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Pulsed laser induced synthesis of scheelite-type colloidal nanoparticles in liquid and the size distribution by nanoparticle tracking analysis

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Abstract

Pulsed laser ablation (PLA) of ceramic target in liquid phase was successfully employed to prepare calcium tungstate ($CaWO_4$) and calcium molybdate ($CaMoO_4$) colloidal nanoparticles. The crystalline phase, particle morphology and optical property of the colloidal nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. The produced stable colloidal suspensions consisted of the well-dispersed nanoparticles showing a spherical shape. The mechanism for the laser ablation and nanoparticle forming was discussed under consideration of photo-ablation process. Nanoparticle tracking analysis using optical microscope combined with image analysis was proposed to determine the size distribution function of the prepared colloidal nanoparticles. The mean size of the $CaWO_4$ and $CaMoO_4$ colloidal nanoparticles were 16 and 29 nm, with a standard deviations of 2.1 and 5.2 nm, respectively.

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Keywords: Pulsed laser ablation; Colloidal nanoparticles; $CaWO_4$ and $CaMoO_4$; Size distribution; Nanoparticle tracking analysis

1. Introduction

Pulsed laser ablation (PLA) of target in liquids has attracted much attention as a new technique to prepare nanocolloidal particles since Henglein, Cotton and their co-workers first developed this synthesis technique [1,2]. It has been demonstrated that laser ablation of various noble metals settled in solvents can produce colloidal nanoparticles of these metals [3–5]. A remarkable advantage of this laser ablation method over chemical synthesis is simplicity of preparation procedures. Moreover, it has shown that the laser ablation in liquids is applicable to prepare nanoparticles of not only noble metals but also compound materials. It was reported that laser ablation of TiO_2, ZnSe, GaAs and CoO [6–9] in various solvents produced nanoparticles of these materials. Above studies on the laser ablation of noble metals and compound materials in liquid led to the formation of stoichiometric nanoparticles, i.e., atomic compositions of the produced nanoparticles were identical to those of the source materials.

In addition, reliable and fast determination of particle size distribution in sub-micrometer ranges still requires a certain challenge for common analytical equipment. Comparative studies [10–12] revealed remarkable differences among size distribution functions derived from different techniques. Generally, the most useful approach tends to be the most expensive and time consuming [13]. While dynamic light scattering provides an advantage of convenient determination, it offers difficulties in dealing with multi-modal distributions [10–13].

Therefore, in this work, a more sophisticated approach, i.e., nanoparticle tracking analysis is represented using Brownian motion of the particles sensed by frequency shift of scattered light. The analysis on the size distribution function calculated from the characteristics of Brownian motion requires the independent detection of a number of individual particles [14–16], leading to the assignment of individual mean square

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displacements and individual particle sizes. In this case, a complete particle ensemble is analyzed collectively, leading to an auto-correlation function that is linked to the particle size distribution. This technique is suitable much for particles in the sub-micrometer range because it requires no specific sample preparation and even allows for a selective analysis of components in particle mixtures. This nanoparticle tracking system can dynamically analyze the paths the particles take under Brownian motion over a suitable period to time (e.g. 10–20 s) and visualize deeply sub-micron particles in real time and in liquids, because motion of the nanoparticles in the sub-100 nm size range can be readily tracked using conventional digital camcorder employed in despite the rapid movement of the nanoparticles.

Calcium tungstate ($CaWO_4$, scheelite) and calcium molybdate ($CaMoO_4$, powellite) are important materials among metal tungstate or molybdate families because they have high application potential in various fields, such as laser host material in electronics [17–19], scintillator in medical applications [20–22], blue phosphor [23–25] in fluorescent lighting devices and MASER materials [26,27]. Various methods, such as Czochralski method, coprecipitation synthesis, combustion method and solid-state reaction have been used to synthesize $CaWO_4$ and/or $CaMoO_4$ [28–31]. However, $CaWO_4$ and/or $CaMoO_4$ particles prepared by these processes are relatively large with irregular morphology, and inhomogeneous compounds might be easily formed because WO_3 and MoO_3 have tendency to vaporize at high temperatures [32]. To overcome this problem, extensive efforts have been made recently to develop alternative synthesis methods such as wet chemical routes [33,34] or pulsed laser ablation processes [35–37].

In this work, we represent a novel synthetic approach to directly produce highly-dispersed $CaWO_4$ and $CaMoO_4$ colloidal nanoparticles using pulsed laser ablation (PLA) of ceramic target in liquid phase without any surfactant. Crystalline phase, particle morphology, nanoparticle forming mechanism and optical property are investigated. Furthermore, a novel method based on simultaneous motion tracking of several individual nanoparticles is proposed for the convenient determination of nanoparticle size distributions.

2. Experimental

2.1. Synthesis of colloidal nanoparticles by laser ablation in liquid

The colloidal nanoparticles of $CaWO_4$ and $CaMoO_4$ were synthesized by the laser ablation of ceramic targets in ethanol using a fourth harmonic (266 nm) Nd:YAG pulse laser (Quentel, France) with a repetition rate of 30 Hz, pulse width of 8 ns and a maximum output of 100 mJ/pulse. The laser beam strikes the surface vertically after passing throughout an optical window and the liquid. Fig. 1(a) shows a schematic diagram for the laser ablation of target in liquid. To avoid the formation of deep holes in the target, the glass cell was displaced under the laser beam using a computer-driven *X–Y* stage with a laser

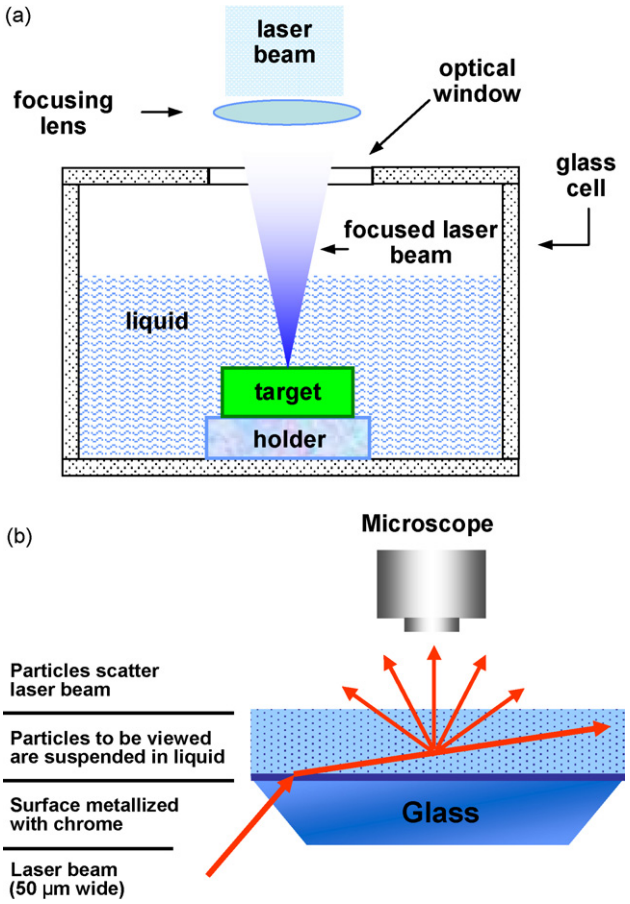

Fig. 1. (a) Schematic diagram for the laser ablation of target in liquid phase. (b) Schematic diagram for detecting nanoparticles in laser viewing module. A laser beam is irradiated into a suspension of nanoparticles in liquid. As the beam hits the particles, the light they scatter can be detected using a conventional microscope.

scanning velocity of 0.5 mm/s and 70–80% overlaps of the laser spot among the consecutive scans.

The $CaWO_4$ and $CaMoO_4$ powders were prepared via a citrate complex route [33,38] and the targets were prepared by compressing the raw powders under a uni-axial pressure of 300 MPa and then sintered at 900 °C in air for 3 h. The prepared $CaWO_4$ and $CaMoO_4$ targets were white-yellow in color. XRD measurements showed that the target had a single phase which was consistent with reported values (insets of Fig. 3, JCPDS Cards 41–1431 ($CaWO_4$) and 29–0351 ($CaMoO_4$)). After removing organic contaminations with ultrasonic cleaner in acetone, the cleaned target was immersed into 60 mℓ ethanol, thereafter the target was irradiated by the Nd:YAG pulsed laser. The laser beam was focused on the target with a beam size of about 1 mm in diameter using a lens with a focal length of 50 mm. The depth of the target immersed into the ethanol was kept about 20 mm. The colloidal suspensions consisting of the well-dispersed $CaWO_4$ and $CaMoO_4$ nanoparticles were prepared by laser ablation for 6 h at room temperature.

Surface morphology of the $CaWO_4$ and $CaMoO_4$ ceramic targets after laser ablation was observed using a scanning electron microscope (SEM, JEOL, JSM 5900 LV, Japan) for investigation on the laser ablation mechanism. The micro-