

Communications

Nanoscale Templates from Oriented Block Copolymer Films**

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Polymers offer unique avenues for the structural control of materials on the nanoscale length scale for the production of nanoporous media, membranes, lithographic templates, and scaffolds for assemblies of electronic materials.^[1-4] With structures on this length scale, quantum properties of electronic materials are exhibited even at elevated temperatures. The natural length scale of polymer chains and their morphologies in the bulk lie precisely at these length scales and, as such, there is a substantial effort to produce, characterize and use polymeric nanostructures. The ease of processing polymers adds to the attractiveness of polymer-based nanostructures. In comparison to the time-intensive process of sequential writing of nanoscale patterns, nanostructure formation by self-assembly is highly parallel and inherently fast. Block copolymers are ideal materials in this respect, since, due to the connectivity of two chemically distinct chains, the molecules self-assemble into ordered morphologies with a size scale limited to molecular dimensions. Of particular interest are block copolymers that form cylindrical microdomains, since the elimination of the minor component transforms the material into an array of nanopores.

A prerequisite for the use of copolymers is the control over the orientation of the microdomains. In particular, for

cylindrical microdomains, an orientation normal to the substrate surface is desirable. Two different approaches are used to this end. In thin films, random copolymers anchored to a substrate can be used to produce a neutral surface.^[5] For entropic reasons, the microdomains orient normal to the substrate surface.^[6] In a second approach, electric fields were used to orient the cylindrical microdomains parallel to the field lines.^[7-10] The approach relies on the orientation-dependent polarization energy induced when an anisotropic body is placed in an electric field. An anisotropic microphase structure will orient such that the interfaces between the two blocks are aligned parallel to the electric field.

In this article it is shown that cylindrical microdomains of a copolymer film can be used to generate an array of ordered nanoscale pores with well-controlled size, orientation, and structure. To this end, selective etching procedures and a characterization of the samples by quantitative analysis of the X-ray scattering along with electron (EM) and atomic force microscopies (AFM) are described. The processes outlined are shown to be operative over a very large range in sample thickness ranging from 40 nm up to several micrometers. The resulting nanoporous films are promising candidates as membranes with specific transport properties and as templates for electronic and magnetic nanostructured materials.

Figures 1A and 1B show AFM images obtained from a 40 nm-thick film prepared on a neutral substrate after annealing. Cylinders standing perpendicular to the substrate are clearly discernable, particularly in the phase image, since the height variations are very small. Polystyrene (PS) and poly(methylmethacrylate) (PMMA) have significantly different photodegradation properties. PMMA is known to be a negative photoresist, i.e., with ultraviolet (UV) or electron beam irradiation, the polymer is degraded via chain scission.^[11] The chemical processes taking place in PS upon exposure to deep UV radiation, on the other hand, are less well defined, with cross linking, chain scission, and oxidation taking place.^[12] However, under the conditions employed here the effect of cross linking, i.e., a reduction in solubility, dominated. Test exposures were performed on each polymer. After irradiation with a dose of 25 J/cm², a thin PS film is insoluble. A typical value necessary for degradation of PMMA is 3.4 J/cm.^[2,11] Deep UV exposure of ordered P(S-*b*-MMA) should, therefore, lead to a degradation of the PMMA block, whereas the PS matrix becomes insoluble. The degradation products from PMMA can then be rinsed away, leaving a porous film. Compared to the degradation of a PMMA homopolymer, the necessary dosage for complete removal of the PMMA in the copolymer will be higher. Not only is the random scission of the

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[**] T.T.-A. acknowledges the support of the Deutsche Forschungsgemeinschaft. We are grateful to C. Black and L. Raboin for their help with the FESEM. We also wish to thank S. Kline (NIST) for assistance with the SANS measurements. This work was also supported by the U.S. Department of Energy, Office Basic Energy Sciences under contract of DE-FG02-96ER45612, the National Science Foundation Partnership in Nanotechnology under CTR-9871782, the NSF Materials Research Science and Engineering Center (DMR-9809365), and the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities.

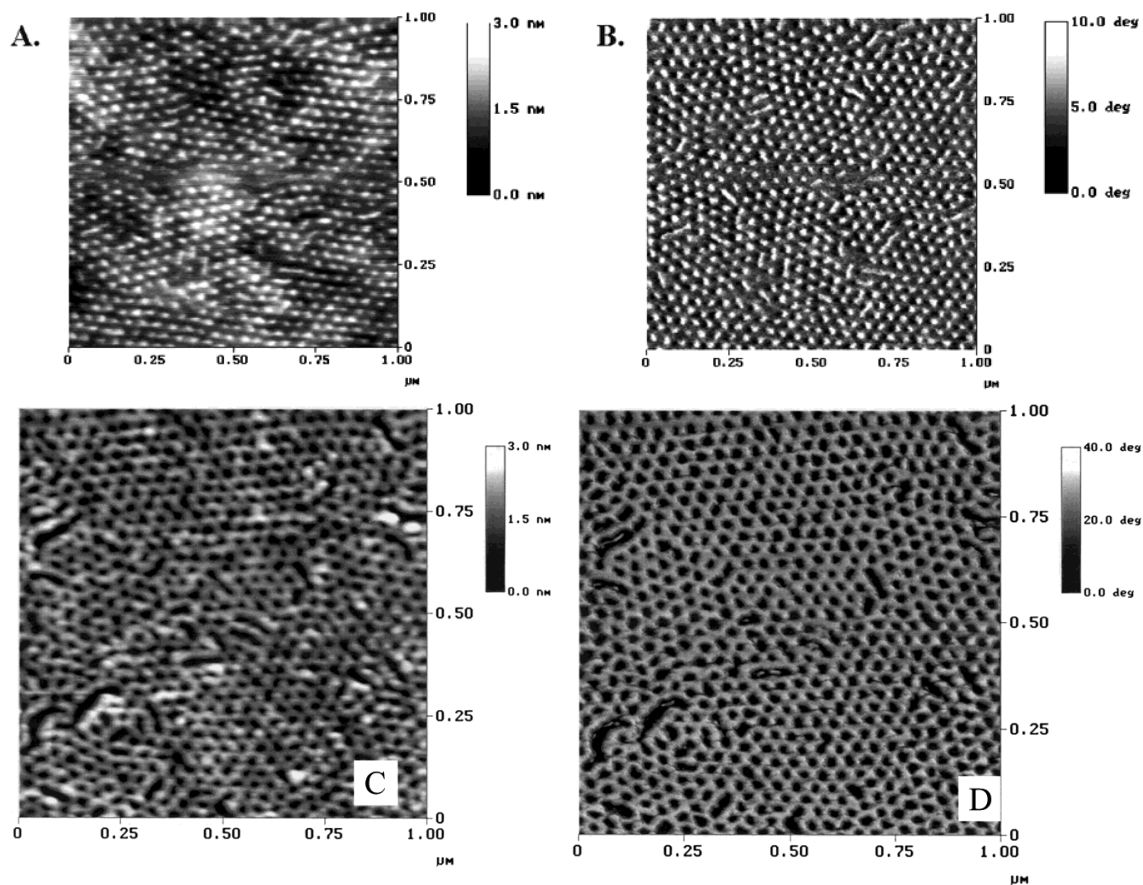


Fig. 1. AFM image obtained from a thin film (40 nm) of P(S-*b*-MMA) on a neutral substrate after annealing at 170 °C in tapping mode, A) shows the height image, B) the phase image. After removal of the PMMA material comprising the cylinders, the height C) and the phase D) images were obtained. Holes at the original locations of the cylinders can be clearly recognized.

PMMA block required, but it is necessary that scission at the junction point of the two blocks of the copolymer occurs so as to affect complete removal of the PMMA block. With thin films, electron irradiation is also possible. In this case, the required dosage is 500 $\mu\text{C}/\text{cm}^2$.

Figures 1C and 1D show AFM images obtained from a film which was exposed to 25 J/cm^2 deep UV radiation, rinsed in acetic acid, a selective solvent for PMMA and then rinsed in deionized water. The image shows an ordered array of circular holes at the positions of the cylinders. The structures can also be imaged by field emission scanning electron microscopy (FESEM) with the advantage that cross-sectional views from a fractured surface can also be prepared. A top and a cross-sectional view are shown in Figure 2. It is evident that the holes go through the entire film.

As mentioned above, an electric field was used to orient the copolymer microdomains in thicker films. Since previous experiments were performed on films with a typical thickness of 10 to 30 μm ,^[10] it is necessary to confirm that alignment in a one micron film could be achieved. Scattering experiments can easily assess the orientation of the mi-

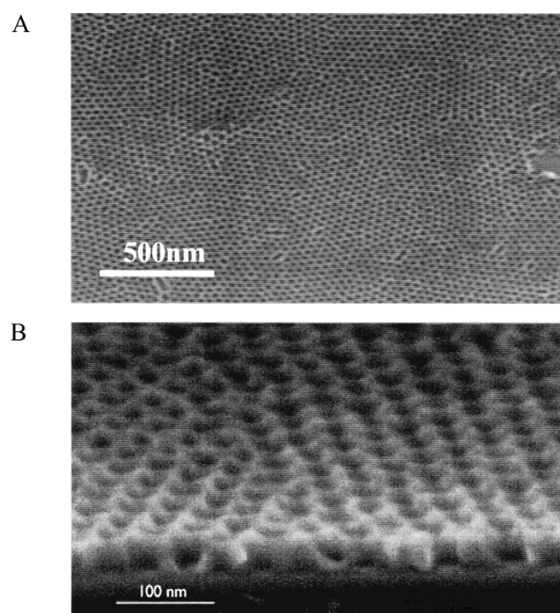


Fig. 2. FESEM image obtained from a thin film of P(S-*b*-MMA) after removal of the PMMA-block inside the cylinders, a) shows a top view, b) a cross-sectional view.

rod domain structure in a thin film. When viewed from the side, a cylindrical structure oriented normal to the substrate is periodic only in the lateral direction. Correspondingly, the scattering pattern emerging from a sample measured at a finite angle of incidence is strongly anisotropic. Figure 3A shows an example of a neutron scattering pattern obtained from a film with a thickness of 800 nm, oriented

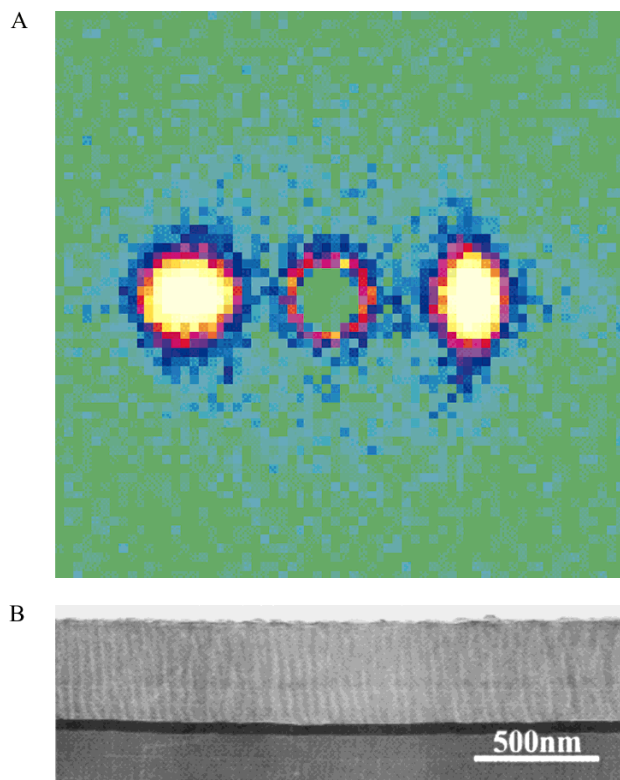


Fig. 3. A) SANS pattern obtained from a P(S-*b*-MMA) film (800 nm) annealed in an electric field of 25 V/μm. The two equatorial reflections indicate a strong orientation of the microphase structure normal to the substrate surface. B) Cross-sectional transmission electron micrograph obtained from a P(S-*b*-MMA) film (800 nm) annealed in an electric field of 25 V/μm. The block copolymer film is lying on top of a dark Au-film, which was used as the lower electrode. The upper electrode has been removed. Cylinders oriented normal to the substrate go all the way through the sample.

in an electric field of 25 V/μm. Two strong equatorial reflections, corresponding to a lattice parameter of 37 nm, are visible, which is the expected result at an incidence angle $\alpha = 45^\circ$. At $\alpha = 0^\circ$, i.e., normal incidence, the scattering consists of a uniform ring (independent of azimuthal angle) indicating that the sample consists of grains of hexagonally close packed cylinders, oriented normal to the surface; however, the lateral packing of the grains is random. An important issue for any nanostructure application of the films is the axial extension of the cylinders, i.e., it is essential that individual cylinders traverse the entire film thickness rather than forming unconnected domains across the film. This issue is addressed in Figure 3B, which shows a transmission electron micrograph (TEM) of a cross-sectional view of an oriented film. The block copolymer film is lying on top of a dark Au film. Reasonable contrast could

be achieved without staining. The brighter PMMA cylinders are clearly discernible. They are oriented normal to the substrate and a substantial fraction extends without defect from one surface to the other. Note that the upper surface shows some roughness, caused by the removal of the upper electrode. The horizontal lines in the image are knife marks having no structural relevance.

It is clear from the results shown that, by a selective removal of the PMMA, an ordered nanoporous material can be produced if the surrounding PS matrix remains intact. FESEM images of the surface of a film that was exposed to 25 J/cm² deep UV radiation, placed in acetic acid, (a selective solvent for PMMA) for 2 h and then rinsed in deionized water, show an ordered array of circular holes, in keeping with the electron microscopy and small-angle neutron scattering (SANS) results.

The small-angle X-ray scattering (SAXS) patterns obtained from a P(S-*b*-MMA) film with cylinders oriented normal to the film surface, before and after degradation of the PMMA, are shown in Figure 4. Prior to degradation, two weak equatorial reflections are seen at $q = 0.027 \text{ nm}^{-1}$ (where $q = (4\pi/\lambda)\sin\theta$, λ is the wavelength and 2θ is the scattering angle), corresponding to a period of 23 nm. An azimuthal scan at this peak position shows that the intensity of the scattering for the initial copolymer film is very weak in comparison to parasitic scattering and the scattering arising from impurities within the film or the electrodes. The positions of the maxima are indicated by arrows in the figure. Shown opposite to these data are the SAXS results obtained on the film after degradation and removal of the PMMA. Clearly, the equatorial reflections have intensified substantially due to the removal of the PMMA. There are several conclusions that can be drawn immediately from these data. First, the retention of the equatorial reflections shows unequivocally, that the microdomain structure of the copolymer has been retained, i.e., the processing involved in the degradation and washing of the PMMA, did not cause a collapse of the structure. Second, the peak remained on the equator showing that the orientation of the pores have remained vertical. Third, the position of the maximum in q has not changed. Consequently, the size scales of the features have not changed with the generation of the nanocylinders. On a more quantitative level, the peak intensity or the total integrated scattering has increased by a factor of 55, which, within experimental error, is in quantitative agreement with the predicted increase by a factor of 53, corresponding to a complete removal of the PMMA. This would not be the case if only part of the PMMA were removed or if the cylindrical pores did not extend from one surface to the other. The enhanced scattering also permits the observation of higher order reflections; $\sqrt{3}$ and $\sqrt{7}$ of the fundamental, quantitatively showing that the hexagonal packing of the nanocylinders normal to the film surface is retained.^[13]

In conclusion, an etching method for P(S-*b*-MMA) copolymers has been presented that allows selective removal

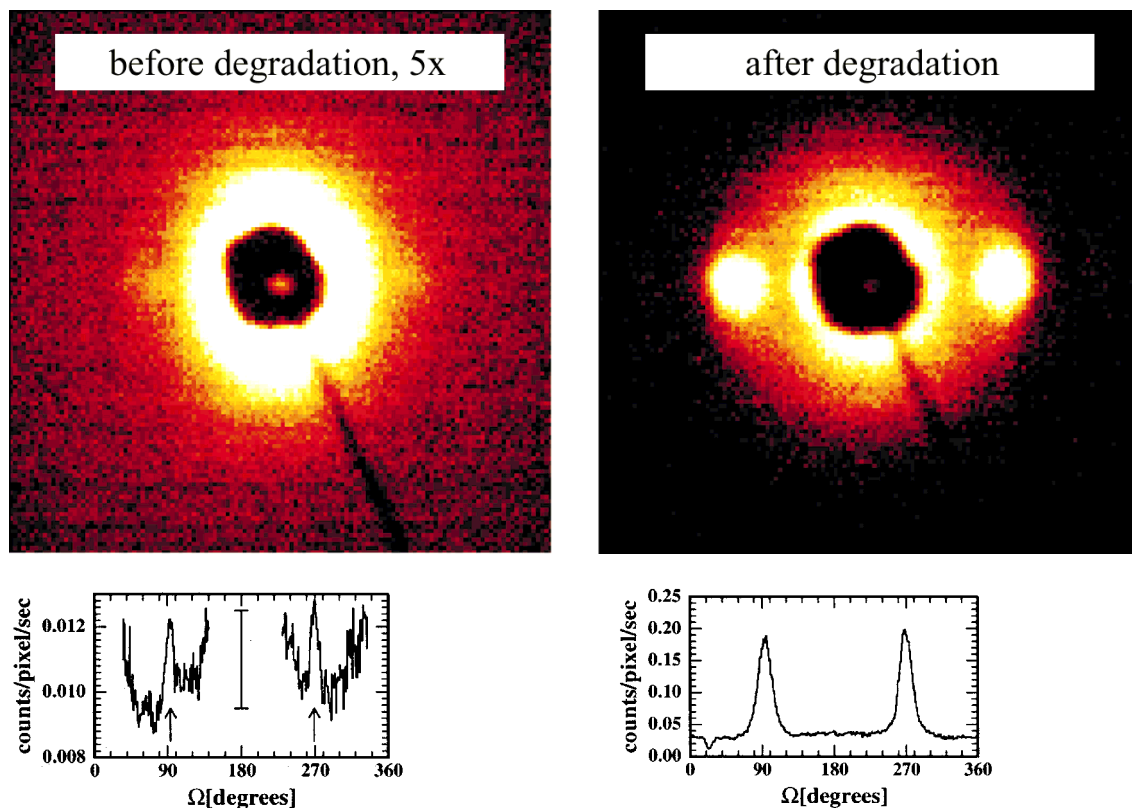


Fig. 4. SAXS pattern of a 1 μm P(S-*b*-MMA) film before and after removal of the PMMA material inside the cylinders. The formation of voids leads to a large increase in scattering intensity consistent with an estimate based on electron densities. The bar shown in the lower left part of the figure shows the expected scattering intensity based on the intensity obtained from the porous structure. For the calculation the contrast factors discussed in the text are used.

of the PMMA microdomains while preventing flow of the PS matrix. Nanoporous films based on self-assembled, block copolymer structures with controlled spatial orientation have been prepared over a large range of sample thicknesses. Such films are promising candidates as templates for the creation of nanostructures.

Experimental

Asymmetric, P(S-*b*-MMA) and P(d-S-*b*-MMA) diblock copolymers were prepared using standard anionic polymerization methods. P(d-S-*b*-MMA) used for SANS and AFM experiments had a weight average molecular weight, M_w , of 73 400 and a polydispersity index of 1.14. For the X-ray experiments, P(S-*b*-MMA) with $M_w = 39\,600$ and $M_w/M_n = 1.08$ was used. Both polymers had a PMMA volume fraction of approximately 30%. Thus, in the bulk, the morphology consists of PMMA cylinders in a PS matrix. Thin films of the copolymer (40 nm thick) were spin-coated from toluene solutions onto Si substrates previously coated with a random copolymer having a styrene fraction of 0.60. As discussed by Mansky et al. [5], such surfaces are essentially neutral. Subsequently, the films were annealed at 170 °C for 72 h under vacuum. Films with a thickness of about 1 μm were prepared by spin-coating from toluene solutions onto a substrate covered with a 100 nm gold layer. The gold layer serves as a lower electrode and as a marker for the TEM. For TEM, the substrate was an Ultem polyetherimide sheet, a material that facilitates microtoming the film into thin cross sections [14]. For the scattering experiments, a 127 μm thick Kapton film was used. The linear absorption coefficient of Kapton is sufficiently small, so that X-ray measurements could be performed in a transmission geometry. The upper electrode, in all cases, was a Kapton sheet (12.7 μm) coated with aluminum. To avoid electrical shorts the Kapton side of the upper electrode was placed in direct contact with the polymer. Samples were heated to

170 °C, well above the glass transition temperatures of the two blocks, and annealed for about 14 h with an electric field applied. To compensate for the higher viscosity of the higher molecular weight of the P(d-S-*b*-MMA), this sample was annealed at 200 °C for 24 h. After annealing, the samples were cooled to room temperature before the field was removed. The upper electrode can be easily removed from the sample in the glassy state.

For UV exposure the samples were placed underneath a mercury UV lamp with maximum emission at 254 nm. Intensity measurements were made with an IL390B Light Bug (International Light Inc.). The intensities are based on the assumption that all intensity is emitted at 254 nm, since the exact spectrum of the lamp used is not known.

SAXS and SANS profiles were obtained with the beam incident on the sample surface at 45°. The scattering arising from the sample was recorded on an area detector. The anisotropy of the scattering pattern can be used to characterize the spatial orientation of the copolymer microdomains. X-ray scattering was performed with Ni-filtered Cu-K α radiation from a Rigaku rotating anode, operated at 8 kW. A gas-filled area detector (Siemens Hi-Star) was used. SANS experiments were performed at the NIST Center for Neutron Research on Beamline NG3.

AFM measurements were performed using a Digital Instruments Nanoscope II in the tapping mode. A JEOL 100CX electron microscope operated at 100 kV was used for TEM. Sections with a thickness of 50 to 100 nm were microtomed using a diamond knife at room temperature. FESEM was performed with a JEOL-JSM 6320FXV and a LEO1560.

Received: December 14, 1999
Final version: February 29, 2000

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Formation of Linearly Arrayed Gold Nanoparticles on Gold Single-Crystal Surfaces**

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Construction of desirable nanostructures is one of the key steps in improving novel advanced technologies such as semiconductor nanodevices, microsensors, and micromachining. Recently developed nanodevice technologies using scanning probe microscopy have allowed us to construct ultrasmall structures on an atomic scale.^[1] However, this method is not adaptable to mass production because it is too slow, especially for sizes of more than a few nanometers. Conventional photolithography techniques are limited to sizes larger than about one hundred nanometers, so the size region between a few nanometers and a hundred nanometers is inaccessible with present production technologies.^[2] Thus, our goal is to develop methods of effective and high-speed construction for making nanostructures of this size.

To solve this problem, self-assembly into a colloidal crystal agglomeration has been widely investigated.^[3–13] When the concentration and surface charge of inorganic nanoparticles of a narrow size distribution are carefully controlled in the course of their preparation, followed by surface modification, the nanoparticles form agglomerates with a highly ordered arrangement. Examples of well-ordered colloidal particles composed of nanosized metal^[4–7,11,14] and semiconductor crystals^[8,9] have been reported. If we can intro-

duce desirable anisotropy into the nanosized colloidal crystals, the techniques may be useful for nanostructure formation. For metal nanoparticles, photoexcitation of surface plasmon modes should be one of the most promising perturbations for modifying the interactions between the particles. The electric field induced by excited surface plasmon modes is highly localized, and the direction of the polarization can be controlled by changing the wavelength and polarization of the light.^[15] There have been exciting reports on structural changes of metal nanoparticles under illumination,^[16–20] but most of them, unfortunately, describe fragmentation and structural deformation of the particles. There have been a few reports on the formation of highly ordered structures, and ordering of colloidal superstructures, by illumination. In this communication, we report anisotropic agglomeration of gold nanoparticles (diameter about 6 nm) modified with organic thiols, by illumination with monochromatic light in aqueous media. The effect of the illumination on the formation of anisotropic superstructures on atomically flat gold (111) surfaces was also investigated. Illumination at 830 nm led to the formation of an anisotropic superstructure on the surface.

Gold nanoparticles were prepared by a conventional method of citric acid reduction of HAuCl₄ in boiling water. Surface modification of gold nanoparticles was carried out by adding thionicotinamide (TNA) to the gold nanoparticle solution obtained.^[21] Structural changes induced by surface modification in solution were monitored by optical absorption and dynamic laser scattering measurements.^[22] The arrangement of gold nanoparticles adsorbed on single-crystal gold (111) surfaces was inspected with a scanning tunneling microscope (STM).^[23] Agglomerated gold nanoparticles in solution were transferred onto single-crystal gold surfaces by immersing the surfaces in solutions containing surface-modified gold nanoparticles. STM observation was carried out in air after blow-drying the gold surface with argon gas to remove excess water. Illumination with unpolarized light (both on the agglomeration in solution and on surfaces) was done with a semiconductor laser (830 nm, 500 mW) and a diode-pump solid-state laser (530 nm, 10 mW).

Figure 1 shows time-dependent spectral changes of a gold nanoparticle solution after adding TNA in the dark and under illumination. In Figure 1a,b, the initial spectrum shows a single absorption peak at 520 nm in the dark, accompanied by evolution of an absorption band at wavelengths beyond 700 nm. After about 300 s, the spectrum had double peaks at 520 and 720 nm. These changes can be attributed to agglomeration of gold due to surface modification by TNA. The two absorption maxima at 520 and 720 nm can be attributed to the excitation of the transverse and longitudinal modes of surface plasmon in anisotropic agglomerates.^[24–27] The modifying reagents should be bound to the gold surface via strongly interacting thiol and/or amide groups.^[19] The formation of such bonds is expected to reduce (in magnitude) anionic surface charges on the gold nanoparticles, leading to an increase in van der

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[**] This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Electrochemistry of Ordered Interfaces" (Nos. 10131244 and 09237105) from the Ministry of Education, Science, Sports, and Culture, Japan.