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THE EFFECTS OF THE AMBIENT LIQUID MEDIUM ON THE ABLATION EFFICIENCY, SIZE AND STABILITY OF SILVER NANOPARTICLES PREPARED BY PULSE LASER ABLATION IN LIQUID TECHNIQUE

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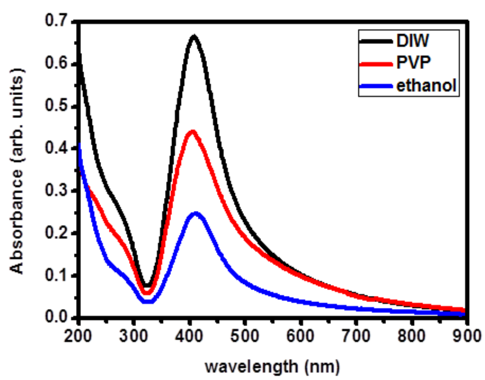
Graphical abstract



Abstract

Silver (Ag) nanoparticles (NPs) were synthesized by pulsed laser (Nd:YAG, 1064 nm) ablation of individual target in various solutions. The influence of deionized water (DIW), ethanol and Polyvinylpyrrolidone (PVP) as ambient medium on the fundamental aspects such as ablation efficiency, particle size and stability of Ag NPs was studied. UV-vis spectrophotometer and transmission electron microscopy (TEM) were used to study the optical characterization and morphological analysis of all the synthesized samples, respectively. Preparation in DIW was carried out as a reference sample. The experiments demonstrated that ablation efficiency and stability of NPs in ethanol medium are lowest than those prepared in PVP medium and the reference sample. PVP medium led to higher stability, lower ablation efficiency and finer average particle size compared to reference sample.

Keywords: Laser ablation, silver nanoparticles, metal colloids, liquid media

Abstrak

Zarah nano (NP) perak (Ag) telah disintesiskan menggunakan ablasi laser denyut (Nd: YAG, 1064 nm) bagi sasaran individu dalam pelbagai larutan. Pengaruh air ternyahion (DIW), etanol dan Polivinilpirolidon (PVP) sebagai medium ambien terhadap aspek asas seperti kecekapan ablasi, saiz zarah dan kestabilan zarah nano Ag telah dikaji. Spektrofotometer Ultra Ungu Nampak dan mikroskop elektron transmisi (TEM) telah digunakan untuk mengkaji pencirian optik dan analisis morfologi semua sampel yang disintesis, masing-masing. Penyediaan di dalam DIW telah dijalankan sebagai sampel rujukan. Eksperimen menunjukkan bahawa kecekapan ablasi dan kestabilan zarah nano dalam medium etanol adalah paling rendah berbanding yang disediakan dalam medium PVP dan sampel rujukan. Medium PVP memberikan kestabilan yang lebih tinggi, kecekapan ablasi yang lebih rendah dan saiz purata zarah yang lebih halus berbanding sampel rujukan.

Kata kunci: Ablasi laser, zarah nano perak, koloid logam, media cecair

1.0 INTRODUCTION

Laser ablation in liquid (LAiL) emerged as a reliable promising technique to obtain metal colloids in water or in organic solvents. LAiL technique has a remarkable feature as procedural simplicity and flexible physical method as well as absence of chemical reagents in solutions compared to other conventional method for preparing metal colloids [1-4]. Thus, pure colloids, which will be proper for further applications, can be synthesized. Another feature characterization of this technique, which prefers it from laser ablation in gas or vacuum, is the influence of the surrounding liquid medium. The liquid medium can lead to physical effects such as confinement and cooling [5-7], and chemical reactions such as oxidation, reduction and stabilizers (capping) regent [8-12]. Mafune` *et al*. [13], have shown that stable platinum (Pt) NPs can be produced by laser ablation technique of Pt target in pure water. Further results have been reported by Compagnini *et al*., [14-16], who shown the prospect of metallic and non-metallic particles preparation via laser ablation in several liquids such as water, ethanol, chloroform, polymer, alkanes and thiol-alkane.

Additionally, they confirmed that the formation of resulting particles in the nanometer size range depend on the liquid used as environment. Other groups of Amendola *et al*., [17], suggested that the concentration, aggregation, and size of gold (Au) NPs prepared by laser ablation in organic solvents can be controlled by changing a few parameters. In the majority of cases, the water medium is favorable in most ablation process because it is cheap, safe medium, exhibits a high heat capacity, and doesn't absorb much light [18]. The fundamental application problem of metallic NPs is connected with the sufficient stability of their dispersions, which prevents the aggregation process. The particles of the metal colloidal solution exhibit unique optical properties which strongly depend on the arrangement of the individual particles in the solution. The aggregated colloidal nanoparticles in which the distance between aggregating spheres becomes small compared with their radius, their optical absorption spectra change from narrow band to broad band and extending into the red shifting [19]. By extending the particles aggregation the particle size increases, thereby the absorption of colloids increases at longer wavelength. To solve such aggregation problems and to control the morphology of these metal colloids, various stabilizers are commonly employed to form barriers between particles by polymer dispersing, surfactants, surface modification and organic agents. Although the research on stabilization of metal NPs colloids has grown up, the effect of Liquid environment parameters on ablation of nanoparticles is still on the way so far.

In this paper, the fabrication of Ag NPs by LAiL of the individual metallic targets in different liquid mediums of DIW, ethanol and PVP is reported. Furthermore, the effect of liquid environment on ablation efficiency, size and stability of ablated species (different sizes of NPs, clusters, free atoms) produced by laser ablation is also discussed in detail.

2.0 EXPERIMENTAL SETUP

Polyvinylpyrrolidone (PVP, Alfa Aesar Co.) having molecular weights of 58, 000, pure ethanol (>99%, Merck) and ultrapure deionized water (pH 7, 18.2 MΩ electrical resistivity) were used as a liquid medium in ablation process. Distilled water and pure acetone (>99%, Merck) were also used to clean working tools in order to avoid any kind of contamination. Metal plate of Ag (99.998%, Alfa Aesar Co.) was used as target material. The target was cleaned in an ultrasonic bath of acetone and ethanol sequentially for 10 min each, and rinsed with DIW. The cleaned target was then fixed on the bottom of a Pyrex vessel filled with 15 mL solution of DIW, 20 mM PVP or ethanol, separately. For comparison, ablation in DIW was conducted as the reference sample. The Ag target in each solution was irradiated at room temperature for 15 min with the fundamental (1064 nm) wavelength of a Q-switched Nd:YAG laser operating at 1 Hz with 8 ns of pulse width. In this case, the laser beam was focused using a lens with a focal length of 100 mm to obtain laser fluence around 15 J/cm^2 on the surface of the Ag target. The ablation vessel was fixed onto a rotating stage to avoid craters formation onto the surface of target and to ensure homogeneous irradiation conditions for the subsequent pulses during laser exposure.

UV-vis measurements were performed using a spectrophotometer (Perkin-Elmer, Lambda 25) and room temperature with a 0.5 cm optimal length cuvette. A transmission electron microscope (TEM, Philips CM 12) operating at an accelerating voltage of 120 kV was used to take the electron images of the nanoparticles. A drop of a sample solution was placed on a carbon-coated copper grid and dried at room temperature. Typically, more than 250 individually particles identified in sight of a given TEM micrograph were measured and the distribution of particle size (in diameter) was calculated.

3.0 RESULTS AND DISCUSSION

Formation of Ag NPs under laser ablation of corresponding metallic targets in liquid environments of DIW, ethanol and PVP is studied. UV-vis optical absorption spectra were taken on each colloidal solution at identical fabricating parameters as shown in Figure 1. The prominent single peak caused by the plasmon transition indicated that the obtained NPs were nearly spherical in the colloidal solution. The ablation efficiency for as-prepared Ag colloids in ethanol was found to be the lowest than what is observed in the other samples, whereas in DIW was higher than that of PVP solution. Mafune´ *et al*. presented a similar result that the production of Ag NPs by laser ablation in organic solution is very low [20]. To compare with the reference sample, the surface plasmon resonance (SPR) peak position of colloids in the PVP solution shifted to short wavelengths, while that of colloids prepared in ethanol does not appreciably shift. These differences may be attributed to different properties (e.g., temperature, pressure, and density) of the plasma after its confinement by each solution. At the high pressure and temperature of plasma plume, ethanol can dissociate to form permanent gases [21]. The formed permanent gases in ethanol solution assemble to bubbles that can be noted during ablation process. The gases bubbles in the path of laser beam combined with ablated species to form metal NPs or may absorb or scatter the laser energy. Thereby, a small portion of the energy reached to the target surface, resulting in a lower nanoparticle concentration.

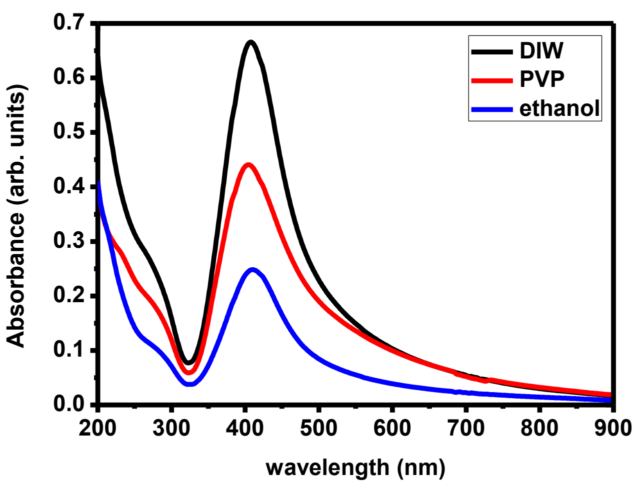


Figure 1 UV-vis absorption spectra of as-synthesis Ag colloids fabricated at laser wavelengths of 1064 nm in different liquid mediums of deionized water, ethanol and PVP

In general, the PVP protective mechanism is divided into three steps [22]: (i) the formation of coordinative bonds between PVP and ions of silver, (ii) the formed structure promotes elements nucleation which leads to the aggregation of small particles as primary nanoparticles, and (iii) steric shielding of the NPs surfaces by physical and chemical bonding to PVP, which inhibited particle–particle contact with each other, thus, the agglomeration of particles. Figure 2 displays the effect of the storage time on the stability of colloidal Ag in each solution of water, ethanol and PVP for two months.

The ablation efficiency and stability of Ag NPs decreased in all colloidal solution. The steric effect of the PVP polymer on the surface of particles prevents aggregating. Therefore, suspensions of NPs obtained in PVP solution are relatively stable but less stable in water, and unstable in ethanol.

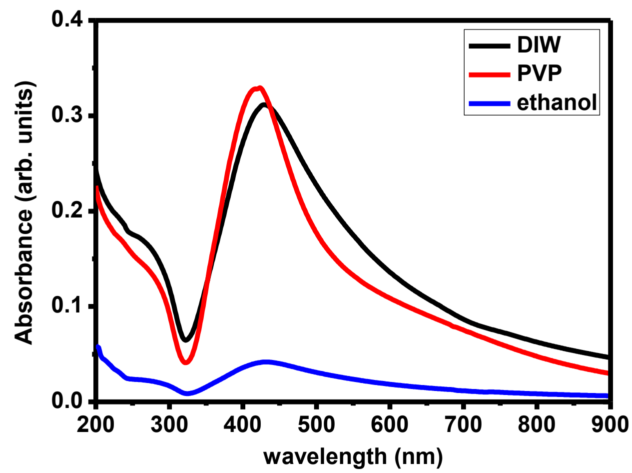


Figure 2 Comparison of UV-vis absorption spectra between Ag nanoparticle colloids fabricated in deionized water, ethanol and PVP after storage time for 2 months

Figure 3 presents TEM micrographs (left side) and the corresponding size distribution histograms (right side) of Ag NPs prepared in water, ethanol and PVP after storage time for two months. TEM results revealed that the prepared Ag NPs are nearly spherical morphology in all liquids. Figure 3a presents the TEM micrograph and size distribution histogram of particles synthesized in PVP that revealed a well-dispersed and narrow size distribution of NPs with smaller average size of 16.36±7.34 nm. TEM results macrograph of Ag NPs obtained in DIW (Figure 3b) are nearly the same as the TEM results of particles in PVP solution, but in this case, more aggregation appeared with the average size of 22.88±9.46 nm and size distribution was broader. In ethanol (Figure 3c), TEM results showed strongly aggregation with string-like structures and broader size distribution of NPs with bigger average size of 26.44±12.10 nm than what is observed in the other samples. These findings are consistent with observations that obtained in Figure 2. The experimental results obtained by studying optical and morphological properties of Ag NPs for each colloidal solution were summarized in Table 1.

Table 1 The average size, ablation efficiency and particle size distribution of Ag NPs prepared in the three different solutions of PVP, deionized water and ethanol

Liquid medium	Average particle size (nm)	Ablation efficiency	Particle size distribution	Stable (a) suspension
PVP	16.36±7.34	high	narrower	yes
DIW	22.88±9.46	low	broad	yes (modest)
Ethanol	26.44±12.10	lowest	narrow	no

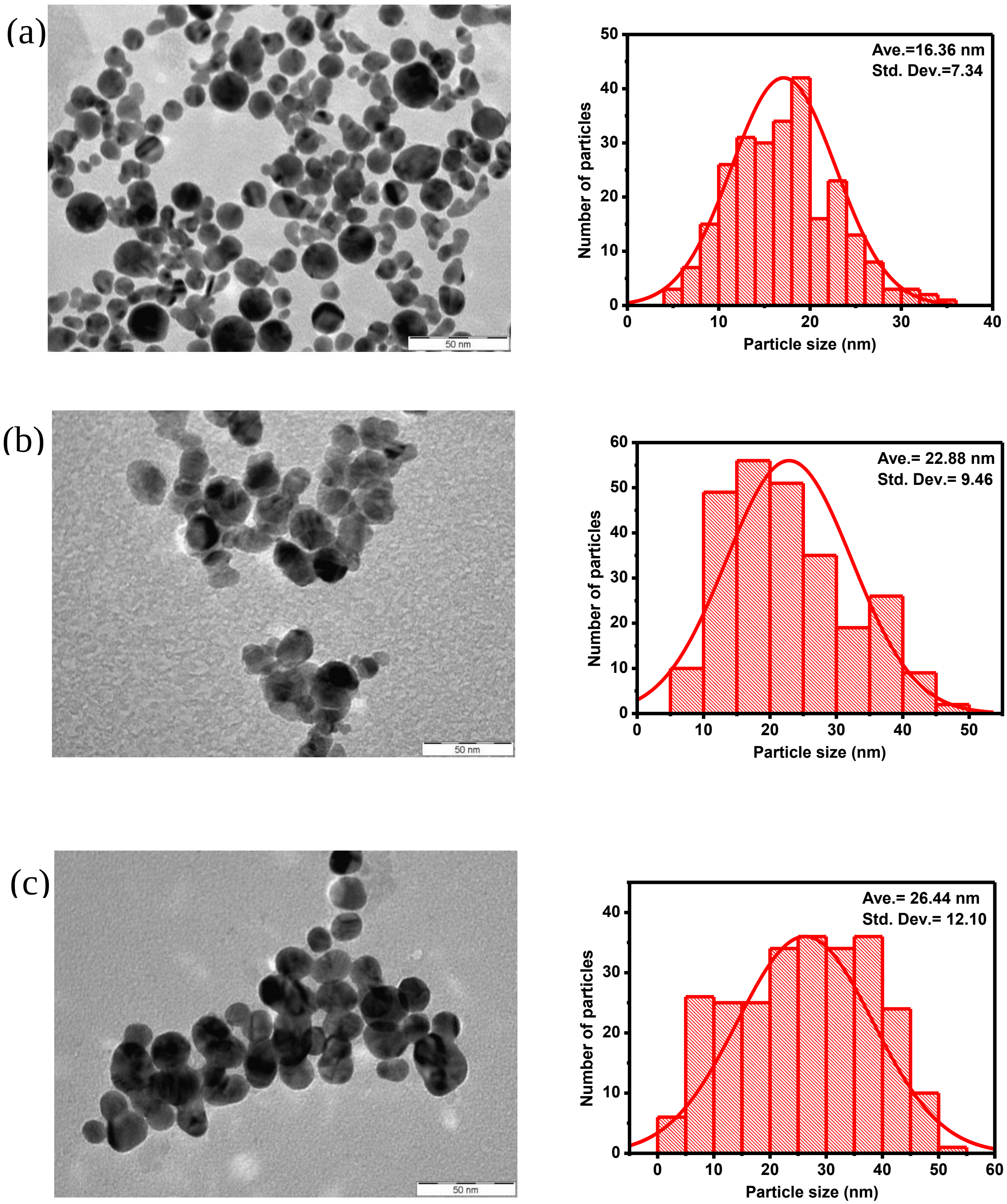


Figure 3 TEM micrographs (left side) and the corresponding size distribution histograms (right side) of Ag NPs produced in (a) PVP medium, (b) deionized water and (c) ethanol

4.0 CONCLUSION

We have successfully obtained silver nanoparticles in DIW, ethanol and PVP medium using the same laser ablation conditions. Pulsed laser ablation of a liquid medium is a unique process which can be applied at ambient conditions with no introduction of disturbing chemical impurities. Effect of liquid media on pulsed laser ablation synthesis of Ag NPs was investigated using DIW, ethanol and PVP. The produced nanoparticles were characterized by UV-vis spectrophotometer and transmission electron microscopy. Not only poor ablation efficiency was observed in ethanol, but the highest aggregation of particles was also detected compared to those of DIW and PVP. DIW resulted in extremely more ablation efficiency of as-prepared nanoparticles than PVP medium. PVP medium was found to act as the best stabilizers and capping agent because it has interacted with ablated matter (atoms, clusters, droplets) and prevent their aggregation. The results deduced that all of the Ag colloidal solutions exhibit absorbance in the visible region, and the wavelength at the maximum absorption band highly shifts towards a longer one with the increased of particles size.

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