Electronic Spectra of Calcium Carbonate Porous Nanostructured Material

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Abstract
For a long time silicon has been kept off from optoelectronic applications due to its indirect band gap, which drastically diminishes light emission efficiency. This setting changed, however, when light emission and optical devices based on nanostructured porous silicon [1] and silicon quantum dots [2] were achieved. Binding electrons and holes inside these structures greatly increases the probability of radiative recombination.

On the other hand, calcium carbonate ($CaCO_3$) is a cheap material with a wide range of applications, whose versatility is mainly due to its use in various fields of industry such as paper, rubber, plastics, and paint industries as a coating pigment, filler, or extender, food, and horticulture. With the recent developments in materials manipulation at nanoscale, nanostructured $CaCO_3$ particles have been investigated and produced for different purposes. Furthermore, $CaCO_3$ applications are determined by a great number of strictly defined parameters, such as the average particle size, the particle size distribution and morphology, specific surface area, brightness, oil adsorption, chemical purity, etc. Concerning bio-applications, many types of micro- and nanoparticles (mostly organic although some inorganic) have been investigated for the use in drug delivery systems [3,4].

On the other hand, porous materials have been the subject of intensive research because of their potential applications in optoelectronics, biotechnology, pharmaceutics, catalysis, etc. Particularly, $CaCO_3$ has shown to be specially useful as a carrier for several substances, such as insulin and hydrophilic compounds, because of its easy production and slow biodegradability [3,4]. Unfortunately, the binding of substances adsorbed in the surface of solid $CaCO_3$ is weak. This suggests that the inclusion of pores in solid $CaCO_3$ particles might enhance its binding efficiency by increasing the available surface for adsorption of other substances. In fact, porous $CaCO_3$ were synthesized and used for capsule preparation. Thus, the versatility of $CaCO_3$ combined with the electronic properties presented by nanostructured porous materials may lead to interesting and innovative applications to a wide range of fields [5]. In particular, luminescence can be helpful in tracking the remaining porous $CaCO_3$ in body fluids when used for drug delivery.

It is the aim of this work to investigate the optical properties of porous $CaCO_3$ by means of computer simulations. A schematic diagram displaying a rectangular porous CaCO3 nanoparticle is shown in Fig. 1(a)-(b) with its respective size distribution of pores. The electronic structure calculation is performed within the effective mass framework.

Figure 2 displays the interband oscillator strength for several combinations of the porosities *p* and pore diameter *D*. As we can see, the energy separations between transitions are very small. This is a consequence of the energy state dependence as a power law scale. Even though we have investigated only the ten lowest states in both conduction and valence bands, we expect that this behavior is also true for a higher number of states. Due to the small energy difference between adjacent states, absorption and luminescence spectra are expected to be very strong and broad even at low temperatures. The authors expect to stimulate experimental efforts to confirm these predictions.

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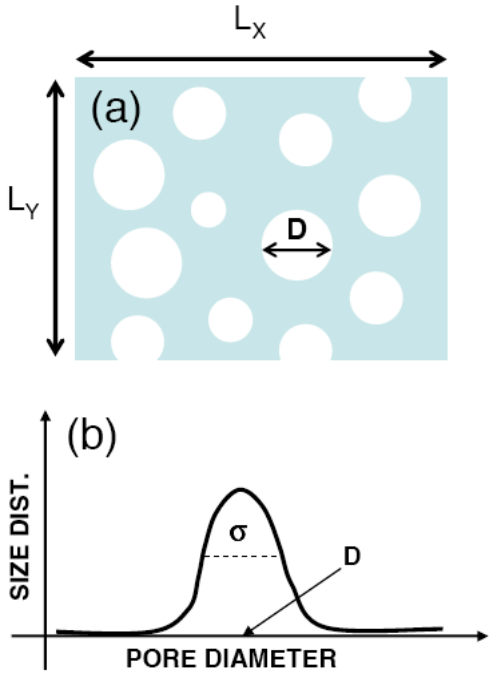

Figure 1. Schematic representation of the porous nanoparticles simulated in this work (a) and its respective size distribution of pores (b). The shaded area represents $CaCO_3$. The pores content is modeled as vacuum.

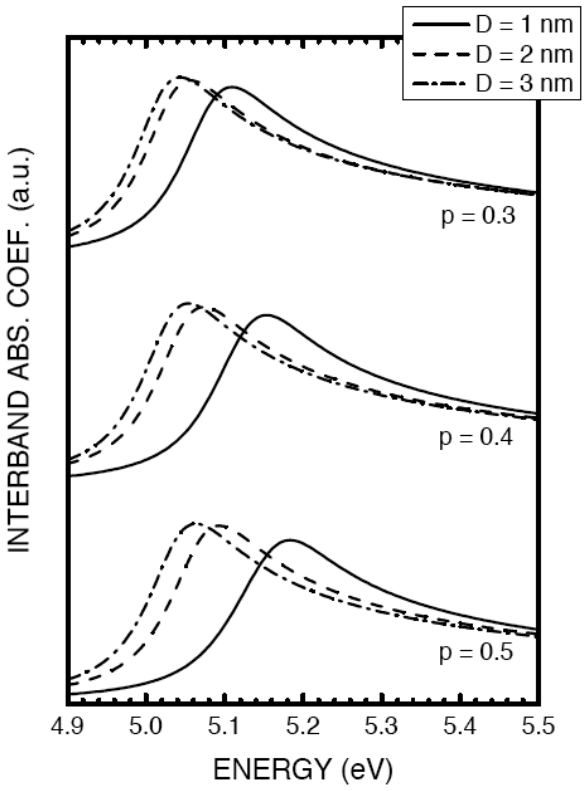

Figure 2. Interband oscillator strength (in arbitrary units) for porous CaCO3 nanoparticles with porosities p = 0.3, 0.4, and 0.5. The average pore diameters are D = 1 nm (solid circle), 2 nm (open circle), and 3 nm (triangle). Each point in this graph were averaged over 40 samples.