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Synthesis of $Mg(OH)_2$, MgO, and Mg nanoparticles using laser ablation of magnesium in water and solvents

Tran X. Phuoc [a,*], Bret. H. Howard [a], Donald V. Martello [a], Yee Soong [a], Minking K. Chyu [b]

[a] National Energy Technology Lab, P.O. Box 10940, MS 84-340, Pittsburgh, PA 15236, USA
[b] Department of Mechanical Engineering and Material Science, University of Pittsburgh, 648 Benedum Hall, 37000 O'Hara Street, Pittsburgh, PA 15261, USA

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ABSTRACT

Laser ablation of magnesium in deionized water (DW), solutions of DW and sodium dodecyl sulfate (SDS) with different concentrations, acetone and 2-propanol has been conducted. The results showed that ablation in acetone and 2-propanol yielded MgO and Mg nanocrystallites as isolated particles and agglomerated chains probably intermixed with organic residues resulting from the alteration/decomposition of the solvents under the high-energy conditions. Brucite-like $Mg(OH)_2$ particles were mainly produced by laser ablation of Mg in either DW or DW–SDS solutions. Ablation in DW yielded particles of fiber-like shapes having a diameter of about 5–10 nm and length as long as 150 nm. Materials produced in DW–SDS solutions were composed of various size and shape particles. Some had rough surfaces with irregular shapes. Small particles were about 20–30 nm and larger particles were about 120 nm. Particles with rod-like, triangular, and plate-like shapes were also observed.

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1. Introduction

Laser ablation in liquid has been considered as an attractive technique for the preparation of nanoparticles and nanomaterial fabrications. The technique has been used to generate nanoparticles and nanomaterials by ablating metals and metal oxides in deionized water (DW) and solvents [1–8]. A comprehensive review of past work in this field has been published by Yang [9]. It has also been demonstrated that the technique can generate stable colloids containing nano-sized metal particles without use of any dispersants or surface reactive reagents [4,10–13].

Laser ablation in liquid occurs when a high-power laser beam is focused for an appropriate time onto a solid target that is submerged in a liquid. The solid at the focal point is heated and melts rapidly. Due to the heat transfer from the heated metal spot, the liquid layer immediately adjacent to the solid surface is heated to the same temperature as the solid which is a much higher temperature than the boiling point of the liquid at normal pressure. The liquid is, therefore, vaporized producing a high temperature, high pressure plasma plume containing highly ionized species. The plume expands violently shattering the melted target material into nano-sized clusters which are supercooled by the surrounding liquid. Laser ablation in liquid is simple and it can generate nanoparticles without counter-ions or surface active substances. Since no stabilizing substances are added, the surfaces of the nanoparticles are free of extraneous ions or other chemical species.

Conversely, laser ablation in liquid can be used to control the compositions, particle size, production rate and morphology of the ablated product by tailored selection of liquid medium, surfactants and other additives. This is because the liquid phase not only provides confinement for the plasma expansion and particle kinetic growth processes but also an environment for various chemical reactions between the generated solid clusters and the molecules of the liquid medium.

Several studies of the effects of the liquid environment on the ablation product have been reported. Saito et al. [14] studied laser ablation of copper in polysiloxane. They reported that laser ablation in polysiloxane produced only Cu nanoparticles. This is because ablation in oil effectively isolated the product from atmospheric oxygen and from reaction with water preventing oxidation of the copper particles. Both the particle size and the production rate changed notably depending on the oil types. Tilaki et al. [15] prepared colloidal copper nanoparticles in water and acetone. In water, copper oxide nanoparticles with mean diameter of about 30 nm were produced. The color of the solutions was blue-green and changed to brown-black as the nanoparticles precipitated completely over 2 weeks. In acetone, the particles were much smaller with an average diameter of 3 nm and the solutions remained stable even after 10 months. Dolgaev et al. [16] reported the formation of Ti, Si, Ag, and Au nanoparticles via laser ablation of metal targets in different liquids (H_2O, C_2H_5OH,

* Corresponding author. Tel.: +1 412 386 6024.
E-mail address: tran@netl.doe.gov (T.X. Phuoc).

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$C_2H_4Cl_2$) using a 510.5 nm wavelength Cu vapor laser. Various particle sizes and compounds were formed via reactions of the metal with liquid and they depended on the laser fluences and the nature of the liquid. Kazakevich et al. [1] reported that laser ablation of Ti in ethanol resulted in the formation of Ti nanoparticles having a cubic structure, while ablation in dichloroethane lead to the formation of titanium carbide TiC nanoparticles. In water, the formation of non-stoichiometric oxide TiO_x (where $x = 1.04$) was observed. Tsuji et al. [8] reported a study on laser ablation of Co, CoO, and Co_3O_4 in water and hexane. Nano-sized particles were produced from all materials in both liquids. It was found that atomic compositions of nanoparticles depended on solvent species in which laser ablation was carried out. In water, Co_3O_4 nanoparticles were produced from all materials. In hexane, Co nanoparticles were produced from Co_3O_4 and Co, while CoO particles were predominantly produced from CoO.

Studies of the effects of surfactants and dispersants added to the liquid have also been reported. Zeng et al. [17,18] studied the composition-controlled synthesis of ZnO–Zn composite nanoparticles by laser ablation of a zinc metal target in pure water and in aqueous solutions of sodium dodecyl sulfate (SDS) with different concentrations. They used a pulsed beam of 1064 nm and power from 35 to 70 mJ/pulse. They reported that with different SDS concentrations, the composition and size of the nanoparticles could be controlled over a wide range. High SDS concentrations resulted in high relative amounts of Zn nanoparticles existing as the core in the core/shell nanostructures, whereas low SDS concentrations lead to a high amount of ZnO. Yang et al. [19] carried out a similar study with 532 nm laser beam. Depending on the ablation time and SDS concentrations they reported that the growth mechanism involved an increase of structural complexity from zero-dimensional nanoparticles to one-dimensional nanorods and then broadening into two-dimensional nanoleaf structures.

Similar results were reported by Liang et al. [20] who performed a series of experiments on the formation of brucite ($Mg(OH)_2$) nanostructures by laser ablation of a Mg plate in DW and DW–SDS solutions with different concentrations. They reported that wormhole-like bulk gel was obtained in DW after drying at room temperature. Ultrafine tube-like fibers were formed in lower concentrations of SDS solutions and strip-like rods and large platelets grew preferentially with increasing surfactant concentrations. The morphologies of the $Mg(OH)_2$ crystallites indicated that the surfactant molecules did not act simply as a template, but also could direct the growth either along one direction to yield fibrous, rod-like morphologies or along two directions to yield a platelet-like shape, depending on the concentration of surfactant.

Chandra et al. [21] prepared Cu nanoparticles in organic media with and without stabilizer. Copper nanoparticles of about 9 nm were prepared by laser ablation of a Cu-metal target immersed in isopropanol both in the presence and absence of polyvinyl pyrrolidone (PVP) which served as a stabilizer and a surface modification agent. The samples prepared through ablation for 15 min without PVP protection remained stable for approximately 2 weeks while the protected nanoparticles remained stable for months. Tsuji et al. [22] performed laser ablation of silver plate in aqueous PVP solutions. They showed that the ablation efficiency and the stability of the prepared solutions were increased by the addition of PVP. Such effects were attributed to the increased secondary etching efficiency by the solvent-confined plasma toward the silver target.

Thus, it is clear from the past studies that liquid environments and surfactants can direct the particle growth mechanism and alter the compositions of the nanomaterials produced from a given target material. In this work we present preliminary results on the preparation of magnesium-based nanofluids using the laser ablation in liquid technique. These fluids contain different nanocrystallites of $Mg(OH)_2$, MgO, and Mg depending on whether DW, acetone, or 2-propanol are used. The possible mechanisms by which SDS can direct the growth of $Mg(OH)_2$ nanocrystallites will be also presented.

2. Experimental apparatus

A sketch of the present experimental apparatus is shown in Fig. 1. It consisted of a nano-pulse laser and an ablation cell. The ablation cell had a 125 mm long × 75 mm high T-shape. It was constructed from quartz glass and equipped with three high-energy laser windows. The laser was a single-mode, Q-switched Nd–Yag laser operating at 1064 nm with a pulse duration of 5.5 ns and 10 Hz repetition rate. The laser beam was directed to the ablation cell and focused on the metal target using a 75 mm focal-length lens. If the focal region of the beam is assumed to be cylindrical in shape, the spot diameter can be approximated by $(2\lambda f/\pi d)$ where f is the focal length, λ is the laser wavelength and $d = 6$ mm is the beam diameter. With this laser system, the laser spot diameter was estimated to be 17 μm.

For the present study, the ablation cell was filled with 80 cm^3 of liquid. Magnesium samples (25×25 mm^2 and 1 mm thick, Alfa Aesar, 99.99% purity) were submerged in the cell using a sample holder. The metal samples had a smooth surface and were used as received. In order to have a well controlled laser beam throughout the experiments, the sample holder was placed on a two-dimensional translation stage so that it could be moved around while maintaining a constant focus at the sample surface.

All results reported here utilized the following experimental conditions: test duration of 60 min, the laser beam was 10 mm below the liquid surface, the metal target was 50 mm from the cell window facing the laser beam and a laser fluence of 0.265 J/cm^2 (33042 J/cm^2 at the focal point) was used. The liquid phase consisted of acetone, 2-propanol, DW, and DW–SDS solutions with different concentrations (from 0.001 to 0.08 M).

3. Results and discussions

General observation indicated that when the laser beam struck the Mg surface it created a spark plume that expanded in all directions. The plume emitted light and a cracking noise which were followed by a visible cloud of metal particles leaving the metal surface and dispersing slowly in all directions. Since the laser beam was 10 mm below the liquid surface, the expanding plume was always confined within the liquid and surface disruption was observed. During the ablation in acetone and 2-propanol, the spark plumes appeared larger and the cracking

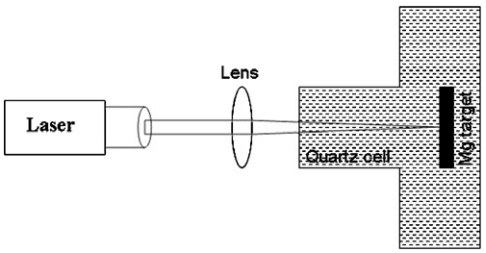

Fig. 1. A sketch of the laser ablation in liquid experiment: laser beam (75 mJ/pulse, 75 mm focal length lens, 17 μm focal point) was horizontal and 10 mm below the liquid surface; cell filled with 80 cm^3 liquid and the ablation duration was 1 h).