Vibrational Spectroscopy 77 (2015) 5–9

Contents lists available at ScienceDirect

Vibrational Spectroscopy

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

Short communication

Raman scattering and optical properties of lithium nanoparticles obtained by green synthesis

Ramón A.B. Álvarez [a], M. Cortez-Valadez [a,*], R. Britto-Hurtado [a], L. Oscar Neira Bueno [b], N.S. Flores-Lopez [a], A.R. Hernández-Martínez [c], R. Gámez-Corrales [d], R. Vargas-Ortiz [e], J.-G. Bocarando-Chacon [f], H. Arizpe-Chavez [a], M. Flores-Acosta [a]

[a] Centro de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-88, 83190 Hermosillo, Sonora, Mexico
[b] Grupo de Espectroscopia y Laser, Universidad Popular del Cesar, C.P. 2503 Valledupar, Cesar, Colombia
[c] Centro de Física Aplicada y Tecnología Avanzada (CFATA), Universidad Nacional Autónoma de México, Campus Juriquilla, Blvd. Juriquilla 3000 Juriquilla, Querétaro, Mexico
[d] Departamento de Física, Universidad de Sonora, Apdo. Postal # 130, Hermosillo, Sonora 83000, Mexico
[e] Universidad Autónoma de Sinaloa, Facultad de Ingeniería Mochis, Ciudad Universitaria, C.P. 81223, Los Mochis, Sinaloa, Mexico
[f] Universidad Tecnológica de Querétaro, UTEQ. Avenida Pie de la Cuesta # 2501, C.P. 76148 Querétaro, Mexico

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form 2 February 2015
Accepted 2 February 2015
Available online 3 February 2015

Keywords:
Lithium nanoparticles
Radial breathing modes
Raman in metal nanoparticles
DFT approximations
Green synthesis

ABSTRACT

The first report on lithium nanoparticles synthesized experimentally is presented. The nanoparticles were obtained using the extract of *Opuntia ficus-indica* through "green synthesis". The optical, structural and vibrational properties were studied through optical absorption, TEM microscopy and Raman spectroscopy. The particles show a size of approximately 5 nm. The absorption bands were found at 315 and 415 nm in the samples after the synthesis of the nanoparticles. One Raman band was detected at around 280 cm^{-1}. Several levels of approximation of the density functional theory and the Hartree–Fock method on the structural and vibrational study of the lithium clusters (Li_n, n = 2–18) are incorporated. A radial breathing mode (RMB) type Raman mode was found for the case Li_n ($n > 3$) in the predicted Raman spectrum. This mode shows the highest relative intensity for each case, and a shift to lower wavenumbers when the amount of atoms in the cluster increases.

1. Introduction

Lithium seems to be the appropriate and irreplaceable element for the improvement of electronic devices such as long-lasting rechargeable batteries. Currently, the development of the nanometric material and nanostructured material sciences, has led to a number of studies that have been focused on developing interactions of lithium with nanometric materials containing: aluminium, titanium, iron, and cobalt [1–4]. This was done with the objective of improving their electrical and electrochemical properties, among others. Mainly by contributing to the efficiency of the fast charging capacity as shown by Hwang et al., who used nanoparticles of nickel oxide [5]. Another results show that Silicon nano-spheres cathodes contribute to the durability of lithium rechargeable batteries.

Other important advantages of metallic nanoparticles are their application in catalysis, fuel cells, optical devices, biomedical use, among others [6–9]. Since these properties regularly depend on the size and morphology of the nanoparticles, it is important to find an effective and low-cost synthesis method. The "green" synthesis with the plant *Opuntia ficus-indica* (*Ofi*) has succeeded for synthesize and stabilize several types of crystalline and amorphous metallic nanoparticles [10–12]. In addition to this, the see-through property of this extract allows the detection of changes in the colour-scheme spectrum, which is visible after the synthesis of the nanoparticles. This facilitates the immediate detection of colloidal nanoparticles in the sample. Consequently, the absorption bands in UV–vis spectrum are detected allowing the study of the plasmonic properties of the nanoparticles. Raman spectroscopy is other technique widely used in the characterization of nanoparticles. This technique facilitates the identification at level of single molecule of materials in the samples [13]. Because of this, Raman spectroscopy is a characterization sensitive to the size [12] and morphology [14] of nanoparticles. The results of our group show evidence of RBM in small metallic nanoparticles [15].

* Corresponding author.
E-mail addresses: manuelcortez@live.com, jose.cortez@unison.mx (M. Cortez-Valadez).

http://dx.doi.org/10.1016/j.vibspec.2015.02.001
0924-2031/

This report shows the synthesis of metallic nanoparticles of lithium with *Ofi* extract. The experimental evidence of the plasmonic properties of lithium nanoparticles is reported for the first time. Low frequency Raman bands were detected after the synthesis of lithium nanoparticles in the extract. A complementary structural and vibrational study in small clusters of lithium was undertaken by the density functional theory. This predictive study showed the existence of vibrational modes in the Raman spectrum of the structures under study. These RBM are located at low wavenumbers matching with the experimental results of Raman spectroscopy.

2. Materials and methods

The extract was taken from a young leaf of the *Ofi* plant. The prickles were removed, in order to peel it and chop it finely. 25 g of the chopped mixture was placed in 50 mL of deionized water, and then placed under magnetic stirring for 30 min at 60 °C. Another solution 0.001 M of LiCl, acted as a precursor solution of the Li ion. Afterwards, 25 mL of the precursor solution was mixed with 3 mL of the plant extract, in order to reduce the Li^+ ions in metallic lithium. The solution was kept at 60 °C for 1 h.

The Raman spectra in the colloidal samples was recorded with the Micro Raman X′plora equipment model BX41TF OLYMPUS HORIBA Jobin IVON with a class 3B argon laser with 20–25 mW, at 532 nm.

2.1. Theory and calculations

The density functional theory at the generalized gradient approximation level B3LYP (Becke's three-parameter exchange functional and the gradient corrected functional of Lee Yang and Parr) combined with the basis set LANL2DZ (the effective core potentials and associated double-zeta valence basis set) were used for the structural and vibrational study of the lithium clusters; both are included in the Gaussian package 09 [16]. Only the cases Li_n ($2 \leq n \leq 18$) were treated, due to computational cost. Additionally, we consider the lithium unit cell at several approximation levels and basis sets. All the structures were optimized; subsequently the vibrational spectrum was obtained to guarantee a local minimum. The Li_n structures were optimized and obtained from the addition or subtraction of one or more atoms in previously reported clusters (Li_{n-1}, Li_{n+1}, Li_{n-2}, Li_{n+2}, etc.). The stationary points on the Li_n potential energy surface, in their lowest electronic states in each case, were initially located and analysed by vibrational spectroscopy using DFT with the hybrid functional B3LYP in conjunction with the LANL2DZ basis set. The stability of the optimized geometries was confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers in the Li_n clusters, guarantee a local minimum in the potential energy surface.

3. Results

Lithium nanoparticles were synthesized in the *Ofi* plant extract. The particles have a crystalline structure and quasi-spherical morphology. The interplanar distance of one of the planes is 2.65 Å, very close to the 2.69 distance reported by Barret [17] which corresponds to one of the crystalline planes with higher intensity (1 0 0) for metallic lithium. The size of the particle is around 5 nm in some the crystalline planes, can be observed with a semi-crystalline morphology, as shown in Fig. 1.

The absorption bands in the ultraviolet spectrum were detected after the reduction of the lithium ion. After 24 h of synthesis processing, optical properties of the samples with colloidal lithium nanoparticles were studied in an aqueous solution. The optical absorption spectrum is shown in Fig. 2. The predictive calculus of the Mie theory [18,19], indicate that the lithium colloidal nanoparticles with spherical morphology and 10 nm diameter, show absorption bands in the ultraviolet spectrum around 310 nm approximately [19]. A deconvolution of the absorption spectrum allows us to view the contribution of the optical properties of the lithium nanoparticles and *Ofi* extract. A band located at 263 nm, is the absorption band of special features of the plant *Ofi* extract. The additional band located at 315 nm have a good agreement with the band referred to above, for the theory of Mie [19] assigned to the surface plasmon in lithium colloidal nanoparticles located in 310 nm. Predictive calculations about the theory of Mie reported previously by our group [11] show a shift towards higher wavelengths when the particle size is increased. Because of this, the band focused on 375 nm could be caused by the surface plasmon in nanoparticles or agglomerates with size greater than 10 nm (Supplementary information).

After the synthesis of the nanoparticles, the Raman band was detected centred approximately at 280 cm^{-1} as shown in Fig. 3. Because the *Ofi* extract does not show Raman bands relevant to the

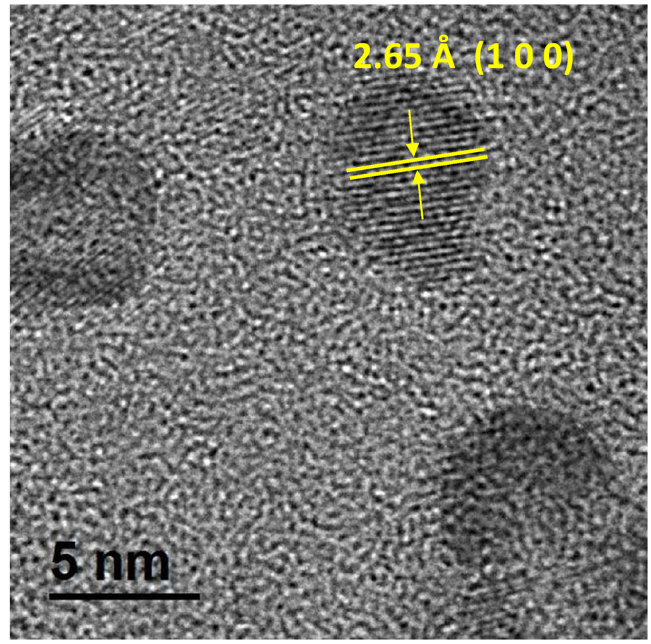

Fig. 1. TEM image of the lithium nanoparticles synthesized in the *Ofi* extract.

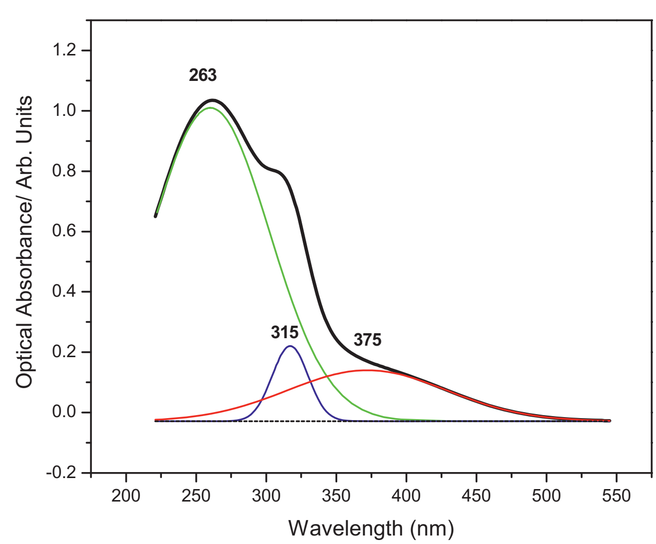

Fig. 2. Optical absorption spectrum of *Ofi* extract with lithium nanoparticles.