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Dendritic Polyelectrolyte-Metal Nanoparticle Complex Aggregates At The Air-Water Interface

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ABSTRACT

Gold nanoparticles are bound to modified partially hydrolyzed polyacrylamide (MHPAM) chains in solution. However, it is interesting to observe that MHPAM-Au complex molecules in solution can be adsorbed to the air-water interfaces to form the dendritic aggregate morphology by addition of Au nanoparticles at interfaces as sorbents using Langmuir-Blodgett technique. The formation mechanism was briefly illustrated

KEYWORDS

Gold nanoparticles;
Dendritic aggregate;
Air-water interfaces.

INTRODUCTION

The structure and morphology of molecules at interfaces has attracted a great deal of attraction because of their importance for practical applications. Examples of applications include mesoporous materials[1], template for nanofabrication[2-7], and nanoscaled metal patterns[8-11]. Significant effects have been made to study the fascinating subjects at interfaces. Among them, the combination self-assembly of polyelectrolyte and nanoparticles at interfaces has been studied extensively[12-16], as they can be used to fabricate nanocomposites and nanopatterning materials fundamental for delivery devices, to control the absorption of nanoparticles into biological cell in gene therapy[17-19], and to do with the flocculation and retention purpose in papermaking processes[20]. From a fundamental point of view, it is interesting to investigate how the conformation of polyelectrolyte and nonaparticle complex is changed and the factors that control the conformation at interfaces.

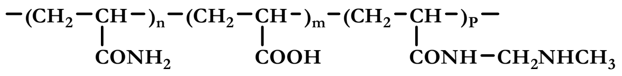
In this work, we observed a novel dendritic morphology formation of a polyelectrolyte (modified partially hydrolyzed polyacrylamide, MHPAM) and gold nanoparticle complex in microsize range on copper grids transferred from the air-soluti on interface.

MHPAM-Au complex molecules in solution can be adsorbed to the air-water interfaces to form the dendritic aggregate morphology by addition of Au nanoparticles at interfaces as sorbents using Langmuir-Blodgett technique. The formation mechanism was briefly illustrated.

EXPERIMENTAL

Chemical

Trisodium citrate, $HAuCl_4 \cdot 3H_2O$ and $NaBH_4$ were purchased from Sigma. Water used through the experiment was purfied by a MilliQ system. All the chemicals were analytical grade. Modified partially hydrated polyacrylamide (MHPAM) was obtained from Beijing Hengju Chemical Agent Co., Ltd, and used without further purification. The structure of MHPAM is shown in figure 1.



$-(CH_2-\underset{CONH_2}{CH}-)_n-(CH_2-\underset{COOH}{CH}-)_m-(CH_2-\underset{CONH-CH_2NHCH_3}{CH}-)_P-$

Figure 1: The structure of MHPAM

Synthesis of Au nanoparticles

3-5nm hydrophilic gold nanoparticles were prepared by the citrate reduction of $HAuCl_4$[21]. A 20 mL aqueous solution containing 2.5 x 10^{-4} M HAuCl4 and 2.5 x 10^{-4} M trisodium citrate was prepared in a conical flask. Next, 0.6 mL of ice-cold, freshly prepared 0.1M$NaBH_4$ solution was added to the solution while stirring. The solution turned pink immediately after adding $NaBH_4$, indicating particle formation. Hydrophobic octadecylamine functional gold nanoparticles were synthesized as follows:[22]

The octadecylamine in an amount of 0.54 g was dissolved into 180mL chloroform. Next, a 0.01mol·L^{-1} $HAuCl \cdot 4H_2O$ solution in 20 mL of chloroform was prepared and added to the octadecylamine solution. The mixture was then sonicated for at least 2 h in the dark, following which, a 0.1-mol·L-1 $NaBH_4$ solution in 20 mL ethanol was added dropwise under rapidly stirring, during which the mixture had an instant color change from light yellow to dark orange/brown. Then the mixture was continuously sonicated for 2 h before the reaction was stopped. Once there action was stopped, the mixture was reduced in volume to about 5 mL by rotary evaporation. The particles were precipitated from chloroform by adding 400 mL anhydrous ethanol and standing at –20°C for 20 h. Then the purple precipitate was filtered with a 0.45mm PTFE filter film, washed with an access amount of ethanol and dried to give about 40 mg product.

Procedures

LB films were formed as follows: 20ml Au nanoparticle colloid solution (d=3~5nm, C=0.4mg/ml) was added to 730ml MHPAM aqueous solution (0.01mg/mL) and placed for 24h to equliulid. A total of 750ml mixed solution was injected into LB trough (FACE HBM, LB Films, JAPAN). Chloroform solution of octadecylamine functionalized gold nanoparticle(0.4mg/ml,100μl) was spread on the subphase and LB film were compressed with a compressing speed of 5cm²/min after 5min for the evaporation of the solvent. Then a carbon-coated copper grid was brought down horizontally by hand to touch the resulting LB films and lifted carefully after a contact time of a few seconds at the desired surface pressures, and transferred LB films of Au-MHAPM complexes were observed by transmission electron microscopy (TEM, JEM 100CX) operating at 100KV.

RESULTS AND DISCUSSION

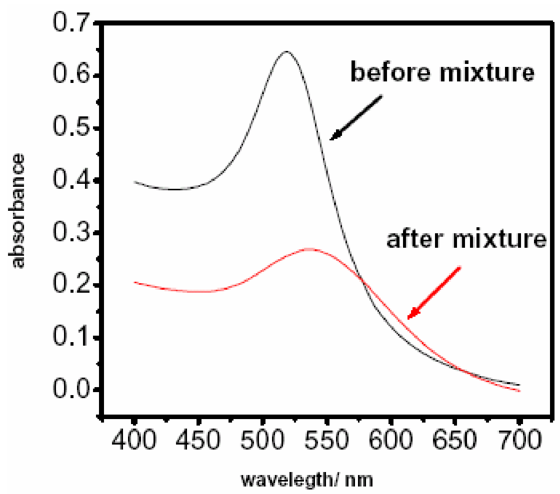


Figure 2: UV-vis spectra of Au nanoparticles before and after the mixture with MHPAM solution

The optical adsorption of Au nanoparticles before the mixtures of Au nanoparticle colloid solution with MHPAM solution shows a peak at 513nm, as show in figure 2a. After the mixture,a apparent shift in the surface plasmon band from 513 to 525nm was observed, as shown in figur 2b. This shift indicted that Au nanoparticles were bound to the MHPAM chains in solution, although the number of Au nanoparticles attached to each individual MHPAM chain has not yet been determined.

TEM images of the resulting LB films of MHAPM-Au complexes transferred onto the carbon-coated copper grids at 12mN/m were observed (see figure 3). For the films transferred, The MHPAM-Au complex molecules were observed to form the morphology of dendritic clusters. Morphologies in our systems are quite similar to in shape to fractal

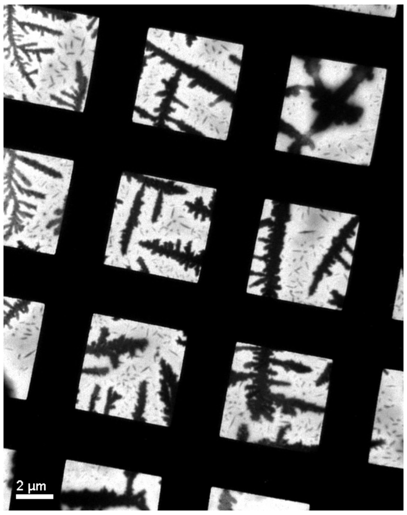


Figure 3: TEM images of Au-MHPAM complexes at various pressures

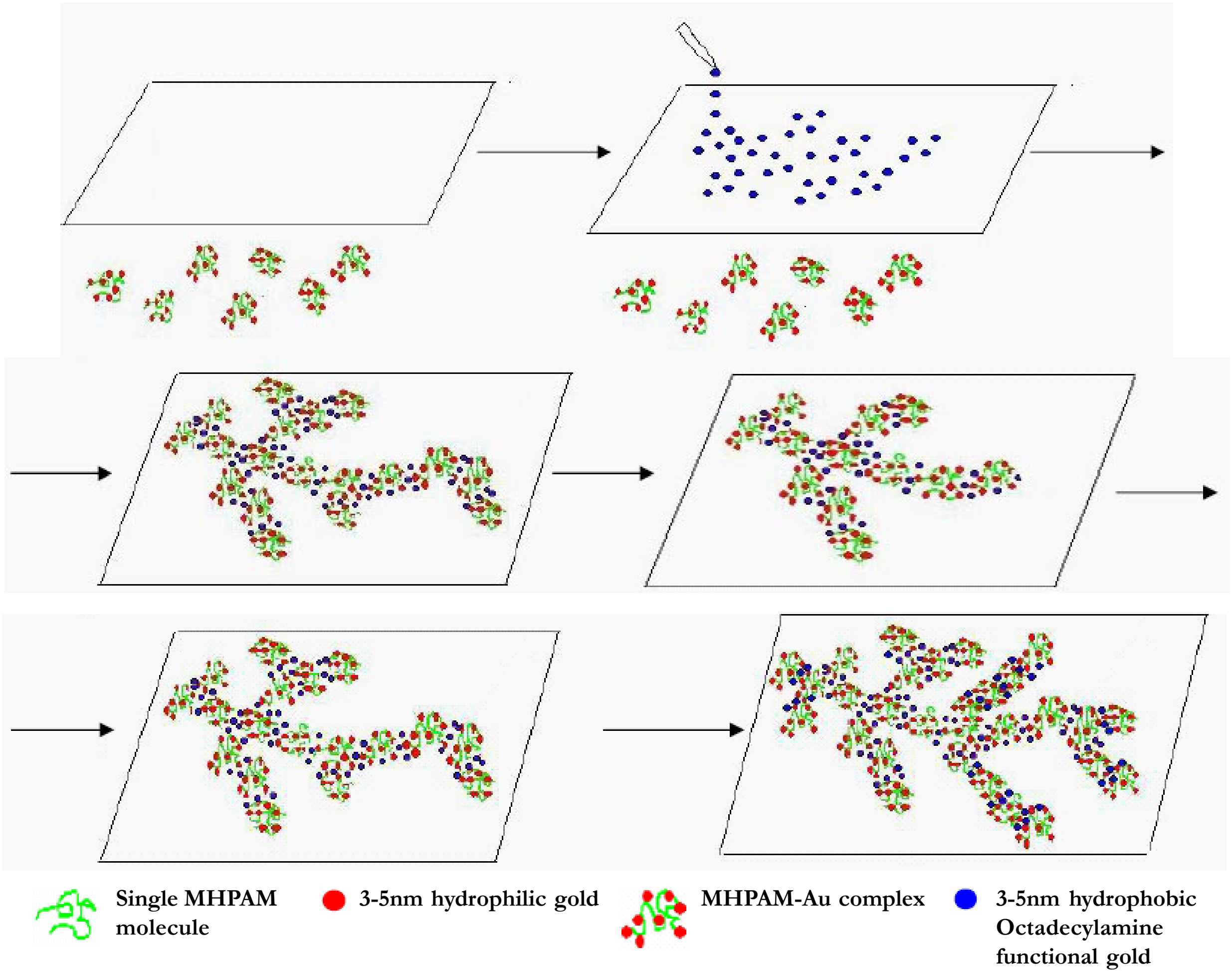


Figure 4: Schematic representation of the growth of Au-MHPAM complexes into fractal dendritic patterns at the air-water interfaces

patterns observed in other systems, practically such as metal dendrites grown by electrodeposition[23,24], two-dimension crystallites grown on a rough surface[25], dendritic crystal grown[26]. Generally, fractals are generally observed in far-from-equilibrium growth phenomena, however, the formation mechanism in our experiments is unlike.

An experimental model is employed to demonstrate the growth process of these dendritic aggregates (figure 4). Gole nanoparticles in solution are attchement to the MHPAM chains due to the strong affinity of Au for the functional groups $-CH_2NHCH_3$[27]. The MHAPM-Au complex molecules show the conformation of coil. When other Au nanoparticles are spread on the air-solution interface, these particles act as absorbates to absorb the MHAPM-Au complex molecules to the air-solution interface from the solution. With the increase of the surface pressure and the delay of time, the possibility of bumps between these molecules increases, this results in the rapid growth of the aggregation. With time elapse, the growth process of these aggregates is countinely in progress and finally microsize morphology of dendritic patterns at the air-water interface is formed.

It is important to note that the formation of dendritic pattern is a result of anisotropy of Au[28]. In the present experimental system, Au nanoparticles of MHPAM-Au complexes are essential for the process of the aggregations. The single crystals of Au particles intrinsically contain a strong crystalline anisotropy. Thus the processes that both Au nanoparticles at the air-water interface absorb MHPAM-Au complex molecules from the solution and clusters-clusters aggregation at the air-water interafce take place along the preferred growth direction. On the other hand, the large MHPAM-Au complex clusters have lower mobility, and they can't change their position or growth direction freely under the agent of anisotropy and grow strictly along the preferred growth direction. Conquently, the final aggregation patter is dendritic. The similar growth behavior of the resulting morphology is decriesed elsewhere[29]. It should be further noted that, when the other experimental procedures is same expect that Au nanoparticles weren't added into the MHPAM solution, the dendritic morphology of LB films wasn't observed. This further indicated that Au nanoparticles in solution played an important role in forming the dendritic patterns at the air-water interface.

CONCLUSION

In this paper, a novel dendritic morphology of the MHPAM-Au complex was observed at the air-water interface. Meanwhile, a possible mechanism is given to meet its occurrence. Au nanoparticles play important role in process of the formation of this pattern, and act as "guide" to induce the aggregating process along the preferred growth direction. Such dendritic patterns enable them to have many conceivable potential applications.

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