Supporting Info

N-heterocyclic carbene and thiol micropatterns enable the selective deposition and transfer of copper films

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Experimental Conditions

Materials. Benzimidazolium hydrogen carbonate salts (**1**•H_2CO_3 and **2**•H_2CO_3) were prepared following procedures described previously.[1] Au/Si substrates were prepared by the University of Western Ontario's Nanofabrication facility (London, ON). All solutions were made with deionized water (Millipore Milli-Q; 18 MU cm resistivity). The reagents were used as received with no further modification unless stated otherwise. Milli-Q water was used for this study for all purposes including electrochemistry and sample rinsing. Sulfuric acid (98%), copper (II) sulfate pentahydrate (99.999%), potassium hexacyanoferrate (III) (≥99%), potassium hexacyanoferrate (II) trihydrate (≥99%), sodium perchlorate monohydrate (98%) and 1-Dodecanethiol (≥98%) were purchased from Sigma-Aldrich (Oakville, On). Quick-setting epoxy adhesive (Armor Coat) was obtained from a local hardware store (Canadian Tire).

The polydimethylsiloxane elastomer kit was supplied by Dow Corning (Sylgard 184 silicone). The kit contains a bottle of base and curing agent.

The Base contains the followings:	The Curing Agent (part B) contains the followings:
Dimethyl siloxane, dimethylivinyl terminated Dimethylvinylated and trimethylated silica Tetra (trimethoxysiloxy) silane Ethyl benzene	Dimethyl, methylhydrogen siloxane Dimethyl siloxane, dimethylvinyl terminated Dimethylvinylated and trimethylated silica Tetramethyl tetravinyl cyclotetra siloxane Ethyl benzene

Preparation of self-assembled monolayers. A transmission electron microscopy (TEM) grid (CF300-CU, mesh 300, Bar: 25 µm Hole: 58 µm) was placed in a plastic petri dish. The polydimethylsiloxane stamp was cast using a 8:1 ratio of base and curing agent. The mixture was well mixed, degassed in the vacuum before solidifying overnight at 75 °C and covering TEM grid as the one shown in Fig. 5a. The PDMS was then removed from the petri dish containing the TEM grid. The part of PDMS that was microstructured, in other words the stamp, was removed from the rest. The stamp was immersed in 10 mM 1-dodecanethiol in ethanol for 5 minutes. It was then removed, dried with a stream of nitrogen, pressed on the electrochemical cleaned Au/Si wafer for 30 seconds and then detached. The modified Au/Si wafer was rinsed with ethanol and dried with a stream of nitrogen before 1-minute immersion in either 10 mM diisopropyl-benzimidazolium hydrogen carbonate (**1**•H_2CO_3) solution or in 10 mM 5-((11-hydroxyundecyl)oxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate (**2**•H_2CO_3) methanol solution. The sample was removed after immersion, rinsed with methanol and dried with nitrogen.

Freshly cleaved gold/silicon wafers were cleaned by sonication in Milli-Q water and ethanol for 10 minutes, respectively. Gold-surfaces were covered with uniform SAMs by immersing cleaned wafers in the respective solutions for 20 hours, rinsing with same solvent and drying with nitrogen gas. The solutions were benzimidazolium hydrogen carbonates (**1**•H_2CO_3 and **2**•H_2CO_3) in methanol and dodecanethiol in ethanol.

Electrochemical conditions. Au/Si wafers were washed by using sonication in water and ethanol, respectively. The wafers were then electrochemically cleaned in 0.5 M H_2SO_4 aqueous solution, by running cyclic voltammetry for 100 cycles between 0 and 1.5 V at a scan rate of 0.5 V/s in prior to further modifications. The reference and counter electrodes are Ag/AgCl/3.0 M KCl and a platinum wire.

Copper reduction was carried out in a home-made electrochemical cell with a 3-eletrode configuration. An Au/Si wafer, a copper wire and a copper wire in glass capillary were used as working-, counter- and reference-electrodes, respectively. Linear voltammetry was performed on bare gold and coated gold substrates between 0 V and -0.8 V at a scan rate of 0.1 V/s in 50 mM $CuSO_4/H_2SO_4$ aqueous solution at pH ≈1. Copper reduction was performed using chronoamperometry in the same electrochemical cell. Au/Si wafers with SAM micropatterns were used as the working electrodes. Two deposition steps were carried out. A more negative potential was used first, followed by a less negative potential for growth to optimize the selectivity of the deposition on two regions of SAMs. The applied potential was referenced to the detected open-circuit potential. The first and second steps are, respectively, 0.75 V and 0.5 V more negative than the open-circuit potential. For example, when an open-circuit potential of 0.27 V was detected, the first deposition was conducted at -0.48 V for 3 seconds followed by a deposition at -0.23 V for 12 seconds.

Cyclic voltammetry measurements on carbene SAMs prepared were carried out with different times using CHI101 gold electrodes. The electrodes were cleaned first with a piranha solution **(must be handled with extreme care and never stored)**, which was prepared by mixing a 3:1 volume ratio of concentrated sulfuric acid to hydrogen peroxide. The electrodes were rinsed thoroughly with Milli-Q water before each electrode was polished using slurries of 0.3 µm and 0.05 µm alumina powders for 3 minutes each. The alumina suspension was then removed by ultrasonicating the electrodes for 10 minutes in Milli-Q water, absolute ethanol and Milli-Q water respectively. Electrochemical cleaning was conducted by running 100 cycles using a pre-programmed CV method; The electrodes were first immersed in 0.5 M of aqueous sodium hydroxide solution and scanned between 0 V and 2 V at a scan rate of 0.5 $V \cdot s^{-1}$. This is followed by exposing the electrodes to a second pre-programmed CV cleaning method of 100 cycles between 0 V and 1.5 V at the same scan rate in a 0.5 M aqueous sulfuric acid solution. All measurements were carried out in 5 mM/5 mM $[Fe(CN)_6]^{3-/4-}$ and 1 M $NaClO_4$.

Scanning electrochemical microscopy (SECM). SECM measurements were carried out using a CHI-900b SECM instrument (CH Instruments, Austin, TX) at room temperature. A Pt wire, an Ag/AgCl/3.0 M KCl electrode and a Pt SECM tip were fitted as the counter electrode, reference electrode and working electrodes, respectively. Au/Si substrates, either unmodified or modified with SAMs, were mounted in the cell and measured without applying any bias. The SECM probe electrode was home-made by sealing a 25 µm diameter Pt wire (99.95%, Alfa Aesar, MA, USA) into a micropipette, which was pulled from a glass capillary 1.5/0.84 mm OD/ID (World Precision Instruments, Inc., FL, USA) using the micropipette puller (PP-83, Narishige, Japan). The electrode was polished using alumina lapping discs (3.0, 0.3 and 0.05 µm, World Precision Instruments, Inc., FL, USA) to RG=5. The electrode was cleaned before each experiment by sonication in water/ethanol (50:50) for 10 mins and electrochemically cleaned by running cyclic voltammetry scans in acid (H_2SO_4, pH ≈1) between 0 and 1.4 V for 100 cycles at scan rate of 0.5 V/s. The electrolyte for the SECM measurement contained 2 mM $K_4[Fe(CN)_6]$ aqueous solution as the redox probe and 50 mM $NaClO_4$ as the supporting electrolyte. A steady current was obtained prior to each approach curve measurement or imaging. The imaging process was carried out with 2 µm increment steps (0.066667s) at an applied potential of 0.7 V.

COMSOL Multiphysics. The experimental approach curves were analyzed and fitted against theoretical curves generated using COMSOL Multiphysics software following reported methods.[2]

Copper structure lift-off. The transfer of fabricated copper structures was carried out by casting epoxy glue over the deposited copper on an Au/Si wafer carefully using molds with diameters of 3 mm. The two components of the epoxy glue were mixed and applied within 3 minutes. The glue was allowed to set further over a period of 24 hours. The glue was then mechanically detached from the substrate along with the patterned copper structures.

Preparation of self-assembled monolayers for X-ray photoelectron spectroscopy Au/Si substrates (thickness of 150 nm Au on a Si wafer with 7 nm of Ti as the adhesion layer) were electrochemically cleaned by cyclic voltammetry in a 0.5 M H_2SO_4 aqueous solutions between 0 V and 1.4 V for 100 cycles at a scan rate of 0.5 $V \cdot s^{-1}$, rinsed with deionized water thoroughly and then rinsed with methanol.

Self-assembled monolayers were prepared by immersion of freshly cleaned Au/Si substrates in 10 mM solutions of the corresponding benzimidazolium hydrogen carbonate salt in methanol for the specified time at room temperature in air. Substrates then were rinsed in methanol and dried under an argon gas (5.0 Praxair) stream.

X ray photoelectron spectroscopy (XPS) was measured on a Kratos Nova AXIS spectrometer equipped with an AlN X-ray source. The samples were mounted on a plain platen sample holder by using double-sided adhesive Cu tape and kept under high vacuum (~ 10^{-8}-10^{-9} Torr) overnight inside the preparation chamber before they were transferred to the analysis chamber (ultrahigh vacuum, ~10^{-10} Torr) of the spectrometer. The XPS data were collected using Al K_a radiation at 1486.69 eV (150 W, 15 kV), charge neutralizer and a delay-line detector (DLD) consisting of three multichannel plates. The spectra were acquired using Vision 2 software and processed using CasaXPS software. The binding energies of all spectra were calibrated to the Au 4f line at 84.0 eV.

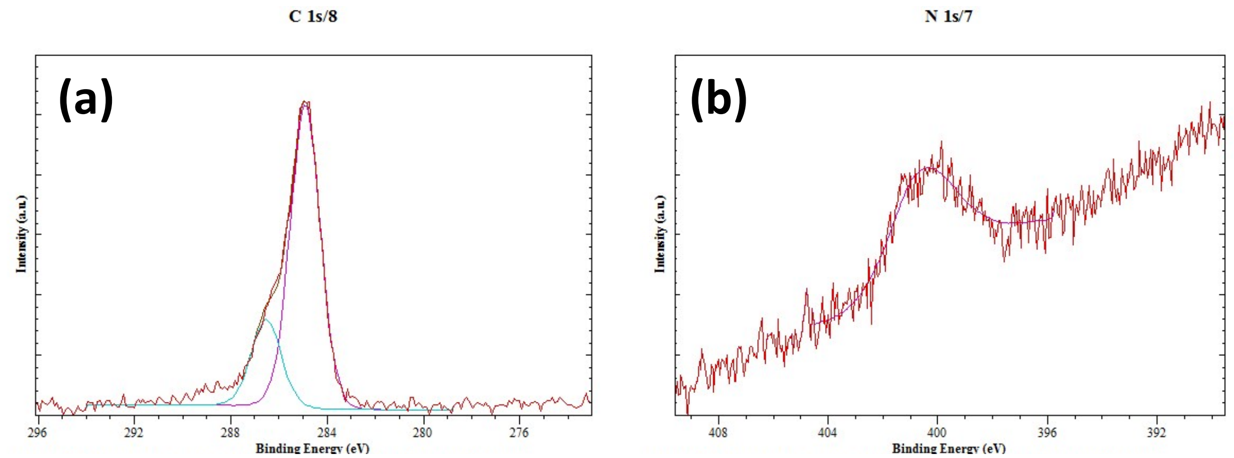

Fig. S1 X-ray photoelectron spectra of (a) carbon and (b) nitrogen signal from **2•Au** formed after immersing gold chip in the methanol solution. The observed C:N ratio is 27:2 (theoretical C:N ratio is 24:2).

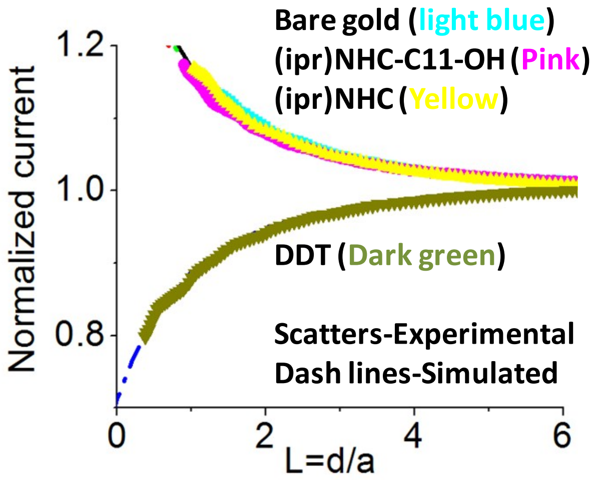

Fig. S2 SECM approach curves obtained from gold surfaces unmodified and modified by different SAMs. Experimental curves (scatters) are fitted with simulated approach curves (dot/dash/continuous lines) for estimating the rate constant, k^0.

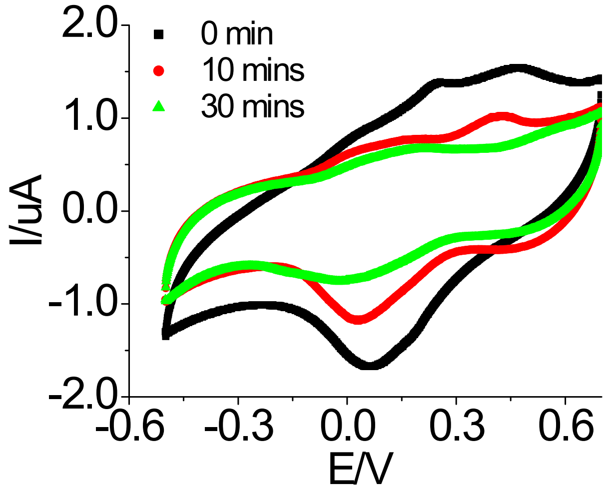

Fig. S3 Cyclic voltammograms of gold surfaces modified with 11-(Ferrocenyl)undecanethiol in a supporting electrolyte of 0.1 M $NaClO_4$. The modified surfaces were immersed in carbene molecule **2** for 0, 10 and 30 minutes.

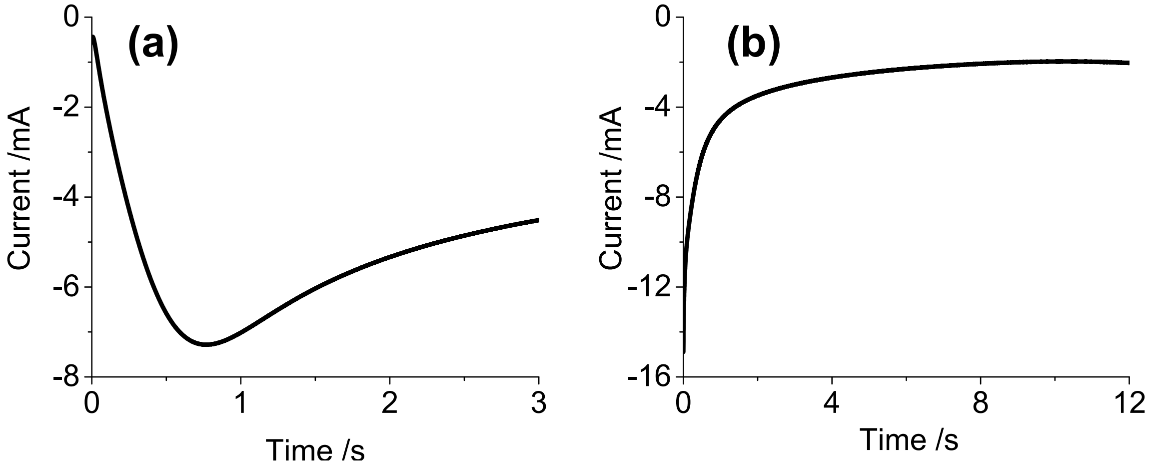

Fig. S4 Two-step electrochemical deposition of copper microstructures by chronoamperometry. (a) Current vs time at a potential of -0.48 V for 3 seconds; (b) current vs time at a potential of -0.23 V for 12 seconds.

1. C. M. Crudden, J. H. Horton, M. R. Narouz, Z. Li, C. A. Smith, K. Munro, C. J. Baddeley, C. R. Larrea, B. Drevniok, B. Thanabalasingam, A. B. McLean, O. V. Zenkina, I. I. Ebralidze, Z. She, H.-B. Kraatz, N. J. Mosey, L. N. Saunders and A. Yagi, *Nature Communications*, 2016, **7**, 12654.
2. (a) P. M. Diakowski and H.-B. Kraatz, *Chem. Commun.*, 2009, DOI: 10.1039/b819876d, 1189-1191; (b) P. M. Diakowski and H. B. Kraatz, *Chem. Commun.*, 2011, **47**, 1431-1433; (c) P. S. Dobson, J. M. R. Weaver, M. N. Holder, P. R. Unwin and J. V. Macpherson, *Anal. Chem.*, 2005, **77**, 424-434.