Vibrational study of hybrid organic-inorganic cadmium sulphide nanocomposites

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The infrared vibrational characterization of optical emission-tunable organic-inorganic nanocomposites containing cadmium sulphide nanoparticles as guest entities in a lamellar host matrix is presented. Nanocomposites were prepared by a simple chemical synthesis that could provide a platform to create functional nanoscale composite structures. The presence of an all-trans conformation of intercalated structurally directing surfactant is confirmed as we elucidate the influence of water molecules on the methylene group vibrations, leading to a unique environment for Cd\textsuperscript{2+} ions to uptake S\textsuperscript{2−} within the nanocomposite to form emissive CdS nanocrystals within the host.

Keywords: Nanocrystals; semiconductors; optical emission tunable.

La caracterización vibracional de compuestos laminares orgánico-inorgánicos de emisión óptica sintonizables que contienen nanopartículas de sulfuro de cadmio como huéspedes es presentada. Nanocompositos fueron preparados usando rutas simples de síntesis química, la cual puede proporcionar una plataforma para la creación de estructuras funcionales a nivel de nanoscale. La presencia de la conformación all-trans en los agentes tensoactivos de las estructuras intercaladas fue confirmada, como también la influencia de las moléculas de agua sobre las vibraciones del grupo metileno. Dando lugar a un ambiente único de iones Cd\textsuperscript{2+} para la absorción de iones S\textsuperscript{2−} dentro del nanocomposito para formar dentro del anfitrión nanocristales de CdS que presentan emisión óptica de energía.

Descriptores: Nanocristales; semiconductores; emisión óptica saturable.

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1. Introduction

Development of a system that allows the investigation of subtle surface-state interactions and reactions resulting in band-gap tunable organic-inorganic nanocomposites has been recently reported [1]. This opens the door to investigations of surfactant-mediated organic-inorganic laminar CdS nanocomposites from fundamental electronic and optical transitions to band-gap and defect emission engineering via a simple chemical synthesis route. The realization of functional nanoscale device materials involving the controlled synthesis, chemical manipulation, and assembly of nanoscale building blocks is a crucial addition to smart opto-electronic nanomaterials [2]. This report concerns the lattice vibrational characterization of the (CdS)\textsubscript{x}(CdCl\textsubscript{2})\textsubscript{y}(CTAB)\textsubscript{z} nanocomposites of a (CdS)\textsubscript{x}(CdCl\textsubscript{2})\textsubscript{y} (surfactant)\textsubscript{z} series.

2. Characterization of Compounds

Scanning electron microscopy (SEM) analyses were performed with a Philips model 515, and the FT-IR spectra were recorded using Perkin-Elmer series 2000 apparatus. The details of the nanocomposite synthesis can be found elsewhere [1].

3. Results and Discussion

The infrared vibrational spectra of the (CdS)\textsubscript{x}(CdCl\textsubscript{2})\textsubscript{y}(CTAB)\textsubscript{z} nanocomposites can be divided and analyzed in two parts: the first is related directly to the surfactant, and the other with the inorganic (host) materials, which in our samples is a CdS-CdCl\textsubscript{2} mixture. The spectrum shown in Fig. 1 represents the vibrational characterization of the hybrid organic-inorganic (CdS)\textsubscript{1.48}(CdCl\textsubscript{2})\textsubscript{1}(C\textsubscript{16}N\textsubscript{33}(CH\textsubscript{3})\textsuperscript{3+}Br)\textsubscript{0.75} nanocomposite.
FIGURE 1. (a) Optical image of CdCl$_2$ (left) and a series of (CdS)$_x$(CdCl$_2$)$_y$(CTAB)$_z$ nanocomposites. SEM images of (b) pure CdCl$_2$ (c) the (CdS)$_{1.48}$,(CdCl$_2$)$_{1}$,(C$_{16}$N$_{33}$CH$_3$)$_{3+}$Br$_{0.75}$ nanocomposite. (d) FTIR spectrum of the same compound as (c). The inset highlights the spectral range from 800-650 cm$^{-1}$.

The absorption energies indicative of methylene group (CH$_2$) stretching in the cetyltrimethylammonium bromide (CTAB) provide a measure of the degree of order/disorder and compactness (here defined to be the inter and intramolecular forces that bind the intercalated organic molecules between the inorganic lamella resulting in minimized chain rotation or twisting, and minimal deformation of the methyl, and methylene groups) of the methylene chain; differences in these vibrational energies may also be a reflection of the relative hydrophilic environments of the hydrophobic methylene chain [3].

For measurements of the surfactant in the solid-state (tightly-bound intercalation, confined volumes and intermolecular interactions), the presence of remnant water molecules in the vicinity of the surfactant molecules permits correlation of the vibrational characteristics of the methylene groups. As a result, the relatively hydrophobic environment of the methylene groups can be correlated with the relatively lower energies (lower wavenumbers) for the CH$_2$ stretching vibrations. The CH$_2$ stretching vibrational energies are known to be higher in aqueous solutions than in the solid state [3].

The energy shifts can be interpreted in terms of the structural order of the methylene group in the nanocomposite. In a more hydrophilic environment, significantly more gauche conformers may be formed in order to reduce the length of contact between the methylene groups and the water molecules. The dimensionality and topotactic process in the intercalated compounds analyzed here, however, evidences surfactant chains with an all-trans conformation.

The infrared measurements of the (CdS)$_{1.48}$,(CdCl$_2$)$_{1}$,(C$_{16}$N$_{33}$CH$_3$)$_{3+}$Br$_{0.75}$ nanocomposite (Fig. 1), and the observed shift among breaks related to the surfactant vibrational mode (solid-state) shows bands at 3028 (+16) cm$^{-1}$ that is attributed to the NH$_3^+$ stretching mode vibration of the surfactant [1]. Intense bands are also observed resulting stretching methyl mode at 2952 (+7), together with bending modes observed at 1416 (+18) and 1380 (0) cm$^{-1}$.

The methylene group can be observed with modes at 2918 (+3), and 2850 (+2) cm$^{-1}$, related to the symmetrical and asymmetrical C–H vibrations, respectively. Other notable bands are located at 1468 (+4) cm$^{-1}$, related to in-plane symmetric angular deformations of the methyl (CH$_3$) species, as well the band at 723 (+7) cm$^{-1}$ that corresponds to the C–H bending mode of the methylene group in the surfactant. The bands at 1487 (0) cm$^{-1}$ and 3021 (+20) cm$^{-1}$ are attributed to the N–H vibrational mode; the H–O–H bending mode of the water molecule is observed. The bands as 966 (0), 908 (+3) cm$^{-1}$ are result from the stretching mode of the C–N bond.

The wavenumber, bandwidths, and integrated intensity of the CH$_2$ stretching vibration bands should be correlated with the gauche/trans conformer ratio of methylene chains in the lamellar composites. Lower frequencies, and narrower band widths, highlight a more ordered structure in the methylene groups, while increasing frequencies and width of these bands are associated with a greater density of gauche conformers and associated disorder [3]. The principal differences in the vibrational spectra of the solid surfactant compared to those of the lamellar nanocomposites, is the observation that all methylene vibrational bands shift to lower wavenumber, implying that the disordered chains have a decreasing number of gauche conformers (less disorder). Preliminary data of a positive delta shift parameter from RMN CP-MAS $^{13}$C experiments in these compounds seems to confirm this hypothesis and will be presented elsewhere.
The second area of interest is related to the cadmium vibrational modes. It is generally accepted that no active CdS mode is observed in the mid-infrared region. The $A_1$ and $E_1$ modes at 243 and 242 cm$^{-1}$ respectively, transverse optical frequencies, and longitudinal mode at 305 cm$^{-1}$ were reported in Ref. 4. Signals from $E_2$ modes attributed to multi-phonon processes are also observed in the range of 85-97 cm$^{-1}$, and 212-207 cm$^{-1}$.

The CdCl$_2$ crystal has two infrared-active modes ($E_u$ and $A_{2u}$) in the long-wavelength limit ($k = 0$). Each infrared-active mode has both transverse optical (TO) and longitudinal optical (LO) components [6]. The layered CdCl$_2$ structure, where every third chlorine layer is in an equivalent position, also it has $D_{3d}$ symmetry with a trigonal axis (the $c$ axis) perpendicular to the plane of the layers. The two infrared-active vibrational modes observed in these nanocomposites are the in-plane $E_u$ (156 cm$^{-1}$) mode and the out-of-plane $A_{2u}$ (239 cm$^{-1}$) mode [6].

The structure of the cadmium chloride-type crystals within each cation layer each ion has six nearest neighbors and since each cation layer is separated by two anion layers, interlayer effects between cations can be ignored [7]. The mid-infrared spectrum of the (CdS)$_{1.48}$(CdCl$_2$)$_{1.7}(C_{16}N_{33}(CH_3)^{3+}Br)_{0.75}$ nanocomposite exhibits two notable bands at 685 and 699 cm$^{-1}$. Neither of these vibrational bands can attributed to either cadmium sulphide or chloride compounds, although recently it was reported that bands at 622 and 572 cm$^{-1}$ are attributed to the presence of an intermediate structure that contains Cd$^{2+}$ ions in a cadmium ethylenediamine chloride nanostructured complex [5, 8].

4. Conclusions

The infra-red vibrational study of novel CdS-containing (CdS)$_{1.48}$(CdCl$_2$)$_{1}$(surfactant)$_{0.75}$ nanocomposites can be summarized as follows:

1. The infrared spectra show the presence of a gauche/trans mix in surfactant molecule conformation after intercalation in the lamellar CdCl$_2$ host matrix. A correlation of the CH$_2$ stretching absorption energies allows classification of the observed degree of order/disorder, compactness (confined volumetric molecular geometries), and increasing disorder of the methylene chain in the nanocomposite.

2. All observations suggest that the relatively hydrophobic state of absorbed surfactant molecules also correlates with changes in the energy of the CH$_2$ stretching vibrational modes.

3. The presence of CdS-CdCl$_2$ complex in the host can only be well described by accounting for the formation of a Cd—S interaction, associated with the vibrational active infrared modes in the mid-infrared area.

4. The formation of the inorganic-organic cadmium chloride/sulphide composites shows the introduction of complexity, and promotes fundamental understanding of size-property correlations at the nanometer scale.

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