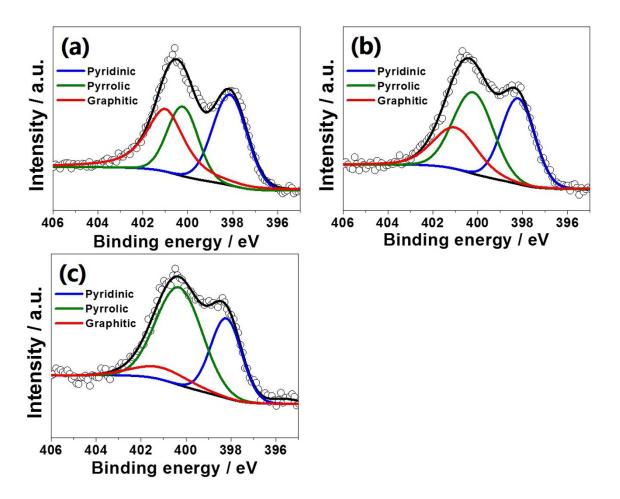


Fig. S2. N 1s spectra of (a) HDCS-L, (b) HDCS-M, and (c) HDCS-H, which were consisted of the pyridinic-N (blue), pyrrolic-N (green), and grphitic-N (red) bond, corresponding to around 398 eV, 400.5 eV, and 401.5 eV, respectively.

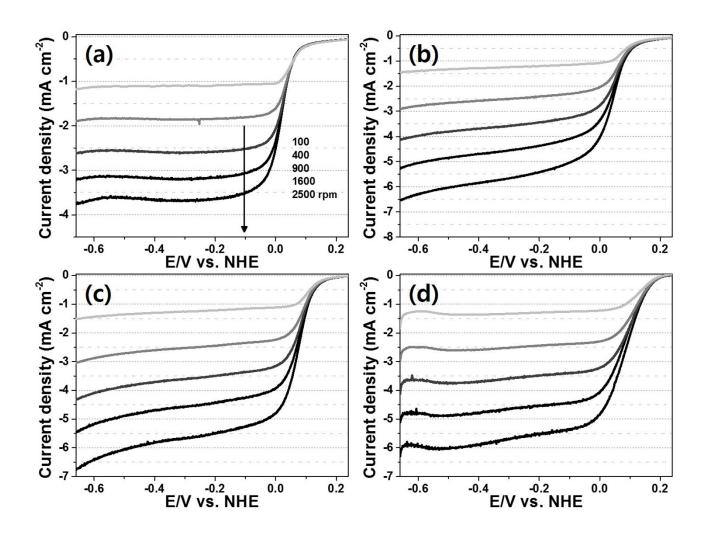


Fig. S3. LSVs of (a) HDCS-L, (b) HDCS-M, (c) HDCS-H, and (d) Commercial Pt electrocatalysts at various rotation speeds from 100 to 2500 rpm in an O₂-saturated 1.0 M KOH electrolyte.

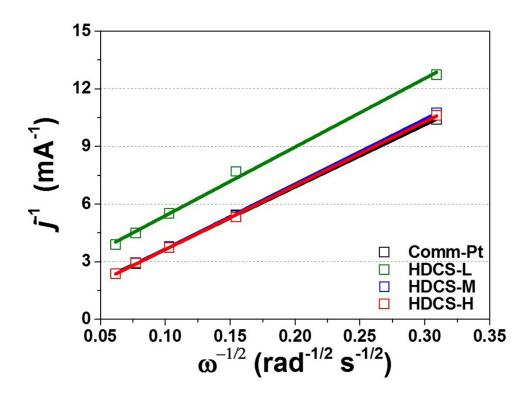


Fig. S4. Koutecky-Levich plots of the HDCSs and Commercial Pt electrocatalysts at -0.46 V.

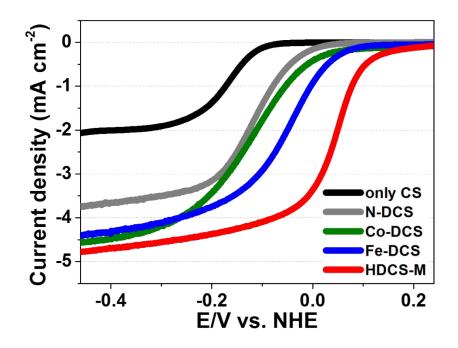


Fig. S5. LSVs of the only CS, N-DCS, Co-DCS, Fe-DCS, and HDCS-M electrocatalysts in an O₂-saturated 1.0 M KOH electrolyte at a rotation speed of 1600 rpm.

To further identify the effect of dopants, we prepared Fe-N, Co-N, and N doped carbon structure (denoted as Fe-DCS, Co-DCS, and N-DCS, respectively) with 5 wt % of Fe-Pc, Co-Pc, and Pc precursors, respectively, in an electrospun solution under same conditions as used for the HDCS-M electrocatalyst. Also, for comparison of the effect of transition metal doping, an un-doped carbon structure (denoted as only CS) was prepared in the absence of M-Pc precursors. As shown in Fig. S5, the catalytic activity of as-prepared electrocatalysts increases the following order: HDCS-M > Fe-DCS > Co-DCS > N-DCS > only CS, which is attributed to well-distributed hybrid bimetallic dopants surrounded by N species as active sites on HDCS-M electrocatalysts. Here, we also note that it has been reported that the coexistence of Fe and Co adatoms bound with N can reduce the binding energy of oxygen molecules on a non-precious electrocatalyst, inducing the modification of eledctronic structures, such as down-shifting of the d-band center, compared to individual Fe-N or Co-N bonding.^{R4} Therefore, we believe this is another reason why we achieved the outstanding ORR activity of the HDCS-M. These findings are consistent with the previously reported results.^{R4-8}

References

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