

Photochemical Growth and Dissolution of Gold Nanorods Promoted by Acetone

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Abstract: The seed-mediated photochemical growth and dissolution of Au NRs promoted by acetone were studied in a single-component surfactant system containing high concentration of HAuCl₄. The results showed that when the ratio of acetone-to-growth solution was higher than 0.1/25(V/V) in the seed-mediated growth solution, Au NRs of higher yield with an aspect ratio of 3.5 (the average diameter of 14 nm) could be rapidly formed; when the acetone-to-growth solution ratio was equal to or lower than this critical value, in contrast, Au NRs formed at chemical aging stage could be dissolved by UV light. In the process of the dissolution, Au NRs underwent a series of changes on the morphology, including the shortening, forming nanospheres and entire dissolution. Further UV irradiation finally made the solution colorless initial state of Au(I)-CTAB complex solution.

Key words: metal materials; gold nanorod; photochemical growth; photochemical dissolution; acetone

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丙酮促进的金纳米棒的光化学生长和溶解

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摘要: 在含有高浓度的 HAuCl₄ 单组份表面活性剂的溶液体系中, 研究了由丙酮促进的金纳米棒晶种媒介的光化学生长和溶解。结果表明, 在晶种媒介的生长溶液中, 当丙酮/生长溶液之比高于 0.1/25(V/V)时, 高产率的金纳米棒(长径比为 3.5, 平均直径 14 nm)能够快速形成; 当丙酮/生长溶液之比等于或低于这一临界值时, 在化学陈化阶段已形成的金纳米棒则在紫外光照射下溶解。在溶解过程中, 金纳米棒发生一系列的形态变化, 包括缩短, 形成纳米球和完全溶解。进一步的紫外照射最终使溶液成为无色的初始 Au(I)-CTAB 络合物溶液状态。

关键词: 金属材料; 金纳米棒; 光化学生长; 光化学溶解; 丙酮

Nowadays, the increasing availability of gold nanorods (Au NRs) with controlled aspect ratio has created widespread interest in their use in biomedical fields for diagnostic application, biological imaging

and photothermal tumor therapy^[1-6]. For the synthesis of Au NRs, the photochemical reduction method^[5-11] is widely used, because it is relatively simple and easy to produce uniform NRs with controlled aspect ratios.

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For this purpose, we have used the seed-mediated photochemical secondary growth for preparing Au NRs in a single-component system of cetyltrimethylammonium bromide (CTAB) system and found that the aspect ratios of Au NRs with an average 10 nm in diameter can be finely controlled in the range of 2.3 to 4.0 by changing Ag^+ ions amount or shortening rods method with ablation^[12]. In order to obtain the high concentration of shorter Au NRs, we tried to increase the concentration of HAuCl_4 in this seed-mediated photochemical secondary growth solution. As a result, a novel phenomenon of the photochemical dissolution of Au NRs promoted by acetone was observed. Thereupon, in this work, we study the photochemical growth and dissolution of Au NRs in detail in the

presence of different amount of acetone.

By means of the characterizations of UV-Vis absorption spectrum and transmission electron microscopy (TEM) for the seed-mediated growth solutions and Au NRs samples, the research results show that after the seed-mediated chemical growth to be reached the reaction equilibrium, the shorter Au NRs with high yield not only can be rapidly formed, but also be dissolved by UV irradiation. Both reactions depend on the concentration of acetone. The threshold of acetone concentration was determined in the photochemical growth and dissolution of Au NRs. The entire progress of the photochemical dissolution of Au NRs can be illustrated as in Fig.1.

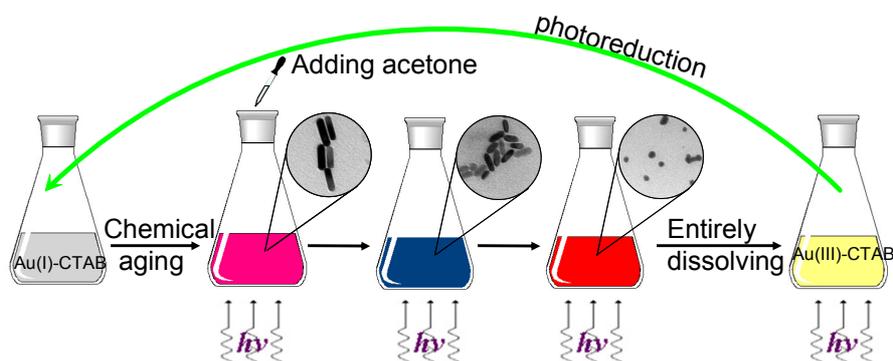


Fig.1 Schematic illustration of the photochemical dissolution progress of Au NRs in the presence of acetone

图 1 在丙酮存在下金纳米棒光化学溶解全过程的示意图

1 Experimental section

1.1 Materials

HAuCl_4 was prepared from pure gold (Au 99.99%). CTAB and sodium borohydride were purchased from Fluka AG (Chemische Fabrik CH-9470 Buchs) and Aldrich, respectively. Double distilled water and analytical-reagents were used throughout the experiments.

1.2 Growth and dissolution of Au nanorods

1.2.1 Growth

Firstly, CTAB-capped Au seed with 3.5 nm of an average size was prepared according to the method reported by El-Sayed et al.^[13]. Then, 10.0 mL of 0.1 mol/L CTAB, 6.8 mL of 3.05×10^{-3} mol/L HAuCl_4 and 2.0 mL of 1.49×10^{-3} mol/L AgNO_3 solutions were

mixed in a quartz conical flask. A freshly prepared 2.2 mL solution of 0.01 mol/L ascorbic acid was added to this solution. After diluting to 25 mL and gently mixing, the color of the mixture solution changed from yellow to colorless and it was used as a growth solution. Next, 50 μL of the prepared seed solution was added to the growth solution, the mixture obtained was aged for 60 min in dark so that the equilibrium of the chemical growth reaction of Au NRs can be reached. Finally, the mixture solution formed was irradiated by UV 300 nm light after adding a certain amount of acetone.

1.2.2 Dissolution

According to above procedure, another same mixture solution was prepared. Then, this solution was irradiated by UV 300 nm light for a somewhat longer

time in the presence of 100 μL of acetone.

1.3 Characterization

The absorption spectra of the seed-mediated growth solutions were taken on a PerkinElmer UV-Vis-NIR spectrophotometer (Lambda 900). Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 TEM instrument operating at an accelerating voltage of 100 kV. The samples of TEM were prepared with drying several drops of the Au NRs solution on carbon-coated copper grids.

2 Results and discussion

2.1 Photochemical growth of Au NRs accelerated by acetone

In order to make Au(I)-CTA^+ complex ions completely reducing as far as possible for growing Au NRs, the method of the photochemical secondary growth is available^[12]. Thus, shorter Au NRs were prepared by this method in the seed-mediated growth solution containing high concentration of HAuCl_4 .

Fig.2-A shows the absorption spectra of the seed-mediated growth solution diluted to 2 times of the volume for 60 min UV irradiation in the presence of various amount of acetone. As can be seen, in the

absence of acetone, the curve a shows a transversal surface plasmon (TSP) band and a longitudinal surface plasmon (LSP) band of Au NRs at around 520 and 800 nm, respectively, and their absorbance is very weak. This also is the same state as the seed-mediated growth solution was aged for 60 min, indicating that the growth of Au NRs was not influenced by UV irradiation. Accompanied with an increase of the amount of acetone, the LSP band maximum shifts to the shorter wavelengths and its intensity increases while the TSP band maximum is not remarkable change (curve b, c, and d). When acetone added was 1.0 mL, the absorbance maximum of the LSP band appeared (curve d). These results show that acetone could promote the photochemical reduction of Au(I)-CTA^+ complex ions to a considerable degree, so that shorter Au NRs with higher yield could be obtained, because the aspect ratio and the yield of Au NRs are determined by the peak position and the absorbance of the LSP band, respectively. The blue shift of the band indicates a decrease in the aspect ratio, and the high absorbance implies an increase in the NRs yield. The TEM image in Fig.2-B shows that the average aspect ratio of Au NRs is about 3.2 (the average diameter of 10 nm).

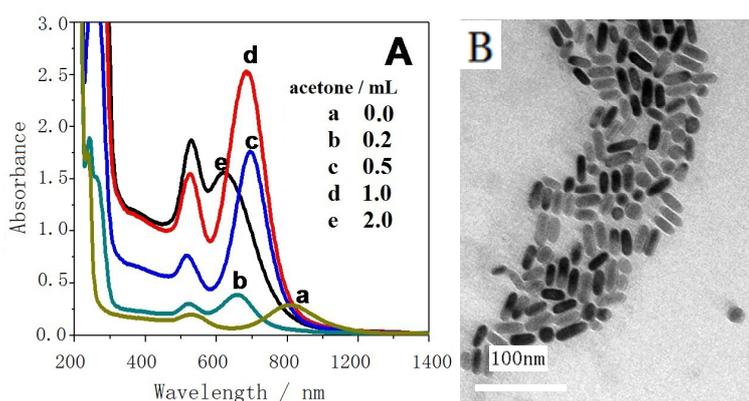


Fig.2 Absorption spectra of the seed-mediated growth solution by UV irradiation for 60 min in the presence of different amount of acetone (A) and TEM image of Au NRs formed in the presence of 1.0 mL acetone (B)

图 2 晶种媒介的生长溶液在不同量的丙酮存在下紫外辐射 60 min 时的吸收光谱图(A) 和丙酮量为 1.0 mL 时形成的金纳米棒 TEM 图像(B)

However, the intensity of TSP band in Fig.2-A curve e is higher than that of the LSP band when the

amount of acetone was further increased. This phenomenon implies that a higher yield of gold

nanospheres was formed as compared to that of Au NRs, because the both absorbance has the additivity property.

It is notable that the photochemical secondary growth could not make rods longer under the given conditions. This indicates that a lot of Au atoms generated in the seed-mediated growth solution did not deposit at the ends of Au NRs formed, or rather, preferentially nucleated and grew to the shorter NRs in high yield.

2.2 Photochemical dissolution of Au NRs

In the seed-mediated growth experiments, an interesting phenomenon of the photochemical dissolution of Au NRs was observed in the presence of a small amount of acetone.

Fig.3 shows the evolution of the absorption spectra of the seed-mediated growth solution aged with an increase of UV irradiation time in the presence of 100 μL of acetone.

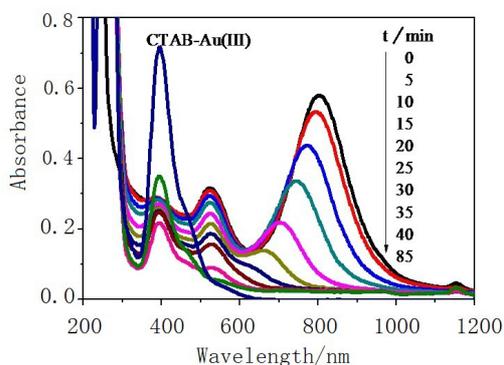


Fig.3 Evolution of absorption spectra of the seed-mediated growth solution aged with an increase of UV irradiation time in the presence of 100 μL of acetone and the absorption spectrum of Au(III)-CTAB complex (curve labeled)

图 3 在 100 μL 丙酮存在下陈化的晶种媒介生长溶液的吸收光谱随 UV 照射时间的演化和 Au(III)-CTAB 络合物的吸收光谱(标记的曲线)

It can be seen that the LSP band maximum of Au NRs formed as a function of irradiation time gradually shifts to shorter wavelengths while the TSP band maximum has a weaker red shift. The intensity of two bands gradually decreases until disappearance. The blue-shift of the LSP band was started after UV

irradiation for 5 min. After 10 min of UV irradiation, a characteristic absorption peak corresponding to Au(III)-CTAB complex appeared at wavelength ≈ 394 nm. After 30 min of UV irradiation, the LSP band maximum of Au NRs disappeared and the characteristic absorption peak at ≈ 520 nm corresponding to spherical Au nanoparticles still existed. However, UV irradiation for 40 min made the absorption peak at ≈ 520 nm quite weak. After continuous 85 min of UV irradiation, a straw yellow solution with the absorption maximum at wavelength ≈ 394 nm was obtained, indicating the entire dissolution of Au nanoparticles.

The changes of absorption spectra reflect the morphological changes of Au NRs. Obviously, under the UV irradiation, Au NRs formed at aging stage were continuously shortened, resulting in spherical nanoparticles, subsequent these particles were further dissolved. Finally, the solution with $\lambda_{\text{max}} \approx 394$ nm absorption spectrum was formed.

In order to verify the morphological changes of Au NRs, we characterized Au nanoparticle specimens obtained after UV irradiation for 25 and 35 min by TEM, respectively. Fig.4 shows the images of these samples. It can be seen that the shortening of Au NRs (Fig.4-A) as compare with Fig.2-B and the formation of nanospheres (Fig.4-B) occurred at different irradiation stage. These results coincide with that predicted in Fig.3 the UV-Vis absorption spectrum curves.

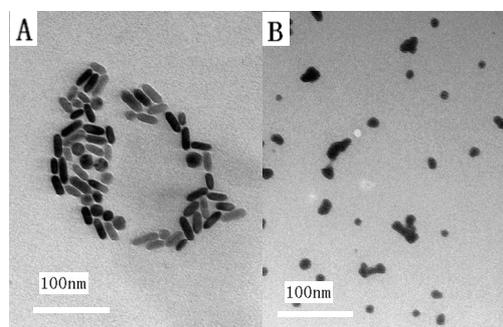


Fig.4 TEM images of Au nanoparticle specimens obtained after UV irradiation for 25(A) and 35(B) min

图 4 在照射 25(A)和 35 min(B)后获得的样品金纳米粒子的 TEM 图像

Based on the above photochemical growth and dissolution of Au NRs, it is clear that a “critical concentration” of acetone plays a key role. This concentration was determined to be 0.1/25 (V/V, i.e. acetone: seed-mediated growth solution). When the ratio of acetone/growth solution is higher than the critical value, shorter Au NRs with a higher yield can be rapidly formed due to the completely photochemical reduction of Au(I)-CTA⁺ complex ions; on the contrary, Au NRs formed are dissolved by UV light.

It is well known that the photochemical reduction of Au(I)-CTA⁺ complex ions is due to the reactions of ketyl radicals^[10] which is the key condition for Au NRs growth. However, for the dissolution of Au NRs in the presence of small amount of acetone, its reaction mechanism may be very complex. According to the absorption spectra in Fig.3 and the TEM images in Fig.4, we consider that when the ratio of acetone-to-growth solution is lower than or equal to the critical value, the growth reaction of Au NRs becomes a non-governable factor in the seed-mediated growth solution. The main role of acetone is to loosen the micellar structure^[7]. In this way, the atoms at the ends of Au NRs CTAB-capped are exposed to a greater degree due to higher curvature. Under the condition of longer UV irradiation, as with the shortening Au NRs by ablation in the previous study^[12], the photon energy and chemical dissolution by oxygen dissolved in the solution are responsible for shape-transformation and the completely dissolution of Au NRs.

In order to further prove the oxidation of Au NRs by O₂ dissolved in the solution, we made other experiment, i.e. the solution described in 1.2.2 was bubbled by nitrogen, and then was irradiated by UV light. Fig.5 gives the comparison of the UV-Vis absorption spectra of this solution with (curve a, b) and without (curve c) nitrogen bubbling. The LSP band maximum for curve b blue-shifts corresponding to curve a, the increase of its absorbance with irradiation time indicates the growth of Au NRs in the presence of small amount of acetone. In contrast, for the solution without bubbling (curve c), the dissolution of Au NRs is the same as result shown in Fig.3. This is

an important evidence of the oxidation of Au NRs (or spherical particles) by O₂ dissolved.

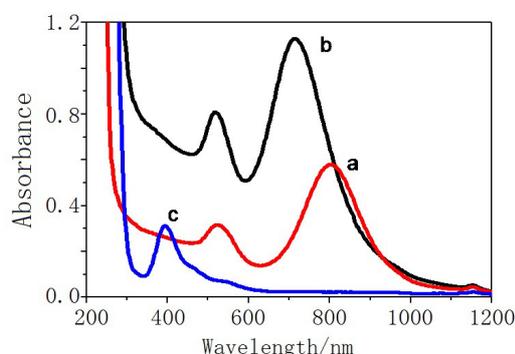


Fig.5 UV-Vis absorption spectra of the seed-mediated growth solution under the condition with (a, b) and without (c) nitrogen bubbling, UV irradiation in turn 0(a), 60(b) and 60 min(c)

图 5 晶种媒介的生长溶液在通(a、b)和不通氮气(c)条件下的 UV-Vis 吸收光谱: a, b, c 的 UV 照射时间依次为 0, 60 和 60 min

In addition, other novel spectral phenomenon was also observed, as shown in Fig.6. That is, the straw yellow Au(III)-CTAB complex solution obtained by dissolving Au NRs was further irradiated by UV light, its absorbance was gradually decreased. After 650 min irradiation, a colorless solution was obtained, indicating the formation of Au(I)-CTAB complex.

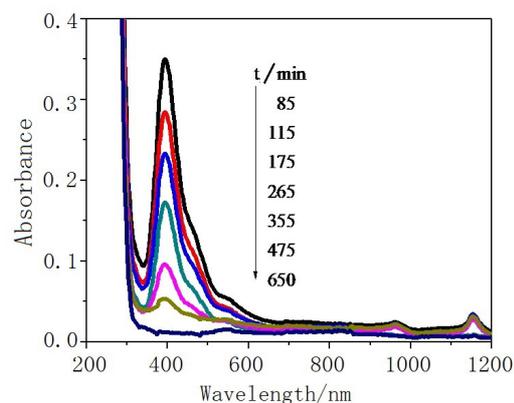


Fig.6 UV-Vis absorption spectra of Au(III)-CTAB complex formed by dissolving Au NRs with UV irradiation time

图 6 金纳米棒溶解形成的 Au(III)-CTAB 络合物随照射时间的 UV-Vis 吸收光谱

In this way, during a full UV irradiation Au NRs formed at the chemical aging stage undergo a series of changes on the morphology, and are finally dissolved to form Au(III)-CTAB complex which is further reduced to the initial Au(I)-CTAB complex ion state. According to the study by Rodríguez-Fernández et al.^[14], Au nanoparticles can be readily oxidized by Au(III) in the presence of CTAB, forming the colorless Au(I)-CTAB complex. However, the formation of the colorless Au(I)-CTAB complex here may belong to other photoreduction reaction mechanism which needs further study.

3 Conclusions

We have proved that acetone either promotes the seed-mediated secondary growth of Au NRs or causes the dissolution of Au NRs formed under condition of UV irradiation in the seed-mediated growth solution containing higher HAuCl₆ concentration. A critical concentration of acetone is a key factor. When the ratio of acetone/seed-mediated growth solution is higher than 0.1/25 (V/V), Au NRs with an aspect ratio of 3.5 (the average diameter of 14 nm) can be rapidly formed in higher yield. When this ratio is equal to (or lower than) above critical value, in contrast, Au NRs formed at the chemical aging stage can be dissolved by UV light. The dissolution of rods has the following stages: shortening, forming nanospheres and entire dissolution, resulting in the middle Au(III)-CTAB complex. This complex can be reduced by further UV-irradiation to the initial Au(I)-CTAB complex state.

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