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Spatially Controlled Assembly of Nanomaterials at the Nanoscale

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A molecular monolayer of 4-nitrothiophenol on gold electrodes is reduced electrochemically when its nitro groups are converted into amino groups by potentiometric scans. The protonated amine with its NH_3^+ functions can be employed to induce the self-assembly of gold nanoparticles at the surface of the electrodes. The electrochemical reaction and the induced assembly process can be controlled at the nanoscale level on the electrodes with a high degree of selectivity. The technology opens up the possibility of fabricating complex multi-nanomaterial nanostructures on the basis of a two-step electrochemical assembly process.

Keywords: Lithography, Self-Assembled Monolayers, Electrochemical Modification, Self-Assembly, Nanostructures.

Significant progress has been made[1–8] during the past few years in the development of chemically specific techniques to immobilize nanoscale components—such as metalloorganic species, organic polymers, carbon nanotubes, metal nanoparticles, proteins, cells, etc.—selectively in spatially well-defined patterns. The bottom-up self-organization of self-assembled nanocomponents which occurs in solution, in combination with top-down lithographic approaches such as UV, X-ray and electron-beam lithography have been pursued[6, 9–13] vigorously as a means of realizing this daunting challenge. Chemical modification of self-assembled monolayers (SAMs), using these radiative lithographic techniques, has provided[6, 9–13] the basis for the earliest demonstrations of the integration of nanolithography with nanoassembly. There is still a pressing need,[1, 7, 8, 14] however, to develop a technique that can control self-assembly at well-defined nanoscale locations with a high degree of selectivity.

In a previous investigation,[15] we have described an approach to control protein immobilization on surfaces, based on SAMs that can switch from bio-inert to bioactive states in response to an applied electrical potential. The approach we have developed is based on an electrochemical reaction in which aromatic nitro (NO_2) groups, self-assembled on gold surfaces, can be chemically modified by a redox process to amino (NH_2) groups, which can then be used to orchestrate the immobilization of the proteins. In this communication, we describe an important advance by demonstrating that this electrochemically based approach can be used to induce the selective assembly of nanomaterials on independently addressed nanoelectrodes. Gold nanoparticles were chosen as the model nanomaterial in order to demonstrate the viability of this modular and generic patterning approach.

Our approach involves (Fig. 1) four major steps.

(1) Micro-or nanoscale gold electrodes are generated by optical or electron-beam lithography.

(2) The electrically addressable gold electrodes are then functionalized with NO_2-terminated SAMs.

(3) To achieve selective modification of individual electrodes, the NO_2 groups are reduced selectively on the electrically addressed electrodes to primary NH_2 groups by electrochemical reduction.[15–18]

(4) The resulting NH_2-terminated patterns on the selected electrodes are employed after protonation of the NH_2 groups to immobilize nanomaterials such as gold nanoparticles.

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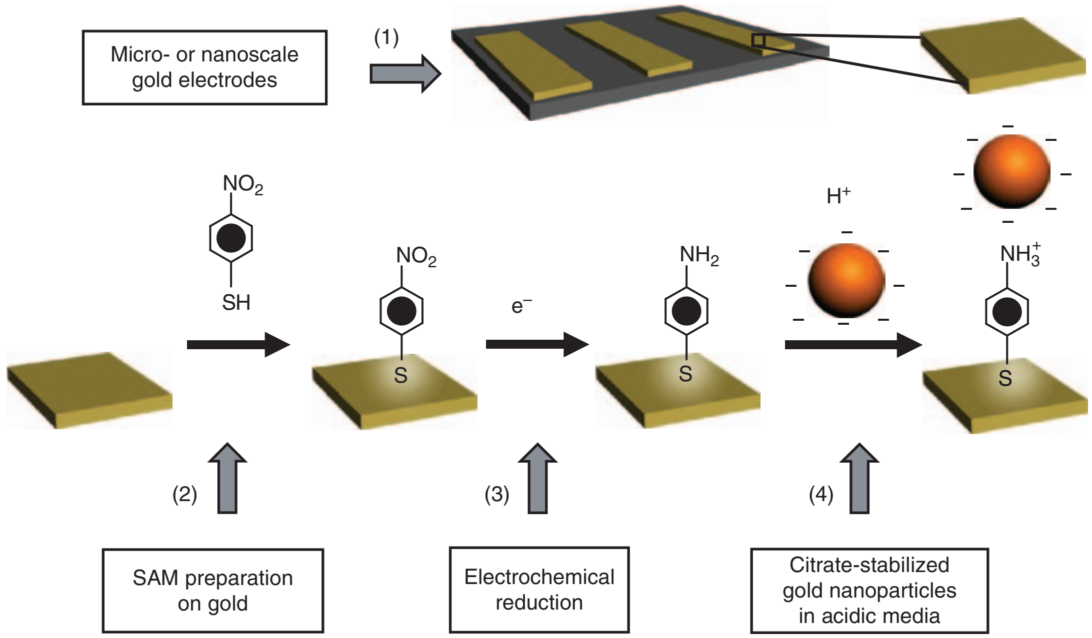

Fig. 1. Schematic illustration of (1) the micro- or nanoscale gold electrodes on glass substrates and (2) their functionalization with SAMs of 4-nitrothiophenol. (3) Upon electrochemical conversion from NO_2 groups on an Au electrode to NH_2 groups, (4) the protonated amines with its NH_3^+ functions are capable subsequently of inducing the self-assembly of Au nanoparticles.

In order to demonstrate that gold nanoparticles are immobilized selectively on NH_3^+-terminated monolayers, our initial experiments focused on converting SAMs of 4-nitrothiophenol electrochemically on large scale gold electrodes. SAMs of 4-nitrothiophenol were prepared as described in a previous paper.[15] Briefly, clean gold substrates (30 nm thick Au on a 10 nm thick Ti adhesion layer on a *n* type Si wafer) were immersed for 12 hours at room temperature in a 0.1 mM ethanolic solution of 4-nitrothiophenol to form the SAMs on the Au surfaces. Pristine 4-nitrothiophenol and converted 4-nitrothiophenol SAMs were previously[15] characterized by cyclic voltammetry and X-ray photoelectron spectroscopy. These previous studies[15] demonstrated that the NO_2-terminated groups in the SAMs of 4-nitrothiophenol on gold surfaces can be reduced electrochemically and selectively to NH_2 groups by applying a negative voltage between the gold surface and its counter electrode in the presence of an electrolyte. In an identical manner, SAMs of 4-nitrothiophenol were electrochemically modified for the immobilization of gold nanoparticles. Electrochemistry was performed with a Princeton Applied Research VMP Multi Channel Potentiostat, using a custom-designed Teflon cell, equipped with the functionalized Au substrate as the working electrode, a Pt wire as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. Electrochemical reduction was carried out by sweeping the potential between 0 and −0.9 V with a 200 mV/s scan rate using 0.1 M KCl aqueous solution as the electrolyte. Subsequently, the electrochemically modified NO_2-terminated SAM was immersed in an Au nanoparticle solution ($pH \sim 4$) for one hour. This aqueous colloidal solution of citrate-stabilized gold nanoparticles (16 nm in diameter) was prepared using a procedure developed by Frens.[19] In the acidic Au colloidal solution, the surface NH_2 groups, i.e., the reduced NO_2-terminated SAM, become protonated, forming NH_3^+ ions, which are then able to bind electrostatically[6, 20–23] to the negatively-charged, citrate-passivated Au nanoparticles, thus immobilizing them on the substrate. An atomic force microscope (AFM) image (Fig. 2(a)) shows a dense monolayer of Au nanoparticles on the electrochemically modified NO_2-terminated SAM, verifying the conversion from NO_2 groups into NH_2 ones. As a control experiment, a pristine 4-nitrothiophenol SAM was treated with the acidic Au colloidal solution as described above. The AFM image (Fig. 2(b)) reveals clearly that gold nanoparticle deposition does not take place on NO_2-terminated SAMs on gold surfaces.

After demonstrating the selective immobilization of gold nanoparticles on the converted 4-nitrothiophenol SAMs on large-scale gold electrodes, we began investigations on microscale electrodes. Optical lithography was used to fabricate the microscale electrodes (20 nm thick Au, with 5 nm thick Ti adhesion layer) on a borofloat glass wafer. A working, a counter, and an idle electrode were fabricated on the chip using a standard lift-off process. The microelectrodes were made to fan out to respective electrical contact pads, that were addressable by a Karl Suss probe station. The procedure for preparing the SAMs was the same as that described[15] previously in the literature for the large-scale electrodes. A drop of 0.1 M KCl aqueous solution was pipetted onto the three microelectrode region,

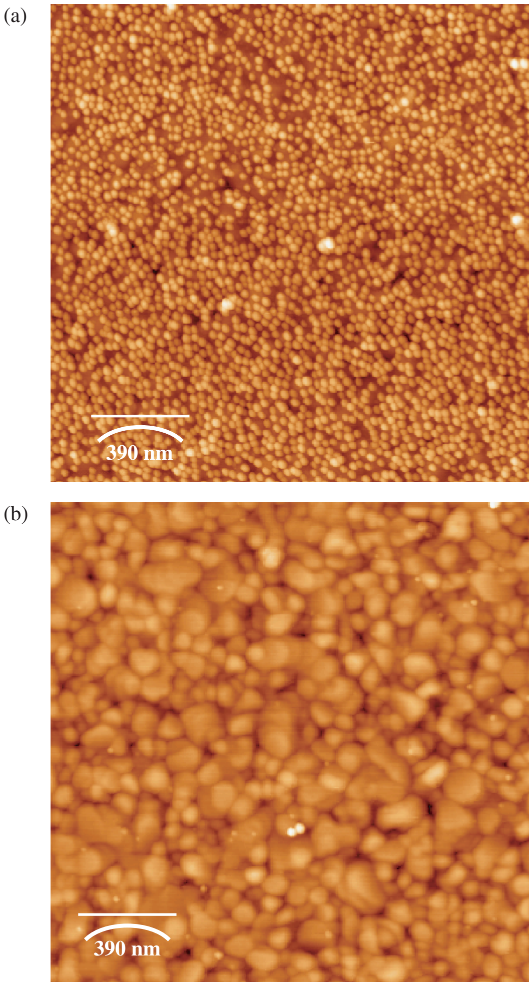

Fig. 2. (a) AFM image of a dense film of Au nanoparticles on an NH$_3^+$-terminated monolayer, which was obtained by electrochemical conversion of the NO$_2$-terminated SAM. (b) AFM image of NO$_2$-terminated control electrode, after incubation in Au nanoparticles. The grain structure of electron-beam deposited gold is clearly visible.

and a Ag/AgCl reference electrode was submerged beneath the surface of the electrolyte droplet. The Ag/AgCl electrode is used to replace the calomel electrode as the reference at the microscale. The minor shift in the reduction potential of the NO$_2$ groups as a result of changing the reference from calomel to Ag/AgCl, as long as it stays within the bounds of the scan window as in this case, is tolerated for the sake of convenience. The CV potential was swept from 0 to −0.9 V. The chip was rinsed with EtOH and Ultra High Pure (UHP) H$_2$O, and the electrodes were immersed in the citrate-stabilized Au nanoparticle solution (pH ∼ 4) for one hour. AFM images (Figs. 3(a) and (b)) of the microelectrodes revealed a dense layer of Au nanoparticles on the working electrode, while the counter and idle electrodes showed very little nanoparticle adsorption.

The final step in the progression was to extend this self-assembly protocol to make it work with nanoscale gold electrodes. Electron-beam lithography was used to fabricate nanoscale electrodes similar to those on the microscale level on a glass slide, except that the electrodes were scaled down to 200 nm wide and separated from each other by 200 nm. A JEOL 5910 SEM, with a retrofit Nano Pattern Generation System (NPGS) unit from JCNabity Lithography Systems, was used to generate nanoscale patterns on a 150 nm thick layer of PMMA (C950) from MicroChem on a glass slide. The other procedures are the same as those described for the microscale experiment, except that (i) extra care was taken to keep the electron beam in focus on account of the non-conducting nature of the glass substrate and (ii) the immersion time in the citrate-stabilized Au nanoparticle solution was limited to 15 minutes, to avoid agglomeration on the electrodes. Note that the reference electrode used was the same as the one used in the microscale experiment, i.e., Ag/AgCl

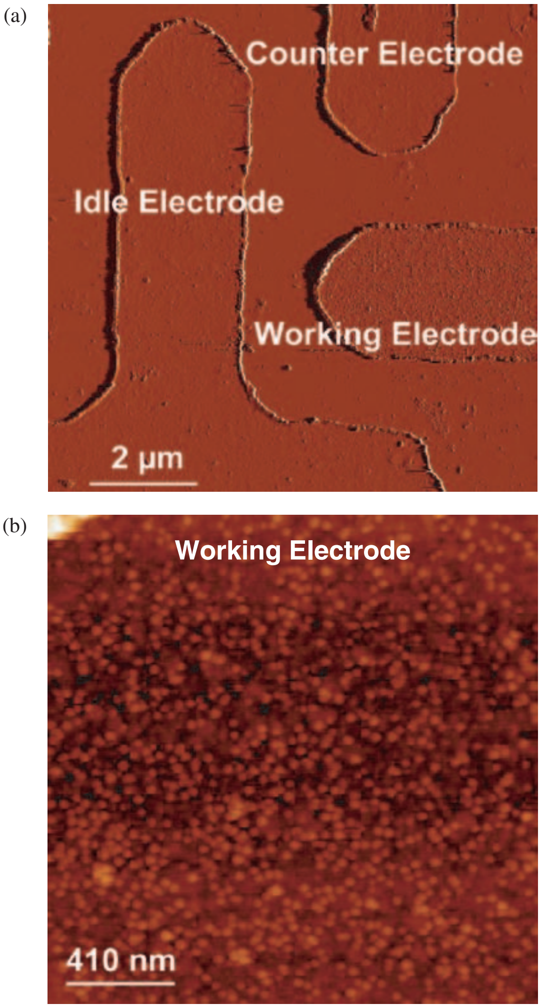

Fig. 3. Controllable self-assembly on microscale electrodes. (a) An AFM phase image showing the counter (top), idle (left) and working electrodes (right) after conversion of the NO$_2$ groups to NH$_3^+$ functions and the self-assembly of Au nanoparticles. The Au nanoparticles are assembled only on the working electrode. (b) An AFM height image of the working electrode, showing the assembled nanoparticles. All electrodes are 2 μm wide.

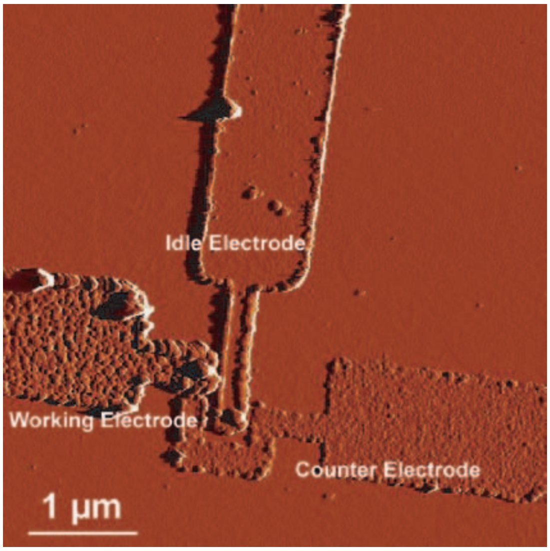

Fig. 4. Controllable self-assembly at the nanoscale. AFM phase image showing the counter (right), idle (top) and the working (left) electrodes, after conversion of the NO_2 groups to NH_3^+ functions and the self-assembly of Au nanoparticles, which assemble on the working and the counter electrode, but not on the idle one.

electrode. An AFM image (Fig. 4) of the nanoelectrodes after the last step of Au nanoparticle attachment shows high density coverage of the Au nanoparticles at the working and counter electrodes, but much lower density at the idle electrode. Unlike the microscale electrodes, the counter electrode in this case was also covered with nanoparticles. This phenomenon could arise from the low potential drop between the counter and the working electrode that comes about as a result of the current being driven through the electrolyte between both electrodes separated by the nanoscale gap. Since at this scale, redox currents (~10 nA @ ~0.1 V) could be comparable to leakage currents in the reference electrode, there could be an activity between the counter and reference electrodes. In order to remove the possible errors caused by the free submerged reference electrode, we have also designed another set of electrodes with the reference electrode introduced on the chip surface in between the working and the counter electrode at a distance of 200 nm from both electrodes. It was found that, even in this case, the counter electrode is covered with Au nanoparticles. The corresponding AFM image is not shown here. Nevertheless, the idle nanoelectrode was always rendered inactivate with very low density of nanoparticles attached, indicating that the potential-induced electrochemical reaction for directed self-assembly can be carried out selectively and specifically on nanoelectrodes with nanoscale spacing.

In summary, the NO_2-terminated groups in the SAMs of 4-nitrothiophenol on individual micro/nanoscale electrodes can be reduced electrochemically and selectively to NH_2 groups by applying a negative voltage between the addressed electrode and its counter electrode in the presence of an electrolyte. We have also shown that the electrochemical addressing of the electrode does not interfere with the idle electrode in its immediate vicinity. This study provides proof-of-principle that self-assembly of nanomaterials onto nanoscale electrodes can be achieved with a high degree of selectively. Since NO_2- and NH_2-terminated surfaces are known to exhibit very different chemical reactivities, the electrochemical approach described in this article, in conjunction with an electrical circuit to address specific electrodes, can provide a programmable electrode array for the self-assembly of various nanomaterials, such as metal and semiconductor nanoparticles, DNA and proteins.[6, 15, 17]

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References and Notes

1. S. Diegoli, C. A. E. Hamlett, S. J. Leigh, P. M. Mendes, and J. A. Preece, *Proc. Inst. Mech. Eng. Part G-J. Aerosp. Eng.* 221, 589 (**2007**).
2. B. Grevin and P. Rannou, *Nat. Mater.* 3, 503 (**2004**).
3. J. X. Huang, F. Kim, A. R. Tao, S. Connor, and P. D. Yang, *Nat. Mater.* 4, 896 (**2005**).
4. J. Liu, M. J. Casavant, M. Cox, D. A. Walters, P. Boul, W. Lu, A. J. Rimberg, K. A. Smith, D. T. Colbert, and R. E. Smalley, *Chem. Phys. Lett.* 303, 125 (**1999**).
5. B. W. Maynor, S. F. Filocamo, M. W. Grinstaff, and J. Liu, *J. Am. Chem. Soc.* 124, 522 (**2002**).
6. P. M. Mendes, S. Jacke, K. Critchley, J. Plaza, Y. Chen, K. Nikitin, R. E. Palmer, J. A. Preece, S. D. Evans, and D. Fitzmaurice, *Langmuir* 20, 3766 (**2004**).
7. P. M. Mendes and J. A. Preece, *Curr. Opin. Colloid Interface Sci.* 9, 236 (**2004**).
8. P. M. Mendes, C. L. Yeung, and J. A. Preece, *Nanoscale Res. Lett.* 2, 373 (**2007**).
9. A. Golzhauser, W. Eck, W. Geyer, V. Stadler, T. Weimann, P. Hinze, and M. Grunze, *Adv. Mater.* 13, 806 (**2001**).
10. Y. H. La, H. J. Kim, I. S. Maeng, Y. J. Jung, and J. W. Park, *Langmuir* 18, 301 (**2002**).
11. Y. H. La, H. J. Kim, I. S. Maeng, Y. J. Jung, J. W. Park, K. J. Kim, T. H. Kang, and B. Kim, *Langmuir* 18, 2430 (**2002**).
12. P. Mendes, M. Belloni, M. Ashworth, C. Hardy, K. Nikitin, D. Fitzmaurice, K. Critchley, S. Evans, and J. Preece, *ChemPhysChem* 4, 884 (**2003**).
13. S. Q. Sun, K. S. L. Chong, and G. J. Leggett, *J. Am. Chem. Soc.* 124, 2414 (**2002**).
14. J. V. Barth, G. Costantini, and K. Kern, *Nature* 437, 671 (**2005**).
15. P. M. Mendes, K. L. Christman, P. Parthasarathy, E. Schopf, J. Ouyang, Y. Yang, J. A. Preece, H. D. Maynard, Y. Chen, and J. F. Stoddart, *Bioconj. Chem.* 18, 1919 (**2007**).
16. C. S. Lee, S. E. Baker, M. S. Marcus, W. S. Yang, M. A. Eriksson, and R. J. Hamers, *Nano Lett.* 4, 1713 (**2004**).
17. J. U. Nielsen, M. J. Esplandiu, and D. M. Kolb, *Langmuir* 17, 3454 (**2001**).

18. H. Tsutsumi, S. Furumoto, M. Morita, and Y. Matsuda, *J. Colloid Interface Sci.* 171, 505 (**1995**).

19. G. Frens, *Nature Phys. Sci.* 241, 20 (**1973**).

20. H. X. He, H. Zhang, Q. G. Li, T. Zhu, S. F. Y. Li, and Z. F. Liu, *Langmuir* 16, 3846 (**2000**).

21. K. Mougin, H. Haidara, and G. Castelein, *Colloid Surf. A-Physicochem. Eng. Asp.* 193, 231 (**2001**).

22. T. Sato, D. Brown, and B. F. G. Johnson, *Chem. Commun.* 1007 (**1997**).

23. T. Zhu, X. Y. Fu, T. Mu, J. Wang, and Z. F. Liu, *Langmuir* 15, 5197 (**1999**).

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