Diamond & Related Materials 82 (2018) 63–69

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Synthesis of MoC@Graphite NPs by short and ultra-short pulses laser ablation in toluene under N_2 atmosphere

Madelyn Madrigal-Camacho[a,b,*], Alfredo Rafael Vilchis-Nestor[b,*], Marco Camacho-López[c], Miguel A. Camacho-López[d]

[a] Posgrado en Ciencia de Materiales Faculty of Chemistry, UAEM, Toluca, Mexico
[b] Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Km 14.5 Toluca-Atlacomulco Road, Campus Rosedal, Toluca, CP 50200, Mexico
[c] Laboratorio de Investigación y Desarrollo de Materiales Avanzados, Facultad de Química, UAEM, Campus Rosedal, Km 14.5 Toluca-Atlacomulco Road, Toluca C.P. 50295, Mexico
[d] Laboratorio de Fotomedicina, Biofotónica y Espectroscopía Láser de Pulsos Ultracortos, Facultad de Medicina, UAEM, Jesús Carranza y Paseo Tollocan s/n, Toluca C.P. 50180, Mexico

ARTICLE INFO

Keywords:
Laser ablation
Short and ultrashort pulses
Molybdenum carbide nanoparticles
Onion-like carbon nanostructures

ABSTRACT

In this work, we present the experimental methods of the synthesis of MoC/MoC@Graphite by laser ablation with short and ultra-short laser pulses by using a molybdenum (Mo) and graphite target. All the experiments were carried out utilizing toluene as liquid medium. During the ablation, a nitrogen (N_2) atmosphere was necessary to avoid the oxidation of the Mo NPs. The structure, composition, and morphology of the NPs were investigated by transmission electron microscopy (TEM-HRTEM-SAED), X-ray diffraction and Raman spectroscopy. The TEM results evidence the formation of two carbonaceous structures: a graphite coating around the NPs and an amorphous carbon matrix that embeds the NPs. It was observed that these structures contribute to avoid the agglomeration and oxidation of the NPs. The size distribution, structure, and agglomeration of the NPs were discussed based on the solvents and also on the duration of the laser pulses.

1. Introduction

Laser ablation of Solids in Liquids (LASL) is one of the most efficient techniques in the synthesis of NPs which is characterized by being relatively simple due to long reaction times, high temperatures or multi-step chemical synthesis procedures not being required [1–3]. The main formation mechanism consists in nucleation during the plasma plume cooling and then, followed by growth and coalescence of NPs [4]. The colloidal solutions produced are stable without adding stabilizing surfactants or ligands and also hazardous or toxic chemical precursors [5] which lead to the generation of pure NPs without residual contaminants and therefore not chemical waste is generated thus contributing to the environment.

Based on the nature of the material, the NPs synthesized may show inhomogeneous particle sizes, agglomeration, and oxidation. One of the ways to avoid these problems is to functionalize the bare NPs by adding a ligand or a surfactant into the colloidal solution just after being synthesized or during the ablation [6–8]. Nevertheless, in this case, the encapsulation of NPs has been developed to form core-shell structures, with the specific aim to avoid the oxidation of the molybdenum.

In order to avoid the oxidation of molybdenum, a carbon coating is a viable and efficient option. The alternative to form this coating is by the laser ablation of a hydrocarbon liquid. It has been reported that laser ablation allows the formation of Onion-like Carbon (OLC) as a coating of the carbide. Currently, these structures are one of the most interesting nanoforms among all the carbon allotropes due to its electrical conductivity, high specific surface area, tribological and catalytic properties, electrochemical energy storage and a high potential in biomedical applications [9–11].

Carbon coating is produced by the effect of the high temperature of the plasma plume which induces a thermochemical decomposition (pyrolysis) of the liquid thus causing the carbon particles generation [5,12,13]. The saturated carbon particles will precipitate and grow as a carbon coating around the NPs during the following rapid quenching process of the laser ablation. The nature of the organic solvent used affects the coating (forming either an amorphous or graphitic coating), and the growth, features, stability, chemical composition and size/morphology of the NPs (some cases are presented in several papers) [14–17].

On the other hand, the synthesis of carbides NPs, specifically

* Corresponding authors at: Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Km 14.5 Toluca-Atlacomulco Road, Campus Rosedal, Toluca, CP 50200, Mexico.
E-mail addresses: mmadrigalc249@alumno.uaemex.com (M. Madrigal-Camacho), arvilchisn@uaemex.mx (A.R. Vilchis-Nestor).

https://doi.org/10.1016/j.diamond.2017.12.019
Received 19 October 2017; Received in revised form 7 December 2017; Accepted 27 December 2017
Available online 28 December 2017

molybdenum carbide by LASL has not been extensively studied [18]. However, the interest in studying this carbide has recently grown due to its catalytic properties (similar to noble metals in many organic chemical reactions) [19–22]. Besides, it is a carbide with a great number of stable phases [23] with a high thermal stability and oxidation resistance [24].

Considering the impact of laser ablation on NPs synthesis and various properties (chemicals, physical, and mechanics) of molybdenum carbide, the present work focuses on the combined implementation of three strategies. Firstly, the experiments were carried out using short ablation time with low energy, thus decreasing the energy cost required for the synthesis of the NPs. Secondly, mitigates the oxidation of the molybdenum by the presence of N_2 atmosphere and by the graphitic coating around the NPs, since Mo is oxidized in organic solvents in O_2 atmosphere using the same ablation parameters. Besides, under oxidizing atmosphere OLC structures were not observed for molybdenum carbide [18,25]. Finally, beyond the synthesis tests, this work also aims to improve the knowledge of the role of the pulse duration in laser ablation regarding size distribution, the morphology of NPs and the formation of a graphitic coating.

2. Experimental

2.1. Laser ablation of Mo and graphite in N_2 atmosphere

The colloidal suspensions were synthesized by using a molybdenum and graphite target (disks with thickness of 3 mm and 3.7 mm respectively, 99.9% purity, Kurt J. Lesker Co.) in toluene (as liquid medium) under a nitrogen atmosphere. The experimental setup used in the laser ablation experiments is shown in Fig. 1.

The experiments were performed by using two different Nd:YAG lasers of short and ultra-short pulses, both with a wavelength of 1064 nm and a repetition rate of 10 Hz. One of them is a nanosecond laser: Surelite Cotinuum (short pulses, $\tau \sim 6$ ns) and the other one is a picosecond laser: Ekspla (ultra-short pulses, $\tau \sim 30$ ps). The incidence angle of the laser beam respect to the normal line of the target was 45° (see Fig. 1).

Firstly, the Carbon NPs were produced by irradiating the graphite for 3 min, using a per pulse laser energy of 25 mJ, which corresponds to a per pulse laser fluence of 3.68 J/cm^2 for ns laser and 0.79 J/cm^2 for ps laser. Finally, the molybdenum target was ablated for 5 min with a per pulse laser energy of 50 mJ, corresponding to a per pulse laser fluence of 7.36 J/cm^2 for ns laser and 1.6 J/cm^2 for ps laser. The NPs suspension was sonicated each minute in order to disperse those precipitated NPs, besides the vapors generated by toluene were removed by inserting a needle into the septum stopper.

2.2. Characterization of samples

The produced NPs were analyzed by TEM (JEOL-2100 with 200 kV acceleration voltage and LaB_6 filament) in order to determine the size distribution, morphology, structure and chemical composition of the NPs and the carbonaceous structures. The sample was prepared firstly by dispersing the NPs in ethanol to eliminate the organic residual components and then the solution was dropped onto a carbon-coated copper grid.

At least 5 representative images were taken for each sample. In order to obtain statistically consistent information. Particle size distributions were obtained by the measurement of more than 100 particles for each sample, employing ImageJ™ software. The average particle size diameters were calculated with the equation $d_{avg} = \Sigma(n_i d_i) / \Sigma n_i$ where n_i is the number of particles of diameter d_i. It is important to mention that HRTEM analysis was performed with DigitalMicrograph™ (DM) software provide by Gatan Microscopy.

To analyze the graphite coating of NPs and the matrix of amorphous carbon formed, microRaman spectroscopy was utilized. The collected powder of NPs (previously washed with ethanol and dried at room temperature) was characterized using a micro-Raman system (LabRamam HR-800 of Jobin-Yvon-Horiba) with a 632.8 nm He-Ne laser as excitation source. To conclude, X-ray diffraction (XRD) was performed to obtain the structural composition of laser ablated NPs. A Bruker D8 Advance system with CuKα radiation and Lynxeye detector (λ = 0.15419 nm, scan step size of 0.03° and time per step of 114 s) was used.

3. Results and discussion

3.1. Laser ablation of Mo in toluene with N_2 atmosphere by using ns laser pulses

All the experiments presented here were carried out in toluene, using a closed system with N_2 atmosphere. It has been proved that using toluene as the liquid medium in the LASL technique carbides NPs and graphite coatings can be obtained. The extreme conditions of high temperature and high pressure of the plasma plume allows the decomposition of the solvent forming ions, radicals, and atoms of Carbon that can combine with the species of metals in the plasma plume [13,26].

The production of the NPs with the N_2 atmosphere system was attempted with both short and ultra-short pulses with the purpose of

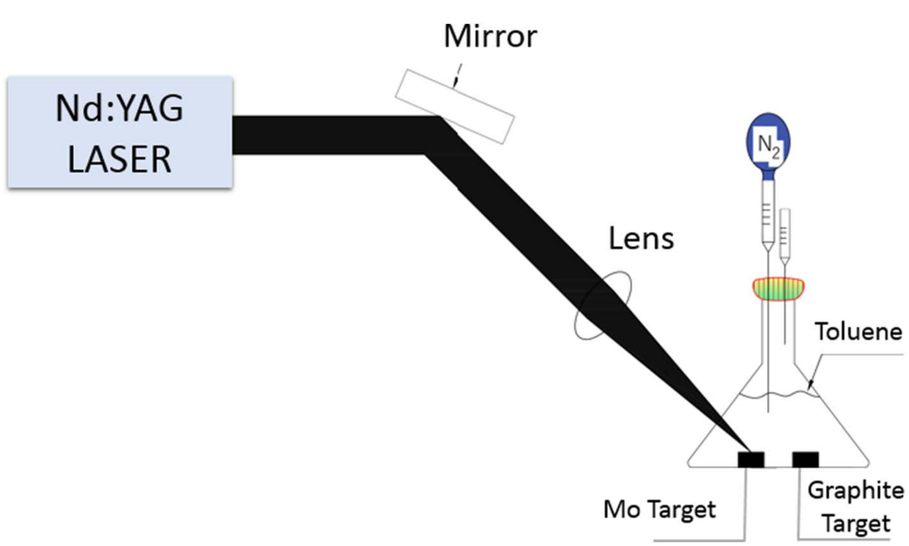

Fig. 1. Experimental setup for the laser ablation experiments in N_2 atmosphere.