Supporting Information

Experimental:

Silicon wafers were cleaned in piranha, and dried in an isopropanol vapor bath prior to metal deposition. A titanium layer 50 Å thick followed by a gold layer 500 Å thick were deposited using an e-beam evaporator. IDA microelctrodes were fabricated at the Stanford Nanofabrication Facility (SNF).

Azide-terminated thiols and tris-(benzyltriazolylmethyl)amine (TBTA) were prepared using previously reported procedures. The click reaction was carried out as follows: the azide-terminated gold surface was exposed to a solution that contains 10 μM Cu(II) TBTA, 8 mM hydroquinone (to ensure that the catalyst was in the active Cu(I) oxidation state), and 1-20 μM ethynylferrocene in 3:1 DMSO/water for a duration of 30 min. The surface was then rinsed with ethanol, dichloromethane, ethanol and finally water.

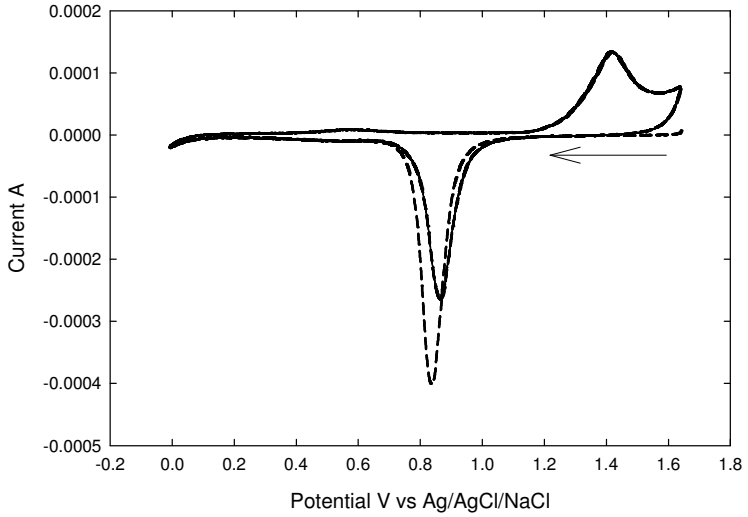

Figure S1: Cyclic voltammogram of a nominally bare gold electrode in 0.5 M aqueous H_2SO_4 starting at arrow. Scan rate 250 mV s^{-1}; dashed line represent the first scan, solid line represents subsequent four cycles.

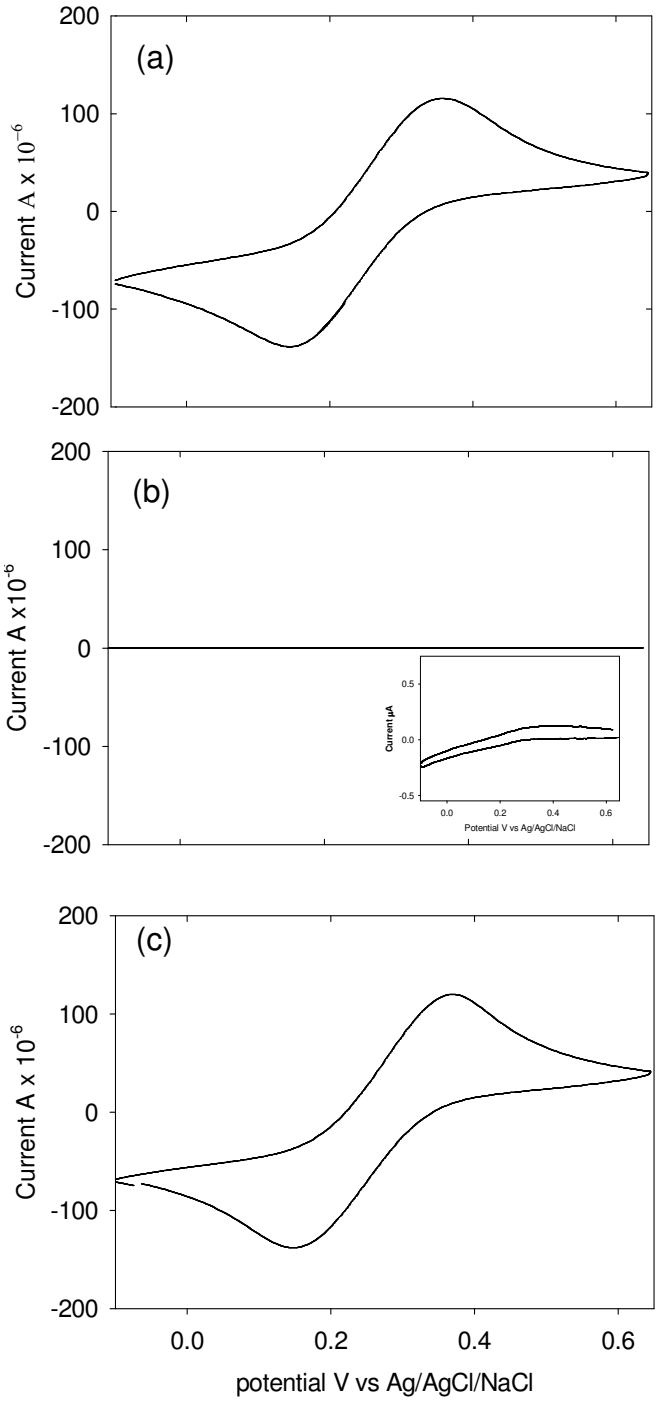

Figure S2: Cyclic voltammetry of 5 mM $K_3Fe(CN)_6$ in 100 mM KCl (a) with bare gold electrode. (b) $HS(CH_2)_{15}CH_3$ self-assembled monolayer after 1 min deposition. (c) After desorption of the thiols. Scan rate 100 mVs^{-1}.

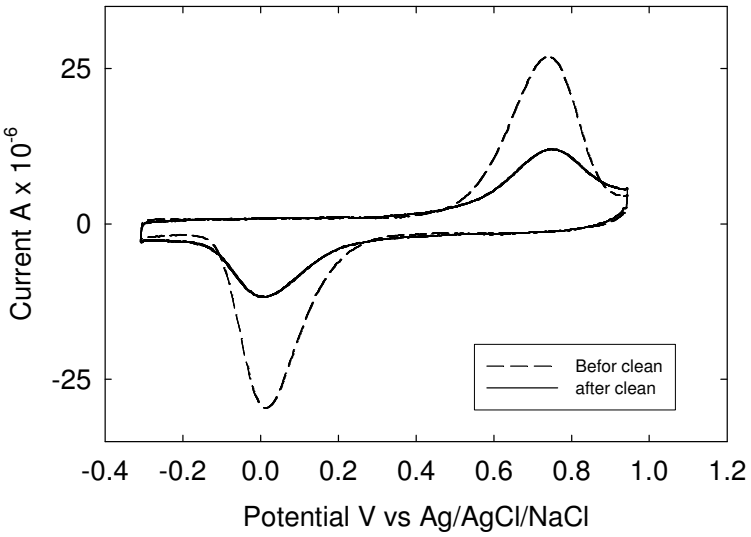

Figure S3: Using $HS(CH_2)_{18}N_3$ and 0.3 mM $HS(CH_2)_{15}CH_3$ in ethanol to form self-assembled monolayer; dashed line represent the ferrocene wave before cleaning the adjacent electrode, solid line after the cleaning procedure. Scan rate 10,000 mV s^{-1}.

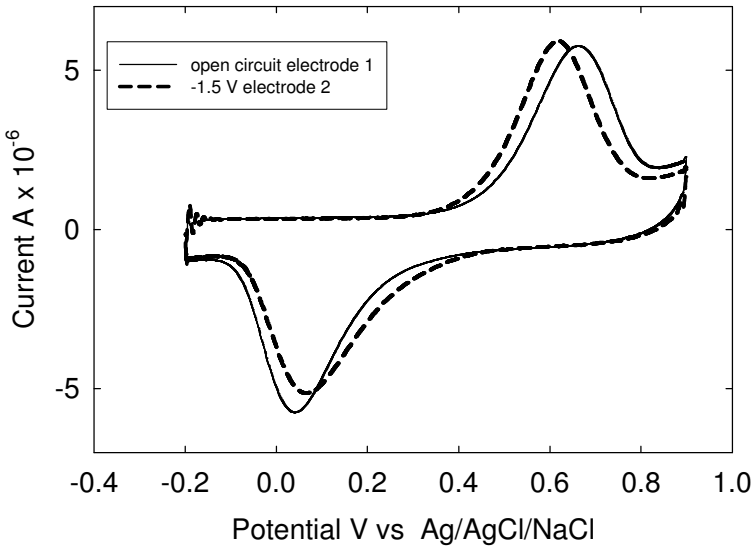

Figure S4: Using $HS(CH_2)_{16}N_3$ and 0.3 mM $HS(CH_2)_{15}CH_3$ in ethanol to form self-assembled monolayer on nominally clean electrodes. Wang procedure for 1 min with electrode 2 (dashed) at -1.5 V vs Ag/AgCl/NaCl and electrode 1 (solid) at open circuit. After rinsing, ethynyl ferrocene with "clicked" to surface azides. Scan rate 5,000 mV s^{-1}.