

Electrostatic model of semiconductor nanoparticles trapped in polymer electrolytes

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MS received 30 September 2011; revised 7 April 2012

Abstract. A simple electrostatic model is applied to study the solvation energy and localization energy to inorganic semiconductor nanocrystallites trapped in polymer and ion conducting polymer electrolytes. The effective mass approximation has been applied to the system. In the single charge configuration, the dielectric constant of the medium has been identified as the selection criteria for hosting the nanoparticles. Solvation energy has been shown to depend on the host medium and the size of the crystallite.

Keywords. Nanocrystals; polymer electrolyte; effective mass approximation; encapsulation.

1. Introduction

Semiconductor nanostructures in recent years have gained considerable importance due to their novel, electrical, optical and device properties (Henglein 1989; Jain 1997). It is well known that the electronic properties of semiconductors undergo drastic change as their size reduces to nanometers. The transition from the band structures in large bulk crystallites to discrete localized energy levels is understood by the quantum confinement. Different approaches have been adopted to calculate the energy gap due to decrease in the crystallite size (Brus 1983; Lippens and Lannoo 1989; Dushkin *et al* 2000). In this paper, attempts have been made to study the ionization potential, solvation of the crystallite and localization energy of the charge in nanometer size inorganic semiconductor crystallite. Efforts have also been made to identify the criteria for selection of proper host material. The matrices chosen are, insulating polymer, polymer electrolyte and water as well.

Most of the experimental results showing encapsulation and trapping of nano-sized semiconductors used polymers and biomembranes as host matrix (Wang *et al* 1987; Gopidas and Kamat 1993; Radhakrishna 1994; Hayes *et al* 2001). Good solvation and binding by polymers have been reported by Bianconi *et al* (1991). In a simple semiconductor, there exists a filled valence band, a well-defined forbidden energy and a vacant conduction band. The ionization in ideal case results to a free electron and a hole trapped in the valence band. In case of small crystallites, the shape of the crystal is important. Though, when prepared, crystallites of various

shapes are reported (Braun *et al* 1996; Bhattacharya *et al* 2009). For simplicity, we choose the spherically symmetric shape of crystallites having radius a . We also assume that the dielectric constant ϵ_2 of the nanocrystallites is the same as that of the bulk material. This crystallite is embedded in a dielectric with dielectric constant ϵ_1 as shown in figure 1.

The crystallite is assumed to be ionized by a single positive charge. No other charge exists in the medium. The electric field due to this point charge terminates at infinity.

2. Theoretical consideration

With the above consideration the potential is derived inside and outside the spherical crystallite by solving the Laplace equation (Bottcher 1973). The potential inside the crystal is given as

$$\phi(r, s) = \sum_{n=0}^{\infty} \left[\frac{(\epsilon - 1)(n + 1)es^n}{\epsilon_2(\epsilon n + n + 1)a^{2n+1}} + \frac{es^n}{\epsilon_2 a^{2n+1}} \right] \times P_1(\cos \theta), \quad (1)$$

where $P_1(\cos \theta)$ is the Legendre polynomial, defined by the angle θ between r and s and ϵ the ratio of ϵ_1/ϵ_2 . Here, we consider the point charge to be very small with a radius r_0 such that it can be treated under Born approximation. The work done in bringing the charge e , through a distance r_0 , from s and $s + r_0$ is then:

$$V(r) = \sum_{n=0}^{\infty} \left[\frac{(\epsilon - 1)(n + 1)}{\epsilon_2(\epsilon n + n + 1)a} \left(\frac{r}{a}\right)^{2n} \right] \frac{e^2}{2} + \frac{1}{\epsilon_2} \frac{1}{|\delta|} \frac{e^2}{2}. \quad (2)$$

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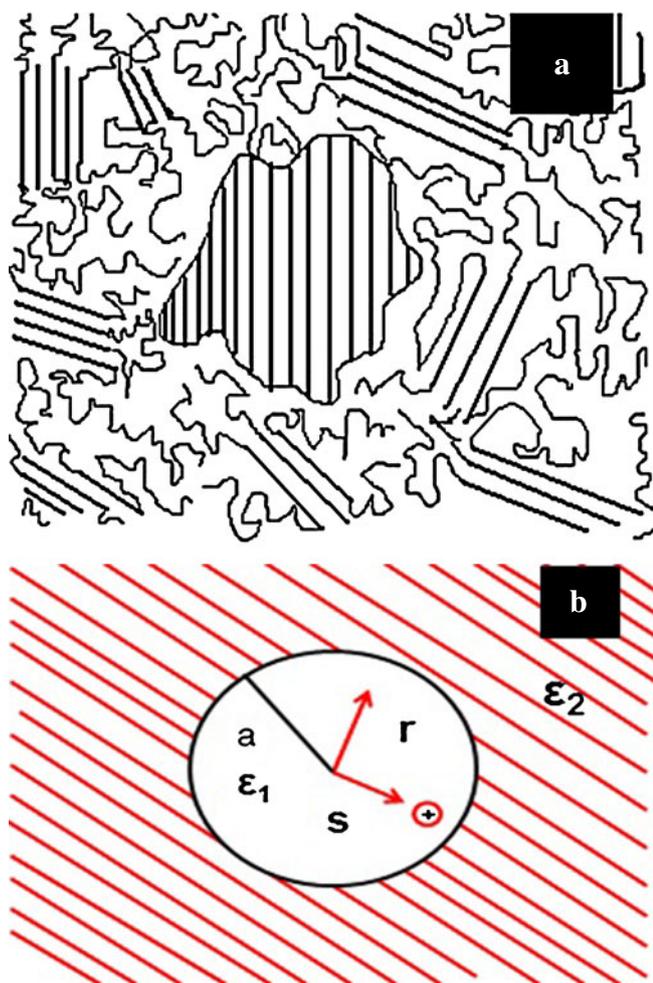


Figure 1. Schematic diagram showing (a) semiconductor nanocrystal of irregular shape embedded in a partially crystalline polymer matrix and (b) a spherical semiconductor nanocrystal embedded in a uniform polymer matrix with dielectric constant ϵ_1 . Semiconductor is shown as singly ionized.

If the external medium is vacuum, then this potential reduces to $e^2/2a|r_0|$. The difference of these two results is the energy stored in the two dielectrics. The energy term reads as:

$$V'(r) = \sum_{n=0}^{\infty} \left[\frac{(\epsilon - 1)(n + 1)}{\epsilon_2(\epsilon n + n + 1)a} \left(\frac{r}{a}\right)^{2n} \right] \frac{e^2}{2} + \frac{e^2}{2|\delta|} \left(1 - \frac{1}{\epsilon_2}\right). \quad (3)$$

The first term in the above expression tends to zero as the size of the nanocrystal becomes large. The other term has no influence of the size variation. The second term indicates that the energy is stored in the medium ϵ_2 , i.e. in the nanoparticles. The first term, hereafter denoted as $U(r)$ is positive for the dielectric combination $\epsilon_2 > \epsilon_1$. In this case, $U(r)$ is the loss of solvation energy as the volume of the nanocrystal (ϵ_2 material) becomes small. If $\epsilon_2 < \epsilon_1$, i.e. $U(r)$ is negative,

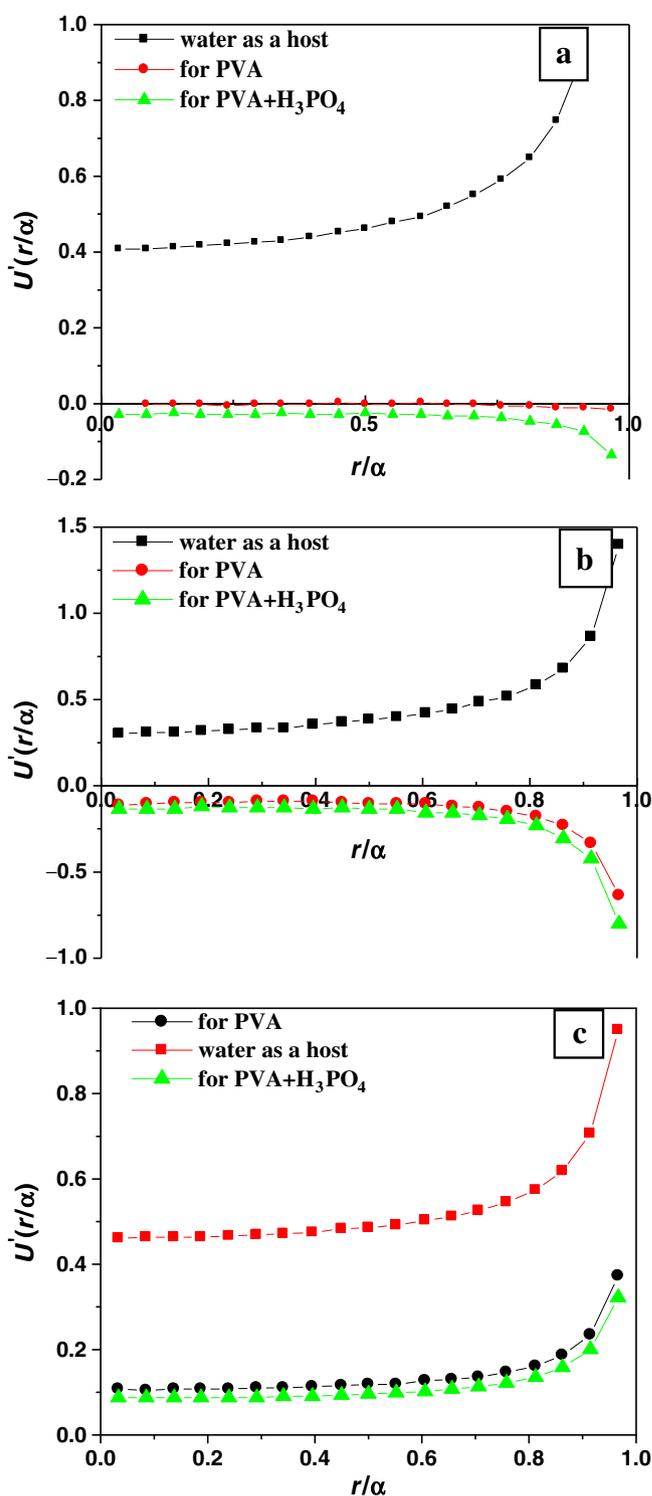


Figure 2. Plot showing variation in reduced potential $U'(r/a)$ with reduced length (r/a) in different media: (a) for CdS, (b) for ZnO and (c) for InSb. Lines marked by (—■—■—) represent water as host, (—●—●—) for PVA and (—▲—▲—) for PVA + H_3PO_4 .

it represents the gain in solvation energy with the same condition. For numerical calculations, we have considered the bulk values of the dielectric constant as ϵ_2 . For the outside

medium, the high frequency (optical range) value of the dielectric constant is considered. The term $U(r)$ is further reduced as $U'(r/a)e^2/2a$, where

$$U'(r/a) = \sum_{n=0}^{\infty} \left[\frac{(\varepsilon - 1)(n + 1)}{\varepsilon_2(\varepsilon n + n + 1)} \left(\frac{r}{a} \right)^{2n} \right]. \quad (4)$$

3. Results and discussion

The reduced potential term $U'(r/a)$ has been calculated for CdS, ZnO and InSb semiconductor crystallites in three different media as water, insulating polymer matrix poly(vinyl alcohol) (PVA) and the ion conducting polymer electrolyte matrix PVA + H₃PO₄ (Singh *et al* 1992). The choice of semiconductors has been made on the basis of their low ε_2 value in ZnO (3.7) and high value in InSb (15.7) (Kittel 1994).

Figure 2(a–c) shows variation in the $U'(r/a)$ with (r/a) . As discussed above for $\varepsilon_2 > \varepsilon_1$, the $U'(r/a)$ comes out to be positive. In all the cases as shown in figure, if the outer medium is water, $U'(r/a)$ comes out to be positive which is in good agreement with the results of Brus (1983). In all polymeric matrices, the term is negative, indicating a strong solvation of the nanoparticle by the medium. In all the experimental results of nanocrystal growth in polymer matrix similar inference has been drawn (Kumar *et al* 2011). Good solvation of the semiconductors by the polymers have been reported to result in the formation of nanocrystallites. ε_2 material ion interacts strongly with the matrix and further coalescence of the particles is restricted by the matrix. In our case, the value of dielectric constant of PVA based electrolyte is not too high. Higher the value of dielectric constant, the better shall be the solvation. This is indicative of the fact that trapping of nanocrystallites in polymeric and glassy matrix always result in isolation of the nucleation centres than in any liquid media. The matrix itself as per its solvation energy, as indicated, works as a capping agent which is normally used in colloidal preparation of QDs and nanocrystallites. This may be used as selection criteria for the host matrix for a particular semiconductor nanocrystal.

With the above considerations, Schrodinger equation for charge in the crystallite is written as:

$$\nabla^2 \psi + \frac{2m^*}{\hbar^2} [V'(r) - E] \psi = 0, \quad (5)$$

where $V'(r)$ is the same potential as in (3) and m^* the effective mass of the electron. Here, we assume that the effective mass remains the same as in the bulk for the nanocrystallite. The wavefunction may be written as a product of the radial $R_l(r)$ and $Y_{lm}(\theta, \phi)$ components. Considering the lowest S eigen function and the potential $V'(r)$ to be infinite, the radial wavefunction results to:

$$\frac{d^2 R}{dZ^2} + \frac{2}{Z} \frac{dR}{dZ} + \left[1 - \frac{l(l+1)}{Z^2} \right] R = 0, \quad (6)$$

where $Z = kr$ and $k = \sqrt{2m^*E}/\hbar$. The solution of the above reads as (Flugge 1971):

$$R_l(r) = \frac{A}{r} \sin nkr. \quad (7)$$

The wavevector $k = \pi/a$ gives the energy eigen values:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2m^* a^2}. \quad (8)$$

In cases where 1s wavefunction dominates, the total energy is:

$$E_n = \frac{\hbar^2 \pi^2}{2m^* a^2} + \frac{e^2}{2a} \bar{V}'. \quad (9)$$

The term \bar{V}' is average over the 1s wavefunction. The first term in this expression is the kinetic energy of the localization and the second term is the potential energy that gives the loss in solvation energy. As the crystallite size decreases, the localization energy term increases faster than the potential energy term. As evident for bulk material, the energy for the localization of charges is very small and the band structure prevails. The variation in energy with the size of the crystallites, based on (9), for CdS, ZnO and InSb are shown in figure 3.

It is to be remarked here that our values differ from those obtained by Brus (1983) and Dameorn *et al* (1989). It is due to the fact that the variational solution obtained by Brus includes 1s and 2s states. In our case, the value calculated is only for 1s. The plot shows a steep increase in the energy value as the crystal radii decreases. As evident from the plot, the localization of the charge is very strong for smaller diameter in our case. As the size of crystallite increases, the potential energy term becomes comparable to the localization term and hence the charge is allowed to move in the bulk system.

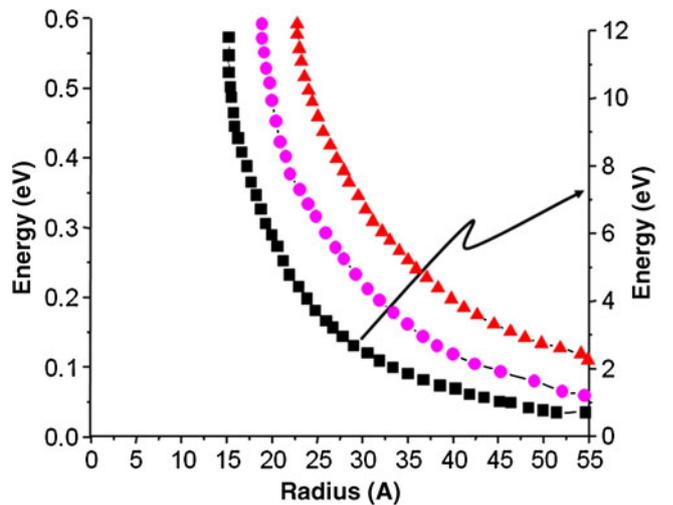


Figure 3. Plot showing variation in localization energy for CdS (—▲—▲—), ZnO (—■—■—) and InSb (—●—●—) with crystallite diameter.

4. Conclusions

From the above discussions, it can be concluded that the materials having high dielectric constant values viz. polymers, biomembranes, zeolites, etc. are the suitable candidates for trapping the nanocrystallites. Also, as the size of crystallite decreases, the electron in the valence band becomes more localized compared to the bulk system and the band structure do not prevail.

Acknowledgement

This work was supported by DST project (SR/S2/CMP-0065/2010), Government of India.

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