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## Gold oxide as a protecting group for regioselective surface chemistry†

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**Selective modification of electrode surfaces is a vital step in the development of many practical applications of self-assembled monolayers (SAMs). This paper describes a protection–deprotection strategy similar to that commonly utilized in organic synthesis, with gold oxide as a protecting layer, to direct self-assembly on one gold electrode in the presence of another.**

Spontaneous formation of self-assembled monolayers (SAMs) of organosulfur compounds is a convenient route to the uniform modification of gold surfaces.<sup>1</sup> Some applications (*e.g.* sensors, photovoltaics, microelectronics, and diagnostic chips), however, require selective modification only on specific regions of a substrate.<sup>2</sup> To meet this need, methods have been developed to print patterns of SAMs on uniform substrates,<sup>1–3</sup> as well as to modify particular features selectively on pre-patterned substrates (*e.g.*, electrode arrays).<sup>1,4–10</sup> This paper describes a facile electrochemical method using gold oxide as a protecting layer to allow the directed self-assembly of monolayers from dialkyl disulfides on selected gold electrodes. This approach integrates the well-established “protection–deprotection” strategy used successfully by synthetic organic chemists for decades into an electrochemical method with potentially broad applicability for the regiochemical control of surface structure. This approach complements our previous work on the site-selective formation of SAMs from alkyl thiosulfates and may provide a route to  $\omega$ -functionality (*e.g.* hydroxyl, vinyl) not amenable to that method.<sup>11–14</sup>

Previously, Rubinstein and coworkers demonstrated that although dialkyl disulfides spontaneously adsorb on gold to form SAMs, they do not adsorb on oxidized gold.<sup>15–17</sup> This behavior contrasts with that of alkanethiols, which form SAMs on gold oxide, presumably by initial reduction to produce elemental gold followed by adsorption.<sup>17–21</sup> The inherent difference in the reactivity of disulfides with gold and gold oxide, coupled with the ease of formation and removal of oxide coatings on gold, offers opportunities analogous to protection–deprotection sequences common in synthetic organic chemistry, for example in the use of silyl groups to temporarily block reactivity at a protected hydroxyl group.<sup>22</sup>

This system also served as an appropriate target because it would extend the types of precursors that can be used for the regioselective formation of SAMs and because dialkyl disulfides exchange much more slowly than alkanethiols with pre-formed monolayers.<sup>23</sup>

To test this approach, we used glass substrates bearing two independently addressable gold electrodes. As shown schematically in Fig. 1, both electrodes initially represented viable sites for chemisorption of disulfide. Oxidation of one of these electrodes produced an oxide coating that rendered it inert to chemisorption. A monolayer could then be adsorbed on the other electrode selectively. After this adsorption step, the first electrode could be deprotected, regenerating a bare gold substrate, onto which a second, distinguishable monolayer could be adsorbed. Gold oxide can be produced electrochemically, by application of an anodic potential in sulfuric acid, and the nature of the oxide can be controlled by the particular potential used.<sup>24–26</sup>

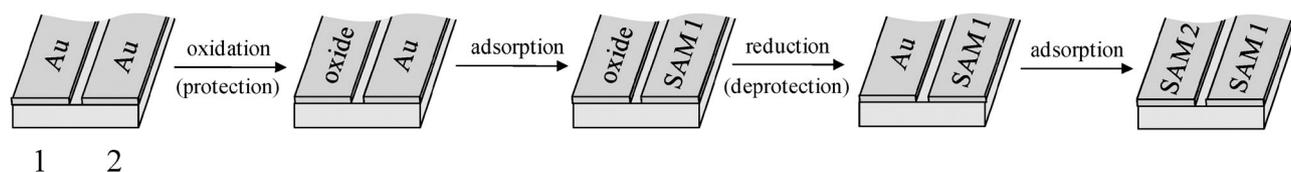
Although this oxide is thermodynamically unstable, films formed in this way are (kinetically) inert over the timescale of the experiments described in this paper.<sup>18,27,28</sup> In our studies, gold oxide was produced electrochemically in 0.5 M sulfuric acid using a standard three-electrode cell comprising a gold working electrode, a platinum wire as the counter-electrode, and an aqueous Ag/AgNO<sub>3</sub> (10 mM) reference electrode. To oxidize electrode **1** (Fig. 1), its potential was held at –0.2 V for 10 s, followed by 1.2 V for 10 s. The sample was then rinsed with deionized water (18.1 M $\Omega$ -cm) and dried under a stream of N<sub>2</sub>.

Analysis by X-ray photoelectron spectroscopy (XPS) confirmed the addition of an oxide coating. A survey scan revealed the presence of gold, oxygen and a small amount of carbon (contamination). A high resolution spectrum in the Au 4f region contained both narrow peaks (fwhm, 0.7 eV) due to elemental gold (84.0 eV, 4f<sub>7/2</sub>; 87.7 eV, 4f<sub>5/2</sub>) and broad peaks (fwhm, 1.3 eV) consistent with a mixed oxide (~85.7 eV, 4f<sub>7/2</sub>; 89.4 eV, 4f<sub>5/2</sub>).<sup>25,26,29–32</sup> A high resolution spectrum in the oxygen 1s region contained a broad peak that could be fit with four components at 529.3, 530.1, 531.1, and 532.5 eV. These binding energies are similar to those reported for gold oxide grown by pulsed-laser deposition and are consistent with a mixed oxide containing both oxo and hydroxyl species.<sup>28–30,33,34</sup> The ratio of Au<sup>3+</sup> to oxygen on this sample was 38 : 62, very close to that expected for Au<sub>2</sub>O<sub>3</sub> (40 : 60).

To assist formation of a SAM on the unmodified electrode (**2**, Fig. 1), its potential was stepped from 0.3 V to –0.9 V,

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**Fig. 1** Schematic representation of a protection–deprotection approach to the selective, sequential modification of neighboring gold electrodes. In the first step, electrode **1** is oxidized electrochemically, which allows electrode **2** to be modified selectively. The oxide on electrode **1** is then reduced to regenerate the bare gold surface, and a second SAM is adsorbed on it. For clarity, the thicknesses of the gold electrodes and glass substrates are not drawn to scale.

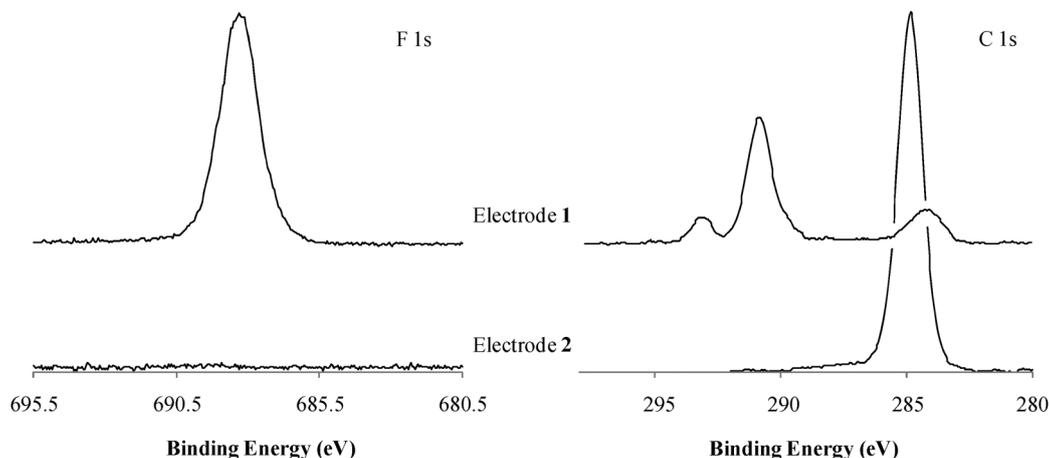
with 5 s at each potential, in the presence of dihexadecyl disulfide. The applied potential served to accelerate the adsorption of dialkyl disulfides on bare gold,<sup>17</sup> and thereby reduce the time required to accomplish the synthetic sequence. Forty of these voltammetric pulses were applied to electrode **2** in a solution containing dihexadecyl disulfide (1 mM) and LiClO<sub>4</sub> (0.1 M) in tetrahydrofuran (THF). In optimization studies, we found that this combination of limiting potentials and number of pulses gave the highest quality monolayers. The sample was then removed from solution, rinsed with THF, and water, and dried under a stream of N<sub>2</sub>. The contact angles of hexadecane (48°) and of water (112°), as well as the ellipsometric thickness (16 Å), were consistent with formation of an ordered monolayer film on the surface.<sup>13,35,36</sup> The contact angles of hexadecane (wetting) and water (55°) on the oxidized electrode **1** indicated that a SAM had not adsorbed on this surface. Ellipsometry also indicated the continued presence of the oxide coating.<sup>34</sup>

High-resolution XPS spectra in the Au 4f region verified that electrode **2** remained in a reduced state after this step (Fig. S1, ESI†). A slight reduction of the oxide film on electrically isolated electrode **1** occurred, perhaps by secondary electrons resulting from the X-ray irradiation used to analyze the sample.<sup>37</sup> To determine the selectivity of SAM formation, high-resolution spectra were also collected in the sulfur 2p region (Fig. S2, ESI†), and these data revealed the presence of thiolate only on electrode **2** (162.1 eV, S 2p<sub>3/2</sub>; 163.3 eV, S 2p<sub>1/2</sub>), consistent with SAM formation only on that electrode.<sup>38</sup> Weak photoemission intensity centered at ~167.5 eV for electrode **1** is consistent with a small amount of sulfate at the surface of

the electrode, presumably from the solution in which that electrode was oxidized.<sup>39</sup> Subsequent treatment of electrode **1** in ethanol (Fig. S1 and S2†) reduced the oxide on that electrode (84.0 eV, Au 4f<sub>7/2</sub>; 87.6, Au 4f<sub>5/2</sub>), while the SAM on electrode **2** remained intact (84.0 eV, Au 4f<sub>7/2</sub>; 87.6, Au 4f<sub>5/2</sub>; 162.0 eV, S 2p<sub>3/2</sub>; 163.3 eV, S 2p<sub>1/2</sub>).

A SAM was then adsorbed on electrode **1** by stepping its potential from 0.3 V to –0.9 V, with 5 s at each potential, in the presence of [CF<sub>3</sub>(CF<sub>2</sub>)<sub>9</sub>(CH<sub>2</sub>)<sub>2</sub>S]<sub>2</sub>. The contact angles of hexadecane (80°) and water (121°), as well as the ellipsometric thickness (9 Å), indicated the presence of a fluorinated SAM on that electrode.<sup>13,40</sup> The contact angles and ellipsometric thickness of the dihexadecyl disulfide SAM on electrode **2** remained the same as before the adsorption of a SAM on electrode **1**.

High resolution XPS spectra in the S 2p region verified the presence of a SAM on both electrodes (electrode **1**, 161.9 eV, S 2p<sub>3/2</sub>; 163.1 eV, S 2p<sub>1/2</sub>; electrode **2** 162.0 eV, S 2p<sub>3/2</sub>; 163.2 eV, S 2p<sub>1/2</sub>). Furthermore, a high resolution spectrum in the F 1s region showed the presence of fluorinated SAM only on electrode **1** (688.3 eV, fwhm 1.6 eV), verifying that no cross-contamination of electrode **2** occurred during monolayer formation (Fig. 2, left).<sup>13</sup> As expected, a high resolution spectrum of electrode **1** in the C 1s region showed three major peaks corresponding to the CF<sub>3</sub>, CF<sub>2</sub> and CH<sub>2</sub> carbons (293.3 eV, fwhm 1.0 eV; 290.9 eV, fwhm 1.1 eV; and 284.3 eV, fwhm 1.5 eV, respectively; Fig. 2, right).<sup>13</sup> A high resolution spectrum of electrode **2** in the C 1s region showed only one peak corresponding to the carbon in the dihexadecyl disulfide (284.8 eV, fwhm 1.1 eV; Fig. 2, right). These results unambiguously



**Fig. 2** High resolution X-ray photoelectron spectrum of electrodes **1** and **2** in the F 1s and C 1s regions after the selective adsorption of a hydrocarbon-bearing SAM on electrode **2** and a fluorinated SAM on electrode **1**.

demonstrate that this protection–reaction–deprotection sequence allows the regioselective modification of independently addressable electrodes on a single substrate.

In summary, we have developed a method that successfully uses gold oxide as a reversible protecting layer for the directed self-assembly of monolayers from dihexadecyl disulfide on gold. This approach is similar to the protection–deprotection scheme used for analogous reasons in synthetic organic chemistry. The analogy is not strict, of course, because the electrodes are independently addressable, and therefore can be selectively protected or deprotected without relying on inherent differences in chemical kinetics. Although there are alternative strategies for reaching a similar target—*e.g.*, reductive desorption,<sup>4</sup> cathodic blocking,<sup>8</sup> or directed electrochemisorption<sup>11–14</sup>—the approach described here may have important advantages in certain applications. For example, this method does not involve thiols or thiolates that could exchange with components of previously adsorbed SAMs, nor does it not produce reactive by-products (such as SO<sub>3</sub>) that could complicate incorporation of nucleophilic functionality into the SAM. This procedure holds promise for microelectronic applications, including sensors, biosensors, and photovoltaics, and ongoing work focuses on its applicability to microelectrodes and its use with ω-functionalized disulfide precursors.

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## Notes and references

- J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103–1169.
- A. Kumar, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1994, **10**, 1498–1511.
- R. K. Smith, P. A. Lewis and P. S. Weiss, *Prog. Surf. Sci.*, 2004, **75**, 1–68.
- C. A. Widrig, C. Chung and M. D. Porter, *J. Electroanal. Chem.*, 1991, **310**, 335–359.
- S.-I. Imabayashi, D. Hobara, T. Kakiuchi and W. Knoll, *Langmuir*, 1997, **13**, 4502–4504.
- P. Diao, M. Guo, Q. C. Hou, M. Xiang and Q. Zhang, *J. Phys. Chem. B*, 2006, **110**, 20386–20391.
- P. Diao, Q. C. Hou, M. Guo, M. Xiang and Q. Zhang, *J. Electroanal. Chem.*, 2006, **597**, 103–110.
- M. Riepl, V. M. Mirsky and O. S. Wolfbeis, *Microchim. Acta*, 1999, **131**, 29–34.
- T. J. Mullen, A. A. Dameron and P. S. Weiss, *J. Phys. Chem. B*, 2006, **110**, 14410–14417.
- L. Niu and W. Knoll, *Anal. Chem.*, 2007, **79**, 2695–2702.
- C.-C. Hsueh, M. T. Lee, M. S. Freund and G. S. Ferguson, *Angew. Chem., Int. Ed.*, 2000, **39**, 1228.
- M. T. Lee, C.-C. Hsueh, M. S. Freund and G. S. Ferguson, *Langmuir*, 2003, **19**, 5246–5253.
- J. P. Labukas, T. J. H. Drake and G. S. Ferguson, *Langmuir*, 2010, **26**, 9497–9505.
- J. P. Labukas and G. S. Ferguson, *Langmuir*, 2011, **27**, 3219–3223.
- R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, 1983, **105**, 4481–4483.
- H. Ron, S. Matlis and I. Rubinstein, *Langmuir*, 1998, **14**, 1116–1121.
- H. Ron and I. Rubinstein, *J. Am. Chem. Soc.*, 1998, **120**, 13444–13452.
- H. Ron and I. Rubinstein, *Langmuir*, 1994, **10**, 4566–4573.
- J. T. Woodward, M. L. Walker, C. W. Meuse, D. J. Vanderah, G. E. Poirier and A. L. Plant, *Langmuir*, 2000, **16**, 5347–5353.
- R. B. A. Sharpe, D. Burdinski, J. Huskens, H. J. W. Zandvliet, D. N. Reinhoudt and B. Poelsema, *J. Am. Chem. Soc.*, 2006, **128**, 15560–15561.
- Z. Zheng, M. Yang and B. Zhang, *J. Phys. Chem. C*, 2008, **112**, 6597–6604.
- P. G. M. Wuts and T. W. Greene, *Greene's Protective Groups in Organic Synthesis*, Wiley-Interscience, Hoboken, 4th edn, 2007.
- C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall and G. M. Whitesides, *J. Am. Chem. Soc.*, 1989, **111**, 321–335.
- K. Juodkazis, J. Juodkazyte, B. Sebekas and A. Lukinskas, *Electrochem. Commun.*, 1999, **1**, 315–318.
- K. Juodkazis, J. Juodkazyte, V. Jasulaitiene, A. Lukinskas and B. Sebekas, *Electrochem. Commun.*, 2000, **2**, 503–507.
- G. Tremiliosi-Filho, L. H. Dall'Antonia and G. Jerkiewicz, *J. Electroanal. Chem.*, 2005, **578**, 1–8.
- H. C. Tsai, E. Hu, K. Perng, M. K. Chen, J. C. Wu and Y. S. Chang, *Surf. Sci.*, 2003, **537**, L447–L450.
- N. Saliba, D. H. Parker and B. E. Koel, *Surf. Sci.*, 1998, **410**, 270–282.
- J. J. Pireaux, M. Liehr, P. A. Thiry, J. P. Delrue and R. Caudano, *Surf. Sci.*, 1984, **141**, 221–232.
- E. Irissou, M. C. Denis, M. Chaker and D. Guay, *Thin Solid Films*, 2005, **472**, 49–57.
- A. Krozer and M. Rodahl, *J. Vac. Sci. Technol., A*, 1997, **15**, 1704–1709.
- To fit the Au 4f<sub>7/2</sub> and 4f<sub>5/2</sub> peaks, fwhm were allowed to float, but were constrained to be equal to each other.
- The component peaks at 531.1 and 532.5 eV are also consistent with adsorbed contaminants: See ref. 29–31.
- K. M. Cook and G. S. Ferguson, *J. Phys. Chem. C*, 2011, DOI: 10.1021/jp207031s.
- H. A. Biebuyck, C. D. Bain and G. M. Whitesides, *Langmuir*, 1994, **10**, 1825–1831.
- C. D. Bain and G. M. Whitesides, *J. Am. Chem. Soc.*, 1988, **110**, 3665–3666.
- T. Dickinson, A. F. Povey and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 298.
- M. C. Bourg, A. Badia and R. B. Lennox, *J. Phys. Chem. B*, 2000, **104**, 6562–6567.
- F. J. R. Nieto, E. Fachini, C. R. Cabrera and A. J. Arvia, *Thin Solid Films*, 2009, **517**, 1534.
- H. Fukushima, S. Seki, T. Nishikawa, H. Takiguchi, K. Tamada, K. Abe, R. Colorado, M. Graupe, O. E. Shmakova and T. R. Lee, *J. Phys. Chem. B*, 2000, **104**, 7417–7423.