Methodological approach to study energetic and structural properties of nanostructured cadmium sulfide by using ab-initio molecular dynamics simulations

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ARTICLE INFO

ABSTRACT

A single wurtzite phase of cadmium sulfide cluster is investigated by ab-initio molecular dynamics simulations at different temperatures, ranging from 100 K to 600 K. In this study we propose a possible procedure to characterize the CdS quantum dots system by means of molecular dynamics calculations using a standard Car-Parrinello scheme. In order to ensure the accuracy of the numerical approach, preliminary calculations to test pseudopotentials, cutoff and box size on both single atoms systems and Cd–Cd, S–S, Cd–S dimers have been performed. Calculated binding energies and bond lengths are obtained in good agreement with experimental data. Subsequently, an uncapped CdS cluster with size below 2 nm, 48 atoms of cadmium and 48 atoms of sulfur, in a wurtzite geometry was structurally optimized to minimize internal stresses. The CdS cluster has been carefully characterized structurally at several temperatures up to T = 600 K. At the temperature of 340 K atomic diffusion on the surface allows the onset of a new stable atomic configuration.

1. Introduction

Nanostructured semiconductors II–VI such as cadmium sulfide quantum dots (CdS QDs) have attracted much attention for their novel optical and electronic properties employed in different technological fields [1,2]. Due to a band gap of 2.58 eV [3], CdS presents high luminescence characteristics and is used in the photovoltaic field for emitting and optoelectronic devices. In addition, novel and interesting properties have been obtained for CdS nanostructure due to the quantum confinement [4–6] that appears when the particle size is close to the excitonic Bohr radius [7]. In this way the band gap is tunable by size, obtaining modulated luminescence properties from synthesis process [8–11]. In fact, many experimental papers have shown that the optical properties of CdS QDs system are strictly connected to the size of the QDs [12,13].

In the last decade, some authors have also investigated several properties of nanostructure materials by using computational approaches [14–24]. Specific results for CdS clusters with different sizes were presented and their geometrical and electronic properties were computed by using ab-initio methods [25–29]. Recently, Wen and Melnik [29] performed an ab-initio molecular dynamics calculation on three different phases of CdS, wurtzite, graphite and rocksalt reporting their potential energy for each temperature between 300 K and 450 K. Some results about structures and electronic properties of stoichiometric cadmium sulfide clusters are also reported by He-Ying and coworkers [27], where the behaviour of the energy gap between HOMO and LUMO orbitals as a function of cluster size is shown. The authors suggest that this parameter could be used as a measure of stability of CdS clusters. In addition the same authors present calculated binding energy (BE) in generalized gradient approximation (GGA) framework for wurtzite and zincblende bulk per cadmium sulfide unit predicting −5.752 eV and −5.668 eV respectively.

The stability of the CdS phase, and particularly the stability of phase between bulk and nanostructure material, continues to be now discussed but not entirely understood [30–33]. In this specific case, two principal crystallographic forms for CdS bulk are wurtzite and zincblende. Wurtzite is the most stable at ordinary pressures and temperatures. There is at least one other crystallographic structure for CdS, the rocksalt configuration obtained at high pressure [34,35]. Several physical properties of clusters are strongly dependent on the particle size when this is reduced below some nanometers. For example, the crystallographic structure is size

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dependent and the most stable wurtzite phase is found for lengths greater than 6 nm. However the exact crystallographic form for small CdS nanoparticles is not yet completely understood and several results are not in agreement. Experimentally, Herron showed that nanoparticles with diameter less than 1.5 nm are amorphous while those around 3.5 nm are cubic. Metastable zincblende structure was prepared by Bandaranayake with size of about 3 nm, by Ricolleau with particles size smaller than 3-4 nm and Kotkata prepared CdS nanocrystals with size around 3-4 nm. However, all those authors found for CdS nanoparticles a wurtzite structure for size greater than 6-7 nm when the sample is heated far from room temperature. In contrast, Murakoshi prepared stable hexagonal CdS under thermodynamic control up to 4.2 nm in size. From theoretical point of view, Junkermeier [16] showed by means of Molecular Dynamics (MD) calculations that uncapped CdS nanoparticles with size around 2 nm are amorphous, in agreement with experimental results by Herron [9] and Vorokh [33].

In this paper we illustrate a calculation procedure to accurately describe the geometrical and structural properties of CdS by means of ab-initio molecular dynamics simulations. In this specific case, preliminary results on single wurtzite cluster of CdS at different temperatures using standard Car-Parrinello molecular dynamics scheme are discussed.

2. Computational details

The results presented in this paper were carried out by using the Car-Parrinello Molecular Dynamics (CPMD) code which employs the density functional theory to efficiently describe the electronic contribution to the ion dynamics [36]. We used a generalized gradient approximation BLYP [37,38] for the exchange-correlation functional already implemented in CPMD package [39]. In addition, we applied a norm-conserving pseudopotentials approach in order to describe the interaction between valence electrons and core ions: in the specific case, a Martins-Trouiller type of pseudopotentials in the Kleinman-Bilander form for S and Cd were employed. All structures, atoms, dimers and cluster, were studied in an empty simulation cell to mimic isolated molecules. Preliminary tests on small Cd and S systems were performed in order to verify the reliability of the pseudopotentials and to accurately determine the box size and the cutoff energy for plane waves. A cubic box with 15.87 Å sides and 30 Ry for plane waves cutoff were used. A CdS cluster with 48 atoms of cadmium and 48 atom of sulfur was built in the wurtzite phase; the temperature of annealing was set in the range from 100 K to 600 K. For 10 K, 100 K, 150 K, 200 K, 250 K, 280 K, 300 K, 330 K, 340 K, 350 K, 370 K, 400 K, 450 K, 480 K, 530 K, 570 K, 600 K the clusters were labeled as CdS0, CdS100, CdS150, CdS200, CdS250, CdS280, CdS300, CdS330, CdS340, CdS350, CdS370, CdS400, CdS450, CdS480, CdS530, CdS570, CdS600 respectively. A time step of 0.125 fs and Nosé-Hoover [40,41] chain thermostat, in order to control the temperature, were used to perform CPMD molecular dynamics simulations. At each temperature, after thermal equilibration, at least 20,000 time steps were used to compute averages. Moreover a CdS bulk structure was built to estimate the performance of DFT method by using the same conditions of the cluster calculations; lattice parameters and band gap energy were obtained for wurtzite supercell containing 5 unit cells and 500 atoms. Band structure was calculated for high symmetry point of the first Brillouin zone in hcp geometry, as reported in [42].

3. Results and discussion

In Table 1 are reported binding energies and geometrical parameters for Cd_2, S_2 and CdS dimers with a cutoff set at 30 Ry. Czajkowski and coworkers [43] reported spectroscopy data of

Table 1
Equilibrium bond lengths and binding energies (BE) for Cd_2, S_2 and CdS dimers. The experimental BE data are from *Handbook of Chemistry and Physics 53*rd *Edition, page F-183*.

Data	CPMD	Experimental
R (Cd–Cd) Å	3.79	4.07–4.33[a]
R (S–S) Å	1.93	1.89
R (Cd–S) Å	2.47	2.52[b]
BE (Cd2) kcal/mol	0.2	2.7
BE (S2) kcal/mol	158.9	101.9–100.7[c]
BE (CdS) kcal/mol	44.2	91
BE (CdS) kcal/mol	44.2	≤ 47[d]

[a] From ref [43].
[b] From ref [26].
[c] From ref [44].
[d] From ref [45].

ground state and excited states for Cd_2 dimer by means of spectroscopy measurements. More specifically, for Cd–Cd the experimental intermolecular distance R is 4.07 Å in agreement to our CPMD results (3.79 Å).

We have obtained satisfactory agreement in the case of CdS intermolecular distance: the experimental results are reported by Gurin [26] (R = 2.52 Å). He-Ying [27] used GGA ab-initio calculation to predict for CdS distance a value of R = 2.36 Å and binding energy BE = 1.557 eV (35.905 kcal/mol), close to our CPMD CdS BE results. For CdS dimer the experimental binding energy is reported in Table 1 by Marquart [45]. In this work, the CdS BE≤47 kcal/mol was obtained, very close to BE = 44.2 kcal/mol computed by using our CPMD calculations. In addition, Fournier [44] reported experimental bond distance for S_2 dimer of R = 1.8892 Å and the relative binding energy BE = 100.7 kcal/mol: intermolecular bond is in good agreement with our CPMD results while the binding energy seems to be quite overestimated.

In order to better determine the performance of the DFT scheme used in this work, we have taken in account a CdS supercells with wurtzite phase containing 5 unit cells (Fig. 1); cell parameters and band gap energy were calculated and subsequently compared with experimental results. For this type of calculation the best cell parameters and band gap energy was obtained by using this specific layout: for wurtzite supercell different cell parameters values a1 and a2 (in hexagonal symmetry they are equals) was employed in order to minimize the potential energy (Fig. 2a). Then the best a1 and a2 values were set and a3 cell parameters was optimized so as to minimize the total potential energy (Fig. 2b). Using these cell parameters we have calculated the band structure of the CdS semiconductor (Fig. 3) whence it is possible to obtain the theoretical band gap. The best structure was found for a3/a1 = 1.59 to compare to 1.63, traditional values for ideal hcp structure.

The values of band gap calculated on gamma point is set around 1 eV, rather different from experimental results. This underestimation of the band gap is well documented in several articles [46–50] and review and it is typical for DFT-GGA approximation. In particular in Ref. [50] is reported 0.9 eV as value of CdS band gap calculated with GGA correction. Fig. 4 shows the side views of the CdS wurtzite structure cluster built with 96 atoms (Cluster96). On the initial structure we performed CPMD molecular dynamics calculation at 10 K to equilibrate the geometry. Then, this equilibrated configuration has been used for an annealing of the cluster up to 400 K. The annealing has been performed slow enough to avoid unphysical melting of the cluster and abrupt changes on the surface. Subsequently the temperature has been raised further to characterize the behaviour of the cluster at high temperatures.

Fig. 5 reports the formation energy per atom calculated for each temperature. Formation Energy (FE) for Cluster96 is defined as the energy difference between final cluster and isolated atoms: