Chemical Lithography by Surface-Induced Photoreaction of Nitro Compounds

Sang Woo Han, Inhyung Lee, and Kwan Kim

Searching for systems of self-assembled monolayers (SAMs) that can be used as templates for chemical lithography, we found that nitro groups on aromatic SAMs are selectively converted on Ag to amino groups by irradiation with a visible laser. 4-nitrobenzenethiol on Ag was thus converted to 4-aminobenzenethiol by irradiating it with an Ar^+ laser. This was evident from surface-enhanced Raman scattering (SERS) as well as from a coupling reaction forming amide bonds. The surface-induced photoreaction allowed us to prepare patterned binary monolayers on Ag that showed different chemical reactivities. Using the binary monolayers as a lithographic template, we induced site-specific chemical reactions, such as the selective growth of biominerals on either the nitro- or amine-terminated regions by adjusting the crystal-growth conditions. We also demonstrated that patterned, amine-terminated monolayers can be fabricated even on gold by using silver nanoparticles as photoreducing catalysts.

Keywords: Surface-induced photoreaction, nitro-to-amine conversion.

I. Introduction

Nano- to meso-scale structures for use in laboratory studies and commercial applications can be realized by controlling chemical functionalities on a nanoscale. Site-selective alternations of surface chemistry provide a means of engineering surfaces that can be used in sensitive optoelectronic and biomimetic devices and sensors. Patterning of the self-assembled monolayers (SAMs) is an excellent strategy for preparing templates that possess variable surface chemical properties. Modification of SAMs can be conducted by conventional [1] or state-of-art destructive lithographic [2] processes, including atomic-beam [3] and proximal-probe [4] methods. Recently, non-destructive processes have also been reported. For instance, chemical reactions can be induced for the terminal groups of organosilane by a catalytically active transition metal-coated atomic force microscope (AFM) tip [5], [6]. A terminal group of organothiol monolayers on gold can also be converted using low-energy electron beams [7].

We recently demonstrated that patterned binary monolayers can be prepared on silver by inducing a surface-induced photoreaction for a SAM of benzyl phenyl sulfide (BPS) on Ag [8]. Irradiation of an argon ion laser (514.5 nm) onto a selected region of BPS SAMs on silver resulted in the formation of benzenethiolate monolayers. The unilluminated sulfides were then replaced with thiols or carboxylic acids by a self-assembly process. This method can produce very robust binary monolayers, but there is one inherent difficulty in that the region of benzenethiolate layers has nano-sized vacancies owing to the removal of the decomposition product, i.e., benzyl radicals. A new system thus needs to be developed that will preserve the overall structural integrity of the primary monolayer even after the surface-induced photoreaction. In our

search for alternative systems, we found that nitro groups on aromatic SAMs on silver are selectively converted to amino groups under irradiation with visible light. Using this photoreaction, we prepared patterned binary monolayers on silver with selectable surface chemical properties. We performed site-specific chemical reactions and patterned crystal nucleation with these monolayers. Moreover, using silver nanoparticles as photoreducing catalysts, we were able to convert nitro groups to amino groups irrespective of the underlying substrates. Its application prospect is very high since amine-group terminated patterned monolayers fabricated on engineering substrates are essential in the development of molecule-based optoelectronic and biomimetic devices and sensors.

II. Experimental

We purchased 4-nitrobenzenethiol (4-NBT), 4-aminobenzenethiol (4-ABT), and 4-cyanobenzoic acid (4-CBA) from Aldrich and 1-Ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) from Advanced ChemTech. These compounds were used as received. Other chemicals, unless specified, were reagent grade, and triply distilled water (resistivity greater than 18.0 MΩ·cm) was used when preparing aqueous solutions.

We prepared the surface-enhanced Raman scattering (SERS) active silver surface by immersing a Ag foil (Aldrich, 0.05 mm thick) in diluted (1:1) HNO_3 [8]. The SERS inactive gold substrates were prepared by resistive evaporation of titanium and gold at about 10^{-6} torr on batches of glass slides. We previously reported the method of preparation of aqueous silver [9] and gold [10] sols. SAMs of 4-NBT or 4-ABT were prepared by immersion of the silver or gold substrates in 1 mM ethanolic solution of adsorbate for about 3 hours.

We obtained SERS spectra with a Renishaw Raman System 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA) and used either the 514.5-nm radiation from a 20-mW air-cooled Ar^+ laser (Spectra-Physics model 163-C4210) or the 632.8-nm radiation from a 17-mW air-cooled He/Ne laser (Spectra-Physics model 127) as the excitation source. All the laser irradiation experiments were conducted in ambient conditions at approximately 40% relative humidity. When required, samples were spun at 3000 rpm by a home-made Raman spinning cell. When Raman images were recorded, the sample was placed below the object lens on an XY-stage (Newport M-462) equipped with a dc motor actuator (Newport 850F), which was controlled by a motion controller (Newport PMC200-P2) [8].

The electrochemical reduction of 4-NBT on a silver surface was carried out in a three-electrode cell using a CH Instrument Model 600A potentiostat. A silver substrate onto which 4-NBT

was self-assembled served as a working electrode. The reference electrode was a saturated calomel electrode (SCE), and a platinum spiral wire was used as the counter electrode. The electrolyte was $NaClO_4$, and all experiments were carried out at room temperature.

We performed the modification reaction with 4-CBA by overnight incubation of the laser-irradiated sample in 0.02 M 4-CBA solution in *N*, *N*-dimethylformamide (DMF) containing 0.02 M EDC as a coupling reagent. The calcite crystallization was conducted by supporting the laser-irradiated sample in a 10 mM $CaCl_2$ aqueous solution in a closed desiccator with vials of solid $(NH_4)_2CO_3$ at the bottom. All experiments were carried out at room temperature for 30 min. After the crystallization step, the substrate was rinsed with water to remove any weakly bound $CaCO_3$ and then blown dry with N_2.

A JSM 840-A scanning electron microscope operating at 20 kV obtained scanning electron microscopy (SEM) images. A Digital Instruments Model Nanoscope IIIa scanning probe microscope in a tapping mode in air at room temperature obtained AFM images.

III. Results and Discussion

1. Surface-Induced Photoreaction of 4-NBT on Ag

The literature has reported several SERS studies regarding the physicochemical properties of aromatic nitro compounds on silver [11], [12]. In most cases, the SERS peaks of the original nitro compounds gradually lost intensities, and a new set of peaks appeared, suggesting that nitro compounds are subjected to photoreaction on the silver surface. Based on these earlier observations, we reexamined the SERS characteristics of 4-NBT on silver.

Figure 1(a) shows the SERS spectrum of 4-NBT adsorbed on a silver foil. When obtaining the spectrum, we spun the silver substrate at 3000 rpm to minimize the occurrence of photoreaction. We attribute the observed SERS peaks entirely to 4-NBT on silver. The complete absence of the S-H stretching peak in the SERS spectrum, observable at 2548 cm^{-1} for pure 4-NBT, indicates that 4-NBT is adsorbed on silver as thiolate after the S-H bond cleavage. On the other hand, the appearance of a prominent SERS peak at 1346 cm^{-1} that can be assigned to the symmetric stretching vibration of the nitro group ($v_s(NO_2)$) indicates that the nitro group is not subjected to change upon the surface adsorption of 4-NBT on silver. Other distinct SERS peaks in Fig. 1(a) can be attributed to either the C-C stretching mode, i.e., at 1573 cm^{-1}, or the in-plane C-H bending modes, i.e., at 1110 and 1082 cm^{-1}.

Figure 1(b) shows the SERS spectrum of 4-NBT on Ag obtained after irradiation with the 514.5 nm line of an Ar^+ laser

(5 mW) for 5 seconds in a static condition, i.e., without spinning the silver substrate. The SERS feature in Fig. 1(b) is substantially different from that in Fig. 1(a). The $\nu_s(NO_2)$ peak is no longer identifiable, and several new peaks appear, for instance, at 1436, 1392, 1192, and 1143 cm^{-1}. This indicates that a certain photoreaction took place for 4-NBT on the silver surface. Since further illumination of the laser light did not affect the SERS spectral feature, the reaction must occur very rapidly. However, we observed no spectral change even after irradiation with a 5 mW Ar$^+$ laser for several hours for pure 4-NBT in a solid state as well as for a 4-NBT solution in ethanol. On the other hand, the Ar$^+$ laser-induced surface reaction hardly took place for 4-NBT on Au. This implies that the SERS spectral change observed in Fig. 1(b) is closely associated with the inherent nature of the silver substrate.

Fig. 2. SERS spectra taken for the laser-irradiated regions of the 4-NBT monolayer (a) before and (b) after the 4-CBA coupling reaction.

We have also confirmed the conversion of the nitro group to amine functionality by monitoring the reaction of the laser-irradiated 4-NBT on Ag with 4-cyanobenzoic acid (4-CBA) in DMF. The as-prepared 4-NBT on Ag did not react with 4-CBA, but the laser-irradiated 4-NBT on Ag readily reacted with 4-CBA to form amide bonds. This is evident from Figs. 2(a) and 2(b), which show the SERS spectra of the laser-irradiated 4-NBT on Ag before and after the coupling reaction with 4-CBA, respectively. We attribute the newly observable peaks at 2234 and 1608 cm^{-1} in Fig. 2(b) to the CN stretching and the aromatic CC stretching modes of 4-CBA, respectively. On the other hand, the appearance of the amide I and II bands at 1650 and 1529 cm^{-1}, respectively, in Fig. 2(b) unambiguously indicates the formation of amide bonds.

2. Formation of Patterned Binary Organic Monolayers on Ag

We demonstrated the potential of our method of producing patterned organic monolayers with selectable surface chemical properties by irradiating the SAMs of 4-NBT on Ag with an Ar$^+$ laser through a copper grid as a photomask. For this experiment, the substrate was moved at a rate of 0.4 μm/s under exposure of laser light. After removal of the grid, the surface was subsequently treated with 4-CBA. Figure 3 shows a typical SERS image obtained from the patterned monolayers after the process. For the production of the image, we selected the SERS peak at 2234 cm^{-1} (Fig. 2(b)) as the most appropriate marker band, indicative of the coupling of 4-CBA to amine functionalities. The light areas in Fig. 3 are due to higher SERS intensity and correspond to the coupled areas. The dimensions of the pattern match closely the actual dimensions of the photomask. Thus, our study shows that the present method can
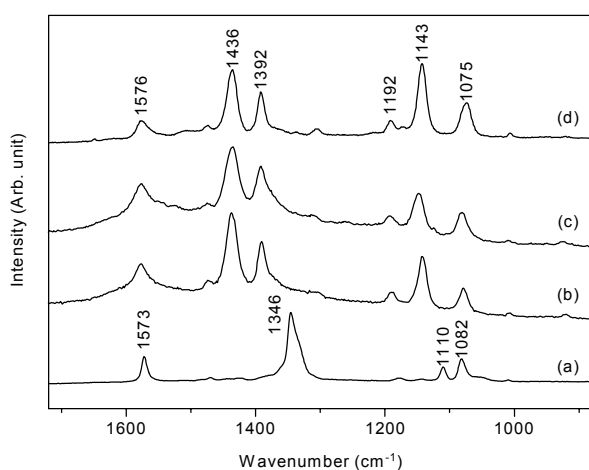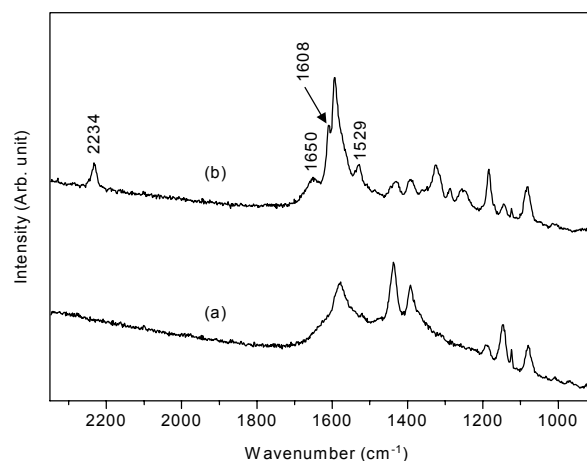

Fig. 1. SERS spectra of 4-NBT on silver taken (a) under spinning at 3000 rpm and (b) under static conditions. (c) SERS spectrum of 4-ABT adsorbed on silver. (d) SERS spectrum of 4-NBT on silver after electrochemical reduction in 0.2 M NaClO$_4$ (aq).

The SERS spectral feature in Fig. 1(b) is coincident with that of 4-aminobenzenethiol (4-ABT) on Ag shown in Fig. 1(c). This suggests that 4-NBT was reduced on Ag to 4-ABT upon illumination with the visible laser. To obtain more firm evidence, we acquired the SERS spectrum of electrochemically reduced 4-NBT on silver in a 0.2 M aqueous NaClO$_4$ solution (Fig. 1(d)). The spectral feature was once again a close match with that in Fig. 1(b). Previous electrochemical studies in aqueous media found that reduction of the surface-immobilized 4-NBT occurs by a complex route but eventually forms amine functionality by a 6-e transfer process [13]. In this light, we attributed the newly observed peaks in Fig. 1(b) at 1436 and 1392 cm^{-1} to the C-C stretching plus the in-plane C-H bending modes of 4-ABT, while we attribute the 1192 and 1143 cm^{-1} peaks to the in-plane C-H bending modes of 4-ABT.
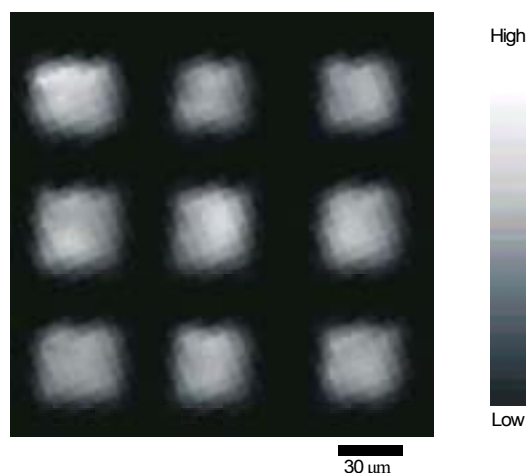
Fig. 3. SERS image of the patterned SAMs on silver after 4-CBA coupling reaction. Image is drawn using the characteristic SERS peak of 4-CBA at 2234 cm^{-1}. The scale bar represents the intensity of the Raman signal.

(a)

(b)

Fig. 4. SEM images of calcite crystals formed (a) on a patterned substrate and (b) on two parallel amine-terminated lines that were generated previously using a focused Ar$^+$ laser.

serve as a means of chemically defined lithography. Since the preparation scheme is very simple, the method must be beneficial particularly when amine-terminated, patterned organic monolayers are needed. In fact, amine-terminated surfaces have been widely used in recent years specifically for the development of biosensors, enzyme-coated electrodes, and DNA computers [14].

Recalling the fact that functionalized organic surfaces can promote the nucleation of inorganic crystals, we subsequently examined whether our patterned monolayers can be used as a template for selective crystal growth. The crystal chosen for this study was calcium carbonate (calcite), one of the most abundant biominerals, which can be grown easily under laboratory conditions [15]. To grow the crystal, the patterned substrates produced by laser-irradiation through a Cu grid were supported upside-down in an aqueous calcium chloride solution to ensure that only particles grown on the substrates are bound to the surface, and then placed in a closed desiccator with vials of solid ammonium carbonate at the bottom. Crystallization of calcite results from the diffusion of carbon dioxide vapor from ammonium carbonate into the solution. Figure 4(a) is a typical SEM image showing the patterns of calcite crystals formed on a sample substrate. Crystallization is restricted to well-defined, nitro group-terminated regions and does not occur on the amine group-terminated areas. The crystallization of calcite only on the nitro group-terminated regions must be associated with the greater affinity of calcium ions for the nitro groups in comparison with the amine groups.

We also examined how the calcite grows on our patterned substrate when the substrate is exposed at the beginning to carbonate ions. For this purpose, a patterned substrate made by
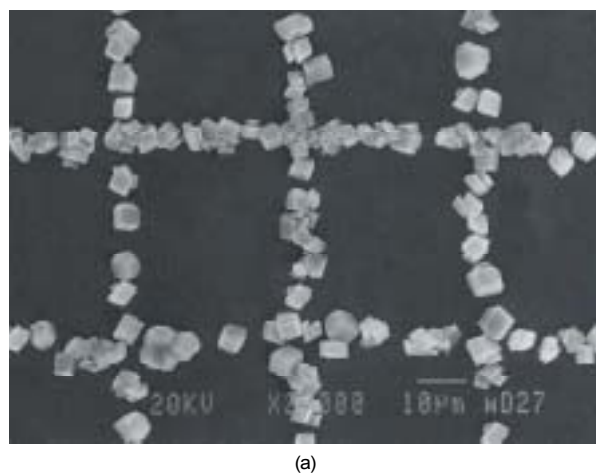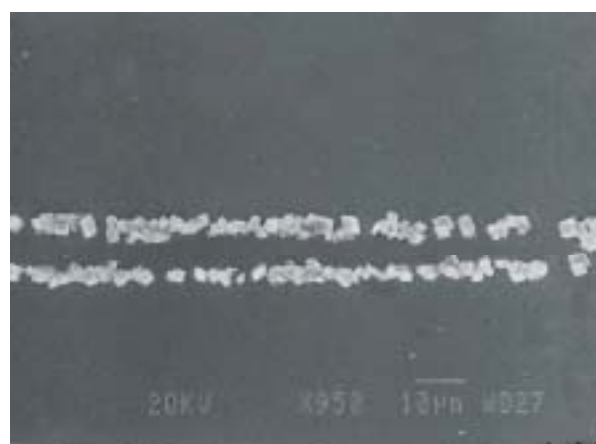
laser-irradiation was supported in pure water and left for a while in a closed desiccator containing vials of solid ammonium carbonate at the bottom prior to adding a calcium chloride solution into water. The crystallization was then restricted to the amine-terminated regions, in contrast with the previous case shown in Fig. 4(a). Considering the preferential binding of carbonate ions to amine groups (amine groups were protonated in our experimental conditions), the crystallization of calcite only on the amine-terminated regions is not unreasonable. In this sense, light-directed crystallization of calcite may be accomplished on silver on demand. To demonstrate its feasibility, after self-assembling 4-NBT on Ag, a focused Ar$^+$ laser was irradiated along parallel lines separated from each other by 10 μm, and then calcite crystals were grown on the substrate, exposing them first to carbonate ions. As shown in Fig. 4(b), the crystals were in fact grown selectively along the two lines that were exposed to the laser beam to produce amine functionality.

3. Formation of Patterned Binary Monolayers on Au by Nanoparticle-Directed Photoreaction

As mentioned previously, the Ar^+ laser-induced surface reaction hardly took place for 4-NBT on Au. In order to use the current lithographic strategy as a general tool for preparing patterned binary monolayers, the limitation on the type of substrate had to be overcome. This was achieved by using silver nanoparticles as photoreducing catalysts. To examine its feasibility, at first we prepared 4-NBT monolayers on a SERS-inactive smooth gold substrate. Silver nanoparticles, prepared by laser ablation of pure silver in deionized water [9], were then spread on the 4-NBT monolayers. Although the gold substrate itself was SERS-inactive, the SERS spectrum of 4-NBT could be obtained with a silver nanoparticle-mediated electromagnetic field enhancement mechanism [16]. Figure 5(a) shows the SERS spectrum of 4-NBT on gold acquired in this way with a 632.8 nm line of a He-Ne laser as an excitation source. The overall spectral feature was nearly the same as that of 4-NBT on silver obtained with spinning (Fig. 1(a)). This clearly indicates that photoreaction of 4-NBT was hardly induced by irradiating with 632.8 nm laser light. Noticeable SERS spectral changes took place, however, when an Ar^+ laser at 514.5 nm was used as the excitation source (Fig. 5(b)). The $\nu_s(NO_2)$ peak is no longer identifiable in Fig. 5(b), and several new peaks appear, for instance, at 1436, 1392, 1192, and 1143 cm^{-1}. This observation is exactly the same as that for 4-NBT adsorbed on Ag and then irradiated with the 514.5 nm radiation (Fig. 1(b)). Hence, photoreaction of 4-NBT can be induced even on gold by using Ag nanoparticles, and the reaction product must be 4-ABT. This implies that Ag nanoparticles can function as photoreducing catalysts even if they are simply spread on the surfaces of SAMs. The potential of the current method to produce patterned organic monolayers on gold has thus been demonstrated as follows.

For selective spreading of Ag nanoparticles onto the 4-NBT SAMs on Au, the so-called μ-molding technique was employed, i.e., a Ag nanoparticle solution was allowed to flow by capillary action into the holes of a prepatterned poly(dimethylsiloxane) (PDMS) stamp [17]. After removing the PDMS mold, the Au substrate was subsequently moved at a rate of 0.4 μm/s under exposure of an Ar^+ laser light. Thereafter, Ag nanoparticles were removed by sonication in water. We then immersed the Au substrate in an aqueous Au nanoparticle solution, expecting that the Au nanoparticles would be immobilized exclusively on the amine-terminated regions. (The Au nanoparticles, prepared by the citrate reduction method, were stabilized with negatively charged citrate ions. Accordingly, these particles could readily be immobilized on the amine-terminated regions through electrostatic interaction because the amine groups were protonated in our experimental conditions. Furthermore, the well-known amine-Au coordination chemistry also increased the strength of specific interaction between Au nanoparticles and amine-terminated regions.) A typical AFM image obtained after the process is shown in Fig. 6. The image clearly shows that the Au nanoparticles were immobilized only on the specific regions of the monolayer. The dimensions of the pattern matched closely the actual sizes of the PDMS pattern used as a template for the Ag nanoparticle array. This proves that the present method can serve as a general tool for the manufacture of amine-functionalized, patterned monolayers on various engineering solid substrates.
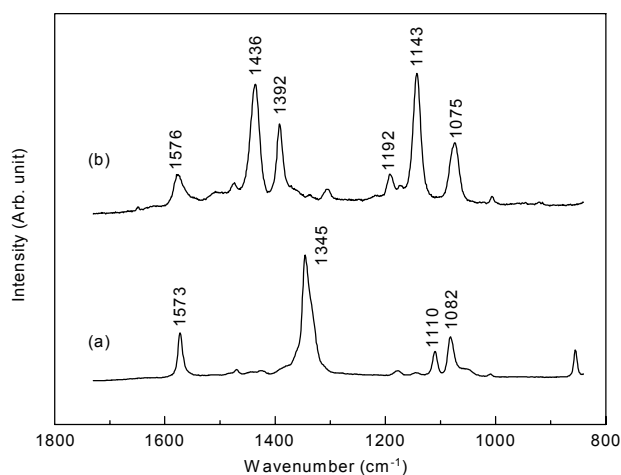

Fig. 5. SERS spectra of 4-NBT SAMs on gold taken after spreading silver nanoparticles onto the SAMs: (a) with 632.8 nm line of He-Ne laser and (b) with 514.5 nm line of Ar ion laser.
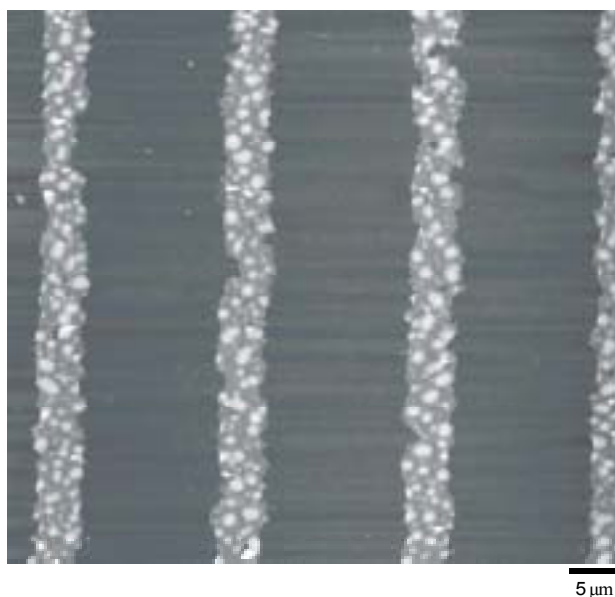

Fig. 6. AFM image of gold nanoparticles immobilized on a patterned substrate.

IV. Conclusion

We observed the chemical transformation of 4-NBT to 4-ABT on Ag by visible laser light irradiation. Based on this, we demonstrated that patterned binary organic monolayers can readily be formulated on a silver substrate by surface-induced photoreaction, preserving the overall structural integrity of the primary monolayer. Such locally modified monolayer surfaces can be used to direct the site-selective self-assembly of a number of different organic and inorganic materials, according to a predefined geometric pattern and a preselected type of chemical functionality. We also demonstrated that patterned monolayers can be fabricated even on gold by using silver nanoparticles as photoreducing catalysts. Our future work will be directed toward the application of the present nondestructive patterning process in various areas of chemical and biological investigations.

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