

Femtosecond laser induced photochemical reaction and configuration change of silver nanorod clusters in aqueous solution

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Abstract

The photochemical reaction processes and configuration change of the silver nanorod clusters in aqueous medium exposed by an 800-nm femtosecond laser and a 532-nm nanosecond laser were studied by surface plasma absorption spectra and transmission electron microscopy. The results indicate that the clusters were quickly fragmented into small nanospheres through the ejection of electrons. Then, the size of the nanospheres decreased gradually due to a series of photochemistry reactions in the surface of Ag nanospheres. Femtosecond laser has better ability to change the size and shape of the material than nanosecond laser.

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1. Introduction

Metal nanomaterials are of great interests due to their unique optical, electrical, catalysis properties, which strongly depend on the size and shape [1,2]. Among them, metal colloids have been the focus of research for many decades as a result of their special properties and promising application. Currently, metal colloids with special structures [3–6] are attracting great interests. Various techniques were used to prepare metal colloids and control their structures, such as templating [7], electrochemistry [8], ultrasonic [9], and photochemistry [3]. Different laser sources were used to prepare nanomaterials, including femtosecond laser. The size and shape of the materials depend on the energy and pulse width of the lasers. Contrasts to the wider laser pulse, femtosecond laser pulse has a great advantage because during the laser pulse no free (transparent) plasma can develop and heat diffusion into the material is minimized [10]. Several groups

studied the effect of femtosecond laser pulse in the preparation and shape control of metal nanomaterials. For example, Sylvestre et al. reported the preparation of smaller gold nanoparticles in aqueous cyclodextrins by laser ablation [11]. Qiu et al. reported the forming of metal nanoparticles in glasses induced by photoreduction through femtosecond laser exposure [12,13]. Link et al. reported the shape change from gold nanorods to near spherical particles by exposure to 800-nm pulsed lasers with different widths (100 fs and 7 ns) and pulse energies. A photothermal reshaping mechanism was proposed [10,14]. Kamart et al. observed wavelength-dependent picosecond laser irradiation-induced photofragmentation of silver nanoparticles. Electron ejection was proposed as the photochemical events that lead to the photofragmentation [15]. In despite of all the studies, the time-evolution of light-irradiation induced change of metal nanomaterials are seldom studied, which is significant for understanding the interaction between metal nanoparticles and laser light. Here, we reported femtosecond laser-irradiation induced fragmentation from Ag nanorod clusters to spherical nanoparticles (minimum size ~ 1 nm) its time-evolutions, contrasts to the nanosecond laser pulse.

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2. Experimental

Silver nanoparticles were prepared using the conventional wet-chemical method [16]. Spherical silver particles were prepared by injection of 1 mL fresh NaBH_4 (0.01 M) solution to an aqueous solution of AgNO_3 (0.02 mM, 100 mL) in the presence of citrate (0.2 M, 1 mL). The mixture solution was deposited at room temperature for 3 months. The color of the solution changed from light yellow to cyan. The absorption spectra were measured with Shimadzu UV-3101PC UV-vis-NIR scanning spectrophotometer. The morphology and size of the particles were observed with a JEM-2010 transmission electron microscope made by Japanese JEOL Company. Laser ablation was carried out with a Ti/sapphire laser (Spectra Physics Co. Ltd.), which provided 110 fs full width at half maximum (FWHM) pulses (wavelength 800 nm, maximum energy 1 mJ/pulse, repetition rate of 1 kHz). For the irradiation experiments, laser energy was 0.33 mJ/pulse. A 532-nm light generated from the Harmonic-Generator pumped by the pulsed Nd: YAG laser (1.06 μm) with a pulse duration of 10 ns, repetition frequency of 10 Hz and the energy is 0.3 J/pulse was used as excitation source. The power density of the irradiation light was 13.2 J cm^{-2} for the femtosecond laser and 750 J cm^{-2} for the nanosecond laser. Three milliliters of the silver hydrosol was placed in a cubic quartz cell with a path length of 1 cm. The sample cell was constantly rotated and moved fluctuate in order to mix the colloidal solution and to ensure that all the particles will be exposed to the laser pulses. During the process the color of the hydrosol changed from cyan to yellow and then to light brown gradually.

3. Results and discussion

Ag particles show surface plasma resonance (SPR) absorption band in visible light resulting from collective oscillations of the free electrons excited by light of a particular wavelength [17]. The SPR absorption of silver nanoclusters is strongly dependent of the particle size, shape, dielectric medium, and surface-adsorbed species. For example, Ag nanospheres have only one SPR absorption band, locating at $\sim 400 \text{ nm}$. One-dimensional Ag nanomaterials such as nanorods or nanowires exhibit two characteristic SPR bands, the transverse and the longitudinal. The location of the transverse SPR is similar to that of spherical particles. That of the longitudinal SPR locates at longer wavelength side and depends on the axial ratio of the longitudinal to transverse size [18]. Fig. 1 shows surface plasmon absorption of Ag nanomaterials before and after irradiation for different time. As shown, before exposure, two absorption bands were observed in the deposited Ag nanomaterials. One appeared around 400 nm, and the other appeared in the range of 550–700 nm. This indicates that the silver nanomaterials should be one-dimensional instead of nanospheres. After being irradiated 5 min, the absorption at 550–700 nm decreased, while a new absorption around 700–800 nm appeared. The new absorption originated from the irregular fragments, which apart from the Ag nanorod clusters. Some fragments were still attached each other like a chain that caused the absorption at long wave region (see Fig. 4). [18] With the increase of the irradiation

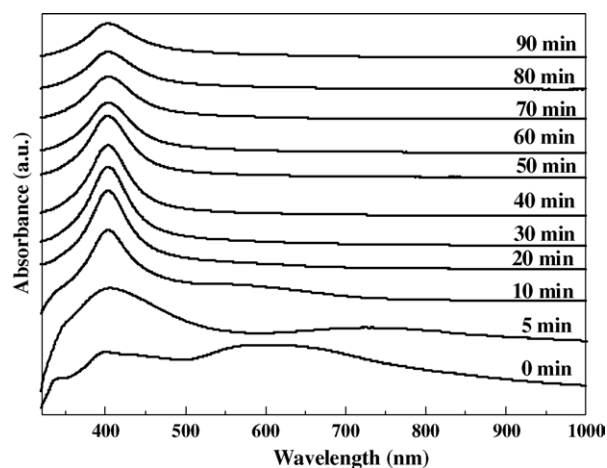


Fig. 1. UV-vis-NIR absorption spectra of silver nanoparticles changed with exposure time (exposed by 800-nm femtosecond laser).

time, the fragments were separated thoroughly, the absorption at 700–800 nm disappeared. After being irradiated for 20 min, the absorption intensity of the silver hydrosol at $\sim 400 \text{ nm}$ increased while the longitudinal SPR absorption decreased drastically and nearly disappeared, indicating that the longitudinal structures were destroyed quickly, and more and more silver nanospheres were formed at the same time. As the exposure time increased continuously, the longitudinal SPR absorption disappeared completely and the transverse SPR absorption decreased gradually. It was also seen that the width of the 400-nm band became broad gradually with the increasing of exposure time. When the free electrons at the surfaces of the small Ag particles are excited by light of a particular wavelength, and size of the particles become smaller than the mean free path of the free electrons, the width of the SPR band should broaden with the decreasing particle size, while the intensity decreases [17,19]. Once these electrons were excited by laser pulse, they do not oscillate at the same frequency like that of the unexcited electrons, thus causing the plasmon absorption band to bleach. The mean free path of Ag is 57 nm at room temperature [17]. The increase of width and the decrease of intensity of the SPR

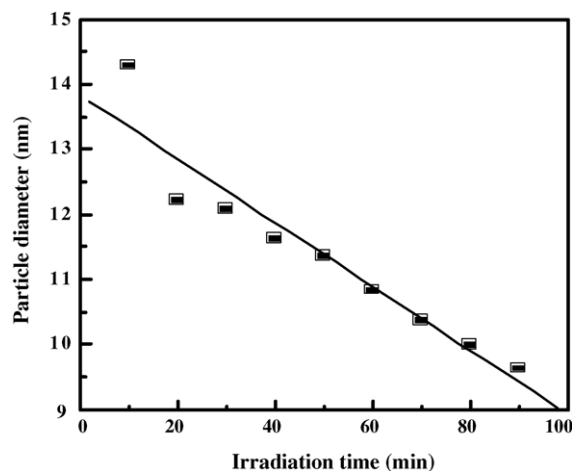


Fig. 2. The size of silver nanoparticles changed with exposure time.

band of Ag particles indicate that the size of the nanoparticles decreases with increasing exposure time. According to the Mie–Drude equation

$$r = \frac{v_F}{\Delta w_{1/2}}, \quad (1)$$

where r is the average crystal radius, v_F is the Fermi velocity of an electron and is constant 1.39×10^6 m/s, and $\Delta w_{1/2}$ is the full width at half maximum of the plasmon absorption in angular frequency [20]. The sizes of the silver particles irradiated for different time were calculated, as shown in Fig. 2. As can be seen, once the one-dimensional Ag nanomaterials were fragmented into nanospheres, the average sizes of the silver nanoparticles decreased linearly and slowly with exposure time.

Fig. 3 shows the change of absorption spectra under the exposure of 532-nm nanosecond laser pulse. After exposure, the absorption intensity of the silver hydrosol at ~ 400 nm increased while the longitudinal SPR absorption decreased and disappeared during the starting 20 min, indicating that the longitudinal structures were destroyed, and silver nanospheres were formed at the same time. After 20 min, the intensity of the absorption at 400 nm increased faintly, and almost changeless after 30 min. Differing from femtosecond laser pulse irradiation, the width of the absorption at 400 had little change, suggesting that the size of the particles did not decrease with the increasing irradiation time. Obviously, the ability of the nanosecond laser pulse to the

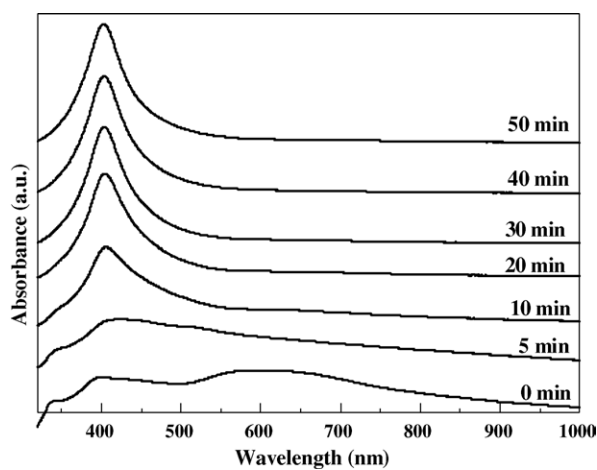


Fig. 3. UV–vis–NIR absorption spectra of silver nanoparticles changed with exposure time (exposed by 532-nm nanosecond laser).

shape change of the nanoparticles was limited even with higher power density.

Fig. 4 shows the TEM images of the silver nanomaterials before and after exposure. The sample before exposure (see Fig. 4a) exhibit as a kind of complicated structure as many rods and slices were bound together, indeed. After exposure 5 min, the one-dimensional structure was destroyed and some irregular pieces were observed (see Fig. 4b), including the chain-like

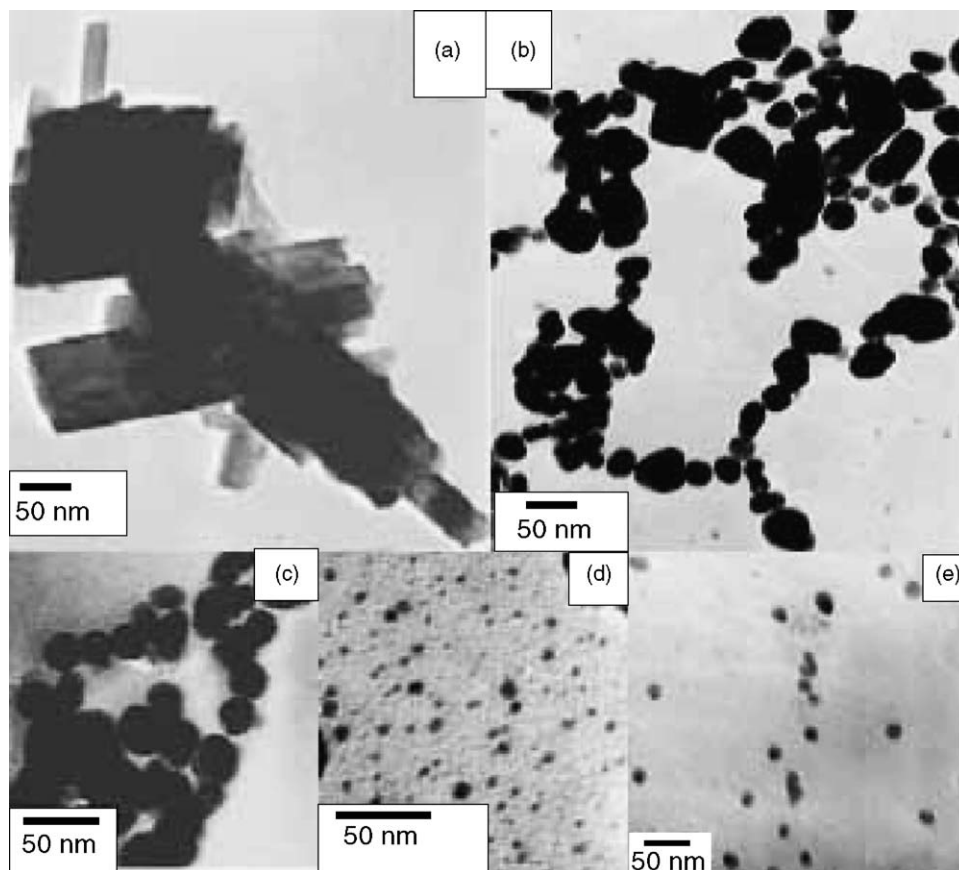


Fig. 4. TEM images of silver nanomaterials: before (a) and after exposure to femtosecond laser pulses for 5 min (b), 90 min taken at different regions (c) and (d); after exposure to nanosecond laser pulses for 50 min (e).

pieces. After exposure 90 min, Ag sphere nanoparticles were formed and the size distribution of the particles was broad (see Figs. 4c and d). The diameter of the larger nanospheres was about 10–20 nm, and the smaller's was about 1–5 nm. The large distribution of the particle sizes may be attributed to inhomogeneous density of the irradiation light. After being irradiated by nanosecond laser, the size of the nanospheres was about 30 nm evenly and no smaller nanoparticles were observed.

Now let's discuss the whole photoreaction processes. Nanoparticles of noble metals show photochemical activity when subjected to femtosecond laser. In the initial time when exposed to the femtosecond laser, the ejection of electrons took place:



This process leads to charging of the surface of the Ag nanorod clusters. As the larger silver nanorod clusters become charged with enough electrons in their surface, intraparticle charges occur, leading to the photofragmentation of nanospheres. The above fast ejection process has been literated [15] by Kamat et al. in detail. We consider that as the size of the nanoparticles is small enough, the particles cannot be fragmented as easily as the larger one, due to the higher binding energy of the small nanoclusters. In this case, the following surface photochemical reaction took place:



Firstly, photo-ionization reaction occurred on the surface of small Ag nanoshells (3.1), and some water molecules were also photo-ionized (3.2). Then, the electrons in the solution were trapped by H^+ and hydrogen was created (3.3). This was confirmed by the appearance of bladders in the whole reaction. After the above reactions were processed to the positive reaction, silver atoms were consumed, in addition, causing the intensity decrease of the SPR absorption of Ag nanoshells. The result of a series of reactions caused the size of the Ag nanospheres to decrease gradually.

4. Conclusions

In conclusions, silver nanorod clusters were irradiated by an 800-nm femtosecond laser as well as a 532-nm nanosecond

laser, in aqueous medium. The clusters were damaged into small nanospheres quickly through the ejection of electrons. Then, the size of the particles decreased gradually due to a series of photochemistry reactions in the surface of Ag nanospheres. The results above suggest that femtosecond laser has better ability to change the size and shape of the material than nanosecond laser.

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References

- [1] Y. Sun, Y. Xia, *Science* 298 (2002) 2176.
- [2] Y.W. Cao, R. Jin, C.A. Mirkin, *J. Am. Chem. Soc.* 123 (2001) 7961.
- [3] F. Kim, J. Song, P. Yang, *J. Am. Chem. Soc.* 124 (2002) 14316.
- [4] Y. Sun, Y. Yin, B.T. Mayers, T. Herricks, Y. Xia, *Chem. Mater.* 14 (2002) 4736.
- [5] R. Jin, Y. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz, *Science* 294 (2001) 1901.
- [6] M. Maillard, S. Giorgio, M. Pileni, *Adv. Mater.* 14 (2002) 1084.
- [7] P. Göring, E. Pippel, H. Hofmeister, R.B. Wehrspohn, M. Steinhart, U. Gösele, *Nano. Lett.* 4 (2004) 1121.
- [8] Y.Y. Yu, S.S. Chang, C.L. Lee, C.R. Wang, *J. Phys. Chem. B* 101 (1997) 6661.
- [9] C. Li, W. Cai, C. Kan, G. Fu, L. Zhang, *Mater. Lett.* 58 (2003) 196.
- [10] S. Link, C. Burda, B. Nikoobakht, M.A. El-Sayed, *J. Phys. Chem. B* 104 (2000) 6152.
- [11] J.-P. Sylvestre, A.V. Kabashin, E. Sacher, M. Meunier, J.H.T. Luong, *J. Am. Chem. Soc.* 126 (2004) 7176.
- [12] J. Qiu, X. Jiang, C. Zhu, M. Shirai, J. Si, N. Jiang, K. Hirao, *Angew. Chem.* 116 (2004) 2280.
- [13] J. Qiu, M. Shirai, T. Nakaya, J. Si, X. Jiang, C. Zhu, K. Hirao, *Appl. Phys. Lett.* 81 (2001) 3040.
- [14] S. Link, C. Burda, M.B. Mohamed, B. Nikoobakht, M.A. El-Sayed, *J. Phys. Chem. A* 103 (1999) 1165.
- [15] P.V. Kamat, M. Flumiani, G.V. Hartland, *J. Phys. Chem. B* 102 (1998) 3123.
- [16] K. Clays, E. Hemdrickx, M. Triest, A. Persoons, *J. Mol. Liq.* 67 (1995) 133.
- [17] R.H. Doremus, *Langmuir* 18 (2002) 2436.
- [18] Y. Sun, Y. Yin, B.T. Mayers, T. Herricks, Y. Xia, *Chem. Mater.* 14 (2002) 4736.
- [19] T. Hayakawa, T. Selvan, M. Nogami, *Appl. Phys. Lett.* 74 (1999) 1513.
- [20] T. Hayakawa, S.T. Selvan, M. Nogami, *J. Non-Cryst. Solids* 259 (1999) 16.