

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

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**Microcontact printed patterns of N-heterocyclic carbenes (NHCs) and thiols were prepared on gold substrates and utilized as templates for the creation of metallic Cu structures using electroplating. The presence of the NHC in the pattern is essential to enable the transfer of the resulting copper microstructures to a second substrate.**

Self-assembled monolayers (SAMs) have been used extensively in patterning of surfaces,<sup>1</sup> in both ‘top-down’ and ‘bottom-up’ approaches,<sup>2</sup> with microcontact printing ( $\mu$ CP), a soft lithography technique, first introduced by the Whitesides group.<sup>3</sup> This technique is often employed to create binary SAM surfaces, which can be used for microelectronics and cellular biology,<sup>1, 4</sup> and also for fabricating copper structures as described by the Buck group.<sup>5</sup> Electron beam (e-beam) lithography can also be employed to create patterns on surfaces either by selectively removing patterns of molecules or by crosslinking aromatic SAMs.<sup>6</sup> The Buck group has studied the application of e-beam patterned SAMs surfaces in the preparation of micro- and nanofabricated gold and copper structures.<sup>7</sup>

For the past 30 years, SAM chemistry has been dominated by sulfur-containing molecules;<sup>8</sup> however, recent reports have shown that N-heterocyclic carbenes (NHCs) can form robust SAMs on gold surfaces that are viable alternatives to thiolate-based SAMs.<sup>9</sup> Ravoo, Glorius et al. have recently described the first example of the use of NHCs in microcontact printing.<sup>10</sup> In this seminal report, transfer of NHC precursors was

accomplished through the use of polydimethylsiloxane (PDMS) stamps coated with NHC precursors. Functional NHCs were employed to generate patterned surfaces that could be functionalized with biomolecules, and survived treatment at elevated temperatures.<sup>10</sup>

Herein, we describe a different method for the preparation of patterned copper/gold surfaces using an approach related to electroplating, which takes advantage of the differential properties of thiol and NHC SAMs. A patterned surface was created by sequential deposition of thiols and NHCs on a gold surface. Following pattern formation, selective overpotential deposition of copper onto the NHC-areas of the patterned gold surface was carried out (Fig. 1). In addition to enabling the site-specific deposition of copper, the NHC SAMs also reduce adhesion between the fabricated Cu-structures and the substrate template, permitting detachment of the Cu-structure and transfer onto a secondary substrate without pattern destruction.

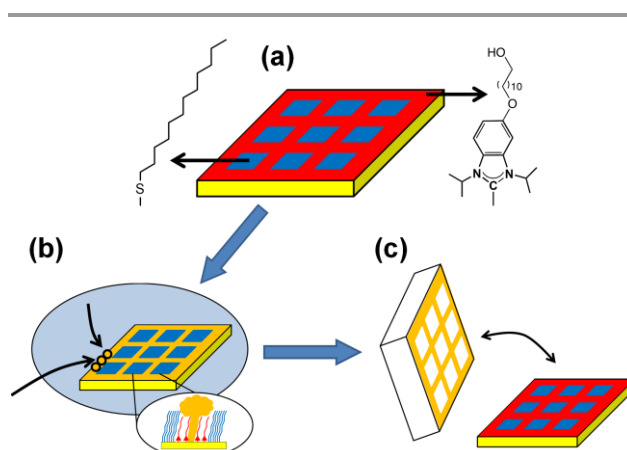


Fig. 1 (a) Preparation micro-patterns consisting of NHC and thiol molecules on gold substrate. (b) Electrochemical deposition of copper microstructures on NHC-areas. (c) Lift off and production of Cu microstructures on secondary substrate.

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The electrochemical reduction of metal ions in solution is the basis for all electroplating applications, and takes place by electron transfer from the electrode to the metal ions in solution.<sup>11</sup> The presence of films, including SAMs, on electrode surfaces typically inhibits electron transfer between the electrolyte and the surface. The film additionally acts as a barrier and reduces the diffusion of metal ions to the surface, thereby hindering the formation of an electroplated layer. In this study, we demonstrate how the ability of NHCs to provide a robust SAM with an electron transfer rate that is intermediate between that of bare gold and thiol-based SAMs enables the preparation of transferable metal patterns.

SAMs were prepared on gold surfaces by immersing gold electrodes in solutions of NHC precursors **1**•H<sub>2</sub>CO<sub>3</sub> and **2**•H<sub>2</sub>CO<sub>3</sub> (Fig. 2a) in methanol for 20 hrs. The presence of the NHCs on the film was verified using X-ray photoelectron spectroscopy (Fig. S1). The ability of these NHC films to support electroplating of Cu was then compared with bare gold, and with thiol-based SAMs on gold (Fig. 2c).

With gold surfaces modified by SAMs of NHC (**1**•Au) and (**2**•Au), the deposition potential on-sets are substantially more negative, such that electroplating of Cu does not take place until voltages reach -0.32 V and -0.38 V, respectively. The difference between NHCs **1** and **2** is the alkyl chain on the back of the NHC, which provides some increased passivation (Figure 2c, green vs. red curves). By comparison, the overpotential reduction of Cu ions to Cu metal happens on bare gold surface takes place as soon as the potential drops below 0 V, showing the inhibiting power of both SAMs (Fig. 2c, black line).

SAMs derived from 1-dodecanethiol (DDT, RS•Au) were also prepared, and were found to be more insulating, with the Cu-

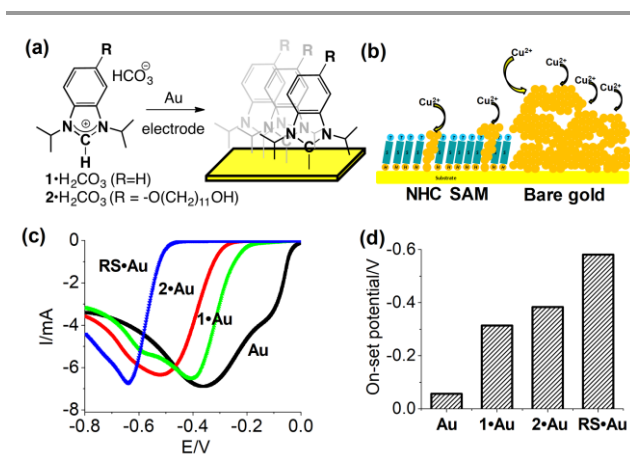


Fig. 2 (a) Preparation of NHC-based SAMs. (b) Illustration of electrochemical reduction of Cu<sup>2+</sup> on modified and unmodified gold surfaces (Au). (c) Comparison of NHC-based SAMs with bare gold and a 1-dodecanethiol SAM (RS•Au) by linear voltammetry. The voltammetry data were obtained in 50 mM CuSO<sub>4</sub> (H<sub>2</sub>SO<sub>4</sub>, pH~1) aqueous solution. (d) Onset potential for an unmodified gold surface and gold surfaces modified with SAMs. A Cu wire capillary was used as a reference electrode.

deposition starting at -0.5 V (Fig. 2c, blue line). This is attributed to the higher density of thiol-based SAMs prepared from unbranched alkyl thiols.<sup>9b,12</sup> As shown below, this difference will be critical to permit the growth of metal films on top of the NHC section of micropatterned films, facilitated by charge and ion diffusion through the NHC portion.

Prior to the preparation of patterned films, we measured the heterogeneous charge transfer properties of the thiol and NHC films by scanning electrochemical microscopy (approach curve mode shown in Fig. 3a). In this mode, electrons transferred from Au surfaces to the redox species, i.e. ferricyanide ions, reduced ferricyanide back to ferrocyanide. The redox process is monitored by the SECM tip. Approach curves for the various films were obtained and evaluated using COMSOL multiphysics (Fig. S2).<sup>13</sup> The rate constants for electron transfer for bare gold and gold surfaces modified with **1**, **2** and DDT are shown in Fig 3b. The rate constant for bare gold was measured to be  $(78.3 \pm 3.8) \times 10^{-4}/\text{cm s}^{-1}$ . By comparison, gold surfaces modified with NHCs **1** and **2** have rate constants of  $(51.8 \pm 4.9) \times 10^{-4}/\text{cm s}^{-1}$  and  $(43.8 \pm 2.8) \times 10^{-4}/\text{cm s}^{-1}$  respectively<sup>(footnote f)</sup>. Consistent with the potential on-set data, the existence of a long alkyl chain at the back of the NHC **2** decreases the rate of charge transfer when compared with NHC **1**, although not dramatically. Dodecane thiol films showed the highest suppression and the rate of charge transfer was reduced down to  $(0.53 \pm 0.09) \times 10^{-4}/\text{cm s}^{-1}$ .

NHC films were compared with unmodified gold by cyclic voltammetry as shown in Fig. 4. Consistent with electron transfer studies, current is suppressed for NHC-modified

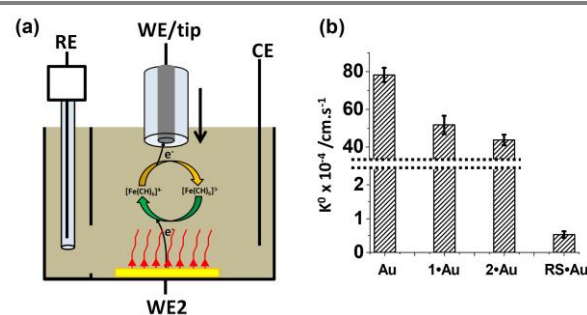


Fig. 3 (a) Illustration of an approach curve measurement by scanning electrochemical microscopy. Working electrode (WE1) is used as the scanning tip while the working electrode (WE2) is the sample surface. (b) Rate constants ( $k^0$ ) for electron transfer as measured from corrected approach curves (Fig. S2), evaluated using COMSOL Multiphysics simulation. A reference electrode (Ag/AgCl/3.0 M KCl) was used for SECM measurement. The SECM solution was 2 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] aqueous solution as the redox probe and 50 mM NaClO<sub>4</sub> as the supporting electrolyte. The gold surfaces were modified by immersing the electrodes in NHCs **1** and **2** and DDT solution for 20 hours, respectively.

<sup>f</sup> These figures for electron transfer were obtained on films prepared by immersion in NHC bicarbonate solutions for 20 h. As shown in Figure 4d, most of the blocking of the surface was completed after 10 minutes, but we chose 20 hrs to obtain an idea of the maximum blockage expected for NHC covered surfaces.

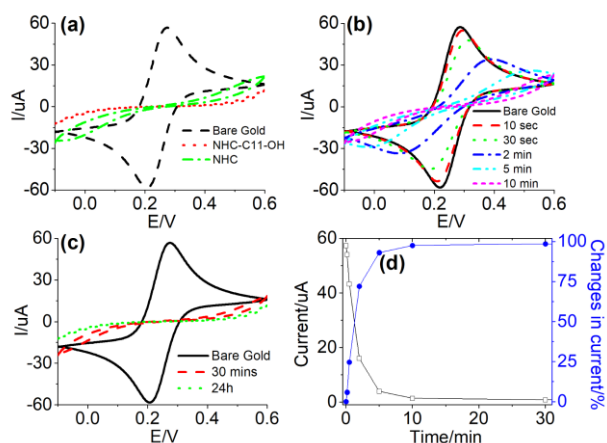


Fig. 4 (a) Cyclic voltammograms for gold surfaces unmodified (dash line, black) and modified with carbene SAMs **1** (dash/dot line, green) and **2** (dot line, red). (b) & (c) Cyclic voltammograms monitoring the electrochemical signal changes triggered by formation of carbene **2** SAM on the surface. (d) Current and changes in current versus time. All measurements were carried out in 5 mM/5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and 1 M  $\text{NaClO}_4$ .  $\text{Ag}/\text{AgCl}/3.0 \text{ M KCl}$  was used as the reference electrode.

electrodes due to the insulating effect of the SAM. The cyclic voltammograms in Fig. 4b show that it only takes 2 minutes for the NHC precursor  $2 \cdot \text{H}_2\text{CO}_3$  to form a layer on gold sufficient to suppress the current and shift the reduction and oxidation peaks further apart.

Having demonstrated that the insulating behaviour of the thin films decreases in order of compounds  $1 \cdot \text{Au} < 2 \cdot \text{Au} < \text{RS} \cdot \text{Au}$ , we needed to decide which surface to prepare first in the micropatterning process, based on the ability of one ligand to withstand replacement by the other. The use of an NHC film as the initial pattern was not feasible due to the possibility of backfilling the less dense NHC SAM with thiol, resulting in film that is too insulating for Cu deposition. However treatment of dodecanethiol films with NHC precursor **1** for extended times (24 h) is known to lead to substantial replacement of the thiol-SAM with the NHC.<sup>9a</sup> To examine the possibility of thiol SAMs surviving NHC treatment at lower exposure times, SAMs were prepared from 11-(ferrocenyl)undecanethiol (FcSH) and treated with solutions of NHC precursor  $2 \cdot \text{H}_2\text{CO}_3$ . The Fc group is introduced to provide a readily quantified signal that serves as an indicator for thiol replacement by NHC (Fig. S3).

As expected, exposure of a SAM prepared from FcSH to NHC **2** showed the loss of the redox signal due to the exchange of thiol by NHC, even at short treatment times. After only 10 minutes, 32 % thiol loss was observed. However, considering that the ferrocene head group will give a significantly more disordered film compared with those prepared from dodecane thiol, we decided to attempt patterning with DDT, and aimed to minimize exposure times to NHC precursors to less than 10 minutes. Since considerable NHC film formation on bare gold was already observed after 5 minutes (see Figure 4), this is a reasonable time frame.

Employing a transmission electron microscopy grid as a mask on a PDMS stamp (Fig. 5a/b), we transferred DDT to a PDMS stamp by immersion in an ethanol solution for 5 minutes. After drying under a stream of nitrogen, the "inked" stamp was pressed to the gold surface for 30 seconds. The modified surface was then immersed in a 10 mM methanol solution of NHC  $2 \cdot \text{H}_2\text{CO}_3$  for 1 minute. The surface was then rinsed with methanol for 30 seconds and dried with a stream of nitrogen gas. Since we are employing the NHC film as the more "lossy" part of the pattern, it is not essential that this be a dense film.

The resulting NHC/thiol patterns were interrogated by SECM, which provides spatial information and information about electron transfer through the respective films. As shown in Fig. 5c, the area functionalized by NHC **2** is brighter than the central DDT squares, since electron transfer is higher in the NHC portion of the film. The dashed line in the image indicates where the cross-sectional profile was taken, (Fig. 5d).

The NHC/DDT patterns were then used to template the formation of a metallic copper grid. Copper reduction was carried out using chronoamperometry with two potential steps at  $-0.48 \text{ V}$  for 3 seconds and  $-0.23 \text{ V}$  for 12 seconds. Using the current over time plots to estimate the reduction charges, the thickness of the copper film was estimated to be approximately 270 nm. As shown in Fig. 5e, copper is deposited primarily on the grid (NHC area) rather than the squares (thiol area), as expected based on the differences in electron transfer between the two films, although there is clearly some copper deposition within the squares as well. This is either a consequence of the NHC replacing some of the thiol during the patterning process, or defects in the thiol film introduced during the overall process.

To illustrate the advantage of deposition on top of the NHC SAM, the copper was detached from the electrode and transferred onto a second substrate surface. The image in Fig. 5f shows the copper grid (bright) after being lifted off the gold

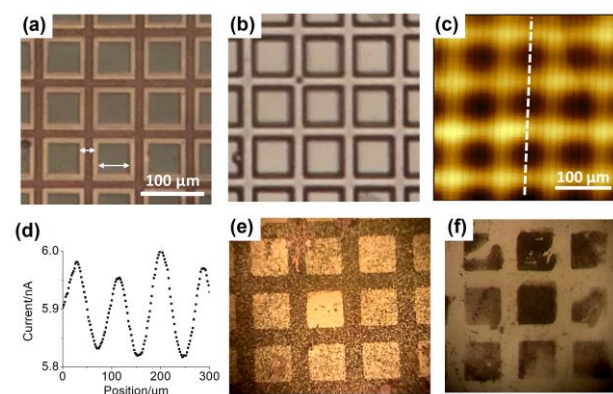


Fig. 5 (a) Optical image of transmission electron microscopy grid (CF300-CU, mesh 300, Bar: 25  $\mu\text{m}$  Hole: 58  $\mu\text{m}$ ) used for casting PDMS stamp shown in (b). (c) SECM image of a micropattern consisting of the NHC (bright yellow grid) and thiol molecules on a gold surface before Cu overpotential deposition. (d) A cross-sectional analysis along the dashed line shown in (c). (e) Optical image of the electrochemically reduced Cu grid (dark) on top of the NHC-covered area. (f) Cu-grid (light) after its transfer to a secondary substrate.

substrate by treatment with an epoxy glue (black). Transfer of the deposited film was enabled by the presence of the NHC SAM, which minimized adhesion between the deposited Cu and the gold substrate.

In conclusion, the recent development of NHC SAM chemistry provides many exciting opportunities in materials science.<sup>14</sup> We have demonstrated that the different properties of NHC SAMs compared to thiol SAMs can be employed to enable selective overpotential deposition of a copper film. Better differentiation between the properties of the two SAMs is likely to lead to a more selective deposition process.

## Notes and references

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