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Rapid synthesis of gold nanorods by the combination of chemical reduction and photoirradiation processes; morphological changes depending on the growing processes†

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Combination of chemical reduction of tetrachloroaurate by ascorbic acid and subsequent ultraviolet photoirradiation resulted in the quick generation of gold nanorods quantitatively, with appreciable shape changes as the reaction proceeds.

Rod-like gold nanoparticles (gold nanorods: NRs) show unique optical properties depending on the size and the aspect ratio.[1–3] A couple of surface plasmon (SP) bands are the distinctive optical characteristics of the NRs. One SP band corresponding to the transverse mode locates in the visible region at around 520 nm, while the other to the longitudinal mode in the near-infrared (near-IR) region. Several approaches for preparing the NRs have been carried out such as templating,[4–6] electrochemical,[7] seeding,[8,9] and photochemical methods.[10,11] The electrochemical[7] and photochemical[11] methods can provide fairly uniform NRs. In the case of the electrochemical method, however, a lot of spherical gold nanoparticles are also formed in the electrolyte. Since the electrochemical method involves complicated conditions such as sonication and constant current electrolysis, it is difficult to improve the uniformity of NRs. The photochemical method, on the other hand, hardly produces the spherical gold nanoparticles, and gives high yields of gold NRs. This method is relatively simple and the shape (aspect ratio) of NRs can be controlled by the amount of silver ions present in the reaction solution. However, it requires very long reaction time of more than 30 hours. The seeding method is rather complicated because it still requires many kinds of reagents and more than two steps to generate the NRs: preparation of gold nanoparticles as seeds and subsequent growth reaction using a different solution.[8,9] In all methods, however, transition states for the growing processes of NRs have not been verified yet.

In this paper, we have found a novel approach to accelerate the photochemical formation of the gold NRs. Substantial reduction of the reaction time and simplification of the reaction solution were achieved by the combined use of chemical and photochemical reactions. During the reaction, we also found reproducible shape changes in the NRs from rectangular, I-shape, and capsule-like as the reaction time proceeded.

The reagent conditions are similar to the previous photochemical method,[11] except for the absence of tetradodecylammonium bromide (TDAB). The reaction solution contained 80 mM of hexadecyltrimethylammonium bromide (CTAB), and 2 mM of hydrogen tetrachloroaurate. Then, small amounts of acetone (65 μL), cyclohexane (45 μL), and certain amounts of silver nitrate solution (10 mM) were added to the reaction solution (3 mL). As the next step, 200 μL of ascorbic acid (AS) (40 mM) was added to the solution. Addition of the AS solution resulted in the instantaneous color change of the solution from pale yellow to colorless. Subsequently, an aliquot of the reaction solution was put into a thin quartz cell (optical path length: 1 mm), and was irradiated by ultraviolet (UV) light from an ultrahigh-pressure mercury lamp (Ushio, USH-500D, 8 mW cm^{-2}) through a band pass filter (Sigma UTVAF-33U) to eliminate the visible light. Absorption spectra from UV to near-IR regions were obtained by a conventional spectrophotometer (JASCO V-570). A multichannel spectrophotometer (Ocean Optics, SD1014DWX) was used to monitor the *in-situ* spectral changes of the solution under the UV-irradiation.

Fig. 1 shows absorption spectra of the reaction solutions before and after addition of 200 μL of AS solution, and those of the UV-irradiated solutions prepared with different amounts of silver nitrate. The absorption peaks of $AuCl_4^-$ at around 380 nm (curve (a)) disappeared instantaneously by the addition of AS (curve (b)), indicating the reduction of $AuCl_4^-$. Since the solution showed no absorption peak in the region from 300 nm to 1000 nm, it is clear that the addition of AS formed no larger gold particles having the SP band.[12] This colorless solution also showed no apparent spectral changes for a few hours, when it was kept in the dark. After the solution became colorless, the UV irradiation was carried out for 10 minutes with different concentration of silver ions. As shown in Fig. 1 (c)–(e) a couple of plasmon peaks characteristic of NRs appeared at about 520 nm and 600–800 nm. The longitudinal plasmon band showed red-shift with increasing the concentration of silver ions. As discussed in the previous paper, the effect of silver ion was crucial for the formation of NRs.[11] A noteworthy difference of the present method as compared with the previous photochemical method is that the absence of TDAB in the reaction solution. NRs having identical absorption profile were formed in spite of the presence or absence of TDAB (see ESI†). Since the effects of TDAB on the thermodynamic behavior of the CTAB-micelle are not clear, removal of TDAB from the reaction solution is very advantageous in simplifying the reaction conditions, and in discussing the reaction mechanism. Fig. 2 shows absorption spectral changes of the reaction

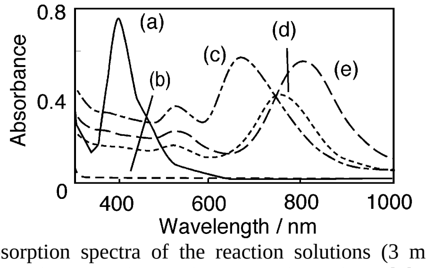

Fig. 1 Absorption spectra of the reaction solutions (3 mL) containing $AuCl_4^-$ (4 mM), CTAB (80 mM), acetone (65 μL), cyclohexane (45 μL), before (a) and after (b) the addition of AS (40 mM, 200 μL), and the spectra when 30 minutes of UV-irradiation is carried out after addition of AS with different amounts of silver nitrate solution (10 mM): (c), 31.5 μL; (d), 60 μL; (e), 200 μL. A thin quartz cell was used for the UV-irradiation and all spectral measurements. Optical path length: 1 mm.

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† Electronic Supplementary Information (ESI) available: effects of hydrophobic ammonium salt (tetradodecylammonium bromide, TDAB). (a): without TDAB, (b): 20 μM of TDAB. See http://www.rsc.org/suppdata/cc/b3/b307836a/

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solution with proceeding the UV-irradiation. The volume of the silver nitrate solution was 200 μL. Two absorption peaks characteristic of the NR could be seen even after only three minutes of UV irradiation. With proceeding irradiation, the longitudinal SP band shifted to longer wavelength region until 30 minutes, but further irradiation showed blue-shift of this SP band.

In order to verify the morphologies of the gold nanoparticles after some irradiation times described in Fig. 2, transmission electron microscopy (TEM) observations were carried out. Fig. 3 shows TEM images of the gold nanoparticles after 5, 30, and 50 minutes of UV irradiation. The images were obtained without fractional centrifugations to purify the NRs. It was shown that the chemical reduction before photoirradiation did not increase a fraction of spherical particles. After 5 minutes of irradiation, cylindrical nanoparticles are formed quantitatively (a), and their shapes are highly uniform. In the case of 30-minutes irradiation, on the other hand, both ends of the NRs are bulged (I-shaped) with high uniformity (b). After 50-minutes of UV-irradiation, some of NRs are rounded at both ends, but not ellipsoidal (c). The blue-shift of the longitudinal SP band started after 30 minutes of UV- irradiation (Fig. 2), which must reflect the morphological changes of the NRs. Transformation of the NRs into thermodynamically stable forms during the reaction is also reported in previous work,[13,14] because of long reaction times (orders of few tenths hours). In our method, however, the photoreaction to form the NR proceeded in only a few minutes, so that the facets of growth direction are likely observed in a shorter irradiation time. It may be reasonable to assume that the cylindrical particles reflect directly the facets of growth direction.[15] The NRs having round corners (Fig. 3(c)) are probably obtained by the realignment of gold atoms induced by UV-irradiation, and the cylindrical particles with bulged ends (Fig. 3(b)) may be one of the transient states of reshaping from the cylindrical particles to the round-corner particles.

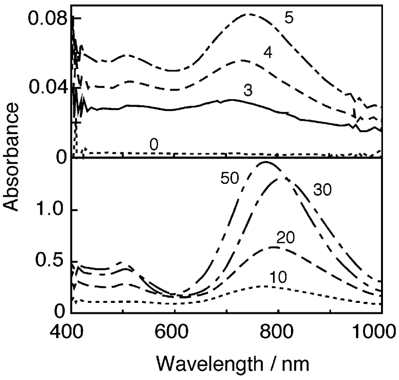

Fig. 2 Effects of UV-irradiation times on the absorption spectral changes of the reaction solution after the addition of AS with 200 μL of the silver nitrate solution. Irradiation time: 0, 3, 4, 5, 10, 20, 30, 50 min. Numbers beside the curves show the irradiation times. Optical path length: 1 mm.

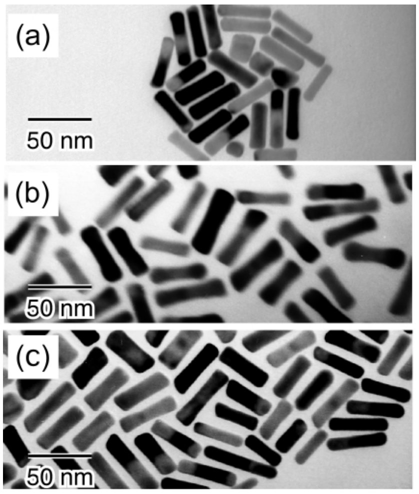

Fig. 3 TEM images of gold NRs obtained from the UV-irradiation of the reaction solution (see caption of Fig. 2) with different irradiation times: (a), 5; (b), 30; (c), 50 min.

In conclusion, the combination of chemical and photochemical processes has succeeded in the drastic acceleration of the photoreactions and simplification of reaction conditions to form the NRs. Hydrophobic quaternary ammonium salts are not essential in this method. The shape of NRs varied depending on the irradiation time. Further investigations, including high-resolution TEM observations, are now in progress.

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