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# Graphite Conjugation of a Macrocyclic Cobalt Complex Enhances Nitrite Electroreduction to Ammonia

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**ABSTRACT:** This work reports on the generation of a graphiteconjugated diimine macrocyclic Co catalyst (GCC-CoDIM) that is assembled at *o*-quinone edge defects on graphitic carbon electrodes. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy confirm the existence of a new Co surface species with a coordination environment that is the same as that of the molecular analogue,  $[Co(DIM)Br_2]^+$ . GCC-CoDIM selectively reduces nitrite to ammonium with quantitative Faradaic efficiency and at a rate that approaches enzymatic catalysis. Preliminary mechanistic investigations suggest that the increased rate is accompanied by a change in mechanism from the molecular analogue. These results provide a



template for creating macrocycle-based electrocatalysts based on first-row transition metals conjugated to an extreme redox-active ligand.

# INTRODUCTION

Since the inception of the Haber-Bosch process over 100 years ago, the nutritional value of industrial ammonia has been realized by over 4 billion births. While over 100 Tg of fixed nitrogen are used as fertilizer each year, only 17% is actually ingested as protein by humans and livestock.<sup>1</sup> The remainder of the fixed nitrogen is converted to various nitrogen oxyanions (including nitrite) and gases by soil organisms and lost to volatilization or in runoff to waterways.<sup>2</sup> Once in waterways, nitrogen oxyanions can lead to eutrophication and hypoxia, ultimately forming aquatic "dead zones".<sup>3,4</sup> In total, eutrophication is estimated to cause \$2.2 billion of damage each year.<sup>5</sup> In addition, high nitrite concentrations are a significant water quality concern due to their toxicity toward humans and animals.<sup>6,7</sup> Nitrite can irreversibly oxidize hemoglobin to methemoglobin, impairing its ability to bind oxygen and leading to respiratory deficiencies.8,5

Because biological denitrification processes are overwhelmed by anthropogenic nitrogen, there is a need for new methods of chemical nitrite reduction that both eliminate damaging waste streams and yield value-added products, such as ammonia. However, nitrite reduction is complicated by a variety of factors. First, nitrite has complex aqueous phase chemistry, with  $NO_2^-$ ,  $HNO_2$ , and  $NO^+$  dominating the speciation, depending on the solution acidity.<sup>10</sup> Additionally, multiple thermodynamically favored nitrite reduction products exist, many of which have similar reduction potentials,<sup>10</sup> presenting a challenge to product selectivity. Finally, intermediate nitrite reduction products such as  $NH_3OH^+$  can react with nitrite in solution to form undesired products such as the greenhouse gas,  $N_2O.^{10}$  Several molecular electrocatalysts have been reported for the reduction of aqueous nitrite.<sup>11–18</sup> While many copper and iron complexes have been shown to catalyze nitrite reduction to NO, N<sub>2</sub>O, NH<sub>2</sub>OH, and/or NH<sub>4</sub><sup>+,19–24</sup> selective reduction is challenging, with the product distribution dependent on applied potential, pH, and/or reaction time.<sup>25–27</sup> Nonetheless, molecular electrocatalysts having excellent product selectivity have been reported, with a leading example being a CoGGH complex (GGH = Gly-Gly-His model tripeptide), which rapidly reduces nitrite to ammonia with high Faradaic efficiency (~90%).<sup>17</sup>

We previously reported investigations into the mechanism of nitrate and nitrite electroreduction to ammonia by the cobalt macrocycle electrocatalyst,  $[Co(DIM)Br_2]^+$  (DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene) (Scheme 1). These studies demonstrated that both the redox activity and H-bond donor ability of the DIM macrocycle are critical for facilitating N–O bond cleavage.<sup>28,29</sup> However, homogeneous catalysts require *sequential* electron transfer and substrate activation, necessitating the formation of high energy redox intermediates for catalysis to occur.<sup>30,31</sup> The driving force for substrate activation is therefore restricted by the

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reduction potential of the catalyst, which may inhibit rapid substrate turnover.<sup>30</sup>

Heterogeneous electrocatalysts, however, exploit strong electronic coupling throughout the electrode band structure, allowing *concerted* electron transfer and substrate activation, which leads to rapid substrate turnover. A number of heterogeneous nitrite reduction electrocatalysts have been reported, particularly with the noble metals Pd and Pt.<sup>32–39</sup> However, quasi-perfect surfaces are usually required for good product selectivity (e.g., N<sub>2</sub> vs NH<sub>4</sub><sup>+</sup>), which is otherwise poor.<sup>40,41</sup> Mechanistic insight that would lead to improved catalyst design is confounded by the dynamic nature of surface sites, which are challenging to tune or characterize.<sup>30,31</sup>

Heterogenization strategies that either immobilize or tether molecular electrocatalysts to electrode surfaces might be anticipated to facilitate tunable active sites. However, the weak physisorption/electrostatic interactions<sup>42,43</sup> or strong covalent linkages<sup>44–50</sup> associated with these strategies often result in poor coupling between the affixed species and the metallic band structure.<sup>31,51</sup> For example, anodic electropolymerization of an iron protoporphyrin on glassy carbon produces a film capable of nitrite reduction; however, this catalyst suffers from poor product selectivity and film instability.<sup>52</sup>

Recently, the Surendranath group introduced a new strategy for creating molecularly well-defined, surface immobilized electrocatalysts, where the native surface topology of an oxidized glassy carbon electrode provides a platform for constructing graphite-conjugated pyrazines as tunable heterogeneous electrocatalysts. Specifically, Schiff base condensation between *ortho*-quinone moieties on the electrode surface and *ortho*-phenylenediamine derivatives generates pyrazine units that are integrated into the conjugated graphite surface.<sup>53</sup> This strategy can be extended to incorporate preformed transitionmetal-based electrocatalysts.<sup>54</sup>

In this paper, we apply this electrode functionalization strategy to prepare the graphite-conjugated analogue of  $[Co(DIM)Br_2]^+$ . The resulting graphite-conjugated catalyst (GCC-CoDIM) has been characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) and shown to be a robust incorporation of the molecular  $[Co(DIM)Br_2]^+$  catalyst into the electrode surface. Notably, GCC-CoDIM reduces  $NO_2^-$  to  $NH_4^+$  with quantitative Faradaic efficiency and with turnover frequency approaching enzymatic rates.

# RESULTS AND DISCUSSION

Chemically modified electrodes are prepared via Schiff base condensation of 1,2-bis(3-aminopropylamino)ethane with anodically treated glassy carbon electrodes under acidic conditions, followed by metalation with Co(II) to yield CoDIM graphite-conjugated catalysts (GCC-CoDIM) (Scheme 2). Nonmacrocyclic imine and/or physisorbed species are cleaved by a washing procedure followed by a reductive scan.  $^{53}$ 



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The modified electrode surface was characterized by X-ray photoelectron spectroscopy (XPS). High resolution XPS spectra of GCC-CoDIM exhibit peaks corresponding to N 1s (Figure 1a top) and Co 2p (Figure 1a bottom) that are absent in unmodified or oxidized glassy carbon electrodes (Figure S17). The N 1s spectrum can be deconvoluted to two peaks centered at 399.2 and 399.9 eV, corresponding to the imine and amine nitrogens, respectively.<sup>55</sup> The Co 2p spectrum displays the  $2p_{3/2}$  and  $2p_{1/2}$  doublet at 781.0 and 796.4 eV, respectively, consistent with Co(III).<sup>55</sup> Importantly, the same N 1s and Co 2p features are observed in the XPS of the molecular [Co(DIM)Br<sub>2</sub>]<sup>+</sup> complex (Figure S18, Table S6). XPS of GCC-CoDIM also provides evidence for exchangeable sites. Specifically, high resolution Br 3d and Cl 2p data obtained after soaking the electrode in 1.0 M KCl show a decrease in Br content with the simultaneous appearance of new Cl signals (Figure S18), providing a final Cl/Co ratio of 2:1. Together, these data support the formation of isolated  $[Co(DIM)Br_2]^+$  sites conjugated to the graphite surface that are capable of ligand exchange. This observation of ligand exchange differs from previously reported graphite-conjugated catalysts,<sup>31</sup> but is consistent with the substitutional lability of 3d metal ions.

X-ray absorption spectroscopy (XAS) for modified high surface area Monarch 1300 carbon black powder was used to interrogate the molecular structure of the GCC-CoDIM surface. The pre-edge feature (7711.2 eV) and edge position (7724.3 eV) in the Co K-edge X-ray absorption near edge spectrum (XANES) correspond to Co(III) in an octahedral environment (Figure 1b).<sup>56,57</sup> Additionally, a fit to the extended X-ray absorption fine structure (EXAFS) spectrum (Figure 1c) is in excellent agreement with the crystal structure of molecular  $[Co(DIM)Br_2]^+$  (Table S2).<sup>28</sup> Specifically, the fit to the EXAFS data shows four N and two Br atoms in the first shell, with two short (1.93(1) Å) and two longer (1.98(1) Å)Co-N distances. These are the same as the Co-N<sub>imine</sub> (1.930(2) Å) and Co-N<sub>amine</sub> (1.975(2) Å) distances observed in the X-ray crystal structure of [Co(DIM)Br<sub>2</sub>]<sup>+</sup>.<sup>28</sup> In addition, the fit also provides two Co-Br distances (2.39(4) Å) which are also the same as in the molecular complex, where Co-Br =2.4009(1) Å. Taken together, the XAS and XPS data demonstrate that the molecular structure of the cobalt ion in  $[Co(DIM)Br_2]^+$  is replicated at the surface of graphite in GCC-CoDIM.

The cyclic voltammogram of GCC-CoDIM in aqueous electrolyte reveals a broad, Gaussian-shaped redox process at  $E_{1/2} = -0.46$  V vs SCE in Figure 2. The linear variation of this peak current with scan rate (Figure 2, inset) indicates a surface-based electrochemical process. This is further sup-



Figure 1. (a) High resolution N 1s (top) and Co 2p (bottom) XPS spectra of GCC-CoDIM after soaking in base solution. (b) Normalized Co Kedge XANES spectrum of CoDIM-modified Monarch 1300 carbon powder. (c) EXAFS spectrum (gold) and fit (blue) in R-space at the Co K-edge absorption of CoDIM-modified Monarch 1300 carbon powder.



**Figure 2.** Cyclic voltammogram of GCC-CoDIM recorded in Arsaturated 0.5 M Na<sub>2</sub>SO<sub>4</sub>, scan rate 100 mV/s. Inset: Plot of  $i_{p,c}$  vs  $\nu$  and the best fit. The plot fits to the equation:  $y = 0.0165x + 5.513 \times 10^{-4}$ ,  $R^2 = 0.999$ .

ported by the small peak-to-peak separation ( $\sim$ 50 mV), which is characteristic of a surface-bound and not freely diffusing species.<sup>58</sup>

Integration of this redox wave allows the surface coverage of GCC-CoDIM to be estimated (Figure S3). Assuming one electron transferred per CoDIM unit, the surface coverage is ~0.56 nmol cm<sup>-2</sup>, comparable to that of previously reported graphite-conjugated species.<sup>53,54</sup> Bromide quantification<sup>59</sup> following acid digestion of the electrode provides a surface coverage of ~0.42 nmol cm<sup>-2</sup>, consistent with the electro-chemically determined value.

The GCC-CoDIM catalyst is highly active toward the electroreduction of aqueous nitrite. With 0.5 M  $Na_2SO_4$  electrolyte, the cyclic voltammogram of GCC-CoDIM in the presence of  $NaNO_2$  exhibits a large catalytic wave with onset potential -1.17 V vs SCE (Figure 3a, blue). No catalytic current is observed in the absence of  $NaNO_2$  (Figure 3a, gold). Importantly, no catalytic current is observed when a functionalized electrode is polished and reimmersed in the electrolyte solution (Figure 3a, red). This indicates that the catalytic current does not arise from leached surface species, but rather a surface-bound electrocatalyst. In addition, independently prepared electrodes exhibit identical activity, demonstrating



Figure 3. (a) Cyclic voltammogram of GCC-CoDIM recorded in Arsaturated 0.5 M  $Na_2SO_4$  (gold), with 250 mM  $NaNO_2$  (blue), and with 250 mM  $NaNO_2$  after polishing the GC electrode (red), scan rate 100 mV/s. (b) Charge passed during CPE with GCC-CoDIM on flexible graphite (FG) (blue) or oxidized FG prefunctionalization (orange) in 0.5 M  $Na_2SO_4$  with 20 mM  $NaNO_2$  for 2 h at -1.4 V vs SCE.

the reproducibility of catalyst preparation (Figure S4). Moreover, the electrocatalytic activity is constant over a wide pH range (Figure S8).

Product quantification following controlled potential electrolysis (CPE) of GCC-CoDIM and 20 mM NaNO<sub>2</sub> at -1.4 V vs SCE shows that the only nitrogen-containing product formed is NH<sub>4</sub><sup>+,60,61</sup> with a Faradaic efficiency of 99.5%. This shows that the GCC-CoDIM electrode retains the excellent

selectivity for NH<sub>4</sub><sup>+</sup> production observed for its molecular analogue,  $[Co(DIM)Br_2]^{+.28,29}$  The linearity of the charge vs time curve for GCC-CoDIM in the presence of NaNO<sub>2</sub> (Figure 3b) indicates that the catalytic activity does not decline over the electrolysis period.

High resolution XPS data of the electrode following CPE show no change in the position of the Co 2p peaks (Figure S16). Moreover, no peaks are observed at ~778.3 eV (the anticipated energy of the Co  $2p_{3/2}$  peak of Co<sup>0</sup>), which excludes the formation of metallic Co nanoparticles. Finally, high resolution N 1s data show no change after 2 h reductive polarization, suggesting that the surface functionalization remains robust under catalytic conditions. Together with the CPE results, this supports the persistence of the surface Co species.

The CPE experiments allow the turnover frequency (TOF) to be determined, TOF = 19.9 s<sup>-1.62</sup> This represents a rate increase of 5 orders of magnitude over molecular [Co(DIM)- $Br_2$ ]<sup>+</sup>, where TOF = 0.0026 s<sup>-1</sup> under similar conditions (CPE at -1.05 V vs SCE).<sup>29</sup> This rate is also orders of magnitude greater than that of the fastest reported homogeneous electrocatalyst, CoGGH, where  $TOF_{max} = 0.18 \text{ s}^{-1}$  at -0.90V vs SCE.<sup>17</sup> Indeed, the rate of nitrite reduction by GCC-CoDIM approaches that of cytochrome *c* nitrite reductase, the biological enzyme responsible for nitrite reduction, where  $TOF_{max} = 528 \text{ s}^{-1} \text{ at } -0.89 \text{ V vs SCE.}^{63} \text{ It is also worth noting}$ that electrocatalytic nitrite reduction by GCC-CoDIM is markedly faster than for heterogeneous nitrite electrocatalysts, including morphologically controlled Pt nanoparticles (TOF = 0.0080  $s^{-1}$ ),<sup>36</sup> and Pd-loaded carbon nanofiber/Ni foam catalysts (TOF =  $0.022 \text{ s}^{-1}$ ),<sup>64</sup> both of which have significantly lower product selectivity.



**Figure 4.** Potentiostatic Tafel data runs collected with GCC-CoDIM in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with 40 mM NaNO<sub>2</sub> (black circles). The slope of the best fit line (red) is 154.5 mV dec<sup>-1</sup>.  $R^2$  = 0.9995.

A Tafel analysis provides preliminary mechanistic insight into catalysis by GCC-CoDIM. Steady-state currents were normalized to the surface concentration of Co as determined by surface process integration in the cyclic voltammogram after ten cycles. The resulting Tafel plot (Figure 4) is linear over an ~0.1 V range, with the slope (154.5 mV/dec) consistent with catalysis controlled by rate limiting single electron transfer, for which the ideal slope value is 120 mV/dec.<sup>65,66</sup> It is possible that the large Tafel slope is due to a nonideal value of the symmetry coefficient ( $\alpha \neq 0.5$ ) caused by the conjugation of pubs.acs.org/JACS

the catalyst to the electrode.<sup>66,67</sup> Similarly large slopes have been observed with other graphite-conjugated catalysts.<sup>30,54</sup> In the case of the molecular electrocatalyst, the rate-determining step was found to be N–O bond cleavage after multiple electron transfer steps.<sup>29</sup> This suggests that graphite conjugation leads to a change in the reduction mechanism from the molecular catalyst  $[Co(DIM)Br_2]^+$ .

## CONCLUSION

In summary, we have demonstrated the straightforward preparation of GCC-CoDIM, which is a graphite-conjugated analogue of the macrocycle complex  $[Co(DIM)Br_2]^+$ , a molecular electrocatalyst for nitrogen oxyanion reduction. Electrode conjugation significantly increases the rate of nitrite reduction, while retaining the high product selectivity and Faradaic efficiency. Preliminary mechanistic investigations suggest that electrode conjugation leads to a change in the reduction mechanism.

This exceedingly tunable platform is expected to provide significant versatility for the design of immobilized macrocyclebased electrocatalysts. Indeed, in contrast to the molecular analogue, where only Co and Ni centers have been installed and ligand modifications are difficult,<sup>68,69</sup> the stepwise synthetic procedure is expected to make access to a wide range of graphite-conjugated macrocycle electrocatalysts facile.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c03427.

Full experimental details (PDF)

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#### Notes

The authors declare no competing financial interest.

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