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Covalent attachment of [Ni(alkynyl-cyclam)]$^{2+}$ catalysts to glassy carbon electrodes.

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Surface modification of glassy carbon electrodes (GCEs) with molecular electrocatalysts is an important step towards developing more efficient heterogeneous CO_2 reduction materials. Here, we report direct anodic electrografting of [Ni(alkynyl-cyclam)]$^{2+}$ catalysts to the surface of GCEs in one simple step using inexpensive earth-abundant chemicals. When modified, these electrodes show reversible electrochemistry in organic solvents with zero peak-to-peak separations (ΔE = 0) and non-diffusive I(V) profiles that are typical for heterogeneous redox materials. CPE of these electrodes showed enhanced formation of H_2 gas relative to CO compared to homogeneous catalysts.

Surface modification of glassy carbon electrodes (GCEs) with molecular catalysts has been one of the most active and promising areas of electrocatalysis in the past decade. Surface modification of electrode materials through the covalent attachment of molecular catalysts is an essential step towards creation of new, scalable, robust electrocatalyst materials with unique structures and properties.[1] These materials can be used in basic electrochemical studies, energy conversion and storage, aerospace, biomedical and semiconductor industries.

Development of surface confined catalytic systems allows combining the most advantageous properties of homogeneous catalysis such as high reactivity and selectivity with those of heterogeneous catalysis - simple product separation, low catalyst loadings and simple catalyst regeneration. In homogeneous electrocatalysis, the diffusion of reactive species to the electrode surface is an important factor that affects the rate of catalysis. Electrodes with surface-attached catalysts represent heterogeneous systems and are capable of increased efficiency due to the absence of catalyst diffusion limitations.

There are only a few reports in the literature of surface modification of GCEs with molecular electrocatalysts, despite the fact that glassy carbon is one of the most common materials used in electrochemistry. Here we report the successful covalent attachment of macrocyclic [Ni(alkynyl-cyclam)]$^{2+}$ electrocatalysts to the surface of GCE. Despite high interest in its catalytic properties there are no previous reports in the literature of a covalent attachment of [Ni(cyclam)]$^{2+}$ to the surface of a GCE.

[Ni(cyclam)]$^{2+}$ is a low cost homogeneous electrocatalyst widely known for its high reactivity towards electrochemical reduction of CO_2 to CO at low potential (-1.2 V vs. NHE) and its ability to operate in aqueous media with high turnover rates and selectivity towards CO production at metal[2,3] and glassy carbon electrodes[4]. Incorporation of a [Ni(cyclam)]$^{2+}$ catalyst to the electrode surface can significantly increase electrocatalytic rates and provide all of the benefits of heterogeneous catalysts. The recent report by Leem *et al.* describes a self-assembled Nicyclam-BTC on ITO glass and its enhanced electrocatalysis for water oxidation[5]. The incorporation of [Ni(cyclam)]$^{2+}$ into an artificial metalloenzyme described by Schneider *et al.* improved the selectivity of CO_2 reduction over hydrogen production by these enzymes[6]. In the paper by Neri and co-workers [Ni(cyclam-COOH)]$^{2+}$ was immobilized onto FTO surfaces for photoelectrochemical CO_2 reduction[7], Kashiwagi *et al.* described polymer encapsulated [Ni(cyclam)]$^{2+}$ at a graphite felt electrode and showed that these modified electrodes can efficiently reduce various organic substrates[8]. Even though glassy carbon surface modification is challenging there are several techniques that allow efficient modification of electrode surfaces, including modification of electrodes through Click chemistry[9], hydrogen plasma treatment[10], electrochemical assisted attachment[11], etc. Anodic electrografting of ferrocenyl derivatives and porphyrins through ethynyl linkages to glassy carbon and other electrode surfaces was previously described by the Geiger group.[12] According to this method, the key step in the mechanism of anodic electrografting through terminal

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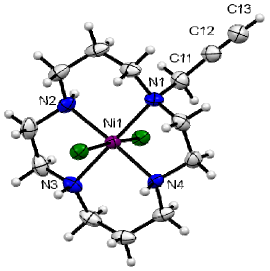

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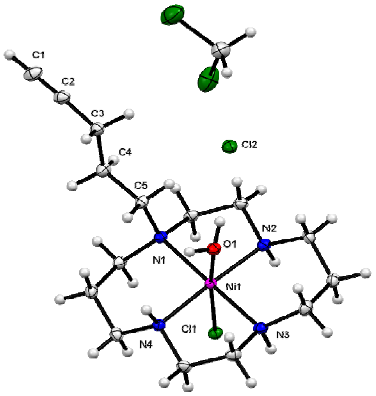

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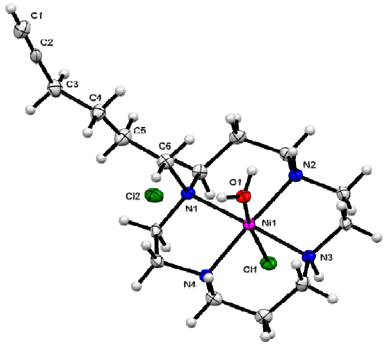
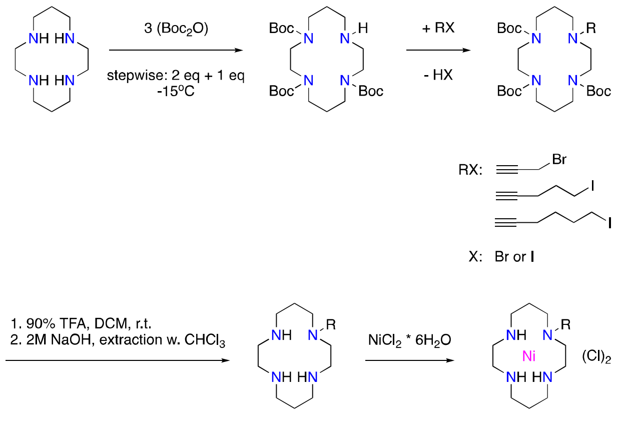


3

alkynes is the formation of alkynyl radicals. One-electron oxidation increases the acidity of the alkyne causing the loss of a proton and formation of alkynyl radicals which react with the surface of a GCE. Following this method, we successfully modified GCEs through the alkynyl radical electrografting procedure with [Ni(alkynyl-cyclam)]$^{2+}$ molecules. Newly modified electrodes were studied using electrochemical methods such as cyclic voltammetry (CV), scan rate dependence, and differential pulse voltammetry (DPV). The linear dependence of peak current versus scan rate confirmed the heterogeneous nature of surface bound redox species.

The synthesis of new alkynyl-cyclam ligands as well as new nickel complexes [Ni-propargyl-cyclam]$^{2+}$ (**1**), [Ni-pentynyl-cyclam]$^{2+}$ (**2**) and [Ni-hexynyl-cyclam]$^{2+}$ (**3**) are described here for the first time. The synthetic route for alkynyl-cyclams includes the following steps: selective tri-Boc-protection of cyclam[13], N-functionalization using propargyl bromide[14], 5-iodo-1-pentyne or 6-iodo-1-hexyne, deprotection in TFA/DCM solution, which resulted in the formation of a trifluoroacetate salt. The salt was basified with 2 M NaOH and the ligand was extracted with chloroform[15] (Scheme 1). The corresponding nickel complexes were obtained using the newly synthesized ligands and nickel chloride hexahydrate ($NiCl_2·6H_2O$). A color change from green to purple was observed upon ligand coordination in anhydrous ethanol. Purple crystals suitable for the X-ray analysis were obtained through vapor diffusion in DCM/pentane. Crystal structures for [Ni(propargyl-cyclam)]$^{2+}$ (complex **1**), [Ni(pentynyl-cyclam)]$^{2+}$ (complex **2**) and Ni(hexynyl-cyclam)]$^{2+}$ (complex **3)** are shown in Figure 1.



Scheme 1. Synthesis of [Ni(alkynyl-cyclam)]$^{2+}$ complexes.

Homogeneous electrochemical CO_2 reduction experiments using the [Ni(alkynyl-cyclam)]$^{2+}$ complexes showed reactivity towards CO_2 reduction in MeCN/water mixtures and are good candidates for further development of a heterogeneous system with attached Ni(alkynyl-cyclam) complexes. Homogeneous CO_2 reduction by [Ni(hexynyl-cyclam)]$^{2+}$ in acetonitrile/water mixture showed catalytic current enhancement at -1.65 V vs. Fc$^{+/0}$ at a glassy carbon electrode under CO_2 atmosphere (Figure S2). Notably, the reduction potential is almost 0.2 V less negative for complex **3** in comparison to the parent catalyst [Ni-cyclam]$^{2+}$ at the same conditions[16]. Similar current increases were detected for complexes **1** and **2** in the presence of 20% water under a CO_2 atmosphere.

Cyclic voltammetry of complex **1** (0.5 mM) in DCM/TBAPF$_6$ solution showed the Ni$^{III/II}$ couple at +0.35 V vs. Fc$^{+/0}$ as well as propargyl oxidation at +1.65 V vs. Fc$^{+/0}$ (Figure 2A). Multiple scans (up to 10 anodic scans) through the alkynyl group resulted in the attachment of [Ni(propargyl-cyclam)]$^{2+}$ at the GCE surface, as determined by CV after thorough rinsing of the modified electrode in DCM and transferring the electrode to a pure electrolyte solution.

Electrodes modified with complex **1** (mod-GCE-1) were studied using cyclic voltammetry and differential pulse voltammetry experiments. The reversible Ni$^{III/II}$ redox couple was observed at -0.1 V vs. Fc$^{+/0}$ and the peak to peak separation $\Delta E_{1/2}$ was nearly 0 V which indicates the heterogeneous nature of the surface attached species and the absence of diffusion limitations (Figure 2B). Scan rate dependence studies were performed on newly prepared electrodes and were taken within the scan rate range of 10 – 70 mV/s (Figure 2C). The peak current of Ni$^{III/II}$ redox couple increased linearly with increasing scan rate. The linear fit is another confirmation of the heterogeneous nature of the surface bound [Ni(propargyl-cyclam)]$^{2+}$ (Figure S7). Similar behavior was observed for a GCE modified with complex **2** (mod-GCE-2) or complex **3** (mod-GCE-3). The CV of complex **2** showed a reversible Ni$^{III/II}$ couple at +0.38 V vs. Fc$^{+/0}$ and the pentynyl oxidation peak at +1.93 V vs. Fc$^{+/0}$ (Figure S5). After 10 scans mod-GCE-2 showed a reversible Ni$^{III/II}$ peak at -0.04 V vs. Fc$^{+/0}$ (Figure S1A) and the scan rate studies showed a linear dependence of peak current vs. scan rate (Figure S8). Cyclic voltammetry of complex **3** in 0.1M TBAPF$_6$ /DCM solution

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showed the $Ni^{III/II}$ redox couple at +0.35 V vs. $Fc^{+/0}$ and the hexynyl oxidation at +1.8 V vs. $Fc^{+/0}$ (Figure S3). A GCE modified with **3** showed reversible $Ni^{III/II}$ redox couple at -0.03 V vs. $Fc^{+/0}$ with minimal $\Delta E_{1/2}$ in pure $TBAPF_6$/DCM solution (Figure S1B). The peak current increased linearly with increasing scan rate similar to the scan rate dependence of mod-GCE-1 (Figure S9). The $Ni^{III/II}$ redox couple of complexes **1**, **2** and **3** for homogeneous solution and surface attached species are summarized in Table S1. The redox potential difference (ΔE) between surface attached species and homogeneous species in solution decreased with the increasing length of a carbon chain linker.

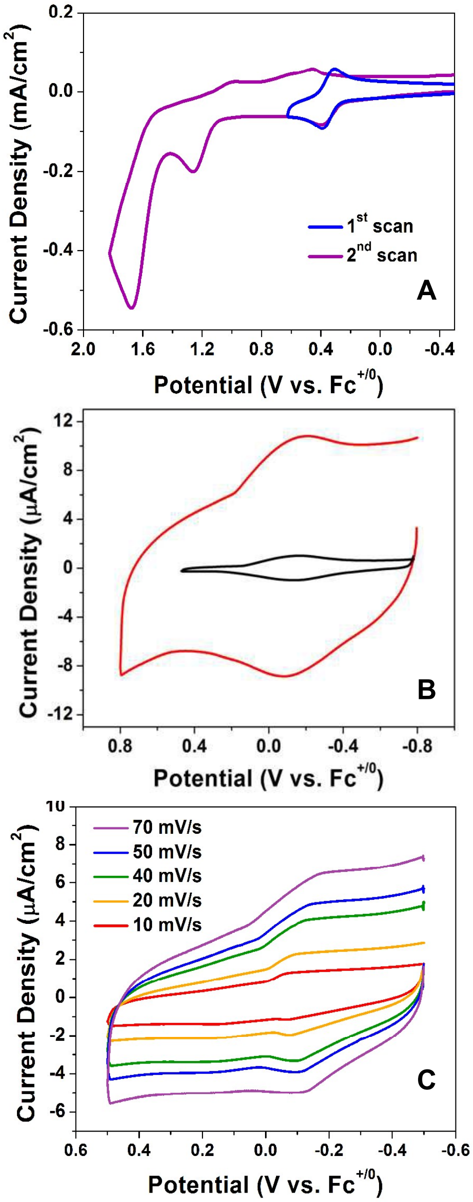

Figure 2. CV of [Ni(propagyl-cyclam)]$^{2+}$ in 0.1 M $TBAPF_6$/DCM solution. Scan rate 100 mV/s **(A)**. CV of mod-GCE-1 in 0.1 M $TBAPF_6$ in DCM. Scan rate 100 mV/s (red), 5 mV/s (black) **(B)**. CV of mod-GCE-1 in 0.1 M $TBAPF_6$ in DCM at various scan rates **(C)**.

Experimental surface coverages were obtained from the differential pulse voltammetry (DPV) and are based on the electrochemical charge (Q) passed through the surface of the electrode. Determination of the surface coverage of modified electrodes was calculated using Equation 1[17]:

$$(1) \quad \Gamma = Q/nFA$$

where n – number of electrons, F – Faradaic constant, A – the electrode surface area, Γ – the surface coverage in moles of adsorbed molecules per cm^2.

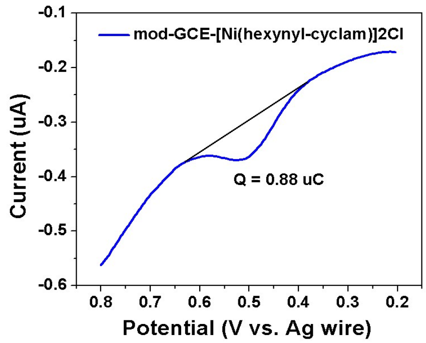

Figure 3. DPV experiment of mod-GCE-3 in 0.1 M $TBAPF_6$/DCM.

DPV experiments for the electrode modified with [Ni(hexynyl-cyclam)]$^{2+}$ showed a charge of 0.88 uC that corresponds to the surface coverage of 1.28×10^{-10} mol/cm^2 and is in exact agreement with the theoretical value of 1.28×10^{-10} mol/cm^2 (Figure 3). Monolayer coverage was determined in all three cases. Detailed surface coverage calculations for GCE modified with complex **1**, **2** and **3** are provided in SI. Theoretical and experimental surface coverages for all modified GC electrodes are summarized in Table 1. Theoretical surface coverages of the modified electrodes were calculated according to previously described methods for Fc molecules[18] and are provided in SI.

Heterogeneous CO_2 reduction experiments using newly modified GCEs were carried out in 0.1 M $TBAPF_6$/MeCN solution with 20% water as a proton source. The CV shows a current increase at -1.45 V vs. $Fc^{+/0}$ under CO_2 and reached a plateau at -2.3 V vs. $Fc^{+/0}$ (Figure 4).

In order to carry out controlled potential electrolysis (CPE) experiments, modified Tokai glassy carbon electrodes with larger surface area (2 cm^2) were prepared by anodic electrografting. CPE experiments were run in CO_2 saturated MeCN/water solution and the headspace of the cell was sampled for gas chromatography analysis. When held at -2.4 V for 1 h, the

Table 1. Theoretical and experimental surface coverage of glassy carbon electrodes modified with [Ni(alkynyl-cyclams)]$^{2+}$.

	mod-GCE-1	mod-GCE-2	mod-GCE-3
Diameter (d, Å)	8.13	10.36	11.23
Charge (uC)	1.54	1.02	0.88
Theor. (10^{-10} mol/cm^2)	2.53	1.62	1.28
Exp. (10^{-10} mol/cm^2)	2.25	1.46	1.28

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average Faradaic efficiency was determined to be 89% for H_2 and 7% for CO (Table S2 and Fig. S13). CPE for homogenous Ni-alkynyl cyclams were carried out at the same conditions with average FE 54% for CO and 39% for H_2. These results are consistent with previous findings that functionalized Ni(cyclam)$^{2+}$ will catalyze CO_2 reduction to CO and H_2[16]. Functionalized -NH groups on cyclam ligand appear to increase H_2 production and lower selectivity for CO. It was also previously shown that the interaction between the cyclam ligand and the electrode surface has a significant influence on the efficiency of Ni-cyclam catalysts, where the flatness of the ligand to the electrode surface facilitates production of CO.[3] Ni-alkynyl cyclam molecules may undergo structural hindrance when attached to the GCE surfaces which resulting in increased evolution of H_2 gas.

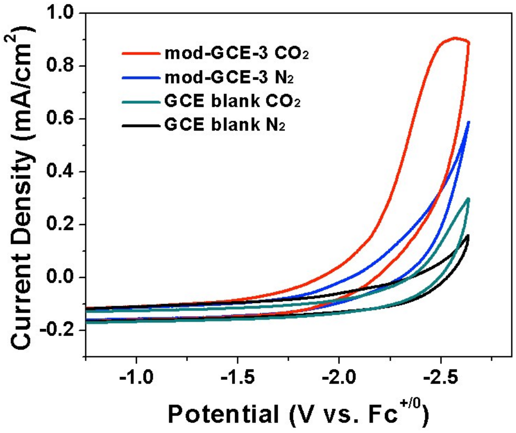

Figure 4. CV of mof-GCE-3 in 0.1 M $TBAPF_6$/MeCN with 20% water under CO_2 (red) and under N_2 (blue) and blank GCE under CO_2 (green) and under N_2 (black).

We have modified the surface of the GCE with [Ni(alkynyl-cyclam)]$^{2+}$ catalysts using direct anodic electrografting. To the best of our knoweledge, this is the first report of the direct attachment of a molecular catalyst to the surface of GCE. Electrochemical studies performed on these electrodes showed that [Ni(alkynyl-cyclam)]$^{2+}$ molecules were attached to the surface in heterogeneous fashion, eliminating diffusion limitations that are typical for homogeneous catalysis. CPE studies of the modified electrodes increased the hydrogen evolution reaction (HER) relative to CO_2 reduction to CO during 1 h electrolysis. Structural configuration and orientation of cyclam ligand plays an important role in product distribution. Functionalized -NH groups on cyclam ligand and orientation of the attached Ni-cyclam catalysts towards the surface of the electrode may also play a crucial role for the selective CO_2 reduction by these systems.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Experimental data including cyclic voltammetry experiments, synthesis and characterization are provided in ESI.

§ CCDC 1580804, 1580806, and 1580807 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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