

LASER-ASSISTED SYNTHESIS OF GRAPHITE ENCAPSULATED ALLOY NANOPARTICLES FOR ENERGY CONVERSION APPLICATIONS

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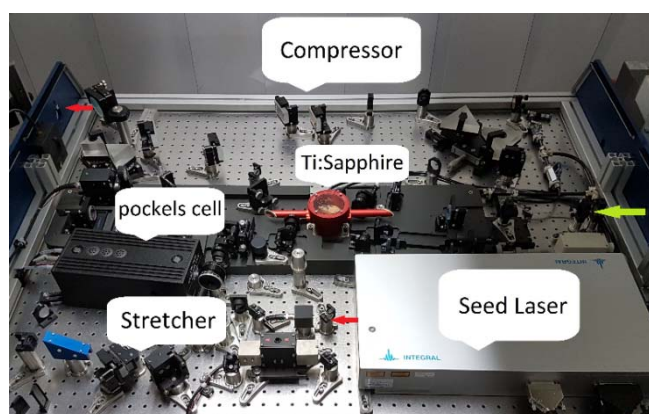
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INTRODUCTION

Pulsed laser ablation in liquids (PLAL) is a novel technique to produce nanomaterials with higher purity for various applications such as biomedicine [1], energy conversion and catalysis. Ultrashort laser pulses are practically important as the physicochemical processes occur in timescales comparable to the natural atomic and molecular oscillation time from femtosecond (10^{-15} s) up to picosecond regime (10^{-12} s) [2]. Moreover due to the thermal non-equilibrium situation of electrons and lattice, the precise and localized material processing with less energy loss can be expected [3]. Graphite shell nanomaterials due to their outstanding optical, mechanical, thermal, electrical properties and high surface area attract more attention in energy conversion applications. They showed a promising potential in transistor, battery, supercapacitor and biosensor. As the efficient heat transfer in electronic packages is of importance, the thermal interface materials (TIMs) were mainly introduced in high-density electronics. Commercial TIMs are generally composed of highly conductive particles such as graphite particles and a matrix for an efficient heat transfer. In the presented work, Ni/Au bimetallic oxide nanoparticles (BONs) with a few nanometer graphitic shell and median size of 10nm were generated by femtosecond laser pyrolysis of butanol solvent on Ni/Au target.

EXPERIMENTAL

The Ni/Au platelets were positioned in a glass cell (height of 15mm) with an optical window allowing the horizontal access of the laser beam (Picture 1). The nanoparticle production was carried out using a commercial femtosecond titanium-sapphire laser (SPECTRA-PHYSICS®, ≤ 400 mW, 800nm, 10 fs, 75 MHz and beam diameter ca. 6 mm). The chirped pulse amplification (CPA) were applied before transferring the seed laser pulse to the Pockels cell [4]. The powermeter (OPHIR Photonics) was placed after diaphragm A3. The maximum output power for the system is ≤ 1 W. The focus position at various liquid media were experimentally evaluated by measuring the ablation area on a silicon target (ImageJ software) as a function of the distance of the focusing parabolic mirror (focal length 101.16 mm). The Gaussian beam radius of 87 micron was calculated. The size distribution study and electron diffraction patterns of laser-synthesized nanoparticles were studied by transmission electron microscope; Philips CM200 TEM (LaB6 cathode, acceleration



Picture 1: The schematic of femtosecond laser set up. The system connected to the motorized XYZ-scanning stage controlled by CNC computer program.

voltage of 200kV, Gatan Orius CCD camera). Energy-dispersive X-ray spectroscopy (EDX) in connection with TEM served for chemical composition studies. High resolution transmission microscopy (HRTEM) was performed by FEI Titan 80-300 equipped with an imaging Cs corrector. The squared diameter of the ablated area (D^2) which is evaluated by optical microscopy is correlated to the Gaussian beam radius (w_0), the pulse energy (E) and the threshold pulse energy (E_{th}) with the assumption of a Gaussian beam profile;

$$D^2 = 2w_0^2 \ln \left(\frac{E}{E_{th}} \right)$$

The laser energy was chosen around 250 μ J to decrease the energy losses during the synthesis. The solvent evaporation by laser cause scattering and shielding of the laser energy and consequently lower productivity. Moreover, the filamentation of ultrashort laser beam in fluid at higher fluences can contribute to energy losses [5].

RESULTS AND DISCUSSION

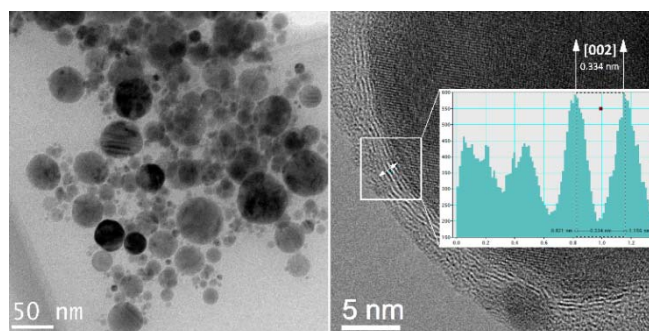
The femtosecond laser ablation of Ni/Au target in butanol at fluence (F) about 1 J.cm⁻² and number of pulses (N) of 1000 led to crystalline Ni/Au BONS with median size of 10 nm. BF-TEM is shown various forms of crystallographic systems and defects (Picture 2). The HRTEM of Ni/Au BONS presented a few atomic layers of graphite shell. The lower polydispersity and median size are observed similar to isopropanol solvent and in comparison to ethanol. In fact, solvents with higher carbon chain length led to the formation of carbonaceous shells, e.g. graphite due to pyrolysis of solvents on hot metallic surface [6-7]. The sublimation, evaporation and disintegration of the solid material occur due to the interaction of the high intensity laser pulse with the surface of the material. Moreover, due to the heat transfer from the molten metal layer and plasma plume to the solvent at the liquid-metal interface, the supercritical liquid can be formed [8]. This can contribute to solvent decomposition and generation of carbonaceous species inside the colloidal solutions.

CONCLUSION

Graphite encapsulated Ni/Au BONS with a thin graphitic shell of a few atomic layers and median size of 10nm were synthesized by femtosecond laser-induced disintegration of butanol solvent. One can assume that the nature of the solvent may play a role in the final chemical composition of nanomaterials. The graphitization of Ni/Au BONS in butanol triggered more colloidal stability due to less agglomeration and particle diffusion.

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Picture 2: BF-TEM, HRTEM and intensity profile of femtosecond laser-synthesized Ni-Au BONS in butanol. ($N = 1000$, $F = 1 \text{ Jcm}^{-2}$).