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Exciton energies of wurtzite CdS nanoparticles

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Abstract

We have determined exciton energies for wurtzite CdS nanoparticles, both theoretically and experimentally. The empirical pseudopotential method has been used to calculate the bulk band structure. The discretization of reciprocal space was considered to get the energy gap and the corresponding exciton energy as a function of the nanoparticles size. The CdS nanoparticles were prepared by colloidal methods and the exciton energies were determined from optical absorption measurements. A good agreement between the calculated and the experimental exciton energies is obtained when an average over the experimental size distribution of the nanoparticles is included in the calculation.

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1. Introduction

Semiconductor particles with radii of tens of nanometers have shown size-dependent properties [1,2]. Because of their potential applications in solar cells [3–5] and other optoelectronic devices [6], growth [7], electronic structure [8], and optical properties [9,10] of II–V compound nanocrystals have been studied extensively. One of the most studied compounds in nanoparticle form is CdS [7,11]. Estimation of exciton energy (EE) in such small particles is important due, among the others things, to its direct dependence on band gap energy [12]. EE as a function of particle

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size has been determined both experimentally and theoretically [13,14]. In general, the spatial confinement affects the electron–hole pair, making it size and structure dependent. The smaller the nanoparticle radius, the higher is the EE value. For small nanoparticles, the wurtzite structure also causes an increase in EE with respect to the values of the cubic one [15].

However, in most of the cases comparison between theory and experiment has been dealt with zinc blende-type CdS nanocrystals and, to our knowledge, a very few samples whose structure is known with certainty to be wurtzite have been reported [14,16]. The reason being that this compound has been synthesized preferably in cubic structure. Using a colloidal route and a size-selective precipitation technique, Vossmeier et al. [16] have obtained CdS nanoparticles with a narrow size distribution, with mean radii ranging from 13 to 39 Å. Due to their sizes, they could not precise the structure of the smaller nanoparticles. Among the bigger ones, according to wide-angle X-ray diffraction and electron microscopy images, two of the samples turned out to be cubic and only one, with mean radius of 22 Å, had hexagonal symmetry. Nevertheless, calculations of exciton spectra by Tomasulo and Ramakrishna [17] suggested that the wurtzite structure could be assigned to those whose structures were undetermined. Rockenberger et al. [14] have analyzed the role of different ligands on the structural properties. Extended X-ray absorption fine structure analysis at several temperatures allowed them to conclude that a couple of cases could be hexagonal, though no emphasis was put on calculating their EE.

Here we report the calculated exciton energies for hexagonal clusters and compare them with experimental results of nanocrystals grown by colloidal methods. We first give a brief description of the calculation, which is based on the Ramakrishna and Friesner approximation [18]. In their approach, the bulk band structure is derived from the empirical pseudopotential method (EPM) and then, assuming a finite-size sample, the bands are discretized. This approximation has successfully explained zinc-blende data and has given insight into the effect of structural changes [17,18]. A description of the experimental procedures of growth and absorption measurement is then given. The size distribution of the samples was determined and included in the calculation. Finally, comparisons of numerical and experimental results as well as the concluding remarks are presented.

2. Theory

A wide variety of bulk properties of solids have been determined by means of the EMP [19]. Here we briefly describe the method, details can be found elsewhere [17,18]. The one-particle Schrödinger equation to be solved includes the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_p,$$

where the so-called pseudopotential V_p accounts for the electron–electron and electron–core potentials. It is written as a plane-wave expansion, like

$$V(\vec{r}) = \frac{1}{Nn_a} \sum_G \sum_{R,j} V_j(\vec{G}) \exp \left[i\vec{G} \cdot (\vec{r} - \vec{R} - \vec{d}_j) \right].$$

Here N is the number of lattice sites in the sample, n_a the number of basis atoms in the unit cell ($n_a = 4$ for wurtzite), v_j is the form factor, \vec{G} are vectors of the reciprocal lattice and \vec{d}_j is the position of the j th basis atom at a lattice site \vec{R} . The summation over lattice sites and j is determined by the lattice structure.

The Hamiltonian matrix elements, in terms of the wave vector \vec{k} , are conveniently written as

$$H_{GG'}(\vec{k}) = -\frac{\hbar^2}{2m} (\vec{G} + \vec{k})^2 \delta_{GG'} + V_s(|\vec{G} - \vec{G}'|) S_s(\vec{G} - \vec{G}') + iV_a(|\vec{G} - \vec{G}'|) S_a(\vec{G} - \vec{G}'),$$

where S refers to the structure factor, V to the form factor and the index $s(a)$ denotes their symmetric (antisymmetric) part. The form factors are fitted to reproduce optical data of the material. Bergstresser and Cohen [20] determined these parameters for wurtzite CdS using 60 plane waves, which gave them a convergence <0.1 eV in the intrinsic band gap. Ramakrishna and Friesner [18] modified three of these parameters slightly for the better agreement of lower bands with those of local-density calculation [21]. On the other hand, Tomasulo and Ramakrishna [17] introduced a spin–orbit correction using also the Bergstresser and Cohen form factors. We have chosen the values as given originally in Ref. [22], without including spin–orbit coupling, for a calculation based on 285 plane waves which gives the bulk energy gap in excellent agreement with the average (2.50 eV) of the values at 0 and 300 K [23].

The discretization of the band has been proposed by Ramakrishna and Friesner [18] to study semiconductor nanoparticles. In this approximation, which will be referred as Discretized EPM (DEPM), the nanocrystal is considered as a finite-size region, for which, in contrast to the bulk, the electrons have a discrete energy spectrum, depending on the boundary shape. The size-dependent band gap, E_g , is determined by the smallest \mathbf{k} vector, whose magnitude times corresponds to the first root of the zero-order spherical Bessel function in the case of a spherical-shaped nanocrystal of radius R . This approach is valid in our case since the difference between the dielectric constants of the nanoparticles and the solvent (acetonitrile) in which they are embedded is very high, 36.64, causing a strong confinement.

On the other hand, the quantum-size effects on the EE have been studied also in case of spherical particles. Within the frame of the effective-mass approximation, it yields the following expression [10,20]:

$$E_x(R) = E_g(R) - \frac{1.78e^2}{\epsilon R} - 0.248E_{Ry},$$

when the electron–hole Coulomb (approx. $1/R$) and correlation energies (approx. E_{Ry}) are included. Here ϵ is the dielectric constant and E_{Ry} is the effective Rydberg energy of the exciton. The average over the size distribution $f(R)$ is, as usually, given by

$$\langle E_x \rangle = \frac{\int f(R)E_x(R) dR}{\int f(R) dR},$$

where $f(R)$ may be Gaussian or Lorentzian form.

3. Experimental section

Colloidal CdS nanoparticles were prepared by mixing different proportions of 1.86×10^{-3} M $\text{Cd}(\text{NO}_3)_2$ and 2.5×10^{-3} M $(\text{NH}_4)_2\text{S}$ solutions prepared in acetonitrile solvent. The solutions were prepared by dissolving 8.79 mg of $\text{Cd}(\text{NO}_3)_2$ in 20 ml of acetonitrile and 1.71 μl of $(\text{NH}_4)_2\text{S}$ in 20 ml of acetonitrile, respectively. To maintain the different concentration of Cd^{2+} and S^{2-} ions in the mixture, different volumetric ratio of the two solutions were mixed. Depending on the concentration of the Cd^{2+} and S^{2-} ions in the mixture, CdS nanoparticles of different sizes were produced and their temporal evolution of growth also varied [24]. With time, the nanoparticles were grown and depending on the initial concentration of Cd^{2+} and S^{2-} ions in the mixture, after a certain time their growth stopped. To interrupt the growth process of the nanoparticles at any moment, a polymer control, 3 mercapto-1, 2-propen-diol $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2$ was used. Optical absorption of the colloidal solutions was measured using a Shimadzu UV3100S spectrophotometer in the interval of 190–800 nm at room temperature. For the transmission electron microscopy (TEM and TED) measurements, the colloidal mixtures (freshly prepared aged) were sprayed over carbon films supported on copper micro-grids after diluting the mixtures 25 to 100 times by acetonitrile. A Jeol FX200 transmission electron microscopy operated at 200 keV was used for the observation samples.

4. Results and discussion

Fig. 1 shows a typical TEM micrograph of CdS nanoparticles with sizes ranging from 5 to 80 Å. A typical transmission electron diffraction (TED) pattern for the samples is shown in Fig. 2. The X-ray diffraction patterns of the samples revealed a predominant hexagonal phase in them [24]. Fig. 3 shows the size distributions, standard deviation (μ) and average radii (x) of the particles. These distributions are fitted to Gaussian or Lorentzian forms.

The absorption spectra of the samples are shown in Fig. 4. All three samples clearly show the effect of the quantum confinement as the EE increases with the decreases of the particle size. Notice how the size distributions broaden the absorption peaks. The exciton energies evaluated from the absorption spectra are 3.22, 2.92 and 2.81 eV for the samples *a*, *b* and *c*, respectively.

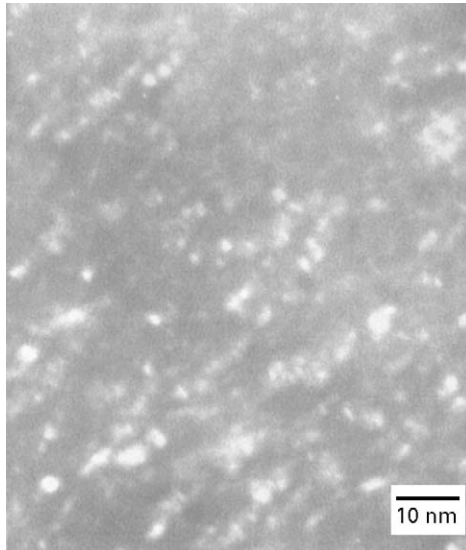


Fig. 1. Typical TEM micrograph of the sample prepared by mixing 1:1 of $\text{Cd}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$ solutions.



Fig. 2. Typical TED pattern of the CdS nanoparticles.

For the calculation of the EE we used bulk parameters, the lattice constant $a_0 = 4.136 \text{ \AA}$ and electron and hole masses, $m_e = 0.19 m_0$, $m_h = 0.80 m_0$, respectively, where m_0 is the free electron mass. Fig. 5 shows the exciton energies as a function of particle size. The continuous line correspond to DEPM(W) wurtzite calculation. The

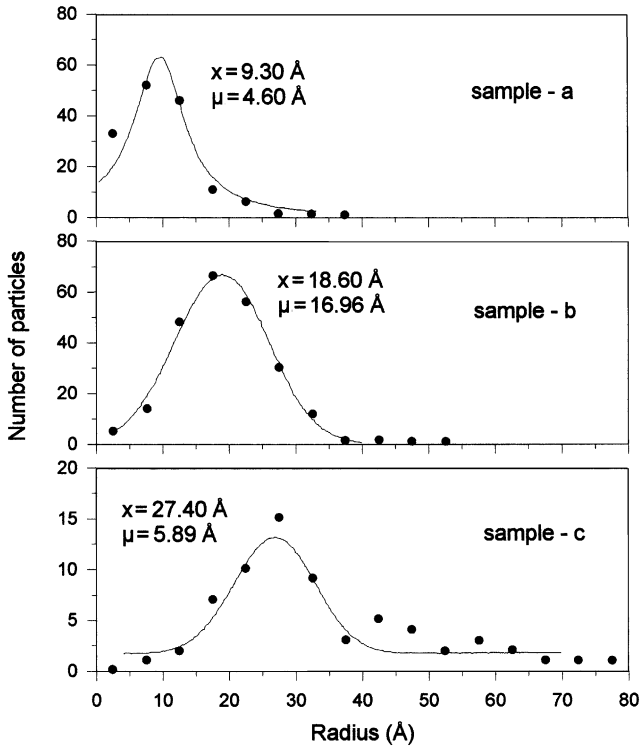


Fig. 3. Optical absorption spectra for the colloidal nanoparticles of samples, at room temperatures, prepared with (a) 1:1, (b) 1:2 and (c) 1:3 ratios of Cd and S ions in the reaction mixture. Because of size distribution of the particles, the absorption bands are broadened. All the spectra were for the freshly prepared colloidal solutions.

dots correspond to the calculation including the size distribution and the black circles to experimentally obtained EE values. A broken line has been drawn as the guide to the eye. The discontinuous line, DEPM(ZB), shows that the EE for the zinc-blende phase is noticeably lower than the wurtzite phase for a fixed particle size. This figure also shows the importance of including the size distribution in the calculation of EE. Deviation of the calculated EE values from the experimental values was reduced when the size distribution of the particle was considered instead of considering the average radius of the particles. For the samples *a* and *b*, the agreement between the calculated and experimental values is good. Whereas, for the sample *c*, the agreement is moderate, which might be due the difference of the parameters of small particles, e.g. lattice constant, dielectric constant and particle form, from their bulk values [20]. Apart from that, as a decrease in the particle size facilitates a structural change from hexagonal to cubic, the coincidence of the exciton peak position of the sample with the calculated zinc-blende exciton value is not surprising. Our results confirm again that the band discretization method is a simple and powerful tool to study properties of semiconductors nanoparticles immersed in solvents with high dielectric constant.

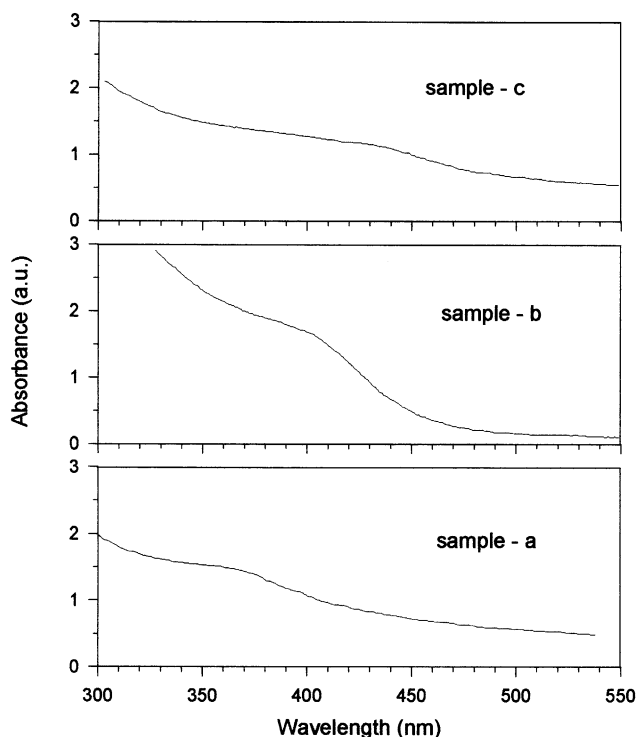


Fig. 4. Size distribution $f(R)$ of grown nanoparticles for the three samples. Sample *a* prepared prepared by mixing 1:1 of $\text{Cd}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$ solutions. Sample *b* prepared with 1:2 of $\text{Cd}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$ solutions and sample *c* prepared with 1:3 of $\text{Cd}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$ solutions.

5. Conclusions

We have presented both experimental and numerical results for exciton energies of wurtzite CdS nanocrystals. For the numerical analysis, an EPM was used to calculate the bulk band structure. Under the assumption of spherical-shaped particles, the bands were discretized and the EE as a function of radius was evaluated. The nanoparticles were grown by colloidal method and characterized by Electron Microscopy and spectrophotometric techniques. Absorption measurements allowed us to obtain the experimental values of exciton energies. The size distributions of the particles obtained from TEM images were included in the calculation of average EE. The calculated EE values are in good agreement with the experimentally determined EE values for the larger nanoparticles. Disagreement between the theory and experiment for the smaller particles might be due the deviation of lattice constant and dielectric constant values for the small nanoparticles from the bulk values and their non-spherical shape.

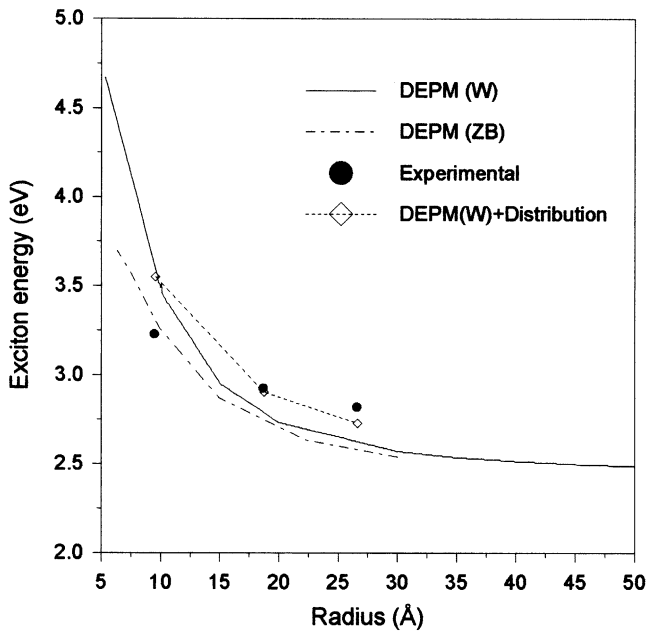


Fig. 5. Exciton energy as the function of particle radius, see text.

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