Molecular Devices

# Self-Assembled Monolayers of Isocyanides on Nickel Electrodes**

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Self-assembled monolayers (SAMs) of thiols on Au(111) surfaces have been examined extensively in recent years as a platform for surface science. They have been used in a number of applications in the areas of molecular electronics and surface-property modulation.[1] In molecular electronics, SAMs of thiol on a gold substrate have been particularly useful in controlling the placement and orientation of molecular electronic components such as wires, diodes, switches, and memories. In the design of molecular electronic components, appropriate interfaces between molecules and electrodes are as crucial as the active organic molecules. To be useful, these interfaces should possess low impedance and high stability. The mismatch between the Fermi level of the electrodes and either the HOMO or LUMO level of the adsorbent molecule generally induces a contact barrier which is the source of contact impedances.[2] So far, the thiol–gold linkage has been mainly considered for composing molecular electronic devices. Gold has an advantage over other surfaces for SAM formation because of its intrinsic inertness in air and high conductivity. However, there are still several limitations of gold surfaces as the electrode for practical molecular electronic applications. Theoretical calculations predicted that the combination of sulfur and gold yields one of the highest contact barriers for charge transport.[3] It is also well-known that SAMs of thiols on gold are thermally unstable.[4] Furthermore, the stochastic behavior of thiols on gold electrodes that results from the breakage of the adsorbent molecule–metal contact have also been observed.[5] The high diffusion mobility of gold atoms makes them less attractive for practical applications because of the limited lifetime of the devices.[6] Therefore, it is meaningful to develop a new combination of chemical linkage groups—alligator clips—and metal electrodes.

Current semiconductor technology employs nickel, tungsten, and their silicon alloys as electrodes for microelectronic devices. In addition, the ferromagnetic character of Ni presents the possibility of expanding the application of such electrodes to spintronic devices.[7] Although there are various reports about the thiol–nickel interaction,[8] the thiol–nickel junction is not as good as the thiol–gold junction for molecular electronic applications. Therefore, it is necessary to develop new alligator clips for Ni substrates. According to theoretical calculations, the isocyanide–nickel junction has significant advantages over the thiol–gold junction and others because of its low charge-transport barriers.[3] There have been several examples of SAMs generated from isocyanides on Au,[9] Pt,[10] Pd,[11] Ag,[9b,12] and Cr.[13] However, the isocyanide–nickel interaction has not yet been explored except for vacuum-evaporated methyl isocyanide ($CH_3NC$) on Ni(100) and Ni(111) surfaces.[14]

Herein, we report the synthesis of ferrocenylalkyl isocyanides and their assembly on polycrystalline Ni surfaces. The ferrocenyl moiety was introduced as a messenger for convenient characterization of monolayers by electrochemical methods to evaluate the surface coverage and thermal stability of SAMs.[15] Additionally, the conformation and binding mode of isocyanide on Ni surfaces, which were characterized by reflection–absorption infrared (RAIR) spectroscopy, are discussed.

We synthesized the ferrocenyl-terminated isocyanide molecules **5** to test their ability to chemisorb on Ni surfaces. In addition to isocyanides, several ferrocenyl-terminated molecules containing reactive functional groups that can potentially chemisorb on Ni surfaces, such as cyanide (**6**), isothiocyanate (**7**), diselenide (**9**), and thiol (**10**), were synthesized (Scheme 1). Polycrystalline Ni surfaces were used as substrates for monolayer formation. Ni surfaces were pretreated by electrochemical reduction (−1.3 V vs. Ag/AgCl, 3 M NaCl) in an aqueous solution of $HClO_4$ (1 M) for 20 minutes prior to use, since Ni is easily oxidized on exposure to air.[8]

The molecular packing and surface coverage of the monolayers were assessed by cyclic voltammetry. Figure 1 shows cyclic voltammograms (CVs) obtained after electrochemically reduced Ni electrodes had been immersed in 0.01 M ethanolic solutions of **5**, **9**, and **10** for 48 hours. Oxidation and reduction peaks were observed at +0.47 and +0.44 V, which correspond to the oxidation and reduction of the ferrocene moiety.[15] However, Ni surfaces immersed for 48 hours in solutions of ferrocenyl-terminated molecules containing azide (**2**), amine (**3**), cyanide (**6**), and isothiocyanate (**7**) functional groups gave featureless CVs similar to those of bare electrodes. These results indicate that **5**, **9**, and **10** were successfully chemisorbed on the electrochemically reduced nickel surfaces. The charge density obtained for SAMs of **5**, **9**, and **10** are clearly different, and they follow the order of isocyanide > thiol > diselenide.

The surface coverage was calculated from the area of ferrocene redox peaks, by assuming that the surface has zero roughness and all chemisorbed molecules are electrochemically active. A surface coverage of $1\times10^{-9}\,\mathrm{mol\,cm^{-2}}$ was obtained from the electrodes modified by a 0.01 M ethanolic solution of **5**. This value is approximately two times larger than the reported value for a well-packed monolayer of ferrocenyl alkylthiols on gold ($4.6\text{–}8\times10^{-10}\,\mathrm{mol\,cm^{-2}}$).[15] The discrepancy for the Ni surface may arise from the rough morphology of Ni surfaces compared to that of gold (see the Supporting Information).

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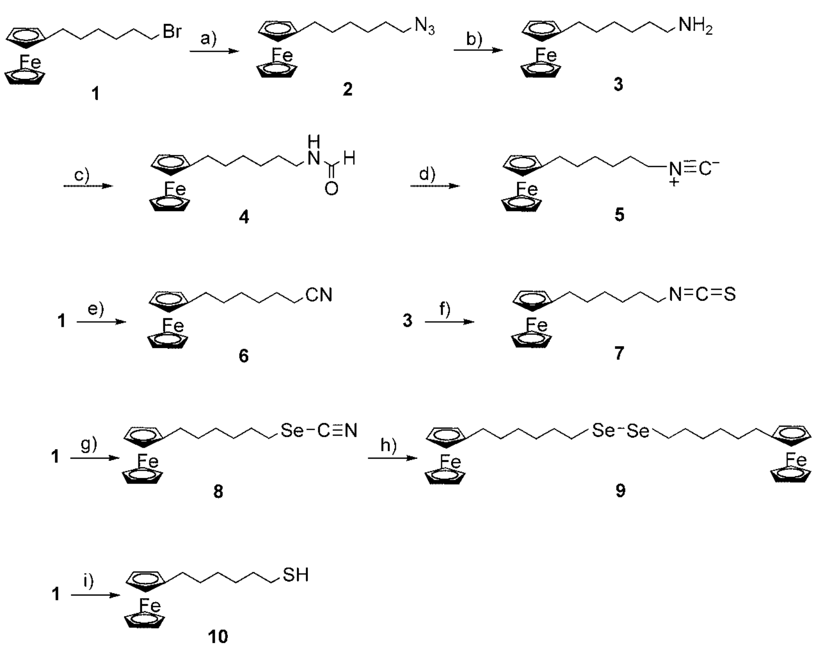

**Scheme 1.** Synthesis of ferrocenyl-terminated molecules containing various functional groups. a) $NaN_3$, DMF, RT, 12 h, 92%; b) lithium aluminum hydride, $Et_2O$, RT, 2 h, 80%; c) ethyl formate, reflux, 18 h, 93%; d) $POCl_3$, triethylamine, THF, 0°C, 2 h, 60%; e) NaCN, DMF, RT, 12 h, 95%; f) di-2-pyridyl thionocarbonate, $CH_2Cl_2$, RT, 1 h, 81%; g) KSeCN, $CH_3CN$, 0°C to RT, 30 min, 92%; h) NaH, DMF, RT, 24 h, 66%; i) thiourea, EtOH, reflux, 18 h and then KOH, reflux, 2 h, 60%.

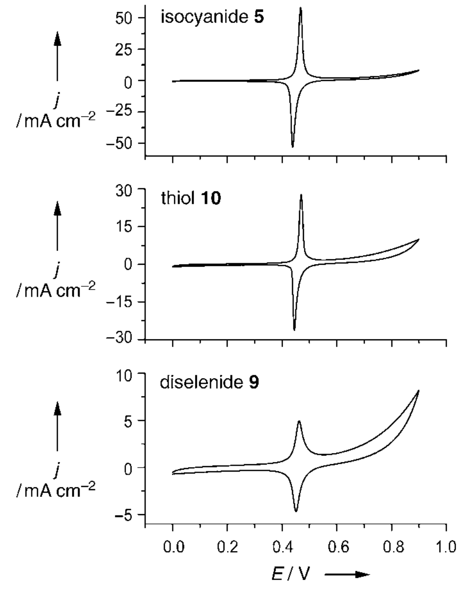

**Figure 1.** Cyclic voltammograms of monolayers of isocyanide **5**, diselenide **9**, and thiol **10** self-assembled on electrochemically reduced nickel surfaces. Electrolyte: 0.1 M $nBu_4NPF_6$ in THF. Scan rate: 0.01 $Vs^{-1}$.

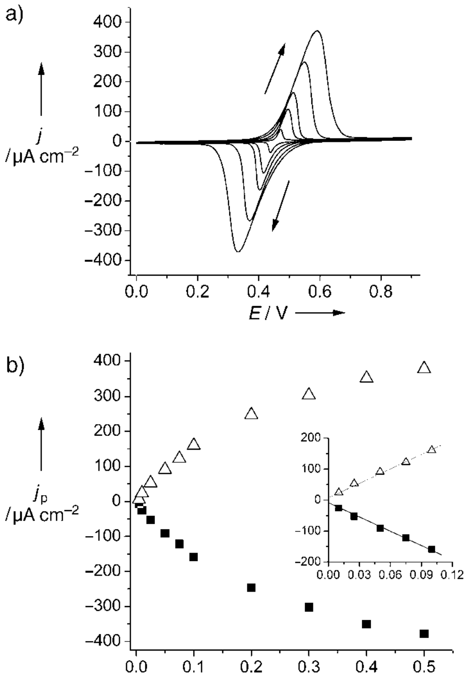

**Figure 2.** a) Cyclic voltammograms of an electrochemically reduced nickel electrode modified with a monolayer of isocyanide **5**. Electrolyte: 0.1 M $nBu_4NPF_6$ in THF. Scan rate: 0.01, 0.05, 0.1, 0.25, and 0.5 $Vs^{-1}$. b) Plot of current density versus scan rate (△ oxidation, ■ reduction) for a monolayer of isocyanide **5** at an electrochemically reduced nickel surface and recorded in 0.1 M $nBu_4NPF_6$/THF. Inset: enlargement of the low-scan-rate region; the line is intended to guide the eye.

The electrochemical responses of monolayers of **5** were shown to be stable when subjected to repetitive cycling at different sweep rates. Only a small loss (5%) in the surface coverage was observed after 100 cycles at 0.2 $Vs^{-1}$. Notably, surface coverage decreased by only 12% when monolayers of **5** were sonicated in THF for 10 minutes. This observation suggests that chemisorbed monolayers are chemically and thermodynamically stable under the given experimental conditions.

When Ni surfaces not treated reductively were used, the surface coverage was $1.9\times10^{-10}$ mol $cm^{-2}$, five times lower than that of the electrochemically reduced Ni surfaces. The surface coverage of the monolayer on the nonreduced Ni surfaces decreased by over 50% of the original value after 100 repetitive scans at 0.1 $Vs^{-1}$. The instability of the monolayers on nonreduced Ni surfaces may be a result of the weak interaction from the physisorption of isocyanides on nickel oxide rather than chemisorption.

Figure 2 shows the CVs of electrochemically reduced Ni electrodes modified with **5** at different scan rates. The peak splitting ($\Delta E_p = E_p^{ox} - E_p^{red}$) increased with increasing scan rate and was larger than that obtained under the same conditions for a monolayer of **5** on polycrystalline gold (data not shown). These phenomena are not consistent with the theory for a reversible redox couple confined to a surface.[16] However, $\Delta E_p$ approaches zero at low scan rates, as expected for a reversible surface-confined redox couple. This behavior can be attributed to a slow electron transfer rate on the timescale of the experiment, where at low scan rates the redox centers remain nearly at equilibrium with the electrode surface.

Another important piece of evidence for a surface-confined faradaic reaction is the linearity between the peak current ($J_p$) and the scan rate ($\nu$), as expressed by Equation (1).[16]

$$j_p = \frac{I_p}{A} = \frac{n^2F^2\Gamma\nu}{4RT} \tag{1}$$

The plot of anodic and cathodic current density against the scan rate is nearly linear at low scan rates, which indicates the existence of a surface-confined faradaic reaction (inset in Figure 2b). At faster scan rates, a deviation from the linearity was observed which is common for slow-electron-transfer kinetics (Figure 2). Along with previous CV results, this electrochemical behavior confirms the fact that a monolayer of **5** was formed on Ni surfaces.

Reflection–absorption infrared (RAIR) spectroscopy has been used to investigate the chemisorption and binding mode of SAMs on various metal surfaces.[15] Figure 3 shows the transmission (a) and RAIR (b) spectra for **5** on a KBr plate and a Ni surface, respectively. In the transmission mode, the characteristic peaks of the hydrocarbon chain and ferrocene unit of **5** appear at 2932 (C–H symmetric stretching), 2855 (C–H asymmetric stretching), 3093 (C–H stretching in ferrocene), 1464 (C–C stretching from the substituted ferrocene), and 1350 cm$^{-1}$ (C–H bending from the substituted ferrocene; Figure 3a). These peaks are also observed in the RAIR spectrum (Figure 3b). This result clearly shows the formation of monolayers of **5** on Ni surfaces. In addition, the binding mode of isocyanides on Ni surfaces was deduced from the RAIR spectrum. While a strong peak for isocyanide stretching is observed in the transmission spectrum at 2147 cm$^{-1}$, the RAIR spectrum on nickel does not show the corresponding peak. In contrast, the isocyanide stretching peak of the monolayers of **5** on gold occurs at 2213 cm$^{-1}$. This result is in agreement with previous reports of isocyanides on gold, and the peak has been assigned to the absorption of isocyanide bonded to the metal surface through the carbon atom of the isocyanide.[9] Considering the surface selection rules for RAIR spectroscopy,[17] the absence of an isocyanide stretching peak in the RAIR spectrum suggests that the chemisorbed isocyanides are bonded through both their carbon and nitrogen atoms, and that they adopt a position parallel to the surface. This observation is consistent with previous studies of methyl isocyanide on Ni surfaces.[14a]

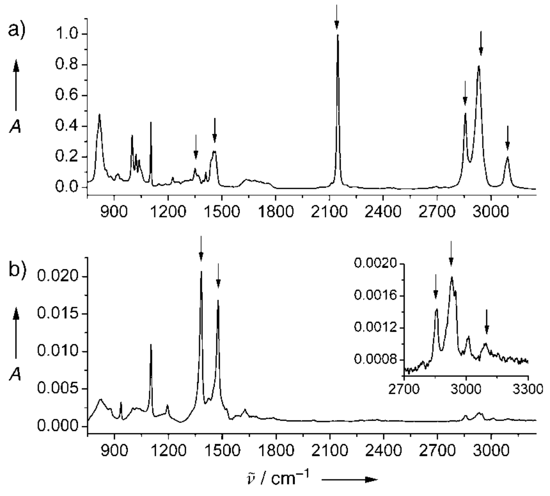

***Figure 3.*** FTIR spectra of **5**: a) transmission on a KBr plate and b) RAIR spectra of a self-assembled monolayer on a nickel surface.

We examined the thermal stability by immersing Ni electrodes modified with **5** into boiling ethanol (78 °C).[18] The surface coverage ($\Gamma$) of the monolayers of **5** was monitored by cyclic voltammetry as a function of boiling time (Figure 4). After three days in boiling ethanol, the surface coverage decreased by about 50 %. Notably, SAMs of **10** on a gold surface lost over 50 % of their surface coverage after one hour in boiling ethanol. The nickel–isocyanide interaction in the present study clearly shows higher thermal stability than the gold–thiol interaction. The peak shape and position in the voltammograms before and after the heating process are constant, which indicates that this experimental condition does not lead to decomposition of the isocyanide compounds on the surface.

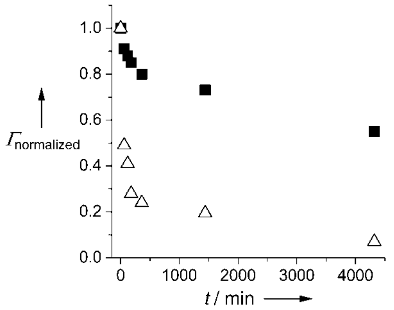

***Figure 4.*** Thermal stability profiles of nickel–isocyanide **5** (■) and gold–thiol **10** (△) as a function of time in boiling ethanol (78 °C).

In conclusion, ferrocenyl-terminated isocyanides were synthesized and tested for surface reaction with Ni substrates. SAMs generated from isocyanides on Ni surfaces were characterized by cyclic voltammetry and RAIR spectroscopy. It was found that SAMs of isocyanides on Ni surfaces have a parallel binding mode and high thermal stability in boiling ethanol. The results indicate the presence of strong chemisorption between isocyanides and the metallic Ni surface. This work is an indication that molecular electronic components with isocyanide groups should be synthesized so that they can be immobilized on substrates more relevant to industrial standards.

## Experimental Section

Experimental details for the synthesis of all compounds, monolayer preparation, cyclic voltammetry, FTIR spectroscopy, and AFM measurements can be found in the Supporting Information.

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