Formation of a Three-Dimensional (3D) Structure of Nanoparticles Using Langmuir–Blodgett Method

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A new approach was proposed to prepare 3D structure of nanoparticles. A kind of ordered superlattice of nanogold was created layer by layer by LB technique. The UV–vis spectra monitored its formation. The TEM images and small-angle X-ray diffraction confirmed the ordered structure.

Particles show various interesting properties[1] that are not observed in the bulk form of a material. For instance, photonic crystals can be constructed by monodispersed particles. In order to apply these novel properties for future devices, particle arrangement methods to produce desired particle assemblies must be developed.

In the past research, an approach had been explored to form 3D ordered structures of nanoparticles, the ligand-induced nanocrystal superlattice formation in colloidal solution.[2,3] An almost perfect example was provided by Zhao et al.[2] They prepared ordered semiconductor Ag_2S nanostructures by using the dodecylthiol as the structure-directing agent. However, the method was difficult to control because of the weak recognition between molecules. On the other hand, some techniques, such as self-assembly, LB technique, and so on could be also used to prepare ordered structures, however, in the past reports, these nanostructures used to be ordered layer by layer[4,5] or have regular particle array on plane.[6–9]

In the letter, we proposed an approach to prepare 3D array of nanoparticles by LB technique. Firstly, a kind of ordered passivated-nanogold monolayer was formed on a LB trough. Then the monolayer was transferred onto solid substrates layer by layer. During the transfer, an organic small molecule was assembled onto the interlayers. Thus, a mixed-molecule-coated nanogold multilayer was built up. The structure was confirmed to be ordered both on plane and in layer by layer by TEM images and small angle X-ray diffraction measurement. This offered a manner to form 3D array of nanoparticles.

The monodispersed nanogolds modified with octadecylamine (ODA) as a surfactant were prepared according to the literature.[10] The nanogolds with a 6.8 nm mean diameter were obtained by size-selective-precipitation[10] and the standard deviation of the particles was 0.69 nm. About 400 μL of the 0.5 mg·mL^{-1} colloid particles in chloroform was spread on the water surface by a 100 μL syringe. After the solvent volatilized, the nanogold particulate monolayer was compressed and expanded repeatedly for several cycles on the LB trough with a barrier. The LB trough was from JiLin University in China. The pressure was from 5 to 10 mN/m. The procedure resulted in the formation of a homogeneous and ordered monolayer of particles. Then the monolayer was transferred onto a pre-hydrophobilized quartz substrate by a vertical LB technique at the pressure of 10 mN/m. After the substrate was dried, it was dipped into 1-phenyl-5-mercaptotetrazole (PMT) aqueous solution (1×10^{-5} mol/L) for 15 min, then the substrate was taken out, washed with distilled water and dried; after this, another monolayer was deposited from LB trough to the substrate again, and then treated with PMT; the process was repeated until the required layers. The formation of the multilayer was monitored by UV–vis spectra measurement in a UV-160IPC Shimadzu instrument. All operations were carried out at about 20 °C.

Figure 1a shows the ODA-coated nanogold monolayer. It exhibits ordered particle structure, which was formed owing to the nature of nanogold, the procedure of compression and expansion cycles on LB trough and the appropriate temperature. After the nanogolds were further modified with PMT again, the ordered structure still remained (Figure 1b).

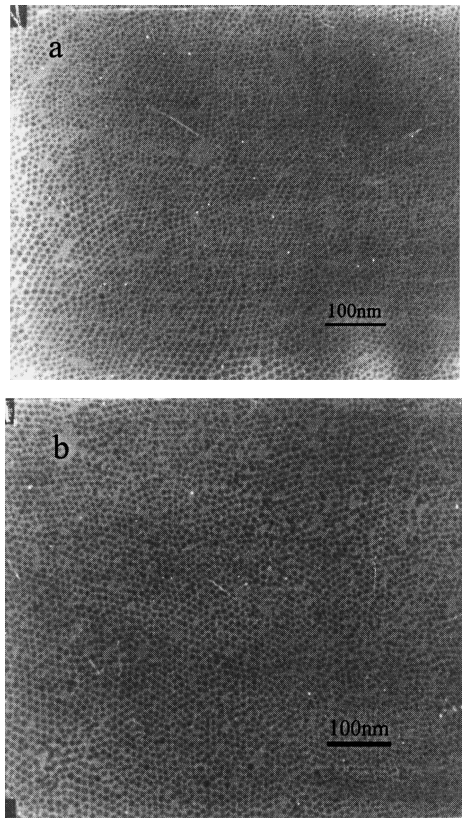


Figure 1. (a) TEM image of ODA-coated nanogolds. (b) TEM image of ODA- and PMT-covered nanogolds.

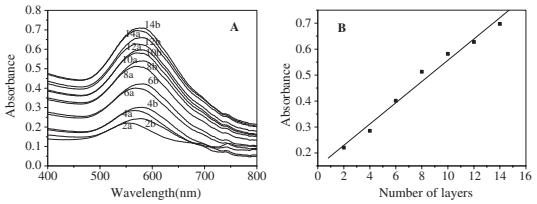


Figure 2. (A) Optical absorption spectra of the multilayer for the 2nd, 4th, 6th, 8th, 10th, 12th, 14th layer (a) before and (b) after the adsorption of PMT. (B) The absorbance at λ_{max} (spectra (a) in Figure 2a) was plotted as the function of the number of layers in the multilayer.

Figure 2A showed the UV–vis spectra of the multilayer, it could be seen that curves (b) were red-shifted compared with curves (a), which showed that PMT was assembled into the layers. The assemblage of PMT slightly changed the original optical properties of ODA-coated nanogold film, which arised from the interaction of nanogold and –SH in PMT. In addition, PMT, as one kind of organic molecules, was assembled into the structure and enriched the construction of the multilayer. Figure 2B showed a good linear relationship between the maximum absorbance of nanogold monolayers transferred from LB trough and the number of layers, which showed the monolayer on LB trough was efficiently transferred.

In order to further investigate the structure of the multilayer, a small-angle X-ray diffraction (SAXRD) pattern of the multilayer was recorded (Figure 3). The experiment was carried out in the Savitzkey–Golay's mode using Cu Kα radiation on a DMAX 2000 diffractometer operating at 40 KV and a current of 100 mA and scanning at $2\theta/^\circ = 0.6$–10°. The pattern showed a very sharp Bragg peak (001), which indicated the multilayer was ordered layer by layer. The peak corresponded to a distance of 11.6 nm. The distance was almost consistent with the value estimated for the particle array in a hexagonal close-packed structure (Scheme 1). If the diameter of the particle was 13.6 nm, and

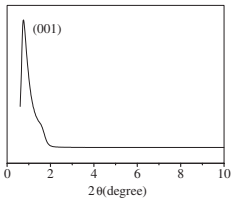
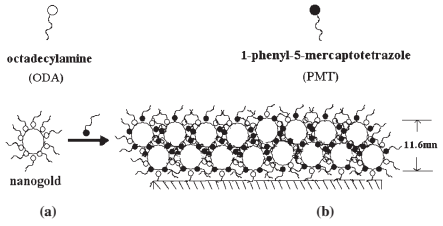


Figure 3. Small-angle X-ray diffraction pattern of a 7-layer multilayer on a quartz substrate.



Scheme 1. Schematics of (a) a nanogold and (b) a lateral view of a unit cell of the superlattice.

the particles were hexagonally close-packed, the period would be 11.8 nm.

In order to visualize the ordered layers, a cross-section plane of the multilayer (5 layers) deposited on a piece of organic glass was viewed on a transmission electron microscopy (Tech Nai Philips instrument) operated at 120 KeV. The sample was prepared by embedding the multilayer into an epoxy resin. The section with thickness as thin as 70–80 nm was cut using an ultramicrotomy with a diamond knife. The image of the cross-section plane was showed in Figure 4A. It was a string of "superclusters." The magnification of one part was showed in Figure 4B. From the image, although the array between layers was not very perfect probably because of the disturbance from the preparation process of the sample for the observation, parallel alignment of particles was still observed. In order to get more regular image, a suggestion was the improvement of the preparation of samples. In addition, if some molecules, such as polyelectrolyte with big molecular weight, not PMT, were assembled into the interlayers, the distance of layers would maybe increase, and it would be more obvious to observe the ordered layer structure. These ideas were in the further experiments.

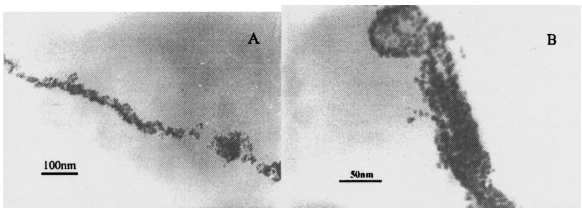


Figure 4. (A) the cross-section plane image of the multilayer (5 layers) deposited on a piece of organic glass. (B) the magnification of one part of Figure (A).

In summary, in this letter, we built up a 3D array of nanoparticles by LB technique. This opened a gateway to form ordered system in nanoparticle architecture. And this method was also a good exploitation for the LB technique.

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