One-dimensional Arrangement of Plasmonic Nanoparticle Chains by Marangoni Flow and Meniscus Recession

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Flexible Au nanoparticle chains were spontaneously aligned into a linear structure at several hundred micrometer scale during evaporation process. 1D alignment was achieved by using Marangoni flow and sequential meniscus recession. Evaporation speed and the incline of substrate strongly affected the resulting structures.

Because of the significant advance in fabrication techniques of nanoparticles for the last couple decades, a wide range of nanoparticles with unique electronic, optical, or magnetic properties can be easily produced with very good control over particle size and shape.[1–3] Since the apparent properties of nanoparticles are substantially affected by their spatial arrangement as well as their inherent characteristics, assembling and positioning nanoparticles at desired locations are important for constructing complex and higher-order functional materials and for modulating their collective properties. Controlled assembly using predefined templates[4] or solvent-drying-induced self-assembly techniques,[5,6] has been extensively investigated for spherical nanoparticles but barely for asymmetric nanoparticles such as nanorods or nanoparticle chains. Herein, we report spontaneous arrangement of long flexible Au nanoparticle chains deposited from a dilute solution during a drying process. Straight and one-dimensionally ordered Au nanoparticle chains at several hundred micrometer scale can be created on a hydrophobic substrate when drying rate and incline of substrate were carefully controlled.

Au nanoparticle chains encapsulated within worm-like block copolymer micelles were used in our experiments. Au nanoparticle chains show unique surface plasmonic properties which can be used as 1D optical conduits.[7] Preparation of straight and aligned nanoparticle chain structures is important for their applications. Au nanoparticle chains are prepared as previously described elsewhere.[7–9] Briefly, Au nanoparticles are first encapsulated within spherical polystyrene-*b*-poly(acrylic acid) (PS_{250}-*b*-PAA_{13}) block copolymer micelles, and then morphological transition of spherical to worm-like micelle was induced by adding 1-(3-dimethylamino)propyl)-3-ethylcarbodiimide methiodide (EDC) to form Au nanoparticle chains. The representative SEM images of Au nanoparticles encapsulated within spherical block copolymer micelles (Au@PS_{250}-*b*-PAA_{13}) and Au nanoparticle chains prepared from PS_{250}-*b*-PAA_{13} are shown in Figure 1. SEM images of Au@PS_{250}-*b*-PAA_{13} showed single, isolated nanoparticles surrounded by copolymer shells of uniform thickness (Figure 1a). As aqueous suspensions of these nanostructures (1 pM in particles) were exposed EDC, the Au@PS_{250}-*b*-PAA_{13} nanoparticles were progressively assembled into long 1D chains. The average length of Au nanoparticle chains was controlled at about one micrometer for our experiments. The formation of nanoparticle chain was also monitored by in situ UV–vis spectrum (Figure 1c). Owing to the surface plasmon coupling between adjacent Au nanoparticles within a chain, the absorption maxima of Au nanoparticle chains shift to longer wavelength. The average diameter of Au was 32 or 52 nm.

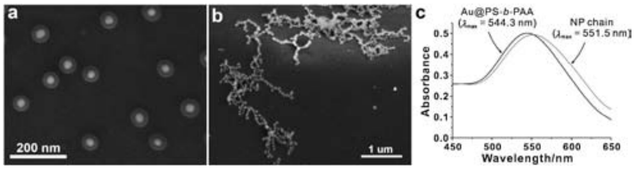


Figure 1. (a) SEM images of spherical Au@PS_{250}-*b*-PAA_{13} ($d_{Au} = 32 \pm 2$ nm). (b) SEM images of nanoparticle chains prepared from spherical Au@PS_{250}-*b*-PAA_{13}. (c) Absorption spectra of spherical Au@PS_{250}-*b*-PAA_{13} ($d_{Au} = 32 \pm 2$ nm) and nanoparticle chains.

To obtain regularly ordered Au nanoparticle chains, we used a solvent-drying-induced self-assembly method. Previous research has shown that an evaporative flux called Marangoni flow can be induced when solution is spread on a substrate forming a pinned contact line.[10–12] Temperature and surface tension gradients induced by nonuniform evaporation within a droplet cause outward flow and carry mass to the edge of the contact line. This Marangoni flow has been successfully used in the formation of close packed two- or three-dimensional arrays from spherical colloidal particles.[13,14] We have tried a similar method to assemble Au nanoparticle chains into an ordered structure. For that, fabricated Au nanoparticle chains were first deposited on a hydrophobic substrate (silicon wafer) from a dilute aqueous solution (5 µL, 1 pM in particles) and then slowly dried under ambient conditions. After completely dry, the morphology was characterized by SEM (Figure 2). SEM image showed a thick circular rim which consists of a large number of nanoparticle

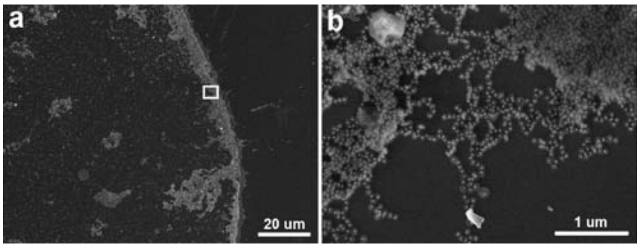


Figure 2. (a), (b) SEM images of nanoparticle chains deposited on a silicon wafer from a solution with a temperature of 25 °C. Image (b) is a zoom-up image of the rectangular area of image (a). Nanoparticle chains are randomly distributed in a circular dried region.

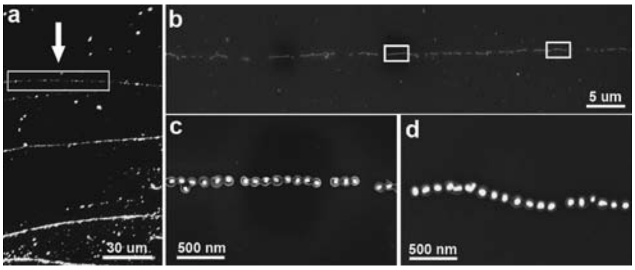
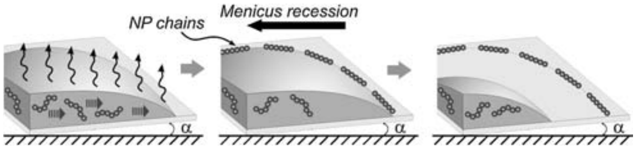


Figure 3. (a) A dark-field optical microscopy image of nanoparticle chains deposited from a hot solution ($T = 70\,^{\circ}\mathrm{C}$). The arrow represents the direction of drying. The highlighted area in a box is shown in right image (b). (b)–(d) SEM image of linearly aligned nanoparticle chains. Image (c) and (d) are zoom-up images of the rectangular region of image (b).

chains. Although it is known that Marangoni flow is weak for aqueous solution, the formation of a thick rim represents that nanoparticle chains migrated to the edge of the contact line by Marangoni flow. However, nanoparticle chains were not regularly arranged by this process. As shown in Figure 2b, nanoparticle chains at the rim were randomly aggregated. No directional order was observed at either the outer or inner part of circle. We attribute this poor ordering to difficulty in close-packing of long flexible chains and weak flow. Unlike colloidal particles, flexible nanoparticle chains are hard to be fitted into a crystal lattice because of their flexible and nonuniform characteristics.

We found that linearly arranged structures from nanoparticle chains can be easily prepared by a slightly modified solvent-drying-induced self-assembly method. We originally expected that the stronger Marangoni flow would be more effective to align nanoparticle chains parallel to the flow. As a way of increasing Marangoni flow, nanoparticle chain solution with higher temperature was deposited. Since the thermal Marangoni stress increases with increase of evaporation speed, a stronger Marangoni flow can be achieved at the higher solution temperature.[11] Interestingly, most nanoparticle chains were aligned normal to the radial direction when a hot solution was deposited. Additionally, unlike the previous case shown in Figure 2, multiple circular lines were found and most nanoparticle chains were aligned on these lines. We postulated that these multiple rings were formed by sequential recession of the meniscus. To facilitate such sequential meniscus recession, nanoparticle chain solution was deposited on a slightly inclined substrate. The dark-field optical microscopy and SEM images shown in Figure 3 were obtained after depositing 5 µL of Au nanoparticle chain solution (70 °C) on a hydrophobic silicon wafer inclined by 10°. SEM images showed that nanoparticle chains are straight and linearly aligned, forming single rows rather than random aggregations. Both line thickness and extent of arrangement in each line varied along the radial direction. In general, the outer ring shows thinner thickness and better arrangement.

Based on our best understanding, we attribute such one-dimensional alignment of nanoparticle chains to combined effects of Marangoni flow and meniscus recession as illustrated in Scheme 1. As shown in Scheme 1, when hot nanoparticle chain solution is deposited on a substrate, nanoparticle chains migrate outward and aligned at the forefront of the contact line.[10] The prealigned structure at the contact line can be locked with a following recession of meniscus. Since the amount of nanoparticle chains migrated to the contact line is dependent on the interval of sequential meniscus recessions, aggregation can be prevented by inducing fast meniscus recession. The interval can be easily controlled by the degree of incline (α). The linearly aligned nanoparticle chains at several hundred micrometer scale without aggregations was achieved at a certain slope of substrate ($\alpha = 10^{\circ}$). Sparsely distributed nanoparticle chain arrays were observed at higher slope, and thicker and more aggregated structures were observed at lower slope.



Scheme 1.

In conclusion, we have successfully demonstrated one-dimensional alignment of Au nanoparticle chains at several hundred micrometer scale by simple solvent-drying-induced self-assembly method. We currently investigate continuous solvent-drying-induced assembly methods to extend our work in macroscopic pattering of Au nanoparticle chains and optical properties of nanoparticle chains prepared on silicon wafers.

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