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Light Driving and Monitoring Growth of Single Gold Nanorods

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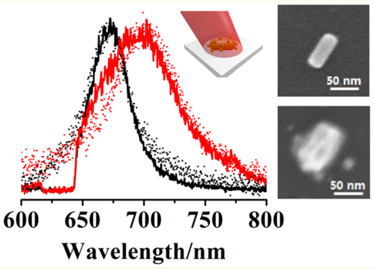
S Supporting Information

ABSTRACT: Growth processes of single gold nanorods (AuNRs) on a glass coverslip surface were monitored in situ via photoluminescence and dark-field scattering spectroscopy. We found that the growth of gold nanorod (AuNR) was light driven and the growth rate was dependent on the excitation light power and polarization. Specifically, the AuNRs can regrow to a larger size upon intense light irradiation, even if the AuNRs have reached an equilibrium state in original growth solution. Furthermore, the resonance wavelength shift during the regrowth was found to be reversible by switching on or off the light illumination. A plausible explanation for such light driven phenomenon could be due to photothermal effects, in which plasmon-induced hot electrons result in Au ions being reduced more easily upon light illumination. These findings suggest a flexible method to control AuNRs synthesis and contribute understanding to plasmon-mediated metal nanoparticle synthesis at the single nanoparticle level.



INTRODUCTION

Metallic nanostructures have unique properties compared with their corresponding bulk forms and have been studied widely in recent decades.[1] The shape, size, and composition of such nanostructures play a critical role in their optical, catalytic, and electronic properties. Many synthetic methods have been developed to prepare metallic nanostructures with various shapes, sizes, and compositions.[1−8] One of them, plasmon-mediated reactions, a class of light-driven, solution-based colloidal syntheses, have progressed from being fascinating phenomena to a controllable experimental tool.[2−4,8,9] For instance, various Ag nanoparticles have been produced in the presence of ultraviolet or visible light since the initial report on Ag nanoprism synthesis.[2] Solution-based Au nanoparticles have also been produced with ultraviolet light irradiation.[4,5] Light can be a valuable tool for influencing nanoparticle growth and realizing anisotropic nanostructures.

AuNRs are particularly interested because of their extraordinary ability to absorb and scatter light. The AuNRs growth can be investigated intermittently with electron microscopy or atomic force microscopy.[10] Most of the previous studies, light-mediated metal nanoparticle synthesis was based on ensemble measurements, such as extinction spectroscopy or transmission electron microscopy. The advent of dark-field microscopy (DFM) has enabled us to observe in situ the growth of a single AuNR on a glass surface in real time.[11,12] Recently, Baumberg et al. implemented the supercontinuum in DFM technique to watch individual AuNRs growth in real time on a millisecond time scale.[12] Therefore, because the light-based DFM method can successfully observe the growth of a single AuNR, it was claimed that the DFM method is an ideal tool to investigate nanoparticle synthesis in real time, as well as other dynamic processes such as molecular switching or sensing applications.[11,12] The following question then arises: does the light perturb the AuNRs growth when the light-based method is employed to monitor the growth process? However, the influence of light on the AuNRs growth process has seldom been reported so far at the single nanoparticle level.

In this study, we investigated the growth process of individual AuNRs on a glass coverslip surface via photoluminescence spectroscopy, which was correlated with the dark-field scattering spectroscopy method. It was found not only that light can monitor the growth process of a single AuNR, but also that light can greatly influence the growth. The AuNRs can regrow further to a larger size under high-intensity light irradiation (e.g., regrowth observed when $I > 0.5$ kW/cm^2 for a 633 nm continuous wave (CW) laser), even if the AuNRs have reached an equilibrium state in the solution. The regrowth rate is dependent on the power, wavelength, and polarization of the illumination with respect to the AuNR resonance band. Moreover, we noticed that the resonance wavelength in the regrowth process was reversible by switching on or off the illumination light. This light-mediated growth mechanism is probably due to the local heating effect, which is enhanced greatly because of the AuNRs' localized surface plasmon resonance (LSPR). These findings suggest a flexible method to control the synthesis of AuNRs, and they are valuable for understanding plasmon-mediated metal nanoparticle synthesis at the single nanoparticle level.

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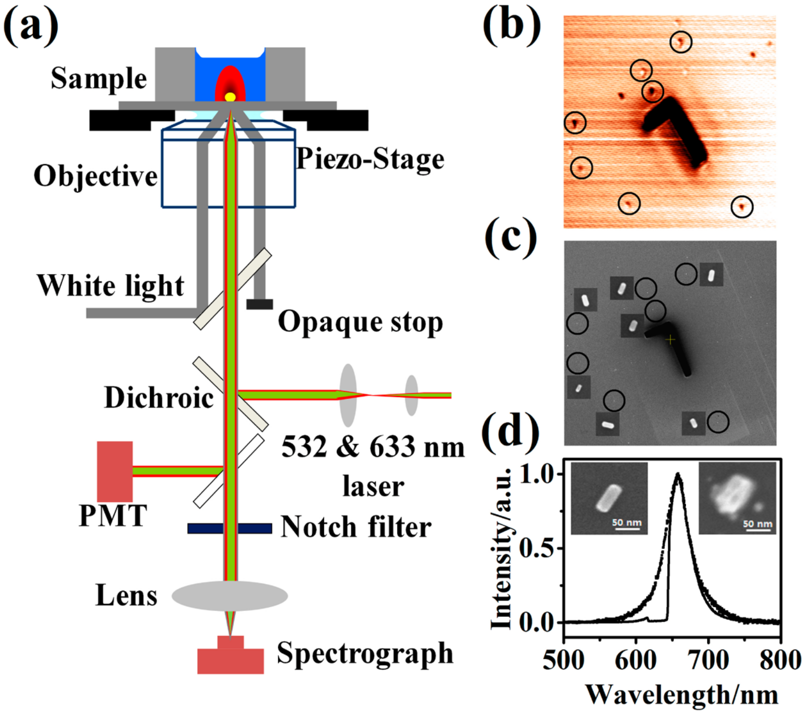

Figure 1. Optical setup schematics: (a) inverted optical system combining optical confocal scanning, white light total internal reflection scattering, and PL; (b) optical confocal scanning image acquired using a CW 633 nm laser; (c) the corresponding SEM at the same 20 μm × 20 μm area. Correlated high-magnification SEM images for corresponding locations; (d) scattering (black dot) and PL spectra (black line) excited by a 633 nm laser; inset: representative SEM images of the AuNRs before and after growth.

■ EXPERIMENTAL SECTION

Chemicals and Glassware. All chemicals were obtained from commercial sources and were used without further purification. All glassware and magnetic stir bars were soaked in freshly prepared aqua regia for hours and then rinsed with deionized water.

Synthesis of AuNRs. AuNRs were synthesized by a seed-mediated method.[6] For the seed solution, $HAuCl_4$ (0.25 mL 10 mM) was mixed with CTAB (10 mL 0.1 M) solution at 28 °C. Then, freshly prepared ice-cold $NaBH_4$ (0.6 mL) was added and the solution was stirred vigorously for approximately 2 min. The solution color changed from yellow to brownish yellow. To the growth solution, $HAuCl_4$ (2 mL 10 mM) was mixed with CTAB (40 mL 0.1 M) solution. Then, $AgNO_3$ (0.25 mL 10 mM) and HCl (0.15 mL 37.5%) were injected. After several minutes of slow stirring, ascorbic acid (0.32 mL 0.1 M) was added and the solution was vigorously stirred for 30 s. The growth solution color changed from dark yellow to colorless. Finally, 20 μL of seed solution was injected into the growth solution, which was mixed well and kept undisturbed at 28 °C for 12 h. After growth, the AuNR solution was purified by centrifugation at 14 000 rpm (5 min, twice) to remove the excess surfactant solution.

AuNRs Immobilized onto a Surface. Clean silica coverslips were coated with 200 nm of ITO film by pulsed laser deposition[13] to sustain the conductivity. Then, the coverslips were treated by oxygen plasma for approximately 5 min and immersed in 5% (v/v) MPTMS alcohol solution for 10 min to silanize their surface.[14] Excessive MPTMS was removed by super-sonication in alcohol. Droplets of AuNR solution were dropped on the MPTMS-functionalized ITO-coated coverslip and left for 5 s. Then, the coverslip was washed thoroughly with deionized water to remove the unbound AuNRs. By tuning the concentration of the AuNR solution, we can obtain a sample in which the average interval between AuNRs is approximately several micrometers. Such an interparticle spacing is suitable for a single nanoparticle detection in our inverted optical system.

Optical System. Our microspectroscopy system is based on an inverted optical microscope (NT-MDT, NTEGRA Spectra, Russia), as shown in Figure 1a.[14] A high-numerical aperture (N.A.) oil-immersion objective lens (N.A. 1.49, 60, TIRF; Olympus, Japan) was used in all measurements. This optical system allowed us to identify individual nanoparticles and measure the PL and white light dark-field scattering spectra from the same nanoparticle in situ.

■ RESULTS AND DISCUSSION

Figure 1a shows the optical setup used in the present study. The microspectroscopy system integrates an optical confocal scanning method, white light total internal reflection scattering, and photoluminescence (PL). The AuNRs were deposited on an ITO-coated glass coverslip.[14] The average separation between the nanoparticles was greater than 1 μm, so that the optical measurements could be performed at the single nanoparticle level. By etching marks on the ITO-coated glass coverslip with a focused ion beam, the same nanoparticle could be identified by an optical confocal scanning and scanning electron microscope (SEM), as shown in Figure 1b and c. Therefore, we can obtain the morphology and spectral information from the same AuNRs. The representative scattering and PL spectra of the same AuNR are shown in Figure 1d. The spectra closely resembled each other, which is related to the AuNR's surface plasmon.[15] Therefore, we can use the PL spectrum as an intrinsic signal to monitor the changes in

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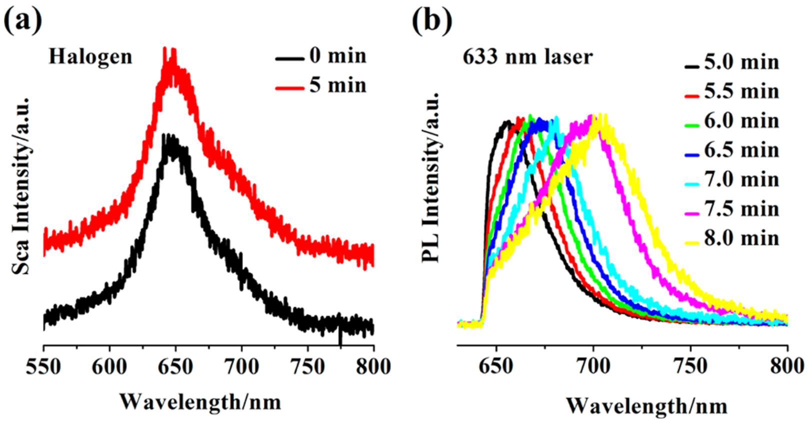

Figure 2. Evolution of scattering and PL spectra of a single AuNR during growth on a surface: (a) scattering spectra acquired with a halogen white light source within 5 min. Spectra are normalized and an offset is implemented for clear observation; (b) PL spectra of the same AuNR acquired with a CW 633 nm laser within the next 3 min.

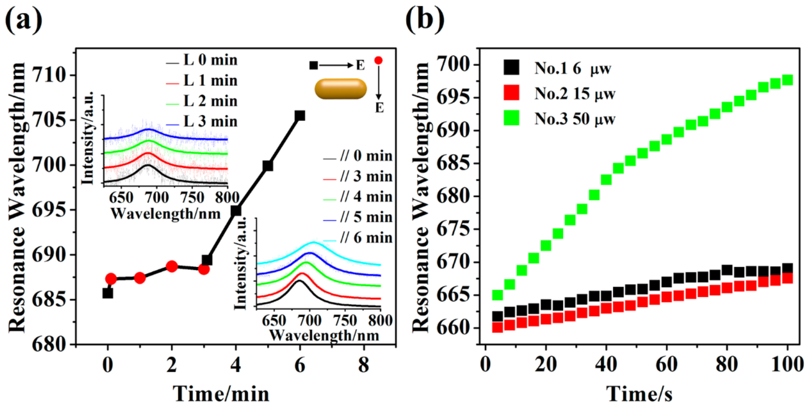

Figure 3. Influence of 633 nm laser illumination on AuNR growth: (a) surface plasmon resonance positions as a function of illumination time for different light polarizations. The red dots (black squares) represent the excited polarization perpendicular (parallel) to the AuNR long axis, respectively. Upper left inset: PL spectra of the AuNR when the excited laser polarization is perpendicular to the AuNR long axis in the first 3 min. Lower right inset: PL spectra of the AuNR when the excited polarization is parallel to the AuNR long axis in the next 3 min; (b) surface plasmon resonance positions as a function of time for various laser power values.

the local dielectric index around the nanoparticle or the changes in the nanoparticles' shape and size.[14]

Watching a single metal nanoparticle grow in situ on a surface has great interest to the community of nanoparticle synthesis. It provides valuable information for understanding the growth process, designing a controllable nanostructure, and aligning nanostructure arrays.[10,12,16] The AuNRs used in the present work were synthesized by the well-known seed-mediated method.[6] The growth time of AuNRs in the ensemble solution was approximately 12 h, which is enough to reach an equilibrium state for the AuNRs. With longer growth time, the extinction spectra showed no obvious changes (as shown in Supporting Information, Figure S1a), meaning that the AuNRs reached an equilibrium state in the growth solution. Then, the prepared AuNRs were deposited onto an ITO-coated glass coverslip. As for the AuNR regrowth on the surface, a few drops of freshly prepared growth solution (CATB 9 mL 0.1 M, AA 100 μL 0.1 M, $HAuCl_4$ 675 μL 10 mM, $AgNO_3$ 60 μL 10 mM, and HCl 45 μL 37.5%)[17] were added to the growth cell on the coverslip with immobilized AuNRs. At first, we monitored the growth of individual AuNRs illuminated with a halogen lamp. The scattering spectra of the AuNRs usually did not show any obvious change, even after 30 min. A representative scattering spectrum after 5 min is shown in Figure 2a. Then, we replaced the halogen lamp with a CW 633 nm laser and recorded its PL spectra. Interestingly, the peak position of the PL spectra was gradually red-shifted within the next 3 min, as shown in Figure 2b. During the growth process illuminated by the 633 nm laser, the longitudinal plasmon band of the AuNR red-shifted from 655 to 705 nm. It should be noted that we measured many nanoparticles and most of them presented similar properties; the results shown in Figure 2 are just a representative case.

The results shown in Figure 2a are different from previous work reported by Novo et al.[11] In that work, the DFM scattering peak of the AuNR red-shifted ~20 nm after 8 min. In our experiment, the scattering showed no obvious change, even after 30 min. We think that this difference is primarily owing to the different AuNRs samples used in the regrowth process. In the present study, the AuNRs already reached equilibrium in the growth solution after 12 h of solution-based growth. However, in ref 11, the AuNRs sample grew only 1 h in the growth solution and had great chemical activity for further regrowth. In Figure 2b, when the 633 nm CW laser was focused on the AuNR, an obvious red shift of the surface plasmon was observed within 3 min. The red shift of the PL spectra may have been caused by the deposition of Au atoms onto the AuNR surface. To confirm this, control experiments were performed using growth solution without any $HAuCl_4$ or in

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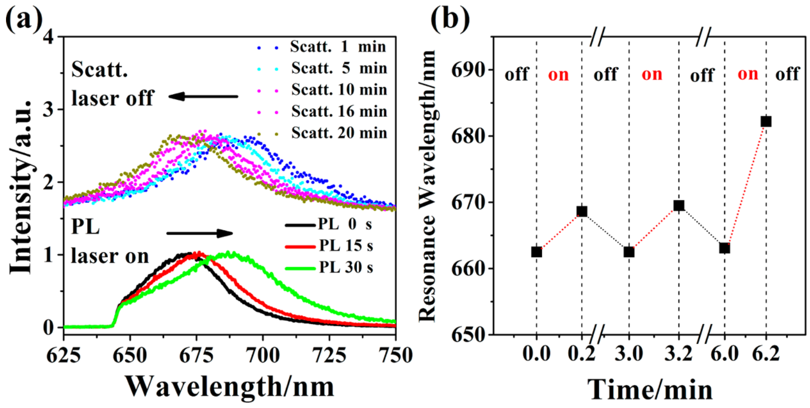

Figure 4. AuNR reversible growth: (a) evolution of AuNR PL spectra (solid lines) by 633 nm laser continuous illumination and the scattering spectra (dots) when the 633 nm laser was switched off; (b) AuNR growth on the surface with alternate light switching on or off. The surface plasmon resonance position presents reversible features.

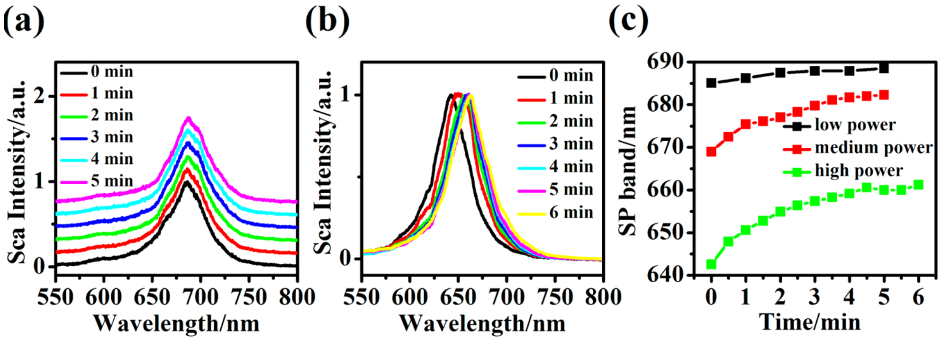

Figure 5. Influence of supercontinuum source illumination on the AuNR regrowth; (a) low illumination power; (b) high illumination power; and (c) surface plasmon resonance positions as a function of time for different excited power.

pure aqueous solution, we did not find any spectral shift (data not shown here). We also added the grown AuNRs into in new fresh growth solution for the ensemble measurements, the spectra only change slight as shown in Figure S1b. These results imply that the red shift of the PL spectra was caused by the AuNR growth. To further confirm light-induced regrowth, both intermittent and continuous laser illumination were tested, that is, the light was switched on shortly when the PL was recorded, or the light was always switched on (Supporting Information, Figure S2). We found that only for the situation in which the laser was kept on did the AuNRs' surface plasmon present a red shift. These results are also consistent with the SEM characterizations before and after the regrowth, as shown in Figure 1d. These control experiments demonstrate that the continuous illumination of light is necessary for AuNRs growth.

To further investigate the influence of laser illumination on the AuNRs growth, we changed the polarization and power of the 633 nm excitation laser. In Figure 3a, we set the laser polarization perpendicular to the AuNR long axis. The surface plasmon band of the AuNR did not change within 3 min. Then, the laser polarization was tuned parallel to the AuNR long axis, and a quick and clear red shift of the surface plasmon band appeared. The insets in Figure 3a show the spectra as a function of growth time. These results clearly show that the excitation laser polarization influences the AuNR growth rate on the surface. That is due to the polarization dependent absorption coefficient related with the AuNR's longitudinal resonant band. Then, we changed the excitation laser power, as shown in Figure 3b. The laser power affects not only the growth rate but also the magnitude of the resonance peak red shift. When the laser power is low, the red-shift rate of the surface plasmon band was slow and the shift of LSPR peak was small. When the laser power was increased, a faster and larger red shift of the LSPR peak was observed.

Interestingly, for some AuNRs, the resonant peak red-shift during the regrowth process is reversible. For instance, when the laser illumination was switched off after the AuNR had grown for a few seconds, the AuNR resonant peak blue-shifted back again. This was confirmed by scattering measurements after the AuNR first grew with laser illumination for a while, as shown in Figure 4a, because the halogen lamp would not induce AuNR regrowth as demonstrated above. Furthermore, as shown in Figure 4b, if the laser illumination was switched on and off alternatively, the AuNR's LSPR peak showed reversible oscillations. The AuNRs should grow lager when the LSPR peak red-shifts. Although the resonant peak reversibility should not be sufficient enough to evidence that the shape and surface of the AuNR recovered intact, more efforts is still needed to reveal whole truth of such reversible phenomena. Additionally, we found that these reversible properties are dependent on the illumination power and the regrowth time. For example, the resonant peak cannot blue-shift back if the duration of the regrowth is over 1 min under high intensity light illumination. And we noticed that some AuNRs did not show reversible properties, which implies that the specific surface or local environment may be leads to an irreversible growth process. Perhaps, the plasmonic tweezer effect happens in the initial growth process when the laser was switched on, and some intermediate or gold complexes were formed near and adsorbed onto the AuNRs' surface; then, these complex disassociated when the laser was switched off. However, a reasonable mechanism for this reversible process remains to be identified.

In addition, we also investigated the influence of a 532 nm laser on the AuNR growth (Supporting Information, Figure S3). Similar to the 633 nm laser, in dark conditions, the AuNR surface plasmon remained, which implies that the AuNR did not grow, or at least grew very slowly. Once the illumination of the 532 nm laser was switched on, a quick and obvious red shift of the AuNR resonance band can be seen. However, for the 532 nm laser, there are less polarization effects on the AuNR regrowth with respect to the results of the 633 nm laser. This is owing to the depolarization effect of the 532 nm laser for the excitation of the AuNR surface plasmon.[14] A CW laser at a wavelength of 785 nm was also implemented and could induce the same AuNR regrowth as the 633 nm laser (data not shown here). The polarization-dependent behaviors of different lasers are related to the AuNR's LSPR band.[14,15] We noticed that the PL spectral shape often cannot maintain a single Lorentz peak as the AuNRs grow further. Most of the PL spectra after long regrowth time become broad with low intensity. That means that the size of the nanoparticles becomes larger and their shapes change. Meanwhile, the surface of the AuNR would not be atomically smooth after the high-power light-induced regrowth, as shown in Figure 1d.

To demonstrate more details of the light illumination effect, we also used the supercontinuum source to investigate the regrowth process. The scattering spectra of single AuNRs were measured with a supercontinuum source at various power values, as shown in Figure 5. When the supercontinuum power was low, the surface plasmon band presented a slight red shift within a few minutes. As the supercontinuum power increased, a significant red shift appeared. This result directly confirms that the light power affects the regrowth rate of AuNRs. In a recent report, the supercontinuum was used to observe single AuNR growth in real time.[12] In that experiment, the illumination intensity was greater than 10 MWcm^{-2}, and such a strong light source definitely affected the AuNR growth. Therefore, they observed that the surface plasmon red-shifts by ~90 nm within 80 s. In that experiment, the light cannot be implemented only as a monitoring tool, as it also influences the growth rate.

How does light irradiation affect AuNR growth on a surface? We think that a plausible explanation is the photothermal effect.[9,18,19] When the light is illuminated on the AuNR, the light can be absorbed effectively because of the AuNR's LSPR, which can explain the excitation polarization and wavelength dependence. The free electrons excited by the light cause heterogeneous local temperatures between the AuNR and the growth solution. The AuNR surface should have a higher temperature than their surrounding solution because of hot electrons induced by light illumination. These electrons are more energetic, which will result in more gold ions being reduced. In short, the AuNR illuminated by the laser would result in hot electrons. These hot electrons break the former equilibrium and induce the deposition of more gold atoms on the AuNR surface. Once the light was switched off, the equilibrium thermal distribution was reversed. The gold atoms near AuNRs' surface would be dissociated into the solution again, leading to the scattering or PL spectra peaks blue-shifting back. Nevertheless, substantial efforts are still needed to explore the true mechanism, for examples, the effect of a highly concentrated electromagnetic field near the AuNR on the chemical reaction rate, the reactant diffusion rate near the AuNR, or the plasmonic tweezer effect, but these are is beyond the scope of this article. Our findings provide a flexible way to investigate the AuNR synthesis process and contribute to understanding to plasmon-mediated metal nanoparticle synthesis at the single nanoparticle level.

■ CONCLUSIONS

We report visible light-driven AuNR growth on a surface at the single nanoparticle level. The PL and scattering spectroscopy were implemented to monitor the regrowth process of the AuNRs in real time. The growth rate is dependent on the excitation power and polarization. The resonance wavelength shift during the regrowth is reversible by simply switching light on or off. It is believed that the mechanism of such light-driven growth is related to photothermal effects of the AuNRs. The energetic hot electrons due to LSPR assisted photothermal effect may be responsible for the gold atom reduction or dissociation near the AuNR surface. Our findings provide a way to control the AuNR size and its LSPR properties at the single nanoparticle level based on light. This experimental scheme is a good platform to explore the light-driven metallic nanoparticle growth mechanism, although more effort is necessary before its full mechanism is revealed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b04029.

> Extinction spectra of the AuNRs for control experiments with long time regrowth or with new growth solution; Illumination time dependent AuNRs growth by the 633 nm laser; Influence of 532 nm laser illumination on the AuNRs growth. (PDF)

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Notes

The authors declare no competing financial interest.

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