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Surface Functionalization

Heterogeneous Catalysis through Microcontact Printing**

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The chemical toolkit for the modification of inorganic surfaces with organic molecules has grown enormously in recent years. Much of the underlying science has been driven by developing technologies[1] such as biomolecular and chemical sensing,[2] molecular electronics,[3] light harvesting,[4] and others. These applications all have certain requirements that place unique demands on the chemistry, which often impact more than just the choice of substrate or organic modifier. For example, electronic communication between surface-bound organic molecules and the underlying substrate may be necessary. Other application-specific requirements include rapid and efficient surface attachment reactions that provide 1) high surface coverage, 2) protection of the underlying substrate against oxidation,[5] and/or 3) control over molecular orientation.

The ability to pattern the organic monolayer spatially is a common requirement. The technique of microcontact printing (μCP) permits[6] the patterned transfer of a molecular ink onto a surface using an elastomeric stamp. The transferred molecules may form a self-assembled, high coverage monolayer, e.g., thiols on gold[6b,e] or silanes on silicon dioxide.[7] Alternatively, μCP can promote the spatially selective reaction between an already surface-bound molecule and a molecular ink. This concept has been demonstrated for 1) the patterning of peptides using amide[8] coupling chemistry, 2) the formation of thermodynamically stable imine[9] bonds, and 3) for the promotion of the Huisgen 1,3-dipolar cycloaddition, yielding[10] a triazole link between a surface-bound moiety and the ink molecule. Both the triazole- and amide-coupling reactions typically require catalysts or additional stoichiometric reagents, such as carbodiimides, when performed in solution. However, within the unique environment[11] created when the surface-bound and molecular ink reagents are brought into close contact using a stamp, the reactions have been reported[10,11] to proceed—at least to some extent—without these additional components.

The organic functionalization of surfaces is heterogeneous, involving a solid-surface reacting with solution- or gas-phase reagents. The two-dimensional nature of surfaces also means that steric effects can either impose kinetic barriers upon thermodynamically favored chemical processes, or they can impart kinetic stability to certain non-equilibrium surface structures.[12] The presence of kinetic barriers, in turn, implies that different chemical approaches towards functionalizing surfaces with organic components might lead to different coverages and/or surface structures.

Here, we investigate four different chemical pathways (Scheme 1 a–d) relevant to the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction.[13] Three of those pathways lead to surfaces functionalized with organic molecules.[5,11,14] At the outset, our practical goal was to identify surface-functionalization protocols that are capable of attaining 1) spatial selectivity, 2) high surface coverage, and 3) rapid reaction kinetics. Our ultimate goal is to achieve a fundamental understanding of how different reaction pathways influence the chemical outcome as it applies to the organic functionalization of surfaces.

The four pathways illustrated in Scheme 1 a–d vary with regard to how the reaction components (**1**–**7** and the Cu source) are introduced to one another. A Cu catalyst is required for the CuAAC reaction to proceed to any appreciable extent in each scheme. Probes **5**–**7**, when attached to surfaces, are respectively designed for specific redox, X-ray photoelectron spectroscopy (XPS), or fluorescent signatures, thus allowing for the full characterization of the functionalized surfaces using complementary techniques. Scheme 1 a summarizes a homogeneous, solution-based pathway in which 1-azidohexane (**3**), 1-octyne (**4**), and $CuSO_4{\cdot}5H_2O$/ascorbic acid[13b] react in solution, and provides a reference against which the surface chemistries can be compared. Under conditions chosen to simulate those relevant to surface functionalization (20-fold excess of **4** relative to **3**), the

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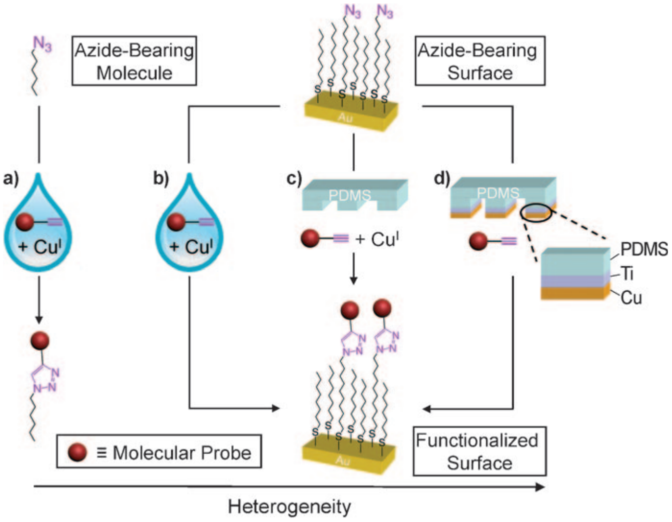

Scheme 1. Various routes to affect the Cu^I-catalyzed azide–alkyne coupling (CuAAC) in different environments: a) Solution: A solution reaction where azide, alkyne, and catalyst participate in a homogeneous reaction; b) Solution–Surface: A heterogeneous reaction where dissolved alkyne and catalyst react with a surface bound azide; c) Reagent-Stamping: A heterogeneous reaction where the alkyne and catalyst are brought into contact with a surface-bound azide in the condensed phase; d) StampCat: A heterogeneous reaction where immobilized copper catalyzes the reaction of an alkyne with a surface bound azide in the condensed phase.

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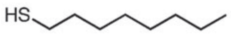

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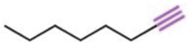

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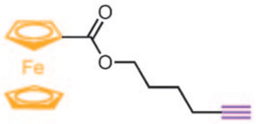

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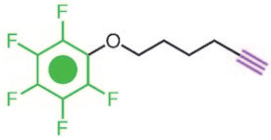

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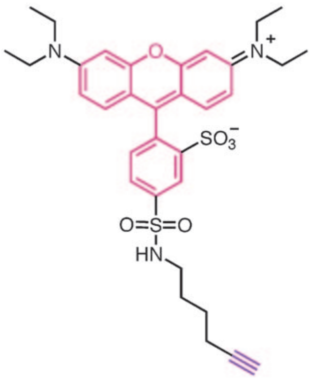

CuAAC reaction proceeded to 95 % conversion[15] during 6 h. This finding is a useful baseline for comparison of the kinetics of the reactions performed through each of the heterogeneous surface reactions (Scheme 1 b–d).

The substrates for the CuAAC reactions described in Scheme 1 b–d were composed of azide functionalities tethered to undecyl alkyl chains as self-assembled monolayers (SAMs) on gold and silicon oxide through terminal thiol and silane groups, respectively. Following on the work of Collman et al.,[14a,b] the monolayers on Au were deposited from a 1:1 mixture of two thiols (azidoundecanethiol and octanethiol) to form mixed monolayers[16] in which the relatively long, projecting azido functions are accessible for reaction. Glass slides functionalized with azide moieties were created in a two-step process[10] whereby a bromoundecylsilane SAM is converted to the azido-terminated SAM through nucleophilic displacement of the bromide by sodium azide. The Solution–Surface approach (Scheme 1 b) introduces both the alkyne-terminated molecules and the Cu^I catalyst, dissolved in a solution placed in contact with the surface. Similar chemistry has been reported previously on Au[14a,b] and other[17,18] substrates. The Reagent-Stamping method (Scheme 1 c) employs μCP methods—using polydimethylsiloxane (PDMS) stamps—to introduce both the alkyne-containing reactant and the Cu^I catalyst to the surfaces by the (solventless) contacting of inked stamps onto the surfaces. Finally, the StampCat procedure (Scheme 1 d) utilizes a PDMS stamp coated with a thin Cu metal film. The stamp itself catalyzes the spatially-selective reaction between a small-molecule alkyne and the azide surface, also under solvent-free conditions.

Elastomeric stamps are often modified[19] to improve their ability to transfer various inks for μCP, generally by increasing the loading potential of the stamp. The CuAAC reaction may be catalyzed in both the solution[13b,20] and solid phase[21] using heterogeneous catalysis in the form of a copper metal source. We hypothesized that a Cu-coated elastomer would similarly catalyze the coupling between surface-bound azides and terminal alkynes. Thus, we modified cured PDMS stamps via electron-beam deposition of a 10 nm Ti adhesion layer followed by a 50 nm Cu layer. The resulting metal-coated flat or patterned stamps retained most of their elasticity and were used in the StampCat process.

Surfaces functionalized according to Schemes 1 b–d were characterized by water contact angle, XPS, FTIR, and cyclic voltammetry (CV) measurements. For Scheme 1 c and d, flat, non-patterned stamps were utilized. For the experiments on surfaces following the CuAAC reaction with each molecular probe (**5**–**7**), all measurements other than CV were carried out after the relevant reaction steps had proceeded to completion (see below). For the reaction of an Au surface with **5**, CV measurements were carried out to validate the formation of a covalent linkage between **5** and the surface, and to follow the reaction kinetics of Scheme 1 b–d.

Cyclic voltammetry measurements were utilized to confirm the formation of a covalent bond between the surface and **5**, and to quantify the extent of the reaction. Figure 1 displays CV data, collected for a mixed monolayer of **1** and **2** that was functionalized by StampCat of **5**. The linear increase

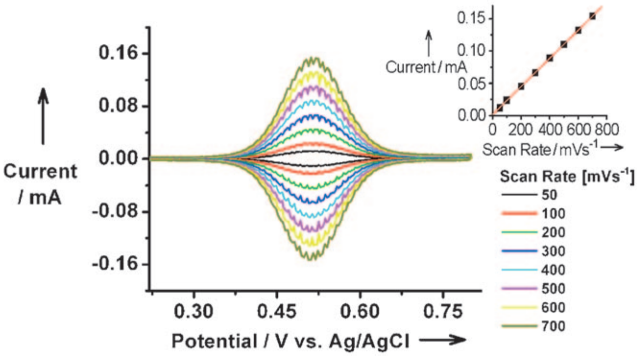

Figure 1. Electrochemical measurements at various scan rates, indicating covalent functionalization of ferrocene-containing ink **3** through StampCat. Proof of covalent attachment is supported by the linear plot of current versus scan rate. Inset: current recorded at +0.51 V for each scan rate. The electrolyte was 1 M $HClO_4$.

in current as a function of scan rate, and the identical values for the peak potential for both oxidation and reduction of the ferrocene, indicate covalent surface attachment of the ferrocenyl moieties. A square-root dependence of current on scan rate would be expected for similar redox behavior if the electroactive components were dissolved in solution. Similar spectra were obtained for surfaces functionalized with **5** employing the Reagent-Stamping and Solution–Surface schemes. Integration of these spectra confirmed that similar efficiencies were obtained using all three schemes.

Further spectroscopic proof of surface functionalization was obtained by XPS. The StampCat process using the pentafluorophenolic ether **6** demonstrated a pronounced change (Figure 2a,b) in the XPS spectra of the F 1s region as a consequence of the addition of a highly fluorinated molecular entity onto the surface. Surfaces functionalized with **5**, using the Reagent-Stamping process, displayed similar changes in their XPS spectra. Figure 2c presents high-resolution XPS spectra of the N 1s region, and shows two peaks at 400 and 404 eV with an intensity ratio of 2:1, similar to other reports for azide groups on gold[14b] and graphitic[17] surfaces. After functionalization with **5**, a single feature in the N 1s region is observed (Figure 2d). These changes for CuAAC functionalized surfaces were common to every situation we investigated, and are also consistent with literature observations.[14a,b] For surfaces functionalized with **5**, changes in the Fe 2p region of the spectrum revealed (Figure 2f) the presence of an Fe-containing molecule.

External reflectance IR spectroscopy also revealed the presence or absence of azide functions at the surface (Figure 3) by measurement of a large peak centered on 2103 cm^{-1} that arises from the azide symmetric stretching mode. Upon either StampCat or Reagent-Stamping of **5**, the integrated peak intensity is attenuated by ca. 90% while a Solution–Surface reaction with **5** leads to its complete disappearance. These results suggest azide consumption resulting from triazole ring formation and hence the functionalization of the surface in general. Water contact angle measurements also lent qualitative support to the idea that all three methods proceed with comparable reaction efficiency (see Supporting Information).

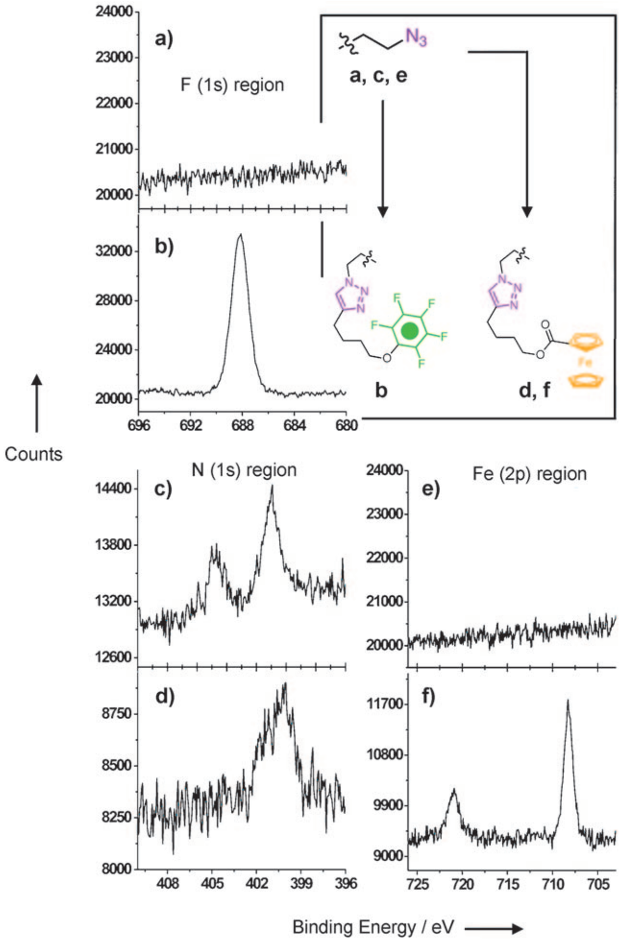

Figure 2. XPS data demonstrating the functionalization of azide-terminated Au substrates (**a**, **c**, and **e**) with pentafluorobenzene **6**-containing (**b**) and ferrocene **5**-containing alkynes (**d** and **f**). The StampCat CuAAC reaction is demonstrated in the F 1s region before (**a**) and after (**b**) the reaction with the pentafluoro alkyne **6**. The Reagent-Stamping CuAAC reaction is demonstrated in the N 1s and Fe 2p regions of the XPS before (**c**, **e**) and after (**d**, **f**) the reaction with the ferrocene-containing alkyne **5**.

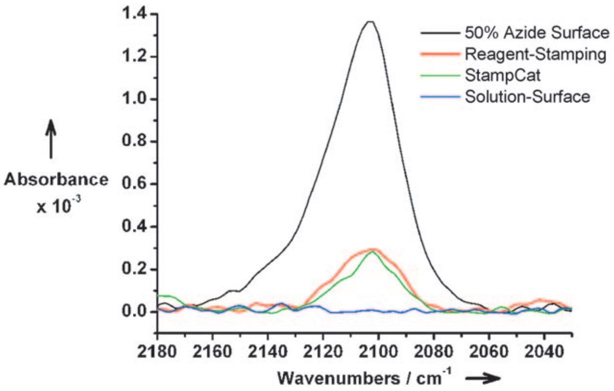

Figure 3. IR spectra demonstrating the reduction of the azide stretch after functionalization with the ferrocene-containing ink **5** using the Reagent-Stamping, StampCat, and Solution–Surface methods.

The solution-based homogeneous reaction (Scheme 1 a) provided a baseline for comparison with the heterogeneous, surface-based reactions of Schemes 1 b–d. Under the conditions employed to approximate[22] those expected for surface-based reactions, the reaction proceeds (Figure 4 c) to > 95 % conversion within 400 min with a half-life around 1 hour. The homogeneous CuAAC reaction is known to demonstrate complicated kinetics. Under catalytic conditions in copper, Finn and co-workers[23] found the reaction to demonstrate different rate orders in copper depending on concentration and ligand choice. Thus, rather than elucidate the rate law for the conditions described above, we used them as a rough benchmark for the kinetics of the different surface functionalization approaches.

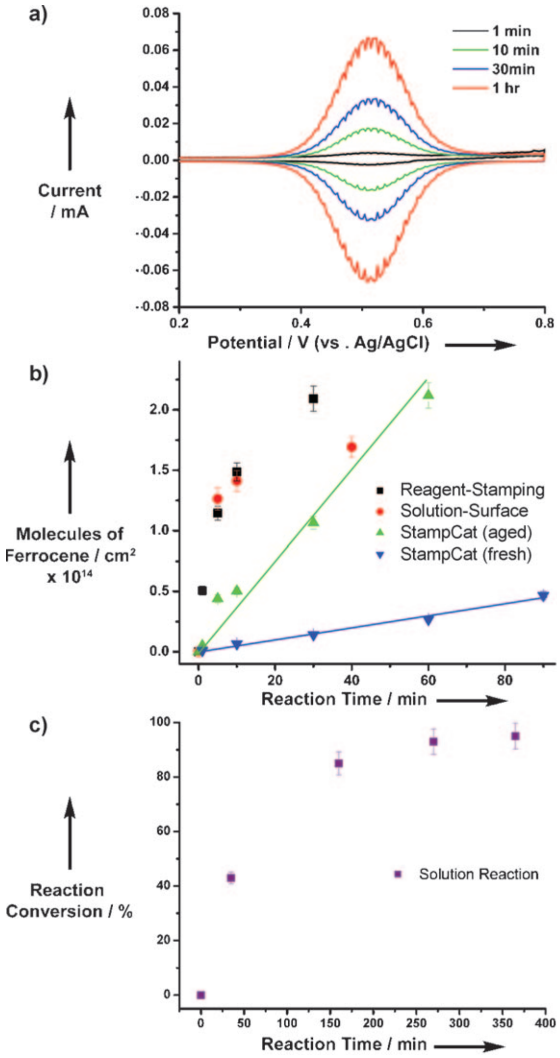

Figure 4. The kinetics of CuAAC catalysis for Schemes 1 a–d. a) Cyclic voltammograms, collected (at 300 mVs^{-1}) as a function of stamping time, for the StampCat process. Coverage increases with longer stamping times (using aged stamps). b) Plot demonstrating the conversion of azide surfaces to surfaces functionalized with **5**, as a function of time, for all three surface-based reactions (Schemes 1 b–d). For the StampCat process, reaction kinetics for stamps that were used within an hour of metal deposition, and for stamps that were aged in air for 24 h, are shown. Both exhibit linear response functions on this plot, as indicated by the straight lines that are drawn to guide the eye. c) Reaction conversion versus reaction time for the Solution reaction (Scheme 1 a) between 1-azidohexane (**3**) and 1-octyne (**4**), as measured by ^{1}H NMR spectroscopy.

The measured rates (using cyclic voltammetry) of the chemical processes summarized in Schemes 1 b–d are shown in Figure 4. For these experiments, the attachment of **5** to azide-presenting Au surfaces was monitored as a function of reaction (or stamping) time. When making the StampCat measurements, a new Cu-coated PDMS stamp was used in the microcontact printing of the surfaces produced for each time point. Two different StampCat kinetic series were investigated: one in which freshly deposited CuPDMS stamps were employed (fresh) and another in which the stamps were allowed to age for 24 h (aged). The integrated intensity of the CV spectra increased (Figure 4 a) as a function of reaction (or stamping) time for all methods, and permitted calculation of ferrocene coverage at the surfaces. That all three methods produced coverages at a maximum of 2×10^{14} molecules cm^{-2} at extended reaction times indicates that the CuAAC proceeds to completion, in agreement with previous measurements[14b] made on the same mixed monolayer surfaces. Plotting the number of functionalizing ferrocene molecules per cm^2 as a function of the reaction time provides (Figure 4 b) a means to monitor the kinetics of each CuAAC process.

The Reagent-Stamping process produced fully functionalized surfaces at the highest rate, with complete conversion being attained within 30 min. In comparison, the StampCat process using aged stamps catalyzed the reaction at half the rate, generating complete coverage after 1 hour. Interestingly, a comparison of the two kinetic curves reveals different operable rate orders, with the Reagent-Stamping displaying what appears to be pseudo-first order exponential growth and the StampCat process zero-order linear growth. Zero-order reaction behavior was also observed when freshly deposited Cu-coated PDMS stamps were used in the StampCat process, but the rate was lower, producing ten-fold less coverage after 60 min of stamping time. The Solution–Surface reaction proceeded at a very high rate initially, producing surfaces functionalized with over 1.2×10^{14} ferrocene molecules per cm^2 after 5 min. However, the efficiency plummets in the later stages of the reaction, only producing fully functionalized surfaces (containing 2×10^{14} molecules cm^{-2}) after 180 min[24] of reaction. This non-linear kinetic behavior for the Solution–Surface method is comparable to the pseudo-first order exponential growth of the Reagent-Stamping method, a feature that can be attributed to an abundance of Cu^I catalytic centers available for reaction when employing both of these methods. The Solution–Surface process produced fully functionalized surfaces slower than either Reagent-Stamping or StampCat (using aged stamps).

The StampCat process involving the CuAAC reaction is dependent on the catalytic Cu metal coating being present. When bare PDMS or platinum-coated stamps were used for the functionalization of the azide-coated gold surfaces, there was no electrochemical evidence (Figure 5) of the CuAAC reaction having occurred with ferrocene alkyne **5**. This was unexpected based upon a previous report[10] of quantitative copper-free click reaction onto glass surfaces. An electrochemical analysis of surfaces functionalized with **5** provides a

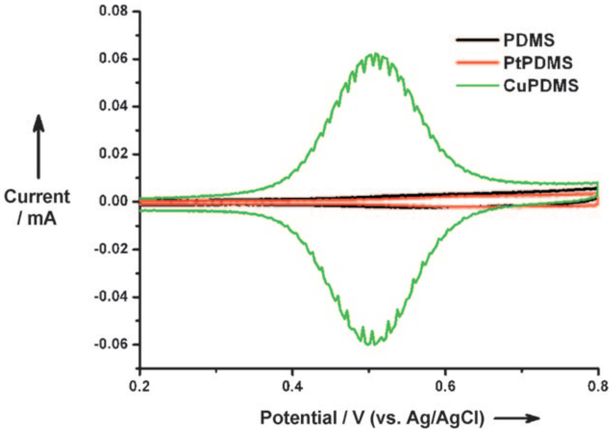

Figure 5. No ferrocene functionalization was observed for stamping with Pt-coated PDMS or bare PDMS for 1 hour in comparison to the high functionalization observed for stamping using Cu-coated PDMS.

quantitative assessment of reaction efficiencies. The earlier work employed highly sensitive but non-quantitative surface characterization methods. We appreciate now that the reaction without a catalyst results in very limited conversion, even over prolonged reaction times.

In an effort to interrogate the nature of the StampCat process, the reaction efficiencies achieved from stamps with freshly deposited Cu films, and those with Cu films that had been aged for 24 h (Figure 4b) were compared. Both situations exhibit linear response functions in terms of ferrocene functionalization versus time, indicating a similar chemical mechanism. However, the aged stamps yielded fivefold more ferrocene coverage at 60 min than the freshly coated stamps, implying that the aging process increases the concentration of the active catalytic species on the Cu-coated stamps. While the homogeneous CuAAC reaction is catalyzed by free Cu^I ions, heterogeneous versions of the reaction have been reported[20,21] in which surface-bound CuO and Cu_2O species are thought[20b,25] to be responsible for the catalysis.

Studies of the oxidation of Cu surfaces[26] indicate that Cu_2O is the predominant initial surface species formed under conditions that are most similar to those for the stamps aged in air for 24 h. It is this Cu_2O coating which most likely acts as the active heterogeneous catalyst in the StampCat process. The stamps with freshly-deposited Cu films are less catalytically active because they contain fewer catalytically active Cu_2O surface sites. The aged Cu-coated PDMS stamps also lose their activity over repeated stampings (see Supporting Information), implying that the surface Cu_2O film is somehow disturbed or depleted during the first stamping event.

The ability to produce spatial surface patterns is a key advantage of µCP methods. It is possible that the active catalyst from the StampCat scheme is either the solid surface of the stamp itself, or potentially Cu^I ions that leave the stamp and diffuse through an adsorbed water layer at the stamp or wafer surface. Thus, we used the StampCat method to react the azide-presenting glass surface with a micro-patterned stamp containing the fluorescent alkyne **7**. We reasoned that, for long stamping periods, the finer features of the stamp would be washed out of the stamped pattern, if the catalyst originated from diffusing[27] Cu^I ions. Otherwise, the stamped pattern would reflect the fine structure of the stamp itself. The stamped patterns were measured using confocal fluorescence microscopy, and compared (Figure 6) alongside atomic force microscopy (AFM) images of the surface of the Cu-coated PDMS stamp.

AFM of the Cu-coated PDMS stamp reflected the molded pattern of 3 × 5 µm lines (Figure 6a), but also revealed a finer structure of submicrometer width lines at a pitch of about 1 µm. This pattern likely arises from contraction of the PDMS stamp when it is removed from the vacuum of the metal deposition chamber. In any case, both the patterned and the fine-structure features are observed in the fluorescence micrographs of the glass surface. This observation, coupled with the above described results that PDMS-only stamps, or Pt-coated PDMS stamps do not promote the surface click reaction to any appreciable extent, confirms that the catalyst for StampCat is likely the (oxidized), Cu-coated surface of the PDMS stamp. The StampCat process can clearly be harnessed[28] to generate impressively small feature sizes for µCP.

We have explored multiple pathways for achieving Cu-catalyzed, surface functionalization of azide-modified surface. One particularly novel pathway is the StampCat method, in which a Cu-coated elastomeric stamp is utilized to catalyze the reaction heterogeneously, and with spatial selectivity, between molecules with pendant alkynes and surface-bound azides. The StampCat method enables solvent-free, fast and efficient surface functionalization. The mechanism and kinetics of the StampCat pathway are contrasted with three other schemes that vary primarily in terms of the increasing range of reactant and reagent immobilization for the CuAAC reaction.

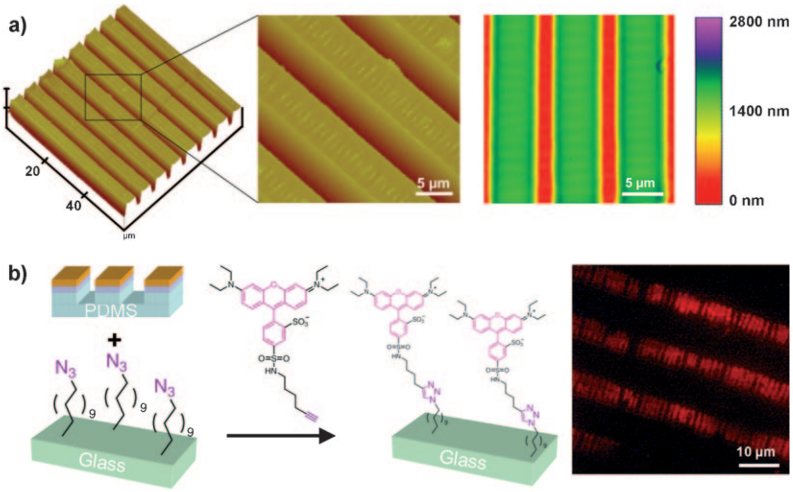

Figure 6. a) AFM investigation of a CuPDMS patterned stamp topography where both the large line patterns (present before metal deposition) and metal ripples (as a consequence of metal deposition) are observed. b) StampCat of the fluorescent alkyne **7** onto azide-functionalized glass slides using the patterned CuPDMS stamp produces lines of stripes that are observed by fluorescent microscopy. The ripple pattern transfer is consistent with heterogeneous catalysis.

A linear rate order is observed for metallic Cu film based catalysis while pseudo-first order behavior is exhibited by freely diffusing Cu^{I} catalytic processes. The CuAAC reaction is becoming an increasingly important approach towards chemically functionalizing surfaces, and these studies should provide a firmer understanding of how that reaction can be harnessed for application-specific uses.

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