Nanostructures

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Laser-Modulated Ordering of Gold Nanoparticles at the Air/Water Interface

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Construction of controlled, organized nanostructure assemblies has been among the most challenging aspects of nanotechnology research and development. While "top-down" lithography techniques have predominated,[1] new "bottom-up" self-assembly methods have garnered increasing interest as viable alternatives.[2–4] In particular, self-assembled monolayers at the air/water interface (i.e. Langmuir monolayers) have been proposed as promising vehicles for surface patterning of metallic and semiconductor nanostructures.[5,6] Such soft lithography approaches have generally employed condensed monolayers of amphiphilic substances as templates for organization of metal nanoparticles on water.[7,8] In these systems, the edges of the condensed amphiphilic domains usually constitute the framework for assemblies of two-dimensional monolayer structures. Herein we describe unique long-range ordering of gold nanoparticles (Au NPs, diameter approximately 3 nm) that occurs when mixed monolayers of the NPs and an unsaturated fatty acid are irradiated with low-intensity laser light. We demonstrate the formation of a network of elongated Au "wires", which can be transferred onto solid substrates. Remarkably, ordering of the Au NPs occured only at zero surface pressure, in which the mixed monolayers exist in highly fluid phases. We show that this unusual and seemingly counterintuitive phenomenon is reversible and is due to local heating of the monolayer surface by the laser irradiation in a very narrow temperature range.

Figure 1 compares the surface-area/pressure isotherm of a mixed monolayer of elaidic acid and dodecanethiol-capped Au NPs (0.2 mol% Au, ‒‒‒) with the isotherms of the individual components elaidic acid (——) and dodecanethiol-capped Au NPs (diameter ca. 3 nm, prepared by a modified Brust method,[9] -----). The isotherm of elaidic acid reflects the formation of a liquid-expanded (LE) phase immediately after deposition of this fatty acid on the water surface.[10] The monolayer of alkyl-capped Au NPs, on the other hand, forms a condensed phase. The compression isotherm of the mixed monolayer indicates a LE monolayer similar to pure elaidic acid but slightly shifted to higher molecular areas owing to the presence of the Au NPs.

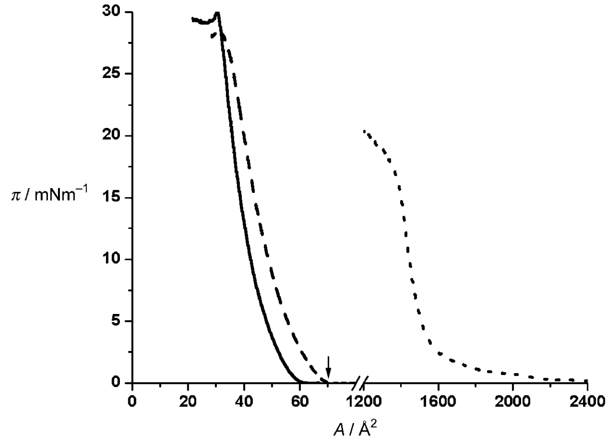

Figure 1. Compression isotherms at 22 °C. Pure elaidic acid (——), dodecanethiol-capped Au NPs (-----), and mixed monolayer of Au NP/elaidic acid (0.2% gold, ‒‒‒). The arrow indicates the molecular area in which irradiation experiments were carried out.

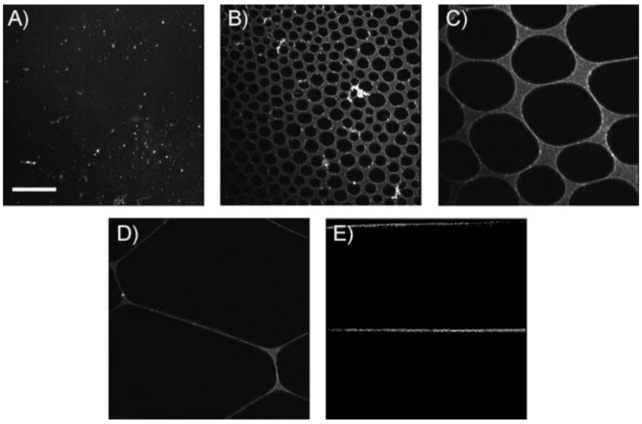

Figure 2. BAM images of Au NP/elaidic acid Langmuir monolayers at different laser intensities. The percentage values indicate laser power used for monolayer irradiation prior to image acquisition: A) 0%; B) 40%; C) 60%; D) 80%; E) 90%. Scale bar (corresponding to all images) is 100 μm. $T = 22$ °C.

We have further examined the fluid Au NP/elaidic acid monolayer in situ at a 0 mN m^{-1} surface pressure (indicated by the arrow in Figure 1) using Brewster angle microscopy (BAM, Figure 2). BAM analysis employs a circularly polarized laser to visualize monolayers formed at the air/water interface through the effects of the deposited substances upon the light refracted at the water/monolayer interface.[11,12] Figure 2 depicts BAM images recorded after exposure of the Au NP/elaidic acid films to differently modulated intensities of the BAM laser beam (wavelength of 532 nm, maximal power 50 mW).

The BAM images in Figure 2 demonstrate that modulation of the power of the laser beam irradiating the monolayer

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resulted in dramatic modifications of film structure. At nominally zero laser power (the image was recorded immediately after switching on the laser beam, Figure 2A) the BAM image indicates a rather homogenous monolayer displaying dull reflectance of the Au NPs randomly dispersed on the water surface. Examination of the same mixed monolayer after application of higher laser intensities, however, reveals a remarkable reorganization of the alkyl-capped Au NPs (Figure 2B–E). Specifically, irradiation of the monolayers with more intense lasing for approximately 60 seconds gave rise to an interconnected network of condensed Au NP regions (Figure 2B,C), which turned into highly uniform narrow wires that finally reached several millimeters in length (Figure 2D,E).

The laser-induced structured films exhibited high stability and could be transferred from water onto solid substrates without disrupting the Au organization. Figure 3 depicts BAM images obtained on glass substrates of Au NP/elaidic acid monolayers irradiated at different laser powers and subsequently transferred onto the solid surface. The images in Figure 3 demonstrate that the same highly-ordered Au structures were retained following transfer to solid surfaces.

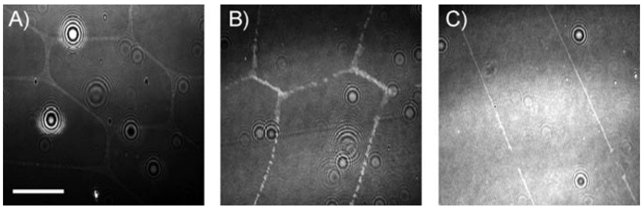

Figure 3. BAM images of mixed Au NP/elaidic acid films transferred onto glass substrates after irradiation with different laser intensities: A) 70%; B) 80%; C) 90%. Scale bar is 100 µm.

We further examined the sub-micrometer organization of the alkyl-capped Au NPs using transmission electron microscopy (TEM, Figure 4). The TEM images demonstrate that the microscopic Au wires observed in the BAM experiments (Figure 2D, E and Figure 3) comprise elongated and interconnected thin strips of Au NP assemblies. The thin "nanowires", each containing numerous Au NPs, are oriented in the direction of the microscopic strips, essentially forming their outer interfaces.

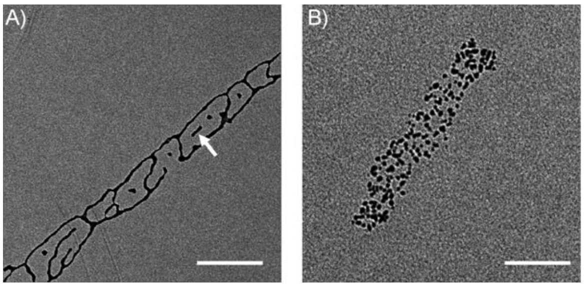

Figure 4. TEM images of Au wires. A) Section of a Au wire (scale bar 2 µm); B) magnification of a Au NP nanowire fragment showing the individual NPs (scale bar 50 nm).

To elucidate the factors responsible for the laser modulation of the film structures, we recorded BAM images of a mixed monolayer of dodecanethiol Au NPs and elaidic acid at zero surface pressure as a function of slight variations of the temperature of the water subphase (Figure 5). At a temperature of 22.0 °C the film displays reflectance of the Au NPs uniformly distributed on the water surface (Figure 5A). However, increasing the water temperature slightly to 22.5 °C (Figure 5B) resulted in dramatic segregation of the Au NPs, highly similar to the effect induced by laser irradiation (depicted in Figure 2). Further increase of the water temperature to 23 °C (Figure 5C) gave rise to organized structures of the Au NPs. It should be emphasized that the monolayer organizations recorded in Figure 5 were completely reversible and solely determined by the water temperature. Furthermore, if the temperature was set higher than 23 °C, the Au NPs formed solidified aggregates that did not subsequently dissociate.

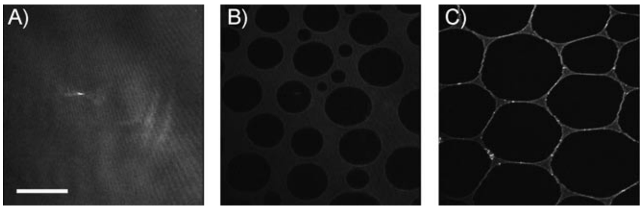

Figure 5. BAM images of Au NP/elaidic acid Langmuir monolayers at different temperatures. A) 22.0 °C; B) 22.5 °C; C) 23.0 °C. Scale bar is 100 µm.

The experiments presented in Figure 5 indicate that the structural reorganization induced by laser irradiation at different intensities can most likely be ascribed to local heating of the liquid-expanded Au NP/elaidic acid monolayers by the laser beam. The pronounced temperature-induced ordering of the Au NPs, apparent on both the millimeter scale (Figure 2 and Figure 3) and the sub-micrometer scale (Figure 4) is unique. The very small temperature range in which ordering of the Au NPs occurred suggests that a "phase window" exists in the liquid-expanded monolayer. In such a state of the monolayer, a slight increase in temperature disrupts the interactions between the fatty acids and embedded alkyl-capped Au NPs, leading to the formation of the highly organized two-dimensional Au NP structures stabilized by the attraction between the alkyl capping agents of adjacent Au NPs.

Overall, this study points to an intriguing phenomenon in which hierarchically ordered Au NP structures are induced by laser irradiation of mixed monolayers comprising Au NPs and fatty acids. Uniquely, ordering of the metal NPs was achieved only in the liquid-expanded (i.e. fluid) phase of the mixed monolayer. Such laser-modulated ordering could be exploited for construction of uniform long-range Au structures at the air/water interface. We have further detected similar organized Au NP structures in mixed monolayers containing other unsaturated fatty acids, underlining the generality and versatility of the concept.

Experimental Section

$HAuCl_4$, tetradecylammonium bromide, sodium borohydride, dodecanethiol, and elaidic acid were obtained from Sigma–Aldrich (St. Louis, MO) and used as obtained. Chloroform and toluene were HPLC grade (Frutarom Ltd.). Elaidic acid was dissolved in chloroform at a final concentration of 2 mm. The desired molar fraction (0.2 mol%) of Au NPs was achieved by mixing the appropriate quantities of parent solutions of each compound. The water subphase used in the Langmuir trough was doubly purified by a Barnstead D7382 water purification system (Barnstead Thermolyne, Dubuque, IA), at 18.3 mΩ resistivity.

Synthesis of the dodecanthiol-capped Au NPs was carried out according to the Brust procedure[13] with slight changes,[9] based on a two-phase (toluene/water) reduction of $HAuCl_4$ in the presence of the stabilizing ligand. Briefly, $HAuCl_4$ (100 mg) was dissolved in water (10 mL) and transferred to toluene (40 mL) by mixing with tetradecylammonium bromide (500 mg). Dodecanethiol (0.0147 mL) was added to the vigorously stirred solution. Finally, $NaBH_4$ (200 mg) in water (1 mL) was added. After 10 min the solution appeared dark brown, indicating the formation of Au NPs. The solution was stirred overnight to ensure completion of the reaction. The organic phase was washed with 2 m H_2SO_4 and water in a separation funnel and subsequently evaporated in vacuum to near dryness. The resultant dodecanethiol-capped Au NPs were precipitated by addition of ethanol (60 mL). After separation by filtration, the precipitate was washed three times with ethanol and once with 2-propanol and dried in vacuo to yield the Au NPs (34.9 mg) as a black wax, which was easily dissolved in chloroform (final concentration 3.12 $mg\,mL^{-1}$). The Au NPs were characterized by UV/Vis spectroscopy and TEM. The average diameter of the particles was approximately 3 nm.

All surface-pressure/area isotherms were recorded on a computerized Langmuir trough (model 622/D1, Nima Technology Ltd, Coventry, UK). The surface pressure was monitored using a 1 cm filter paper as a Wilhelmy plate. For each isothermal compression experiment, the desired amount of elaidic acid/Au NP mixture in chloroform was spread on the water subphase and equilibrated for 15 min, allowing for solvent evaporation prior to compression. Compressions were carried out at a constant barrier speed of 8 $cm^2\,min^{-1}$.

For TEM, films at the desired surface pressures were transferred horizontally onto 400 mesh copper formvar/carbon grids (Electron Microscopy Sciences, Hatfield, PA, USA). TEM images were recorded on a Jeol JEM-1230 transmission electron microscope (JEOL LTD, Tokyo, Japan) operating at 120 kV.

A Brewster angle microscope (NFT, Göttingen, Germany) mounted on a Langmuir film balance was used to observe the microscopic structures in situ. The light source of the BAM was a frequency-doubled Nd:YAG laser with a wavelength of 532 nm and 50 mW primary output power in a collimated beam. The BAM images were recorded with a CCD camera. The scanner objective was a Nikon superlong working distance objective with a nominal 10× magnification and diffraction-limited lateral resolution of 2 μm. The images were corrected to eliminate side-ratio distortion originating from a nonperpendicular line of vision of the microscope.

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