

Control of Anisotropy of Metal Nano-dots Arrayed on Glass Substrate via Photoexcitation under Applying Electric Field in Solution

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Large-scale and well-ordered Ag nano-dot arrays were prepared via improved nano-sphere lithography technique based on the spreading polystyrene particles onto water-air interface. A hexagonally closed-packed monolayer structure of polystyrene particles with relatively large area ($> 1 \text{ cm}^2$) was prepared on a glass substrate as a template for the preparation of well-ordered periodic triangular Ag dot array. The template was also used to fabricate rod-like chained Ag dots array. Optical absorption using polarized light shows clear optical anisotropy correlated with the polarization direction to long axis of the chained Ag dots array. The structure showed very strong Raman scattering at near-infrared excitation. The degree of anisotropy of the individual rod-like structure was increased via polarized photo-illumination under applying a static electric field in solution. Polarized light perpendicular to the long axis of the chained dots resulted in increase of the degree of anisotropy as well as uniformity of the array.

Key words: nano-sphere lithography, surface-enhanced Raman scattering, plasmon absorption, metal nano-dot array, near-infrared Raman, anisotropy

1. INTRODUCTION

Structural control of metal dots and rods in a size range less than 100 nm is one of most important targets at current nano-technology.¹ Although recently developed techniques via self-assembled processes,²⁻⁵ such as nano-sphere lithography (NSL)⁶⁻⁸, allow us to obtain well-ordered periodic super-structure in the corresponding size range, we now recognized that introduction of controlled anisotropy into these ordered structures is next important issue for novel device construction. To improve techniques for structural control, we have proposed a novel idea using localized photo-excitation process at metal nanostructures in solution.⁹⁻¹¹ The electromagnetic field induced by excited surface plasmon is highly localized, and the direction of its polarization can be controlled by changing the wavelength and polarization of illumination light. Thus, if the localized field can be utilized to induce electrochemical reactions, such as metal dissolution and deposition, the effect can be applied to change and/or control the metal nanostructures. We also proved that applying a static electric field in solution under the photo-excitation is useful to improve the efficiency of the photo-reaction.^{9, 10}

In this report, we improved the technique of NSL originally developed by P. Van Duyne *et al.*⁶⁻⁸ to prepare two-dimensional arrays of anisotropic Ag nano-dots in a large-scale. Characteristics of the optical properties of the array were investigated using different size of the polystyrene spherical particles as the template. After the optimization of the preparation conditions, the anisotropy was introduced to the Ag dot array via

repeated evaporations with the different angles between the surface normal of the sample substrate and the deposition beam. The deposition angles were also optimized to obtain relatively intense Raman scattering at near-infrared (NIR) excitation (785 nm). The size and anisotropy of the Ag dots in the array were tuned by the photo-illumination under applying a static electric field in solution.

2. EXPERIMENTAL

Periodic triangular-Ag dot arrays were prepared by NSL^{7, 8} or angle-resolved nanosphere lithography (AR-NSL)⁶ technique. The template was prepared using monodisperse polystyrene (PS) particles (Polysciences Inc.) with diameters from 3 μm to 350 nm. Aqueous PS solutions were concentrated to 10 wt.%, and then diluted by ethanol. As well as previously documented drop-coating method⁶⁻⁸, we adapted the other method using PS monolayers prepared on liquid-gas interfaces to improve the quality of the array.¹² The PS solutions (30 μl) were dropped on convex surface of a watch glass immersed in Mill-Q water (Fig.1 (a, c)). Thin water layer on the glass surface leads to uniform spreading of PS particles on the liquid-gas interface. After the spreading of PS particles to water surface, the layer was packed tight by the addition of 10 μl of 2% sodium dodecyl sulfate (SDS) aqueous solution. The change in the surface tension of the water around the PS layer results in the formation of well-ordered monolayers with low density of defects, dislocations, and vacancies on the liquid-water interface (Fig.1 (b, d)). The prepared monolayer with high quality was then

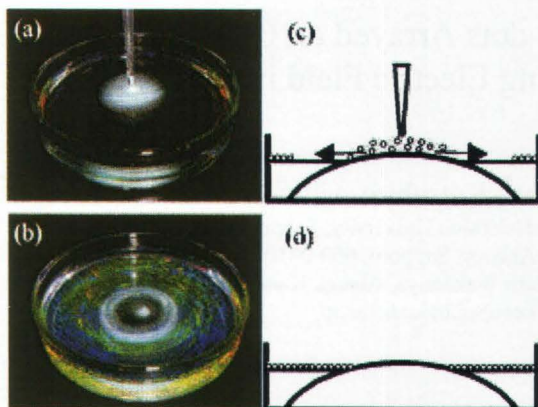


Fig. 1. Images of fabrication process; just after dropped solution containing PS particles ($D = 350$ nm) onto a top of the convex surface of the watch glass (a, c); after spreading on the surface of water surface and formation of closed-pack monolayer of PS particles (b, d).

lifted off from the water surface using cleaned glass substrate (Fig.2). The Ag films were deposited onto the PS monolayer prepared on the glass substrate. After the Ag deposition, the PS mask was removed by sonication in ethanol for 3 min.

Raman spectra were recorded using a commercial Raman microprobe spectrometer (System 2000, Renishaw) which was modified for NIR excitation. The light source was a continuous-wave, single-frequency semiconductor 785-nm diode laser. The expanded NIR beam was focused onto the sample using an water-immersion objective lens with 100 times magnification and a numerical aperture of 1.0 (Olympus). The estimated spot size of irradiation was ca. $1 \mu\text{m}$, with the output intensity of $30 \mu\text{W}$.

Application of an electric field to the Ag nanoparticle array on the glass immersed in solution was conducted employing a two electrode cell. Two platinum wires ($d = 0.5$ mm, 99.99%) separated by 2.5 cm were fixed onto a Teflon plate. The glass substrate of the Ag nanoparticle array was fixed in a square hole on the Teflon plate between the platinum wires. The surface plane of the glass substrate was adjusted to be parallel to the wires and the Teflon plate. The Ag nanoparticle array and the platinum wires were immersed in $1 \mu\text{M}$ KCl aqueous solution. Following immersion, an external electric bias voltage of 50 V was derived from a DC power supply.

3. RESULTS AND DISCUSSION

Compared with the conventional method via drop-coating, the method using spreading the PS layer on the air-water interface resulted in a successful preparation of well-ordered Ag dot array structure with

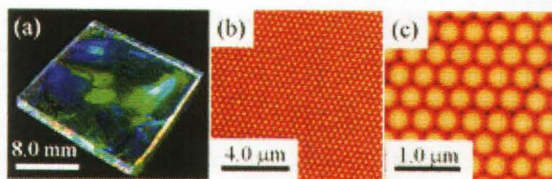


Fig. 2. Optical image (a) and AFM images (b, c) of closed-pack monolayer of PS particles on glass substrate.

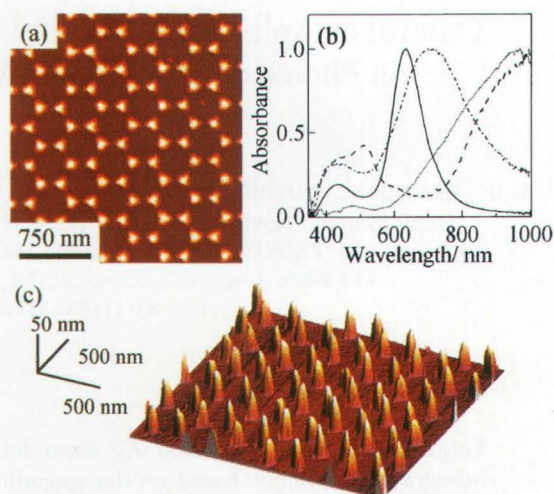


Fig. 3. (a, c) AFM images of triangular Ag dots array using 350 nm diameter PS particles; (b) absorption spectra of Ag dots prepared by PS particles with the diameter of 350nm (solid line), 600 nm (dot-dashed line), 750 nm (dotted line) and 1000 nm (dashed line).

relatively large areas ($> 1 \text{ cm}^2$) on a glass substrate. Fig. 3 shows typical AFM images of triangular Ag dot array and absorption spectra. The lengths of the perpendicular bisectors of the equilateral Ag triangles fabricated using PS particles with different diameters 350, 600, 750, and 1000 nm were ca. 130, 180, 250, and 300 nm, respectively. The heights of them were ca. 30 nm. Typical plasmon absorptions correlated to the sizes and the structures of Ag dots were observed.⁵⁻⁷ It should be noteworthy that the spectra were not dependent upon the observed area within ca. 1 cm^2 , indicating the uniformity of the structures of Ag dots as well as a well-defined periodicity of the arrays. As to the origin of the

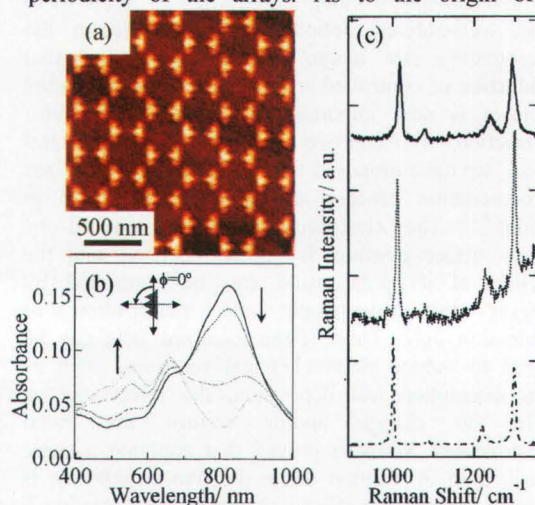


Fig. 4. (a) AFM image of chained Ag dot array ($D = 350$ nm, $\theta = 0^\circ, \pm 15^\circ$); (b) polarized absorption spectra (polarization angle to the long axis, ϕ , was change from 0° to 90° by 30°) (c) NIR Raman spectra of 4,4'-bipyridine; adsorbed on chained Ag dot array ($W_{\text{ex}} = 30 \mu\text{W}$, $t_{\text{ex}} = 5$ s; solid line), 20 mM aqueous solution ($W_{\text{ex}} = 1 \text{ mW}$, $t_{\text{ex}} = 500$ s; dotted line), bulk crystal ($W_{\text{ex}} = 1 \text{ mW}$, $t_{\text{ex}} = 500$ s; dashed line).

well-defined structure, contribution of the added SDS can be considered for change of the surface tension of the PS layer. Controlled packing of the PS particles on the air-water interface, induced by the addition of SDS, resulted in the formation of the well-ordered hexagonally closed-packed structure of the PS particles. The structure can be also maintained during the evaporation of water after the liftoff of the monolayer from the interface.

The uniformity and the periodicity of the Ag dot array were maintained after the repeated evaporation with different angles (θ) to prepare Ag chained structure (Fig. 4 (a)). Absorption spectra measured by polarized light showed two distinct peaks attributed to a transverse and a longitudinal mode (Fig. 4 (b)).^{6, 13, 14} When the polarization of the illuminated light coincides with the long axis of the chained structure, absorption maximum is observed at a longer wavelength. Polarized excitation with the short axis leads to absorption at shorter wavelength. The apparent change in the absorption maximum depending upon the polarization angle proves the formation of the well-ordered chained structure. In the present system, the well-aligned angle dependence of the polarization direction was observed at relatively large area ($> 1 \text{ cm}^2$). Although anisotropic Ag dots array structures prepared by drop-coating were already reported previously, the angle dependence was only observed at very limited and small areas, typically less than $25 \mu\text{m}^2$.⁶ The present result of large-scale anisotropy proves the advantage of the method at the air-water interface for the preparation of large-scale periodic array of Ag chained structure on a glass substrate.

The chained Ag dots array shows another very interesting optical property. The characteristic absorption at NIR region led to significantly enhanced Raman scattering from adsorbed molecules on the surface of the metal dot.¹ Fig. 4 (c) shows the Raman spectrum of bipyridine molecules adsorbed on the surface of the Ag dots array, comparing spectra measured under the conditions without enhancement. Raman scattering signals attributed the ring breathing mode and that coupled with C-H bond deformation of bipyridine molecules were enhanced significantly at the chained Ag dots array, even at relatively low excitation power (W_{ex}) and short exposure time (t_{ex}). An empirical signal enhancement factor, which was determined from the peak integration ratio of the SERS vibration at 1015 cm^{-1} to the unenhanced signal from the solution of a defined sample concentration, was found to be greater than 10^4 . Strong enhancement could be attributable to the chained Ag particulate with a unit size in ca. 100 nm. It is known that strong electromagnetic field localized at valley between connected metal particles leads to a significant enhancement in Raman scattering when an incident light energy matches to the excitation energy of a localized surface plasmon of the anisotropic structure.¹⁵⁻¹⁷ Relatively strong scattering from the chained Ag dots array shown here proves possible application as a sensor matrix for ultra-sensitive molecular detection.

Further structural tuning in the anisotropy of the chained Ag dots was achieved via polarized photo-illumination under applying an electric field in

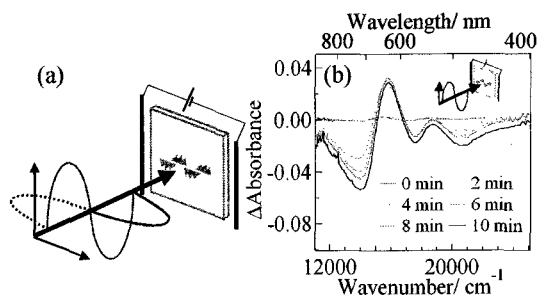


Fig. 5. Differential absorption spectra of chained Ag dot array under polarized photo-illumination applying an external electric field (20 V/cm) in 1 μM KCl aqueous solution; schematic illustration of the experiment was also shown. Measurements were performed six times at intervals of 2 min.

solution. Fig. 5 shows schematic presentation of the experimental setup. The illuminated light was polarized to parallel or perpendicular to the long axis of the chained structure. The structural change was monitored as the change in the optical absorption in visible to NIR region. Upon the illumination under applying electric field, the gradual change in absorption shown in Fig. 5 was observed. The changes were not apparent without photo-illumination or electric field. The addition of 1 μM KCl was also indispensable to induce the spectral change. The decrease in the absorption at visible and NIR region is attributable for the deformation of the chained Ag dots. We have shown that photo-induced dissolution and deposition processes of Ag nano-dots on the glass substrate can be accelerated by applying static electric field in solution.^{9, 10} The change in the absorption observed in the present system reflects the structural change of the chained Ag nano dots in the size range less than a few nm.^{13, 14}

The change in the anisotropy was characterized by polarized-light angle dependence of the optical absorption of the chained Ag dots array. Fig. 6 (a) shows polarized-angle dependence of the absorption maximum observed at several different samples of as-prepared chained Ag dots array. The clear angle dependence reflects the well-defined anisotropy of the chained Ag dots array.⁶ Difference between maximum peak wavenumber at the different angles also reflects the averaged aspect ratio of the chained Ag dots in the array.

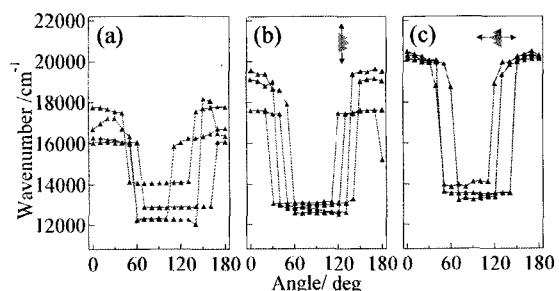


FIG. 6. Maximum peak wavenumber of polarized absorption spectra measured at different ϕ ; before photo-illumination and applying electric field (a), after photo-irradiation with the light polarized to parallel to the chain under applying electric field (b), after perpendicular photo-irradiation under applying electric field (c).

Approximately 4000 cm^{-1} of the maximum difference at the as-prepared sample agrees with previously documented value of chained Ag dots prepared by similar manner.⁵

After the photo-illumination under applying electric field for 10 min, the angle dependence was changed as shown in Fig. 6 (b), (c). Both at the parallel and perpendicular polarized illumination to the long axis of the chained Ag dots, the maximum peak wavenumber shifted to higher values. The differences between maximum peak wavenumber also increased to be approximately 6000 cm^{-1} . These changes in the optical properties after the polarized photo-illumination indicate that the anisotropy of the chained Ag dots increased by the present treatment.

We have proved that photo-illumination to metal nanostructures induces photoelectrochemical dissolution / deposition via plasmon excitation when the system is kept under appropriate electrochemical condition.¹⁸ In the case of the metal nanoparticle on insulating substrates, such as glass, the external static electric field accelerate the photoreaction.^{9, 10} At the present system, the degree of anisotropy of the chained dots was increased via selective excitation of the specific plasmon mode of the metal structure.

When the modified angle dependences achieved by the parallel excitation of the long axis (Fig. 6 (b)) is compared to those with perpendicular excitation (Fig. 6 (c)), the difference between the samples is fairly small at the latter case. The result indicates that polarized excitation perpendicular to the long axis of the chained Ag dots improves anisotropy as well as the uniformity of the structure of the chained Ag dots. Although anisotropy was also improved at the parallel excitation, the difference between samples is still large as comparable to those at as-prepared samples. The results demonstrate the effect of selective excitation of the specific plasmon mode on the structural control of the metal nano-dot structure. Characteristics of the optical properties imply that anisotropy of metal dots can be controlled in the size range less than a few tens of nm.

4. SUMMARY

Large-scale and well-ordered Ag nano-dot arrays were prepared successfully via improved nano-sphere lithography technique based on the spreading polystyrene particles onto the water-air interface for the preparation of a hexagonally closed-packed structure of polystyrene particles with relatively large areas ($> 1\text{ cm}^2$) as a template. Chained Ag dots arrays were also prepared by repeated evaporation using the template. The array shows clear optical anisotropy correlated with the polarization direction to the array structure. The structure showed very strong Raman scattering at near-infrared excitation. The anisotropy of the chained dots was improved via polarized photo-illumination under applying a static electric field in solution. Further improvements in the techniques for the control of nano-structure as well as uniformity of anisotropic arrays may lead to the preparation of novel devices for ultra-sensitive molecular recognitions.

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