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Investigation of different liquid media and ablation times on pulsed laser ablation synthesis of aluminum nanoparticles

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ABSTRACT

Aluminum nanoparticles were synthesized by pulsed laser ablation of Al targets in ethanol, acetone, and ethylene glycol. Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) images, Particle size distribution diagram from Laser Particle Size Analyzer (LPSA), UV–visible absorption spectra, and weight changes of targets were used for the characterization and comparison of products. The experiments demonstrated that ablation efficiency in ethylene glycol is too low, in ethanol is higher, and in acetone is highest. Comparison between ethanol and acetone clarified that acetone medium leads to finer nanoparticles (mean diameter of 30 nm) with narrower size distribution (from 10 to 100 nm). However, thin carbon layer coats some of them, which was not observed in ethanol medium. It was also revealed that higher ablation time resulted in higher ablated mass, but lower ablation rate. Finer nanoparticles, moreover, were synthesized in higher ablation times.

1. Introduction

Physical and chemical properties of aluminum (Al) and particularly its powder, are favorable enough to make them applicable in a variety of applications such as alloy powder metallurgy parts for automobiles and aircrafts, heat shielding coatings of aircrafts, corrosion resistant, conductive and heat reflecting paints, conductive and decorative plastics, soldering and thermit welding, pyrotechnics and military applications (rocket fuel, igniter, smokes, and tracers) [1]. Size reduction and its effects on material properties are matter of interest in the last decades, and nanomaterials are interesting since they often exhibit better performance than conventional ones due to increase of the specific surface area [2]. As a case in point, Al nanoparticles are more explosive than their micro-size particles, and their activities significantly increases by further size reduction [3].

High purity powders and nanopowders of active metals such as Al are not easily synthesized inasmuch as their rapid oxidation occurs easily. Laser ablation in liquid media is the recently developed synthesis method and has introduced a new prospect toward production of pure active nanoparticles, provided that the appropriate synthesis parameters are opted [4]. Not only can pure nanoparticles be synthesized in this way, but also oxide, carbide, or alloy nanoparticles are producible if corresponding elements be present either in ablation medium or in target. Besides, easiness and size control are other important privileges of this technique [4–11].

Three main steps contribute in laser ablation synthesis method and formation of nanoparticles from a target immersed in liquid. Only in a short period of time, typically about a few microseconds, all these steps take place and nanoparticles are synthesized [4,11]. Laser pulse, first, heats up the target surface to the boiling point, and thus, plasma plume containing vapor atoms of target is generated. Then, plasma expands adiabatically; and finally, nanoparticles will be generated when condensation occurs [4]. During the condensation step, first, nucleation takes place; then fine nuclei either collide and stick to each other or new materials precipitate on them which result in growth. Nanosized hard agglomerates can form as a result of strong covalent or ionic bonds between nuclei. These hard agglomerates may also stick together by weak van der Wales or covalent–ionic bonds and bring about soft agglomerates, which can be broken to hard ones by severe agitation [12].

Synthesis parameters such as laser wavelength, laser energy, pulse width, liquid media type, and ablation time can notably affect the product characteristics [4–11]. Until now, assorted kinds of liquids have been used as laser ablation media such as distilled or de-ionized water [8,12–16], ethanol [8,13,14,16,17], acetone [13,16], ethylene glycol [15], hexane [11], and decane [18]. A thin oxide layer may cover the synthesized nanoparticles, which is found to be thinner in acetone medium than in ethanol [13], and in ethanol is also thinner than in water [8,13,14,17]. In addition, finer nanoparticles can be generated in acetone [16] and in ethanol [8,13,14,16] compared to water medium.

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Increase of the ablation time is anticipated to bring about higher ablated mass [19–22] and finer nanoparticles with narrower size distribution [20,23]. In long ablation times, however, the ablation rate decreases. It occurs when high concentrations of nanoparticles in produced colloidal solution blocks the laser path, and thus, a part of laser energy is absorbed by formerly synthesized nanoparticles instead of the target surface [20].

In spite of the fact that various metallic nanoparticles have been synthesized by this technique, scarcely is laser ablation synthesis of Al nanoparticles reported and limited numbers of related articles have been published in the last few years [12,17,24]. Hence, the effect of different liquid media and ablation time on pulsed laser ablation synthesis of aluminum nanoparticles will be discussed in this paper.

2. Experimental procedure

Targets with dimensions of about 2.5 cm × 2.5 cm were cut from a 2-mm thick aluminum 1050 sheet, which proved to contain 99.4 wt.% Al and negligible amounts of other alloy elements based on quantometery analysis. Targets were washed and ground by sand papers of numbers 800, 1200, and 2500, in ethanol medium in order to exclude their superficial oxide layers and to prevent the simultaneous oxidation. Absolute ethanol with 99.6–99.9% purity (produced in Bidestan Co., Iran), acetone with 99% purity (produced in Dr. Mojallali's Lab Co., Iran), and ethylene glycol (produced in Merk Co.) were used as laser ablation media.

A pulsed Nd:YAG laser (EKSPLA Co.) was used to generate laser pulses with wavelength of 1064 nm, full width at half maximum (FWHM) of 6 ns, and repetition rate of 10 Hz. Laser energies of 280–400 mJ/pulse were exerted, but only samples produced by the same energy will be compared. Targets were immersed in 100 ml liquid and ablated for 5, 10, and 15 min by normal incident laser beam, which passed horizontally. The beam diameter on target was tried to be kept constant, about 3 mm, by a focal lens (f = 100 mm), and its position on target was changed and the solution was stirred every 3–4 min of ablation. Each target sample was weighed before and after the ablation by a digital weigher with 0.1 mgr precision to determine the ablated mass.

UV–visible spectra of the colloidal Al nanoparticles were taken by a Carry100 spectrophotometer after they were homogeneously dispersed by ultrasonic. Unlike ethanol and ethylene glycol, acetone is not transparent at all for the wavelengths shorter than 300 nm. To overcome the problem, 5 ml of colloidal solutions containing synthesized nanoparticles in acetone was selected. For each sample, acetone was evaporated in room temperature and in flowing air. Then, 5 ml of ethanol was added to the remained precipitations, and the resulted solutions were dispersed by ultrasound. Finally, UV–visible absorption spectra of nanoparticles synthesized in acetone were taken.

Size distribution diagrams and mean diameter of Al nanoparticles were calculated by LB-550 model of Laser Particle Size Analyzer (LPSA). Synthesized nanoparticles were observed by Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images. SEM and TEM microscopes were Philips XL30 and Philips CM10, the operation voltage of which were 15 and 100 kV, respectively.

3. Results and discussion

3.1. Effect of liquid media

Effect of different liquid media on UV–visible absorption peak and ablated mass of targets are presented in Table 1.

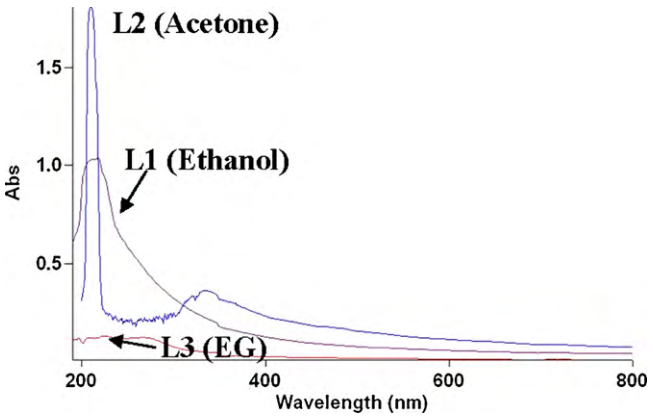

Fig. 1. UV–visible absorption spectra of nanoparticles prepared in three ablation media of ethanol, acetone, and ethylene glycol (λ = 1064 nm, E = 320 mJ/pulse, t = 10 min).

It was obvious that colors of liquids were changed differently within the process. During the laser ablation in ethanol (samples L1 and L4), prepared colloid became opaque slowly, and finally, it tended to pale yellowish color after 10 min of ablation. Acetone medium (samples L2 and L5) became opaque faster than ethanol one, and its color also became gray; finally, it tended to dark grayish color after ablation for 10 min. On the other hand, ethylene glycol (EG) showed totally different behavior, and fine bobbles were formed in front of target L3 after first 15–20 s of ablation. These bobbles apparently prohibited the laser energy to be absorbed by target, which could easily be realized by extremely diminished noises of impacts. Even stopping the ablation and stirring the liquid could not enhance the ablation efficiency in subsequent laser exposures.

Visual comparison of synthesized colloidal samples demonstrated that samples L2 and L5 were darker in color than other ones. They also were unstable, and only after 3–4 h did dark grayish sediments precipitate. Samples L1 and L4 seemed to be more stable than samples L2 and L5, and few pale yellowish sediment could be observed at the bottom of its glassy container after 3–4 days. Sample L3, which did not seem to encompass noticeable amount of Al nanoparticles, remained as transparent as the pure primary ethylene glycol even after 6 months.

UV–visible absorption spectra of products are presented in Fig. 1 (for E = 320 mJ/pulse) and Fig. 2 (for E = 400 mJ/pulse). It is obvious that samples synthesized in ethanol and acetone bear the specific absorption peak of aluminum around wavelength of 210 nm, which proves the presence of Al particles, and not alumina ones [17,24].

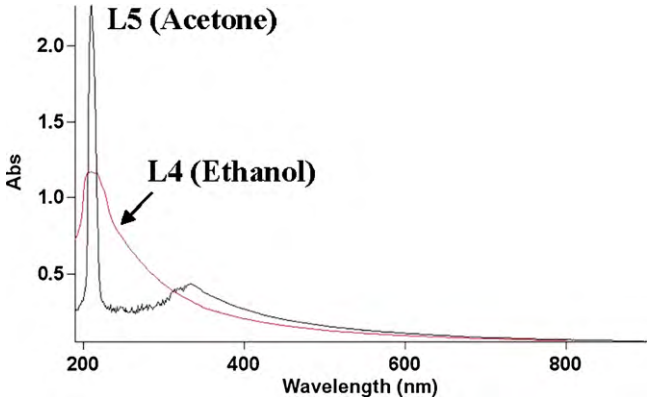

Fig. 2. UV–visible absorption spectra of nanoparticles prepared in two ablation media of ethanol and acetone (λ = 1064 nm, E = 400 mJ/pulse, t = 10 min).