Synthesis of Micronsized Gold Nanoplates at Low Precursor Concentration Using Ionic Liquid as Novel Subphase Solvent

Han Jia and Hongtao Zhou

Abstract—The micronsized gold nanoplates were successfully synthesized under Langmuir monolaver of 1-hexadecyl-3-methylimidazolium bromide (C16mimBr) when the room temperature ionic liquid ethylammonium nitrate (EAN) was used as the novel subphase solvent. Due to strong electrostatic interaction, the C₁₆mim⁺ cations can arrange closely at the EAN surface to form a compact monolayer. At the low precursor concentration, the sizes of obtained gold nanoplates in EAN solution are much larger than that in aqueous solution. The effects of the novel subphase solvent were further demonstrated with the assistance of the energy calculation methods. The delicate equilibrium among nucleation, diffusion and growth rates plays the key role in the formation of larger nanoplates. By the control experiment with a cationic fluorocarbon surfactant, the mechanism was proposed and further demonstrated.

Index Terms—Langmuir monolayers, Ionic liquid, subphase solvent, gold nanoplates.

I. INTRODUCTION

Due to the excellent physical and chemical properties, effective catalysis and great optic properties, gold nanomaterials have been more and more researched in recent years. And these applications are closely related to the shape and size of the particles [1]. Even since the first scientific research of colloidal gold particles by Michael Faraday in 1850s, gold nanoparticles with various shapes have been synthesized through different methods, such as nanowires, nanorods, nanorings, nanoplates and other branched nanocrystals [1]-[4]. Among the above nanostructures, the main interest in the two-dimensional gold nanosheet relies on their potential applications in the fields of the electrochemistry and new nanodevices [5]. Because the intrinsic properties of nonspherical gold nanostructures are highly dependent on their size and shape [6], it is very important to learn how to tune them according to the reaction conditions. Besides, due to the high price of noble metal, it is the most important and challenging part to obtain the nanostructures at lower precursor concentration. Nanoplates with diameters larger than 1 µm are comparatively uncommon [4], and it may be more difficult at lower precursor concentration. There are a large number of techniques used to prepare shape-controlled gold nanoparticles [4], [7]-[9]. Wang et al. demonstrated a facile method to fabricate gold plasmonic microstructures based on the combination of colloidal lithography and a nanotransfer printing method. Poly(dimethylsiloxane) PDMS hemisphere arrays were fabricated through colloidal lithography and used as a "stamp" for the nanotransfer printing [9]. Compared with other methods, the well-defined Langmuir film provides an opportunity to control the formation of nanoparticles in one step. But the obtained nanostructures are lack of variety due to the limit of the 2D air/water interface. Recently, we combined the seed-mediated growth and Langmuir-Blodgett technique to prepare gold nanostructures via a novel two-step procedure [10]. Various gold nanostructures were first pre-formed in aqueous solution by using cyclodextrin as both reducing and capping agent. Due to the continuous growth of the pre-formed gold nanostructures at the air/water interface with the help of the Langmuir monolayers of 1-hexadecyl-3-methylimidazolium bromide, the morphology changes can be observed obviously. In the present work, we try to change the subphase solvent to further develop the traditional Langmuir-Blodgett technique, which has been scarcely reported.

It has been extensively studied to use the ionic liquids (ILs) in solvent extraction and organic catalysis, while it is beginning to use ILs in inorganic synthesis. ILs are a family of non-conventional molten salts that can act as templates and precursors to inorganic materials, as well as solvents [11]. The room-temperature ILs were used to prepare the gold nanostructures widely [12]-[14]. Hierarchical, three-fold single-crystalline gold symmetrical, dendrites were synthesized on different metal substrates including Al, Zn, and Ni in a mixture of ethanol and water with the assistance of an ionic liquid. Structural characterizations suggested that the obtained gold dendrites were grown along the <211> directions, which were seldom reported [13]. Huang et al. prepared three-dimensional dendritic gold nanostructures via an ultrafast one-step homogeneous solution method. Cationic surfactants, decane-1, 10-bis(methylpyrrolidinium bromide), were used as the capping agent and ascorbic acid was used as the reducing agent [14]. But the use of ILs in Langmuir technique as subphase solvent has been scarcely reported.

In this present study, we fabricated the micronsized gold nanoplates at the subphase concentration of 10^{-4} M when the ILs were used as the subphase solvent. Moreover, the bonding energies between HAuCl₄ and solvents were calculated using molecular mechanics to further verify the possible

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mechanism.

were applied [19], [20].

II. EXPERIMENTAL METHODOLOGY

A. Chemicals

 C_{16} mimBr was synthesized according to the literature method [15]. In a typical synthesis, an excess of 1-hexadecylbromine (33.41g, 0.128 mol) was mixed with 1-methylimidazole (10.26 g, 0.125 mol). The mixture was put into a 250 mL flask, refluxed at 75-80 °C for 48 h, then cooled to room temperature. Dichloromethane was removed by using a rotary evaporator under reduced pressure, leaving a white waxy solid. The product was further purified by recrystallization from ethyl acetate at least four times and dried under vacuum for 24 h. The purity of the product was ascertained by an 1HNMR spectrum in CDCl₃.

EAN was synthesized as described by Zhao *et al.* [16]. A portion of 3 M nitric acid was slowly added to the ethylamine solution while stirring and cooling in an ice bath. Water in the resulted solution was first removed with a rotary evaporator and then with a lyophilizer (MartinchristerALPHA1-2). The residual water content of the final product was determined by Karl Fischer titration to be 0.7 wt %, and its melting point was about 11 ℃.

HAuCl₄ and other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd and used as received. And other chemicals related to the synthesis were purchased from ACROS and used as received.

B. Synthesis and Characterization of Gold Nanoplates

The pressure-area (Π -A) isotherm was recorded on a NIMA 611 (Britain) rectangular trough. The subphase concentrations of HAuCl₄ EAN solutions were 10⁻⁵, 10⁻⁴, and 10⁻³ M. After evaporating the spreading solvent for 15 min, the Langmuir monolayers were compressed at room temperature at a continuous barrier speed of ca. 10 cm/min. For the formation of gold nanoplates, an appropriate amount of HAuCl₄ EAN solution was added into a chemostat, and then an appropriate amount of C₁₆mimBr chloroform solution was spread onto the surface of the HAuCl₄ EAN solution with a microsyringe. After the solvent was allowed to evaporate for 15 min, it formed a monolayer with a certain surface pressure. Then the chemostat was put into a desiccator (use as a reaction container) with some aqueous formaldehyde at the bottom. The system was allowed to react for one day at ambient temperature. After the reaction, the nanoparticles formed at the air-water interface were transferred onto Formvar-covered copper grids and quartz slides by the Langmuir-Schafer method for characterization with transmission electron microscopy (TEM) (JEM-100CX II (JEOL)) and UV-vis spectroscopy (HITACHI U-4100), respectively.

C. Calculational Process of the Binding Energy

The calculations were performed with the module Dmol³ of Materials Studio 5.0 package [17], [18]. The generalized gradient approximation (GGA) in the form of the Perdew and Wang exchange-correlation functional (GGA-PW91) for geometry optimization and in the computation of energies

III. RESULTS AND DISCUSSION

Fig. 1 shows the surface pressure-area (Π -A) isotherms of C16 mimBr monolayers formed on the surfaces of pure EAN and the different concentrations of HAuCl₄ in EAN solutions. Surprisingly, the four isotherms almost overlap, which is different from the previous reports [4], [10]. Besides, the limiting molecular areas of C₁₆mimBr in the monolayers are measured to be 11 $Å^2$, which is much smaller than before [4], [10]. When the ionic liquid is used as the subphase solvent, there must be much strong electrostatic interaction between C_{16} mim⁺ and the solvent ions. Due to the relatively low HAuCl₄ concentration, the electrostatic interaction between $C_{16}mim^+$ and $AuCl_4^-$ cannot effectively affect the whole system, resulting in the similar isotherms. If the interaction between C₁₆mim⁺ and the solvent ions can overcome the repulsive forces among C₁₆mim⁺ cations, the C₁₆mim⁺ cations can arrange closely at the surface to form a compact monolayer. Then it is reasonable to find the much smaller limiting molecular areas of C16 mimBr at the surfaces of EAN or the HAuCl₄ EAN solutions.



Fig. 1. Surface pressure-area (II-A) isotherms of monolayers with different subphase solutions.



Fig. 2. TEM images of gold nanoparticles measured 24 h after preparation at a subphase concentration of (a) 10^{-5} M, (b) 10^{-4} M and (d) 10^{-3} M. (c): Size distribution histogram of the obtained gold nanoplates at the subphase concentration of 10^{-4} M. The inset shows the corresponding electron diffraction pattern of a single hexagonal gold nanoplate.

As shown in Fig. 2, the different gold nanostrutures are obtained when the concentrations of HAuCl₄ in EAN solutions are varied. If the HAuCl₄ concentration is much lower (10^{-5} M) , there is tendency for the irregular gold nanoparticles to connect with each other, as well as some shattered nanoplates (Fig. 2a). As the concentration is increased to 10⁻⁴ M, the well-defined triangle, truncated triangle and hexagon gold nanoplates are the main products, which are micronsized with a mean diameter of 4.47 $\pm\,0.29$ um (Fig. 2b-c). The inset of Fig. 2b shows the related SAED pattern obtained by focusing the electron beam on the gold nanoplates on the TEM grid. The SAED pattern reveals that the hexagonal symmetry diffraction spot pattern is generated, indicating that the gold nanoplate is a single crystal with a preferential growth direction along Au {111} plane. When the HAuCl₄ concentration is high (10^{-3} M) , the shapes of gold nanostructures are almost unchanged, and the size is slightly increased. Besides, the thickness of nanoplates is also increased (Fig. 2d). While the water was used as the subphase solvent and the concentration of HAuCl₄ was low (10^{-4} M) , the nanoplates about 500 nm were obtained [4]. If the C₁₆mimBr was not added, the products take the form of uneven and irregular particles (Fig. 3). Based on the above results, we find that both the subphase solvent and the Langmuir film of C₁₆mimBr are the key factors in the formations of larger gold nanoplates.



Fig. 3. TEM image of the nanoparticles without the assistance of the C_{16} mimBr Langmuir monolayers.



Fig. 4. UV/vis spectrum of the Au plates suspended on a quartz substrate.

It is well known that gold nanostructures usually display a very intense color because of the surface plasmon resonance (SPR). We see this clearly at the surface of the subphase after reaction. The products display a very beautiful golden color.

It is demonstrated that the SPR band of gold nanoparticles strongly depended on the size and shape of the nanoparticles [4]. Fig. 4 shows the absorption spectrum of the resulting gold plates deposited on a quartz substrate. For anisotropic metallic nanoparticles, it is well known that two or more plasmon resonances, the transverse and longitudinal bands, are expected. The spectrum of our product shows two distinct plasmon absorption bands around 660 and 1000 nm. Spherical Au particles show an SPR band at approximately 520 nm that is usually red-shifted to longer wavelengths with increasing particle size [10]. The one at about 630 nm may be attributed to this band. The band around 990 nm can be attributed to the longitudinal plasmon band, reflecting the anisotropic nature of the gold nanoplates. The band is broad because of the relatively high polydispersity, both in size and shape, which implies quite a broad range of possible resonance frequencies. An asymmetrical shape may result from the existence of smaller gold plates in the colloidal system.[4] This result is consistent with the TEM images. and coworkers synthesized micrometer-scale Dong single-crystalline Au plates of nanometer thickness by a wet-chemical route. The UV/vis spectrum shows that there are two SPR bands located at about 680 and 925 nm, which arise from the longitudinal plasmon resonance of Au particles [21]. They believe that this provides evidence for the formation of anisotropic Au particles, which is consistent with our results.

During the initial stage of the reaction, The AuCl₄⁻ anions in the subphase can be adsorbed to the air/water interface due to the electrostatic interaction between the AuCl₄⁻ anions and the C_{16} mim⁺ cations in the monolayer. Then the Au³⁺ cations are reduced into Au⁰ with formaldehyde during the reaction. When the quantity of gold atoms reaches supersaturation, they will begin to nucleate and grow into gold nanoclusters in the monolayer, which are nucleation centers and thermodynamically unstable due to insufficient capping with the stabilizing agent [22]. Then AuCl₄ anions will preferentially adsorb on the surface of the preliminary gold particles. Under the induction of C₁₆mimBr Langmuir film, the formation of triangular or hexagonal gold nanoplates is favored [4]. What causes the formation of the larger nanaplates? We think that the rates of the nucleation and growth are the key factors. As has been reported, rapid nanoparticle nucleation affords small, aggregated nanoparticles, whereas slow growth at low temperature leads to thermodynamic stabile nanostructures [23]. The theory of DLA (diffusion-limited aggregation) has been widely applied to the interpretation of the phenomenon of growth and assembly related to a variety of fractal structures [24]. But our case is just thoroughly opposite: the ionic liquid is used as the novel subphase solvent, the interaction between EAN and HAuCl₄ will retard the adsorption process of AuCl₄⁻ into the air/water interface. To confirm the effects, calculations have been carried out to examine the binding energies between AuCl₄ and different solvents, and the calculational models are shown in Fig. 5. The binding energy between the $AuCl_4$ and EAN is -69.24203 eV, while that is -22.19591 eV for the H₂O system. The negative value of energy implies that the process is spontaneous. It can be noted that the binding energies between the AuCl₄⁻ and EAN are much larger than those of H₂O, suggesting that the AuCl₄⁻ anions are more stable in EAN. The rates of the nucleation and growth are much slower than those in the aqueous solution. The ionic liquid has the special ability to control the nucleation, diffusion and growth rates, and the delicate equilibrium among the three rates plays the key roles in the formation process of the larger nanoplates. If the HAuCl₄ concentration in the subphase is high (10^{-3} M) , the sizes of the obtained nanoplates are not increased greatly due to the same reasons. To further verify the formation mechanism, we also used FC-4 as the spreading agent, but "tadpole-shaped" nanostructures were not observed (see Fig. 6). Due to the lack of nucleation centers, the small nanoparticles cannot connect with each other to form the larger structures. The control experiment further confirmed our proposed mechanism.



Fig. 5. The schematic of two calculational models between $HAuCl_4$ and EAN (a) or H_2O (b).



Fig. 6. TEM image of the nanoparticles with the assistance of the FC-4 Langmuir monolayers.

IV. CONCLUSION

In conclusion, we used the ionic liquid EAN as the subphase solvent for the first time. With the help of C_{16} mimBr Langmuir monolayers, the single-crystal gold nanoplates with the size about 4.5 µm, which are much larger at the lower precursor concentration (10^{-4} M). By the quantum mechanism methods, the bonding energies between the AuCl₄⁻ and the solvents were calculated to further clarify the mechanism. The ionic liquid has the special ability to control the nucleation, diffusion and growth rates, which can play the important roles in the formations of the larger nanoplates. The present work provides a new avenue for the preparations of gold nanoparticles using Langmuir-Blodgett technique.

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recovery.

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