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THE SMALL-ANGLE X-RAY SCATTERING AND PHOTON ABSORPTION STUDIES ON THE SYNTHESIS OF SILVER NANOPARTICLES WITH THE LASER INDUCED STRUCTURE CHANGES

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Abstract. The silver nanoparticles were synthesized by mixing 10 ml 0.5 mM $AgNO_3$, 10 ml 0.5 mM trisodium citrate, and 0.6 ml 10 mM N_aBH_4 at room temperature. Right after mixing, the solution turned gold-yellow color indicating that silver nanoparticles were formed. It was discovered accidentally that the produced silver nanoparticles change color from gold to red-brown by laser irradiation during dynamic light scattering measurement (with Argon laser, wavelength 488 nm). The UV-vis absorption spectra of the laser irradiated solutions containing the silver nanoparticles exhibit two absorption peaks centered at 400 nm and about 550 nm wavelength. The intensity of the 550 nm peak increases with increasing laser exposure time while the intensity of the 400 nm peak decreases with increasing exposure time. This indicates the shape transformation from globular particle into short rod-like particle due to the laser irradiation. The small-angle X-ray scattering from the laser irradiated samples also confirm the formation of rod-like particles. The analysis shows that these as-produced silver particles have a mean radius of about 6.6 nm and the laser induced rod-like particles have a length of about 28 nm and a radius of the cross section about 8 nm (an aspect ratio of 1.75). It is likely that laser irradiation can cause closely adjacent globular silver nanoparticles to fuse together to form a rod-like particle.

1. INTRODUCTION

Nanoparticles are very useful as catalysts and sensors in biotechnology [1]. Their optical properties are highly size-dependent. It is desirable to be able to control their size and shape during the synthesis processes. In most cases, globular nanoparticles are most easily synthesized, such as by wet chemical methods with protecting surfactants, in reverse microemulsions, with UV irradiation, or laser ablation in solution [2-6]. In some rare cases, nanocube or nano-prisms were synthesized [7,8]. It is less easy to modify the size or shape of the synthesized nanoparticles in a well controlled manner once it is synthesized. Some studies showed that laser irradiation may induce fragmentation of nano-clusters into smaller nanoparticles, fusing small globular nanoparticles into larger globular particles, or turn rod-like particles into globular particles [9-14]. In this study, we will show that the laser irradiation can induce the fusion of globular silver nanoparticles into short rod-like particles. Both the UV-visible absorption and the small-angle X-ray scattering (SAXS) were used to characterize such a transformation process.

2. EXPERIMENTAL

The silver nanoparticles were synthesized by wet chemical methods similar to the methods developed by N. R. Jana *et al.* [2,3]. The silver nanoparticles were synthesized by mixing 10 ml 0.5 mM $AgNO_3$, 10 ml 0.5 mM trisodium citrate, and 0.6 ml 10 mM N_aBH_4 at room temperature. The UV-vis absorbance

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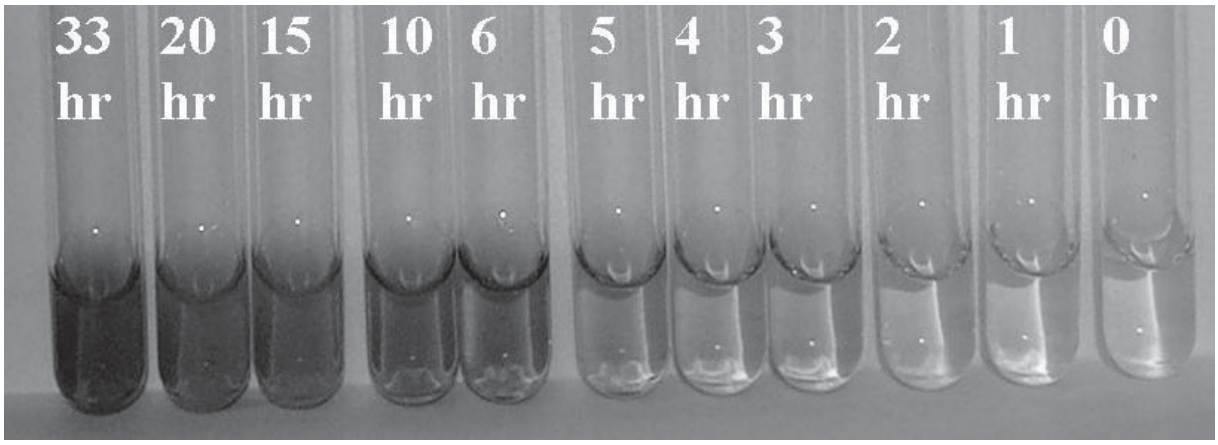

Fig. 1. The aqueous solutions containing the silver nanoparticles for different laser irradiation time.

was measured by HITACHI Spectrophotometer, model U-3410. Small-angle X-ray scattering measurements were carried out at the Department of Engineering and System, National Tsing-Hua University, Hsinchu, Taiwan. The SAXS instrument consists of a Rigaku RU-300 18 KW rotating anode X-ray generator, graphite monochromator, three pinhole collimation system with pinhole sizes of 1 mm, 1 mm, and 2 mm, and an ORDELA area detector (effective area: 20 cm by 20 cm) placed at 2 m from the sample position. The SAXS data were all corrected for background, detector sensitivity, transmission, and normalized to absolute scattering cross sections.

3. RESULTS AND DISCUSSIONS

When the silver nanoparticles were synthesized according to the method described in the previous section, right after mixing, the solution turned gold-yellow color indicating that silver nanoparticles were formed. It was discovered accidentally that the produced silver nanoparticles change color from gold-yellow to red-brown by laser irradiation during dynamic light scattering measurement (with Argon laser, wavelength 488 nm). The Argon laser was operated at 1 Watt and the laser beam was collimated through pinholes and focusing lens. Fig. 1 shows the photo of the sample solutions with different laser irradiation time, from 0 to 33 hours. One can see that the solution color changes gradually from the originally gold-yellow color to red-brown color and the color darkens with longer laser irradiation time. The color of each laser irradiated sample remained stable for months and it indicates the change due to laser irradiation is almost permanent. Fig. 2 shows the UV-visible absorption spectra of these laser irradiated samples. The as-synthesized sample shows only single absorption peak centered at 400 nm wavelength, which is typical for globular silver nanoparticles [6,15,16]. For all the laser irradiated samples they posses two absorption peaks centered at 400 nm and about 550 nm wavelength. The peak height of the 400 nm decreases with increasing laser irradiation time while the peak height of the 550 nm peak increases with increasing laser irradiation time. The existence of the 550 nm absorption peak indicates the appearance of rod-like particles due to the laser irradiation. According to the theoretical calculation [16], the rod-like particles should have an aspect ratio around 1.5 to 2.5 in order to have the 550 nm absorption peak. The broad 550 nm peak implies there is a size distribution of the rod length. The 550 nm absorption peak corresponds to the longitudinal plasmon resonance absorption mode for rod-like particles. The longitudinal plasmon resonance absorption peak will shift to longer wavelength for increasing the aspect ratio of the rod-like particles. The almost no change of this 550 nm peak position indicates that the size or shape of the rod-like silver particles is almost the same for different laser irradiation time. In fact, the rod-like particles have another absorption peak corresponding to the transverse resonance plasmon mode, which is also at the 400 nm wavelength and it can not be distinguished from the 400 nm absorbance peak of the spherical silver nanoparticles. Since the two peaks are slightly overlapped, the absorption spectra are fitted with two Lorentzian functions to accurately determine their peak positions and peak area. Figs. 3-5 shows the absorption spectra together with the

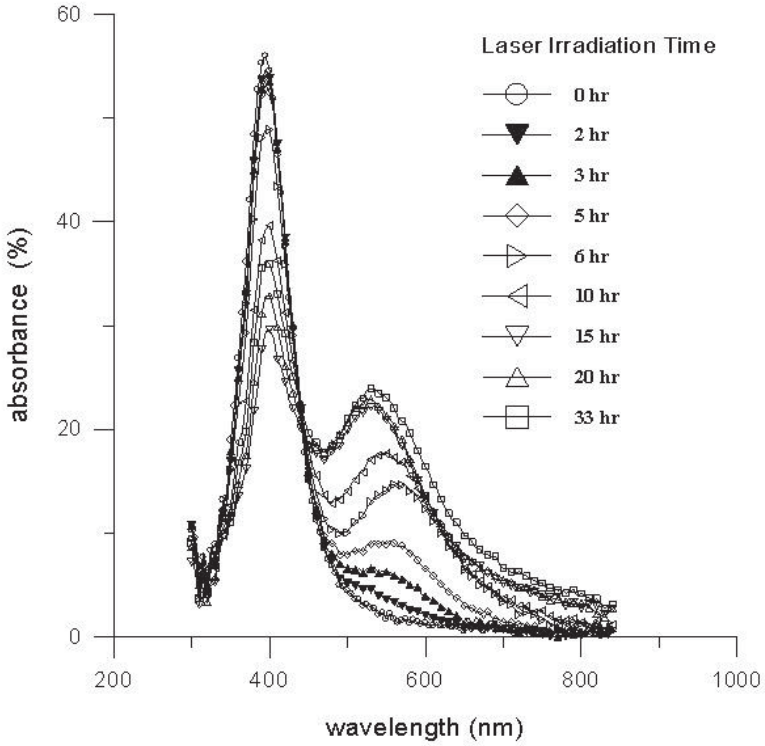

Fig. 2. The UV-vis absorbance spectra of the silver nanoparticles with different laser irradiation time.

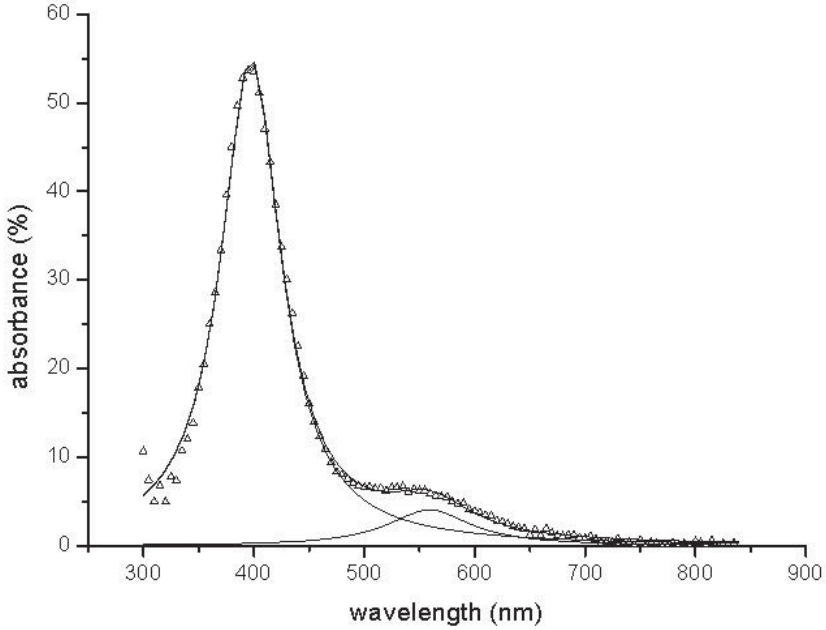

Fig. 3. The UV-vis absorbance spectra of the silver nanoparticles with 3 hour laser irradiation. The spectrum was fitted with two Lorentzian peaks.

fitted results of the separate absorption peaks for 3, 6, and 15 hours of laser irradiation time, respectively. For the 3 hour irradiated sample, the 550 nm peak appears as a small shoulder on the 400 nm peak. The number density of rod-like particles is still small. For this sample, most of the 488 nm laser photons are still absorbed by the spherical silver nanoparticles. As shown in Fig. 4 for the 6 hour irradiated sample, the 550 nm peak is quite visible and the 488 nm laser photons are absorbed equally by the 400 nm peak and the 550 nm peak (both have about the same absorbance for the 488

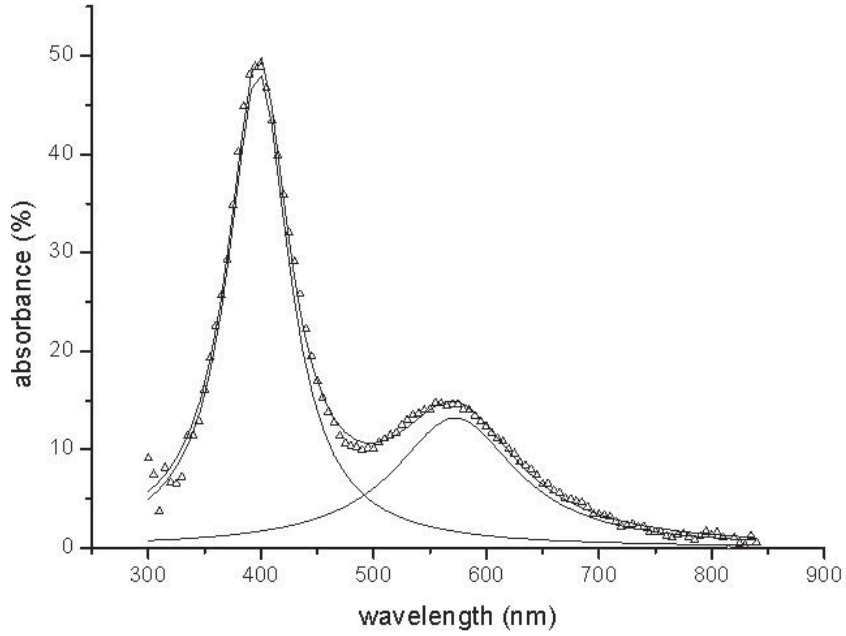

Fig. 4. The UV-vis absorbance spectra of the silver nanoparticles with 6 hour laser irradiation. The spectrum was fitted with two Lorentzian peaks.

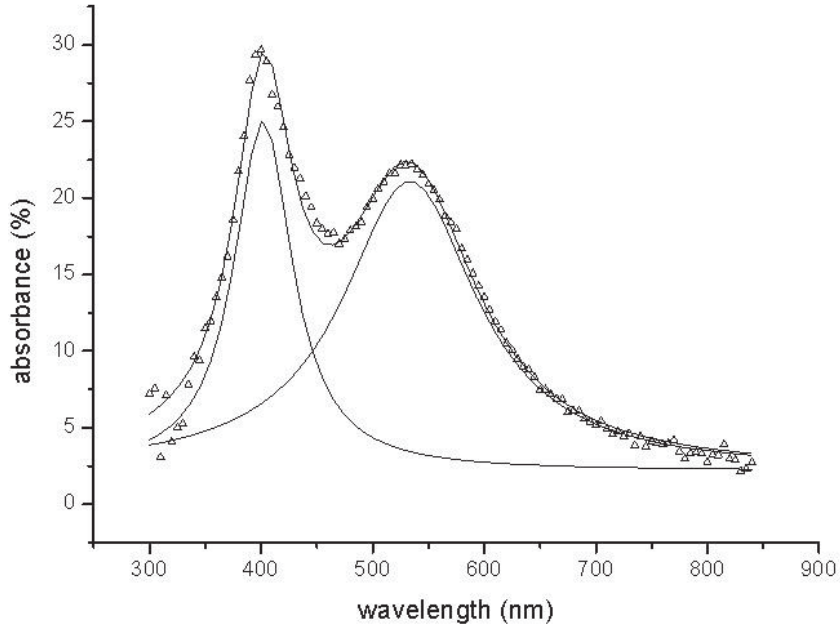

Fig. 5. The UV-vis absorbance spectra of the silver nanoparticles with 15 hour laser irradiation. The spectrum was fitted with two Lorentzian peaks.

nm photons). For the 15 hour irradiated sample, as shown in Fig. 5, the absorption spectra shows a strong and broad 550 nm peak in conjunction with a decreased 400 nm peak. For the 15 hour irradiated sample, most of the 488 nm laser photons are absorbed by the 550 nm peak and the 400 nm absorption peak can only absorb a much smaller fraction of the incident laser photons. The efficiency to turn the remaining spherical particles into rod-like particles will be decreased due to the attenuation of the rod-like particles for their longitudinal and also the transverse plasmon resonance absorption.

Fig. 6 shows the plot of the peak areas of the 400 nm peak and the 550 nm peak as a function of the laser irradiation time. The 400 nm peak area decreases steadily with the laser irradiation time in

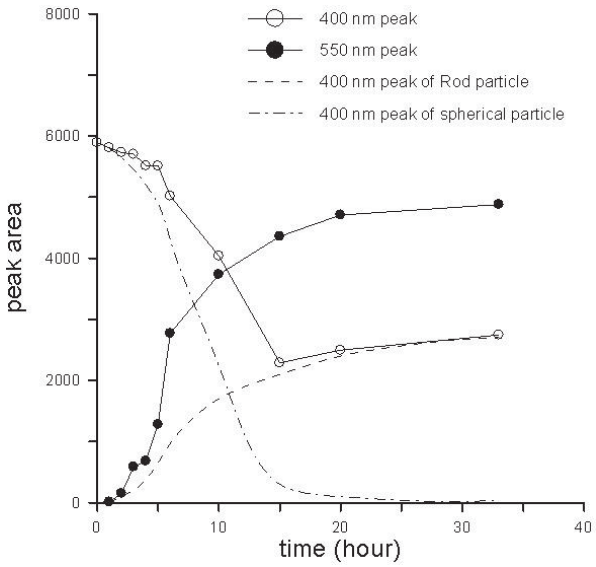

Fig. 6. The two peak areas of the UV-vis absorbance spectra of the silver nanoparticles as a function of the laser irradiation time. The 400 nm peak is decomposed into two components corresponding to the absorption by spherical particles and to the transverse plasmon mode of the rod-like particles (as illustrated by the two dashed lines).

the initial period of 0 to 5 hour irradiation times. The 400 nm absorption peak drops much faster in the period of 5 to 15 hour of irradiation times. A minimum point is reached at the 15 hour irradiation time. The 400 nm peak area increases only slightly from 15 to 33 hour irradiation times. For the 550 nm peak, in the initial 0 to 5 hour irradiation time, the peak area increases steadily with irradiation time. The increase in peak area is faster in the 5 to 6 hour irradiation period. Further increasing the irradiation time, a saturation plateau is gradually approached. In fact, the 550 nm peak area only increase slightly from 15 to 33 hour of irradiation times. As mentioned previously that the 400 nm absorption peak is due to the absorption of the spherical particle and also the transverse plasmon resonance mode of the newly formed rod-like particles. The variation of the 400 nm peak area with the irradiation time can best be understood by separating these two contributions. The decrease of the 400 nm peak area in the 0 to 15 hour period is due to the decrease of the spherical particle number density and the plateau or slightly increase in the 15 to 33 hour period is due to absorption of the transverse plasmon mode of the newly formed rod-like particles. The broken curves in Fig. 6 are illustrative to show the possible contributions of absorption by the spherical particles and the rod-like particles to the 400 nm absorption peak and how they vary with the laser irradiation time. As illustrated in Fig. 6, both the component of the 400 nm absorption peak area due to rod-like particles and the 550 nm absorption peak area vary in a similar way with the irradiation time. The increase in the absorption peak area indicates the number density of the rod-like particles also increases with laser irradiation time. The component of the 400 nm absorption peak area due to the spherical particles decreases steadily to near zero after about 15 hour of laser irradiation. This means that almost all the spherical particles are fused into short rod-like particles in about 15 hours of laser irradiation.

Fig. 7 shows the changes in the absorption peak positions as a function of the irradiation time. For the 400 nm peak, there is no change in the peak position in the whole irradiation period. For the 550 nm peak, the peak position seems to increase slightly from 550 nm to the 570 nm from 2 to 6 hour of laser irradiation, then to decrease to about 535 nm. The slightly decrease in the peak position at long hours of laser irradiation may be due to the photon absorption by the longitudinal plasmon mode of the rod-like particle and to induce slight melting effect to shorten the rod-like particles [14].

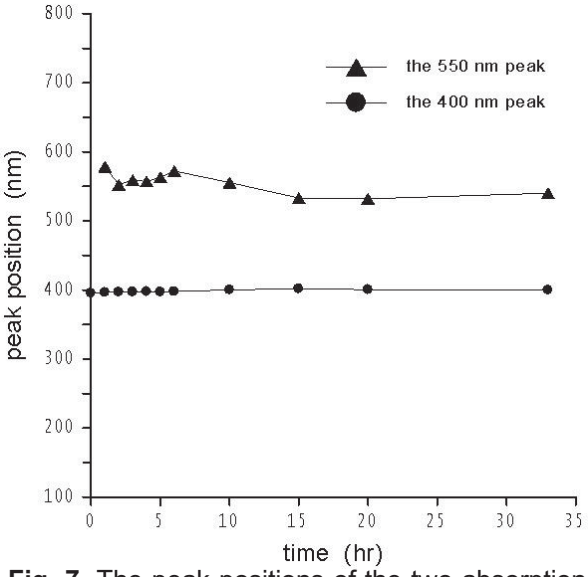

Fig. 7. The peak positions of the two absorption peaks of the UV-vis absorbance spectra of the silver nanoparticles as a function of the laser irradiation time.

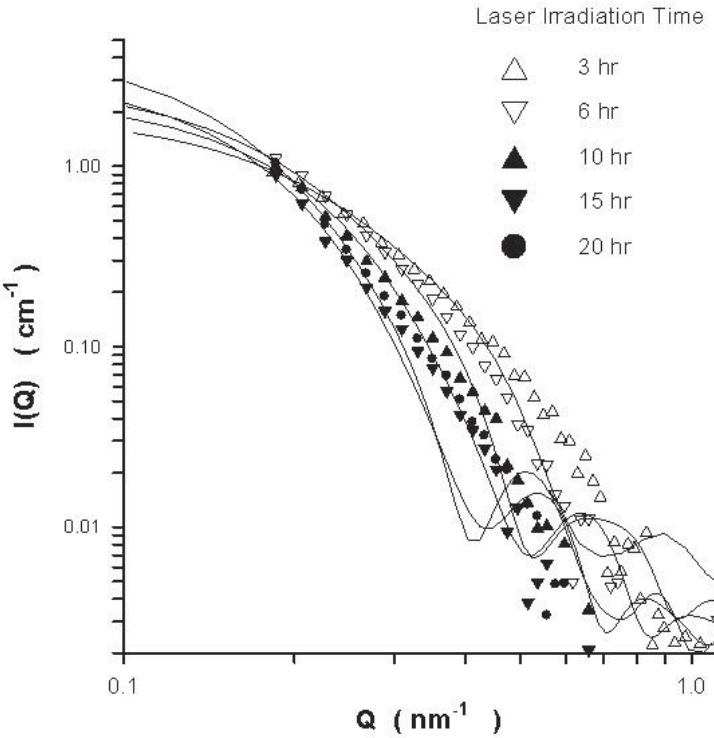

Fig. 8. The measured small-angle X-ray scattering data from the laser irradiated silver nanoparticles. The solid lines are the fitted curves using rod-like particle model.

SAXS is a useful tool to investigate the size and shape of nanoparticles in its original environment. Another advantage is to have the averaged results of the whole sample. The measured SAXS curves are represented as the scattering cross section per unit sample volume $I(Q)$ as a function of scattering vector Q, where Q is the equal to $(4\pi/\lambda)\sin(\theta/2)$, here λ is the wavelength of the incident X-rays and θ is the scattering angle. Fig. 8 shows the measured SAXS curves of these laser irradiated samples in a log-log plot. The solid curves are the fitting results using the rod particle scattering model [17]. To simplify the analysis, the fitting model assumes monodisperse rod-like particles and also neglects the scattering contributions from the spherical particles. The scattering intensity is proportional to the square of the particle volume. From the UV-visible absorption spectra, the laser fused rod-like particles should have an aspect ratio around 2; thus the volume of the rod-like particle should at least two to three times the spherical particles. Also, the number density of spherical particles should decrease to a much smaller value for sample with more than 10 hours of laser irradiation. The results of the rod particle model fitting are listed in Table 1 for the obtained scattering amplitude $I(0)$, the rod radius and length. The scattering amplitude roughly increases with increasing laser irradiation time, and it indicates that the particles in the sample are getting bigger due to laser irradiation. The analysis of the original sample (with laser irradiation) shows that the as produced silver nanoparticles has a mean radius of about 6.6 nm. As listed in Table 1, the mean radius of the rod-like particles increase from 5.8 nm to 9.9 nm while the length increases from 25 to 32 nm as the laser irradiation time increases from 3 to 33 hour. On the average, the rod-like particle has a length of about 28 nm and a radius of 8 nm. From the SAXS results, the aspect ratio of the rod-like particle is equal to 1.75. This number is in good correspondence to the result of UV-visible spectra.

The possible mechanism of such laser irradiation induced globular particle to short rod-like particle transition may be attributed to the fusing of closely adjacent spherical particles. The as-synthesized spherical silver nanoparticles are protected by adsorbing some trisodium molecules on their surfaces to keep them from forming large aggregates and precipitating. The protection by the adsorbed molecules may not be perfect all the time and the heat up by the laser irradiation may cause the protection to fail. The nanoparticles may well

Table 1. The results of the analysis of the small-angle scattering data from the silver nanoparticles with different laser irradiation time using rod-like particle model. The rod-like particle has a length *L* and radius *R* of the cylindrical section. *I*(0) is the scattering amplitude.

Laser Irradiation Time (hour)	*I*(0) (cm^{-1})	*R* (nm)	*L* (nm)
3	1.96	5.8	25.1
6	2.93	7.3	28.0
10	2.40	8.1	24.3
15	3.32	9.8	28.6
20	4.64	9.9	31.9

have chances to be in close contact and surface melting by the laser irradiation can cause the nanoparticles to fuse together. Two to three spherical particles in a chain can be fused to form short rod-like particles in such a process. It seems that the fusing is more likely to occur between spherical particles instead of fusing spherical particles with the rod-like particles to further increase the aspect ratio of the rod-like particle.

4. CONCLUSIONS

In this study we discovered that by using the 488 nm laser irradiation of the as-synthesized silver nanoparticles, the originally spherical silver nanoparticles with radius about 6.6 nm were transformed into short rod-like particles with an aspect ratio of about 1.75. Both the UV-vis absorption and SAXS were successfully used to investigate the transformation process. It is likely that laser irradiation can cause closely adjacent globular silver nanoparticles to fuse together to form a short rod-like particle.

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