DFT study of CdS-PVA film

Vaneeta Bala, S K Tripathi and Ranjan Kumar

Department of Physics, Panjab University, Chandigarh, India

E-mail: vaneetabala@yahoo.com, surya@pu.ac.in, ranjan@pu.ac.in

Abstract. Density functional theory has been applied to study cadmium sulphide-polyvinyl alcohol nanocomposite film. Structural models of two isotactic-polyvinyl alcohol (I-PVA) chains around one cadmium sulphide nanoparticle is considered in which each chain consists three monomer units of \[ -(CH_2-CH(OH))EMALE]}. All of the hydroxyl groups in I-PVA chains are directed to cadmium sulphide nanoparticle. Electronic and structural properties are investigated using ab-initio density functional code, SIESTA. Structural optimizations are done using local density approximations (LDA). The exchange correlation functional of LDA is parameterized by the Ceperley-Alder (CA) approach. The core electrons are represented by improved Troulier-Martins pseudopotentials. Densities of states clearly show the semiconducting nature of cadmium sulphide polyvinyl alcohol nanocomposite.

1. Introduction

In recent years, polymer nanocomposites of II-VI semiconductor compounds have attracted much research interest due to their size dependent structural, electronic, optical and catalytic properties. As the size of nanoparticle approaches to excitonic radius, quantum confinement effect arise which results in size dependent unique properties. Among II-VI inorganic semiconductor compounds, cadmium sulphide (CdS) is regarded as an attractive candidate for optoelectronic devices and solar cells [1]. CdS has a wide direct band gap ~ 2.4 eV with excitonic Bohr radius ~ 3 nm which make it possible to tailor its electronic and optical properties with size. The incorporation of CdS nanoparticles in polyvinyl alcohol matrix has shown significantly enhanced photoluminescence with long term stability [2,3]. Polyvinyl alcohol (PVA) is a water soluble polymer which provides a good control over growth and morphology of embedded nanoparticles. PVA acts as a capping material which binds to nanoparticle through -OH groups of polyvinyl alcohol chains [4]. Various in situ synthetic methods have been used to synthesize CdS nanoparticle/polymer composites [5-7]. Extensive experimental work has been done on CdS Nanocomposites but theoretical studies of these or related systems are very few.

In this paper, we propose three structural models of CdS nanoparticle incorporated within two isotactic-polyvinyl alcohol (I-PVA) chains in different ways utilizing the interaction between Cd and OH group of PVA. Each I-PVA chain contains three monomer units of \[ -(CH_2-CH(OH))EMALE]}. We have performed density functional based calculations to get optimized structures. We also focus our attention on the electronic properties of these proposed structural models.

To whom any correspondence should be addressed.
2. Computational Details
We employ first principles calculations on structural models of CdS nanoparticle embedded in polyvinyl alcohol chains using SIESTA [8] code which is based on density functional theory. It implements the standard Kohn-Sham self-consistent method and valence electrons are described by linear combination of numerical atomic-orbital basis set and the atomic core by norm-conserving pseudopotentials. The pseudopotentials generated using the Troullier and Martins scheme [9] are applied to describe the interaction of valence electrons with atomic core and their nonlocal components are expressed in the full separable form of Kleinman and Bylander [10,11]. The Ceperley-Alder (CA) form local density approximation (LDA) corrections are employed for the exchange-correlation potential [12]. We have used a split valence double- $\xi$ polarized (DZP)-basis set throughout the work. To calculate the self-consistent Hamiltonian matrix elements, the numerical integrals are performed and projected on a real space grid with an equivalent cut-off of 250 Ry. Structural models are relaxed using conjugate gradient algorithm until maximum atomic force is less than 0.04 eV/Å.

3. Results and Discussion
We discuss three structural models of CdS nanoparticle within I-PVA chains. Each PVA chain consists of three repeating units of $[-(\text{CH}_2\text{CH(OH)})-]$ with periodicity of 2.52 Å. C-C and C-O bond distances in zigzag PVA chain are 1.53Å and 1.43 Å respectively with tetrahedral bond angles. Cd-S bond length is observed to be 2.53 Å. The -OH groups in PVA chains are directed towards cadmium sulphide and act as coordination sites for nanoparticles.

3.1 Structural Models
In model A, CdS nanoparticle is suspended within two I-PVA chains (figure 1(a)). Cadmium is surrounded by four sulphur atoms and each sulphur atom is saturated with hydrogen. Cadmium is in the plane of two oxygen atoms of opposite chains. The methyl groups of two chains are separated by 6.61 Å. The incorporation of nanoparticle decreases the intermolecular hydrogen bonding between two polymer chains.

![Figure 1](image1.png)

(a) Model A, (b) Model B and (c) Model C. In these figures red, yellow, grey and green circles represent O, S, C and Cd atoms respectively. Hydrogen bonding is shown by dotted lines.

In model B, Cd is bonded with three sulphur atoms and to one of the PVA chains through interaction of Cd ion with central OH group of the polymer chain (figure 1(b)). Cd-O bond length is observed to be 2.32 Å. Central -OH group of second PVA chain is at a distance of 2.72 Å from Cd. In model C, Cd is coordinated to two hydrogenated sulphur atoms and two polyvinyl alcohol chains through central -OH groups of I-PVA chains (figure 1(c)). O-Cd-O bond angle is observed to be 90°. Intermolecular
hydrogen bonding between I-PVA chains increases as the distance between polymer chains decreases in this model.

3.2 Electronic Structure
We focus our attention on the band gap for these structural models which is very important factor for optoelectronic materials. We have plotted total densities of states (DOS) for above mentioned structural models as shown in figure 2. From DOS, band gap is calculated as 3.90 eV, 3.78 eV and 4.02 eV for models A, B and C respectively. These plots clearly show the semiconducting nature of the composite.

![Figure 2](image_url)

*Figure 2.* Density of states: (a) Model A, (b) Model B and (c) Model C.

4. Conclusion
We have proposed structural models for CdS nanoparticle embedded in PVA chains. All the structures are optimized using density functional theory. We have considered different situations in which nanoparticle can bind to polymer chains through interaction between Cd and -OH groups of PVA. DOS have been plotted for these structural models which reveal semiconducting nature of CdS-PVA composites. In the present study, we have calculated band gap from DOS which is comparable to
experimental results [13,14]. Wide band gap values ensure the use of CdS-PVA composites as a promising material for optoelectronic applications.

Acknowledgements
We are highly thankful to the Department of Physics, Panjab University for providing facility High Performance Computing Centre (HPCC). One of the authors, Vaneeta Bala thanks Department of Science and Technology, Government of India for INSPIRE fellowship.

References

[1] Han Z, Zhang J, Yang X and Cao W 2011 Sol. Energ. Mat. Sol. Cells 95 483
[2] Jung D, Kim J, Nahm C, Nam S, Kim J I and Park B 2012 Mater. Res. Bull. 47 453
[3] Pattabi M, Saraswathi Amma B and Manzoor K 2007 Mater. Res. Bull. 42 828
[4] Wang H, Fang P, Chen Z and Wang S 2007 Appl. Surf. Sci. 253 8495
[5] Mbhele Z H, Salemane M G, van Sittert C G C E, Nedeljković J M, Djokovic V and Luyt A S 2003 Chem. Mater. 15 5019
[6] Mondal S P, Mullick H, Lavanya T, Dhar A, Ray S K and Lahiri S K 2007 J. Appl. Phys. 102 06433
[7] Saikia D, Saikia P K, Gogoi P K, Das M R, Sengupta P and Shelke M V 2011 Mater. Chem. Phys. 131 223
[8] Ordejon P, Artacho E and Soler J M 1996 Phys. Rev. B 53 R10441
[9] Troullier N and Martins J L 1991 Phys. Rev. B 43 1993
[10] Kleinman L and Bylander D M 1982 Phys. Rev. Lett. 48 1425
[11] Bylander D M and Kleinman L, 1990 Phys. Rev. B 41 907
[12] Ceperley D M and Alder B J 1980 Phys. Rev. Lett. 45 566
[13] Mansur H S, Mansur A A P and González J C 2011 Polymer 52 1045
[14] Ghoswami M, Ghosh R, Chakraborty G, Gupta K and Meikap A 2011 Polym. Comp. 32 2017