Electrochemical oxygen reduction catalysed by Ni$_3$(hexaiminotriphenylene)$_2$
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Control over the architectural and electronic properties of heterogeneous catalysts poses a major obstacle in the targeted design of active and stable non-platinum group metal electrocatalysts for the oxygen reduction reaction. Here we introduce Ni$_3$(HITP)$_2$ (HITP = 2, 3, 6, 7, 10, 11-hexaiminotriphenylene) as an intrinsically conductive metal-organic framework which functions as a well-defined, tunable oxygen reduction electrocatalyst in alkaline solution. Ni$_3$(HITP)$_2$ exhibits oxygen reduction activity competitive with the most active non-platinum group metal electrocatalysts and stability during extended polarization. The square planar Ni-N$_4$ sites are structurally reminiscent of the highly active and widely studied non-platinum group metal electrocatalysts containing M-N$_4$ units. Ni$_3$(HITP)$_2$ and analogues thereof combine the high crystallinity of metal-organic frameworks, the physical durability and electrical conductivity of graphitic materials, and the diverse yet well-controlled synthetic accessibility of molecular species. Such properties may enable the targeted synthesis and systematic optimization of oxygen reduction electrocatalysts as components of fuel cells and electrolyzers for renewable energy applications.
The development of heterogeneous oxygen reduction reaction (ORR) electrocatalysts for implementation into fuel cell and electrolyzer cathodes is a major research thrust in the arena of renewable fuel development. Achieving desired architectural and electronic properties of such catalysts remains difficult, however, because several variables must be optimized simultaneously, requiring synthetic tunability that is rarely available in the solid state. Desirable characteristics of an ORR electrocatalyst include: high active site density, reproducible synthesis and catalytic activity, stability in the electrolyte and in oxygen and peroxide, and low overpotential relative to the thermodynamic 4e⁻/O₂ oxidant reduction potential of 1.23 V (versus the reversible hydrogen electrode, RHE). One structural motif that has proven successful in catalysing ORR with high activity and physical robustness is the M-Nₓ unit, where M = a non-platinum group metal (for example, Fe, Co, Ni, Cu) chelated in a nitrogenous environment. These structures were popularized after the 1964 report by Jasinski¹ that detailed the high ORR activity of cobalt phthalocyanine complexes blended with electrically conductive acetylene black. The ability of oxygen to chemisorb onto these M-Nₓ sites without degrading the material fuelled extensive investigations of ORR on M-Nₓ-containing catalysts²–⁵. Though active towards ORR, M-Nₓ complexes have shown inconsistent stability in various electrolytes, motivating high-temperature treatment of the materials to enhance catalyst longevity and electrical conductivity³,⁶. Thermal treatment indeed increased the stability of the materials, but introduced new challenges in maintaining synthetic control over structure formation, identifying the catalytic active sites, and establishing structure–function relationships useful for catalyst optimization and mechanistic understanding. Thus, the search for active, intrinsically conductive, and chemically and electrochemically stable ORR electrocatalysts possessing well-defined and tunable active sites continues.

One class of materials that could answer these challenges is metal-organic frameworks (MOFs). These materials are compelling choices for electrocatalytic applications because their high surface area maximizes active site density, and their tunable chemical structure affords tailor-made microenvironments for controllable reaction conditions within the pores. Despite their promising features, MOFs have rarely been used for electrocatalytic applications because they are typically electrical insulators⁶–¹¹. Recently, synthetic advances have given rise to conductive MOFs, some of which exhibit encouraging properties as electrocatalysts¹²–¹⁶, but to our knowledge none have been experimentally shown to mediate ORR electrocatalysis.

Here we introduce Ni₃(HITP)₂ (HITP = 2, 3, 6, 7, 10, 11-hexaiminotriphenylene), a conductive two-dimensionally layered material structurally reminiscent of the long-studied M-Nₓ ORR electrocatalysts (Fig. 1)¹⁷, as a representative of a new class of highly ordered ORR electrocatalysts exhibiting ORR activity and electrical conductivity (σ = 40 S cm⁻¹)¹⁷ with no post-synthetic treatment or modification. In addition to possessing ORR activity competitive with the most active non-platinum group metal (nPGM) electrocatalysts to date, Ni₃(HITP)₂ retains 88% of its current density and undergoes no visible morphological degradation during prolonged electrochemical cycling. This study highlights conductive MOFs as a powerful platform for the development of tunable, designer electrocatalysts. It is noted that MOFs have been used as scaffolds for ORR electrocatalysts formed from high-temperature (> 600 °C) pyrolysis¹⁸–³⁷ as well as incorporated into composites containing graphene oxide and porphyrin additives⁷,². Whereas such materials indeed exhibit competitive ORR activity, the pyrolysis involved in their preparation eliminates the crystallinity and synthetic control inherent to MOFs. Our aim herein is to introduce a multi-faceted handle on imposing in a controlled manner structural, chemical and electronic properties on our material for reaction-targeted, MOF-based electrocatalyst design.

Results

Synthesis and quantification of Ni₃(HITP)₂. Ni₃(HITP)₂ can be grown solvothermally as a thin film on a variety of electrode surfaces using synthetic conditions mimicking those employed for the synthesis of bulk material¹⁷. Glassy carbon disk electrodes (5 mm diameter) served as the working electrodes for all investigations described herein unless otherwise noted, and all potentials are referenced to RHE. Deposition of Ni₃(HITP)₂ onto the glassy carbon electrodes typically afforded loadings of ~ 5 µg of MOF. The loadings were determined precisely in each case by atomic absorption spectroscopy (AAS) and verified by inductively coupled plasma-mass spectrometric (ICP-MS) measurements. The thickness of the film was analysed by atomic force microscopy. Ni₃(HITP)₂ films grown on glassy carbon electrodes have a thickness of ~ 120 nm, whereas films grown on indium tin oxide exhibit a similar morphology with a thickness of ~ 300 nm (Supplementary Fig. 1).

ORR activity of Ni₃(HITP)₂. Cyclic voltammograms of Ni₃(HITP)₂ thin films on glassy carbon rotating disk electrodes recorded in the absence of O₂ revealed a significant double layer capacitance that increased with increasing scan rate (Supplementary Fig. 2), reflecting the high surface area of the modified electrodes³⁸. Indeed, Ni₃(HITP)₂ exhibits a Brunauer–Emmett–Teller-specific surface area of 629.9 ± 0.7 m² g⁻¹, as calculated from its nitrogen adsorption isotherm (Supplementary Fig. 3). Under O₂ atmosphere, the material reduces oxygen with an onset potential (j = −50 µA cm⁻²) of 0.82 V in a 0.10 M aqueous solution of KOH (pH = 13.0; Fig. 2). The measured ORR onset potential is competitive with the most active nPGM ORR electrocatalysts reported thus far⁹ and sits at an overpotential of 0.18 V relative to Pt (Eonset = 1.00 V).

Notably, cyclic voltammetry of the film on indium tin oxide electrodes shows the same ORR activity as the films on the glassy carbon electrodes (Supplementary Fig. 4), verifying that the MOF does not simply enhance the ORR activity of the glassy carbon electrode but rather acts as a stand-alone ORR electrocatalyst regardless of the substrate.

Figure 1 | Ni₃(HITP)₂ structure. Perspective view of the two-dimensional layered structure of Ni₃(HITP)₂ (ref. 17).

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Stability of Ni₃(HITP)₂ during ORR. Steady-state potentiostatic measurements at $E = 0.77$ V showed that 88% of the initial current density is retained over 8 h (Supplementary Fig. 5), in-line with other nPGM ORR catalysts. Cyclic voltammetry of the modified electrode after the durability study showed no shift in the diffusion-limited region of the polarization curve, indicating that any alterations to the material during electrocatalysis were not significant enough to decrease the mass transport properties of the Ni₃(HITP)₂ film (Supplementary Fig. 6). Moreover, cyclic voltammetry of the electrolyte after these 8 h, using a fresh unmodified glassy carbon electrode, indicated no leaching from the Ni₃(HITP)₂ films, evidencing the heterogeneous nature of the catalyst. Additionally, ICP-MS and AAS analyses of films before and post electrolysis indicated the same quantity of Ni, suggesting that no part of the catalyst, homogeneous or heterogeneous, is lost from the films during catalysis (Supplementary Tables 1 and 4).

Characterization of Ni₃(HITP)₂ before and after ORR. Spectroscopic, microscopic and diffractometric techniques enabled analysis of the film before and after ORR catalysis. X-ray photoelectron spectroscopy (XPS) of catalyst films before and after catalysis revealed an increase in binding energy of the Ni₃p envelope region (850–885 eV) by +1.0 eV (Supplementary Fig. 7). Also visible by XPS was a shoulder peak that was present in the Ni₃p region before ORR (399 eV) which disappears after catalysis (Supplementary Fig. 8). Importantly, though the catalyst may undergo minor structural rearrangement during ORR, the high activity is largely retained over extended steady-state measurements, that is, neither access to the active sites nor the integrity of the active sites themselves is severely compromised during prolonged electrocatalysis. The structural robustness was supported by Raman spectroscopy conducted on the unused film, the film after submerison in the 0.10 M KOH electrolyte, and the film after electrochemical cycling under either N₂ or O₂. There were no missing or additional Raman bands for any of the altered films compared with the spectrum of the unused film (Supplementary Fig. 9). Additional evidence supporting the stability of the film was observed in scanning electron micrographs (SEMs) of the film taken before and after ORR catalysis (Supplementary Fig. 10). No perturbations in the morphology of the film were observed upon electrochemical cycling under O₂. Finally, grazing incidence X-ray diffraction of the Ni₃(HITP)₂ film before and after ORR catalysis showed retention of the long-range order in the ab plane of Ni₃(HITP)₂ during ORR, further highlighting the structural stability of this catalyst during electrochemical cycling under O₂ (Supplementary Fig. 11).

ORR kinetics on Ni₃(HITP)₂. Using standard rotating ring-disk electrode experiments (Supplementary Fig. 12) and assuming that catalytically competent sites within Ni₃(HITP)₂ are distributed homogeneously throughout the film and not just on the surface, lower limit turnover frequencies (TOFs), determined by AAS, were found to be 0.042 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹ and 0.052 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹ for H₂O₂ and H₂O production, respectively, at $E = 0.79$ V. Quantifying the Ni content in the same films by ICP-MS gave lower limit TOF values of 0.046 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹ and 0.056 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹ for H₂O₂ and H₂O production, respectively, also at $E = 0.79$ V (Supplementary Tables 1–6). The TOF values for H₂O₂ and H₂O production increase by one order of magnitude to 0.491 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹ and 0.466 electrons [Ni₃(HITP)₂]⁻¹ s⁻¹, respectively, at 0.67 V. If the active sites in Ni₃(HITP)₂ are the Ni atoms, the lower limit TOFs derived from AAS quantification of Ni are 0.014 electrons [Ni]⁻¹ s⁻¹ and 0.017 electrons [Ni]⁻¹ s⁻¹ for H₂O₂ and H₂O production, respectively, at $E = 0.79$ V. Minimum TOF values calculated from the ICP-MS quantification of Ni were 0.005 electrons [Ni]⁻¹ s⁻¹ and 0.019 electrons [Ni]⁻¹ s⁻¹ for H₂O₂ and H₂O production, respectively, also at $E = 0.79$ V. Notably, the intrinsic ORR turnover frequencies for Ni₃(HITP)₂ could exceed the values reported here because the Ni quantification methods do not distinguish exclusively electroactive Ni sites; if some fraction of the potentially active sites are not catalytically competent because of mass transport limitations within the films, the ORR current-to-active-site ratio would increase, consequently increasing the TOF.

Mechanistic insight into ORR on Ni₃(HITP)₂. The activation-controlled Tafel plot generated from Koutecky–Levich (K–L) data (Supplementary Fig. 13) revealed a Tafel slope of $-128$ mV dec⁻¹ (Fig. 3). This Tafel slope corresponds to an irreversible one-electron pre-equilibrium process, likely indicating the formation of the superoxide anion as the rate-limiting step (theoretical Tafel slope $= -120$ mV dec⁻¹). The total number of electrons transferred during ORR was determined using the inverse of the slope of the K–L plots, termed the $B$ factor.
heating the modified electrode in methanol at 65 °C for 20 h, Ni3(HITP)2 and related materials may be strong candidates for implementation into direct methanol fuel cells where methanol tolerance of the anodic and cathodic catalysts is a necessity. High stability in the presence of methanol is not observed for Pt-based electrocatalysts, a major hurdle currently slowing direct methanol fuel cell development.

Further insight into the robustness of Ni3(HITP)2 during ORR was achieved using several spectroscopic and microscopic techniques to probe the catalyst structure before and after catalysis. The +1 eV shift in the Ni2p XPS after ORR catalysis could be indicative of a Ni–O interaction or, alternatively a strengthening of the ligand field as electron density around the imine decreases. The loss of asymmetry in the N1s region of the XPS after catalysis is consistent with an alteration of the ligand field during prolonged electrocatalysis. Furthermore, any subtle alterations of the film affected neither the film’s microstructure nor the polarizability of the Ni3(HITP)2 bonds as shown by SEM and Raman spectroscopy, respectively. The stability of the catalyst in aqueous media is industrially advantageous given the lower cost of water-based electrolytes.

To the best of our knowledge, the foregoing results demonstrate for the first time electrocatalytic ORR activity in a well-defined, intrinsically conductive MOF. Clearly, the faradaic efficiency for water production should be increased for maximizing energy density in industrial settings, but such a goal may be more tractable with MOFs, whose well-defined structures provide the ability to systematically investigate a number of variables including the metal centre identity, valency and coordination environment. Structure-function and mechanistic studies will facilitate understanding, development, and diversification of this material into a platform structure primed for the targeted design of other ORR electrocatalysts.

Methods
Characterization of the Ni3(HITP)2 film. Samples were prepared for ICP-MS and AAS analysis by sonication of the modified electrode buttons in concentrated ICP (OmniTrace purity, 67–70% w/w; EMD) grade nitric acid for 4 h. The electrode buttons were removed from the acid, and the acid was diluted to 2% v/v with Milli-Q water. ICP-MS was conducted on an Agilent 7900 at the MIT Center for Environmental and Health Sciences (Cambridge, MA, USA). An external calibration curve was generated with a nickel standard (1,000 p.p.m. in 2% HNO3; Ultra Scientific) diluted to 0, 15, 30, 60 and 120 p.p.b. in 2% ICP grade nitric acid. Argon flowing at 1.06 l min<sup>−1</sup> was used as the carrier gas. The ICP-MS data was analysed by MassHunter 4.1 software.

Graphite furnace AAS was conducted on a Perkin Elmer AAAnalyst 600 GFAAS (property of the Lippard Group, MIT, Cambridge, MA, USA). An ICP grade Ni standard (1,000 p.p.m. in 2% HNO3) (Ultra Scientific) was diluted to 100 p.p.b. in 2% HNO3. The AAS was performed in serial dilution with a nickel calibration curve at 0, 25, 50, 75 and 100 p.p.b. nickel calibration points. The nickel content was probed by monitoring the optical absorption at λ = 232.0 nm. The graphite furnace temperature was ramped from 110 to 2,500 °C during AAS analysis. The AAS results were analysed by WinLab32 for AA, version 6.5.0.2066.

Atomic force microscopy was conducted in the MIT Institute for Soldier Nanotechnologies (Cambridge, MA, USA) using a Veeco Dimension 3,100 scanning probe microscope (Veeco Digital Instruments by Bruker) equipped with a Nanoscope V controller. Images were recorded in tapping mode in the air at room temperature (23–25 °C) using an Al reflex coated silicon micro cantilever (AC240TS-R3, Asylum Research). The scan rate was set at 1.0 Hz. The atomic force microscopy results were analysed by Gwyddion 2.43 software.

XPS was conducted at the Harvard Center for Nanoscale Systems (Cambridge, MA, USA) on a Thermo Scientific K-Alpha XPS. A survey scan was taken and C, N, O and Ni were probed with a pass energy = 30 eV, beam width = 400 μm. Data analysis was executed with the Advantage 5.98 software programme.

Raman spectroscopy was conducted on a Horiba Raman spectrophotometer (property of the Myerson Group, MIT, Cambridge, MA, USA) operated at 457 nm
with a hole diameter of 500 μm, a silt size of 100 μm, a range of 100–300 cm−1, a 100× magnification lens, a laser intensity of 39 Å, and 2× runs with three accumulations per sample. Scanning electron microscopy was conducted at the Harvard Center for Nanoscale Systems (Cambridge, MA, USA) on a Zeiss Ultra Plus FE-SEM with an InLens detector at a working distance of 10 kV, and 200× magnification. Data analysis was executed with SmartSEM V05.04.02.00 software. Grazing incidence X-ray diffraction was conducted at the MIT Center for Materials Science and Engineering (Cambridge, MA, USA) on a Bruker D8 Discover Diffractometer with a Vantec 2.0 two-dimensional detector, a Cu Kα X-ray source (1.5405 Å), and a tube voltage and current of 40 kV and 40 mA, respectively. The diffraction patterns were collected in a grazing incidence geometry with a grazing incidence angle of 3.6°. The blank indium tin oxide slide and the black flaky solid had settled at the bottom of the reaction vial. The electrode was removed from the reaction mixture and heated in Milli-Q water (20 ml) at 65°C for 5 h. The CH3OH was removed and the electrode was heated at 65°C for 4 h in a capped vial, rinsed with Milli-Q water, then dried under a stream of air. The working electrodes were then subsequently polished with 100, 30 and 5 μm diamond alumina powder from BASI. Unless otherwise noted, all electrochemical experiments were conducted with a Bio-Logic SP200 potentiostat/galvanostat in a custom 2-compartment electrochemical cell. Rotating disk and rotating ring-disk electrode studies were conducted with a Bio-Logic VMP3 potentiostat in a two-compartment cell with a glass frit separating the working electrode from the auxiliary electrode. Experiments were performed in two parts: (i) the working electrode was rotated at 0.1014 V versus Pt mesh; reference electrode = Hg/HgO (1.00 M KOH); working electrode = blank glassy carbon button (5 mm diameter) or glassy carbon button modified with Ni3(HITP)2 film and inserted in a polyarylether-ether ketone rotating ring disk electrode (RRDE) tip with a platinum ring; rotation rate = 2000 rpm; scan speed = 5 mV s−1; atmosphere = N2 or O2 sparged for 10 min through a fitted sintered glass frit and sparged throughout the entirety of the experiment. The potential was held at E = 0 V versus OCP to −0.300 V versus Hg/HgO (0.567 V versus RHE). The electrolyte solvent window was established by cycling a blank glassy carbon button under N2 atmosphere. ORR activity of the unmodified glassy carbon was observed by cyclic voltammetry (CV) of modified glassy carbon electrode vs. Hg/HgO (OCP) to E = 4.00 V versus RHE. These controls preceded data collection of Ni3(HITP)2-modified glassy carbon under N2 and O2 atm. When relevant, a potential of E = 1.23 V versus RHE was applied to the Pt ring disk for oxidation of the ORR products. A 20% collection efficiency was applied for quantification of the ORR products using the current measured at the Pt ring disk.

Determination of the 2-and-4-electron ORR TOFs. The background-subtracted ring current (Supplementary Fig. 12) was taken for each potential probed during potentiodynamic ORR experiments. A linear fit (Slope = 0.807, 0.787, 0.767, 0.747, 0.727, 0.707, 0.687, and 0.667 V) then divided by 1,000 to calculate current passed in A = Cs−1 (I = Q/I). That current was divided by 0.2 to account for the 20% ring collection efficiency, then divided by Faraday’s constant (96,485.3636 C mol−1) and multiplied by Avogadro’s number (6.022 × 1023 electrons per mol) to determine the number of electrons transferred per second divided by the number of nickel sites as determined by AAS and ICP-MS, respectively, to convert the 2-electron ORR TOF to electrons per nickel site per second according to the two nickel quantification methods (that is, AAS and ICP-MS) (Supplementary Tables 2 and 5). Alternatively, the number of electrons transferred per second was divided by the number of Ni3(HITP)2 units to convert the 2-electron ORR TOF to electrons per Ni3(HITP)2 formula unit per second. The number of Ni3(HITP)2 formula units was directly calculated from the number of nickel sites derived from the two nickel quantification methods. In the main text, the TOF is expressed as a range defined by the values calculated using the two employed nickel quantification methods.

To determine the TOF for 4-electron ORR, the background and collection efficiency-corrected ring current was subtracted from the disk current (A) (Supplementary Fig. 12) to obtain the current passed during 4-electron ORR. The current (A) was divided by Faraday’s constant then by number of nickel or Ni3(HITP)2 sites to calculate the TOF (electrons per nickel site per second, or electrons per Ni3(HITP)2 formula unit per second, respectively) during 4-electron ORR according to the two employed nickel quantification methods (Supplementary Tables 3 and 6). In the main text, the TOF is expressed as a range defined by the values calculated using the two employed nickel quantification methods.
ORR proton order study. Potential was measured over 25 min at a constant current I = −5 mA while varying the pH from 12.89 to 11.54 in the 0.10 M KOH electrolyte titrated with 1.0 M HClO4.

References

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Author contributions
T.F. assisted with the RRDE experimental setup and design of electrochemical procedures. Y.S. provided electrochemical equipment. D.S. conducted Ni isotermals and Brunauer–Emmett–Teller surface area analysis of Ni(HPTP), L.S. conducted atomic force microscopy measurements. E.M.M. prepared all samples for electrochemical
investigations and all other analyses, and conducted the reported experiments. E.M.M., T.F., Y.S. and M.D. contributed to data analysis. E.M.M. and M.D. wrote the manuscript.

Additional information
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