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Preparation of starch stabilized silver nanoparticles with spatial self-phase modulation properties by laser ablation technique

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Abstract Silver nanoparticles inside the starch solution have been successfully fabricated by laser ablation of a silver plate immersed in starch solution. The ablation has been done using a Q-switched Nd:YAG laser at 10 Hz repetition rate. The starch solution allows for the formation of silver nanoparticles with uniform particle diameters and well dispersed. The ablation was performed at different time durations to study the influence of the laser ablation time on efficiency of particle formation and sizes. The Spatial Self-phase modulation phenomena which can determine the nonlinear optical property of the samples were also investigated for starch solutions containing silver nanoparticles.

1 Introduction

Nanoparticles (NPs) are engaging, very interesting materials with high potential applications in a vast research area. For example, the ability of metal NPs to increase the nonlinear refractive index of material has been well known [1]. Many physical and chemical methods have been applied for the fabrication of NPs [2–4], but preparation of metal NPs by laser ablation (LA) of metal plate in a liquid medium is an alternative method. The advantage of LA in liquid over in vacuum or gas is that the used solvent during LA process can provide physical impacts such as cooling and confinement [5, 6]. Previously, adducts effect on the size of NPs and stability in solutions has been reported [7, 8]. The preparation of NPs by LA of silver plates in polyvinyl pyrrolidone (PVP) aqueous solutions has been studied before and was found to have NPs in PVP solution which were more stable as compared to the NPs prepared in pure water [9, 10]. PVP also prevented aggregation of ablated atoms, clusters and droplets produced by LA in the solution, and subsequently PVP influenced the particle size.

Starch which is a polymer of hexacarbone monosaccharide-D-glucose as a single helix structure [11], as shown in Fig. 1, can cover the surface of the metal NPs by hydroxyl groups as a capping agent. This is due to the surface of many

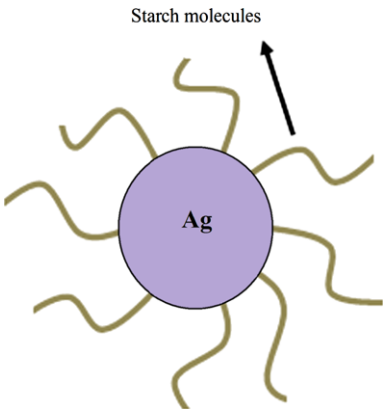

Fig. 1 The schematic representation of Ag-NPs stabilized by starch molecules

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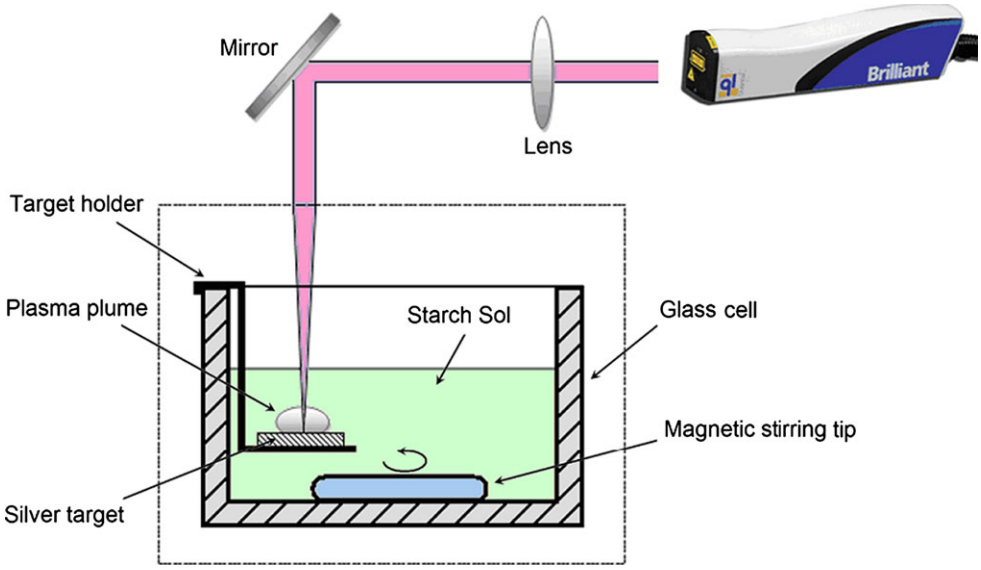

Fig. 2 Schematic diagram of the LA experimental setup

metallic NPs such as Ag, Au, and Cu which is negatively charged [12]. Many researchers showed the ability of starch as a suitable dispersant or stabilizer for the preparation of metal NPs [13, 14] but this ability has not been tested for preparation by the LA technique. Starch is available easily, eco-friendly and economical as compared to other stabilizers available on the market.

When an intense electromagnetic wave propagates in a medium, it changes the refractive index of the medium and induces nonlinearity in the refractive index. This change in the refractive index then reflects back on the wave, by changing its propagation characteristics. As a result of this interaction, some interesting phenomena can be observed. One of these phenomena is beam divergence and a diffraction pattern in the far-field after propagation of the beam through the medium. This spatial redistribution of transverse cross-section of the laser beam profile is well-known as spatial self-phase modulation (SSPM) [15]. In this article, we report both the preparation of silver nanoparticles (Ag-NPs) in a starch solution using the LA technique and the investigation of SSPM phenomena on the prepared sample.

2 Experiment

The design of experimental setup that was applied for the preparation of Ag-NPs is shown in Fig. 2. A silver plate (Sigma-Aldrich, 99.99% purity) was located in a glass cubic cell and containing 20 ml of freshly aqueous starch (1 wt%) solution. The silver plate was first cleaned using an ultrasonic bath for 30 min and then immersed in the starch solution (Fig. 2). For ablation, a pulsed Q-switched Nd:YAG laser (Brilliant) with 10 Hz of repetition rate, 100 mJ/pulse, and pulse duration of 5 ns at its original wavelength (1064 nm) was directed at the silver plate surface for ablation to produce Ag-NPs. The laser beam was focused at the plate vertically by a 25 cm focal length lens and a flat mirror. The solution was magnetically stirred during ablation process to disperse the produced NPs. The ablation has been done for different duration times (15, 30, 45, 90 min) at room temperature. The characterization of the prepared Ag-NPs was done with a UV–Visible double beam spectrophotometer (Shimadzu) and a Transmission Electron Microscopy (TEM, Hitachi H-7100). Particle diameters were obtained by software UTHSCA (Ver. 3) and analyzed using

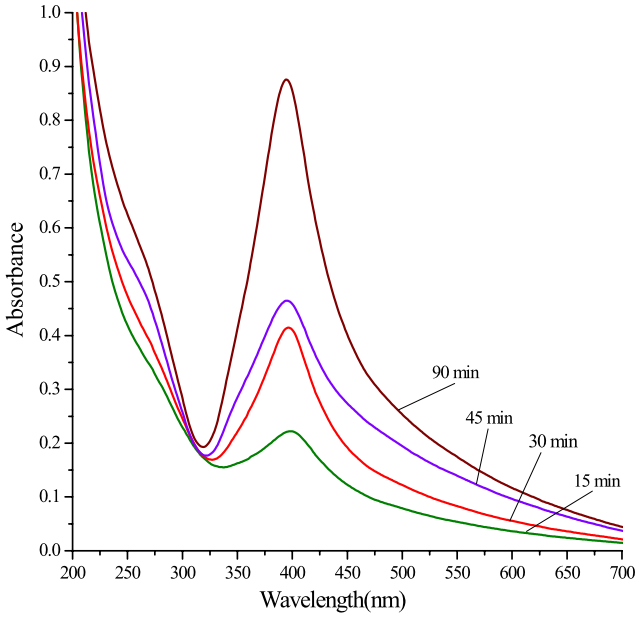

Fig. 3 UV–Visible absorption spectra of samples containing Ag-NPs prepared for different ablation times in starch solution

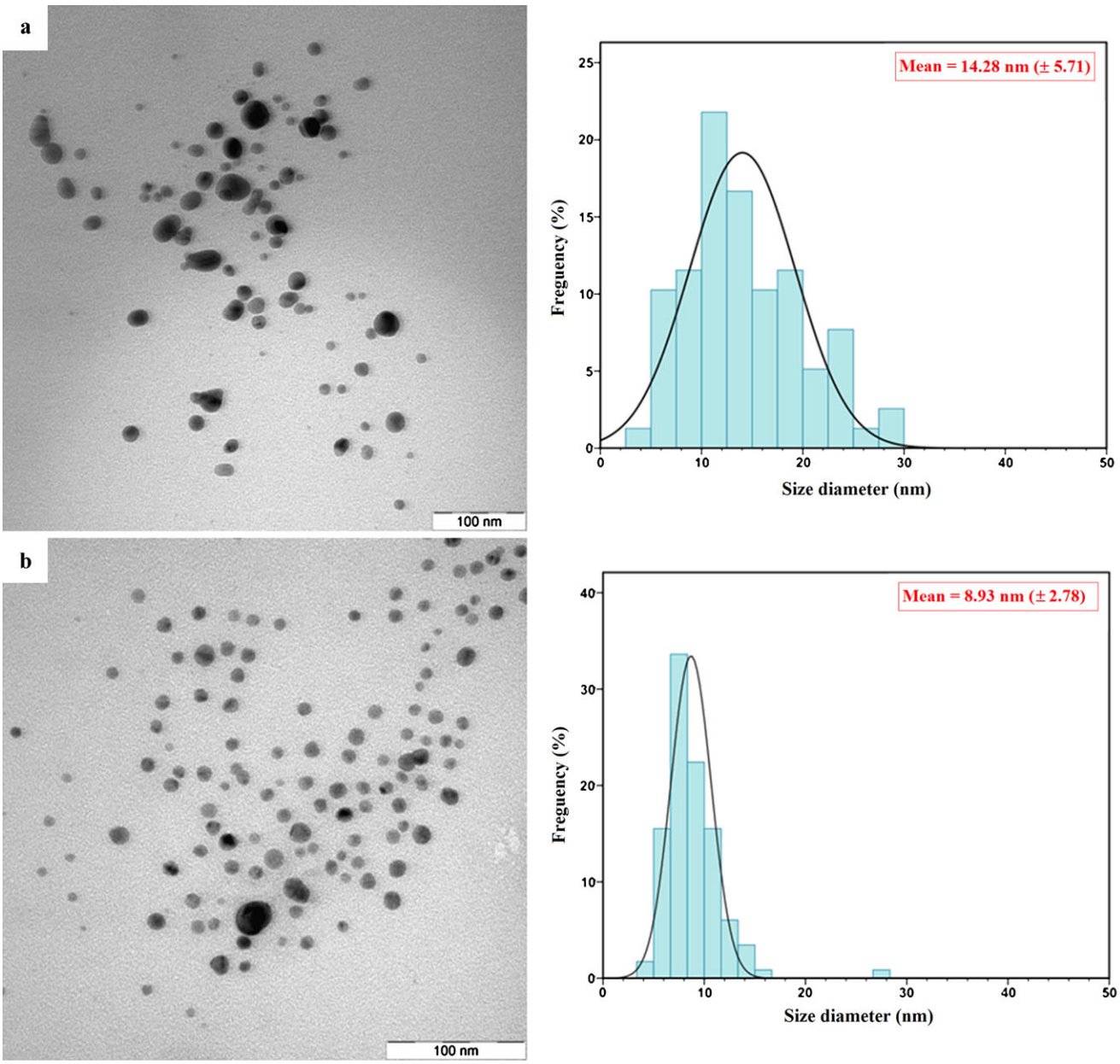

Fig. 4 TEM images and typical of statistical graphs for Ag-NPs in starch solution under (**a**) 30 and (**b**) 90 min ablation times

SPSS statistics software (Ver. 17). To compare the efficiency of stabilizer, we filled the container with twice distilled water as a reference sample and ablated the silver plate under similar experimental conditions for 30 min.

To investigate the SSPM phenomena on the prepared samples, a diode pumped solid state CW laser (LDCU8/7870) of 405 nm wavelength and 50 mW power was applied. The laser beam was focused by a 21 cm focal length lens then passed through a 1 mm thickness sample contained in a quartz cell. The cell was located at the distance where the incident beam diverged on the sample entrance plane. The far-field diffraction patterns were appeared on a screen at 50 cm behind the sample and recorded by a CCD camera. The response time to the beam by the sample was determined by placing a variable-speed chopper in front of the lens.

3 Results and discussion

The color of solutions appeared transparent at the beginning of the LA process and finally turned light yellow for shorter and dark yellow for longer ablation times. The dark yellow color indicates high Ag-NPs concentration which was confirmed by UV–Visible absorption spectra. Figure 3 shows the absorption spectra of the solution containing Ag-NPs

Table 1 The particle diameters of prepared Ag-NPs in starch solution at different ablation times and in distilled water (*)

Ablation time (min)	Mean diameter (nm)	Standard deviation (nm)
15	16.05	7.19
30	14.28	5.71
45	12.68	5.13
90	8.93	2.78
30*	23.12	9.37

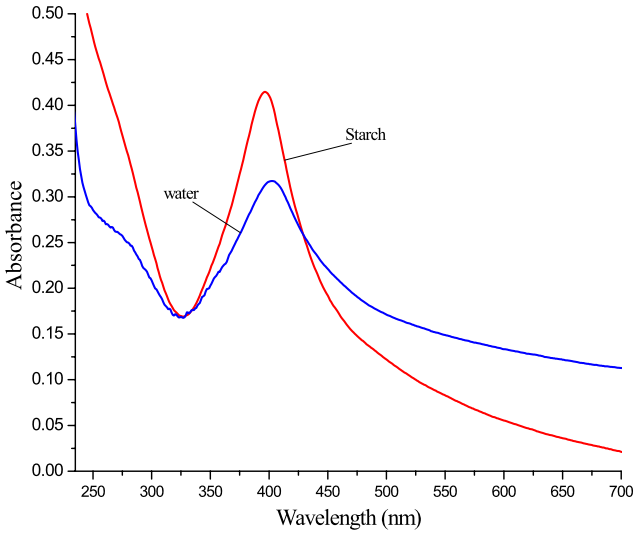

Fig. 5 UV–Visible absorption spectra of samples containing Ag-NPs in starch solution and in distilled water prepared at 30 min ablation time

when the silver plate was ablated by constant power under different ablation time durations. The narrow and symmetric peak at about 400 nm and the broad tail extending toward the UV wavelength range are the characteristic features of Ag-NPs solutions [16]. The peak at 400 nm and the tail part around 250 nm originated from the particle plasmon excitation and the interband transition, respectively [17]. The spectra peaks are prominent and single at 400 nm, which shows that the NPs present in the solution are spherical [18]. Increasing the ablation time increases the NPs formation efficiency and the absorbance. The blue shift also appears at longer times in the spectrum which indicates reduction of particles size. The reducing particles size with increasing ablation time can be explained by the way that at longer ablation times the interaction of produced NPs from the plate with laser light will increase. The result of this interaction is the fragmentation of NPs to smaller sizes, and therefore the obtained particles at longer ablation times are smaller [18].

The interband transition also increases at longer ablation times which can be attributed to increasing NPs formation. The electron micrograph and the corresponding NPs size distribution prepared under 30 and 90 min ablation times are shown in Fig. 4. The diameter of Ag-NPs was about 14.28 nm for 30 min, and decreased to 8.93 nm for 90 min ablation times. The other diameters obtained and their corresponding standard deviations are listed in Table 1. It can be observed that the mean diameter of particles decreases as the ablation times become longer.

In comparison with distilled water (Fig. 5), the peak intensity is decreased and shifted towards a higher wavelength. TEM photographs and Ag-NPs size distributions prepared in distilled water are shown in Fig. 6. Both figures support the conclusion that the obtained particles sizes in starch solution are considerably smaller compared to those in distilled water. The dispersion of Ag-NPs prepared in starch solution was clearer compared to that in distilled water as shown in the TEM image. The decrease in size can be explained by the interaction between the starch molecules and the produced particles by LA. The formation of NPs during the LA process is through phase transition, nucleation and crystal growth of emitted materials such as silver atoms, clusters and droplets from the silver plate [19]. Starch can adsorb NPs and prevent aggregation and growth.

The Ag-NPs formation efficiency in starch solution is higher compared to that in water. This is explained by the ablation products which when emitted from the silver plate will be confined by the solvent, and this confinement becomes stronger when the solvent has more density and viscosity. The generated plasma already confined near solids is high pressured and therefore can etch the surface [20, 21] and again generate NPs. This process is called secondary ablation [22]. Therefore, it can be concluded that the increase in the ablation efficiency of starch solution results from the increase in the secondary ablation process is due to the increase of density and viscosity of solvent by starch.

The other interesting phenomenon which is observable from Fig. 5 is an increase in interband transition peak for starch compared to water. This is due to the increase of formation efficiencies of NPs in starch solution.

Figure 7 shows images of the beam spot size when the sample is located behind the lens focal length. The increase in the beam diameter after passing through the samples indicates that the beam diverges. In other words, the sample behaves like a negative lens when a laser beam passes through it. Additionally, as it is shown clearly, diffraction pattern are formed on the screen and this phenomenon increases when the concentration of NPs increases. The results show that the presence of the Ag-NPs in the starch induces the nonlinear refractive index in the medium and causes the SSPM effect in laser beam propagation [23–25]. The response time of around 1 ms was obtained from the beam diffraction pattern, and this relatively long time duration confirms that this phenomenon is due to the thermal effect.

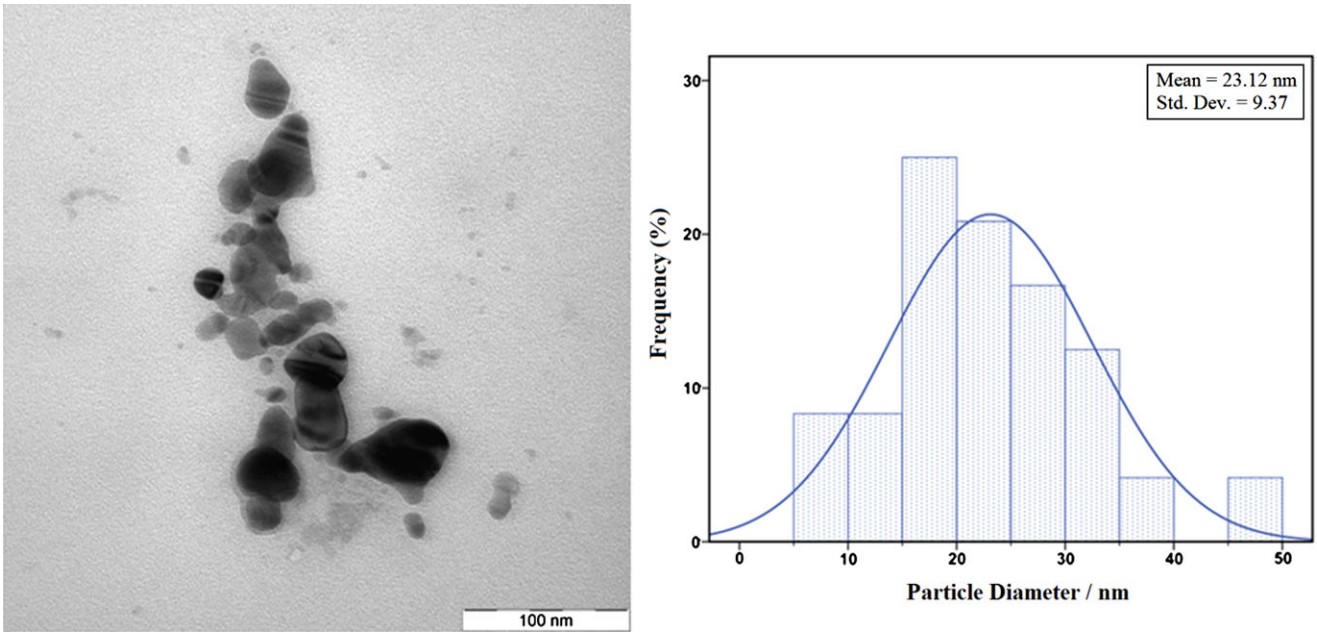

Fig. 6 TEM image and typical of statistical graph for Ag-NPs in distilled water

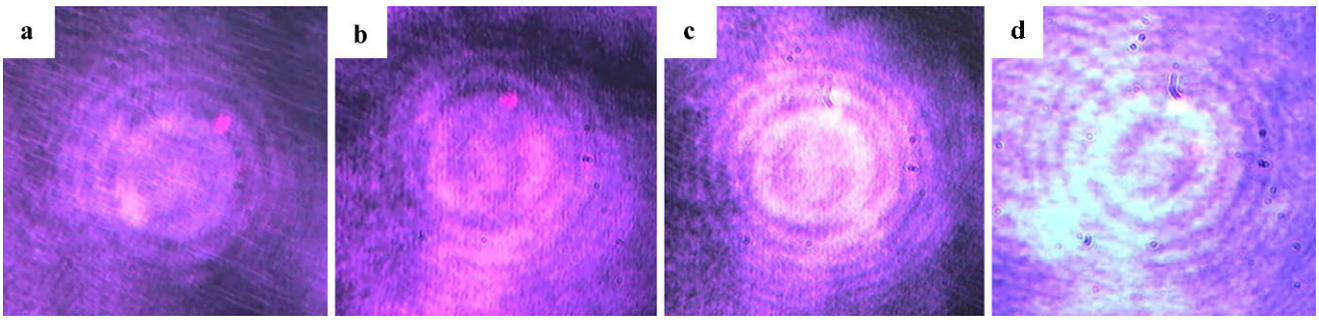

Fig. 7 The far-field diffraction patterns of laser beam after propagation through Ag-NPs in starch solutions prepared at different ablation times (**a**) 15, (**b**) 30, (**c**) 45, (**d**) 90 min

4 Conclusions

The Ag-NPs were successfully prepared in aqueous starch solution under different ablation time durations. The obtained results showed that particle sizes decreased with increasing ablation times. The nonlinear optical property of starch solution containing Ag-NPs with different concentrations was also studied. The results showed that the increase of Ag-NPs in starch solution had increased the nonlinear optical property of the samples which is due to the thermal effect.

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