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### **TOPICAL REVIEW**

# Charging and quantum size effects in tunnelling and optical spectroscopy of CdSe nanorods

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#### Abstract

We summarize our correlated scanning tunnelling microscopy and optical spectroscopy investigations of the electronic level structure and single-electron charging effects in CdSe quantum rods. Both optical and tunnelling spectra show that the level structure depends primarily on rod diameter and not on length. With increasing diameter, the bandgap and the excited state level spacings shift to the red. The level structure is assigned using a multi-band effective-mass model. The tunnelling spectra also exhibit, depending on the tunnel-junction parameters, single-electron charging effects that yield information on the degeneracy of the electronic states.

#### 1. Introduction

Colloidal semiconductor nanocrystals are a model system that manifests the transition from the molecular limit to the bulk solid-state regime [1-3]. Their size-tunable electronic properties yield significant potential applications ranging from opto-electronic nano-devices [4-6] to biological fluorescence tagging [7]. Shape control of such colloidally prepared nanostructures has been recently achieved by modifying the synthesis to obtain rod shaped particles-quantum rods (QRs) [8, 9]. QRs exhibit electronic and optical properties that differ from quantum dots (QDs). For example, unlike the spherical dots, QRs demonstrate linearly polarized emission [10, 11] leading also to polarized lasing [5]. In addition to size and shape, nanocrystals' charging may also significantly influence their electrical and optical properties. In our recent work [12] we combined optical and tunnelling spectroscopies on CdSe QRs and correlated the experimental

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data with the level structure calculated using a multi-band effective-mass model for an infinite potential well. However, the experimental set-up in both optical and tunnelling measurements was tuned so as to avoid QR charging.

In this paper we present further studies of the electronic level structure of CdSe QRs, and its dependence on rod length and diameter, by correlating tunnelling and optical spectroscopic data with calculations performed for a finite potential-well model. Additionally, tunnelling experiments and simulations investigating single-electron charging phenomena were performed in order to resolve the degeneracy of different QR energy levels, as done previously for QDs [2, 13]. Our study provides significant insight into the evolution of the electronic structure from zero-dimensional QDs to one-dimensional quantum wires.

The combination of scanning-tunnelling and optical spectroscopies has proven to be a powerful approach to decipher the level structure of spherical nanocrystal QDs [2, 14]. While in the optical spectra, allowed valence band (VB) to conduction band (CB) transitions are



Figure 1. TEM images of two CdSe QR samples with average length  $\times$  diameter of (a) 29 nm  $\times$  3.7 nm and (b) 33 nm  $\times$  6.5 nm. The scale bar is 100 nm.



**Figure 2.** Schematic diagram of the DBTJ configurations used to acquire the tunnelling spectra. The QR in (a) is deposited directly on HOPG, while that in (b) is anchored to a gold substrate via DT molecules. The equivalent circuit is shown in (c).

detected [15, 16], in tunnelling spectroscopy the CB and VB states can be separately probed, providing complementary information on the level structure [2, 13, 17-19]. Moreover, single-electron charging effects may yield information on the degeneracy of the electronic states. Such data can provide an important benchmark for theoretical models of the level structure in strongly quantum-confined nanostructures, as was demonstrated for spherical QDs [20-22]. Multiband effective-mass approaches [15, 16, 23], atomistic pseudo-potential theory [20] and semi-empirical tight-binding modelling [21, 22] were used to describe measured QD sizedependent level spectra. Recently, both multi-band effectivemass theory [24] and the pseudo-potential approach [25, 26] were applied to calculate the size-dependent energy levels in QRs.

#### 2. Experimental section

CdSe QRs were grown using the well developed methods of colloidal nanocrystal synthesis, resulting in rods that are overcoated by organic ligands [8, 27, 28]. The growth process was monitored by the absorption spectra taken during the synthesis, and terminated upon reaching the desired QR size. Good control over the QR shape and size distribution was achieved, as portrayed in figure 1, which presents transmission electron microscope (TEM) images of two different QR samples. The size distribution of the rods was determined from such images, by measuring at least 200 particles for each sample, and was found to be on the order of  $\pm 10\%$  for the diameters and  $\pm 15\%$  for the lengths.

For the scanning tunnelling microscopy (STM) measurements the QRs were deposited on a conducting substrate applying two different methods, resulting in two distinct sample configurations. The tunnelling spectra (dI/dV versus V characteristics) were measured at 4.2 K by positioning the tip above a *single* QR, thus forming a double-barrier tunnel junction (DBTJ) configuration. In the first deposition method,



**Figure 3.** STM topographic images of CdSe QRs deposited on HOPG (a), and attached to gold via DT molecules (b). Image (a) shows a cluster of rods, about 25 nm long and 4 nm in diameter, and the inset focuses on a single QR. Image (b),  $200 \times 200 \text{ nm}^2$  in size, exhibits both clusters and isolated QRs, with sizes around  $30 \times 5 \text{ nm}^2$ . The surface morphology of the bare gold film is presented in the inset ( $300 \times 280 \text{ nm}^2$ ), in which atomic steps and dislocations typical of Au(111) surfaces are seen.

which is illustrated in figure 2(a), the QRs were spin-coated on highly oriented pyrolitic graphite (HOPG) from a highly diluted QRs-hexane (or toluene) solution to obtain a 'QR/HOPG configuration'. The tip was retracted far away from the QR, thus suppressing single-electron charging effects [13, 14, 19]. In addition, CB (VB) states appear at positive (negative) sample bias and the peak separations are close to the real OR level spacing. The second method is presented in figure 2(b), in which the QRs were anchored to an atomically smooth gold surface via hexane dithiol (DT) molecules, yielding the 'QR/DT/Au configuration'. These DT molecules increase the QR-substrate distance, and the tunnelling rate in this junction typically becomes slower in comparison to the tip-QR junction. Consequently, single-electron charging effects become significant [2, 3], as opposed to what is typically observed for the QR/HOPG system. Moreover, the peak separations were often much larger than the real QR level spacing, due to the effect of voltage division between the two tunnelling junctions [13, 18, 19]. In both methods, as shown theoretically for QDs, the applied voltage does not much affect the level spectrum [21, 22, 29]. Hence, the dI/dV versus V spectra yield direct information on the QR level structure and singleelectron charging effects.

Low-temperature (T = 10 K) optical spectroscopy was measured on QRs embedded in a free-standing polymer film, in particular photoluminescence excitation (PLE) measurements, which probe the size-dependent absorption level structure of nanocrystals. Here, one measures the excitation spectra using a narrow detection window on the blue side of the inhomogeneously broadened photoluminescence (PL) peak. The detection window selects a subset of the inhomogeneous sample, and sharply structured excitation spectra were obtained. The measurements were carried out on different QR samples where the rod diameter and length were varied systematically.

#### 3. Results and discussion

Figure 3(a) presents STM images of QRs deposited on HOPG substrates (measured at 4.2 K). Clusters of QRs were often observed, showing their tendency to aggregate on the HOPG surface (consistent also with the TEM images), but in many cases isolated single QRs were also found (see the inset).



**Figure 4.** (a) dI/dV versus V tunnelling spectra at 4.2 K for CdSe QRs deposited on HOPG. The QR dimensions (length × diameter) are marked above each curve in nanometres. For clarity, the spectra were shifted horizontally to position the bandgap symmetrically relative to zero bias. CB1, CB2 and CB3 at positive bias, and VB1 at negative bias, denote the main peaks of the spectra that are addressed in the text. (b) PLE spectra at 10 K for six CdSe QR samples: (A) 60 nm × 6.7 nm,  $E_{det} = 2.00 \text{ eV}$ ; (B) 30 nm × 6.5 nm,  $E_{det} = 2.01 \text{ eV}$ ; (C) 11 nm × 5.8 nm,  $E_{det} = 2.03 \text{ eV}$ ; (D) 31 nm × 3.8 nm,  $E_{det} = 2.25 \text{ eV}$ ; (E) 21 nm × 3.7 nm,  $E_{det} = 2.16 \text{ eV}$ ; (F) 11 nm × 3.2 nm,  $E_{det} = 2.25 \text{ eV}$ , with the zero energy representing the position of the detection window,  $E_{det}$ . Relevant optical transitions are denoted as I, II and III. The structure above 0.7 eV results from overlapping peaks of the excitation lamp that could not be completely normalized out.

Figure 3(b) presents an STM image of QRs on a gold substrate. These substrates were smooth at the atomic level, thus enabling one to clearly identify the adsorbed rods. The gold surface exhibited large terraces, atomic-height steps and dislocations running along the  $\langle 110 \rangle$  directions, typical of (111) oriented gold films (see inset). The images in figure 3(b) were acquired at room temperature, where the tip–sample drift was too large for reliable measurements of local single-rod *I–V* tunnelling spectra. Only at cryogenic temperatures were STM images and spectroscopy of isolated CdSe QRs realized on both gold and HOPG.

#### 3.1. Size-dependent QR level structure

In order to study the length and diameter dependence of the QR electronic level structure, various samples were investigated with average QR dimensions ranging from 3.5 to 7 nm in diameter and from 10 to 60 nm in length, with aspect ratios varying between 3 and 12.

We first describe our single QR tunnelling spectra measured in the QR/HOPG configuration (see figure 2(a)), where charging effects are suppressed and the spectra yield (nearly) direct information on the energy levels. These spectra demonstrate that the QR level structure, in particular the bandgap, depends primarily on the diameter of the QRs, and not on their length. This behaviour is depicted in figure 4(a), showing tunnelling spectra measured on QRs of different diameters and lengths. Most significantly, the region of suppressed tunnelling conductance (null density of states) around zero bias, associated with the quasi-particle energy gap, is red shifted upon QR thickening from about 2.4 eV in the upper curve (d = 4 nm) to about 2.1 eV in the lower curve (d = 6 nm). This trend was not observed as clearly for the spacing between the CB ground state (CB1) and the



**Figure 5.** Energy gap versus QR radius (a) and QR length (b). The tunnelling data (empty squares, size digitized due to radii uncertainty) and the model (solid and dashed curves represent finite and infinite potential wells, respectively) correspond to the energy separations VB1–CB1. The optical data (solid circles) were determined from the first absorption peak and corrected for the electron–hole Coulomb interaction; see the text.

first excited state (CB2). Level CB3 was observed in about 50% of the measured rods, where the current did not reach the saturation limit before resolving this level. Some of the spectra contain additional small peaks that could be attributed to excited longitudinal states, having nodes along the QR axis.

The VB is considerably more dense and complex and its level structure was not reliably resolved in our tunnelling spectra; thus we only denote the first (ground state) peak as VB1. Further insight regarding the QR level structure, including the excited VB levels, is gained by correlating the tunnelling spectra with allowed optical VB to CB transitions, and both measurements with theoretical calculations.

We now turn to discuss the optical spectroscopy measurements. The optical absorption spectra also showed that the bandgap red-shifts with increasing diameter and has no significant variation with rod length, as reflected in the positions of the absorption onset and PL peak (see [30] and figure 5). The PLE spectra presented in figure 4(b) are less structured as compared with those measured on QDs [15] due to the increased sources of inhomogeneous broadening in rods and due to the intrinsically less discrete level structure. A striking feature is the nearly identical level structure observed for the three QR samples of large diameter (traces A-C), which differs significantly from the spectra measured on the thinner rods (traces D-F), although in each group the aspect ratio varies from 3 to about 6. This shows clearly that not only does the bandgap of the rods depend mainly on the diameter, but also the excited optical transitions. This property demonstrates the quasi-one-dimensionality of the QRs in the range studied here, in the sense that the QR radius is smaller than the bulk exciton Bohr radius in CdSe (5.7 nm), while the length is larger. Thus, strong confinement pertains for the radial direction only, while weak confinement is approached for the axial direction. We note here that for InAs rods, where the Bohr radius is much larger (~32 nm), the bandgap decreased systematically with increasing QR length (up to a few tens of nanometre) [9].

To accompany the experimental results and to assist in their interpretation, we used an effective-mass approximation approach in order to calculate the electronic structure of the QRs, following the formalism developed by Sercel and Vahala for quantum wires [31]. The same basis functions as in [31] were employed, using the following notation for the quantum numbers: n, the principal number, and  $F_z$  and  $L_z$ , the

projections of the total and envelope angular momenta along the z axis, respectively. Here  $F_z = J_z + L_z$  where J is the zone centre Bloch angular momentum of the bulk bands. The finite length of the rods brings about an additional quantum number denoted by m (associated with the number of nodes along the QR axis, m-1), replacing the continuous wavevector  $k_z$  in [31], and accordingly the eigenfunction is multiplied by a factor  $\exp(imz)$ . Within this model, and for the m = 1 states, CB1 ( $L_z = 0$ ) is twofold (spin) degenerate, while higher CB states ( $|L_z| > 0$ ) are fourfold degenerate, as  $L_z$  can accept positive and negative values.

More details about the calculations, and results for an infinite potential well, are given in [12]. Also the model exhibits a much stronger dependence of the energy levels on radius as compared to length. We denote hereafter the first three m = 1 CB states as CB1, CB2 and CB3. The calculated (lowest) VB levels were divided into three groups of closely spaced (effectively degenerate) states denoted as VB1, VB2 and VB3. We note that each of these levels contains contributions of various  $L_z$  components, resulting in weak selection rules for optical transitions, thus complicating the assignment of the optical spectra.

In figure 5(a) we compare the radial dependence of the measured bandgaps (optical and tunnelling) with our theoretical calculations. The gap extracted from the optical measurements (solid circles) and the gap identified in the tunnelling data (empty squares) are plotted along with the calculated energy gap, VB1 - CB1. In order to compare with the quasi-particle (tunnelling) gap, the measured excitonic (optical) gap was corrected for the electron-hole Coulomb As a first approximation, we modified the interaction. expression given in [32] for QDs,  $1.8e^2/kr$  (where k is the dielectric constant), to take into account the fact that strong confinement holds primarily for the radial dimension of the QRs. We thus replace the radius, r, by  $(r^2a_0)^{1/3}$  where  $a_0$ is the bulk CdSe Bohr radius, 5.7 nm. A relatively good agreement between the calculated and measured energy gaps is found for both tunnelling and optical experiments. However, the tunnelling gaps are higher in energy, as was previously observed for QDs [2]. This can be ascribed to the effect of voltage division in the DBTJ, namely, to the non-vanishing voltage drop on the OR-substrate junction, enlarging the measured level spacing [13, 18, 19], and to the overestimated QR radii measured by STM due to convolution with the tip [2].

In figure 5(b) we plot the measured bandgaps as a function of QR length. It is evident that both optical and tunnelling gaps do not show any clear dependence on QR length (in contrast to the dependence on radius). The scatter in the data, partly due to variations in the diameters for rods of similar length, masks any possible (small) length dependence.

Turning now to the excited levels, figure 6 shows spacings of the PLE transitions with respect to the bandgap transition, along with levels CB2 and CB3 measured with respect to CB1, detected by tunnelling. The data are presented as a function of the bandgap measured in each experiment, thus eliminating the possible problem of QR radius estimation mentioned above. PLE transition I (relative to  $E_g$ , solid circles) correlates well with the calculated level separation between VB1 and VB2, enabling us to assign it to the transition from VB2 to the CB ground state, CB1.



**Figure 6.** Excited energy states versus energy gap. The respective separations between the tunnelling peaks are denoted by open symbols. Spacings between the PLE transitions and the optical energy gap are presented by solid symbols. The calculated energy level separations are depicted by the lines and marked. VB2 to CB2 corresponds to |CB2–CB1| + |VB2–VB1|. Inset: an illustration of the excited optical transition from different VB states to CB states.

The assignment of PLE transition II is not as straightforward. In the lower-energy-gap (thick rods) regime,  $E_{\rm g}$  < 2.12 eV (solid inverted triangles), as well as in the regime of  $E_g > 2.25$  eV (solid diamonds), this transition corresponds fairly well with the calculated level separation CB2 - CB1. Therefore, it appears that PLE transition II takes place from the VB ground state (VB1) to CB2. This interpretation gains further support from the relatively good correlation with the CB2 - CB1 level separation extracted from the tunnelling experiment (empty squares) in the regime where the corresponding bandgaps overlap (considering, again, the voltage-division-induced enlargement in the tunnelling experiments). However, in the intermediatebandgap regime, the experimental data for PLE transition II appear to merge with those of PLE transition III (upwards pointing triangles), which was observed only for thick (lowbandgap) QRs. Moreover, in this region the calculated VB2 to CB2 transition (shown as a dashed line) also seems to correspond with the PLE data, complicating the assignment of PLE II.

In this intermediate regime there may be an avoided crossing behaviour, which is not completely resolved in our data. The difficulty in resolving this phenomenon, and the PLE assignment in general, arises from the broad PLE peaks (about 200 meV) that appear in our spectra, under which several transitions could overlap. Compared with QDs, the experimental PLE data are significantly broader for rods and therefore it is much more difficult to provide unambiguous level assignment. This behaviour matches the theoretical model that exhibits a complex and dense VB level structure (depicted also in the STM spectra). Additionally, the spectral lines in both experiments are further broadened due to the contribution of excited *m*-levels. This reflects the significant increase in the density of states for rods compared with dots, as part of the manifestation of the transition from a zerodimensional to a quasi-one-dimensional system.

#### 3.2. Single-electron charging effects

In figure 7(a) we present a tunnelling spectrum of a single QR measured in the QR/DT/Au configuration (solid curve). As



**Figure 7.** dI/dV versus V tunnelling spectra (solid curves) of two similar CdSe QRs (25 nm × 4 nm), one (a) attached to gold via DT molecules, showing single-electron tunnelling effects, and the other (b) deposited on HOPG, exhibiting merely resonant tunnelling. The dashed curves represent simulations calculated using the theory for single-electron tunnelling, shifted vertically for clarity (the more complex VB was not simulated). In both cases we used the same values for the bandgap and CB2 – CB1 level spacing, thus the two fits differ only in the tunnelling junction parameters; see the text. The numbers below the fit in (a) denote the charging state of the QR.

shown previously for QDs [13], the DT layer may promote single-electron charging due to the reduction in the QR-tosubstrate tunnelling rate. Indeed, the main difference from the spectra measured in the QR/HOPG configuration, presented in figures 4(a) and 7(b), is the appearance of peak multiplets attributed to single-electron charging multiplets, which may reflect the degeneracy of the corresponding levels [2, 3, 33]. At positive bias, right above the energy gap, a doublet is clearly observed, signifying that the CB ground state, CB1, is doubly (spin) degenerate, as expected for a particle in a cylindrical box. The inter-doublet spacing corresponds, up to voltage division enlargement [14], to the single-electron charging energy. The spectra at higher positive bias (above 2 V) are more complicated and hard to interpret, as will be further discussed below. In short, the two first smaller peaks are attributed to tunnelling through the CB2 states while the CB1 level remains un-occupied (un-charged). The next two peaks correspond to the condition where the CB1 level is occupied, and the CB2 levels become charged. However, intrinsic (onset of field emission) and experimental (saturation of the pre-amplifier) limits of the available voltage range in the tunnelling spectra did not allow us to fully resolve the CB2 level degeneracy (which appears to be higher than two). InAs QRs, having a narrower bandgap [9], are promising candidates for investigating the degeneracy of the excited energy states. The simulated spectra, presented as dashed curves in figure 7, corroborate our discussion above concerning the charging effects.

The spectra were simulated using the theory for singleelectron tunnelling in a DBTJ configuration, modified to treat nanoparticles having a discrete level spectrum [14]. Since the QRs in both cases were very similar in size (~25 nm × 4 nm), we used the same values for the bandgap and CB2 – CB1 level spacing,  $E_g = 2.20 \text{ eV}$  and  $\Delta_{CB} = 0.39 \text{ eV}$  (which correspond well with our energy level calculations). The fits differ only in the tunnelling junction parameters. The capacitance values are  $C_1 = 1.9 \times 10^{-19}$  F and  $C_2 = 8.4 \times 10^{-19}$  F for spectrum (a), while  $C_1 = 1.1 \times 10^{-19}$  F and  $C_2 = 50 \times 10^{-19}$  F in (b). The lower  $C_2$  for case (a) may reflect the increased QR–substrate distance due to the DT layer. The important difference between these two pairs of parameters is the ratio,  $C_1/C_2$ , which is

much larger in (a). This ratio determines the voltage division between the two junctions,  $V_1/V_2 = C_2/C_1$ , and consequently the ratio between measured and real level spacing,  $1 + C_1/C_2$ . In spectrum (a) this enlargement effect is significant, resulting, e.g., in an apparently large energy gap (note the difference in the bias scales between the two frames). The typical charging energy found in our experiment (inter-multiplet peak separation) was about 160 meV, after correcting for the voltage division effect, comparable to our previous observation for InAs ODs. More pronounced is the effect of the tunnelling rate ratio between the two junctions. In the QR/HOPG case it is  $\Gamma_2/\Gamma_1 = 10$ , suppressing charging effects, whereas  $\Gamma_2/\Gamma_1 = 0.71$  for the QR/DT/Au configuration, enhancing QR charging. The numbers below the fit in the latter case (figure 7(a)) denote the number of excess electrons on the QR. The simulation shows, as discussed above, that tunnelling through the CB2 levels may take place without charging the CB1 level. The probability for that is small for the parameters used in the simulation, resulting in two small peaks in the simulated spectra, in good agreement with experiment.

#### 4. Conclusions

Combined optical and tunnelling spectroscopy measurements provide a powerful tool for investigating the level structure of semiconductor QRs. The experimental data obtained for CdSe QRs, from both optical and tunnelling measurements, show that the level structure is dominated by radius rather than by length, and they correspond to model calculations with reasonable agreement. This behaviour depicts the quasione-dimensional nature of the QRs even for aspect ratios as small as three and lengths above ~10 nm. This can be qualitatively understood by considering the dimensions of CdSe QRs compared with the bulk exciton Bohr radius. For rods longer than 10 nm, the weak confinement regime is already approached for the long dimension (the axis), while strong confinement still persists for the lateral dimension in the diameter regime studied.

These electronic properties allow one to select a desired QR length and tune its optical or electrical properties at will, using the diameter. This ability is of significant importance for future nanotechnology applications of QRs. The single-electron charging multiplets measured on these nanocrystals clearly revealed the degeneracy of the CB ground state, but further investigations on QRs made of narrow-bandgap semiconductors are still needed in order to reveal the degeneracy of excited states.

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