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Radial breathing modes in silver selenide quantum dots

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ABSTRACT

Silver selenide (Ag_2Se) quantum dots obtained in synthetic zeolite F9 through ion exchange are reported in this work. A hydrothermal reaction was conducted between the zeolite–Ag^+ system with Na_2SeSO_3. Quantum dots smaller than 10 nm were measured by Transmission Electron Microscopy (TEM). The particles have a cubic structure with a phase lm-m (229). A shoulder centered at 150 cm^{-1} was experimentally detected after the synthesis of quantum dots by Raman Spectroscopy. The Density Functional Theory (DFT) was employed to determine a possible allocation to the Raman band detected. The LSDA (Local Spin Density Approximation) approximation levels and B3LYP (Becke's three-parameter Exchange functional and the gradient corrected functional of Lee, Yang and Puar) were employed in combination with the basis set LANL2DZ (Los Alamos National Laboratory 2-double-ζ) to study the structural and vibrational properties in minimum energy clusters $(AgSe)_n$. Radial Breathing Modes were detected between 150 and 252 cm^{-1} for these levels of approximation.

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1. Introduction

The interest for semiconductor nanoparticles and quantum dots from different scientific disciplines has been growing rapidly. The main reason for this is the physical dependency of their size properties [1–4], which differ greatly from the size properties in bulk state. This refines the band structure and optical and electrical properties [5], through quantum refinement. In recent years, the activity of selenide nanoparticles in living organisms as well as their size-dependent optical properties has attracted attention for research [6–8]. Likewise, recent studies have been focused on the preparation of selenide from different metals [2,9]. This compound has been applied for the elaboration of commutation devices, additionally, it belongs to the family of superionic conductors [10]. Silver selenide is a narrow-band-gap semiconductor between 1.13 and 1.31 eV for low temperature phase [11]; it presents high ionic and electronic mobility and a high electrical resistivity, which makes it a compound suitable for a wide variety of applications. The synthesis methods used for the elaboration of selenide nanoparticles and quantum dots materials are varied, among which we can find chemical, sonochemical, electroplating, hydrothermal and green synthesis methods [6–8,12]. These methods are adjusted to the needs, equipment and resources available for the elaboration of nanostructures. The competitive advantages obtained from cheaper methods are important. Including the properties of the small particles to be explored, for which the use of natural or synthetic zeolite generates big expectations due to the intrinsic capacity of the ionic exchange it possesses [12,13].

It is possible to perform “in vivo” analysis in samples of tissues, cells, blood, etc.; through Raman spectroscopy, penetrating the samples at a depth of hundreds of micrometers. Furthermore, quantum dots allow the amplification of Raman Spectroscopy (SERS). Even though most of the quantum dots that have been studied until now contain toxic elements such as Pb, Cd, Hg, etc., that hinder a vibrational study “in vivo”, the main purpose of this study is to get stable Ag2Se quantum dots in a biocompatible matrix (zeolite) for potential applications on SERS in the vibrational study of “in vivo” samples.

This work presents the synthesis and structural and vibrational characterization of Ag_2Se quantum dots in F9 synthetic zeolite. New vibrational modes located at low wave numbers are detected experimentally due to the effect of quantum confinement after the synthesis of silver selenide quantum dots. DFT complements the study of vibrational modes in low energy structures $(AgSe)_n$. Radial Breathing Modes (RBM) are found in the small clusters analyzed. RBM in other materials allow a correlation between the position of the Raman modes and the diameter of the structure [14,15].

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Graphene has a relation with the position of the Raman bands and the number of layers [16]. In other cases, it has been possible to determine the specific correlation between the RBM and the number of atoms in the particles (quite small metallic particles) [17]. The presence of RBM in quantum dots clearly confirms that small materials show vibrational characteristics that differ from those present in bulk materials. The presence of RBM at low wavenumbers in the Raman Spectrum facilitates the detection of Ag_2Se quantum dots in "in vivo" samples, without an elaborate study of TEM. It is important to consider that the presence of RBM at low wavenumbers does not interfere with the Raman Bands of organic compounds at higher wavenumbers.

Given that RBM are assigned principally to carbon nanotubes, this work intends to bring a theoretical hypothesis with experimental evidence, of the existence of RBM in small particles of silver selenide, through a vibrational analysis in Raman Spectroscopy.

2. Materials and methods

Ag_2Se quantum dots were obtained from commercial F9 zeolite from Waco Chemicals Inc. (Na_2O Al_2O_3 2.5 SiO_2 27 H_2O). Silver is incorporated to zeolite through the intrinsic property of zeolites of exchanging ions of the same or different size and charge. To do so, the zeolite is incorporated in 25 ml of $AgNO_3$ solution with a molarity of 0.75 M for 0.3 h, in thermal treatment at 50 °C. Subsequently, zeolite–Ag^+ system is obtained after the sample is filtered, cleaned and dried at room temperature. The ion Se^2 reacts with Ag^+ when in contact with zeolite–Ag^+ in 1 ml Na_2SeSO_3 (Sodium selenosulfate) at 1 M for 0.25 h.

A small quantity of a powder sample (approx. 5 mg) was placed in a glass microscope slide for the study of vibrational spectroscopy at room temperature in standard conditions. The samples were characterized by Raman Spectroscopy in a Micro Raman X0plora BX41TF OLYMPUS HORIBA Jobin IVON with a 3B argon laser with 20 to 25 mW, at 532 nm.

For TEM measures, the powder sample mixed with water. A drop of colloidal water was placed on a copper micro grid coated with carbon. Afterwards, the sample was vacuum dried at room temperature for 4 h. The images were obtained through Transmission Electron Microscopy (TEM JEOL, model JEM-2010F, with an acceleration voltage of 200 KeV).

3. Theory and calculations

The Density Functional Theory (DFT), included in GAUSSIAN 09 software [18] was used to obtain minimal energy structures and allocate vibrational modes. The $(AgSe)_n$ $(2 \leq n \leq 9)$ clusters were optimized at LSDA approximation levels (Local Spin Density Approximation) and B3LYP (Becke's three-parameter exchange functional and the gradient corrected functional of Lee, Yang and Puar) [19] combined with the base-set LANL2DZ (the effective core potentials and associated double-zeta valence) [20]. The Raman bands in predicted spectrum show low wave numbers. After the analysis of the predicted vibrational modes in each spectrum and after proving the nonexistence of negative frequencies, it can be confirmed that the structures are local minimum and not transition states. The study of the evolution of Raman bands with respect to the number of atoms in each cluster is performed for both approximation levels. Structures conformed by maximum 18 atoms were considered in order to find low energy $(AgSe)_n$ structures. It was not possible to consider bigger structures due to the computational price required for this approximation level. The initial structures considered in the study were: diverse geometries of triangular, cubic and tetragonal types etc. As well as structures reported in the literature of oxide clusters, metallic clusters and semiconductor clusters [21–23].

4. Results and discussion

TEM microscopy images in Fig. 1a show Ag_2Se quantum dots. These particles possess high distribution at approximately 5336 particles/μm^2. Fig. 1b shows bigger isolated particles found in the samples. These particles show clearly the formation of well-defined crystal planes. The interplanar distances found at 2.07 and 2.45 Å correspond approximately to those reported at 2.04 and 2.50 Å, attributed to planes (2 1 1) and (2 0 0) corresponding to the cubic phase Im-3m (229) of Ag_2Se. The particle sizes from Fig. 1a vary mainly from 4 to 9 nm. The particle size histogram in Fig. 1c allows to determine the predominant size of quantum dots (7 nm).

The forbidden band width (E_g) calculated from the experimental optical absorption spectrum (Supplementary material) for Ag_2Se quantum dots corresponds to 1.376 eV, and is slightly higher than the reported experimentally from 1.31 eV [11]. It can be attributed to the average size of the quantum dots obtained experimentally. The $(AgSe)_n$ clusters obtained at the approximation level B3LYP/LANL2DZ are shown in Fig. 2 with their respective symmetry point group, after the minimization of energy. Subsequently, the energetic difference in the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) is calculated at the B3LYP/LANL2DZ level. The parameters obtained are shown in Fig. 3, some values fluctuate around 1.3 eV. The measurements in Raman Spectroscopy in Fig. 4 show the presence of a band centered at 150 cm^{-1}. These do not show the Raman bands characteristic of bulk Ag_2Se, probably due to the small size of the particles. The active modes in Raman were detected for $(AgSe)_n$ clusters through DFT. Fig. 4 shows a progressive RBM observed in all the cases, located between 150 and 225 cm^{-1} for the approximation level B3LYP/LNL2DZ. This mode is different from the rest of the harmonic frequencies calculated due to the higher relative intensity and the Raman spectrum predicted on each cluster. The F9 zeolite shows a characteristic band located approximately at 509 cm^{-1} associated to the Si–O–Al vibrations [24]. Since F9 zeolite does not show Raman bands at low wave numbers, it is suitable for the study of vibrational properties in quantum dots and small nanoparticles. DFT at the approximation levels (B3LYP/LANL2DZ) and (LSDA/LANL2DZ) were used to allocate the Raman band detected at low wave numbers. Fig. 5a shows the dependency of RBM with respect to the number of atoms in each case for the approximation levels LSDA/LANL2DZ and B3LYP/LANL2DZ. The RBM modes appear in every case at higher wave numbers than those obtained at the approximation level B3LYP, due to the undervaluation in the interatomic bond length shown at the approximation level LSDA. The bond distance for AgSe is 2.634 Å, similar to 2.630 Å [25]. A triangular structure was obtained for $(AgSe)_2$, with a length between the bonds Ag–Ag and Se–Se of 2.96 Å and 2.95 Å, respectively. From the structures $(AgSe)_{4-9}$ a periodic behavior is observed for the development of tubular structures. This behavior is clearer in $(AgSe)_9$, in such a way that these structures can represent early stages of the growth of silver selenide nanowires, etc. [26].

Fragmentation energy is defined as the difference in energy between the cluster or molecule and the fragmented components. This stability parameter is widely used to identify the structures with higher energy for their fragmentation or for those that show lower energy. This parameter implicitly shows information of the stability of the cluster. The fragmentation energy of the clusters is described by Eq. (1):

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