Catalytic reduction of nitro-group terminated monolayers by Ag nanoparticles; a novel strategy for site-selective patterning of organic monolayers†

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We have demonstrated that site-selective patterning of organic monolayers can be accomplished simply by inducing Ag nanoparticle-mediated catalytic reduction to occur on the desired regions of those monolayers.

The patterning of self-assembled monolayers (SAMs) of organic molecules is an excellent strategy for preparing templates that possess variable surface chemical properties.[1] This can be accomplished either by utilizing conventional photolithography or by destructive atomic beam and proximal-probe lithographic processes.[2] In recent years, a number of non-destructive processes have also been reported, *e.g.*, atomic force microscope (AFM) tip-based lithography.[3] All of these currently available methods have their own weakness, however. The destructive lithographic processes have to be conducted in an expensive ultra-high vacuum system. AFM tip-based lithography is time-consuming, and it has to be performed on the SAMs on flat substrates.

In this regard, it is highly desirable to develop simple but cost-effective chemical lithographic processes that can be applied even to SAMs on uneven solid substrates under ambient conditions. As one simple example, amine-group terminated patterned monolayers can be prepared on silver by inducing a surface photoreaction from 4-nitrobenzenethiol (4-NBT) SAMs on Ag using an Ar$^+$ ion laser at 514.5 nm.[4] On the other hand, it has been discovered that Ag nanoparticles physically in contact with 4-NBT SAMs can induce, simply by irradiating with visible laser in ambient conditions, the photolytic reduction of the nitro-to amine-group. This is indicative of the usefulness of Ag nanoparticles' property of acting as a moderate photoelectron emitter.[5]

Recently, site-selective patterning of SAMs has also been accomplished by inducing reductive reactions to occur *via* the injection or spreading of borohydride droplets or particles onto the desired regions of the monolayers;[6] NaBH$_4$ may also generate H$_2$, but it can easily be purged out under ambient conditions since the H$_2$-mediated catalytic reaction usually occurs on active catalysts such as Pd–C or Raney Ni under high pressure.[7] Regarding this matter, it is of interest that coinage metal nanoparticles, such as Ag, can function as microelectrodes for the catalytic reduction of organic compounds by BH$_4^-$ ions in solution phases.[8] Catalysis is presumed due to the efficient nanoparticle-mediated electron transfer from BH$_4^-$ ions to the organic compounds. The addition of BH$_4^-$ ions to aqueous silver sol has also been known to lower the surface potential of Ag nanoparticles.[9] The required potential of the nanoparticles has been claimed to lie between the potential thresholds of the donor (*e.g.*, more negative, BH$_4^-$) and the acceptor (*e.g.*, more positive, aromatic nitro compounds).[8b] These characteristics of Ag nanoparticles may be applied efficiently to the patterning of organic SAMs, and a minute amount of catalytic nanoparticles is expected to considerably lower the required concentration of BH$_4^-$ ions, and also to minimize the possible damage of SAMs and/or substrate caused by the usage of reductants.

In this work, we demonstrate that Ag nanoparticles dispersed in borohydride solution efficiently relay electrons used for the

reduction of the terminal functionality of SAMs anchored on a solid substrate. Based on this, we were able to prepare amine-group terminated patterned monolayers *via* Ag nanoparticle-mediated catalytic reduction of 4-NBT SAMs on a vacuum-evaporated flat Ag surface.

Spectroscopic verification of the chemical transformation of SAMs generally necessitates the introduction of sophisticated instrumentation, but a judicious choice of solid substrates for the SAMs makes it possible to use popular means such as infrared and Raman spectroscopies. The μm-sized Ag particles used in this work have proven to be useful in allowing the acquisition of infrared as well as Raman spectra of chemical species adsorbed thereon.[10] The diffuse reflectance infrared Fourier transform (DRIFT) spectral pattern is comparable to the reflection–absorption infrared (RAIR) spectral pattern of the same adsorbate assembled on a flat silver substrate, implying that the usual infrared surface selection rule is applicable even on powdered silver. On the other hand, the Raman spectrum acquired is the surface-enhanced Raman scattering (SERS) spectrum of the adsorbate on silver. Another advantage is that high quality SERS spectra can be obtained from the μm-sized Ag particles not only using blue light, *e.g.*, 514.5 nm, but also using red light, *e.g.*, 632.8 nm, as the excitation source.

Fig. 1A(a) and A(e) show the DRIFT spectra of 4-NBT and 4-aminobenzenethiol (4-ABT) SAMs on 2 μm-sized Ag particles, respectively (see ESI†). Distinct spectral differences between 4-NBT and 4-ABT are noticeable in the region 1500–1200 cm^{-1}. The N–O stretching band is distinctly identifiable at 1341 cm^{-1} for the 4-NBT SAMs. Fig. 1A(b) and A(c) show the DRIFT spectra of 4-NBT on Ag soaked in 1 and 10 mM sodium borohydride solution for 10 min, respectively. In fact, the spectral pattern of 4-ABT on Ag is not affected at all by coming into contact with borohydride solution (data not shown). It can be seen, however, that the DRIFT spectral pattern of 4-NBT on Ag becomes the same as that of 4-ABT on Ag upon coming into contact with > 10 mM borohydride solution. Considering the fact that 4-NBT itself is not reduced to 4-ABT even by 200 mM BH$_4^-$ in solution (confirmed by the UV/Vis spectral analysis; see ESI Figure S1†), the present observation indicates that μm-sized Ag particles provide a catalytic route for the reduction of 4-NBT to 4-ABT. Fig. 1A(d) shows the DRIFT
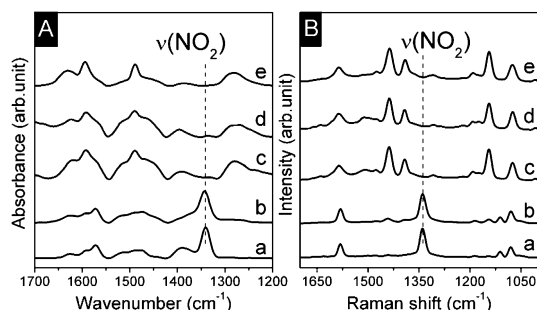

Fig. 1 A: DRIFT spectra of (a) 4-NBT/Ag (μm), (b) and (c) 4-NBT/Ag (μm) soaked for 10 min in 1 and 10 mM NaBH$_4$ solution, respectively, (d) 4-NBT/Ag (μm) soaked in 1 mM NaBH$_4$ solution containing 10 μM AgNO$_3$ for 10 min, and (e) 4-ABT/Ag (μm). B: SERS spectra for the samples corresponding to the DRIFT spectra taken using the 632.8 nm line as an excitation source.

spectrum of 4-NBT on Ag that has been soaked for 10 min in 1 mM borohydride solution containing 10 μM AgNO₃. It is evident that the presence of merely 10 μM Ag⁺ ions results in the complete conversion of 4-NBT to 4-ABT on Ag. This clearly suggests that small Ag nanoparticles, that have been produced by the borohydride, have acted as catalysts for efficient electron transfer from the borohydride to 4-NBT on Ag.

In the Introduction, we mentioned that surface-induced photo-reduction takes place for 4-NBT on Ag upon irradiation at 514.5 nm. The same photoreduction does not occur, however, using the radiation at 632.8 nm. We have thus recorded a series of SERS spectra for the samples corresponding to the DRIFT spectra shown in Fig. 1A using the 632.8 nm line. Fig. 1B(a) shows the SERS spectrum of 4-NBT on Ag. As observed by DRIFT spectroscopy, almost no 4-NBT is converted to 4-ABT by 1 mM borohydride while the reduction does take place by coming into contact with a 10 mM borohydride solution (see Fig. 1B(b) and B(c)). Fig. 1B(d) shows the SERS spectrum of 4-NBT on Ag treated with a 1 mM borohydride solution containing 10 μM AgNO₃. Its spectral features are observed to be identical to that of 4-ABT on Ag in Fig. 1B(e). This is also in good agreement with the observation made by DRIFT spectroscopy. It is thus clearly understood that the nitro-to-amine group conversion can be induced and accelerated by nano-sized Ag particles even in a borohydride solution of fairly low concentration, e.g., 1 mM.

The reduction potential of silver is known to depend on the size of silver particles.[8] It is uncertain, however, whether the reduction potential of silver is also dependent on the surface roughness. Nonetheless, we observed in this work that μm-sized Ag particles could also act as an electron relaying catalyst. It may be conceivable that nano-sized Ag particles are inevitably present in any sample of μm-sized Ag powders. Or, any cationic silver ions present on the powdered silver (such as Ag₂O) may be reduced to nano-sized particles by borohydride to act as catalysts. We have to remember that 4-NBT is not reduced to 4-ABT even by 200 mM BH₄⁻ in solution phase. We also note that the SAMs of 4-NBT on thick SERS-active Au substrates can be converted to 4-ABT on Au by 200 mM BH₄⁻, however.[6] Since there were no nano-sized Au particles, it would be indicative of the importance of the surface roughness in an electron relay system. We may then be curious as to whether the nitro-to-amine group conversion will take place by borohydride when 4-NBT is assembled, for instance, on a very smooth, SERS-inactive Ag substrate. Fig. 2A(a) and A(f) show the RAIR spectra of 4-NBT and 4-ABT on vacuum-evaporated Ag substrates, respectively. Fig. 2A(b) to A(d) show the RAIR spectra of 4-NBT on Ag taken after soaking in 5, 50, and 200 mM NaBH₄ for 10 min, respectively. It is evident that chemical reduction indeed takes place on contact with > 50 mM BH₄⁻. This seems to indicate that even a flat noble metal can function as an electron relay system. Fig. 2A(e) shows the RAIR spectrum of 4-NBT on Ag that has been immersed for 10 min in 1 mM BH₄⁻ containing 10 μM AgNO₃. It is remarkable that the nitro-to-amine group conversion is completed under very mild reduction conditions. This clearly supports the contention that nano-sized Ag particles are very effective electron relaying catalysts.

Based on the above observations, we have prepared amine-group terminated patterned monolayers via Ag nanoparticle-mediated catalytic reduction of 4-NBT SAMs on a vacuum-evaporated flat Ag surface (see ESI†). In Fig. 2B is shown an AFM image of Au nanoparticles selectively adsorbed onto the patterned amine-groups
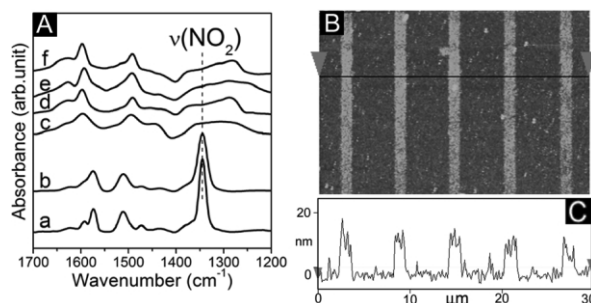

Fig. 2 A: RAIR spectra of SAMs on vacuum-evaporated flat Ag; (a) 4-NBT/Ag (flat), (b) to (d) 4-NBT/Ag (flat) taken after soaking for 10 min in 5, 50, and 200 mM NaBH₄ solution, respectively, (e) 4-NBT/Ag (flat) immersed in 1 mM NaBH₄ solution containing 10 μM AgNO₃ for 10 min, and (f) 4-ABT/Ag (flat). B: AFM image (30 μm × 20 μm) of Au nanoparticles selectively adsorbed on the patterned amine-groups that have been produced by the catalytic reduction of 4-NBT to 4-ABT on a vacuum-evaporated flat Ag. C: Representative cross-section image.

that have been produced from nitro-groups by Ag nanoparticle-mediated catalytic reduction; this selectivity results from the electrostatic interaction between the negatively charged Au nano-particles and the positively charged amine groups in acidic Au sol solution.[11] Cross section analysis in Fig. 2C also supports the adsorption of Au nanoparticles (∼17 nm) on the patterned SAMs.

In summary, we have demonstrated that site-selective patterning of organic monolayers can be accomplished simply by inducing Ag nanoparticle-mediated catalytic reduction to occur on the desired regions of monolayers. Such a reaction is simple but effective and benign, and also possible under ambient conditions. The present strategy can thus be adopted as an environmentally friendly and versatile means of fabricating functional polymeric thin films as well as patterned monolayers. It can also be applied to a variety of substrates including non-flat and non-metallic surfaces in contrast with the usual soft lithography. This surely gives the proposed method an advantage over the existing lithographic methods.

Notes and references

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