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Synthesis and Assembly of Gold Nanoparticles in Organized Molecular Films of Gemini Amphiphiles

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Generation and assembly of gold nanostructures were investigated in the organized molecular films of a series of gemini amphiphiles. The chloroauric acid, dissolved in the aqueous subphase, was incorporated into the monolayers of the gemini amphiphiles containing ethyleneamine spacers through an interfacial assembly. The in situ formed complex monolayers were transferred onto solid substrates, and gold nanoparticles were generated in the film by a chemical or photochemical reduction. Discrete gold nanoparticles with an absorption maximum at 550 nm were generated in the films by photoirradiation, while different gold nanostructures were obtained by chemical reduction. Depending on the chemical reductant, various shape and assembly of gold nanostructures were obtained. When reduced by hydroquinone, a tree-branched assembly of the nanoparticles was obtained and the film showed a broad band centered at around 900 nm. When NaBH₄ was applied, crooked nanowires or assembly of nanoparticles were obtained, depending on concentration, and the film showed absorption at 569 or 600 nm. Furthermore, by combining the photochemical and chemical reduction methods, i.e., the chloroaurate ion-incorporated film was initially irradiated with UV light and then subjected to chemical reduction, the optical absorption of the formed gold nanostructures can be regulated.

Introduction

Fabrication of gold nanoparticles and nanoparticulate films has drawn extensive attention in recent years due to their unique optical properties and potential application in transistor, chemical sensor, optical device, biomedical and electrochemical fields, and so on.^{1–7} The optical properties of individual nanoparticles are mainly determined by their size,⁸ shape,⁹ and dielectric environment.¹⁰ Thus, many excellent ways of synthesis have been developed to explore the size- and shape-controlled nanoparticles.^{11–14} On the other hand, the properties of metal nanoparticles can also be tuned by their interparticle interactions and dipole–dipole interactions.^{15–17} Among these factors, the

dependence of surface plasmon band on the interparticle distance is interesting. When single particles aggregate into larger ensembles, the collective nanoparticles may exhibit specific optical properties that are different from those of the individual nanoparticles.¹⁸ Therefore, it is also quite important to control the assembly of nanoparticles either in two-dimensions or in three-dimensions in order to obtain the nanostructures with tunable optical properties.^{19,20}

Great efforts have been devoted to the preparation of the organized assemblies of functionalized gold nanostructures through layer-by-layer assembly,^{21–24} electrophoretic deposition,^{25,26} self-assembled monolayers,^{27,28} Langmuir–Blodgett (LB) technique,^{29–32} and so on. Among these methods, the LB

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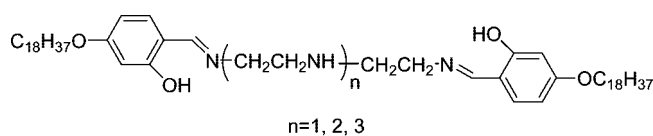
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technique as well as the Langmuir–Schaefer (LS) technique occupies an important position to fabricate nanoparticulate films, because not only the size distribution can be controlled in LB and LS films but the organic templates can be tuned in order to produce nanoparticles with various shapes and optical properties.^{33–35} It has been reported that upon photoirradiation on the LB films containing chloroaurate ions, gold nanoparticles of different dimensionalities and shapes could be generated.³⁶ In addition, surface-functionalized gold nanostructured films were obtained from gold colloids by choosing proper amphiphiles as templates.³⁷ The hybrid nanocomposite films were fabricated by the adsorption of the gold nanoparticles on polymeric LB films.^{38,39} Sastry et al. have reported the formation of various gold nanostructures by reduction in situ of chloroaurate ions that were stabilized by surfactants at the air/water interface.⁴⁰ Although various gold nanostructures were fabricated in these systems, the modulation of optical properties is very limited. In this paper, we report the synthesis and controllable assembly of gold nanoparticles by both chemical and photochemical method in the LB or LS films using a set of gemini amphiphiles. Gemini amphiphile can be regarded as a dimeric amphiphile in which two amphiphiles were covalently linked by a spacer through their headgroups.^{41–43} Gemini amphiphiles have a wealth of parameters, such as the length of the hydrophobic chain, the type of counterions, and the flexibility and polarity of the linker group (spacer), which can be regulated to show a good performance either in solution or at the interface. Previously, we have shown a good control of gemini amphiphiles on dye aggregation,⁴⁴ DNA condensation,⁴⁵ and POM functionalities⁴⁶ through the interfacial organization. In this paper, we will show the controlled synthesis of gold nanoparticles in the organized molecular films. We have found that the chloroaurate ions could be incorporated into the monolayers of the designed gemini amphiphiles and the formed films can be further used to generate gold nanostructures. Upon photoirradiation, discrete nanoparticles were obtained in the films. Upon chemical reduction, different nanostructures can be obtained depending on the reductants. Furthermore, by combining the photochemical and chemical methods, the optical properties of the formed nanostructures can be regulated. The evolution of metallic gold nanoparticles has been monitored by UV–visible spectroscopy. Produced gold nanoparticles were also character-

Scheme 1. Molecular Structures of Gemini Amphiphiles Used in This Work



ized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and transmission electron microscopy (TEM).

Experimental Section

Materials. The gemini-type Schiff base amphiphiles GNn ($n = 1, 2, 3$) were prepared by following the procedure described previously,⁴⁷ and the structures are shown in Scheme 1. Solvents used in this work were obtained from Beijing Chemicals and distilled before use. Ultrapure deionized water (Millipore-Q, 18 MΩ cm) was used for all the solution preparations. Trisodium citrate, citric acid, hydroquinone, and sodium borohydride were purchased from Beijing Chemical Plant. Chloroauric acid and octadecylamine (ODA) were purchased from Aldrich and used as received.

Procedures. 1. *Incorporation of the AuCl₄⁻ Ions into the Monolayers.* The spreading of films on water and chloroauric acid subphase and the film transfer were performed on a KSV minitrough (KSV instruments, Helsinki, Finland). The monolayer was formed by carefully spreading the chloroform solution of GNn on 0.1 mM chloroauric acid aqueous solution. After waiting 20 min for the evaporation of the chloroform, surface pressure–area (π – A) isotherms were recorded with a compression speed of 7.5 cm²/min at 20.0 ± 0.2 °C. For AFM measurement, the LB monolayer film was transferred onto a freshly cleaved mica plate by the vertical dipping method, and Langmuir–Schaefer multilayer films were fabricated onto quartz plates for UV–vis spectroscopy measurement. In transferring the monolayer to the solid substrates by the LS method, the plate was held parallel to the surface and lowered to touch the monolayer. After touching the film for 30 s, the plate was slowly lifted up to leave the surface and then the film was let dry in the air or N₂ atmosphere for 5 min. The process was repeated and up to 60-layer films could be fabricated successfully.

2. *Generation of Gold Nanoparticles in the Films.* After the complex film was transferred onto solid plates, gold nanostructures were produced by photochemical or chemical reduction. In photochemical reduction, the transferred films were irradiated with a UV light, which was put 20 cm away from the film. The generation of the gold nanoparticles in the film was monitored by the UV–vis measurement. The UV irradiation lasted for several hours until the absorption band of gold does not change. In the chemical reduction method, the film was immersed into an aqueous solution of hydroquinone or sodium borohydride with different concentrations. After a certain time, the film was pulled out, washed with water, and then subjected to the UV–vis or other measurements. We also carried out a third way to generate the gold nanoparticles in the film. We first irradiated the film with UV light for a short time and then subsequently dipped the film into hydroquinone solution for further reduction. The produced gold nanostructures were characterized by AFM, TEM, and XPS measurements. For the TEM measurement, the monolayer at the air/water interface was first transferred onto a carbon-coated copper grid and then treated by the same procedure.

Measurements. UV light irradiation of LS films was performed with a 500 W UV lamp. UV–vis spectra of the films were obtained by a JASCO UV-550 spectrophotometer. AFM images were recorded using tapping mode (Nanoscope IIIa multimode system, Digital Instruments, Santa Barbara, CA) with silicon cantilever probes. All AFM images were shown in the height mode without any image processing except flattening. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was about 3 × 10⁻⁹ mbar.

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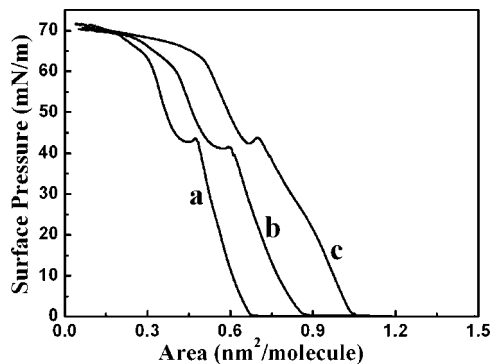


Figure 1. Surface pressure–area isotherms of GN1 (a), GN2 (b), and GN3 (c) monolayers on 0.1 mM chloroauric acid aqueous solution subphase at 20 °C.

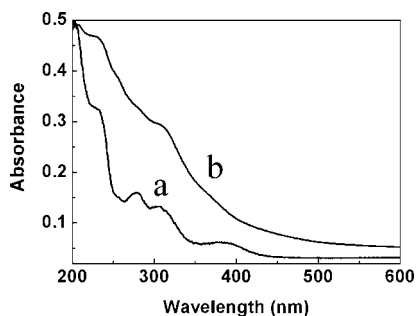


Figure 2. UV–vis spectra of 40-layer GN2 LS films transferred from water (a) and 0.1 mM chloroauric acid aqueous solution (b) subphases at 20 mN/m.

The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. TEM measurement was done on a JEOL TEM-1011 electron microscope.

Results and Discussion

Incorporation of AuCl_4^- Ions into Monolayers. Figure 1 shows the surface pressure–area isotherms of GN n amphiphiles on 0.1 mM chloroauric acid subphase. In a previous paper, we have shown that the three gemini amphiphiles could form stable condensed monolayer films on water surface with nearly the same limiting molecular area of 0.54 nm²/molecule.⁴⁷ When AuCl_4^- ions existed in the subphase, obvious changes are observed. First, the liftoff molecular area, where the surface pressure begins to appear, increases significantly with the length of spacer of gemini amphiphiles, and the values of 0.64, 0.82, and 1.04 nm²/molecule are obtained for GN1, GN2, and GN3 monolayers, respectively. Second, there appears an obvious inflection point in the pressure range of 42–44 mN/m for each monolayer. These data clearly indicate that there is an interaction between the GN n monolayers and AuCl_4^- ions in the subphase. Since the pH of 0.1 mM chloroauric acid is 3.7, the gemini amphiphiles could be protonated. The electrostatic interaction between gemini amphiphiles and negatively charged AuCl_4^- ions is supposed to be responsible for the complex film formation at the interface. Due to the adsorption of these AuCl_4^- ions to the spacer of the gemini amphiphile, the spacer could stay on water surface, resulting in the increment of the liftoff molecular area.

The spreading films of GN n from chloroauric acid subphase were transferred onto solid substrates for further functionalization. Figure 2 shows the UV–vis spectra of GN2 LS films on quartz plates transferred at a surface pressure of 20 mN/m. Since the transferred LS films from three amphiphiles have similar spectra,

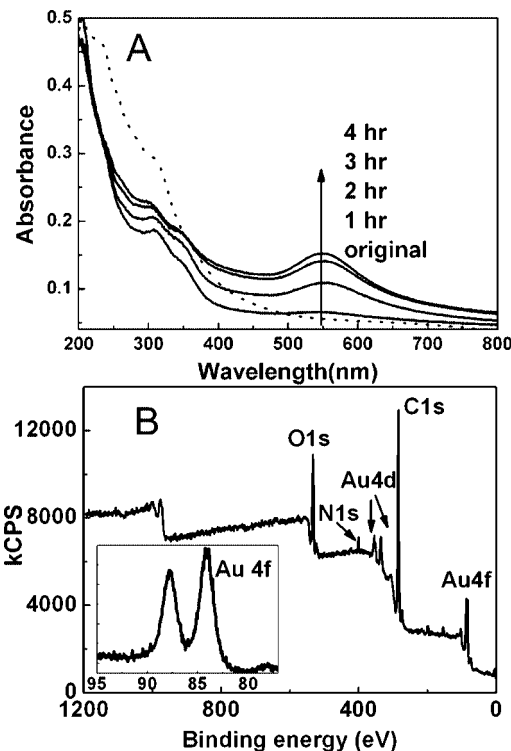


Figure 3. (A) UV–vis spectral changes of the GN2/ AuCl_4^- film as a function of the irradiation time: dashed line, before reduction; solid lines, after irradiation for 1–4 h (from bottom to up). (B) XPS spectra of the film after reduction for 4 h.

we take the spectrum of GN2/ AuCl_4^- complex film as an example to show the change on different subphases. For the spectrum of GN2 multilayer films prepared from water subphase (Figure 2a), absorption peaks appear at 231, 278, 304, and 387 nm. The former three peaks can be assigned to electronic absorption localized on the aromatic ring or azomethine group of the ligand, and the latter peak is designated as the charge-transfer band.^{47,48} When the film was deposited from the chloroauric acid subphase, the peak at 387 nm disappeared, as shown in Figure 2b. This suggests the protonation of the spacer as well as the electrostatic interactions between GN2 and AuCl_4^- ions. It should be remembered that AuCl_4^- species have absorption at around 300 and 230 nm. In the absorption spectra of the complex film, these bands were overlapped with the absorption of GN n .

Generation of Gold Nanoparticles in the Transferred Complex Films. The complex monolayers were transferred onto solid substrate and the gold nanoparticles were generated in the films by photochemical, chemical, and combined photochemical and chemical reduction methods. Different nanostructures as well as the optical properties were obtained.

1. UV-Generated Gold Nanoparticles. When the AuCl_4^- ion-incorporated film was irradiated by the UV light, gold nanoparticles were found to be generated, a process which was monitored by the UV–vis spectral measurement. The three gemini did not perform with obvious differences in the generation of gold nanostructures; thus, we discuss GN2 as our example. Figure 3A shows the UV–vis spectral changes of a 40-layer GN2/ AuCl_4^- film as a function of irradiation time. Upon irradiation for 1 h, an absorption band was newly observed at 550 nm, which can be assigned to gold plasmon band, suggesting the formation of gold nanoparticles in the film. Upon further

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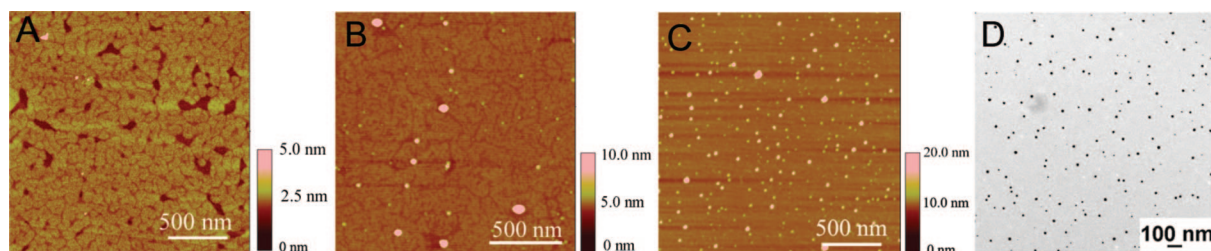


Figure 4. AFM images of GN2/AuCl₄[−] film before (A) and after photochemical reduction for 1 h (B) and 2 h (C). (D) TEM image corresponding to film C.

irradiation, this peak increased its intensity but without changing its absorption position. Upon measuring the XPS spectra of the irradiated film, the spin doublet peaks of Au 4f were observed to appear at 84.1 and 87.7 eV in XPS, as shown in the inset of Figure 3B, confirming the generation of zerovalent gold in the film.⁴⁹

AFM images provide further information about the change in the film before and after photochemical reduction. As we reported previously, the GN n films from water surface were uniform and structureless. When the film was transferred from chloroauric acid subphase, wormlike domains were observed, as shown in Figure 4A. Upon irradiation, the wormlike structure was gradually destroyed and some dotted domain formed in the film, as shown in Figure 4B. After 2 h of reduction, discrete tiny gold nanoparticles were generated (Figure 4C). The generated gold nanoparticles were further confirmed by the TEM characterization, as shown in Figure 4D, which indicated that gold nanoparticles with an average diameter of 9.8 nm were generated in the film upon UV irradiation.

2. Chemically Reduced Gold Nanoparticles. Photogenerated gold nanoparticles have been studied extensively, but there are few reports about the chemically generated gold nanoparticles in LS films. Herein, we investigated the synthesis of gold nanoparticles in organized molecular films. First, GN n /AuCl₄[−] LS complex films of 40 layers were immersed in 0.05 M hydroquinone solution, whose pH value was adjusted to 3.6 by 0.1 M citrate/citric buffer solution. This pH was selected because it is close to that of chloroauric acid solution, and thus, the structures of GN n /AuCl₄[−] complex films can be maintained. After reduction for 3 h, the color of the quartz plates changed from colorless to blue. Upon measuring the UV–vis spectra of the film, as shown in Figure 5A, a rather broadened absorption band centered at around 900 nm appeared. The XPS data have confirmed that only zerovalent Au existed in the film (data not shown). Thus, it can be concluded that the broadened absorption band is assigned to the reduced gold nanoparticles. There have been many reports on the gold plasmon band at longer wavelength, which usually corresponds to a resonance over much larger distances, such as nanoshell⁵⁰ or nanorods,⁵¹ or the closely packed aggregates^{52–54} of a large number of nanoparticles. In order to make clear the formed nanostructures in our organized molecular films, we have measured the AFM and TEM of the gold nanostructures formed in the film, as shown in Figure 5. Different from those gold nanoparticles formed by the photochemical

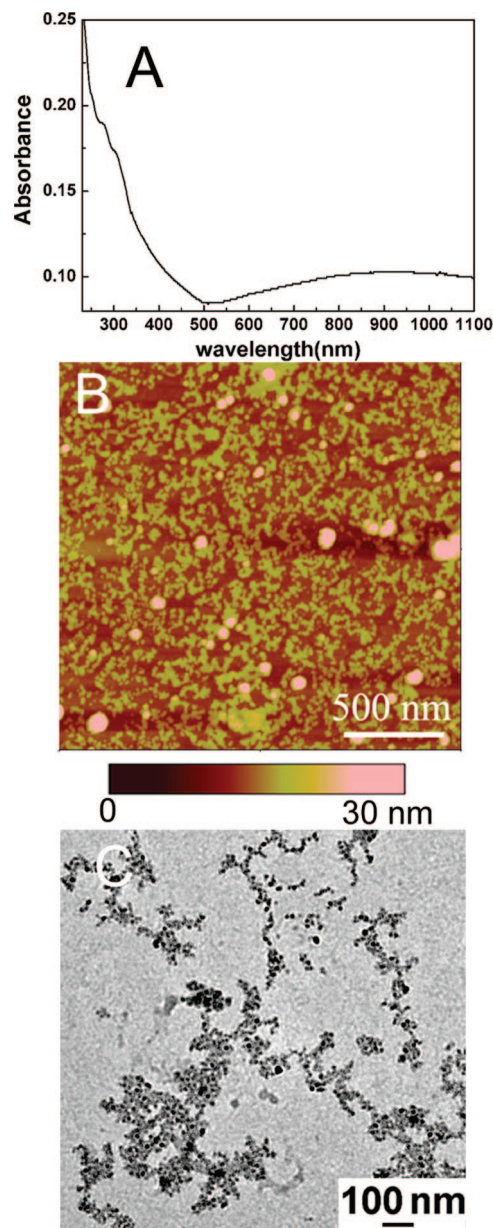


Figure 5. UV–vis spectra (A), AFM (B), and TEM (C) images of GN2/AuCl₄[−] complex films after immersion in hydroquinone solution for 3 h.

reduction, closely connected aggregates of the nanoparticles were observed in the AFM images (Figure 5B). The TEM micrograph (Figure 5C) further confirmed that the aggregates were composed of several nanoparticles. These nanoparticles were not distributed randomly. Several of them connected to form short branched aggregates extending to different directions. This clearly indicated that the broadened absorption in UV–visible

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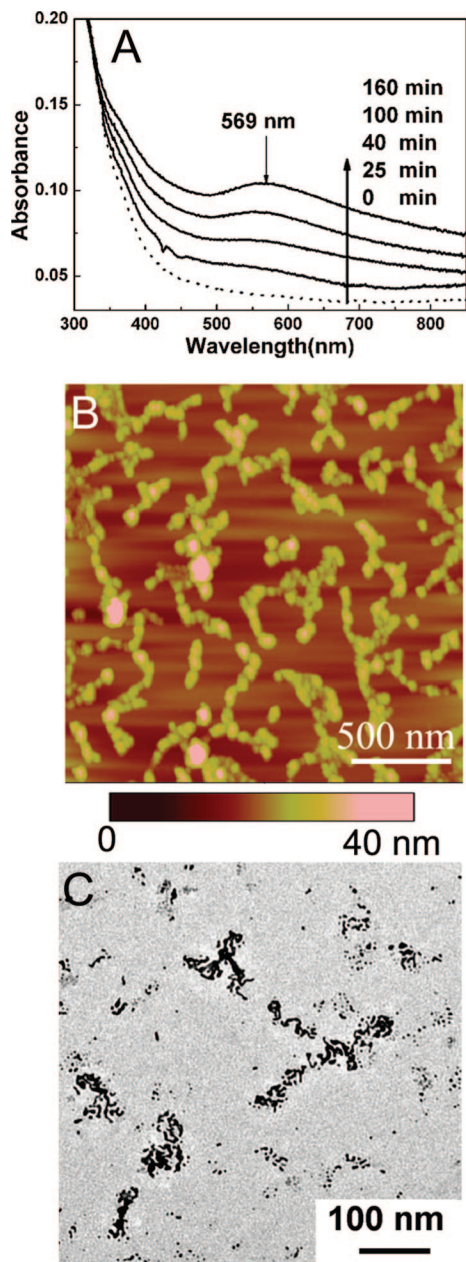


Figure 6. (A) UV-vis spectra of GN2/AuCl₄⁻ complex films after immersion in 0.05 M NaBH₄ aqueous solution over 160 min: dashed line, the spectrum before reduction; solid lines, spectra after reduction for 25–160 min (from bottom to top). (B) AFM and (C) TEM images of complex films after reduction for 25 min.

spectroscopy is caused by the tree-branched assembly of the gold nanoparticles in the film.

Besides hydroquinone, we also tried the generation of the gold nanostructures in the film by NaBH₄. A 40-layer film was immersed in 0.05 M sodium borohydride aqueous solution for different times, and their UV-vis spectra were monitored at different time intervals, as shown in Figure 6A. After 25 min, the plasmon absorption band appeared at around 569 nm. With the time increase, the intensity of the absorption band increases. The broad absorption band at 569 nm is also related to the formation of the aggregates or anisotropic nanostructures in the film. The formed nanostructures were further investigated by the AFM and TEM measurements. AFM (Figure 6B) revealed that some larger nanoparticles were formed in comparison to the case of hydroquinone as reducing agent. In addition, these larger nanoparticles further assembled into crooked nanowires. The

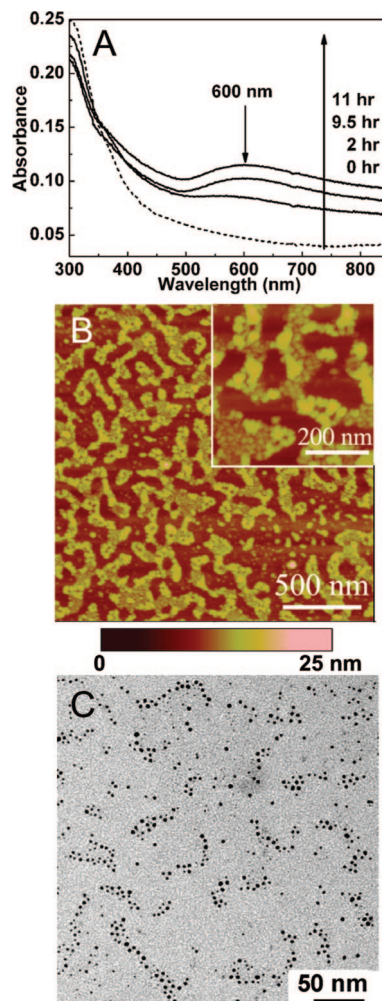


Figure 7. (A) UV-vis spectra of GN2/AuCl₄⁻ complex films after immersion in 0.003 M NaBH₄ aqueous solution over 11 h: dash line, the spectrum of the film before reduction; solid lines, spectra after reduction for 2–11 h (from bottom to top). (B) AFM and (C) TEM images of complex films after reduction for 4 h.

TEM images (Figure 6C) confirmed that these larger nanoparticles in AFM images were some fused one-dimensional nanostructures, and they further formed crooked ensembles.

The concentration of reductants may also impose much influence on the reducing speed and finally affects the size or shapes of produced gold nanoparticles. We diluted sodium borohydride to 0.003 M and investigated the generation of the gold nanostructures in the film. Similar optical spectra were recorded, as shown in Figure 7A. However, the gold surface plasmon band shifted to a little longer wavelength at 600 nm after reduction for 9.5 h. From both the AFM and TEM measurements, it was seen that discrete nanoparticles were generated and they aligned in certain directions.

In order to ensure the above changes of the UV-vis spectra are assigned to gold, blank experiments had been done. When GN_n LS films from water subphase were immersed in hydroquinone and sodium borohydride solution, respectively, no absorption band appeared in the visible range.

It should be noted that the gemini amphiphiles play an important role in the formation of the above chemically reduced gold nanostructures. We did the parallel experiment by using a conventional amphiphile, octadecylamine (ODA), instead of the gemini amphiphiles. It has been found that when ODA/AuCl₄⁻ films were immersed in hydroquinone solution, no gold absorption

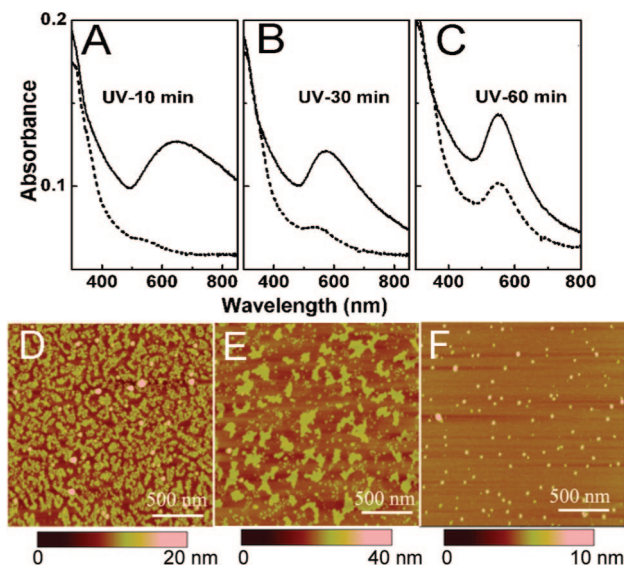


Figure 8. UV-vis spectra of 40-layer GN2 LS films first irradiated (dash lines) for 10 min (A), 30 min (B), 60 min (C), respectively, and then immersed in hydroquinone solution for 3 h (solid lines). AFM images of GN2 monolayer first irradiated for 10 min (D), 30 min (E), and 60 min (F), respectively, and then all reduced by hydroquinone for 3 h.

band appeared, even after reduction for 36 h. Moreover, if the ODA/AuCl₄[−] complex films were immersed in the chemical solution for even longer time, part of the films would peel off from the substrates. If the ODA/AuCl₄[−] complex films were immersed in sodium borohydride, the film peeled off within 1 h and no gold band appeared. However, the complex film of GN_n/AuCl₄[−] were stable enough to let gold nanostructures generate in the film, even in the case of wet-chemical reduction. This may be due to the fact that the gemini amphiphiles have two headgroups, which can anchor the film on the substrates firmly.

Generation of the Gold Nanoparticles by Combining the Photochemical and Chemical Reduction. On the basis of the above results, distinct gold nanostructures could be produced by changing reductants or reducing methods. By combining the two methods, a further control on optical properties of generated gold nanostructures can be realized. We first irradiated the film with UV light and then reduced the AuCl₄[−] ions with hydroquinone. Figure 8 shows the UV-vis spectral changes of the film upon UV-irradiation and subsequent chemical reduction. When a 40-layer GN2/AuCl₄[−] complex film is exposed to UV light for 10 min, a slight increase in absorption at around 550 nm is observed (dash line in Figure 8A), which indicates that part of the chloraurate ions in the film has been reduced to zerovalent gold. This film is subsequently immersed into a hydroquinone solution of pH 3.6 for 3 h, and then a broad peak appears at around 640 nm (solid line in Figure 8A). The obvious red-shift from 550 to 640 nm suggests that aggregation of particles happened in the films. However, compared with the films reduced only with hydroquinone, the absorption band is narrowed and appears at shorter wavelength. If we initially irradiated the film for 30 min and then let it reduced in hydroquinone, then the gold absorption band shifts to a shorter wavelength of 570 nm (solid line in Figure 8B). In the case of the films exposed to UV light for 60 min, the absorption does not shift before and after reduction in hydroquinone solution, suggesting that the growth process of gold nanoparticles was uniform. This gradual change of optical properties of the gold nanostructures indicates that the initially photoproduct nanoparticles may act as the seeds for the next growth in solution, and by controlling the seeds' growth, the

optical properties of the gold nanostructures can be controlled easily.

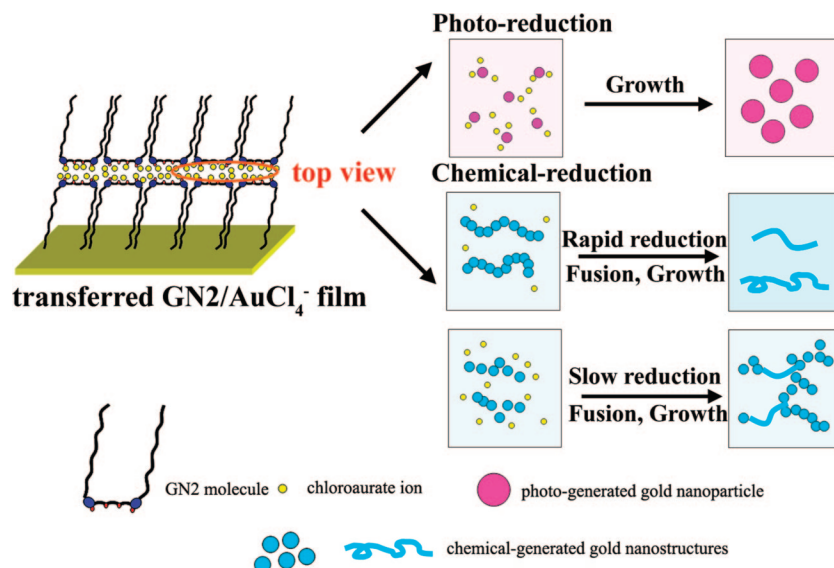
AFM was used to check the gold nanostructures formed in the film, as shown in Figure 8D–F. When the illumination time is 10 min, fractal gold nanostructures are still the main construction in the film after complete chemical reduction in solution (Figure 8D). This topology is quite similar to the film reduced by hydroquinone without irradiation. When the illumination time is increased to 30 min, many more single spherical particles can be observed, but some fractals still exist occasionally (Figure 8E). As the irradiation time is prolonged to 60 min, only single small particles (Figure 8F) can be seen after reduction with hydroquinone, and the topology is similar to that obtained by only photochemical reduction. It is noted that by simply changing photochemical and chemical reduction time, the optical properties and assembly of gold nanoparticles can be controlled in a large wavelength range, and this may have important application in optical devices, chemical sensor, and so on.

Discussion

The generation of gold nanoparticles is an important topic in current nanoscience and technology. The LB technique is an effective way to synthesize and assemble the nanoparticles. Previously, some groups have reported the generation of nanoparticles in the LB films. In that case, conventional amphiphiles were used. In the present work, we used gemini amphiphiles that have a poly(ethyleneamine) spacer. It seems that the use of the gemini amphiphiles has some advantages. First, it helps the film to grasp the AuCl₄[−] ions onto substrate firmly. Thus, we could get the nanoparticles even through reducing in aqueous solution, which was difficult when conventional amphiphiles were used. Second, the gemini amphiphiles can act both as capping agents and confinement environment to let the nanoparticles assemble in a two-dimensional way.

During photogeneration, due to the confinement of the AuCl₄[−] ion in the films, only tiny discrete nanoparticles were obtained, as shown in Scheme 2. In the photogeneration method, neither the ions nor the formed nanoparticles can immigrate and thus uniform as well as separated nanoparticles were mainly obtained. While in solution, the immigration of both the ions and the produced nanoparticles was possible, resulting in the assembly or organization of the nanoparticles in the film. At the solid/liquid interface, assembly of these nanoparticles is greatly dependent on their generation speed. If the reduction proceeds quickly, such as in a concentrated NaBH₄ solution, a large number of tiny gold nuclei may be generated simultaneously as soon as the film is immersed in NaBH₄ solution. With the help of water flow, they can interact with each other and fuse into one-dimensional nanostructures to lower the surface energy. On the other hand, if the speed is low, such as in the case of hydroquinone, fewer nanoparticles were produced at a certain reaction time. Thus, the fusion and growth of the nanoparticles are not continuous and can be stopped at a certain place and grown into another direction. Therefore, we obtained the tree-branched assemblies. When dilute NaBH₄ was used as reductant, many fewer nanoparticles could be produced at the same reduction time due to the overly low concentration of NaBH₄. The produced nanoparticles are thus far from each other and cannot interact until more gold ions were reduced and larger nanoparticles were generated. Therefore, ensemble of single nanoparticles was obtained. In the assembly of the nanoparticles, the gemini amphiphile may also play an important role. Due to the strong hydrophobic interaction of the hydrophobic tails and repulsion between the spacers, the growth of the nanoparticles in the film

Scheme 2. Schematic Illustration on the Generation of Gold Nanoparticles by Photochemical and Chemical Reduction in GN2/AuCl₄⁻ Complex Film



layer was not straight. Thus, we obtained crooked nanowires in the case of rapid reduction but tree-branched assembly in the low-speed reduction.

When the photochemical and chemical reduction methods were combined, some gold nanoparticles can be generated first by UV illumination. Upon subsequent reduction in the solution, these preformed nanoparticles can act as seeds and grow into different nanostructures. When small gold seeds were initially formed by irradiation, high surface energy promotes these nanoparticles to further assemble into larger structures in the subsequent reduction in the solution, resulting in absorption at a longer wavelength. On the other hand, when the initial irradiation time is increased, more large discrete nanoparticles were produced. Then upon immersion in reductant solution, reduced Au(0) will grow with the photoproduced seeds, and thus we obtained the spectra similar to those nanoparticles generated only by UV irradiation. We herein provided a very simply way to control the aggregates and optical properties of gold nanostructures by adjusting the initial irradiation time.

Conclusion

In this paper, we have clearly revealed the effect of gemini amphiphiles on the in situ formation and assembly of the gold nanoparticles in the organized molecular films. Compared with

conventional amphiphiles, gemini amphiphiles showed a better capability of immobilizing the chloroaurate ion onto the solid substrate, which is an important premise to gain metallic nanoparticles in films by chemical method. Furthermore, the gemini amphiphiles could provide a confined environment for the assembly of the in situ reduced gold nanoparticles. By using different reducing methods, the shape and interparticle distances of particles can be controlled; thus, various nanostructures such as the discrete nanoparticles, crooked nanowires, and the tree-branched assemblies could be obtained. This study extends the research on the synthesis of metallic particles in films from conventional amphiphiles to other special amphiphiles and provides a very convenient method to modulate the optical properties in a large wavelength range, which will be important in designing optical devices based on different gold nanostructures. Moreover, besides gold nanoparticles, other noble metallic particles with various shapes and size distribution should be also produced by choosing the proper types of amphiphiles.

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