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Nanophotothermolysis of Poly-(vinyl) Alcohol Capped Silver Particles

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Abstract Laser-induced thermal fusion and fragmentation of poly-(vinyl) alcohol (PVA)-capped silver nanoparticles in aqueous medium have been reported. PVA-capped silver nanoparticles with an average size of 15 nm were prepared by chemical reduction technique. The laser-induced photofragmentation of these particles has been monitored by UV-visible spectroscopy and transmission electron microscopy. The morphological changes induced by thermal and photochemical effects were found to influence the optical properties of these nanoparticles.

Keywords Nanoparticles · PVA · Silver · Surface plasmon · Thermolysis

Introduction

Ultrafine metal particles in the nanometer regime have various interesting properties compared with bulk metals because of their quantum size effects, so they hold promise as advanced materials with new electronic, magnetic, optical, and thermal properties, as well as new catalytic properties [1]. Metal nanoparticles (NPs) are certain to be the building blocks of the next generation of electronic, optoelectronic and chemical sensing devices [2]. One of the most important applications of metal NPs is as catalysts [3]. The activity of a catalyst largely depends on the particle size. Several methods have been employed to control the particle size in solution. A common feature of those methods is that the size control is achieved by changing the reaction conditions, for example, adding surfactants as protective agents, changing pH, concentration of reactants, etc. However, once metal NPs are synthesized, it is very difficult to break them effectively, particularly, when their diameter is less than 50 nm. Thus, the size-manipulation of metal NPs remained a major challenge for materials scientists and physical chemists. The first successful attempt was reported by S. Koda et al. [4, 5]. They have employed short-laser pulses to induce photofragmentation of pure metal NPs (gold and silver). However, in recent time polymer-protected metal NPs have gained much attention than that of pure metal NPs, owing to their extensive applications in bio-medical engineering (as sensors and drug-delivery agents), site-selective catalysts, and optoelectronic components, etc. Hence, it is necessary to apply the Koda-technique to achieve the smaller polymer-capped metal NPs. The only appreciable effort was made by P. V. Kamat and co-workers to investigate the photofusion and fragmentation of thionicotinamide capped gold NPs [6]. However extension of this technique to other metal NPs capped with other polymers has not been explored. In the present communication, we have made an approach to investigate the fusion and fragmentation of PVA capped silver NPs induced by continuous laser irradiation. The laser induced photo-fragmentation of these particles has been monitored by UV-visible spectroscopy and transmission electron microscopy. The morphological changes induced by thermal and photochemical effects were found to influence the optical properties of these NPs.

Experimental

PVA capped silver NPs were synthesized by a chemical reduction technique using $NaBH_4$ (Extra pure, Junsei

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Chemicals Co., Ltd.) as reductant, poly-(vinyl) alcohol (1,500) (98.0%, Showa Chemical Co., Ltd.) as a stabilizer and $AgClO_4 \cdot H_2O$ (99.999%, Aldrich Chem. Co.) as the source for the Ag^{4+} ion. Exact experimental procedures are as follows: 97 mL of distilled water was placed in a 250 mL glass beaker in an ice bath. A calculated quantity of 1 mM silver perchlorate followed by 100 mM sodium borohydride and 3 mM of trisodium citrate was added to the above beaker under vigorous stirring. This solution was used as the reference colloid. Then PVA capped samples were prepared by inserting 1 wt% of poly-(vinyl) alcohol to the reaction mixture instead of trisodium citrate. This was used as the experimental colloid. A transparent bright yellow color was observed immediately in both the cases due to the formation of the silver colloid. UV-vis spectra were taken by a UV-visible spectrophotometer (UV-2550, Shimadzu). TEM images were collected to investigate the morphology of NPs (JEM-2010, JEOL). Laser irradiation experiments was carried out in a quartz cuvette (10 mm × 2 mm) by using 325 nm continuous laser radiation with a power of 9 mW/cm^2.

Results and Discussion

UV-vis spectra of the silver NPs recorded in the aqueous medium is shown in Fig. 1. PVA-capped silver colloid has shown the surface plasmon band at 390 nm (silver colloid obtained in the presence of trisodium citrate also showed the surface plasmon band at this position). This confirms the formation of PVA capped silver nanoparticles. Before the laser irradiation the native PVA capped silver colloids exhibit a prominent surface plasmon band at 390 nm. Upon laser irradiation of PVA capped silver NPs suspension for

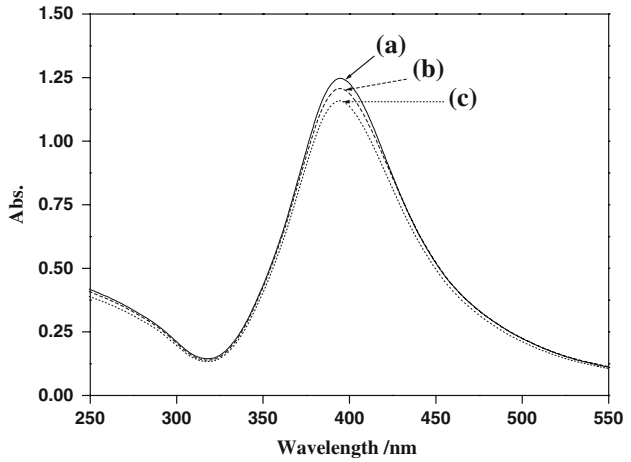

Fig. 1 UV-visible spectra of PVA capped silver NPs in aqueous suspension (**a**) before laser irradiation, after laser irradiation for (**b**) 5 min, and (**c**) 30 min

5 minutes, a slight blue shift (~4 nm) in the plasmon band was observed. The full-width at half-maximum (FWHM) of the spectrum also decreased after irradiation. This effect is due to the formation of larger size aggregates (which has decreased the particle concentration) caused by photochemical reaction. The morphological changes of the PVA capped silver NPs caused by the laser irradiation were investigated by transmission electron microscopy and are shown in Fig. 2. The average size and its standard deviation of three different particles—as-synthesized, 5 min, and 30 min laser irradiation—were investigated. Particle size was estimated by using JEM-2010, JEOL transmission electron microscope at a magnification of 150,000 on an average of 1,000 particles. Native PVA capped Ag particles were clearly shown to have an average size of 15 nm. The samples taken after 5 and 30 min of laser irradiation were found to have particles with average size of 46 and 8 nm respectively. Native PVA capped silver NPs prepared by chemical reduction technique were all most spherical in shape with a diameter of 15 nm (Fig. 2a). The TEM image also shows the presence of cluster islands, each consisting of several NPs that are in close contact. The samples taken after 5 min of laser irradiation shows the formation of large size particles that are nearly spherical (Fig. 2b). These large size particles which are well separated from each other do not exhibit optical transitions that correspond to aggregation effects. These results are similar to those observed by Kamat et al. [6]. The TEM image (Fig. 2b) supports the hypothesis that aggregates of PVA capped silver NPs undergo fusion to form larger NPs even under short-term laser irradiation. Although these nanoclusters have grown in size (46 nm), they are well separated from each other, thus ceasing the aggregation effects on the absorption spectrum. No such changes were noticed for bare silver NPs [4]. Even it was not observed for sodium dodecyl sulfate (SDS) stabilized silver particles. Similar effect was also observed by Kamat et al. for gold nanoparticles. We expect that bare silver nanoparticles do not show such photofusion effect because individual particles are well separated (even if they form larger clusters due to Ostwald ripening in the absence of stabilizer) and thus the heat gained from laser excitation is quickly dumped into the surrounding aqueous medium. However, the nature of the capping agent is expected to play a major role in this process. Capping agent has two major roles in the whole process. (i) It has to make the metal particle surface photochemically active to react with the laser radiation by capturing the photoejected electrons, (ii) To hold the heat generated in this process for a critical period to cause photo-thermal melting of the nanoparticles [6, 8–10]. Poly-(vinyl) alcohol (mp ≈ 230 °C) is expected to be more effective in the above two processes than that of sodium dodecyl sulfate (mp ≈ 200 °C). When the laser irradiation

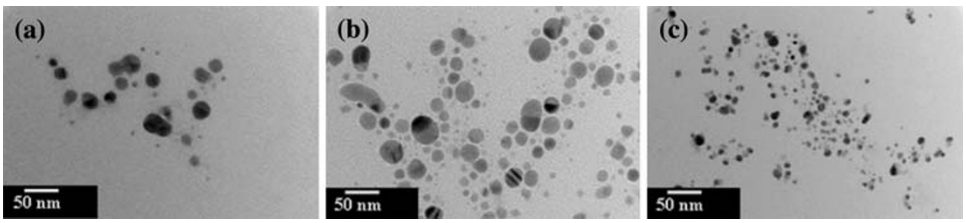

Fig. 2 TEM images of PVA capped silver NPs in aqueous suspension (**a**) before laser irradiation, after laser irradiation for (**b**) 5 min, and (**c**) 30 min

was continued for 30 min, fragmentation of these nanoclusters were observed (shown in Fig. 2c), which produced NPs with average size of 8–10 nm. However, this was not reflected in the UV-vis spectrum. This was expected to be either due to the formation of aggregates that has ceased the fragmentation effect or due to the excitation damping of the surface charge. However the exact mechanism is still under investigation.

The phase of the NPs has been investigated by X-ray diffraction technique. As shown in Fig. 3, resultant product has shown all the major peaks of metallic silver with fcc structure, which has supported the results obtained from HRTEM analysis. A slight change in the intensity of the XRD peaks has been noticed which is expected to be due to the change in the crystallite size of the PVA capped silver particles before and after laser irradiation. The mean crystallite diameter was calculated (using Scherrer's formula) to be 16.3, 42.7, and 11.4 nm for the native PVA-capped silver nanoparticles, samples obtained after 5 and 30 min of laser irradiation respectively. These values are in good agreement with the results obtained from TEM images (Fig. 4).

Two possible physical mechanisms were suggested that could lead to the laser-induced explosion of NPs; thermal

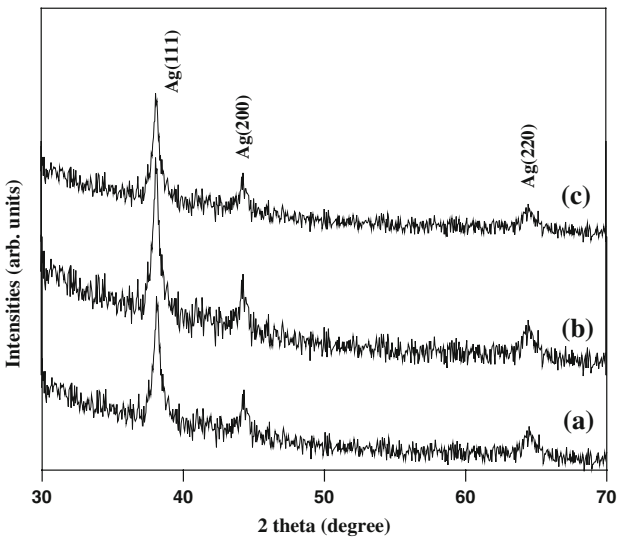

Fig. 3 XRD patterns of PVA capped silver NPs in aqueous suspension (**a**) before laser irradiation, after laser irradiation for (**b**) 5 min, and (**c**) 30 min

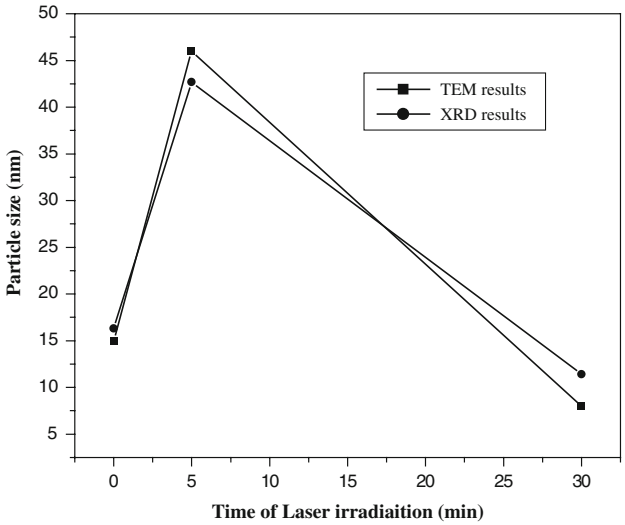

Fig. 4 Graph showing the comparison of the particle size obtained from XRD and TEM results

explosion through electron-phonon excitation-relaxation, and Coulomb explosion through multiphoton ionization. We have tried to explain our results by considering the thermal explosion via electron-phonon excitation-relaxation concept. This phenomenon was expected to be the melting (fusion) of aggregates to form larger spherical particles during initial stages of laser irradiation. Since surface-modified silver NPs exists as aggregates it was expected that the energy gained from the absorbed photons to be dispersed as excess heat to the neighboring particles and thus to induce their fusion. Similar laser-induced fusion is not observed in bare silver NPs [7, 8]. When laser was irradiated for longer time, particle promptly approaches the melting point. If there are some cracks in the parent particle, then it may explode to fragments. Smaller particles of about 10 nm may be thus produced [9, 10].

Conclusion

In conclusion, at long-term continuous laser irradiation we have observed the photothermal fragmentation of PVA capped silver NPs. Similar results have been observed by pulsed laser irradiations by other researchers. It was expected that the photoejection of electrons followed by

the charging-up of the metal surface is a possibility that could lead to the particle fragmentation. The surface-complexed PVA may also play a role by capturing the photoejected electrons at the silver surface.

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