Nucleation and growth of nano-gold colloidal lattices

Toshihiko Sato*[a] David Brown[b] and Brian F. G. Johnson[b]

[a] *Hitachi Cambridge Laboratory, Hitachi Europe Ltd., Cavendish Laboratory, Madingley Road, Cambridge, UK CB3 0HE*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*

A two-dimensional array of 10 nm gold colloidal particles is formed by a submonolayer deposition technique using a bifunctional aminosilane followed by a mobility-restoration treatment with alkanethiol, converting the disordered submonolayer deposition to a highly-ordered two-dimensional array.

Driven by interest in the quantum-confined electronic properties of nanometer scale metal/semiconductor particles, the investigation of nanostructured materials is becoming an exciting area of interdisciplinary research. The device application[1,2] of these nanostructured particles requires techniques of ordering particles in one-, two- or three-dimensional structures; such requirements for nanoarchetecture provide challenges to sample preparation technology. Recently, a method for depositing nanometer-scale gold colloidal particles on SiO_2 surfaces was demonstrated using alkylsiloxane molecules as an adhesion agent.[3] The self-limiting nature of this method stopped the deposition at submonolayer coverage density. The compatibility of this method with conventional electron beam lithography was tested and the deposition was carried out only on prescribed positions on the substrate surface. Further, highly-ordered, hexagonally-packed two-dimensional (2D) lattice formation was observed by the electrophoretic deposition of a colloidal gold from the bulk solution onto a carbon-coated electron microscope grid.[4] It was also shown that metal particles including gold and other transition metal clusters can form densely packed monolayers on electron microscope grids when they are ligated by organic surfactant molecules.[5]

In this work, the method of forming a hexagonally-packed 2D lattice of nanoparticles on a SiO_2-grown Si substrate is described using a gold colloid solution in combination with organic surfactant treatments of both the substrate and colloid particles. We have been successful in performing surfactant ligation of the gold colloidal particles after they are immobilised on a substrate surface by a bifunctional aminosilane. By this reaction scheme, the switching between mobile/immobile conditions takes place in the gold colloid adsorption.

This method starts with the submonolayer coating of a SiO_2 surface with 10 nm gold colloidal particles (GCP) from solution (*viz.* a citrate sol with an average size of *ca.* 10 nm and a size variation of *ca.* 10% standard deviation prepared according to the recipe described in ref. 6) using the method described in ref. 3. A Si substrate covered with a thermally-grown SiO_2 (200 nm thick) was cleaned by brief (*ca.* 30 s) oxygen plasma ashing. Immediately afterwards, the sample was immersed in a 2.3 mM aqueous solution of a bifunctional aminosilane [*i.e.* 3-(2-aminoethlyamino)propyltrimethoxysilane, APTMS [$(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$] for 5 min. After the APTMS immersion, the sample was rinsed in two distilled water baths, dried with a nitrogen gun, and placed in a 120 °C oven for 30 min to complete Si–O bond formation. The APTMS treatment replaces the hydroxy groups (OH) adsorbed on the SiO_2 substrate with APTMS molecules forming a siloxane bond between the Si on one end of the APTMS molecules and an oxygen atom on the SiO_2 surface. As a consequence, the amino group attached on the other end of the APTMS molecule is oriented away from the substrate. These amino groups on the APTMS molecules immobilise gold particles onto the substrate because of the affinity of the amino group to the gold [see Fig. 1(*a*)].[3]

The APTMS treated sample was then immersed in the GCP for 8–12 h, rinsed with two distilled water baths, and dried with a nitrogen gun. This procedure gave a sub-monolayer coating of the GCPs. Since immobilised particles on the substrate are still covered with ionic adsorbates of citrate ions,[7] there is always an electrostatic repulsive force between the colloidal particles. Therefore, the GCP deposition automatically stops before it reaches a close-packing density.[3] Fig. 2(*a*) shows a scanning electron micrograph of the submonolayer coated sample (the observation was carried out using S-900, Hitachi, which has an in-lens type electron optics and a cold cathode electron gun). The micrograph demonstrates a disordered particle deposition with the inter-particle spacing of 10–50 nm.

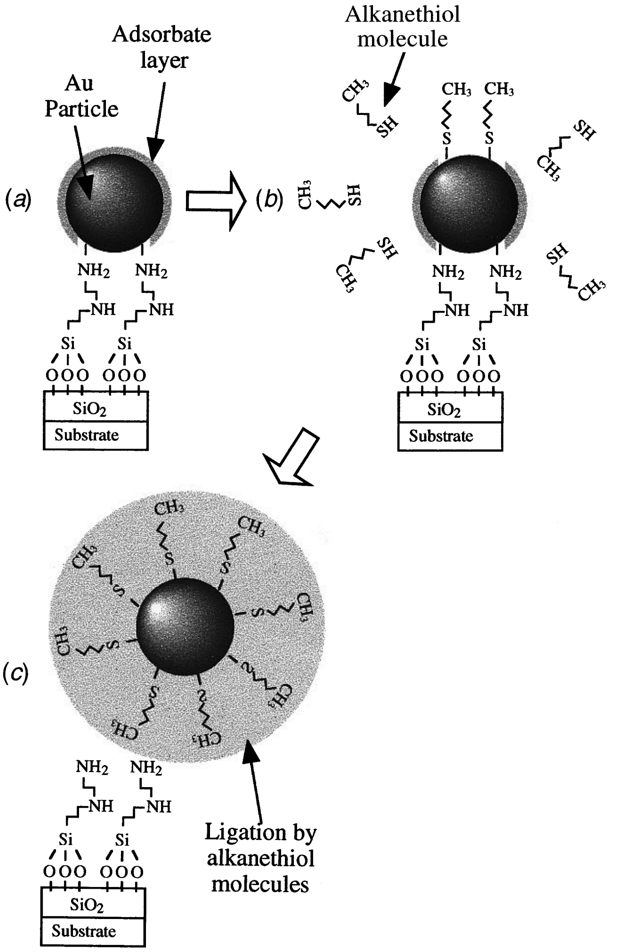

Fig. 1 Mobility restoration mechanism by a displacement reaction. (*a*) Gold colloidal particle immobilised by a bifunctional aminosilane. (*b*) Ligation of gold particles by alkanethiol molecules displacing the adsorbates and Au–NH_2 bonds. (*c*) Mobility restoration by complete ligation of the gold particle.

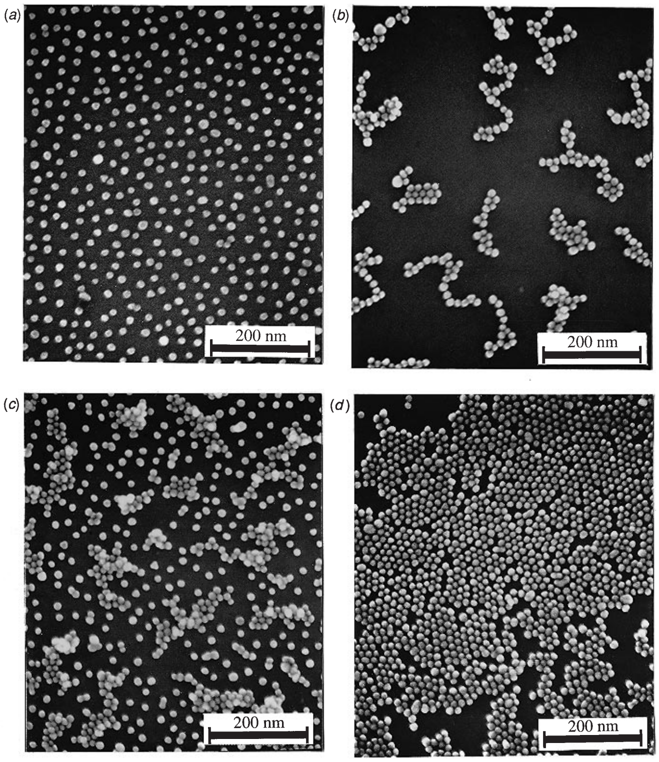

Fig. 2 Scanning electron micrograph observation of the gold particle crystal nucleation and growth. (*a*) Disordered submonolayer deposition of gold particles from a gold colloid solution using a bifunctional amino silane. Nominal particle size is 10 nm (10% standard deviation). (*b*) Nucleation of gold colloidal crystal initiated by the mobility restoration reaction induced by alkanethiol treatment. (*c*) Additional particle supply from the gold colloid solution on the vacant sites between the nuclei formed in the previous process. (*d*) Highly-ordered two-dimensional gold particle lattice formed by the repetitive application of gold colloid immobilisation and disorder-to-order conversion.

After the sub-monolayer GCP coating, an alkanethiol treatment was carried out to initiate the nucleation of the 2D structure of GCPs. The sample was immersed in a 5 mM ethanolic solution of dodecane-1-thiol $[Me(CH_2)_{11}SH]$ for *ca.* 24 h, and rinsed with an ethanol bath, and dried with a nitrogen gun. Because of the strong affinity of sulfur to gold, this treatment replaces citrate adsorbates with the alkanethiol molecules [Fig. 1(*b*)]. In addition to the adsorbate removal, the bonding between the sulfur and gold can even displace the bonding between the amino group and gold. This results in the complete ligation of the gold particle with alkanethiol molecules [Fig. 1(*c*)]; as a consequence, since the molecular binder of the bifunctional aminosilanes are detached from the gold particles, once immobilised particles are now released from the substrate and acquire some mobility on the substrate surface.

Because of the restored surface mobility, particles move and collide with each other on the substrate surface. However, because of the short-range steric repulsion due to the alkanethiol ligation, the particles will not undergo diffusion-limited aggregation which results in 'fractal' structures;[7] instead, they form hexagonally-packed ordered nuclei and grow two-dimensionally given the particle supplies from the migration of GCPs on the substrate surface. Fig. 2(*b*) shows a scanning electron micrograph of a sample after the alkanethiol treatment showing the initiation of ordered 2D nuclei.

Fig. 2(*b*) also shows that the nuclei are deposited with substantial spacing between them. These vacant areas are expected to be covered with the bifunctional aminosilanes. Therefore, when the sample is immersed in the GCP solution again, additional particles can land on those vacant spaces from the GCP solution and are immobilised on the substrate. Fig. 2(*c*) shows a scanning electron micrograph of the sample after the second GCP solution immersion. Individual GCPs are filling the vacant spaces with similar inter-particle distances to that of the first GCP solution immersion.

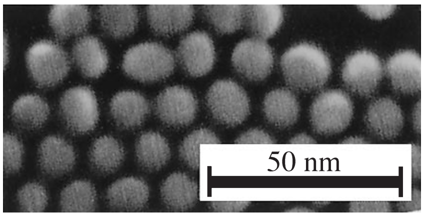

Fig. 3 Scanning electron micrograph of a highly-ordered two-dimensional array of 10 nm gold particles

Then, the alkanethiol treatment are applied to the sample after the second GCP solution immersion in order to mobilise them and grow the nuclei larger. In this sense, the second GCP solution immersion is playing a role supplying additional materials for the growth of GCP grains. Repetitive application of the GCP immersion with the subsequent alkanethiol treatment enlarges the GCP grain size further. After four repetitions, the grains with different orientations are connected with each other and reach a continuous film of GCP with a densely packed two-dimensional order as is shown in Fig. 2(*d*). Further repetition of the GCP immersion and alkanethiol treatment, however, did not improve the monolayer coverage density; instead, multilayer growth becomes dominant.

From micrographs with a greater magnification as shown in Fig. 3, the average gap between the particles is estimated to be about 2 nm, which is about the twice the thickness of a self-assembled monolayer of dodecanethiol on Au(111) (*i.e.* 1.2 nm).[8] This confirms that the inter-particle distances are determined by the steric repulsion between the alkanethiols attached on the gold particle surfaces.

In conclusion, a highly-ordered two-dimensional array of 10 nm gold particles was formed by the surfactant treatment of both the substrate and gold particles. A bifunctional amino-silane treatment of the substrate immobilised the gold particles from a gold colloid solution with a coverage density of a submonolayer. Subsequent alkanethiol treatment converted the disordered deposition to an ordered one by giving surface mobility to the gold particles. Repetitive applications of immobilisation and disorder-to-order conversion grew the two-dimensionally ordered GCP grains until they were connected together.

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