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Photoluminescent colloidal Cu@C-NPs suspensions synthesized by LASL

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ABSTRACT

In this work we report the synthesis of photoluminescent carbon-coated copper nanoparticles (Cu@C-NPs) based colloidal suspensions, using the laser ablation of solids in liquids technique (LASL). LASL experiments were carried out by ablating a Cu solid target immersed in acetone as the liquid medium with ns-laser pulses (1064 nm) of a Nd-YAG laser. In all experiments the per pulse laser fluence and the repetition rate frequency were kept constant and the ablation time was varied. The as obtained Cu@C-NPs suspensions were optically characterized with absorption and photoluminescence spectroscopies. Raman spectroscopy was used to give evidence of the carbon shell deposited around the Cu NPs. TEM results showed that 10 nm spheroids Cu@C-NPs were obtained. The as obtained Cu@C-NPs suspensions displayed out a PL emission band similar to that for carbon nanoparticles suspensions obtained by the same technique. We have found that the blue-green PL emission band intensity is mainly dependent on the ablation and aging time of the samples. The Cu@C-NPs-based colloidal suspensions can be proposed as multifunctional due to its absorbance and emission properties.

1. Introduction

One of the key benefits of a material in the nanoscale is that its properties considerably differs from the bulk material of the same composition, feature which can be easily altered by varying its size, shape or chemical environment, allowing the possibility to have nanomaterials with well-defined properties for specific applications [1–3]. Nanomaterials of almost any material can be produced i.e., metallic, semiconductors, ceramics and among; and their chemical, physical and optical properties can generally be controlled by the route of synthesis used [4,5], either during or after by a post-synthesis treatment, a surface passivation, for example. In order to tune the properties of nanomaterials, numerous chemical, physical and biological routes of synthesis have been implemented during the past decades [6–8]. An increasing route of synthesis for the production of nanomaterials is the physical method termed laser ablation of solid targets in liquid media (LASL). The increase of its use is mainly because this technique of synthesis is considered as chemically clean (green), simple, versatile and fast; and because through it, nanomaterials from almost whatever bulk material can be obtained [5,6,9,10]. It is necessary to point it out that through the LASL route, different experimental parameters as laser fluence, pulse duration, irradiation time, and among, can be modified in order to have a reasonable control of the nanoparticle size [5], however the grow mechanism of nanoparticles through this technique is very chaotic and the complete information for the perfect control of nanoparticle sizes is still missing. The main goal of the present work is to use LASL route to produce copper-based photoluminiscent nanoparticles.

Copper based-metallic nanomaterials, termed copper nanoparticles (Cu-NPs) have been attractive in different areas by virtue of their useful properties such as the good thermal and electrical conductivity at a much lower cost than silver or gold. Due to its plasmon surface resonance, copper nanoparticles exhibit enhanced nonlinear optical properties, which can result in many applications in optical devices and nonlinear optical materials [11,12]. Due to its potential applications, several routes of synthesis have been implemented for the production of Cu-NPs [11–17]. Only to cite some of them, it can be referred the chemical reduction of copper sulfate method [11], photochemical synthesis [13], laser ablation in liquids [14–17], biological routes [18], and among. It has also been reported the synthesis of small

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fluorescent atomic copper clusters via electrochemical synthesis [19]. The synthesis of copper/copper oxide nanoparticles through solution plasma [20] or via Gram-negative bacterium [21] and the production of electrically conducting copper iodide (CuI) nanoparticles synthesized at room temperature via chemical routes have also been reported [22]. In particular, the production of copper-based nanoparticles using the above mentioned LASL technique requires times of synthesis as short as 100 s [16], which is very short compared with the typical 2–3 h for the chemical routes [12]. Inkjet-printed electronics [12], SERS technique [14], as antibacterial activity agents [18], or optoelectronic applications [22], are only some of the specifics applications of Cu-NPs reported.

Beside of the close-pure Cu-NPs, it has interestingly been reported the synthesis of copper nanoparticles covered with carbon, which have mainly been designed in order to protect the Cu-NPs to the agglomeration phenomena, or to prevent the unwanted degradation phenomena or oxidation, which impacts on its applications. With the aim to have a better understanding and control of the carbon-shell covering the copper-core, the production of carbon-coated copper nanoparticles (Cu@C-NPs) have been possible performing different route of synthesis. To cite some examples, these are synthesized using flame spray synthesis [23], solid-state reduction reactions [24], by detonation decomposition of Cu ions [25], in ionic liquid under microwave heating [26], using hydrothermal methods [27], laser ablation [28,29] and among. Cu-NPs encapsulated in multi-shell carbon cages using Cu-phthalocyanine as precursor material [30] or by multi-layer graphene through metal-organic chemical vapor deposition method [31] or reducing flame synthesis [32], have also been reported. The prevention of the undesired degradation phenomena was also reached by incorporating linear carbon chains [33] containing *sp* hybridization either as alternating triple and single bonds (polyynes). The benefits of the carbon-shell on a copper-core on its applications have been exemplified, indicating that the carbon shell prevents the oxidation, which allows the possibility to use these as temperature or pressure sensors completely exposed to air [23], being also suitable to replacing the expensive noble metal nanoparticles utilized in the conductive inks [30]. Another advantage is due to the carbonaceous shells, preventing the oxidation and aggregation of metal copper, was proposed to be useful to improve the catalytic performance of copper nanostructures [27]. Multifunctional optical applications due to its absorbance and fluorescence properties, like as biomedical, sensor and lubricant ones have been proposed for Cu@C-NPs [28,29,34,35]. It is necessary to point it out that agglomeration can be prevented by adding dispersant or surfactant agents to the solution after its synthesis, however when LASL technique is used, this effect can be reached after some minutes [27,36].

Motivated on the potential applications of copper-core carbon-shell (Cu@C-NPs) nanoparticles, the aims of this paper are focused to report on the one hand, its synthesis using LASL technique, considered as a simple and versatile route; on the other hand show its photoluminescent response and its correlation with the carbon-shell presence. To obtain the Cu@C-NPs, the ablation of copper bulk immersed in acetone was performed at different ablation times. The effect of the ablation time and aging time on the optical properties of the as-well prepared copper suspensions was analyzed, concluding that Cu@C-NPs are formed and the carbon shell is the responsible for the photoluminescence.

2. Experimental

2.1. Synthesis of colloidal Cu@C-NPs in acetone

Colloidal Cu@C-NPs suspensions were obtained using the laser ablation of solids in liquids technique (LASL). The ablation experiments were carried out as is illustrated in Fig. 1A. A copper disk (2.54 cm diameter×0.635 cm long, 99.999% pure, Kurt J. Lesker Co.) was the solid target, which was immersed in 10 ml of pure acetone (*Sigma- Aldrich Co.*), using a glass vessel of 20 ml. By focusing laser pulses (30 mJ per pulse) on the surface of the copper disk by means of a 135 mm focal length lens, the ablation was initiated; the copper disk was manually moved to prevent ablation in the same place, which could change the focus conditions. It is necessary to indicate that the laser beam was not exactly focused on the copper surface; the spot beam have 0.125 cm^2 area (0.2 cm diameter), which is reduced to 0.005 cm^2 area (0.04 cm diameter), giving a laser fluence, according to the power per pulse, 5 J/cm^2. A pulsed Nd:YAG laser (*Minilite II, Continuum*) emitting at 1064 nm and operated at 15 Hz of repetition rate was used in all experiments. Samples for irradiation times of 30, 60, 120, 180, 240 and 300 s (sec) were prepared. Even when through LASL technique many experimental parameters can be tuned in order to control the final properties of the prepared nanoparticles [5], the goal of this study is to elucidate the effect of the irradiation time on the produced copper nanoparticles when keeping constant the solvent, repetition rate frequency, laser fluence and wavelength used for the synthesis. Based on our experimental experience related with LASL technique, flammable solvents as acetone could flame during its interaction with the laser pulses, however it was found to occur when the level of the solvent is slightly above to the target or when the laser beam interacting with the target produces small drops; both possibilities were not present in the LASL experiment reported here, ignition of the acetone was not observed.

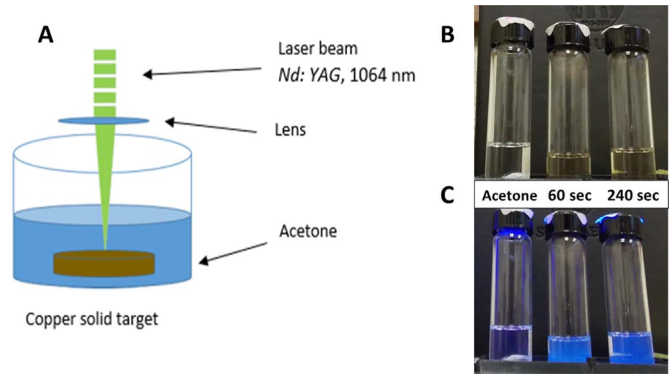

Fig. 1. A-Experimental setup for the Cu@C-NPs synthesis and appearance of the Cu@C-NPs suspensions under white (B) or UV (C) light illumination for different irradiation times and pure acetone. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. 1B and C shows optical images of the samples under white light and UV (370 nm) illumination, respectively. For comparison purposes, acetone was also included in the picture. In Fig. 1B one can observe a brownish coloration in the liquid similar (samples obtained at 60 and 240 s of ablation time) to that observed in the carbon nanoparticles suspension obtained by LALS from a carbon target immersed in acetone under the same laser parameters previously reported by our group [37]. In Fig. 1C blue photoluminescence is observed in samples illuminated with a UV (370 nm) lamp (pictures were taken after 30 days of the synthesis). The photoluminescence observed in these copper nanoparticles in acetone is similar to that observed in the carbon nanoparticles suspensions in the same solvent reported by our group [37,38].

2.2. Optical and structural characterization

The optical features of the as-obtained Cu@C-NPs and carbon suspensions were investigated by using absorption and photoluminescence spectroscopies. Optical absorption spectra of the suspensions were taken using a double beam spectrophotometer (Perkin-Elmer, Lambda 650) from 320 to 900 nm. A quartz cuvette with an optical path length of 10 mm was used for the optical characterization. The