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**TITLE:** Theory-driven design of electrocatalysts for the two-electron oxygen reduction reaction based on dispersed metal phthalocyanines

**AUTHORS:** Yang Wang, Zisheng Zhang, Xiao Zhang, Yubo Yuan, Zhan Jiang, Hongzhi Zheng, Yang-Gang Wang, Hua Zhou, Yongye Liang

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# Theory-driven design of electrocatalysts for the two-electron oxygen reduction reaction based on dispersed metal phthalocyanines

Yang Wang,<sup>1,+</sup> Zisheng Zhang,<sup>2,+</sup> Xiao Zhang,<sup>3,\*</sup> Yubo Yuan,<sup>1</sup> Zhan Jiang,<sup>1</sup> Hongzhi Zheng,<sup>1</sup> Yang-Gang Wang,<sup>2</sup> Hua Zhou,<sup>4</sup> Yongye Liang.<sup>1,5\*</sup>

<sup>1</sup>Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055.

<sup>2</sup>Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055.

<sup>3</sup>State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027.

<sup>4</sup>X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Lemont, IL, 60439.

<sup>5</sup>Guangdong-Hong Kong-Macao Joint Laboratory for Photonic-Thermal-Electrical Energy Materials and Devices, Southern University of Science and Technology, Shenzhen 518055.

\*Corresponding authors: Y. Liang: liangyy@sustech.edu.cn, X. Zhang: zhangx\_energy@zju.edu.cn.

<sup>+</sup>Equally contributed to this work.

## Abstract

The two-electron electrochemical reduction of oxygen is an appealing approach to produce hydrogen peroxide. Metal and heteroatom-doped carbon (M-X/C) materials have recently been recognized as compelling catalysts for this process, but their performance improvement is generally hindered by the ill-defined structures of active sites. Here we demonstrate a theory-driven design of catalysts for oxygen reduction reaction based on molecularly dispersed electrocatalysts (MDEs) with metal phthalocyanines on carbon nanotubes. Density functional theory calculations suggest that nickel phthalocyanine (NiPc) favors the formation of  $^*\text{H}_2\text{O}_2$  over  $^*\text{O}$ , thus acting as a selective catalyst for peroxide production. NiPc MDE shows high peroxide yields of ~83%, superior to the aggregated NiPc and pyrolyzed Ni-N/C catalysts. The performance is further enhanced by the introduction of cyano group (CN). NiPc-CN MDE exhibits ~92% peroxide yields and good stability. Our studies provide a new perspective for the development of heterogeneous electrocatalysts for hydrogen peroxide production from metal macrocyclic complexes.

## Keywords

metal phthalocyanine, oxygen reduction reaction, peroxide, theory-driven design, molecular engineering

## Introduction

Driving economically important chemical reactions with renewable electricity offers an intriguing opportunity to replace current energy-intensive processes.<sup>1-3</sup> For example, the electrochemical oxygen reduction reaction (ORR) through the two-electron ( $2e^-$ ) pathway is considered as an environmentally benign alternative of the industrial anthraquinone method to produce hydrogen peroxide ( $H_2O_2$ ), which is widely used as a green oxidizer in bleaching, waste water treatment, and chemical industry.<sup>4-6</sup> An ideal electrocatalyst should possess high activity toward the  $2e^-$  pathway to the peroxide product and suppress the competing  $4e^-$  process to water. Platinum (Pt) or palladium (Pd) alloys with mercury (Hg) have been demonstrated as selective electrocatalysts for the  $2e^-$  pathway in ORR.<sup>7-8</sup> However, the toxicity of Hg and the limited reserve of noble metals are not preferred for practical applications.

Carbon-based materials doped with earth-abundant elements are compelling candidates as efficient and affordable electrocatalysts.<sup>9-14</sup> Carbon nanotube, graphene, and activated carbon with oxygen-containing functional groups were reported to be selective in  $2e^-$  ORR.<sup>15-18</sup> Embedding coupled boron-nitrogen (BN) domains into graphitic carbon showed enhanced selectivity and activity for reducing  $O_2$  to  $HO_2^-$  compared to the catalysts with individual B or N doping.<sup>19</sup> In addition to metal-free catalysts, metal and heteroatom-doped carbon (M-X/C) catalysts with isolated heteroatom-coordinated metal moieties, one type of single-atom catalysts (SACs), have also been exploited for  $H_2O_2$  production.<sup>20-23</sup> A series of M-N/C (M = Mn, Fe, Co, Ni and Cu) catalysts with proposed M-N<sub>4</sub> active sites were synthesized to investigate their performance in ORR and the Co-N/C catalyst showed preference for the  $2e^-$  pathway in acidic condition.<sup>24</sup> Moreover, SACs with transition-metal centers coordinated by different heteroatoms, such as O and S, were also reported to show high selectivities for the  $2e^-$  reduction pathway in ORR.<sup>25-28</sup> However, lacking of well-defined structures and co-presence of various types of active sites prevent understanding the structure-performance relationships and catalyst design principles in these SAC catalysts.

Metal macrocyclic complexes, such as metal phthalocyanines and porphyrins with well-defined M-N<sub>4</sub> moieties, have been attractive electrocatalysts since the report of

cobalt phthalocyanine as an active ORR catalyst.<sup>29-31</sup> For instance, iron phthalocyanine (FePc) has been reported efficient in catalyzing ORR through the 4e<sup>-</sup> pathway to water.<sup>32-33</sup> However, the performances of metal complexes in heterogeneous form are often limited by their low electric conductivity issue.<sup>34-36</sup> Hybridizing metal macrocyclic complexes with nanocarbon materials were found to promote their catalytic performances.<sup>35, 37-38</sup> In the carbon dioxide reduction reaction, achieving molecular dispersion on conducting supports is beneficial to reveal the intrinsic performance of molecular catalysts and establish catalyst design principles.<sup>39-40</sup> In addition, previous reports of heterogeneous molecular ORR catalysts mainly focused on optimizing the performance toward the 4e<sup>-</sup> pathway with little exploration for the 2e<sup>-</sup> pathway to peroxide production.<sup>30, 41</sup>

In this work, we present a theory-driven design of electrocatalysts based on molecularly dispersed electrocatalyst (MDE) consisting of dispersed metal phthalocyanines (MPcs) on carbon nanotubes (CNTs) for electrochemical production of peroxide. From density functional theory (DFT) calculations, we identify nickel phthalocyanine (NiPc) as a selective catalyst for 2e<sup>-</sup> ORR with experimental peroxide yields of ~83% in the form of MDE, in contrast to FePc MDE that is selective for 4e<sup>-</sup> ORR. Achieving molecular dispersion of NiPc with well-defined Ni-N<sub>4</sub> sites is important to the high peroxide selectivity as proved by the lower peroxide yields of the physically mixed NiPc and CNT (containing aggregated NiPc) and a pyrolyzed Ni-N/C SAC. Moreover, molecular engineering of NiPc MDE with the introduction of cyano groups to the Pc ligand (NiPc-CN MDE) further enlarges the free energy preference to the 2e<sup>-</sup> pathway and enhances the selectivity for the electrochemical production of peroxide. NiPc-CN MDE exhibits high peroxide yield of ~92% in the potential range of 0.70~0.20 V versus reversible hydrogen electrode (RHE).

## Experimental Methods

### Preparation of MPc MDEs

The preparation of MPc MDEs was based on a reported procedure with the control of ratio between MPcs and CNTs.<sup>40</sup> NiPc and FePc were obtained from commercial

sources and NiPc-CN was synthesized according to a reported method.<sup>40</sup> Briefly, 30 mg purified CNTs were dispersed in 25 ml of N,N-dimethylformamide (DMF) with the assistance of sonication, in which a calculated amount of MPcs in 5 ml of DMF was added to obtain a well-mixed suspension. The mixture was further sonicated for 30 min and then stirred at room temperature for 20 h. Subsequently, the precipitate was collected by centrifuge and washed with DMF (three times) and ethanol (twice). Finally, the collected precipitate was lyophilized to yield the final product.

### Electrochemical measurements

4 mg of MPc MDEs and 10  $\mu$ l of 5 wt.% Nafion solution were dispersed in 990  $\mu$ L ethanol under ultrasonication to form a homogeneous ink. 13  $\mu$ L catalyst ink was loaded onto the glassy carbon (GC) disk electrode (5.5 mm in diameter) of a rotating-ring-disk-electrode (RRDE) to achieve a catalyst loading of  $\sim 0.2$  mg  $\text{cm}^{-2}$ . The ink of NiPc+CNT was prepared by dispersing 2.8 mg of NiPc, 1.2 mg of CNT and 10  $\mu$ l of 5 wt.% Nafion solution in 990  $\mu$ L ethanol under ultrasonication, then loaded onto the GC electrode. The RRDE experiments were conducted with a four-electrode system using saturated calomel electrode (SCE) as the reference electrode (calibrated with a home-made RHE), a graphite rod as the counter electrode and the catalyst modified GC disk electrode as the working electrode, while the Pt ring electrode was kept at 1.5 V (vs. RHE, the same for following potentials unless otherwise stated) for all experiments. The disk and ring electrodes were rotated at a speed of 1600 rpm (Pine research). Electrolytes (0.1 M KOH) were saturated with  $\text{O}_2$  by bubbling for 30 min prior to each experiment and a flow of  $\text{O}_2$  was maintained over the electrolyte during reaction. Linear sweep voltammetry (LSV) was conducted by scanning the disk electrode potential with a scan rate of 5 mV/s. For stability test, the disk electrode potential was kept at 0.5 V. Experiments were also performed under an argon environment to record the background currents of the disk and ring electrodes, which were subtracted from the currents under  $\text{O}_2$ . The peroxide yield and electron transfer number ( $n$ ) were determined by the following equations:

$$\text{Peroxide yield (HO}_2^-) = 200 \times \frac{I_r/N}{I_d + I_r/N} \%$$

$$n = 4 \times \frac{I_d}{I_d + I_r / N}$$

where  $I_r$  is ring current,  $I_d$  is disk current and  $N$  is current collection efficiency of the Pt ring electrode (0.28, calibrated with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ).

## Computational Methods

DFT calculations of gas-phase MPc molecules catalyzing ORR were conducted using the Gaussian 09 program.<sup>42</sup> B3LYP functional<sup>43</sup> with D3 correction (Becke-Johnson damping)<sup>44</sup> was adopted for calculation.<sup>45</sup> The all-electron 6-31G\* basis set (for H, C, N, O)<sup>46-48</sup> and the Stuttgart-Dresden (SDD) basis set containing all double- $\xi$  valence with effective core potentials (ECPs)<sup>49</sup> (for Ni, Fe) were used. The geometric structures were all optimized at 298.15 K and under 1 atm. The Harmonic vibrational frequencies were computed with no imaginary frequency found for all reaction intermediates. The Gibbs free energies of high- and low-spin forms of all intermediates were calculated with the harmonic potential approximation to determine the ground states. The electrocatalytic mechanisms were investigated with the computational hydrogen electrode (CHE) model.<sup>50</sup> Additional details of computational methods are available in the Supporting Information.

## Results and Discussion

### Theoretical calculations of MPcs catalyzing ORR

To understand how the central metals in MPc molecules affect the product selectivity in ORR, DFT calculations of the free energy changes of ORR through the  $2e^-$  and  $4e^-$  pathways were conducted on FePc and NiPc at 1.23 V vs. RHE. The calculated free energy diagrams suggest distinctly different ORR behaviors of FePc and NiPc (Figure 1a). On FePc,  $\text{O}_2$  is first adsorbed on the Fe center, followed by a proton-coupled electron transfer (PCET) process to form  $^*\text{OOH}$  with an uphill free energy change. The divergence of the  $2e^-$  and  $4e^-$  pathways came from the preference of  $^*\text{OOH}$  reduction with a protonation mechanism to  $^*\text{H}_2\text{O}_2$  or an O-O cleavage to  $^*\text{O}$ . The downhill free energy change to form  $^*\text{O}$  and the large free energy increase required for the generation of  $^*\text{H}_2\text{O}_2$  indicate a high preference for the  $4e^-$  reduction pathway on FePc, consistent

with high selectivities of  $\text{O}_2$  reduction to water/hydroxide of Fe macrocyclic complexes and Fe-based SACs in previous reports.<sup>34, 51</sup> By contrast, the  $\text{*OOH}$  intermediate (generated from  $\text{O}_2$  through an  $\text{*O}_2$  intermediate with two uphill free energy changes) on NiPc shows a slight downhill free energy change to generate  $\text{*H}_2\text{O}_2$ , while the formation of  $\text{*O}$  in the  $4\text{e}^-$  reduction pathway is energetically uphill (Figure 1a). In contrast to FePc, the reversed trend in free energy changes to form  $\text{*H}_2\text{O}_2$  and  $\text{*O}$  on NiPc suggests the preference for the  $2\text{e}^-$  reduction pathway. Therefore, NiPc molecules are predicted to be selective electrocatalysts for  $2\text{e}^-$  ORR to peroxide product (Figure 1b).

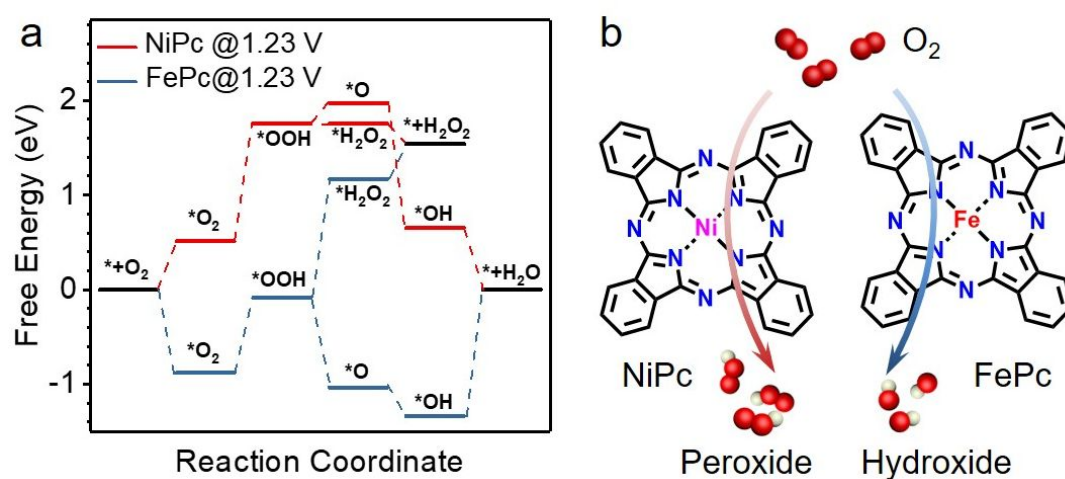


Figure 1. Theoretical calculations of ORR catalyzed by MPcs. (a) Calculated free energy diagrams of ORR through the  $2\text{e}^-$  and  $4\text{e}^-$  reduction pathways on NiPc and FePc at 1.23 V. (b) Schematic presentation of ORR selectivity on NiPc and FePc based on DFT calculations.

### ORR performance of MPc MDEs and aggregated MPcs

Dispersed NiPc and FePc molecules were supported on CNTs via  $\pi$ - $\pi$  interactions to fabricate MPc MDEs according to our previous method<sup>40</sup> to examine the calculated trends in ORR. The metal contents in MDEs were controlled to be  $\sim 0.7$  wt.% (Table S1), which were measured by inductively coupled plasma mass spectrometry (ICP-MS). The electrochemical behaviors of NiPc MDE and FePc MDE were first investigated in  $\text{O}_2$ -saturated 0.1 M KOH electrolytes with the RRDE setup ( $0.2 \text{ mg cm}^{-1}$  catalyst loading). The MDEs were drop-coated on the disk electrode as the working electrode



to reduce  $O_2$ , while the ring electrode (Pt) was maintained at 1.5 V to detect the produced peroxide. FePc MDE shows more positive onset potential (0.94 V at -0.025 mA, corresponding to a current density of  $\sim -0.1 \text{ mA cm}^{-2}$ ) than that of NiPc MDE (0.79 V) (Figure 2a). The current of FePc MDE is saturated to -1.41 mA at  $\sim 0.58$  V. The saturation current for NiPc MDE is about -0.63 mA at the same potential. The peroxide yield and  $n$  of MPc MDEs calculated from the disk and ring currents are depicted in Figures 2b and S1, respectively. NiPc MDE shows good peroxide yields of  $\sim 83\%$  in the potential range of 0.70–0.53 V, which decline at more negative potentials. Correspondingly,  $n$  of NiPc MDE is below 2.34 in the potential range of 0.70–0.53 V, which gradually increases to 2.83 from 0.53 to 0.20 V (Figure S1). In contrast, low peroxide yields of  $\sim 1\%$  together with  $n$  above 3.97 in the potential range of 0.70–0.20 V are observed with FePc MDE (Figures 2b and S1), confirming its strong preference toward the  $4e^-$  reduction pathway. These results indicate that the preferred ORR pathways of NiPc MDE and FePc MDE are the  $2e^-$  and  $4e^-$  reduction pathways, respectively, which are consistent with the DFT calculations (Figure 1a).

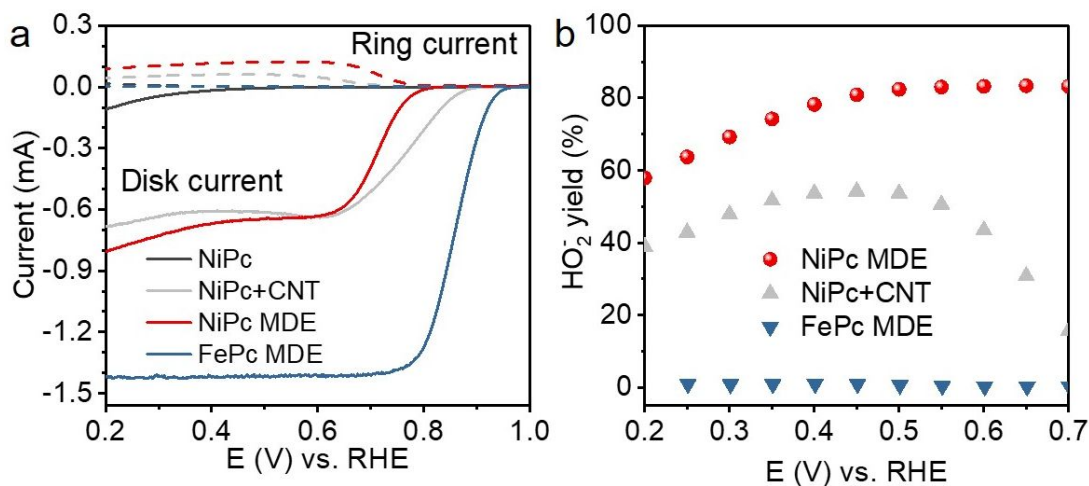


Figure 2. ORR performance of MPc-based electrocatalysts on RRDE. (a) Disk and ring currents of NiPc, NiPc+CNT, NiPc MDE, and FePc MDE in  $O_2$ -saturated 0.1 M KOH electrolytes on RRDE test rotating at 1600 rpm. (b) Calculated peroxide yields of NiPc MDE, NiPc+CNT, and FePc MDE.

The effects of aggregation state of NiPc were further investigated. The NiPc molecules directly deposited on substrates easily form aggregates due to the strong

intermolecular interactions (Figure S2). Due to the poor electric conductivity and limited exposure of active sites of aggregated NiPc, the neat NiPc electrode shows minimal activity in ORR (Figure 2a). Therefore, we physically mixed NiPc with CNTs (denoted as NiPc+CNT) to enhance the conductivity. LSV shows that the physically mixed NiPc+CNT possesses higher activity than that of neat NiPc (Figure 2a). Although NiPc+CNT exhibits even more positive onset potential than NiPc MDE, the low peroxide yields of NiPc+CNT (under 60% in the potential range of 0.70~0.20 V) suggests its much less preference towards the  $2e^-$  pathway compared to NiPc MDE (Figure 2b). Topological defects and N-dopants have been considered as active sites for ORR.<sup>11</sup> However, Pc MDE (prepared by anchoring Pc molecules on CNTs) without metal centers shows inferior ORR activities and selectivity for the  $2e^-$  pathway compared to NiPc MDE (Figure S3). These results suggest the critical role of dispersed Ni centers rather than the N-dopants or topological defects in the selective electrocatalysis of  $2e^-$  ORR.

To investigate the origin of the different ORR behaviors of neat NiPc, NiPc+CNT, and NiPc MDE, their structures were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM (Figure S4a) and SEM (Figure S4b) images of NiPc MDE show the bundles of multi-walled carbon nanotubes and excluded the formation of nano-sized or micro-sized NiPc aggregates. The isolated bright spots in the high-angle annular dark field (HAADF) image of NiPc MDE obtained with a Cs-corrected scanning transmission electron microscope (STEM) indicate the existence of single-Ni sites, suggesting the molecular dispersion of NiPc on CNTs (Figure S5). No appreciable signature peaks of NiPc molecules are observed in the Raman spectrum of NiPc MDE (Figure S6), which could be due to the low content of NiPc in NiPc MDE. On the contrary, physically mixed NiPc+CNT contains micro-sized NiPc aggregates, as revealed by SEM and confirmed by EDS mapping of the Ni signals (Figures S4c and S7).

Electrochemical impedance spectroscopy (EIS) was further conducted to gain insights of the ORR kinetics of the NiPc catalysts in aggregated and dispersed states.

The Nyquist plots in Figure S5d show that the charge transfer of NiPc MDE for ORR

is more favorable than that of NiPc and NiPc+CNT. The neat NiPc exhibited the largest charge transfer resistance, in agreement with its low activity from LSV (Figure 2a). It should be noted that DFT calculations with individual NiPc molecule catalyzing ORR suggest high selectivity toward the  $2e^-$  transfer pathway, which is only observed in dispersed NiPc as in NiPc MDE but not in aggregated NiPc as in NiPc+CNT. These results emphasize the importance of correlating free energy diagrams calculated with individual catalyst molecule with the electrocatalytic performance of dispersed molecular catalysts rather than aggregated molecules.

### Comparison with the pyrolyzed Ni-N/C SAC

SACs have gained extensive attention recently due to their superior electrocatalytic properties. In electrocatalytic applications, SACs were generally fabricated by pyrolyzing metal salts and N-containing organic precursors at high temperature. However, these pyrolyzed SACs easily contained parasitic active sites due to the insufficient structural control during the high-temperature synthesis.<sup>52</sup> For comparison, a nickel SAC with Ni-N<sub>x</sub> structures (denoted as Ni-N/C) was synthesized by pyrolyzing a Ni-containing zeolitic imidazolate framework (ZIF) precursor according to the reported method with minor modifications.<sup>53</sup> The Ni content of the Ni-N/C catalyst was also controlled to be ~0.7 wt.% (measured by ICP-MS) to compare with NiPc MDE. TEM images of Ni-N/C suggest the absence of metallic Ni particles in the catalyst (Figure S8). The XRD pattern of Ni-N/C only shows broad features attributable to graphitic carbon (Figure S9),<sup>53</sup> further indicating the absence of metallic Ni or crystalline Ni-containing compounds. The Fourier-transformed extended X-ray adsorption fine structure (FT-EXAFS) curve of Ni-N/C exhibits a peak at ~1.4 Å (without phase correction) corresponding to Ni-N coordination, but little signal at ~2.1 Å corresponding to Ni-Ni coordination (Figure S10), confirming the presence of single Ni sites in Ni-N/C.

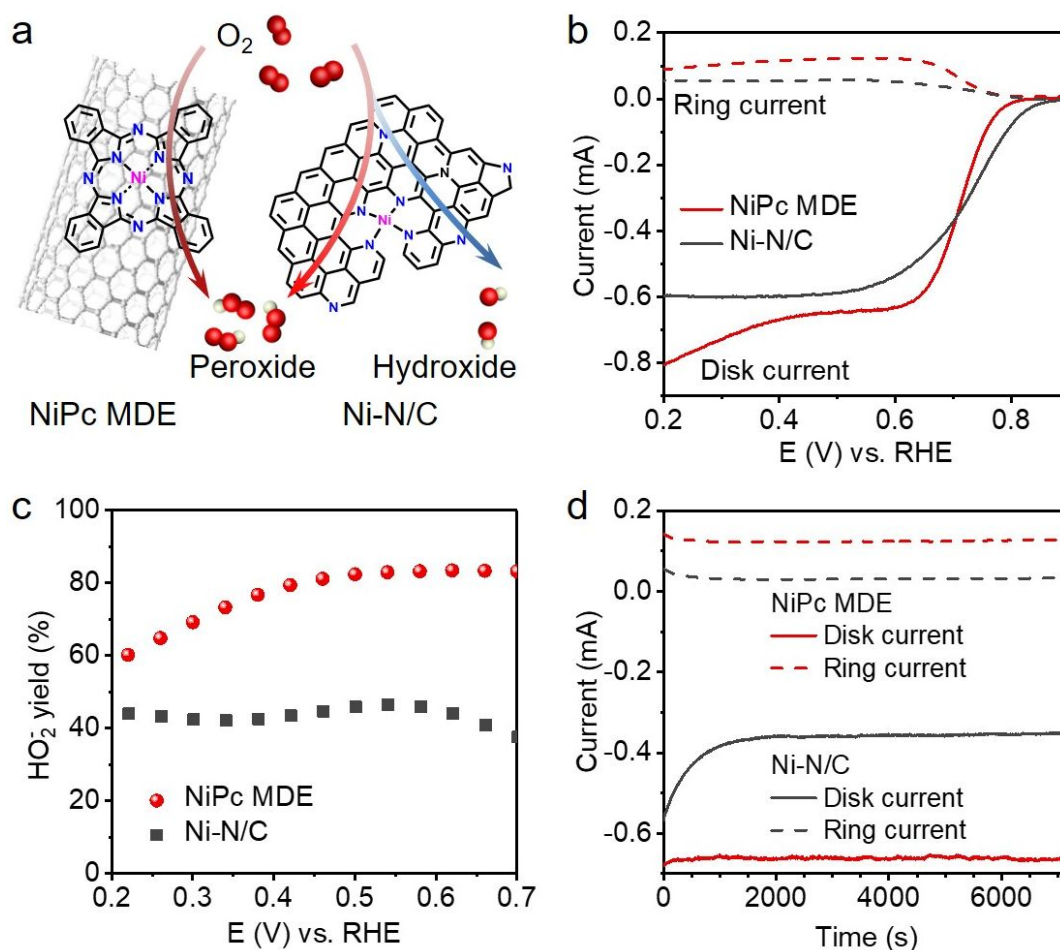


Figure 3. Comparison of electrocatalytic ORR performance between NiPc MDE and Ni-N/C. (a) Schematic presentation of ORR with NiPc MDE and Ni-N/C. (b) Disk and ring currents of NiPc MDE and Ni-N/C in O<sub>2</sub>-saturated 0.1 M KOH electrolytes. (c) Calculated peroxide yields of NiPc MDE and Ni-N/C. (d) Stability tests of NiPc MDE and Ni-N/C under the constant potentials of 0.50 V for the disk electrode and 1.50 V for the ring electrode.

Although no Ni particles are observed, parasitic active sites such as N-doped carbon sites could still present in the Ni-N/C catalyst,<sup>54-55</sup> which are known to be active for 4e<sup>-</sup> ORR (Figure 3a). The ORR performance of the Ni-N/C catalyst was further characterized in the RRDE setup with identical conditions as NiPc MDE. From the LSV curves (Figure 3b), Ni-N/C possesses more positive onset potential (0.83 V) than that of NiPc MDE (0.79 V). The peroxide yields of Ni-N/C are under 43% with *n* larger than 3.1 in the potential range of 0.70~0.20 V (Figures 3c and S11). The much worse

selectivity of the Ni-N/C catalyst toward the  $2e^-$  reduction pathway than that of NiPc MDE is attributed to the structural heterogeneity in the pyrolyzed Ni-N/C catalyst. Additionally, the stability tests were carried out at the constant potentials of 0.50 V for the disk electrode to conduct ORR and at 1.50 V for the ring electrode to detect generated peroxide. As shown in Figure 3d, Ni-N/C shows obvious decay of both the disk and ring currents in the first half hour, suggesting the instability of the pyrolyzed structure. By contrast, NiPc MDE exhibits much better stability without appreciable decay of the disk and ring currents during the measurement. Therefore, the molecularly dispersed and well-defined Ni-N<sub>4</sub> sites in NiPc MDE render it a better ORR catalyst for the  $2e^-$  reduction pathway than the pyrolyzed Ni-N/C. NiPc MDE can be a model catalyst system to establish the relationship between the active site structure and electrocatalytic performance.

### Molecular engineering of NiPc MDEs for ORR

A unique advantage of the MDE system is the capability of manipulating the properties of the active sites and the associated electrocatalytic performance through molecular engineering. Hence, we seek to further improve the performance of NiPc MDE for  $2e^-$  ORR for peroxide production with the introduction of pedant groups to the Pc ligand. We examined nickel phthalocyanine substituted with electron-withdrawing cyano groups (NiPc-CN, nickel(II) 2,3,9,10,16,17,23,24-octacyano-phthalocyanine, see Figure 4a inset for molecular structure) as an ORR catalyst by DFT calculations. The free energy diagrams suggest that, similar to NiPc, NiPc-CN shows strong preference toward the  $2e^-$  reduction pathway and the energy difference of generating  $^*H_2O_2$  over  $^*O$  is enlarged from 0.22 eV with NiPc to 0.37 eV with NiPc-CN (Figure 4a), indicating that NiPc-CN can be a more selective catalyst for  $2e^-$  ORR.

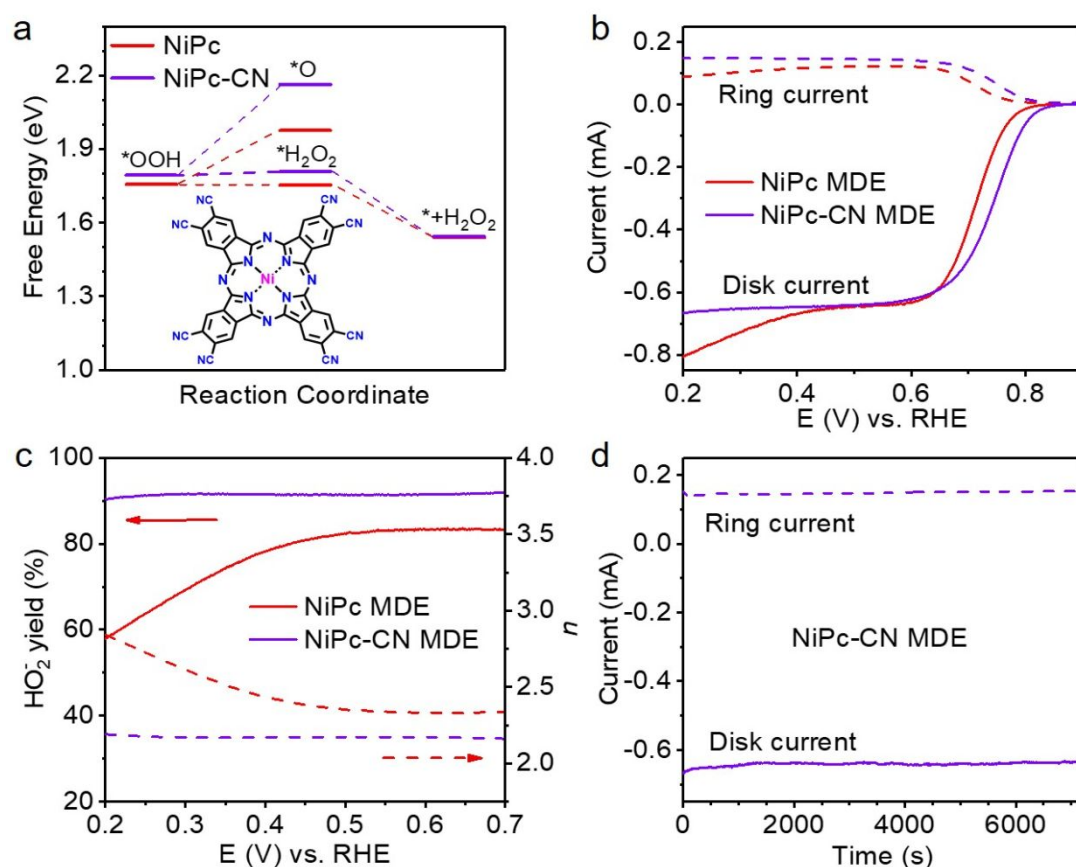


Figure 4. Enhanced ORR electrocatalysis with NiPc-CN MDE. (a) Calculated free energy diagrams of ORR through the 2e<sup>-</sup> and 4e<sup>-</sup> reduction pathways on NiPc and NiPc-CN at 1.23 V. Inset shows the molecular structure of NiPc-CN (b) Disk and ring currents of NiPc and NiPc-CN MDEs in O<sub>2</sub>-saturated 0.1 M KOH electrolytes. (c) Calculated peroxide yields and *n* of NiPc and NiPc-CN MDEs. (d) Stability test of NiPc-CN MDE under the constant potentials of 0.50 V for the disk electrode and 1.50 V for the ring electrode.

NiPc-CN MDE was synthesized (Figure S12) and characterized with the RRDE setup. The LSV curve shows more positive onset potential of NiPc-CN MDE (0.82 V) than that of NiPc MDE (0.79 V) (Figure 4b). Moreover, the saturation current for NiPc-CN MDE remains similar in the potential range of 0.60~0.20 V together with constant ring currents. The peroxide yields of NiPc-CN MDE were calculated to be ~92% from 0.70 to 0.20 V, superior to NiPc MDE with decreased peroxide yields below 0.45 V (Figure 4c). The enhanced peroxide yields of NiPc-CN MDE are consistent with the

improved preference toward the  $2e^-$  reduction pathway from DFT calculations with the introduction of cyano groups (Figure 4a). NiPc-CN MDE also shows good stability in ORR with little decay in the disk and ring currents and the peroxide yields during the operation (Figure 4d). The performance of NiPc-CN MDE for oxygen reduction to peroxide is among the best for the reported single-metal and non-precious metal catalysts, demonstrating high peroxide selectivity of  $\sim 92\%$  at a wide potential window in alkaline conditions (Table S2).

## Conclusions

In summary, driven by rational catalyst design with DFT calculations, we identify NiPc MDE as a good ORR catalyst for the  $2e^-$  reduction pathway and further enhanced its performance through molecular engineering. The enhanced NiPc-CN MDE with cyano group substitution shows superior selectivity with peroxide yield of  $\sim 92\%$  in the potential range of 0.70~0.20 V. The molecularly dispersed and well-defined Ni-N<sub>4</sub> sites on CNTs endow NiPc MDEs higher  $2e^-$  selectivities than the aggregated NiPc and pyrolyzed Ni-N/C catalysts. These results also imply that the MPc MDE system can act as excellent model electrocatalysts for the establishment of the relationship between active site structures and electrocatalytic performances of molecular catalysts and SACs.

## Supporting Information

Supporting Information is available and includes [Supporting Methods, Supporting Figures 1-12, Supporting Tables 1-2, and Supporting References 1-12].

## Conflict of Interest

There is no conflict of interest to report.

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