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Covalent Attachment of Catalyst Molecules to Conductive Diamond: CO_2 Reduction Using "Smart" Electrodes

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Supporting Information

ABSTRACT: We report here covalent attachment of a catalytically active cobalt complex onto boron-doped, p-type conductive diamond. Peripheral acetylene groups were appended on a cobalt porphyrin complex, and azide—alkyne cycloaddition was used for covalent linking to a diamond surface decorated with alkyl azides. The functionalized surface was characterized by X-ray photoelectron spectroscopy and Fourier transform IR spectroscopy, and the catalytic activity was characterized using cyclic voltammetry and FTIR. The catalyst-modified diamond surfaces were used as "smart" electrodes exhibiting good stability and electrocatalytic activity for electrochemical reduction of CO_2 to CO in acetonitrile solution.

Tethering electrocatalytically active molecules to conductive surfaces combines the advantages of highly efficient conversion of electrical energy into chemical energy with the convenience, stability, and low catalyst loadings of heterogeneous catalyst systems.[1] The boron-doped, p-type conductive crystalline diamond surface is especially suitable as a cathode because of its high overpotential for hydrogen production and stability under reductive conditions.[2] Taking advantage of these properties and the facile electrode/molecule electron transfer rates available through surface immobilization, we report here the covalent attachment of a cobalt CO_2 reduction catalyst[3] to a conductive diamond surface, creating "smart" electrodes that can electrochemically catalyze CO_2 reduction at −1.5 V vs Ag/Ag^+/3 M NaCl in anhydrous acetonitrile.

Extensive efforts to devise appropriate catalysts for CO_2 reduction have been made,[3,4] and metalloporphyrins [abbreviated here as M(Por)] represent an important class of catalysts for this process.[3,4f] However, their electrochemical utility has been hindered by poor solubility in reductively stable solvents. Developing heterogeneous M(Por) systems is one strategy for overcoming this limitation, and metalloporphyirns containing earth-abundant metals such as Co are of particular interest for CO_2 reduction.[5] Although Co(Por) catalysts physically adsorbed onto surfaces or porous substrates have demonstrated CO_2 reduction,[6,7] covalent attachment of the catalysts onto solid substrates promises greater stability and ease of characterization. To this end, reports have shown covalent attachment of the CO_2 electroreduction catalyst Re$(CO)_4$(bipyridine) onto TiO_2 via a carboxylate linkage,[4k] and mesoporous silica-immobilized Fe(Por) is also relevant to this discussion.[8] However, neither of these oxide substrates is ideal for the strongly reductive conditions necessary for CO_2 reduction.

Aramata and co-workers reported Co(Por) attachment to glassy carbon via an amide linkage;[9] however, this attachment is still susceptible to protonation in an acidic reductive environment. Here we utilized a photochemical grafting method previously developed by us[1h,10] to link a monolayer of 10-undecen-1-ol onto hydrogen-terminated surfaces of microcrystalline, boron-doped "electrochemical grade" diamond (Element Six, Inc.) using UV light (254 nm), forming a very stable sp^3—sp^3 C—C linkage at the diamond—molecule interface.[1h] The resulting alcohol-terminated surface could subsequently be converted to an azide-terminated surface by mesylation followed by treatment with sodium azide.[1h]

We prepared Co(Por^{alkyne}) (**1**) [Por^{alkyne} = (5,10,15,20-tetra-*p*-ethynylphenylporphrin)] bearing four alkyne groups using the modified procedure by Lindsey.[11] An active Co(Por^{alkyne}) complex was covalently grafted to the azide-functionalized diamond surface[1h] via the Cu^I-catalyzed azide—alkyne cycloaddition (CuAAC or "click") reaction,[12] as shown in Figure 1a. The cycloaddition reaction employed a modified procedure based on several known porphyrin "click" reactions in the literature.[13] Notably, a 1:3 (v/v) tetrahydrofuran/ethyl acetate solvent mixture was used to accommodate the drastically different solubilities of the reactants. The progress of the covalent grafting of the porphyrin was monitored by Fourier transform IR spectroscopy (FTIR) as a function of reaction time by observing the azide stretching vibration near 2090 cm^{-1} (see Figure 1b and the Supporting Information). Figure 1b shows the FTIR spectrum before and after the cycloaddition of Co(Por^{alkyne}) to the azide on the diamond surface (**1-Diamond**). The intensity of the azide stretch at 2090 cm^{-1} was reduced by 80% after the "click" reaction. A control reaction using non-alkyne-functionlized Co(TPP) (TPP = *meso*-tetraphenylporphyrin) following the same procedure was performed (**2-Control**), in which case the azide peak remained unchanged under the same conditions (Figure 1c). From these data, we can conclude that the surface azide groups react specifically with the alkynes under these reaction conditions.

After the reaction, the samples were further characterized by X-ray photoelectron spectroscopy (XPS). Figure 1d shows the Co(2p) region of the XPS spectra of the two samples. In **1-Diamond**, where Co(Por^{alkyne}) was used, Co $2p_{1/2}$ and $2p_{3/2}$

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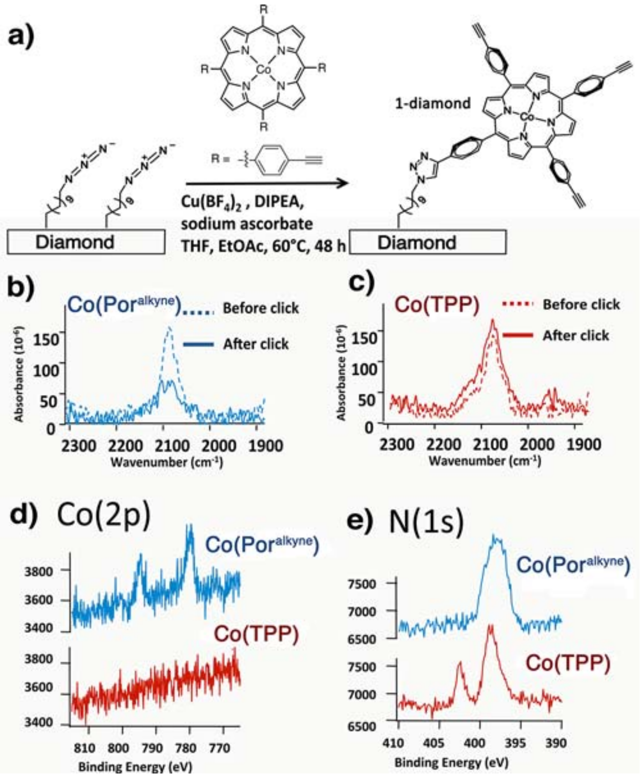

Figure 1. (a) Attachment of Co(Por^{alkyne}) (**1**) onto an azide-functionalized diamond surface by the "click" reaction to form the surface adduct **1-Diamond**. (b) FTIR spectrum showing the azide asymmetric stretching region before and after the "click" reaction. (c) FTIR spectrum of **2-Control**. (d) Co(2p) and (e) N(1s) regions of the XPS spectra of the "clicked" Co(Por^{alkyne})−diamond adduct **1-Diamond** and **2-Control** obtained using Co(TPP).

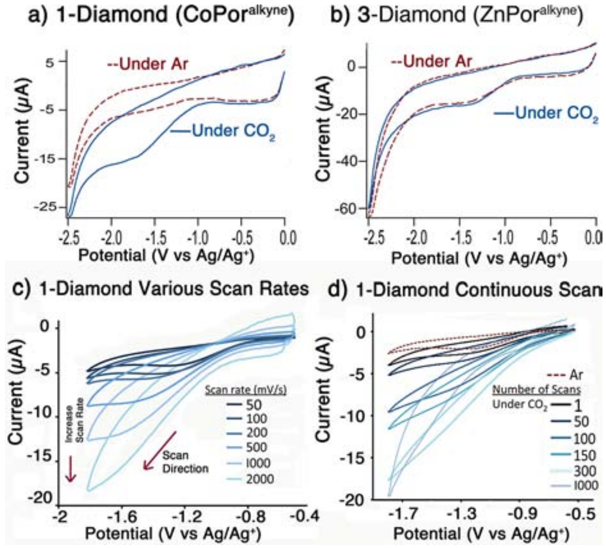

Figure 2. CV data in 0.1 M Bu_4NPF_6 in acetonitrile: (a) **1-Diamond** under Ar and CO_2 at a scan rate of 3 V/s. (b) **2-Control** under Ar and CO_2 at a scan rate of 3 V/s. (c) **1-Diamond** under CO_2 at various scan rates. (d) **1-Diamond** under CO_2 at a scan rate of 50 mV/s for up to 1000 cycles and under Ar at a scan rate of 50 mV/s (dotted line).

peaks are prominent. In contrast, no Co peak was observed on the diamond surface for **2-Control**, revealing that no significant physical adsorption took place. Therefore, we conclude that the Co peaks shown in **1-Diamond** arise from Co(Por^{alkyne}) covalently attached to the functionalized diamond surface. The XPS N(1s) region is also informative (Figure 1e). The **2-Control** sample showed unreacted azides on its surface, featuring two characteristic N 1s peaks at 399 and 403 eV with a peak area ratio of 2:1.[1c] The central nitrogen atom in the azide moiety is more electron-deficient than the other two and thus appears at a higher binding energy. As shown for **1-Diamond**, the disappearance of the peak at 403 eV and the broadening of the peak at 399 eV confirmed the formation of a 1,2,3-triazole linkage through the "click" reaction. On the basis of the intensity of the Co XPS peaks, the surface coverage of **1-Diamond** was determined to be 3.8×10^{13} Co/cm^2 (see the Supporting Information for details).

Cyclic voltammetry (CV) scans exhibiting **1-Diamond**-catalyzed electroreduction of CO_2 in anhydrous acetonitrile are presented in Figure 2. In the presence of CO_2, there was an abrupt onset of catalytic current at approximately −1.55 V vs Ag/Ag$^+$ (approximately −1.93 V vs Fc/Fc$^+$) at a scan rate of 3 V/s, whereas essentially no current was observed in the absence of CO_2 (Figure 2a). As a control, we also tethered catalytically inactive Zn(Por^{alkyne}) (**3**) onto diamond (**3-Diamond**) using the above protocol, and its surface coverage, 1.0×10^{13} Zn/cm^3, was very similar to that of **1-Diamond**. The Zn complex showed one-electron reduction of the porphyrin ligand at −1.2 V both with and without CO_2,[9] but no catalytic current was observed. Therefore, we conclude that neither the diamond substrate nor the alkane monolayer catalyze the electroreduction of CO_2. Figure 2c shows CVs measured at various scan rates. The reductive current increased with increasing driving force. Plots of current (i) versus scan rate (ν) (see the Supporting Information) showed that a slightly better fit was obtained for $i \propto \nu$ (as expected for surface-tethered redox functionality with no diffusion) than for $i \propto \nu^{1/2}$ (as expected for a diffusion-limited process). The reduction potential of −1.55 V vs Ag/Ag$^+$ (−1.93 V vs Fc/Fc$^+$) is close to the value of −1.89 V vs Fc/Fc$^+$ reported by Fujita and co-workers for electrochemical reduction of CO_2 using Co^{II}(Por) in homogeneous solution.[3]

The stability of this catalytic system was tested as shown in Figure 2d. For up to 300 cycles (scan rate, 50 mV/s; voltage range, −0.5 to −1.8 V vs Ag/AgCl), the catalytic current feature actually increased, suggesting that the porphyrin was likely adopting a more favorable configuration. A catalytic current was still observed after 1000 cycles, although the shape of this feature had changed, suggesting a further change in the nature of the catalyst environment. The catalytic current was persistent to >1000 cycles, suggesting a remarkably stable catalyst. The turnover frequency of this system was estimated to be 0.8 s^{-1} for a 16 h period under a constant potential of −1.8 V.[14]

Mechanistic insights from the previously reported solution measurements[3] indicate that the active species is a doubly reduced "Co(1)(Por$^{\bullet-}$)" species that produces CO and CO_3^{2-} as products.[3] We confirmed the evolution of CO from **1-Diamond** via FTIR spectroscopy, using an electrochemical cell directly coupled to a cylindrical gas transmission cell. Spectra were acquired at 0.5 cm^{-1} resolution to resolve the individual ro-vibrational lines of the CO product. Figure 3 shows the FTIR spectrum after reduction of CO_2 on **1-Diamond** along with the experimental spectrum of CO and a calculated spectrum based on the HITRAN database.[15] Because the small surface area of the electrode exposed only <1 pmol of catalyst,

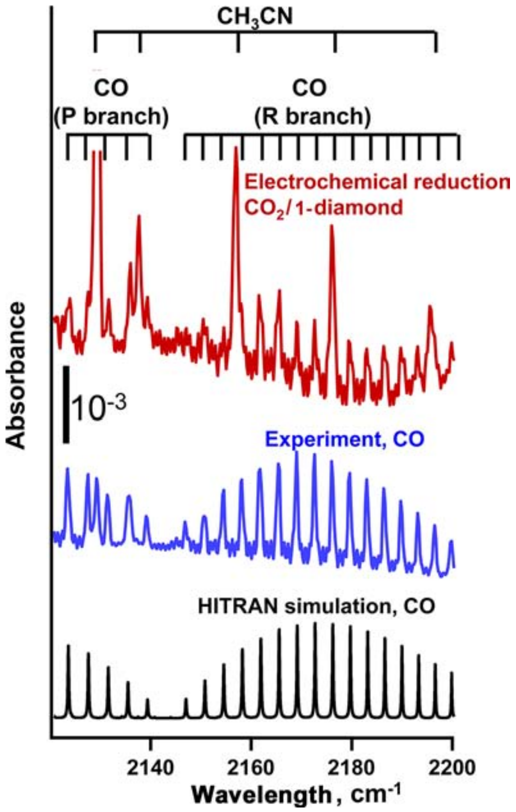

Figure 3. FTIR spectra showing the production of CO via electrochemical reduction of CO_2 on the **1-Diamond** surface. Also shown are the experimental spectrum of CO and a simulated CO spectrum obtained using parameters in the HITRAN spectroscopic database.[15] Peaks due to the CH_3CN solvent were confirmed by NIST reference spectra.[16]

we were not able to detect other possible products. However, observation of the CO product was unambiguous.

In summary, our results demonstrate that a molecular catalyst, Co(Por), can be robustly linked to a relatively inexpensive diamond substrate to yield an extremely stable surface-immobilized catalyst system that is active for electroreduction of CO_2, combining the high stability of the diamond surface with the high activity and selectivity of the molecular catalyst. Furthermore, this method is promising for the surface attachment of Fe(Por) and other tetrapyrrole macrocycles, metallocorrins, metallophthalocyanines,[1b] and metallocorroles with well-demonstrated CO_2 reduction ability.[4i,j,14] Since the diamond surface is also stable under oxidizing conditions,[4f] oxidation reactions with the Co(Por) catalyst can also be performed.[1h]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of the metalloporphyrins, details of functionalization of the diamond surface, FT-IR characterizations of the functionalization progress, method for the surface coverage calculation, and scan rate dependence of the current. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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