

Spontaneous Assembly of Organic Thiocyanates on Gold Surfaces. Alternative Precursors for Gold Thiolate Assemblies

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The discovery of spontaneous assemblies of organic thiols on gold surfaces¹ has proven to be a major advance for chemists and surface scientists in disciplines ranging from biomedicine^{2,3} and sensors^{4,5} to electronics.^{6,7} Of particular value is the ability of the molecules to rearrange or migrate to give self-assembled monolayer (SAM) films⁸ and to tolerate a wide variety of functional groups.^{1,9}

One of the drawbacks to this technique is the propensity of organic thiols to oxidize to disulfides,¹⁰ which is especially frustrating in the case of aromatic thiols. Furthermore, α,ω -dithiols, which are prone to polymerization both in solution and on the surface, form multilayers rather than monolayers.¹⁰ If protected thiols are used, in situ deprotection adds extraneous material to the reaction, which can be problematic.¹¹ An additional drawback to using a protecting group is that the cleavability required for in situ deprotection/assembly often requires a protecting group too labile to withstand many reaction conditions. An ideal system would be a thiol-protection moiety that is air, moisture, and light stable and yet requires no auxiliary agents for assembly on a surface. To that end, we have found a thiocyanate to be an excellent precursor for thiolate assemblies. These easily synthesized molecules can be assembled on gold surfaces directly in a variety of solvents and are an excellent complement to free thiol and protected thiol assembly procedures.¹²

In a typical experiment, gold substrates were prepared by thermal evaporation of chromium (15 nm) and gold (150–200 nm) onto Si (100) wafers at 10^{-6} Torr. Gold samples were exposed to the assembly solutions (1–10 mM, MeOH or EtOH for the aliphatic species, MeOH with THF for solubility of the aromatic species) for 24–36 h after which assembly was complete. Samples were removed from the solution, sonicated and rinsed with the same solvent, and dried with a nitrogen stream.

The product of the thiocyanate assembly resembles gold thiolate SAMs. Powder X-ray photoelectron spectroscopy (XPS) analysis of **1** clearly shows the thiocyanate functional group with an electron binding energy of 164.8 and 166.0 eV corresponding to S 2p^{3/2} and S 2p^{1/2} signals (Table 1). The C 1s and N 1s signals for the SCN group appear at 286.3 and 399.2 eV, respectively. After assembly, the XPS signals for S 2p shift to 162.0 and 163.3 eV, with no apparent N 1s or C 1s signals for CN_(ads). The locations of the sulfur peaks overlay precisely with the binding energies seen for a sample of an aromatic thiol, **2**, assembled onto gold. In the same manner, the SAMs of the alkanethiocyanate, **4**, showed sulfur binding energy identical to those assembled from the free alkanethiol **5**. Although not definitive, this further suggests that the alkanethiols lose their proton upon chemisorption, a longstanding question in thiol-gold chemistry.¹³

To better understand the mechanism of this phenomenon, assemblies of **1** were examined by XPS before full monolayer

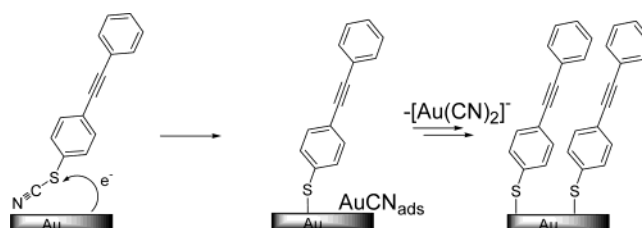
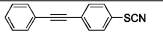
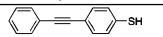
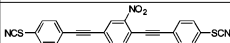
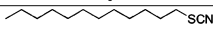
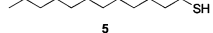


Figure 1. Proposed mechanism for thiocyanate assembly.

Table 1. X-ray Photoelectron Spectroscopy Characterization

Molecule	X-ray photoelectron binding energy (eV)					
	Solid phase material ^a				Surface-bound material ^b	
	S 2p ^{3/2}	S 2p ^{1/2}	C 1s (SCN)	N 1s (SCN)	S 2p ^{3/2}	S 2p ^{1/2}
	164.8	166.0	286.3	399.2	162.0	163.3
	163.1	164.3			162.0	163.3
					162.2, 165.2	163.5, 166.3
					161.8	163.0
	163.6	164.8 ^c			161.9	163.0

^a Referenced internally against the C 1s signal at 284.5 eV. ^b Referenced internally against the Au 4f signal at 84.0 eV. ^c Literature value.²⁰

coverage was achieved. This revealed both gold-bound sulfur signals as well as gold-bound cyanide (N 1s at 399.5 eV).¹⁴ Combined with previously published electrochemical studies on the reduction of RSCN,^{15,16} we propose a surface-mediated reduction of the thiocyanate to give CN and the S covalently bound to the surface. The lack of CN_(ads) XPS signal¹⁷ in the fully assembled monolayers suggests that the cyanide group (a known etchant for gold) may leave as an [Au(CN)₂]⁻ species, resulting in a layer of assembled thiolate (Figure 1). The relative bond strengths of Au–S, Au–Au, and Au–CN, approximately 40, 53, and 90 kcal/mol, respectively,^{13,18,19} make other mechanisms less attractive.

For the alkanes, the monolayers are slightly inferior to those prepared from the free thiol. Measurements of passivation by cyclic voltammetry²¹ atop Au¹/Cr/Si showed a decrease in peak current from the pristine gold surface (Figure 2a); however, the decrease is not as large as for the free thiol-prepared surface.

The differences in assembly quality are also apparent by contact angle and ellipsometric measurements (Table 2). This difference is not related to the rate of assembly (studied over 4 days) but is in fact an inherent characteristic of the thiocyanate assembly.

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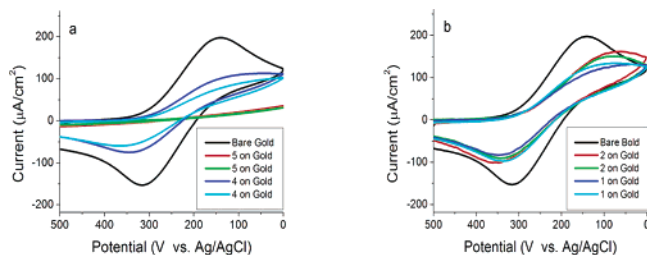
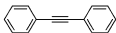
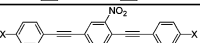


Figure 2. Electric field was applied to the SAMs in aqueous solutions with 1 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl with a sweep rate of 100 mV/s to show the passivation ability of the SAMs in two experiments for each case. (a) Comparison of electrode passivation for aliphatic species **4** and **5**. (b) Comparison of passivation by the aromatic species **1** and **2**.

Table 2. Film Thickness ($\pm 10\%$) Determined by Single-Wavelength Ellipsometry and Contact Angle ($\pm 5\%$) (Water) Measurements

Molecule	Measured ellipsometric thickness (\AA)		Contact angle (degrees, static)	
	X=SH	X=SCN	X=SH	X=SCN
$nC_{12}H_{25}-X$	16.4	12.2	105	97
	14.6	13.8	80	78
		18.7		

Grazing angle IR studies further confirm this difference in monolayer coverage. The value for the $\nu_{as}(CH_2)$ mode at 2922 cm^{-1} for a monolayer made from $C_{12}SCN$, compared to $C_{12}SH$ SAMs measured in the same apparatus at $2918\text{--}2919\text{ cm}^{-1}$, implies differences in packing.²² Quantitative analysis of the monolayer by XPS suggests that for every 100 sulfurs bound to gold during alkanethiol assembly, a comparable alkylthiocyanate assembly contains approximately 90 sulfur atoms.

The aromatic system compares more favorably with its thiol counterpart. Examination of the monolayers by ellipsometry shows virtually no difference in thicknesses. The same is true for the passivation effects where experiments show nearly identical current transport (Figure 2b). We attribute this difference in apparent quality between aromatic and aliphatic systems to the difference in packing densities of the two systems.^{23,24}

Further advantages of the thiocyanates are their exceptional stability to ambient conditions. Samples of 4-thiocyanoaniline, a particularly sensitive compound when prepared as a thiol, showed no decomposition when left exposed to open laboratory conditions for 4 months. Similar stability was seen in all of the thiocyanates that were prepared for this study. Solutions of these compounds are significantly more stable over typical assembly time periods (24–72 h) than the analogous solution of free thiols; the free thiol never needs to be present in solution for assembly to occur.

A common problem, particularly associated with dithiol assembly, is mitigated with the thiocyanate route. No disulfide-based polymerization¹⁰ was detected in assemblies of **3** by ellipsometric measurements (Table 2) or XPS; one SCN end group remains chemically intact, while the other is covalently attached to Au (Table 1). These assemblies were carried out in ambient conditions (open to air), which would cause dithiol compounds to form multilayers within minutes even upon the trace presence of air. Finally, the

SCN functional group is easily accessible in aliphatic systems from a simple S_N2 reaction²⁵ or in aromatic systems from the aniline via the diazonium salt.²⁶

In summary, we have demonstrated a simple technique for depositing thiolate-based SAMs onto gold without the need for ancillary reagents during deprotection and assembly. This technique is ideal for aromatic systems and dithiol-derived molecules. It is also suitable for use with alkanethiols, provided that the lower packing density is acceptable.

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Supporting Information Available: Synthetic details and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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