

Development of size and shape dependent model for bandgap of semiconductor nanomaterials

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A simple theoretical model is developed to study the effect of size and shape on the bandgap of semiconductor nanomaterials. It is found that bandgap increases by decreasing the size, which depends on the shape considered. The results obtained are compared with the available experimental data as well as with those based on earlier models. Different models predict similar trend of variations. However, such an excellent agreement with experimental data particularly in low size range using a simple model is never seen earlier. The model reduces the number of input parameters and includes more shapes as compared with earlier studies. This demonstrates the simplicity and wide applicability of the present model due to which it can be used to study the size and shape dependence of bandgap of different semiconductor nanomaterials of current interest in science and technology.

Keywords: Bandgap; semiconductor; size; shape; nanomaterial.

1. Introduction

As size of materials reduces to nanoscale, the behavior of materials changes dramatically, which has led to new technological applications. This gives tuneable properties and may find immense potential applications in different areas.^{1–5} It is well known that semiconductor materials are used in solar cells^{6,7} and other ultra-small devices. Due to high surface to volume ratio, the properties of nanomaterials are different from their bulk counterparts. The proportion of atoms at the surface is no longer negligible as they possess higher energies than atoms in the interior.^{8,9} The bond energy model describes how the dangling bonds modify the properties of materials at nanoscale.

Semiconductor compounds, having durability of their electronic as well as optical properties by three-dimensional confinement of carriers, have attracted much

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interest in science and technology.¹⁰ Thus, the study of the quantum confinement in semiconductors is a subject of intense study. It has been found that bandgap increases with decreasing particle size of semiconductor materials, having a large value as compared to the bulk materials.^{11–15} In order to understand the size dependence of bandgap, different approaches have been adopted. Most of these have been used for material larger than several nanometers and are approximate when the size of the material is less than 10 nm.^{1,16–19} Some efforts have been made to understand the effect of size and shape on bandgap in terms of cohesive energy and melting temperature.²⁰ These authors discussed a thermodynamic model for the size dependence of bandgap of low-dimensional semiconductor compounds using size dependence of melting temperature. It has been found that bandgap of nanomaterials increases by reducing the size. Such studies have also been repeated by Singh *et al.*²¹ using size dependence of melting temperature as reported by Qi^{8,9} based on bond energy model. It should be mentioned here that such studies are limited only up to three shapes *viz.* spherical, nanowire and nanofilm. At present, it has been well accepted that there exist a number of shapes of nanomaterials in addition to these shapes. Thus, it is legitimate and may be useful to develop a simple model which includes more shapes and provides a better information as compared with earlier work. In this paper, an effort has been made to achieve this.

2. Theoretical Formulation

Li and Li²⁰ reported the following relation for the size dependence of bandgap (E_g) which reads as follows:

$$\frac{\Delta E_g(n)}{E_g(b)} = 1 - \frac{E_a(n)}{E_a(b)}, \quad (1)$$

where

$$\Delta E_g(n) = E_g(n) - E_g(b). \quad (2)$$

Equations (1) and (2) give the following relation:

$$\frac{E_g(n)}{E_g(b)} = 2 - \frac{E_a(n)}{E_a(b)}, \quad (3)$$

where n represents for nanomaterials and b for bulk materials. $E_a(n)$ and $E_a(b)$ are the activation energies of nano and the bulk materials, respectively. An important property of material science using which we can understand several thermodynamic properties of the material is the cohesive energy.²² Actually, cohesive energy is responsible for atomic structure, thermal stability, atomic diffusion, crystal growth and several other properties.

Based on the Lindemann criteria²³ of melting, which is valid for both bulk and nanocrystal^{24,25} the relationship among melting temperature (T_m), Debye temperature (θ_D) and cohesive energy (E_c) could be obtained. According to this criterion, a crystal melts when the root mean square amplitude of atoms reaches a certain friction of interatomic distance as reviewed by Shanker and Kumar.²⁶

Combining with Einstein's explanation for the low temperature specific heat of crystals, a simple expression of the relationship between melting temperature and Debye temperature has been written.²⁶ This shows that the square of Debye temperature is directly proportional to the melting temperature. From Lindeman's criteria, melting temperature is directly proportional to cohesive energy. Thus, $\theta_D^2(b) \propto T_m(b) \propto E_C(b)$. It has been assumed that relationship can be extended to the nanorange as the first-order approximation.²⁷ Thus, $\theta_D^2(n)/\theta_D^2(b) = T_m(n)/T_m(b) = E_C(n)/E_C(b)$. It has been discussed by Yang and Li²⁸ that in general the relationship between $E_C(n)$, $E_a(n)$ and $E_v(n)$ can also be expressed as first-order approximation as discussed by Guisbiers.²⁹ This gives

$$\frac{E_c(n)}{E_c(b)} = \frac{E_a(n)}{E_a(b)} = \frac{E_v(n)}{E_v(b)} = \frac{T_m(n)}{T_m(b)}, \quad (4)$$

where E_c is the cohesive energy, E_a is the activation energy, E_v is the vacancy formation energy. In this paper, we used Eq. (4) for melting temperature and activation energy. Combining Eqs. (3) and (4) gives the following relation:

$$\frac{E_g(n)}{E_g(b)} = 2 - \frac{T_m(n)}{T_m(b)}. \quad (5)$$

Thus, it may be discussed that the model for the size dependence of bandgap depends on the size dependence of melting temperature. No doubt, different models exist for size dependence of melting temperature. In this work, we include widely cited models of melting temperature for comparison purposes.

Jiang *et al.*³⁰ discussed that the size dependence melting temperature of a crystal is given by²⁵

$$\frac{T_m(n)}{T_m(b)} = \exp \left[-\frac{2S_{\text{vib}}}{3R \left(\frac{D}{D_0} - 1 \right)} \right], \quad (6)$$

where S_{vib} is bulk vibrational melting entropy and R is the ideal gas constant. For nanoparticle D means diameter, for wire D is its diameter and for thin film D denotes its thickness. D_0 means the critical diameter for which almost all atoms of the particle are located on its surface. It depends on the dimension of crystal and is defined as

$$D_0 = 2(3 - d')d, \quad (7)$$

where $d' = 0$ for nanoparticle, $d' = 1$ for nanowire $d' = 2$ for thin film and d is the atomic diameter. Thus, the method can be used to study size and shape effect on nanoparticle, nanowire and nanofilm only. Combining Eqs. (5) and (6) gives the relation for size dependence of bandgap as used by Li and Li²⁰ for nanoparticles. The results have been compared with the experimental data and other theoretical predictions. It has been found that the bandgap increases with decreasing particle

size. These authors²⁰ noted that there exist some deviations also. It should be mentioned that Jiang *et al.*³¹ studied size dependence of cohesive energy and modified Eq. (6). The model has been used by Lu *et al.*³² to study the size, shape and dimensionality dependent melting temperature of nanocrystals, which reads as follows^{31,32}:

$$\frac{T_m(n)}{T_m(b)} = \left[1 - \frac{1}{\left(\frac{12D}{D_0} - 1\right)} \right] \exp \left[-\frac{2\lambda S_{\text{vib}}}{3R\left(\frac{12D}{D_0} - 1\right)} \right]. \quad (8)$$

Using Eqs. (5) and (8), we have the following relation:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left[1 - \frac{1}{\left(\frac{12D}{D_0} - 1\right)} \right] \exp \left[-\frac{2\lambda S_{\text{vib}}}{3R\left(\frac{12D}{D_0} - 1\right)} \right], \quad (9)$$

where $\lambda = 1$ for spherical nanoparticle, nanowire and nanofilm.¹ Equation (9) has been used by Lu and Meng¹ to study $E_g(n)$ of GaN nanoparticle and nanowire.

By considering surface effects, Qi^{8,9} proposed the formulation for the size and shape dependent properties of nanosolids, which is based on the size dependent of cohesive energy. The detailed analysis is available elsewhere^{8,9} and mathematical form reads as follows:

$$\frac{T_m(n)}{T_m(b)} = \left(1 - \frac{N}{2n} \right), \quad (10)$$

where n is the total number of atoms of a nanosolid and N the surface atoms. It has been discussed that the method is applicable for nanoparticle, nanowire and nanofilm as discussed by Qi.^{8,9} Now, combining Eqs. (5) and (10) gives the following relation:

$$\frac{E_g(n)}{E_g(b)} = \left(1 + \frac{N}{2n} \right). \quad (11)$$

The values of $N/2n$ have been provided by Qi^{8,9} for respective shapes, *viz.* nanoparticle, nanowire and nanofilm. Thus, Eq. (11) can be used to study the size and shape effect on $E_g(n)$. Thus, it is pertinent to mention here that the models discussed above may be used for few shapes.²¹ At present, it is well recognized that nanomaterials are possible in different shapes.^{1,33} For this purpose, Bhatt and Kumar (BK)³⁴ developed very simple model. In this paper, we develop the theory to study the size and shape effect on bandgap of nanomaterials, which includes the number of shapes. According to the BK model³⁴ the size and shape dependence of melting temperature reads as follows:

$$\frac{T_m(n)}{T_m(b)} = \left(1 - \frac{N}{2n} \right)^k, \quad (12)$$

where k is the dimensionless parameter, as discussed earlier³⁴ with its value as $k = 2$. Now combining Eq. (5) and Eq. (12), we get the following relation:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{N}{2n}\right)^2. \quad (13)$$

It should be mentioned that Eq. (12) reduces to the relation of melting temperature (Eq. (10)) as reported by Qi^{8,9} for $k = 1$. A detailed analysis for this purpose has already been provided elsewhere³⁴ and therefore not repeated in this paper. In Eq. (13), the value of $N/2n$ depends on size and shape of nanomaterials. It is pertinent to mention here that the application of Eq. (13) needs the value of $N/2n$. Qi⁸ reported a simple geometrical method with all possible steps to determine the values of $N/2n$ as reviewed by Bhatt and Kumar.³⁴ We have compiled these values in Table 1 (see Ref. 8 for geometrical steps). Using these values of $N/2n$, we get the relations for size and shape dependence of bandgap, using Eq. (13) as given below

For Film:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{0.666d}{h}\right)^2. \quad (14)$$

For Dodecahedral:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{0.898d}{a}\right)^2. \quad (15)$$

For Icosahedral:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{1.323d}{a}\right)^2. \quad (16)$$

For Wire:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{1.333d}{L}\right)^2. \quad (17)$$

For Spherical:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{2d}{D}\right)^2. \quad (18)$$

For Hexahedral:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{2d}{a}\right)^2. \quad (19)$$

For Octahedral:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{2.449d}{a}\right)^2. \quad (20)$$

For Tetrahedral:

$$\frac{E_g(n)}{E_g(b)} = 2 - \left(1 - \frac{4.898d}{a}\right)^2. \quad (21)$$

In this paper, we used these relations to study the size and shape dependence of bandgap of different nanomaterials.

3. Results and Discussion

In this paper, we have thus developed a simple model to study the size and shape effect on bandgap of nanomaterials. To judge on the validity of the model developed, we applied this to different semiconductor nanomaterials. We selected those materials for which experimental data^{35,36} are available, so that we can judge on the validity of the theory proposed. In addition to this, we also included the earlier studies (Eqs. (9) and (11)) for comparison purposes. The input parameters required are given in Table 1.^{8,20,34} The results obtained using Eqs. (9), (11), (13) are reported in Figs. 1–5 along with the available experimental data.^{35,36} It is observed that different formulations give similar trends of variation *viz.* bandgap increases by decreasing the size. The results obtained by Eq. (9) are somewhat smaller as compared with the results obtained by Eqs. (11) and (13). Moreover, the results obtained by Eq. (13) are in better agreement with the available experimental data. This demonstrates the validity of Eq. (13) developed in this paper. It should be mentioned that Eqs. (9), (11), (13) are based on different analytical approaches. Thus, they give different results.

It is pertinent to mention here that all the models discussed in this paper to study the size and shape dependence of bandgap are based on the size dependence of melting temperature or cohesive energy. Three widely used models *viz.* Nanda model, Jiang model and BK model, based on different physical origins have been discussed by Chhabra and Kumar.³³ These authors³³ studied the size dependence of cohesive energy and melting temperature of different nanomaterials. It has been discussed that the suitability of Jiang model and Nanda model depends on the material

Table 1. Input data used in the present work.^{8,20,34}

Shape	$N/2n$	Material	$E_g(b)$ (eV)	S_{vib} (J/g-atom K)
Film	0.666 d/h	ZnTe	2.39	12.26
Dodecahedral	0.898 d/a	ZnSe	2.82	6.80
Icosahedral	1.323 d/a	CdS	2.50	8.314
Wire	1.333 d/L	CdSe	1.74	6.596
Spherical	2 d/D			
Hexahedral	2 d/a			
Octahedral	2.449 d/a			
Tetrahedral	4.898 d/a			

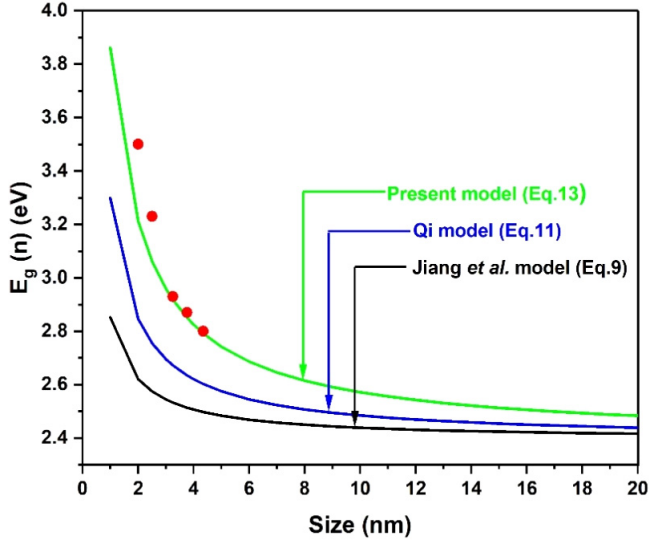


Fig. 1. (Color online) Size dependence of bandgap of ZnTe (spherical), • represent experimental data.³⁵

considered (see Table 2 in Ref. 33). Moreover, BK model works well for all the materials considered. This supports the suitability and applicability of the BK model used in this paper. As discussed above, the shape effect is very useful to understand the behavior of matter at nanoscale. An important aspect of the present model is that it includes more shapes as compared with earlier studies (Eqs. (9) and (11)). In earlier studies, only three shapes can be considered *viz.* spherical, nanowire and

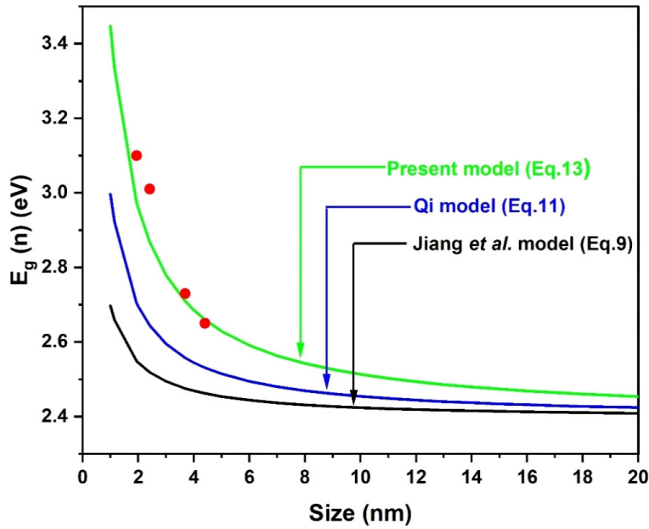


Fig. 2. (Color online) Size dependence of bandgap of ZnTe (nanowire), • represent experimental data.³⁵

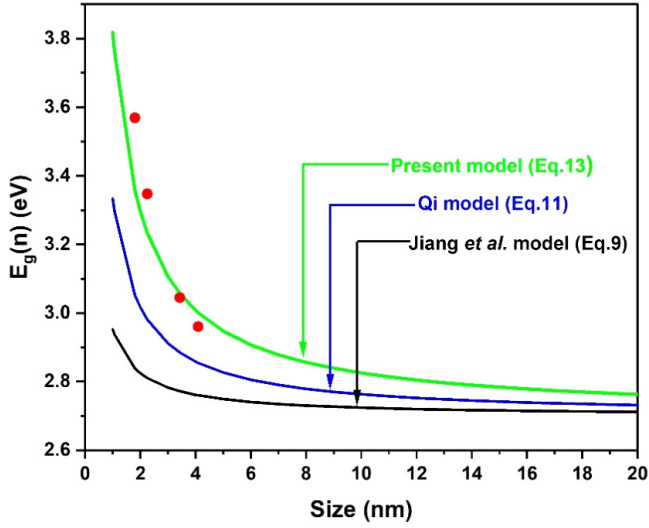


Fig. 3. (Color online) Size dependence of bandgap of ZnSe (nanowire), • represent experimental data.³⁵

nanofilm due to the limitations of the model. In this work, an effort has been made to increase the number of shapes. Using the values of $N/2n$ as given in Table 1, we obtained the relations for size dependence of bandgap for different shapes (Eqs. (14)–(21)). We used our formulation to compute $E_g(n)$ for different nanomaterials under variable conditions of size and shape *viz.* ZnTe, ZnSe, CdS, CdSe. The results obtained are reported in Figs. 6–9.

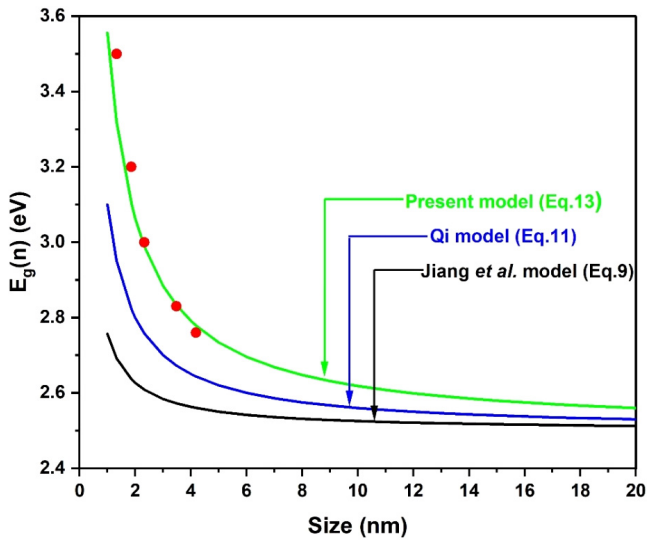


Fig. 4. (Color online) Size dependence of bandgap of CdS (nanowire), • represent experimental data.³⁶

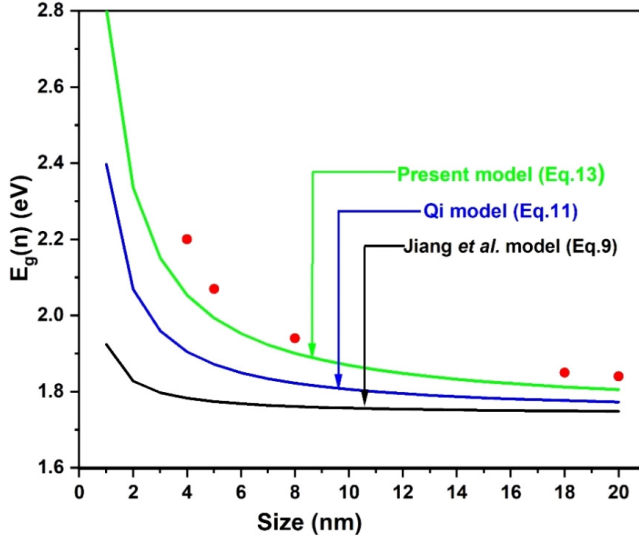


Fig. 5. (Color online) Size dependence of bandgap of CdSe (nanowire), • represent experimental data.³⁶

It is observed that bandgap depends on the shape also in addition to the size. The systematic trends of variations are observed for different shapes considered in this work *viz.* Tetrahedral, Octahedral, Hexahedral, Spherical, Wire, Icosahedral, Dodecahedral, Film. For a particular size, bandgap is highest for tetrahedral shape and minimum for Film. For other shapes, the values lie in between these two shapes. To confirm the situation, we have repeated our study to different nanomaterials of

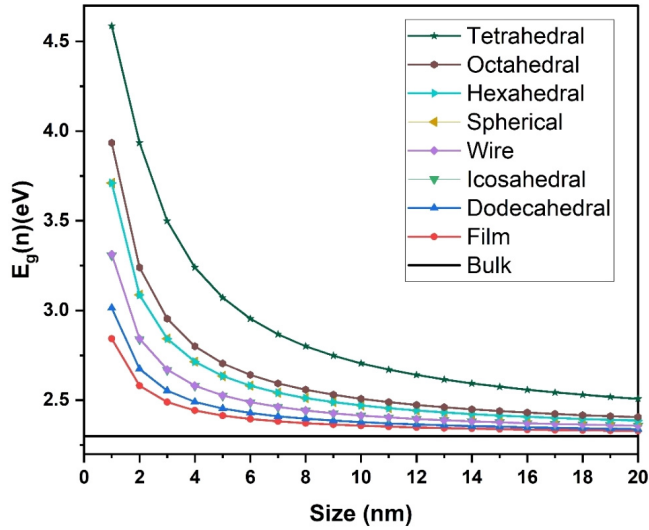


Fig. 6. (Color online) Size dependence of bandgap of ZnTe for different shapes.

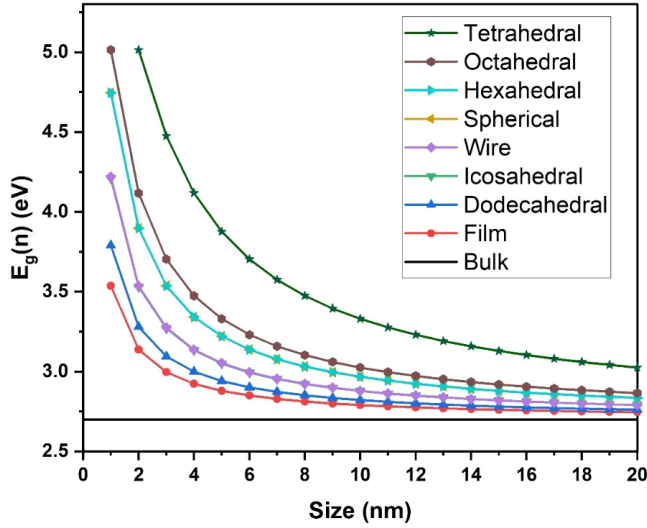


Fig. 7. (Color online) Size dependence of bandgap of ZnSe for different shapes.

current interest. The results thus obtained are reported in Figs. 6–9. It is found that the variation depends upon the surface to volume atomic ratio. This has been considered in the present model in the form of $N/2n$. We have also computed these values for ZnTe as an example for different size and shape and reported in Fig. 10. Decreasing the size increases the surface to volume atomic ratio ($N/2n$), which increases the bandgap for different shapes for different materials considered in this work.

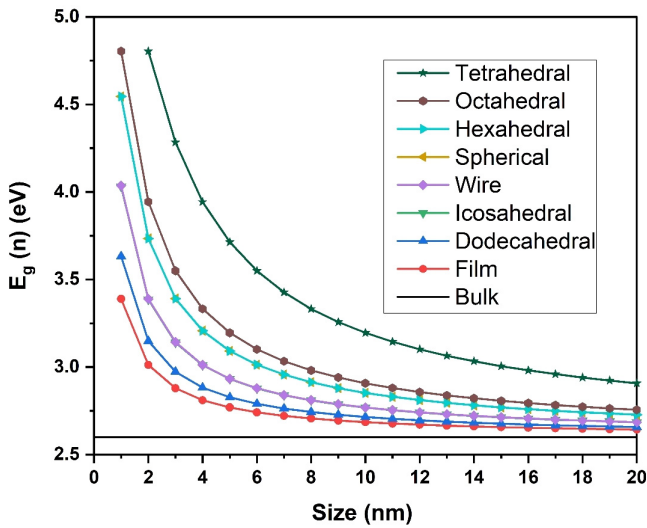


Fig. 8. (Color online) Size dependence of bandgap of CdS for different shapes.

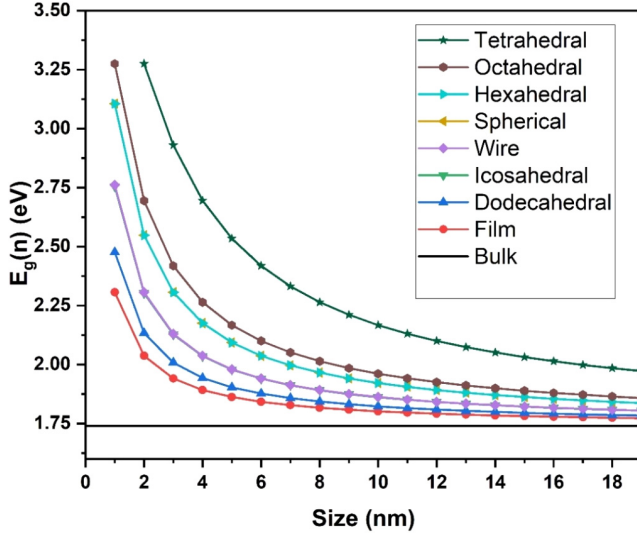


Fig. 9. (Color online) Size dependence of bandgap of CdSe for different shapes.

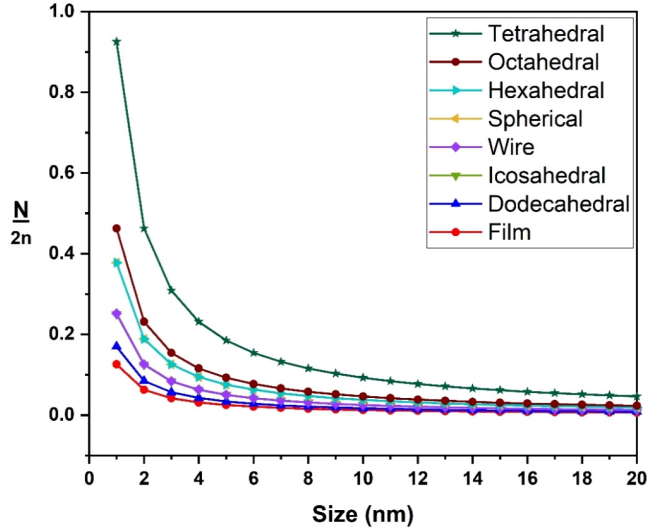


Fig. 10. (Color online) Size dependence of surface to volume atomic ratio ($\frac{N}{2n}$) for ZnTe.

4. Conclusions

A simple theoretical method based on the bond energy model is developed. The formulation is applied to study the size and shape dependence of bandgap of different nanomaterials. The results obtained are compared with the earlier findings in the light of available experimental data. A good agreement between the model predictions and experimental data supports the validity of the model developed in

this work. It is observed that the present theory gives the better results as compared with earlier formulations. It is discussed that the results depend on surface to volume atomic ratio, which has been considered in this work. Due to simplicity and applicability of the model, it may be used to understand the behavior of nanomaterials under varying conditions of size and shape.

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