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SHORT COMMUNICATION

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Fractal metal nanoparticle aggregates morphology formation mediated by polyelectrolyte/surfactant complex films at interfaces

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Abstract In this work, the gold nanoparticle self-assembly behavior of mica-surface-confined polyelectrolyte/surfactant complex films was investigated. First, modified partially hydrated polyacrylamide (MHPAM)/hexadecyltrimethylammonium bromide (CTAB) complex films were deposited on the mica surface using Langmuir–Blodgett technique. Then, the preadsorbed MHPAM/CTAB complex film mica plate was dipped into the gold aqueous solution and the interesting fractal nanostructured gold network was formed. In addition, the effect of dipping time on gold nanoparticle self-assembly morphology was studied. The mechanism of formation process is briefly proposed.

Keywords Self-assembly · Polyelectrolyte/surfactant · The fractal

Introduction

Metal nanoparticle assembly into one, two, and three dimensions has recently been of great interest due to their unique optical, electronic, and magnetic properties [1–6]. Numerous papers have been published for the construction of metal nanoparticle assembly. Among them, one-dimensional nanoparticle assembly is one of the most popular research fields due to its potential applications in optics and as an interconnect product in small-scale devices [7–9].

While these methods represent a significant advancement, they have predominately focused on the ordered structures of nanoparticle assembly; very little is known about the disordered structures of nanoparticle assembly. Such disordered structure is named 'fractal pattern'. Metallic fractal patterns play important roles in many physical processes, especially toward future nano-optics [10]. In a fractal system, the strongly multiple scattering of electromagnetic waves causes a great change in the photon-transport behaviors and this phenomenon has got the name 'Anderson localization of light', similar to photonic crystal [11]. However, only a few papers have been focused on the preparation of metallic fractal nanoparticle assembly despite their potential applications in optics. Campion and Kambhampati [12] reported a large enhancement of Raman scattering from the metallic fractal clusters. Safonov et al. [13] reported the formation of silver nanoparticle fractal aggregates with highly localized laser-excited optical modes. Samuelson et al. [14] more recently described the synthesis of branching fractal 'nanotree'. The process involves the self-assembled growth of nanoparticles via the vapor–liquid–solid growth mode, followed by the sequential seeding of branching structures. Therefore, investigations on the fractal morphology of metal nanoparticle assembly are worthwhile for more detailed theoretical and technological studies. We report herein a type of the fractal nanostructured gold network aggregates of a mica-surface-confined polyelectrolyte film. The mechanism of formation process is also proposed.

Experimental section

Materials Hexadecyltrimethylammonium bromide (CTAB) was of analytical reagent grade (Beijing Xi Zhong Chemical Factory) and was purified by extraction with diethylether followed by three phases of recrystallization from anhydrous ethanol. After recrystallization, there was no minimum in a plot of surface tension vs concentration [trisodium citrate (Fisher), $HAuCl_4 \cdot 3H_2O$ (Sigma), and $NaBH_4$ (Mallinckrodt)]. Modified partially hydrated polyacrylamide (MHPAM) with a molecular weight of

0.8×10^7 g mol^{-1} was obtained from Beijing Hengju Chemical Agent and used without further purification. The structure of MHPAM is shown in Fig. 1.

Preparation of preadsorbed MHPAM/CTAB complex film on mica surface The surface pressure (π)–surface area (A) isotherm of a spread film was obtained by an LB trough (length × width 700×40 mm, FACE HBM, Japan) equipped with a Wilhelmy plate for monitoring the surface pressure. The entire film balance is trapped in a container to avoid contamination and air currents. The accuracy on the surface pressure is ±0.1 mN m^{-1}. Before each experiment, the trough was thoroughly cleaned with acetone and dichloromethane. The surface area was compressed by moving a Teflon barrier at the speed of 20–25 cm^2 min^{-1}.

Owing to good solubility in water, CTAB or MHPAM molecules alone cannot form a stable monolayer at the air–water interface. However, the strong electrostatic interactions between the negatively charged –COO– groups along the MHPAM chains and CTA^+ headgroups make MHPAM/CTAB complexes able to form a stable film at the air–water interface. The MHPAM/CTAB complex films were obtained as follows.

CTAB was dissolved in chloroform to make a 1.0-mM solution, and then 100 μl of CTAB solution were dropped on the subphase MHPAM aqueous solution interface (c=0.01 mg ml^{-1}) with a microsyringe. A 5-min period was allowed for solvent evaporation before compression was started. The π–A isotherm is shown in Fig. 2. Figure 2 clearly confirms the coadsorption of MHPAM and CTAB molecules at the air–water interface and the formation of highly surface-active MHPAM/CTAB complex films. Then, the MHPAM/CTAB complex films were compressed to the surface pressure of 12 mN m^{-1}. The freshly cleaved mica plate was brought down horizontally by hand to touch the monolayer and lifted carefully after a contact time of a few seconds. This is the so-called horizontal lifting method [15].

Preparation of aqueous Au nanoparticles A 20-ml aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M trisodium citrate was put in a conical flask, and then 0.6 ml of ice-cold, freshly prepared 0.1 M $NaBH_4$ solution was added to the solution while stirring (Fig. 3). The color of the solution turned to pink immediately after adding the $NaBH_4$ solution, indicating particle formation with a diameter of about 4.8 nm as confirmed by transmission electron microscopy (TEM, JEM 100CX).

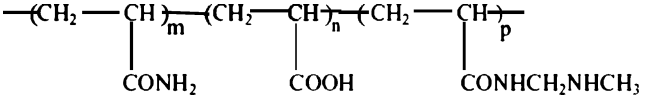

Fig. 1 Structure of MHPAM

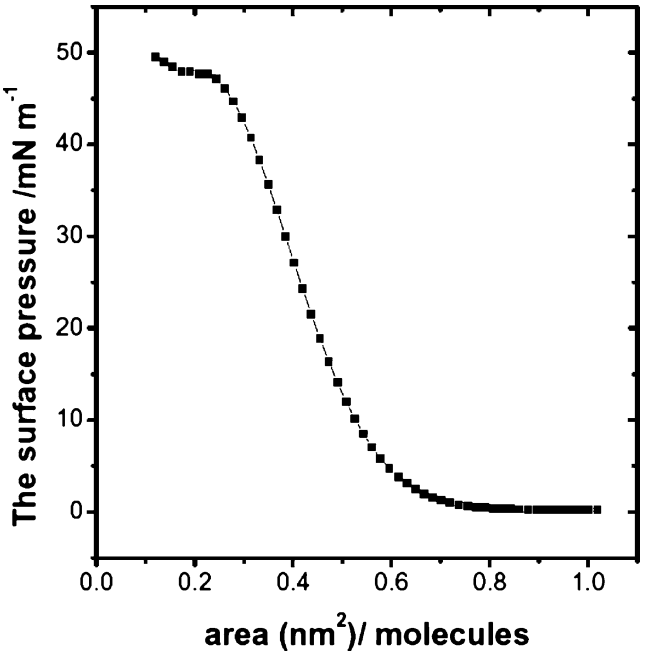

Fig. 2 Isotherm of surface pressure vs mean molecular area

Atomic force microscopy (AFM) A Nanoscope IIIa AFM (Digital Instruments, CA, USA) was used for imaging the morphology of the CTAB/MHPAM complex films on

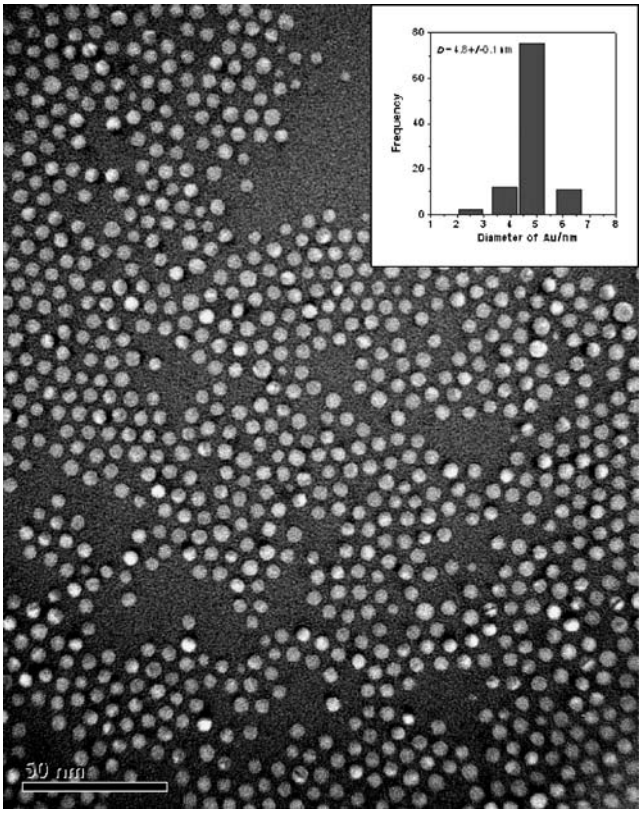

Fig. 3 The size distribution of aqueous Au nanoparticle

mica surfaces. All images were captured using silicon cantilever in tapping mode. Each mica sample was freshly cleaved just before use. The AFM image is shown in the height mode without any image processing except flattening.

Results and discussion

Figure 4 shows the AFM image morphology of MHPAM/CTAB complex films adsorbed to mica surfaces from the interface between the air and the MHPAM aqueous solution. Mica surface is observed to form closely packed nanofiber film morphology. As we have known, there are two approaches that could be expected to produce the assembly of nanoparticles mediated by polyelectrolytes. First, nanoparticle assembly could be prepared by in situ generation of metal nanoclusters by the chemical reduction of a metal salt contained within a polyelectrolyte matrix. The polyelectrolyte matrix not only acts as a template for their synthesis but also imparts the necessary stability by providing a barrier against agglomeration of the metallic nanoparticles formed during and after the reduction process. The second approach involves the assembly of polyelectrolyte scaffolds at first and then the nanoparticles are adsorbed to the polyelectrolyte chains. The latter approach is relatively simple and effective. In our experiments, the closely packed nanofiber film morphology of a MHPAM/CTAB complex film could be formed on mica substrate from the descriptions above. In addition, the functional groups $–CH_2NHCH_3$ of MHPAM molecules have high affinity to Au [16]; it is reasonable to expect that gold nanoparticle assembly can be performed using the latter approach.

Figure 5 shows a typical sequence of AFM images of gold nanoparticles assembly mediated by MHPAM/CTAB complex film at various times after the preadsorbed MHPAM/CTAB complex film mica plate was dipped into the aqueous gold solution and dried rapidly by a stream of nitrogen. Larger changes were found in complex film morphology. When the mica plate modified by the MHPAM/CTAB complex film was dipped into gold aqueous solution, water molecules wet the mica surface and destroy the intactness of complex film, which results in the formation of holes in the complex film, as shown in Fig. 5a at 2 s. The cross-section profiles of Fig. 5a show the height and width of some holes on the mica surface. In addition, a few gold nanoparticles are bound to the complex films. With the dipping time increased, at 5 s more water molecules continue to wet the mica surface and push the MHPAM/CTAB complex films into changing to string morphologies; the nanoparticles adsorbed accumulate along the direction of the strings and the fractal gold nanoparticle network structure is formed. Figure 5b clearly shows that the strings of MHPAM/CTAB complex films are interconnected, leading to the formation of the fractal

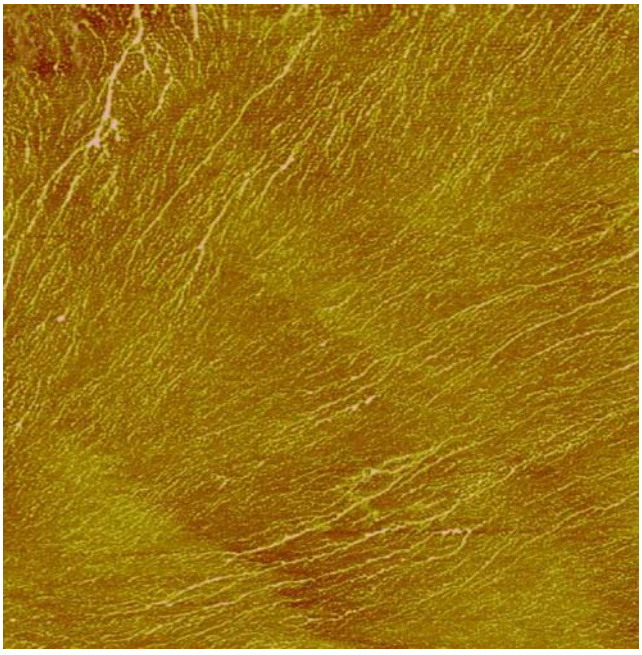

Fig. 4 A representative AFM image of MHPAM/CTAB complex film adsorbed to mica surface. The scanned areas are 2,000×2,000 nm^2

gold nanoparticle network morphology. The gold nanoparticle shows a height of about 4.5 nm in cross-section profiles of Fig. 5d, which is in very good agreement with the TEM images of Fig. 3. With the elapse of time, however, the wetting interaction forces between water molecules and mica surfaces rupture the interconnection of the strings and destroy the fractal network structures to some extent. The image of Fig. 5e, observed at 15 s, clearly shows that the strings of MHPAM/CTAB complex films are broken at their weakest points, and the fractal gold nanoparticle network structures are somewhat destroyed. Figure 5f shows that the interconnection of strings of the MHPAM/CTAB complex films is completely destroyed. The separated MHPAM/CTAB/Au complex aggregates are randomly distributed on the mica surface. The network structures are eventually completely destroyed.

The formation mechanism of the observed structure is a two-step process: an initial wetting effect [17] of water molecules on the hydrophilic mica surface during dipping stage and the complete evaporation of water droplets rapidly upon further drying by a stream of nitrogen when the mica plate was taken out of the solution. Our experimental method is actually similar to the water-droplet-assisted method reported elsewhere [18–22], in which the formation of nanoporous or microporous structures of polymer films was reported. In their studies, the polymer dissolved in volatile solvent was dropped onto the substrate. The evaporation of the solvent caused a cooling on the polymer solution surface. As a result, the water vapor was condensed into water droplets at the

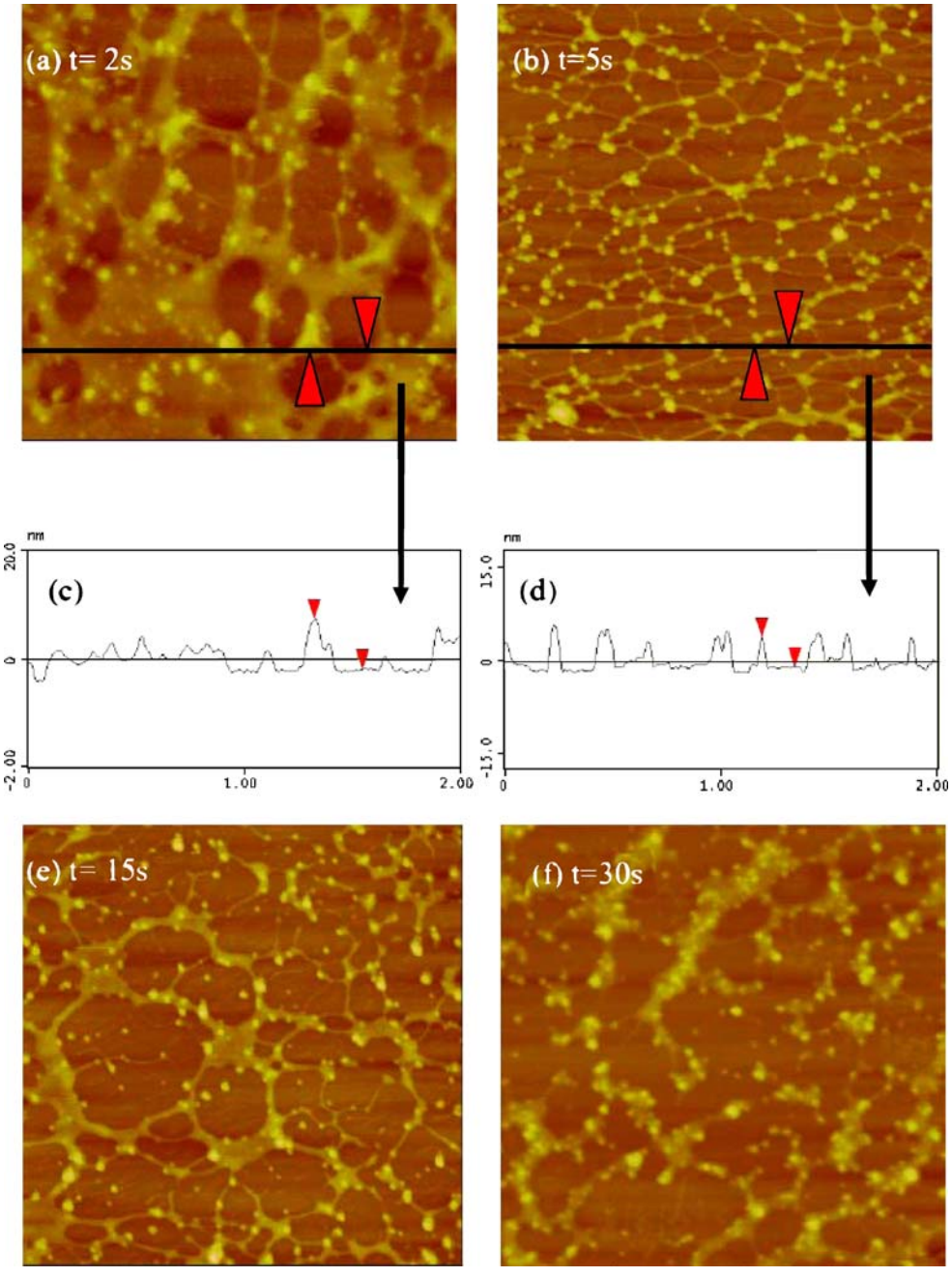

Fig. 5 Series of AFM images of the morphological change process of gold nanoparticles assembly mediated by MHPAM/CTAB complex film on a mica surface at various times. The scanned areas are 2,000×2,000 nm^2

polymer solution surface. After the complete evaporation of the solvent and water, traces of water droplets still remain in the polymer film, leading to an observed porous structure. Here in our experiment, the water molecules were similarly inevitably presented in the preadsorbed MHPAM/CTAB complex film on mica surfaces during the dipping stage. When the mica plate was lifted up from the solution, the water molecules changed into the water drops and the rapid evaporation of water droplets left the observed structure morphology on mica surfaces. From the above results, it seems that the dipping time has a big effect on the gold nanoparticle assembly morphology. By controlling the appropriate dipping time, we believe that results on other nanoparticle organizations can also be achieved such as that of Ag, Pt, and Pd.

Conclusion

In this paper, the fractal gold nanoparticle network aggregates morphology was formed on the mica surfaces. We presented the effect of dipping time on the morpho-

logical change process of gold nanoparticle assembly mediated by MHPAM/CTAB complex films and explained the formation mechanism in terms of the water-droplet-assisted method on the mica surfaces. By controlling the appropriate dipping time, it is possible to obtain the metallic fractal aggregates of nanoparticles. Such fractal patterns enable them to have potential applications in nano-optics.

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