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Unveiling the Activity Origin of Electrocatalytic Oxygen Evolution over Isolated Ni Atoms Supported on N-doped Carbon Matrix

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Abstract

Exploring highly efficient electrocatalysts for the oxygen evolution reaction (OER) and unveiling their activity origin are pivotal for energy conversion technologies. Herein, we report atomically distributed Ni sites over N-doped hollow carbon matrix as a promising electrocatalyst for OER in alkaline conditions. Significantly boosted activity is observed after the decoration of active Ni sites with well-controlled coordination geometry. Results of X-ray absorption spectroscopy investigation and density functional theory calculation reveal that the effective electronic coupling via the Ni-N coordination can move down the Fermi level and lower the adsorption energy of intermediates, thus resulting in the facilitated OER kinetics.

Keywords: single-atom catalysis, electronic coupling, hollow carbon matrix, oxygen evolution reaction

Electrochemical water splitting is expected to be an attractive approach for addressing the forthcoming fossil fuel depletion and environmental issues. Oxygen evolution reaction (OER), which occurs at the anode in the water splitting process, suffers from intrinsically sluggish kinetics and thus restricts the overall efficiency of the energy conversion.^[1-3] Therefore, highly efficient electrocatalysts for reducing the overpotential of OER are required to improve the efficiency of water splitting. RuO₂ and IrO₂ are the benchmark OER electrocatalysts with appreciable turnover frequencies at moderate overpotentials. However, their widespread applications are limited by the scarcity and high cost.^[4-5] While great endeavor has been devoted to improving the performance of earth-abundant electrocatalysts for replacing the precious metal-based catalysts, the catalytic performances of currently developed electrocatalysts are still not very satisfactory.^[6-9]

Among various promising alternatives, single-atom catalysts (SACs) with the isolated active sites have attracted tremendous interest and emerged as a new frontier in electrocatalysis.^[10-15] Compared with traditional metal particle-based electrocatalysts, SACs possessing the refined coordination geometry and the strong metal-support interaction provide the maximum atomic efficiency.^[16-20] These characteristics offer an ideal model for developing highly efficient electrocatalysts and exploring the origin of the activity. Though great efforts have been devoted, the electronic structure of SACs has remained elusive and the origin of OER activity of SACs is still not clear. These actualities impede the understanding of these catalysts and the design of new SACs for water splitting.

Here, we report a facile approach for constructing isolated Ni and N atoms decorated on hollow carbon matrix (HCM@Ni-N), and further determine its atomistic structure and the correlation with electrocatalytic activity towards the OER. The configurations of the decorated heteroatoms are

identified by the X-ray absorption spectroscopy investigations, which confirms that the isolated Ni atoms are coordinated with surrounding N atoms in unsaturated coordination geometry. The measured OER performance of HCM@Ni-N is corroborated with theoretically computed adsorption energetics. Combining experimental and theoretical approaches, we reveal that effective electronic coupling via the Ni-N coordination is critical for regulating the OER mechanism. Specifically, we believe that the electronic coupling can significantly move down the Fermi level, which may cast great influence on the adsorption of intermediates as well as the final OER kinetics.

The synthetic procedure of HCM@Ni-N is shown in **Figure 1a**. First, the core-shell silica@resorcinol formaldehyde (SiO₂@RF) nanospheres are synthesized as the precursor.^[21] Field-emission scanning electron microscopy (FESEM) images reveal the spherical morphology of the obtained sample, while transmission electron microscope (TEM) observations confirm the core-shell structures (Figure S1, Supporting Information). Subsequently, a layer of methylimidazole-Ni (MI-Ni) is coated on the surface of SiO₂@RF by evaporating the mixture of SiO₂@RF, MI and Ni(NO₃)₂ under decompression conditions at 70 °C. As indicated by FESEM observation, the obtained SiO₂@RF@MI-Ni preserves the spherical morphology (Figure S2, Supporting Information). The as-prepared SiO₂@RF@MI-Ni is converted into HCM@Ni-N through pyrolysis and acid etching processes. The carbonization of SiO₂@RF@MI-Ni is studied by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. An obvious exothermic process together with a quick weight loss starts at ~100 °C and ends at ~580 °C (Figure S3, Supporting Information). This process corresponds to the transformation of RF into carbon matrix, accompanied by the gradual fusion of Ni-N species into the matrix. Finally, the sample is etched by diluted HF for removing SiO₂ and other unstable species, and the HCM@Ni-N electrocatalyst is obtained. The control samples of HCM, N-

doped HCM (HCM@N) and isolated Ni atoms decorated HCM (HCM@Ni) (Figure S4, Supporting Information) with nearly identical morphology are also constructed by the similar synthetic method.

FESEM observation of HCM@Ni-N shows the well-maintained spherical morphology with nearly intact shells (Figure 1b, c). TEM observations not only demonstrate the inner hollow space in the porous architecture of HCM@Ni-N, but also confirm that no nanoparticle or cluster is present in HCM@Ni-N (Figure 1d-f). To further determine the atomic structure, annular dark-field (ADF) imaging has been conducted on an aberration-corrected scanning transmission electron microscope (STEM) system. As observed in the Figure 1g, isolated single Ni atoms are clearly observed on the carbon support, which is the direct evidence for the existence of atomically distributed Ni sites over the HCM@Ni-N. The high-angle annular dark field (HAADF)-STEM and related elemental mappings of C, N and Ni confirm that the atoms are distributed uniformly over the entire nanosphere (Figure 1h, i). The HCM@Ni-N has also been studied by the energy-dispersive X-ray spectroscopy (EDX) and linear EDX scanning (Figure S5 and S6, Supporting Information).^[22] The obtained results further verify the uniform distribution of Ni species over the entire particle. As measured by inductively coupled plasma mass spectrometry (ICP-MS), the loading amount of Ni is about 1.27 wt.% in HCM@Ni-N. The X-ray diffraction (XRD) pattern of HCM@Ni-N displays only typical diffraction peaks of graphitic carbon (Figure S7, Supporting Information). All above characterizations imply that Ni species should exist in the form of isolated atoms.

We have conducted X-ray absorption fine structure analyses for confirming the coordination geometry of the Ni species.^[23-24] As shown in **Figure 2a**, HCM@Ni-N exhibits similar Ni K-edge extended X-ray absorption fine structure (EXAFS) magnitude to that of HCM@Ni and presents the main peak at about 1.49 Å. No obvious peak for the Ni-Ni interaction is observed. These results

further demonstrate that Ni atoms should exist in the single-atomic form in the hybrids.^[25] Further quantitative EXAFS curve fitting analyses for HCM@Ni-N and HCM@Ni confirm that the coordination numbers in the first coordination sphere of Ni center are estimated to be 4.1 and 4.3 at the distance of 1.91 and 1.88 Å, respectively (Figure 2b, c, Figure S8 and Table S1, Supporting Information). The coordinatively unsaturated Ni centers with square-pyramidal configuration are thus confirmed.^[26-28] For better identifying the structures in atomic scale, X-ray absorption near-edge structure (XANES) spectroscopy is applied for its higher sensitivity in confirming the three-dimensional arrangement of atoms around the photo-absorber (Figure 2d). The apparent distinction of XANES profiles between HCM@Ni-N and Ni foil directly rules out the Ni-Ni interaction in HCM@Ni-N. On the other hand, the characteristic pre-edge peaks at about 8342 eV arising from a 1s-4p_z shakedown transition are observed in HCM@Ni-N and HCM@Ni, confirming that the square-planar configuration of a Ni center with high D_{4h} symmetry.^[29-30] We have also performed wavelet transform (WT) analysis for verifying the coordination environments of Ni centers. A WT intensity maximum near 6.0 Å⁻¹ arising from the light atom coordinator is well resolved at 1.0 to 2.0 Å for HCM@Ni-N and HCM@Ni, whereas an intensity maximum at ~7.9 Å⁻¹ related to the Ni-Ni coordination is absent (Figure 2e). These findings clearly verify the unsaturated coordination geometry of the isolated Ni sites in the hybrids of HCM@Ni-N and HCM@Ni.^[31]

To further examine the coordination environment and charge transfer related to the isolated Ni sites, C K-edge and N K-edge XANES spectra are also investigated. The C K-edge spectra of HCM@Ni-N and HCM@N are dominated by the two characteristic peaks arising from the carboatomic rings (**Figure 3a**). The peaks at about 285.7 eV and 288.5 eV are related to the C-C π^* transition and C-C σ^* transition, respectively.^[32] Three obvious peaks are observed at ~401.5 eV,

~402.5 eV and ~406.9 eV in the N K-edge XANES of HCM@N, arising from π^* transition of C-N-C, N-₃C and σ^* transition of C-N, respectively (Figure 3b).^[33] In contrast to the Ni-free hybrid HCM@N, HCM@Ni-N exhibits an additional peak at about 399.4 eV, corresponding to the presence of π^* transition from C-N-Ni bonding. Moreover, slight shifts of the peaks to lower binding energy are also observed, confirming the charge transfer from Ni atoms to the carbon matrix via the Ni-N bonding.^[33]

X-ray photoelectron spectroscopy (XPS) and Raman spectra have also been acquired for further providing structural information. The high-resolution XPS spectrum of Ni 2p in HCM@Ni-N shows peaks corresponding to Ni 2p_{3/2}, Ni 2p_{1/2} and related satellite peaks. It should be noted that no peak assigned to zero-valence nickel is observed, indicating that the nickel atoms are mostly coordinated with the surrounding nitrogen atoms (Figure 3c).^[14,15] The high-resolution N 1s spectrum of HCM@Ni-N displays four deconvoluted peaks ascribed to Ni-N (399.6 eV), pyridinic N (400.6 eV), pyrrolic (401.9 eV) and graphitic N species (402.6 eV) (Figure 3d and Figure S9, Supporting Information).^[16] Raman analysis is also performed for analyzing the structure of carbon matrix (Figure 3e). The D band peak at about 1350 cm⁻¹ is induced by defects while the G band peak at about 1585 cm⁻¹ is highly dependent on the first-order scattering of the E_{2g} mode of sp²-C domains.^[34] It can be observed that the structural disorder of carbon matrix can be improved by the Ni and N dopants, evidenced by the increased intensity ratios of I_D/I_G from HCM (0.97) to HCM@Ni-N (1.09) (Figure 3e).^[35] N₂ sorption isotherms are investigated to reveal the textural information of the material (Figure 3f and Figure S10, Supporting Information). The highly porous structure of the HCM@Ni-N architecture is clearly confirmed by the typical type-II isotherm.

The well-solved atomistic structure with the direct Ni-N coordination provides an ideal model to probe the electronic structure modulation in determining the catalytic activity. Density functional theory (DFT) simulations are first conducted for obtaining insights into the electronic nature and the consequent OER energetics (Figure S11, Supporting Information). The calculated distributions of charge densities confirm the obvious changes after the Ni decorations (Figure S12, Supporting Information). The newly emerged electronic states should be ascribed to the hybridization between Ni (3d orbital) and the surrounding nonmetal atoms (Figure S13, Supporting Information). Compared with the densities of state of HCM@Ni, a leftward shift of the of Ni-3d orbital in HCM@Ni-N around the Fermi level (E_F) can be well observed (Figure S14 and Figure S15, Supporting Information).^[36] Both the bonding and antibonding states deviate from the E_F , indicating the greater covalency of the Ni-N bond in HCM@Ni-N. The calculated d-band center levels of HCM@Ni-N and HCM@Ni are confirmed as -2.04 and -0.94 eV, respectively. According to the d-band center theory, the d-band of catalyst could interact strongly with the highest occupied molecular orbital of the adsorbate, and the lower electron density near the E_F will facilitate the desorption of adsorbate.^[37] In other words, the introduction of N dopant greatly modifies the 3d orbital distribution of Ni in HCM@Ni-N, resulting in the significantly improved charge polarization of Ni. This makes the HCM@Ni-N less active in chemical bonding with other species, and thus substantially reduces the energy barrier and promotes the OER kinetics (Figure 4b).^[3, 6]

The free energy pathways of the OER process are monitored by simulating the adsorption energies of the intermediates. Generally, a four-step OER reaction proceeds through OH*, O*, OOH* and O₂* (Figure 4c and d).^[38] The limiting reaction barrier is an important criterion for evaluating the catalytic activity, which is confirmed by the free energy of the rate-determining step (RDS). For

pristine HCM and HCM@N, the conversion of OOH^* to O_2^* is the RDS with the largest reaction free energy of 4.14 eV and 3.6 eV, respectively. The effective polarization between isolated Ni and coordinated N atoms cast great influence on the RDS in the catalytic process. For HCM@Ni, a much lower limiting barrier of 2.36 eV is observed with the formation of O_2^* as the RDS. Moreover, for HCM@Ni-N, the RDS is completely changed to the oxidation of OH^* to O^* with the smallest limiting barrier of 1.83 eV. This indicates the much easier dissociation of H_2O on the HCM@Ni-N, leading to the promoted reaction kinetics and modified reaction mechanism. Our simulation results verify that the unsaturated Ni atoms should be the dominant active centers and the electronic coupling between Ni and surrounding N atoms could induce electronic redistribution, and the lower electron density near the E_F can significantly improve the OER activity.

The performances of the electrocatalysts toward OER are then measured in 1 M KOH solution to verify the predictions from DFT calculation. Figure 4e presents the iR -compensated polarization curves of the catalysts recorded by linear sweep voltammetry (LSV). It can be observed that the pristine HCM shows very poor or negligible OER activity. Although both HCM@N and HCM@Ni show improved electrocatalytic activities, the positive effects of the sole N or Ni decoration on the OER activity are very limited. In contrast, HCM@Ni-N gives greatly improved catalytic performance. To achieve the OER current density of 10 mA cm^{-2} , HCM@Ni-N requires a small overpotential of 304 mV, much lower than that of HCM@Ni (489 mV), HCM@N (502 mV) and RuO_2 (393 mV) under identical conditions (Figure S16, Supporting Information). These results not only demonstrate the synergistic effect of the Ni-N electronic coupling, but also verify that HCM@Ni-N is among the most active SACs based OER electrocatalysts (Table S2, Supporting Information).

The OER kinetics are then analyzed by Tafel plots (Figure 4f). The Tafel slope for HCM@Ni-N

(76 mV per decade) is much smaller than that of HCM@Ni (187 mV per decade) and HCM@N (203 mV per decade), verifying the important roles of Ni-N electronic coupling in promoting the reaction kinetics.^[39] To study the durability of the HCM@Ni-N electrocatalyst, long-term electrolysis at a constant current has been conducted (Figure 4g). As observed from the chronopotentiometry (CP) curve, the HCM@Ni-N electrocatalyst could maintain the current density of 20 mA cm⁻² for 12 h with only ~1.2% increase in the required potential. Moreover, chronoamperometry measurement at a fixed potential has also been conducted over extended periods. The current densities of HCM@Ni-N remain stable over 12 h with small degradation, further suggesting the outstanding stability in the OER process (Figure S17, Supporting Information). The characterizations for HCM@Ni-N after the OER test including XRD, FESEM, TEM and XPS investigations have also been conducted (Figure S18 and S19, Supporting Information). There is no obvious change for the morphology and no formation of aggregated particles after continuous operation for 12 h, further confirming the high stability of the hybrid electrocatalyst. Electrochemical impedance spectroscopy has also been used to investigate the charge transfer kinetics. The fitted results clearly demonstrate the fast OER kinetic process on the HCM@Ni-N electrocatalyst (Figure S20 and Table S3, Supporting Information).^[40]

The catalytic performance of electrocatalysts in acidic media (0.5 M H₂SO₄) has also been investigated, which displays an identical catalytic activity trend as that in the alkaline solution. HCM@Ni-N exhibits the best electrochemical performance with an overpotential of 403 mV for achieving the current density of 10 mA cm⁻² (Figure S21a, Supporting Information). To further understand the nature of the isolated Ni atoms, we have also investigated the influence of thiocyanate ions (SCN⁻) on the OER activity of the HCM@Ni-N catalyst. The metal catalytic sites are widely known to be deactivated by the SCN⁻ under acidic conditions. With the introduction of SCN⁻ (20 mM)

into the acidic electrolyte, the overpotential of the HCM@Ni-N catalyst at the current intensity of 20 mA cm⁻² increases from 493 to 537 mV (Figure S21b, Supporting Information). Further increasing the concentration of SCN⁻ to 30 mM does not result in additional deactivation of HCM@Ni-N, indicating that nearly all isolated Ni sites have been blocked. This value is still much lower than that of HCM@N without Ni decoration. These experimental studies further elucidate that the decorated Ni sites should not be the sole origin for the high OER activity and the effective electronic coupling via the Ni-N coordination contributes greatly to the final catalysis.

In summary, we have developed a facile strategy to decorate isolated Ni centers into N-doped carbon matrix. EXAFS and XANES investigations reveal unambiguously that the isolated Ni centers in HCM@Ni-N adopt an unsaturated coordination geometry with direct Ni-N bonding. DFT calculations suggest that the electronic structure of the isolated reaction centers not only governs the OER activity but also the reaction mechanism. The effective electronic coupling via the Ni-N coordination can move down the E_F and lower the adsorption energy of intermediates, resulting in the facilitated OER kinetics. As a result, the HCM@Ni-N electrocatalyst shows high OER performance and excellent stability. The present work reveals a correlation between catalytic activity and electronic structure of the isolated active sites, and thus sheds some light on the origin of high activity of many single atom catalysts.

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Figures and Captions

Figure 1. (a) Schematic description of the synthetic process of HCM@Ni-N: (I) coating of methylimidazole (MI)-Ni species, (II) annealing under high temperature, (III) etching of SiO₂. (b, c) FESEM images, and (d-f) TEM images of the HCM@Ni-N nanospheres. (g) The atomic-resolution ADF-STEM image of HCM@Ni-N. (h, i) HAADF-STEM image of HCM@Ni-N, and related EDX elemental mappings.

Figure 2. (a) Ni K-edge EXAFS spectra of HCM@Ni, HCM@Ni-N and Ni foil. (b) Fourier transform of the experimental EXAFS spectrum in K space and the best fitting result for HCM@Ni-N. (c) Fourier transform of EXAFS spectrum in R space and the best fitting result for HCM@Ni-N. (d) Co K-edge XANES spectra of Ni foil, HCM@Ni and HCM@Ni-N. (e) WT for the k^3 -weighted EXAFS signals of Ni foil, HCM@Ni and HCM@Ni-N.

Figure 3. (a) C K-edge and (b) N K-edge XANES spectra of HCM@Ni-N and HCM@N. (c) XPS Ni 2p spectra and (d) XPS N 1s spectra of HCM@Ni-N. (e) Raman spectra of HCM and HCM@Ni-N. (f) N₂ sorption isotherms of HCM@Ni-N.

Figure 4. (a) Calculated distribution of charge density for HCM@Ni-N. (b) Schematic band diagrams of HCM@Ni and HCM@Ni-N. (c) Proposed mechanism of O_2 evolution over HCM@Ni-N. (d) Free energy diagram at 0 V for OER over HCM, HCM@N, HCM@Ni and HCM@Ni-N. The dashed lines indicate the rate-determining step. (e) LSV curves and (f) the related Tafel plots of the electrocatalysts. (g) CP response at the current density of 20 $mA\ cm^{-2}$ for the HCM@Ni-N.

For Table of Content Entry

A well-defined Ni single-atom catalyst supported on N-doped carbon matrix is synthesized and used as a model system for corroborating measured electrocatalytic activity for the oxygen evolution reaction with theoretically computed adsorption energetics. This work unveils the dominant electroactive centers from the Ni-N sites for oxygen evolution reaction, which will shed light on future design of efficient electrocatalysts.