Two-Dimensional Conductive Ni-HAB as a Catalyst for the Electrochemical Oxygen Reduction Reaction

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**ABSTRACT:** Catalytic systems whose properties can be systematically tuned via changes in synthesis conditions are highly desirable for the next-generation catalyst design and optimization. Herein, we present a two-dimensional (2D) conductive metal–organic framework consisting of M-N₄ units (M = Ni, Cu) and a hexaaminobenzene (HAB) linker as a catalyst for the oxygen reduction reaction. By varying synthetic conditions, we prepared two Ni-HAB catalysts with different crystallinities, resulting in catalytic systems with different electric conductivities, electrochemical activity, and stability. We show that crystallinity has a positive impact on conductivity and demonstrate that this improved crystallinity/conductivity improves the catalytic performance of our model system. Additionally, density functional theory simulations were performed to probe the origin of M-HAB sites’ binding strength. They suggest that M-HAB’s organic linker acts as the active site with the role of the metal being to modulate the linker sites’ binding strength.

**KEYWORDS:** metal–organic frameworks, electrical conductivity, electrocatalysis, active sites, oxygen reduction reactions, density functional theory

**INTRODUCTION**

The oxygen reduction reaction (ORR) is an important electrochemical process for fuel cell applications (4e⁻ process) and the electrochemical production of hydrogen peroxide (2e⁻ process) as an energy efficient alternative to the traditional anthraquinone-based process. Noble metal-based catalysts such as Pt and Pd-Hg are the current state-of-the-art for the 4e⁻ and 2e⁻ process, respectively, exhibiting low overpotentials and high stabilities. Despite their outstanding performance, their scarcity and expense of the noble metals is a particular true for the electrochemical production of hydrogen peroxide, which due to the low stability of the product, has to be performed under relatively milder conditions and with a different experimental setup than the 4e⁻ ORR.¹,² Thus, intensive research efforts have been devoted to developing cost-effective catalysts based on earth-abundant elements, such as nonprecious metal/metal oxide catalysts, carbides, nitrides, and metal-free carbon materials. Central to these efforts is the engineering of catalysts with optimal ORR binding energetics and highly accessible, dense active sites for high catalytic performance.

Previously, low-cost molecular systems containing M-N₄ macrocyclic complexes have been demonstrated as high performing ORR catalysts,³ where the M-N₄ motif represents a catalytically active site composed of a single metal species coordinated to four nitrogens. Although molecular catalysts with M-N₄ units have exhibited notable activity,⁴ the low electrical conductivity of molecular catalysts requires a large amount of conductive additives (e.g., carbon black), resulting in a significant dilution of active site density on a per mass basis. Considering this, a catalyst design that can maximize the density of M-N₄ units in a conducting matrix would be highly desirable.⁵ To address this issue, pyrolysis of M-N₄ containing precursors into a carbon matrix has been attempted to enhance the stability and electrical conductivity of the catalyst.⁶ However, after pyrolysis, the chemical nature and conformation of the active centers are often extensively altered with unidentifiable defects, which presents a challenge in determining the nature of the active sites.⁷ Thus, a bottom-up synthesis approach with well-defined building blocks would be ideal to realize M-N₄ rich catalysts due to a much more benign synthesis procedure compared to pyrolysis.

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Herein, we report a new synthesis procedure to obtain highly conductive two-dimensional (2D) metal–organic frameworks (c-MOFs) with dense M-N4 units, namely, M-HAB (M = Cu, Ni; HAB = hexaaminobenzene), as catalysts for the ORR.\textsuperscript{10} M-HAB is a highly tunable materials system, and by varying synthesis conditions, we demonstrate that M-HAB can provide a great platform for the study of ORR activity with respect to the identity of the metal species and the catalyst’s electrical conductivity.\textsuperscript{11−14}

A similar 2D MOF based on the hexaiminotriphenylene (HITP) linker and Ni(II) node, which has a larger triphenylene-based unit (Figure 1), has been previously reported.\textsuperscript{15,16} With a combination of experimental results and theoretical calculations, we found that the identity of the metal plays a key role in determining the catalytic activity of M-HAB by modulating the electronic environment around the highly conjugated organic networks. Previously, theoretical calculations on Cu- and Ni-HAB were performed but neglected any active site other than the direct metal cation.\textsuperscript{17} Our theoretical analysis, however, suggests that the preferred active site is in-plane with the 2D c-MOF matrix with ORR intermediates binding strongly to multiple N-H groups of the M-N4 moieties (Figure 4). Such sites (referred to as linker sites herein) exploit the large degree of conjugation in the MOF framework, which facilitates the formation of strong hydrogen-bond interactions with the ORR intermediates. We also studied the effect of conductivity in the same framework by tuning the synthetic conditions. We successfully prepared Ni-HAB catalysts with improved crystallinity and electrical conductivity. High crystallinity was found to correlate positively with ORR activity with high onset potentials of 0.8 V vs RHE to achieve 1 mA/cm\textsuperscript{2} in a rotating disk electrode (RDE) setup. The catalyst

Figure 1. Synthetic scheme for the c-MOF M-HAB. Left: chemical structure of the molecular linker utilized herein, hexaaminobenzene (HAB, black), with the structure of a larger topological analog hexaaminotriphenylene (HITP, green) shown for comparison. Right: c-MOF M-HAB structure; the use of a relatively small HAB linker results in a framework with a high density of active sites.

Figure 2. (a) Comparison of PXRD patterns of Ni-HAB samples before and after the buffer treatment (0.1 M KOH buffer). (b) N\textsubscript{2} sorption isotherms of Ni-HAB-H/Ni-HAB-L. BET surface area L: 180 m\textsuperscript{2}/g, H: 129 m\textsuperscript{2}/g. (c) SEM images of M-HAB before and after electrochemical catalytic testing.
demonstrates stability for over 20 h at 0.5 V vs RHE applied potential with a moderate selectivity toward hydrogen peroxide.

RESULTS AND DISCUSSION

Synthesis of Ni-HAB-H and Ni-HAB-L. We recently reported 2D conductive MOFs, namely, M-HAB (M = Ni, Cu), where the HAB linkers are bridged by transition metal species with square planar geometry (Figure 1). Due to the smaller size of the HAB linker compared to its topological analog, HITP, the M-HAB system can achieve a denser packing of M-N₄ units with an underlying (2,3)-honeycomb topology.

The structure of synthesized Ni- and Cu-HAB products were confirmed by powder X-ray diffractions (PXRD), which show a good agreement with our previously reported 2D honeycomb eclipsed structures (Figure 2a). The previously reported synthetic conditions used 100% H₂O as the solvent, which yielded Ni-HAB with much poorer crystallinity compared to Cu-HAB. Thus, we further optimized the synthesis conditions to yield a Ni-HAB product with crystallinity comparable to Cu-HAB, which allows for a fairer control of the effects of crystallinity on the ORR activity. The Ni-HAB product with higher crystallinity was synthesized by using dimethyl formaldehyde (DMF) (1:1, v/v) at an elevated temperature (75 °C) and will henceforth be referred to as Ni-HAB-H, while the lower crystalline product will be referred as Ni-HAB-L. Having M-HAB catalysts synthesized with comparable crystallinity, we tested their chemical and electrochemical stability and found that, under harsh electrolyte treatment (0.1 M KOH), the crystallinity of Cu-HAB severely degrades over 24 h (Figure S2). Similarly, Cu-HAB suffers from an electrochemical degradation, especially at lower potential (Figure S3). For instance, Cu-HAB generated a large irreversible current at around 0.3 V vs RHE, which is indicative of degradation, considering that the mass transport-limited current for the full 4e⁻ ORR process is only about 6 mA/cm².

Having characterized their identical structures evidenced by PXRD patterns and similar particle sizes, we tested the chemical stability of Ni-HAB-H and Ni-HAB-L in the same electrochemical testing condition indicated by the well-maintained PXRD patterns after the buffer treatment.

ORR Activity of Ni-HAB-H and Ni-HAB-L. Cyclic voltammograms (CV) of the catalysts were measured on a glassy carbon rotating ring disk electrode (RRDE) setup mentioned in the Supporting Information with a spin rate of 1600 rpm. Catalysts were prepared by an ink-based drop-casting process. The net current presented was calculated by subtracting the double-layer capacitance under high N₂ flow with the absence of O₂. While scanning electron microscopy images reveal that there was no noticeable changes in size and morphology after the catalytic testing (Figure 2c), for the Ni-HAB-H sample, the onset potential was determined to be 0.8 V vs RHE with fast kinetics, reaching a mass transport-limited current at 0.7 V vs RHE. Despite the similarity in the
The energetics of all computed structures as well as the corresponding structure found at Catalysis-Hub.org.25,26

This is likely attributed to less exposure of active sites on the surface of Ni-HAB-L and/or slow mass transport. Because the high-crystallinity product (Ni-HAB-H) contains more crystalline domains with better accessibility than the low crystalline product, the more amorphous features of Ni-HAB-L results in a lower density of exposed/accessible active sites as well as a slower mass transport. Additionally, the ring current indicates that both Ni-HAB-H and Ni-HAB-L show a moderate selectivity toward H2O2 of around 50% (Figure 3a,d), despite the electrochemical active surface areas (ECSA) of the Ni-HAB-H and Ni-HAB-L being comparable (Figure S1). Therefore, the enhancement in the reactivity of Ni-HAB-H relative to Ni-HAB-L is most likely due to the enhancement in crystallinity and conductivity rather than differences in intrinsic active site activity.

Stability of Ni-HAB during the ORR. Electrochemical stability under operating conditions is a crucial requirement for catalyst performance. Steady-state potentiodynamic measurements at a saturation current of 0.5 V vs RHE show that nearly 100% of the initial current density was retained over the 20 h of potential hold for both the ring and disk currents on Ni-HAB-H (Figure 3b). This indicates a more promising result compared with the previously reported Ni-HITP structures with respect to their onset potential and the rate to reach the mass transport-limited current.10 Additionally, a thorough stability test was performed at a lower operating potential, which is at a much harsher reducing potential than what is reported for Ni-HITP. Both the ring and disk currents are recorded and have shown no major changes in both the activity and selectivity over the 20 h testing period. Cyclic voltammetry measurements before and after the 12 h potential hold show no change in the entire potential region for the ORR (Figure 3c,f). The lower crystallinity sample, Ni-HAB-L, however, showed a notable decrease in the ORR and H2O2 current over a potential hold of 12 h and irreversible redox features, as shown by cyclic voltammetry in the 0.2−1.1 V vs RHE voltage window. One plausible decomposition mechanism for MOFs is the over-reduction of the metal center, which causes further leaching of the metal species out of the framework. Additionally, we believe that, due to the lower effective density of intrinsic M-N4 active sites and the relatively lower conductivity of Ni-HAB-L compared to its counterpart Ni-HAB-H, the electron transport (the assumed rate determining step) is inhibited, resulting in slower onset kinetics.

Electrical Conductivity of M-HAB. The electrical conductivities of bulk Ni-HAB catalysts were measured using four-point probe measurements with pelletized powders. As expected, the more crystalline Ni-HAB-H exhibited a conductivity over an order of magnitude larger than that of Ni-HAB-L (conductivity of 1.050 and 0.086 S/cm for Ni-HAB-H and Ni-HAB-L, respectively). It is worth noting that Ni-HAB-H presents a slightly lower Brunauer−Emmett−Teller (BET) surface area of ~130 m²/g than that of Ni-HAB-L (~200 m²/g), which may be ascribed to a lower contribution from the mesoporous regime arising from inter-particle
The ORR activity volcano (Figure 4b) relates the ORR LP to the adsorption energy of $\Delta G_{\text{ads,OH}}$ by invoking scaling relations to express the adsorption energies of *OOH and *O in terms of $\Delta G_{\text{ads,OH}}$. Figure 4b shows that the metal binding sites for Ni-HAB, Cu-HAB, and Ni-HITP (squares) lie to the right of the volcano maximum ($\Delta G_{\text{ads,OH}} = 0.86$ eV) and therefore bind *OH too weakly to have high activity. Conversely, the linker-mediated mechanism on Ni-HAB has strengthened *OH binding, resulting in a high LP (0.67 V) that is comparable to platinum. Comparing the M-HAB and M-HITP motifs for M = Ni, Figure 4b shows that the activity on the metal site is similar between these two MOF structures with limiting potentials of 0.10 and 0.12 V vs RHE and *OH free energies of adsorption ($\Delta G_{\text{ads,OH}}$) of 1.87 and 1.81 eV, respectively. Conversely, the activity and *OH adsorption free energies vary drastically between the linker centered pathway ($\Delta \Delta G_{\text{ads,OH}}$ (HITP – HAB) = 0.8 eV and $\Delta \Delta \text{LP}$ (HITP – HAB) = 0.3 V vs RHE), indicating that the linker may play an important role in modulating the ORR activity in 2D c-MOFs containing M-N$_4$ sites. Additional computational data for M-HAB was included from a recent report for M = Os, Fe, Ir, and Pt, and the activities for the corresponding pure metal crystals are reproduced from literature. In general, the pure metal crystals bind much stronger than the corresponding M-HAB catalyst, which presents an interesting avenue to activate transition metals on the strong binding side of the volcano by supporting them into an HAB framework.

**CONCLUSIONS**

Herein, we demonstrated the synthesis of M-HAB (M = Ni, Cu) catalysts of varying crystallinity/conductivity via synthetic modulation and successfully studied the contribution of crystallinity/conductivity toward the ORR behavior of these systems. Ni-HAB-H exhibits an earlier onset potential compared to the catalyst with poorer crystallinity, possibly due to the fewer defects and better electron conduction in Ni-HAB-H. The catalytic performance was largely dependent on the metal species with Cu-HAB being much less active and stable under the given electrochemical potential. Additionally, our theoretical modeling suggests that the in-plane linker site acts as the active center. In addition to being a promising candidate for ORR fuel cell applications, the favorable stability of Ni-HAB may also allow for the elucidation of the ORR pathway on the M-HAB platform via in situ studies.

**EXPERIMENTAL SECTION**

**Materials and Instrumentations.** All reagents and starting materials were purchased from Sigma-Aldrich or Alfa Aesar and were used without further purification. Hexamaminobenzene (HAB) was synthesized according to literature. Powder X-ray diffraction was carried out on a BRUKER D8 venture single crystal diffractometer equipped with a Cu-sealed tube (\(\lambda = 1.54 \text{ Å}\)) using capillary at 50 kV and 1 mA. Scanning electron microscopy (SEM) analysis was performed on a field emission-scanning electron microscope (Magellan 400 XHR) at 5 kV. Gas adsorption was measured using a Micromeritics ASAP 2020, and the BET surface areas were calculated using its software. Electrical conductivity measurements were carried out using a Keithley 4200 SCS parameter analyzer.

**Synthesis of Ni-HAB-H with High Crystallinity.** A solution of 105 mg (0.36 mmol) of nickel nitrate hexahydrate [Ni(NO$_3$)$_2$·6H$_2$O] was dissolved in a mixture of 25 mL of DMF (dimethylformamide) and 20 mL of water in a round bottom flask. The solution was preheated on an oil bath at 75 °C for 15 min. Afterward, 50 mg of HAB-3 HCl (0.18 mmol) in 5 mL of H$_2$O was added into the nickel...
Electrocatalysis and Energy Conversion. The resulting black powder was washed with acetone and dried under vacuum at 80 °C for 2 h.

Electrochemical and Chemical Stability Tests. Stability tests of M-HAB were performed in a KOH aqueous buffer solution (0.1 M). As-synthesized samples (~10 mg) were suspended in 2 mL of 0.1 M KOH for 24 h at room temperature. Afterwards, the sample was further washed with water and acetone. The nanosheets were subsequently treated by typical activation procedures mentioned previously. After being dried under vacuum for 3 h at 75 °C, the samples were degassed on an ASAP2420 adsorption system for 2 h at 80 °C. These samples were then measured for N2 sorption at 77 K. Finally, all samples were characterized by powder X-ray diffraction to confirm the crystallinity (Figure 2a).

Electrochemical stability of the materials was tested by holding the potential at 0.5 V vs RHE for 12 h, and the current was measured during the process. Three regular 10 mV/s scans between 0.2 and 1.1 V vs RHE were conducted before and after the 12 h potential hold to ascertain the change in activity over time.

Electrochemical Characterizations. All electrochemical tests were carried out under alkaline conditions with 0.1 M KOH in water (1 kg P250-1 Potassium Hydroxide Certified ACS, Fisher Chemical). The pH was measured to be 13 by a pH meter unless otherwise noted. The measurements were conducted through either a rotation ring disk electrode (RRDE) or rotation disk electrode (RDE) setup in a four/three-electrode setup utilizing a graphite rod counter electrode, a ring disk electrode (RDE), or rotation disk electrode (RDE) setup in an electrolyte from that obtained in an O2-saturated electrolyte. The ORR activity was quantified by cyclic voltammetry. The ORR products were measured by the working electrode in an H2-saturated electrolyte, and a value of 0.959 V, referenced to RHE, was obtained. The ORR activity was determined by subtracting the current obtained in an N2-saturated electrolyte from that obtained in an O2-saturated electrolyte. The theoretical limiting potentials determined for all systems of interest and summarized in a volcano plot. Further details on the DFT methodology, calculation of adsorption free energies, and other computational methodologies can be found in the Supporting Information.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c09323.

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