Published in final edited form as:

Appl Surf Sci. 2018 July 31; 447: 535–541. doi:10.1016/j.apsusc.2018.04.007.

Indirect photopatterning of functionalized organic monolayers via copper-catalyzed “click chemistry”

Mackenzie G. Williams and Andrew V. Teplyakov*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States

Abstract

Solution-based lithographic surface modification of an organic monolayer on a solid substrate is attained based on selective area photo-reduction of copper (II) to copper (I) to catalyze the azide-alkyne dipolar cycloaddition “click” reaction. X-ray photoelectron spectroscopy is used to confirm patterning, and spectroscopic results are analyzed and supplemented with computational models to confirm the surface chemistry. It is determined that this surface modification approach requires irradiation of the solid substrate with all necessary components present in solution. This method requires only minutes of irradiation to result in spatial and temporal control of the covalent surface functionalization of a monolayer and offers the potential for wavelength tunability that may be desirable in many applications utilizing organic monolayers.

Keywords

Photopatterning; Surface chemical modification; Surface functionalization

1. Introduction

The ability to tune the surface properties of materials by chemical modification with molecular-scale precision is a target objective for various fields that focus on the development of small-scale devices for different applications, such as catalysis, microprocessor manufacturing, sensing, and microelectromechanical systems. Chemical methods devoted to this process have attracted tremendous interest from science and engineering communities [1,2].

In the last few decades, “click chemistry” has gained traction as an effective means of surface modification [3]. “Click chemistry” is a general term that describes modular reactions that are efficient and selective. Described by Meldal [4] and Sharpless and Fokin [5], the copper (I) catalyzed azide-alkyne dipolar cycloaddition (CuAAC) is lauded as the gold standard of “click” reactions and has been widely-utilized as a means of anchoring molecular and larger structures to a substrate. The thermally-induced cycloaddition results in a mix of regioisomer products; however, the presence of the copper (I) catalyst allows the reaction to proceed at room temperature, resulting in the selective formation of the 1,4-

*Corresponding author. andrewt@udel.edu (A.V. Teplyakov).

disubstituted triazole product [5]. This has been effectively used for surface modification of a number of different substrates [6–8], and even for building layered structures with components much larger than molecular size [9–12].

Another important aspect of substrate modification for the purpose of microfabrication is maintaining control over adsorbate placement for patterned surfaces. A number of techniques have been developed and utilized to create micropatterns on various materials [13–16]. Traditional photolithographic methods are often used for surface patterning. To produce high-resolution features, this process requires multiple steps and materials including etching, photoresist application and removal steps, and often, cleanroom environments. Furthermore, the photolithographic steps themselves may result in damage to, or defects in, the patterned surface [17,18]. A combination of photolithographic patterning with “click chemistry” by using traditional resist-based patterning methods, followed by a solution-based “click” reaction to produce spatially-controlled modification with the high selectivity of attachment [19] is a promising route for efficient surface patterning; however, the very use of resist-based methods can easily damage the organic or biological layers that are patterned. To avoid this damage, alternative patterning techniques based on self-assembled monolayers (SAMs) can sometimes be employed instead [20]. Microcontact printing allows for reproducible patterning over a large area and completely eliminates the need for photochemical steps. The stamp itself, however, must be fabricated using more complicated techniques and undergoes deformation during the stamping process [20,21]. As an alternative, scanning probe lithography is capable of producing more highly-resolved features but is a slower process because the features must be written individually [20]. Shadow masking produces patterns based on photochemical reactions by irradiation through a mask. Like microcontact printing, patterning can be achieved quickly and over large areas using this method, although resolution is limited by diffusion, as well as the mask features and diffraction limit [20].

Thus, new photochemistry-based methods that combine high precision with relatively gentle treatment of the surface are needed. An extensive review by Tasdelen et al. on externally stimulated (including light-mediated) click reactions summarizes the recent advances in the field to promote photo-reduction of copper (II) to copper (I) to catalyze the cycloaddition [22]. Direct photoreduction of copper (II) has been successfully applied to catalyze the azide-alkyne “click” reaction, but may require long irradiation times [22–26]. Indirect reduction by irradiation of a photoinitiator to generate a radical system that reduces copper(II) to copper(I) is the alternative approach that proceeds more quickly and offers wavelength tunability to make it appropriate for different systems [23,27]. This affords the ability to avoid photo-degradation of sensitive organic functionalities (such as the decomposition of azides [28] or oxidation/desorption of thiols [29] upon exposure to ultra-violet irradiation) and materials (such as those undergoing bioorthogonal processes) [30,31]. Furthermore, the use of this “click reaction,” which can proceed in a number of different solvents, makes it amenable to certain biological applications (such as biosensors), which may otherwise be impossible in specific solvent systems [32]. This approach is ubiquitous in the field of polymer chemistry [21,28,33–35], where parts of polymer films can be modified chemically with high efficiency. Here we demonstrate the utility of a similar approach to selectively modify and pattern organic monolayers on solid substrates. In addition to high

efficiency, simplicity, and low cost, this gentle method does not damage the chemically modified self-assembled monolayers and offers potential wavelength tunability that may be desirable in a variety of applications involving photosensitive materials [13]. This approach offers a potential alternative to non-line-of-site deposition techniques to achieve conformal filling over high aspect-ratio features.

2. Experimental section

2.1. Azide modification of the gold substrate

A pre-fabricated gold-coated wafer (1000 Å gold thickness on silicon wafer support with titanium adhesion layer, Sigma Aldrich) was cleaned in piranha solution (1:3 (by volume) hydrogen peroxide (30%, Fisher Scientific):concentrated sulfuric acid (98%, Fisher Scientific)) for five minutes, followed by cleaning in Milli-Q water (18 MΩ·cm, Quantum EX, EMD Millipore) for five minutes in order to remove organic contaminants. It was then rinsed with hydrochloric acid (37%, Fisher Scientific), Milli-Q water, ethanol (200 proof, Decon Labs), and dried in a stream of nitrogen. The substrate was added to a 7 mM ethanolic solution of 1-azidoundecan-11-thiol (synthesized following a modified procedure outlined in the Supplementary Information) for 24 h, then was washed with ethanol, dichloromethane (Certified ACS, Fisher Scientific), and water, and dried in a stream of nitrogen

2.2. Patterned monolayer formation by click-chemistry

A solution containing 5 µL 3,4,5-trifluorophenylacetylene (Aldrich^{CPR}, Sigma-Aldrich), 4.3 mg Irigacure 819 (BASF), and 5.3 mg copper sulfate pentahydrate (>99%, Sigma-Aldrich) in 1 mL methanol (Certified ACS, Fisher Scientific) was thoroughly mixed and was prepared no more than 6 h prior to monolayer formation and stored in darkness. Immediately following substrate preparation, washing, and drying, the alkyne solution was drop cast onto the substrate. The substrate was covered with a coverslip and photomask. The sample was placed between glass slides and irradiated for 5 min at 365 nm using an Omnicure S2000 lamp with an intensity of 30 mW/cm². The irradiation time was optimized based on saturation of the signal detected by X-ray photoelectron spectroscopy. Following irradiation, the samples were immediately washed twice in ethanol, once in dichloromethane, and twice more in ethanol, followed by drying in a stream of nitrogen gas.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) was performed on the samples to observe patterning and monitor the surface chemistry following irradiation. A Thermo Scientific K-Alpha+ instrument equipped with an Al Kα source ($h\nu = 1486.6$ eV) at a take-off angle normal to the surface was used. The measurements were performed at a base pressure of 5×10^{-9} mBar. Mapping mode was performed with an X-ray spot size of 100 µm and spot step size of 200 µm. Snapshot spectra were obtained for the binding energy regions of interest and images were processed with Advantage software (version 5.952) and interpolated to 512 points. Survey spectra were collected over a binding energy range of 0–1000 eV, with a pass energy of 100 eV, step size of 1 eV, and dwell time of 10 ms. High resolution spectra were collected with a pass energy of 60 eV, step size of 0.1 eV, and dwell time of 50 ms. The

number of high resolution scans collected per binding energy region varied between 5 and 30. The Au $4f_{7/2}$ peak at 83.8 eV was used to calibrate all spectra. Casa XPS software was used for data processing and peak fitting.

Density functional theory (DFT) calculations were performed using the Gaussian 09 Suite [36] of programs with B3LYP functional and 6-311+G(d,p) basis set. Geometry optimization and prediction of the core level binding energies for N $1s$ and C $1s$ were performed. The computationally-predicted binding energies were calibrated with a correction factor of 10.03 eV for N $1s$ and 11.97 for C $1s$ for the 6-311G+(d,p) basis set, based on the previously published procedure [37,38].

3. Results and discussion

A fluorine-tagged alkyne ($C_8H_3F_3$, trifluorophenylacetylene) was chosen as a reactant to be attached to the azide-terminated self-assembled monolayer on gold due to the strong XPS signal observed for this compound in the F $1s$ region that can be used to follow the reaction quantitatively. A solution containing the alkyne molecule, a copper (II) species, and commercially-available photoinitiator (Irgacure 819, which absorbs most strongly below 440 nm) was drop cast onto the azide-modified substrate, as illustrated in Scheme 1. Upon irradiation, the photoinitiator reduces the copper species which catalyzes the reaction to form the product in Scheme 1. A more general view of this approach, summarized in Scheme 2, illustrates how this photoreduction can be applied to result in a patterned substrate. At short timescales, only the irradiated areas should react with the fluorine-tagged alkyne to form the triazole product. The masked regions inhibit photo-reduction of copper, and by extension, attachment of the alkyne. Of course, the resolution of the patterned features is limited by diffusion of the copper species.

Following irradiation and washing of the samples to remove physisorbed species, XPS imaging was performed on the resulting surface. Fig. 1 displays these maps for specific binding energy regions of interest, with the images (a), (b), (c), and (d) representing the N $1s$, F $1s$, Au $4f_{7/2}$, and C $1s$ regions, respectively. In all instances, the patterning can be clearly observed. For the N $1s$ and Au $4f_{7/2}$ regions, the irradiated areas appear darker than the masked areas. This indicates that less nitrogen and gold are detected in these areas, which is expected in the event of triazole formation as the nitrogen-modified gold substrate is partially obstructed by the fluorinated phenyl ring, compared to the masked areas in which the ring should not be present. The opposite shading is observed in the F $1s$ and C $1s$ regions, where the irradiated areas appear brighter than the masked regions. This indicates successful adsorption of the trifluorophenylacetylene, which should be marked by increased fluorine and carbon signals. The XPS maps are fully consistent with the presence of trifluorophenylacetylene located in the areas that were irradiated; however, a closer look at the spectra is required to determine the chemical species involved.

In order to understand the nature of the binding of the trifluorophenylacetylene to the azide-modified substrate, high resolution XPS spectra in the important binding energy regions of this system were collected. They are presented in Fig. 2. The top high-resolution spectrum in Fig. 2(a) was collected from the center of one of the irradiated areas in the maps in Fig. 1.

The bottom spectrum (Fig. 2(b)) was collected in a masked region on the sample shown in Fig. 1. The leftmost panel in Fig. 2 shows the large difference in the F 1s signal detected between irradiated and masked areas. In Fig. 2(a), the large peak is consistent with the high signal observed in the patterned spots in Fig. 1(b). The masked region reveals only a very small, albeit detectable amount of fluorine in 2(b), which may be explained by inefficient attachment by triazole ring formation as the cycloaddition reaction will take place regardless of the presence or absence of a copper (I) catalyst; however the former is much more efficient [4,5].

Similarly, the third panel from the left, which illustrates the high-resolution C 1s region, shows an increased carbon signal on the irradiated region. Additionally, a peak at 287.5 eV is clearly observed on the spectrum collected on the irradiated area. This is consistent with the presence of C-F [39] and the binding energy shift from the C-C peak at 286.4 eV is consistent with that determined from density functional theory calculations (see Supplementary Information). The Au 4f peaks, shown in the rightmost panel of Fig. 2 show a higher signal on the masked surface than the irradiated surface which is to be expected and is fully consistent with the map in Fig. 1(c). Again, this is expected as the covalent attachment of the fluorinated alkyne molecule will attenuate the detected signal originating from gold.

The N 1s signal can be observed in the second panel from the left. The bottom spectrum (b) shows the nitrogen signal of the masked area and two peaks can be observed: a larger feature at approximately 400.5 eV and a smaller one near 404.5 eV. These peaks are consistent with the nitrogen atoms in the surface azide groups [9,10,40–42]. DFT computational methods were used to optimize the structures of the precursors and triazole product and predict the theoretical binding energies of the nitrogen atoms. The predicted energies of 400.9 eV, 401.5 eV, and 404.3 eV can be assigned to the nitrogen atoms of the azide group: ***N=N=N-***, ***N=N=N-***, and ***N=N=N-***, respectively (bolded and italicized for clarity). The colored bars underneath spectrum (b) indicate these theoretically predicted energies for the correspondingly-colored atoms in the model. The experimental binding energies are in good agreement with the predicted energies and indicate that the azide groups on the surface remain intact even after interaction with the alkyne solution and the washing steps. Spectrum (a) in the N 1s binding energy region shows only one broad feature in the irradiated area that is consistent with the formation of the triazole ring [9,10,40]. This feature can be deconvoluted into the three features corresponding to the nitrogen atoms in the triazole ring based on the computationally-predicted binding energies. The colored bars under the spectrum, located at 400.5 eV, 401.5 eV, and 402.5 eV, represent the theoretical energies of the corresponding nitrogen atoms in the model. The agreement between the theoretical and experimental results, as well as the stark difference between the features observed on the masked and irradiated areas of the surface provide evidence that the trifluorophenylacetylene is bound to the surface by the triazole ring.

The XPS features in the N 1s and F 1s were integrated and compared in order to approximate the monolayer coverage of fluorine in both the masked and irradiated regions. It was assumed that the nitrogen signal detected originates from a full monolayer of azide-terminated adsorbates on the substrate. If the distance between adjacent alkyl linkers on a

Au (1 1 1) surface is about 5 Å [43], this corresponds to approximately 1.26×10^6 azide functional groups per μm^2 of substrate. Taking into account the atomic sensitivity factors of 1.00 for F 1s and 0.38 for N 1s [44], the ratio of the F:N regions in the masked sample (Fig. 2(b)) is 0.365 which corresponds to about one fluorine atom to three nitrogen atoms. This ratio on the irradiated region (Fig. 2(a)) increases to an apparent ratio of 2.08, or two fluorine atoms per nitrogen atom which is in excess of a full monolayer (expected 1:1 ratio). To confirm the reliability of these results, N 1s and F 1s spectra averages were collected in multiple irradiated and masked spots on the XPS maps (Fig. 1(a) and (b)). The average F:N values of 0.32 ± 0.02 (masked) and 1.46 ± 0.29 (irradiated) are consistent with about a third of a monolayer of the fluorinated molecule in masked regions and approximately 1.5 monolayers equivalent in irradiated spots. It is possible, though unlikely, that the large ratio is due to screening of the azide by the fluorinated molecule. It is reasonable to attribute the excess fluorine to degradation or removal of the nitrogen-containing species. Regardless, the relative amounts of fluorine and nitrogen detected by XPS show that a greater degree of attachment is facilitated by irradiation and that attachment affects the entire monolayer but does not form polymers or thick multilayers. Furthermore, a comparison of the areas of the two major species in the C 1s region in Fig. 2(a) (irradiated region), corresponding to fluorinated carbon and non-fluorinated carbon provides a ratio of about 0.3 for C-F to other carbon species. This is slightly in excess of the 3:16 (0.19) ratio expected for attachment of the fluorinated alkyne molecule, but in agreement with the conclusions drawn from the F:N ratio, indicating that the modification by click chemistry introduces on the order of a single monolayer equivalent (or slightly more) of fluorine labels calibrated by the resulting triazole ring formation.

If this reaction does indeed depend on the photo-reduction of the copper (II) species to efficiently drive the reaction, rather than a direct photo-initiation of the cycloaddition process itself, it is important that all components (irradiation of alkyne and azide functional groups, copper (II), and photoinitiator) are necessary for the patterning reaction to occur. A control study was performed to determine if patterning occurs in the absence of any of these components. To determine whether irradiation is necessary for efficient patterning of the surface, the solution containing the fluorinated alkyne molecule, copper sulfate pentahydrate, and photoinitiator was drop cast onto the azide-modified substrate. The sample was placed between the glass slides and allowed to react for 5 min in the dark before being washed. The XPS map, seen in Fig. 3(a), shows no evidence of patterning on the surface, indicating that irradiation is required for the reaction to occur in this timeframe. To determine whether the photoinitiator is required, a solution containing the alkyne molecule and copper sulfate pentahydrate was drop cast onto the modified substrate and irradiated through the photomask for 5 min before being washed. Fig. 3(b) shows the resulting map of the surface. No patterning is observed which suggests that the irradiation itself is not sufficient to reduce the copper to catalyze the reaction and that the uncatalyzed thermal cycloaddition is inefficient within the given timeframe.

Finally, a solution containing the alkyne molecule and photoinitiator, but no copper (II), was drop cast onto the substrate and irradiated for 5 min through the mask before being washed. Fig. 3(c) shows the resulting surface and here, a faint pattern is detected, suggesting that the irradiation of the photoinitiator may promote the cycloaddition. The efficiency of this

reaction is very low compared to the sample in which all necessary components are present (Fig. 3(d)). High-resolution XPS spectra were collected in the F 1s region of the irradiated (unmasked) regions of Fig. 3(c) and (d) and can be observed in Fig. 3(e) and (f), respectively. From the relative intensities of the F 1s signal on the irradiated regions in Fig. 3(e) and (f), it was determined that irradiation in the presence of Cu (II) results in more than six times the signal resulting from irradiation without copper. This result confirms that irradiation of the photoinitiator to reduce the copper (II) to catalyze the cycloaddition is required to achieve a significant degree of surface patterning by this “click” reaction.

As a consequence of the “click” reaction being driven by photoreduction of the copper species rather than direct photo-initiation of the cycloaddition, the resolution of the patterned features is necessarily limited by copper diffusion across the surface. This has been shown to occur during patterning processes in polymeric systems which are based on indirect copper photoreduction [21,28] and can be directly observed by the differences in the diameters of the patterned spots observed in the images despite the fact that the windows of the photomask were uniform in size. Although problematic for very high-resolution patterning, the diffusion of the copper species offers potential for functionalization over three-dimensional features. As a non-line-of-site deposition technique, this method would allow for conformal filling of high aspect ratio features with a uniform coating of the targeted functional group that may otherwise be difficult to achieve with a fast wet chemistry approach. Furthermore, the potential wavelength tunability of this process by using different photoinitiator systems makes it amenable to different substrate and adsorbate combinations that might be otherwise compromised by photo-degradation.

4. Conclusions

A solution-based photochemical method for spatially-controlled surface modification of organic monolayers on solid substrates is presented. Covalent surface attachment of an alkyne-functionalized probe molecule to the azide-functionalized organic monolayer on gold is achieved by photo-induced reduction of copper (II) to initiate the azide-alkyne dipolar cycloaddition. The process occurs over the timescale of a few minutes and efficient, reproducible patterning is achieved. Spectroscopic analysis of the surface chemistry is in agreement with the expected triazole ring formation as predicted computationally. Control studies confirm that efficient binding and patterning occur only upon irradiation of the photoinitiator, copper (II), and necessary functional groups and provide further support that the reaction relies upon indirect photo-reduction of the copper species by a free radical photoinitiator. This method lends itself to further customization of irradiation parameters, based on the photoinitiator utilized, for patterning with substrate and adsorbate systems of varying stabilities or tendencies to undergo competing reactions. Diffusion of the reduced copper center limits the achievable resolution but also suggests potential for this modification method as a viable alternative to more time-consuming, vacuum-based non-line-of-site deposition techniques to result in conformal coating for diverse applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also partially supported by the National Science Foundation (CHE1057374 and DMR1609973 (GOALI)) and the NASA Delaware Space Grant College and Fellowship Program (NASA Grant NNX15AI19H). The authors acknowledge the NIGMS 1 P30 GM110758 grant for the support of core instrumentation infrastructure at the University of Delaware. The authors would also like to thank Professor T. P. Beebe, Jr. and Dr. R. Pupillo (Surface Analysis Facility, University of Delaware) for XPS training and support. The authors are deeply appreciative of the help and support in the synthesis of 1-azidoundecan-11-thiol by Professor J. Koh and Mr. B. Rupert. Finally, the authors would like to extend acknowledgement and sincere thanks to Professor C. Kloxin, Mr. A. Shete, and Dr. S. Ma for their assistance in setting up and performing irradiation experiments and for the helpful discussions and advice.

References

1. Gao F, Teplyakov AV. Challenges and opportunities in chemical functionalization of semiconductor surfaces. *Appl Surf Sci.* 2016; 399:375–386.
2. Williams, MG., Teplyakov, AV. Chemical functionalization of surfaces: preparation for secondary chemical modification. *Encycl Interfacial Chem Surf Sci Electrochem.* 2017. <https://doi.org/10.1016/B978-0-12-409547-2.13559-0>
3. Nicosia C, Huskens J. Reactive self-assembled monolayers: from surface functionalization to gradient formation. *Mater Horiz.* 2014; 1:32–45.
4. Tornøe CW, Christensen C, Meldal M. Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J Org Chem.* 2002; 67:3057–3064. [PubMed: 11975567]
5. Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. A stepwise Huisgen cycloaddition process: copper (I)-catalyzed regioselective “Ligation” of azides and terminal alkynes. *Angew Chemie – Int Ed.* 2002; 41:2596–2599.
6. Chassaing S, Bénétiau V, Pale P. When CuAAC “Click Chemistry” goes heterogeneous. *Catal Sci Technol.* 2016; 6:923–957.
7. Zheng S, Yang Q, Mi B. Novel antifouling surface with improved hemocompatibility by immobilization of polyzwitterions onto silicon via click chemistry. *Appl Surf Sci.* 2016; 363:619–626.
8. Devaraj NK, Collman JP. Copper catalyzed azide-alkyne cycloadditions on solid surfaces: applications and future directions. *QSAR Comb Sci.* 2007; 26:1253–1260.
9. Williams MG, Teplyakov AV. Building high-coverage monolayers of covalently bound magnetic nanoparticles. *Appl Surf Sci.* 2016; 388:461–467. [PubMed: 27789916]
10. Liu Y, Williams MG, Miller TJ, Teplyakov AV. Nanoparticle Layer Deposition (NPLD) for highly controlled multilayer formation based on high-coverage monolayers of nanoparticles. *Thin Solid Films.* 2016; 598:16–24. [PubMed: 26726273]
11. Upadhyay AP, Behara DK, Sharma GP, Bajpai A, Sharac N, Ragan R, et al. Generic process for highly stable metallic nanoparticle-semiconductor heterostructures via click chemistry for electro/photocatalytic applications. *ACS Appl Mater Interf.* 2013; 5:9554–9562.
12. Etschel SH, Portilla L, Kirschner J, Drost M, Tu F, Marbach H, et al. Region-selective deposition of core-shell nanoparticles for 3D hierarchical assemblies by the Huisgen 1,3-dipolar cycloaddition. *Angew Chemie – Int Ed.* 2015; 54:9235–9238.
13. Xia YN, Whitesides GM. Soft lithography. *Annu Rev Mater Sci.* 1998; 37:551–575.
14. Smith RK, Lewis PA, Weiss PS. Patterning self-assembled monolayers. *Prog Surf Sci.* 2004; 75:1–68.
15. Walker AV. Toward a new world of molecular devices: making metallic contacts to molecules. *J Vac Sci Technol A Vac, Surf, Film.* 2013; 31:50816.
16. Craighead HG, James CD, Turner AMP. Chemical and topographical patterning for directed cell attachment. *Curr Opin Solid State Mater Sci.* 2001; 5:177–184.
17. Montoya J, Levit L, Englisch A. A study of the mechanisms for ESD damage to reticles. *IEEE Trans Electron Packag Manuf.* 2001; 24:78–85.

18. Zhang K, Deng X, Fu Q, Meng Y, Zhao H, Wang W, et al. Photolithography-compatible templated patterning of functional organic materials in emulsion. *Adv Sci*. 2016; 3:1500304.
19. Wang J, Wu F, Watkinson M, Zhu J, Krause S. "Click" patterning of self-assembled monolayers on hydrogen-terminated silicon surfaces and their characterization using light-addressable potentiometric sensors. *Langmuir*. 2015; 31:9646–9654. [PubMed: 26274063]
20. Schmaltz T, Sforazzini G, Reichert T, Frauenrath H. Self-assembled monolayers as patterning tool for organic electronic devices. *Adv Mater*. 2017; 29:1605286.
21. Adzima BJ, Tao Y, Kloxin CJ, DeForest CA, Anseth KS, Bowman CN. Spatial and temporal control of the alkyne-azide cycloaddition by photoinitiated Cu (II) reduction. *Nat Chem*. 2011; 3:256–259. [PubMed: 21336334]
22. Tasdelen MA, Kiskan B, Yagci Y. Externally stimulated click reactions for macromolecular syntheses. *Prog Polym Sci*. 2016; 52:19–78.
23. Tasdelen MA, Yilmaz G, Iskin B, Yagci Y. Photoinduced free radical promoted copper(I)-catalyzed click chemistry for macromolecular syntheses. *Macromolecules*. 2012; 45:56–61.
24. Ritter SC, König B. Signal amplification and transduction by photo-activated catalysis. *Chem Commun*. 2006:4694–4696.
25. Tasdelen MA, Yagci Y. Light-induced copper(I)-catalyzed click chemistry. *Tetrahedron Lett*. 2010; 51:6945–6947.
26. Wang B, Durantini J, Nie J, Lanterna AE, Scaiano JC. Heterogeneous photocatalytic click chemistry. *J Am Chem Soc*. 2016; 138:13127–13130. [PubMed: 27673341]
27. Sakamoto M, Tachikawa T, Fujitsuka M, Majima T. Three-dimensional writing of copper nanoparticles in a polymer matrix with two-color laser beams. *Chem Mater*. 2008; 20:2060–2062.
28. Shete AU, El-Zaatari BM, French JM, Kloxin CJ. Blue-light activated rapid polymerization for defect-free bulk Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) crosslinked networks. *Chem Commun*. 2016; 52:10574–10577.
29. Huang J, Dahlgren DA, Hemminger JC. Photopatterning of self-assembled alkanethiolate monolayers on gold: a simple monolayer photoresist utilizing aqueous chemistry. *Langmuir*. 1994; 10:626–628.
30. Kumar A, Biebuyck HA, Whitesides GM. Patterning self-assembled monolayers: applications in materials science. *Langmuir*. 1994; 10:1498–1511.
31. Mrksich M, Whitesides GM. Using self-assembled monolayers to understand the interactions of man-made surfaces with proteins and cells. *Annu Rev Biophys Biomol Struct*. 1996; 25:55–78. [PubMed: 8800464]
32. Michel R, Lussi JW, Csucs G, Reviakine I, Danuser G, Ketterer B, et al. Selective molecular assembly patterning: a new approach to micro- and nanochemical patterning of surfaces for biological applications. *Langmuir*. 2002; 18:3281–3287.
33. Alzahrani AA, Nair DP, Smits DJ, Saed M, Yakacki CM, Bowman CN. Photo-CuAAC induced wrinkle formation in a thiol-acrylate elastomer via sequential click reactions. *Chem Mater*. 2014; 26:5303–5309.
34. El-Zaatari BM, Shete AU, Adzima BJ, Kloxin CJ. Towards understanding the kinetic behaviour and limitations in photo-induced copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reactions. *PCCP*. 2016; 18:25504–25511. [PubMed: 27711587]
35. Chen RT, Marchesan S, Evans RA, Styan KE, Such GK, Postma A, et al. Photoinitiated alkyne-azide click and radical cross-linking reactions for the patterning of PEG hydrogels. *Biomacromolecules*. 2012; 13:889–895. [PubMed: 22332589]
36. Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., et al. Gaussian 09, Revision B.01. 2009.
37. Zhao J, Gao F, Pujari SP, Zuilhof H, Teplyakov A. Universal calibration of computationally predicted N 1s binding energies for interpretation of XPS experimental measurements. *Langmuir*. 2017; 33:10792–10799. [PubMed: 28921989]
38. Leftwich TR, Teplyakov AV. Calibration of computationally predicted N 1s binding energies by comparison with X-ray photoelectron spectroscopy measurements. *J Electron Spectros Relat Phenom*. 2009; 175:31–40.

39. Hatada R, Baba K. Preparation of hydrophobic diamond like carbon films by plasma source ion implantation. *Nucl Instrum Methods Phys Res B*. 1999; 148:655–658.
40. Liu Y, RamaRao N, Miller T, Hadjipanayis G, Teplyakov AV. Controlling physical properties of iron nanoparticles during assembly by “Click Chemistry”. *J Phys Chem C*. 2013; 117:19974–19983.
41. Devadoss A, Chidsey CED. Azide-modified graphitic surfaces for covalent attachment of alkyne-terminated molecules by “click” chemistry. *J Am Chem Soc*. 2007; 129:5370–5371. [PubMed: 17425323]
42. Gouget-Laemmel AC, Yang J, Lodhi MA, Siriwardena A, Aureau D, Boukherroub R, et al. Functionalization of azide-terminated silicon surfaces with glycans using click chemistry: XPS and FTIR study. *J Phys Chem C*. 2013; 117:368–375.
43. Vericat C, Vela ME, Salvarezza RC. Self-assembled monolayers of alkanethiols on Au(111): surface structures, defects and dynamics. *PCCP*. 2005; 7:3258–3268. [PubMed: 16240039]
44. Wagner, CD., Riggs, WM., Davis, LE., Moulder, JF., Muilenberg, GE. *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer Corporation; Eden Prairie, MN: 1979.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apsusc.2018.04.007>.

Fig. 1. XPS maps of the patterned surface in the (a) N 1s, (b) F 1s, (c) Au 4 $f_{7/2}$, and (d) C 1s binding energy regions.

Fig. 2. High-resolution XPS spectra collected (a) on an irradiated portion of the sample, and (b) on a masked portion of the sample. The colored lines underneath the spectra in the N 1s region indicate the theoretical binding energies of the correspondingly-colored nitrogen atoms in the models, as determined by density functional theory calculations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3.

XPS maps in the F 1s binding energy region of (a) a non-irradiated sample containing the alkyne, Cu(II), and photoinitiator, (b) a sample containing the alkyne and Cu(II), but no photoinitiator, irradiated through the photomask, (c) a sample containing the alkyne and photoinitiator, but no Cu(II), irradiated through the photomask, and (d) a sample containing all necessary components (alkyne, Cu(II), and photoinitiator), irradiated through the photomask. The spectra in (e) and (f) show the average F 1s XPS spectra in the boxed areas in maps (c) and (d), respectively.

Scheme 1.

Formation of the triazole ring between the azide-terminated self-assembled monolayer and trifluorophenylacetylene resulting from photoinitiated reduction of Cu(II).

Scheme 2.

Overview of the patterning procedure involving irradiation through a photomask to result in spatially-controlled attachment of a molecule to the modified substrate.