

Coulomb blockade of electron transport in a ZnO quantum-dot solid

Aarnoud L. Roest, John J. Kelly, and Daniël Vanmaekelbergh^{a)}

Debye Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands

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The temperature dependence of electron transport was studied in an assembly of ZnO quantum dots. The number of electrons per quantum dot was controlled by the electrochemical potential. For assemblies permeated with organic electrolyte solutions, the electron conductance measured in the linear response regime shows an activation energy of 80–120 meV. Our analysis indicates that this is due to Coulomb blockade of electron transport. © 2003 American Institute of Physics.
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Quantum-dot solids, formed by assembly of semiconductor nanocrystals, may find application in electronic and optoelectronic devices, such as light-emitting diodes, lasers, photodiodes, solar cells, and electrochromic windows. Due to quantum confinement, the nanocrystal building blocks of such solids have a set of discrete conduction and valence energy levels with atom-like *S*, *P*, symmetry. Semiconductor nanocrystals are, therefore, referred to as quantum dots or artificial atoms. The energy separation between the electron levels may be considerably greater than the thermal energy $k_B T$ which opens the possibility of exploring the quantum properties of such solids, even at room temperature.¹

The electronic properties of quantum-dot solids are determined by the energy levels of the nanocrystal building blocks, the electronic coupling between them and the occupation of the energy levels with electrons or holes. Thus, in the study of electron-conducting quantum-dot solids, the number of electrons per quantum dot $\langle n \rangle$ in the assembly is a key parameter. Using an electrochemical transistor setup with a film consisting of ZnO quantum dots, we have shown that $\langle n \rangle$ can be controlled by the electrochemical potential,^{1,2} The electronic charge in the ZnO nanocrystals is compensated by ions present in the electrolyte solution that permeates the assembly. This principle of electrochemical gating has also been demonstrated recently with other quantum-dot solids based on CdSe nanocrystals.³ Long-range electron transport in the nanocrystal assembly can be studied by measuring the conductance in the linear response regime, i.e., between a source and drain electrode using a very small bias (1–10 mV) such that the source-to-drain current through the quantum-dot assembly is proportional to the bias. For an assembly of ZnO quantum dots, permeated with an aqueous electrolyte solution, we have shown that there are two quantum regimes in the electron transport.¹ If the average electron number $\langle n \rangle$ is smaller than 2, electron transport occurs predominantly by tunneling between the atom-like *S* orbitals, while tunneling between *P* orbitals prevails if $\langle n \rangle$ is above 2 and, hence, the *S* levels are completely occupied. Studies of long-range transport in the linear response regime form a valuable extension to transport studies under strongly non-equilibrium conditions, e.g., with a large electric field over the film and/or photoexcitation of charge carriers.^{4–6}

Here, we report on the temperature dependence of electron transport through assemblies of ZnO quantum dots (the average diameter is 4.3 nm) permeated with an aqueous electrolyte solution and with two nonaqueous solutions based on ethanol or propylene carbonate solvents (with 0.1 M tetrabutylammonium perchlorate).⁷ The linear conductance between source and drain, G_{sd} , at a given electron number $\langle n \rangle$, was measured in a broad range between room temperature and the freezing point of the solutions. Since $\langle n \rangle$ is independently controlled by the electrochemical potential of the assembly, the temperature dependence of the electron conductance in the linear response regime should reveal fundamental aspects of electron transport through a quantum-dot solid, such as effects due to size-dispersion of the nanocrystals or Coulomb repulsion between the electrons.

The synthesis of the colloidal ZnO nanocrystals and the preparation of the nanocrystal assemblies have been described elsewhere.⁸ The conductance was measured with the electrochemical transistor setup placed in a liquid-helium flow cryostat equipped with a sample heater to stabilize the temperature between 224 K and room temperature.

The ability to accommodate electrons in the ZnO quantum-dot assembly depends strongly on the nature of the electrolyte solution that is present in the pores. This is demonstrated in Fig. 1, which shows the average electron number

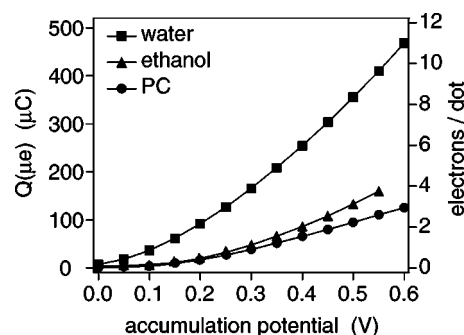


FIG. 1. The electron charge injected into an assembly of ZnO quantum dots as a function of the accumulation potential of the assembly. The assembly has been permeated with an aqueous electrolyte solution (0.2 M phosphate buffer, pH=8) and with two organic solutions of ethanol and propylene carbonate. The corresponding average number of electrons per quantum dot $\langle n \rangle$ is obtained from the injected charge and the number of quantum dots in the film (see Ref. 9).

^{a)}Electronic mail: d.a.m.vanmaekelbergh@phys.uu.nl

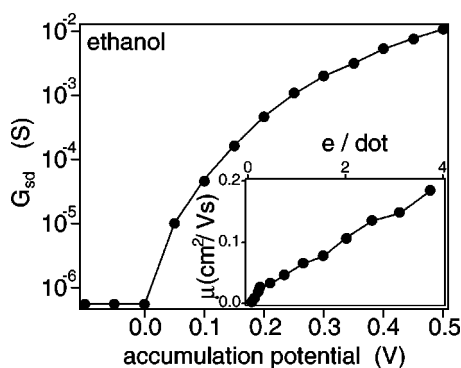


FIG. 2. The conductance of an assembly of ZnO quantum dots permeated with an ethanol electrolyte solution measured between a source and drain electrode as a function of the accumulation potential. Inset: the calculated electron mobility as a function of the electron occupation number of the quantum dots.

$\langle n \rangle$ versus the accumulation potential (i.e., the electrochemical potential of the assembly referred to that at which electron injection starts). The ZnO quantum-dot assembly was permeated with an aqueous solution and subsequently with ethanol and propylene carbonate solutions.⁷ For the aqueous electrolyte solution, the average electron number $\langle n \rangle$ is roughly a factor of 2 larger than that for the organic solutions at the same accumulation potential. The results were reproducible, and did not depend on the sequence of the experiments. Similar results were obtained with assemblies consisting of smaller or larger nanocrystals. Quenching of the highest occupied molecular orbital-lowest unoccupied molecular orbital optical transition and transitions at higher energy showed that the injected electrons occupy the delocalized atom-like *S* and *P* orbitals, and that charge storage in localized surface states is not important.¹ Therefore, the results presented in Fig. 1 indicate that the strong decrease in the electronic capacitance of the porous nanocrystal electrodes upon replacement of the aqueous solution by an organic one must be caused by an increase of the electrostatic charging energy per injected electron.

Figure 2 shows the electron conductance G_{sd} , measured with a small source-drain bias (1–10 mV), for a ZnO quantum-dot assembly permeated with an ethanol electrolyte solution as a function of the accumulation potential. The conductance rises steeply as soon as electrons are injected into the assembly, and increases by four orders of magnitude when the electrochemical potential is increased to 0.5 V. Similar results have been obtained with films permeated with an aqueous and a propylene carbonate electrolyte solution. In accordance with the optical results, this shows that the injected electrons occupy delocalized conduction orbitals, not localized surface states. The electron mobility can be obtained from the measured conductance, the electron density in the film and the geometry of the transistor. A typical plot of the electron mobility as a function of increasing average electron number is shown in the inset of Fig. 2: the mobility increases gradually with increasing $\langle n \rangle$. Due to the size distribution of the nanocrystals in the assembly, there is a considerable energy overlap in the *S* and *P* electron levels. Transport occurs by tunneling between *S* orbitals at $\langle n \rangle < 2$ and by tunneling between *S* and *P*, and *P* and *P* orbitals at higher electron occupation. In contrast to ZnO nanocrystal

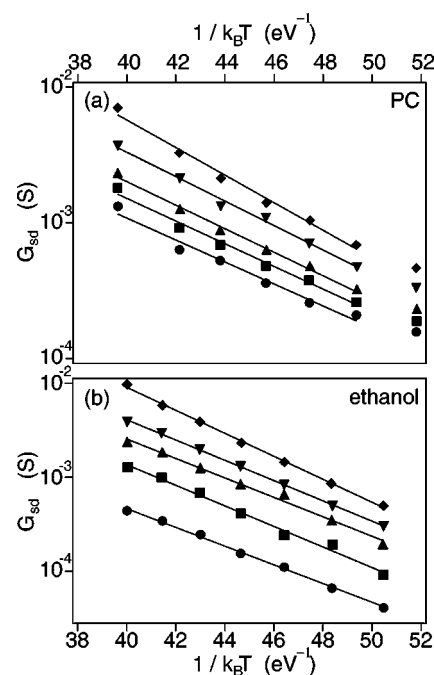


FIG. 3. The source-drain conductance of an assembly of ZnO quantum dots permeated with a propylene carbonate electrolyte solution [Fig. 3(a)] and with an ethanol electrolyte solution [Fig. 3(b)] as a function of $1/k_B T$. The results were obtained at different accumulation potentials and thus different electron occupation numbers. Figure 3(a): from bottom-to-top $\langle n \rangle$ is 1.2, 1.5, 1.8, 2.2, and 3.0, respectively. Fig. 3(b): $\langle n \rangle$ is 0.8, 1.2, 1.7, 2.0, and 3.5, respectively.

films permeated with an aqueous electrolyte solution,¹ a sharp transition between transport via *S* orbitals and via *P* orbitals is not observed here.

Figure 3(a) shows a plot of the logarithm of the conductance versus $1/k_B T$, measured with an assembly permeated with a propylene carbonate electrolyte solution.⁷ The data were acquired between 293 K and the freezing point of propylene carbonate (224 K). The results obtained below the freezing point were not reproducible, probably due to damage in the quantum dot film or at the contacts. The film conductance is presented for different electron occupation numbers between 1.2 and 3. For a given $\langle n \rangle$, the conductance increases exponentially with temperature. The thermal activation energy of electron conductance, obtained from the slope of the $\ln G_{sd}$ vs $1/k_B T$ plots, is 81 meV (± 5 meV) for $\langle n \rangle = 1.2$ and 101 meV for $\langle n \rangle = 3$. The results obtained with assemblies permeated with an ethanol electrolyte solution⁷ are very similar [Fig. 3(b)]; the thermal activation energy varies from 100 meV (for $\langle n \rangle = 0.8$) to 122 meV ($\langle n \rangle = 3.5$). Our results suggest that the thermal activation energy of conductance increases slightly with increasing electron occupation of the quantum dots in the assembly. We remark here that thermally activated electron transport was generally observed for ZnO quantum-dot assemblies (for diameters of 3.9, 4.3, and 5.0 nm) permeated with an *organic* electrolyte solution (e.g., ethanol and propylene carbonate). In contrast, ZnO assemblies permeated with an *aqueous* electrolyte solution show a conductance which is independent of the temperature in the accessible range between 273 and 310 K.

Thermally activated long-range charge carrier transport has been observed in molecular crystals,¹⁰ self-assembled superlattices of gold¹¹ and cobalt¹² nanocrystals, and assembled

blies of CdSe quantum dots.⁴ The thermal activation energy obtained from the temperature dependence of the conductance varied between 10 and 200 meV depending on the system studied. The temperature dependence of the conductance has been commonly attributed to electron–electron repulsion, i.e., Coulomb blockade. The thermal activation energy found in the conductance should then reflect the electrostatic charging energy needed to add an electron to a molecule, a metallic nanocrystal, or a semiconductor quantum dot.

We have observed that the electronic conductance of a ZnO quantum dot assembly permeated with an *aqueous electrolyte solution* is not thermally activated. This shows that the energy mismatch between the conduction *S* (or *P*) levels of adjacent quantum dots (which is due to the dispersion in size of the ZnO nanocrystals) is so small that it does not lead to a detectable temperature dependence of the conductance. Thus, by analogy, we can conclude that the strong temperature dependence of the electron conductance observed for assemblies permeated with an organic electrolyte solution is not due to inelastic tunneling caused by energy mismatch. It is thus very likely that the thermally activated conductance is due to the repulsion between conduction electrons in a quantum dot; i.e., Coulomb blockade of electron transport.

Further support for Coulomb blockade of electron transport is obtained by analyzing our results on the basis of a theoretical model provided by Beenakker.¹³ The model considers electron transport through a single quantum dot embedded between a source and a drain electrode. The conductance is calculated for the linear response regime, i.e., very small source-drain bias, as was used for the conductance measurements discussed in this work. According to Beenakker, Coulomb blockade of electron transport occurs if two conditions are fulfilled: (i) the coupling between the quantum dot and the electrodes is weak, this means that the tunneling rates Γ must be sufficiently small: $\Gamma \ll k_B T/h$ and (ii) the electrostatic charging energy for adding an electron to a dot must be sufficiently large, i.e., $e^2/C > 4k_B T$ (C being the capacitance of the dot). The degree of electronic coupling between the orbitals of adjacent quantum dots in the film can be obtained from the measured electron mobility μ , using the Einstein–Smoluchowski equation, i.e., $\mu = (e/k_B T)\Delta^2/\tau$ (Δ is the length over which the electron is transferred in one tunneling event, taken here as the diameter of the nanocrystal). We find that the mobility is typically of the order of 0.1 cm²/V s (see Fig. 2) which gives a rate of tunneling between two adjacent nanocrystals of 1.4×10^{10} /s; 400 times smaller than the tunneling rate $k_B T/h$ which marks the onset of coherence. It is thus clear that the electronic coupling between the ZnO quantum dots in the assembly is relatively weak, and that Coulomb blockade should occur if the charging energy is larger than $k_B T$. We have observed that for films permeated with an organic electrolyte solution the thermal activation energy of the conductance is about 100 meV, thus four times $k_B T$. For quantum-dot assemblies permeated

with water, the conduction did not depend on the temperature, which indicates that the charging energy is smaller than $k_B T$. This is in accordance with the result of the electron capacitance measured with ZnO quantum-dot assemblies⁹ which show that in aqueous solvents the charging energy can be neglected while it plays an important role in assemblies permeated with propylene carbonate or ethanol. The reason for this difference remains unclear. We remark here that the dielectric constant of the ethanol (24.3) and propylene carbonate (64) electrolyte solutions is not very different from that of water (81). In addition, we have used solutions with a similar and high ionic strength in all cases. The only difference between the aqueous and organic solutions is the proton concentration. The buffered aqueous solution has a proton concentration of about 10^{-8} M, while the proton concentration is much lower in the ethanol solution and practically zero in the propylene carbonate solution. Perhaps, due to their extremely small size, protons may play a special role in the screening of the electronic charge in the ZnO quantum dots. We suggest that in aqueous solutions the electron–electron repulsion in a quantum dot is strongly screened by protons adsorbed at the surface of the ZnO nanocrystals or inserted into the ZnO lattice.⁹

In summary, we have presented evidence for a Coulomb blockade of long-range electron transport in an assembly of weakly coupled ZnO quantum dots where electron transport occurs by non-coherent tunneling between adjacent quantum dots.

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