Chapter 3

Long-range electron transport in assemblies of ZnO quantum dots: the effects of quantum confinement, Coulomb repulsion and structural disorder

In this chapter we compare the results for aqueous electrolytes described in the previous chapter with the results obtained with propylene carbonate solutions. The storage and long-range transport of electrons in a porous assembly of ZnO quantum dots is found to depend strongly on the interpenetrating electrolyte. The screening of the electron charge is less effective in the case of an assembly permeated with a propylene carbonate electrolyte solution. The effect of temperature on the conductance of ZnO assemblies permeated with propylene carbonate and ethanol is reported.
3.1 Introduction

When an electron is added to an otherwise neutral nanocrystal it will occupy the lowest conduction level; the corresponding orbital is strongly delocalized with respect to the atomic scale and occupies the space of the nanocrystal. Insulating nanocrystals with a diameter in the 1-10 nm range, therefore, possess discrete conduction (and valence) energy levels corresponding to orbitals with atom-like symmetry (denoted as $S$, $P$, $D$). The set of discrete energy levels depends both on the chemistry and on the size and shape of the nanocrystal. For a number of insulating nanocrystals, such as InAs, CdSe and PbS, these discrete energy levels have been studied with resonant electron tunnelling spectroscopy using an STM [1, 2]. The results are found to be in fair agreement with sophisticated electronic structure calculations based on the pseudopotential [3] or tight-binding methods [4].

Colloidal nanocrystals can be assembled to form solids. In most cases the Van der Waals interactions between the surface molecules of the nanocrystals form the driving force for self-assembly. If the size-distribution of the nanocrystals is sufficiently small, ordered arrays (also called superlattices), quantum-dot solids or artificial solids are formed by self-assembly [5, 6]. These arrays represent the analogue of crystals consisting of ordinary atoms. The optical and electrical properties of quantum-dot solids will be determined by the energy levels of the individual nanocrystal building blocks and the degree of overlap of these orbitals in the solid [7].

Figure 3.1 shows the set of energy levels ($S$, $P$, $D$, etc.) and the $S$ and $P$ conduction orbitals of a nearly spherical, but faceted ZnO quantum dot with a diameter of 3.9 nm, calculated by a tight-binding model. The energy separation between the conduction orbitals in such a small nanocrystal is about 300 meV. This means that quantum confinement effects should play a role in the optical and electrical properties of such systems, also at room temperature. The contour plots of the squared $S$ and $P$ wave functions show atom-like symmetry. They also give an idea of the degree of electronic coupling that can occur if the nanocrystals are assembled into a solid.

Experimental research on the electronic and optical properties of quantum-dot solids requires that the number of electrons (holes) per nanocrystal building block (further denoted as the electron number $n$) can be varied in a controlled way. We have used an electrochemical gating principle to control the electron number in porous assemblies of nanocrystals. Briefly, the nanocrystal assembly forms the bridge between a source and a drain electrode and the source-nanocrystal assembly-drain system forms a polarizable working electrode in an electrochem-
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Figure 3.1: Atom-like $S$ (A) and $P$ (B) electron orbitals for a ZnO quantum dot (the black dots present the Zn and O atoms). (C): The energy levels calculated for a 3.9 nm quantum dot. The energy of the levels is relative to the conduction band of bulk wurtzite ZnO. The results are obtained with the $S, P, D, S'$ tight-binding method.
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The electron number can be gradually increased from zero by changing the electrochemical potential to more negative values with respect to a reference electrode. The positive ions in the electrolyte solution in the pores of the assembly provide the counter charges for the electrons present in the nanocrystals. Electrochemical gating is an example of three-dimensional charge compensation which is of central importance for the electronic properties of single-phase solids and permeated two-phase solids [8, 9]. The electron density in the sample can be varied from zero to high values. Thus, studies with an electrochemical gate form a valuable addition to previous studies performed with a simple two-electrode set-up in which electron transport was investigated applying large electric fields [10–12]. We remark that in our case the entire film is uniformly charged with electrons in contrast to two-dimensional charging in a conventional field effect transistor or a strongly biased two-electrode system.

In Chapter 2 we described a study of the storage of electrons in an assembly of ZnO quantum dots permeated with an aqueous electrolyte [8]. We found that in this case the average electron number $\langle n \rangle$ could be varied in a controlled way between zero and twelve in a potential range in which ZnO is chemically stable. Clearly, the charging energy for the addition of one electron is very small due to the very effective screening of the Coulomb repulsion between the electrons present in one ZnO quantum dot. Furthermore, it was shown that long-range electron transport in such assemblies is determined by the overlap of the atom-like orbitals. A first quantum regime in which transport occurs by tunnelling between the $S$ orbitals is found for $\langle n \rangle < 2$; it could be distinguished from a second regime, for $\langle n \rangle > 2$, where tunnelling between the $P$ orbitals prevails.

In aqueous electrolytes the storage and transport of electrons is determined by the quantum-confined energy levels of the ZnO nanocrystals; the charging energy can be neglected. It is, at present, not clear why the charging energy is so small. Furthermore, it is not clear to what extent the chemistry at the ZnO nanocrystal/electrolyte internal interface is important. In order to address these issues, we have performed an extensive study of the storage and electron transport in a ZnO quantum-dot assembly permeated with a propylene carbonate (PC) electrolyte. Our choice for PC was determined by the fact that it cannot form hydrogen bonds with the ZnO surface molecules and solvates positive ions less strongly than water. We have used similar assemblies as in the previous study consisting of ZnO nanocrystals with diameters in the 3-5 nm range. Here, we present a detailed comparison between the characteristics of electron storage and transport in a ZnO quantum-dot assembly permeated with water and propylene carbonate. For the sake of comparison we include in this chapter results and some discussion from...
3.2 Experimental

The synthesis of the colloidal ZnO nanocrystals [13] has been described in detail in Section 2.2.1. The particle size of the washed ZnO quantum dots was determined with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The diameter of the quantum dots used in the present work is 3.9±0.9 and 4.3±1.0 nm. The maximum error which is made in the determination of the diameter of the quantum dots with TEM and XRD is estimated to be 15% in accordance with the value stated by Hoyer and Weller [14].

Transparent films of pure wurtzite ZnO quantum dots were made by spin-coating the solution of ZnO particles on a (transparent) conducting substrate. Very flat and optically transparent films are formed with this technique [15]. The thickness of the layer was obtained by profilometry (Tencor Instruments alpha-step 500). The thickness of the various ZnO layers is about 200 nm in the present work. For the measurements of the long-range transport gold substrates were used (30 nm thick gold deposited on a 5 nm thick adhesion layer of chromium on a flat glass substrate). Between the electrodes there was a non-conducting gap, 10 μm wide and 1 cm long.

The film was heated after each spin-coating step for 15 minutes to remove the solvent. Low temperatures (90-110°C) were used to prevent neck formation between the dots. The low temperature and the thorough washing procedure of the sol are necessary to observe the phenomena which are described in the present work. The absorption spectrum of the ZnO layer shows a slight red-shift with respect to the absorption spectrum of the original washed ZnO sol (see Section 2.2.1). This confirms that the quantum properties of the individual ZnO nanocrystals are preserved in the film. A slight red-shift was also seen if the layer was not heated but only dried in ambient air conditions. The film preparation and properties are different from much of the work that has been published, where often a high-temperature anneal (400°C) was used to convert the as-deposited film to a porous ZnO film. This always resulted in an increase of the particle size and a coarser structure and, sometimes, substantial light scattering could not be avoided.

The zinc and lithium content of the films was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after dissolution of the films in diluted HCl. This chemical analysis showed that lithium was not present above its detection limit (0.5 at.% relative to zinc) after the washing procedure.
From the amount of ZnO and the average volume per quantum dot the number of quantum dots in the film is estimated. From this number and the injected charge, the average number of electrons per dot $\langle n \rangle$ is obtained (see also Section 2.5).

The aqueous electrolyte was an argon-purged 0.2 M phosphate buffer (pH = 8) and was made by adding pure NaOH to phosphoric acid. Here the reference electrode was a Ag/AgCl electrode, and the counter electrode a platinum sheet. Otherwise, anhydrous propylene carbonate (PC) with 0.1 M tetrabutylammonium perchlorate (TBAClO$_4$) was used. In this electrolyte a silver rod served as a quasi reference electrode. The quasi reference electrode potential was calibrated with the ferrocene/ferrocinium couple and was found to be 200 mV vs. Ag/AgCl. The experiments in PC were carried out in a nitrogen-filled glovebox to keep the electrolyte free of oxygen and water. The ethanol and propylene carbonate were used without further purification. The water content of the pure solvents was 0.2% and 0.3% respectively.

The low-temperature electrochemical measurements were performed using a liquid-helium flow-cryostat equipped with a sample heater to stabilize the temperature between 150 K and room temperature.

### 3.3 Results and Discussion

#### 3.3.1 Electron Storage

We have investigated the storage and long-range transport of electrons in ZnO quantum-dot assemblies permeated with aqueous and non-aqueous electrolyte solutions. The differential charge $\Delta Q(\mu_e)$ injected into the quantum-dot layer was measured per 50 meV increase of the electrochemical potential $\mu_e$ of the source-drain electrode system (the source and drain electrodes are kept at the same potential). The differential charge is shown for the injection of electrons into ZnO quantum-dot layers permeated with the phosphate buffer (Figure 3.2A) and the propylene carbonate electrolyte (Figure 3.2B). Nanocrystals with a mean diameter of 3.9 and 4.3 nm were used.

If a sufficiently negative potential is applied, electrons can be stored in the ZnO nanocrystals. The onset potential of electron injection depends on the average size of the quantum-dot building blocks in the ZnO layer. Electron injection occurs at potentials of about -0.65 and -0.60 V in water, and -0.30 and -0.20 V in PC for the 3.9 and 4.3 nm diameter particles, respectively. A variation of the pH of the phosphate buffer in the range 7-10 did not change the charging characteristics apart from a shift of the onset potential, which corresponded nicely to
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Figure 3.2: The differential charge $\Delta Q(\mu_e)$, expressed as electrons per dot, measured upon successive potential steps of 50 mV, in a ZnO quantum-dot assembly permeated with an aqueous phosphate buffer or 0.1 M TBACIO$_4$ in PC as a function of the electrochemical potential. The average diameter of the quantum dots is indicated in the figure.
Nerstian behaviour. Similar results were found by Noack et al. [16]. The differential capacitance function of the quantum-dot layers permeated with water, shows two waves for an assembly of 3.9 nm quantum dots; the function suggests three waves in the case of an assembly with 4.3 nm quantum dots. The significance of these steps was already discussed in Chapter 2. In PC some small steps can also be seen for both sizes of quantum dot. Integration of the differential charge from Figure 3.2 gives the cumulative charge, \( Q(\mu_e) \), in the quantum dots:

\[
Q(\mu_e) = \frac{1}{\Delta V} \int_{\mu_{e, onset}}^{\mu_e} \Delta Q(\mu_e) d\mu_e
\]

Here \( \Delta V \) is the size of the potential step. From the cumulative charge and the known number of quantum dots in the film (see Section 3.2), the average number of electrons per ZnO quantum dot \( \langle n \rangle \) can be obtained as a function of the electrochemical potential (see Figure 3.3). It is evident that the larger nanocrystals
contain more electrons than the smaller ones at the same accumulation potential (i.e. the potential versus the onset potential of electron injection). For example, in the assemblies permeated with water, at an accumulation potential of 0.5 V, the larger nanocrystals contain about 8 electrons per quantum dot whereas the smaller ones have about 6 electrons per dot. This efficient electrochemical ‘gating’ is typical for the case in which the transistor layer is permeated with an aqueous electrolyte [14, 15, 17]. At the same accumulation potential in PC about 1.5 and 1.0 electrons can be stored in the ZnO quantum dots for the 4.3 and 3.9 nm quantum dots, respectively. This is much less than in water. The electrochemical gating is, therefore, much less effective in PC. Furthermore, we found that the charging characteristics in aqueous and non-aqueous electrolyte solutions are independent of the cation that was used as a counter charge; i.e. the differential charge function did not change on replacing Na$^+$ with the tetrabutyl- or tetramethylammonium cation.

Figure 3.4 summarizes the capability of electron storage in ZnO assemblies permeated with water or PC. We plot the average number of electrons per dot for an accumulation potential of -0.5 V. It is clear that considerably more electrons

\textbf{Figure 3.4:} The average number of electrons per quantum dot at an accumulation potential of -500 mV. The results are shown for ZnO films, prepared from nanocrystals of several sizes, permeated with water and PC.
per quantum dot can be stored using water as compared to PC at the same accumulation potential. This difference becomes relatively larger as the size of the quantum dots becomes smaller. We conjecture that the high electrochemical gating efficiency in water is due to the presence of protons ($10^{13}$ cm$^{-3}$ at pH = 8). The concentration of protons in the aprotic electrolytes used in this work is many orders of magnitude lower. Protons can adsorb on the ZnO surface or even be inserted into the ZnO nanocrystals [18]; the cations are, therefore, very close to the electrons in the ZnO dots which results in an efficient screening of the electron charge.

The electrons in the ZnO nanocrystals can be located in delocalized $S$, $P$, and higher energy conduction orbitals, or in trap states. In order to investigate the
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possibility of trapping, we measured the quenching of the optical absorbance of the HOMO-LUMO and higher energy transitions of the ZnO quantum-dot layers on varying the electron occupation. The absorbance in the energy range between 3.3 and 4 eV is quenched significantly when electrons are present in the films (Figure 3.5).

The quenching signal \(-\Delta A(h\nu)\) becomes broader in energy at higher energies and increases in intensity when the electron density increases. At low electron occupation \(\langle n \rangle < 2\) the HOMO-LUMO is quenched, while at higher electron occupation optical transitions between other energy levels are also quenched. In Figure 3.6, the integrated absorbance difference, \(-\int \Delta A(h\nu)d(h\nu)\), is plotted as a function of the average number of electrons per quantum dot \(\langle n \rangle\), in the ZnO layers prepared from 4.3 nm quantum dots. Similar results are obtained when films are used with quantum dots of a different size. The results are shown for a layer permeated with water (■) and with PC (●). The relative absorbance is defined as the decrease of the absorbance between 3.3 and 4.0 eV divided by the total absorbance between 3.3 and 4.0 eV at 0.0 V (i.e. at zero quenching). The

**Figure 3.6:** The relative absorbance as a function of the average number of electrons for the water and PC systems. The relative absorbance is defined as the quenching of the absorbance between 3.3 and 4.0 eV divided by the total absorbance between 3.3 and 4.0 eV without quenching. The IR absorbance is shown in the inset as a function of \(\langle n \rangle\) (the measurement was performed in PC).
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total absorbance between 3.3 and 4.0 V was the same for assemblies permeated with PC or the phosphate buffer.

The integrated absorbance difference increases almost linearly with the injected charge and the process is completely reversible in the potential range between 0 and -1.2 V in water and between 0 and -1 V in PC. A striking result is that in water approximately twice the number of electrons per dot are needed to obtain the same quenching of the absorbance. We do not have an explanation for this effect. Furthermore, the quenching of the UV-absorbance vanishes only when \langle n \rangle goes to zero and the IR absorbance increases as soon as electrons are injected into the ZnO assembly permeated with PC as shown in the insert of Figure 3.6. The details of the IR measurements are discussed in Chapter 4. This shows that all electrons are located in S, P and higher energy atom-like conduction orbitals and that electron localization in surface states is not important. The idea that electron trapping in localized band gap states is not important is further supported by the prompt and strong increase of the conductance of the quantum-dot layer observed as soon as electrons are present in the dots (see Section 2.3.2). In agreement with this, electrochemical results obtained with ZnO single crystals have shown no or only minor effects of interfacial band gap states [18]. Still, our results with quantum-dot assemblies are surprising, since the number of ZnO surface sites in a quantum dot is very large.

The differential charge (i.e. capacitance) functions presented in Figure 3.2 reflect the consecutive filling of the two-fold degenerate S and six-fold degenerate P orbitals by electrons. These results can be understood on the basis of the thermodynamic framework for electron addition to quantum dots proposed by Zunger and co-workers [3]. In this framework, the electrochemical potential for electron addition to a quantum dot is considered, taking into account the quantum-confined single-particle energy levels, the dielectric polarization due to the electron charge and Coulomb repulsion between the electrons occupying delocalized conduction orbitals. Addition of the first three electrons to an otherwise neutral quantum dot can be described by:

\[
S^0 + e \rightarrow S^1 \quad \mu_e(S^{0/1}) = \epsilon_S + E_{pol}
\]

\[
S^1 + e \rightarrow S^2 \quad \mu_e(S^{1/2}) = \epsilon_S + E_{ee} + E_{pol}
\]

\[
S^2P^0 + e \rightarrow S^2P^1 \quad \mu_e(P^{0/1}) = \epsilon_P + 2E_{ee} + E_{pol}
\]

Equations 3.2 to 3.4 give the electrochemical potentials for injection of the first, second and third electron in a ZnO quantum dot. These electrochemical potentials
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Figure 3.7: Fit of the potential dependence of the differential charge (experimental data are indicated by •’s), normalized as the number of added electrons per 50 mV per quantum dot, as a function of the electrochemical potential. The ZnO assembly is permeated with an aqueous solution. The experimental results are obtained with an assembly of 3.9 (upper figure) and 4.3 nm (lower figure) nanocrystals. The solid lines give the best fit obtained with the sum of single-electron addition functions. The addition functions $\Delta Q(S^0 \rightarrow S^1)$ and $\Delta Q(S^2P^0 \rightarrow S^2P^1)$ (dotted lines) are calculated with a model that takes into account the quantum-confined single-particle energy levels, $\varepsilon_S(d)$, $\varepsilon_P(d)$, ... and a very small Coulomb repulsion ($E_{ee}(d) < kT$). The overall $S$ and $P$ energy levels are also shown (dashed lines). The $D$ energy levels are omitted for clarity. The size-distribution used for the best fit is shown in the insert.
Figure 3.8: Fit of the potential dependence of the differential charge (experimental data are indicated by •'s), normalized as the number of added electrons per 50 mV per quantum dot, as a function of the electrochemical potential. The ZnO assembly is permeated with a propylene carbonate solution. The experimental results are obtained with an assembly of 3.9 (upper figure) and 4.3 nm (lower figure) nanocrystals. The solid lines give a fit with a sum of single-electron addition functions. The single addition functions $\Delta Q(S^0 \rightarrow S^1)$, $\Delta Q(S^1 \rightarrow S^2)$ (dotted lines), ... are calculated with a model accounting for quantum-confined single-particle energy levels, $\varepsilon_S(d)$, $\varepsilon_P(d)$, ... and a size-dependent Coulomb repulsion energy (200 and 130 meV for 3.9 and 4.3 nm dots, respectively).
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depend on the energy of the orbitals ($\epsilon_S$ and $\epsilon_P$), the self-polarization energy per added electron ($E_{pol}$) and the electron-electron repulsion energy ($E_{ee}$) \[3\]. The differential charge functions can now be fitted with a sum of single-electron addition functions calculated with Equations 3.2 to 3.4 and a size-distribution for the ZnO nanocrystals in the assembly (Figure 3.7 and 3.8). The size-distributions used here are presented as inserts in Figure 3.7. The diameter dependent single-particle energy levels $\epsilon_S(d)$ and $\epsilon_P(d)$ are obtained from tight-binding theory (see also Section 4.2). The self-energy (i.e. polarization energy) $E_{pol}(d)$ and the repulsion energy $E_{ee}(d)$ are assumed to be proportional to $d^{-1}$ \[19\].

Figure 3.7 shows the single-electron addition functions $\Delta Q(S^0 \rightarrow S^1)$ and $\Delta Q(S^2P^0 \rightarrow S^2P^1)$, and the total fit for the results obtained with an assembly permeated with an aqueous solution. We find that the experimental results can be fitted very well with a small value for the repulsion energy $E_{ee}$, i.e. $E_{ee} < kT$. As a consequence of the negligible repulsion energy, the addition curves $\Delta Q(S^0 \rightarrow S^1)$ and $\Delta Q(S^1 \rightarrow S^2)$ overlap. In addition, the width of the functions is entirely determined by the size dispersion. The difference in electrochemical potentials corresponding to the maxima of the single-electron addition functions reflect the energy difference between the $S$, $P$ and $D$ electron levels. For the 3.9 nm ZnO nanocrystals, we find $\epsilon_P-\epsilon_S = 300$ meV and $\epsilon_D-\epsilon_P = 333$ meV, while for the larger 4.3 nm dots $\epsilon_P-\epsilon_S = 256$ and $\epsilon_D-\epsilon_P = 284$ meV. These results are in fair agreement with the single-particle separations measured with IR absorption spectroscopy (see Section 4.5.2) \[20\]. Due to the size-distribution of the ZnO quantum dots in the assembly, there is a considerable overlap between the single-electron addition functions of the $S$ and $P$ orbitals. This is of key importance for understanding the characteristics of long-range transport, discussed in the next section.

The results obtained in PC are strikingly different (see Figure 3.8). They can only be fitted if a large Coulomb repulsion energy is taken into account: $E_{ee}(d)$ is 220 and 130 meV for the quantum dots of 3.9 and 4.3 nm, respectively. As a consequence, the single-electron addition curves $\Delta Q(S^0 \rightarrow S^1)$ and $\Delta Q(S^1 \rightarrow S^2)$ are clearly separated, and the overlap with $\Delta Q(S^2P^0 \rightarrow S^2P^1)$ is very strong. Thus, at a given electrochemical potential (for instance $V = -0.6$ V) a considerable fraction of the (largest) quantum dots contain an electron in a $P$ orbital, while the smallest quantum dots have no or one electron in the $S$ orbitals. As a result of the large charging energy observed in PC, the electron number is considerably smaller than in ZnO nanocrystal assemblies permeated with water (see Figure 3.4).

$E_{ee}$ in PC is 100-200 meV which is considerably larger than in aqueous electrolytes. The dielectric constants of water (81) and PC (64) are almost similar and
cannot explain this difference. We believe that adsorption of protons on the ZnO surface can strongly reduce the values of $E_{\text{pol}}$ and $E_{\text{ee}}$.

In order to fit the differential capacitance functions obtained in PC, an additional broadening effect on the single-electron energy levels has to be taken into account. The origin of this broadening of the single-electron energy level distribution is not clear. Because of the weak screening of the Coulomb repulsion, it is possible that electron-electron repulsion between adjacent quantum dots cannot be neglected.

### 3.3.2 Long-range electron transport

In order to measure the characteristics of long-range electron transport in the ZnO quantum-dot assemblies, the electrochemically gated transistor is used. At a given electrochemical potential, thus a given $\langle n \rangle$, a small potential drop is applied between the source and drain ($V_{sd} = 1-10$ mV), and the current $I_{sd}$ is measured. We found that $I_{sd}$ is linearly dependent on $V_{sd}$ for these small values of $V_{sd}$ [15].

The linear conductance, $G = R^{-1} = I_{sd}/V_{sd}$, is presented as a function of $\langle n \rangle$ in Figure 3.9 for assemblies of 3.9 and 4.3 nm dots permeated with the phosphate buffer. Note that the conductance starts to increase from a very low value to much higher values as soon as electrons are injected into the films.

For the 3.9 nm quantum dots, the conductance increases linearly with $\langle n \rangle$, for $0 < \langle n \rangle < 2$, and for $2 < \langle n \rangle < 8$. Note that in the second range the slope of the $R^{-1}$ and $\langle n \rangle$ plot is larger. This suggests that there are at least two regimes characterized by a different electron mobility $\mu$. The same trends are observed with the quantum dots of 4.3 nm in size. In this case, $R^{-1}$ increases again if $\langle n \rangle > 8$. The electron mobility can be calculated using:

$$
\mu \equiv \frac{\partial \sigma}{\partial N_e} = \frac{d}{eLt} \times \frac{\partial G}{\partial N}
$$

(3.5)

Here, $\sigma$ is the specific electron conductivity (S·cm$^{-1}$), $N$ is the average electron density (cm$^{-3}$), and $e$ is the elementary charge. $L$, $d$, and $t$ define the ZnO bridge dimensions and represent the width and length of the insulating gap and the thickness of the ZnO layer in this gap, respectively. There are clearly two regimes with a constant mobility. For the films with 3.9 nm dots the electron mobility is $17 \times 10^{-3}$ cm$^2$/Vs and $66 \times 10^{-3}$ cm$^2$/Vs respectively for $0 < \langle n \rangle < 1.5$, and $2.5 < \langle n \rangle < 8$. This is equivalent to an electron diffusion coefficient or diffusivity $D$ of $0.4 \times 10^{-3}$ cm$^2$/s and $1.5 \times 10^{-3}$ cm$^2$/s. In the first range, the electrons occupy predominantly $S$ levels and in the second predominantly $P$ levels. We in-
Figure 3.9: The source-drain conductance $R^{-1}$ and the corresponding electron mobility $\mu$ as a function of $\langle n \rangle$. The electrochemically gated ZnO transistor is permeated with the phosphate buffer in this experiment. The average diameter of the quantum dots is indicated in the figure.
Figure 3.10: The source-drain conductance $R^{-1}$ and the corresponding electron mobility $\mu$ as a function of $\langle n \rangle$. The electrochemically gated ZnO transistor is permeated with PC in this experiment. The average diameter of the quantum dots is indicated in the figure. The lines through the points are a guide to the eye.
fer that the mobility in the first regime corresponds to tunnelling via the $S$ orbitals and in the second corresponds to tunnelling via the $P$ orbitals. There is a transition range between these two regimes at around $\langle n \rangle = 2$ where both $S$ and $P$ orbitals are involved in long-range transport. This agrees with the overlap of the $S$ and $P$ density-of-states observed in the differential capacitance function (Figure 3.7). The two regimes for the electron mobility in the films with 4.3 nm dots can also clearly be seen. However, the transition range between the two regimes is broader due to the stronger overlap between the $S$ and $P$ density-of-states as can be seen in Figure 3.7. The variation in $\mu$ for a given regime ($S$ or $P$) in the aqueous electrolyte was about 10% for electrodes from different batches, but the relative magnitude of $\mu_{P-P}/\mu_{S-S}$ was always close to 4. The ratio of 4, found in every sample, can be understood more quantitatively by applying the Einstein-Smoluchowski formalism. Electron hopping between the $S$ orbitals of neighboring quantum dots corresponds to a mobility:

$$\mu_{S-S} = \frac{(e/k_B T) \Delta^2}{\tau_{S-S}}$$

$\Delta$ is the length over which the electron is transferred in one tunnelling step (i.e. the diameter of the quantum dot) and $\tau_{S-S}$ the typical time between two tunnelling events. Electron diffusion via $P-P$ orbital tunnelling corresponds to:

$$\mu_{P-P} = \gamma (e/k_B T) \frac{\Delta^2}{\tau_{P-P}}$$

Here $\gamma$ accounts for the higher density of the $P$ orbitals per unit of energy ($\gamma$ should be 3 if the width of the $P$ single-electron functions were the same as that of the $S$ functions). Thus, the fact that $\gamma$ is larger than 3 must be due to the larger spatial extension of the $P$ orbitals with respect to the $S$ orbitals. In agreement with this, tunnelling through $P$ orbitals in resonant tunnelling experiments through a single quantum dot leads to a somewhat larger current increase as compared to that for tunnelling through $S$ orbitals [2].

With assemblies consisting of 4.3 nm quantum dots, the electron mobility increases again for $\langle n \rangle > 8$. Although the electron mobility does not really flatten off at $\langle n \rangle = 11$, the expected ratio for $\mu_{D-D}/\mu_{P-P}$ of 10/6, corresponds very well to the empirical value of 1.6 which we obtain from our results. Since $\Delta$ corresponds to the diameter of a ZnO quantum dot, we calculate that the rate for $S-S$ orbital tunnelling in 3.9 nm particles $1/\tau_{S-S}$ is $3 \times 10^9 \text{s}^{-1}$, while the $P-P$ tunnel rate $1/\tau_{P-P}$ is $3.7 \times 10^9 \text{s}^{-1}$. By comparison, the rates of resonant tunnelling in a
single-quantum dot device with metal/dot tunnel barriers of 1 nm in width are two orders of magnitude smaller [2].

We conclude that there is a weak to moderate coupling between the atom-like orbitals of the quantum-dot building blocks. In Chapter 2 we showed that long-range electron transport in ZnO quantum-dot assemblies is non-coherent [8]. This means that the electron wave functions do not extend over several quantum dots: tunnelling occurs by step-wise tunnelling from dot to dot.

In Figure 3.10 the linear conductance and the calculated electron mobility in PC is presented as a function of $\langle n \rangle$. $R^{-1}$ increases with increasing $\langle n \rangle$ but unlike the result for assemblies permeated with water, quantum steps cannot easily be distinguished. The line through the data points is a guide to the eye. For the assembly with 3.9 nm ZnO nanocrystals, the mobility gradually increases for $0 < \langle n \rangle < 3$. A range with a constant mobility is not found here. This behavior can be understood by comparison of Figure 3.7 and 3.8. The filling of the $S$ levels with a second electron overlaps strongly with the filling of the $P$ levels. Therefore, the electron mobility changes much more gradually from $S$-$S$ tunnelling via $S$-$P$ tunnelling to $P$-$P$ tunnelling. The results with an assembly of 4.3 nm dots, however, suggest that there are again two regimes, i.e. tunnelling via the $S$ orbitals for $0 < \langle n \rangle < 1$ and tunnelling via the $P$ orbitals for $2.5 < \langle n \rangle < 4.5$. In between these two ranges there is again a gradual increase in the electron mobility due to larger overlap of the $S$ and $P$ single electron functions.

Remarkably, the electron mobilities are two to three times larger than for quantum-dot films permeated with water. Similar results were reported in another study [15]. The increased mobility in quantum-dot films permeated with PC compared to films permeated with water must be due to subtle changes in the tunnelling barriers between the quantum dots. Since the rate of tunnelling depends exponentially on the width ($W$) and the height ($V$) of the barrier, $\tau_{-1} \sim \exp(-W\sqrt{8m_eV/\hbar^2})$, subtle microscopic changes in the structure of the film will have measurable effects on the long-range mobility. For instance, the strong affinity of water for the ZnO surface might lead to a Zn(OH)$_2$ layer between two ZnO nanocrystals in the assembly which will increase the width of the tunnelling barrier. The adsorption of protons on the ZnO surface may also lead to changes in the height or width of the tunnelling barrier between two nanocrystals.

In our quantum-dot films, structural disorder is mainly related to the dispersion in the size of the quantum dots. The fact that we do not find a conductor-to-insulator transition, theoretically expected in the potential range at around $\langle n \rangle = 2$, is due to the simultaneous filling of $S$ and $P$ orbitals. For quantum-dot films permeated with aprotic solvents, the electron-electron repulsion energy seems to
enlarge the effects of the size-dispersion. As a result, the mobility increases gradually as $\langle n \rangle$ increases above two (see Figure 3.10B). Structural disorder in the quantum-dot assembly, and thus in the tunnelling distances, may also have a dispersive effect on the electron mobility (see Equations 3.6 and 3.7).

### 3.3.3 Temperature dependence of the electron transport

Here, we report on the temperature dependence of the electron transport through an assembly of ZnO quantum dots. We have studied a porous assembly of ZnO nanocrystals permeated with an aqueous electrolyte solution (the phosphate buffer with pH = 8) and two aprotic electrolyte solutions, 0.1 M tetrabutylammonium perchlorate in ethanol and in propylene carbonate. We have measured the conductance $G$ of the quantum-dot assembly between a source and drain electrode in a broad temperature range between room temperature and the melting points of the solvents (156 K for ethanol and 224 K for propylene carbonate). Since $\langle n \rangle$ is independently controlled, the temperature dependence of the conductance gives direct information on the temperature dependence of the electron mobility in the assembly of quantum dots. Thus, the effect of several phenomena, such as the energy mismatch between electron energy levels due to a dispersion in the size of the quantum dots and the Coulomb repulsion between the electrons in a quantum dot can be studied.

The striking difference between a ZnO quantum-dot assembly permeated with an electrolyte solution with water or with an aprotic electrolyte solvent such as ethanol or propylene carbonate is demonstrated in Figure 3.11. For nanocrystals with an average diameter of 4.3 nm, $\langle n \rangle$ can reach eleven if the assembly is permeated with water. However, $\langle n \rangle$ is at most three and four for PC and ethanol, respectively. This was also observed for quantum dots of different sizes (see Section 3.3.1). These results indicate that the electric charging energy, corresponding to the addition of an electron to a ZnO quantum dot, is much larger if the assembly is permeated with an aprotic solvent. This is confirmed by measurements of the differential capacitance for electron injection as a function of the electrochemical potential showing that the electric charging energy is smaller than $k_B T$ for assemblies permeated with water, but 4-6 times $k_B T$ for an aprotic solvent (see Section 3.3.1).

Figure 3.12 shows the source-drain conductance of a ZnO quantum-dot assembly permeated with ethanol as a function of the accumulation potential. The conductance increases promptly as soon as electrons are injected in the assembly. The conductance can increase by four orders of magnitude in the stability range.
Figure 3.11: The electron charge injected in an assembly of ZnO quantum dots (average diameter of the quantum dots is 4.3 nm) as a function of the accumulation potential of the assembly. The assembly has been permeated with an aqueous electrolyte solution and with the two aprotic solutions, i.e. 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 Section 2.5).

of the assembly. Similar results have been obtained with films permeated with propylene carbonate and water (see Section 2.3.2). This strongly indicates that the injected electrons occupy delocalized atom-like orbitals, not localized band gap states. This has been confirmed by optical and near-infrared spectroscopy (see Section 3.3.1) [20, 21]. A typical plot of the electron mobility in ethanol as a function of increasing electron number is shown as an inset in Figure 3.12: the mobility increases gradually with \( \langle n \rangle \), which is very similar to the results in propylene carbonate (see Section 3.3.2). A striking difference between aqueous and aprotic electrolyte solutions is that with aprotic electrolyte solutions the conductance and mobility of the quantum-dot film depend strongly on the temperature.

Figure 3.13A shows the conductance as a function of \( 1/k_B T \) measured with an assembly of ZnO quantum dots (4.3 nm in diameter) permeated with PC. The data were acquired between 293 K and the melting point of PC (224 K). The results obtained below the melting point of PC are not very reproducible, probably due to mechanical damage of the quantum-dot film and the film/metal contacts. The plots correspond to different accumulation potentials and thus to different
3.3. Results and Discussion

Figure 3.12: The conductance of an assembly of ZnO quantum dots permeated with an ethanol electrolyte solution (average diameter of the quantum dots is 4.3 nm) measured between a source and drain electrode as a function of the accumulation potential. Inset: The electron mobility as a function of the electron occupation number of the quantum dots.

electron occupation numbers (1.2 < \langle n \rangle < 3). In all cases, the logarithm of \( G_{sd} \) decreases linearly with \( 1/k_B T \) in the range \( 40 < 1/k_B T < 50 \). The data acquired at 224 K in PC are positioned slightly above the linear fits. The results show that the conductance increases exponentially with increasing \( T \); the thermal activation energy obtained for the slope of the plots is 81 meV (±10 meV) for \( \langle n \rangle = 1.2 \) and 101 meV for the maximum occupancy of the assembly; i.e. \( \langle n \rangle = 3 \). The results obtained with assemblies permeated with ethanol are very similar (Figure 3.13B); the thermal activation energy varies from 100 meV (for \( \langle n \rangle = 0.8 \)) to 122 meV (\( \langle n \rangle = 3.5 \)). Our results seem to indicate that the thermal activation energy increases slightly with increasing occupation of the quantum dots.

Thermally activated long-range charge carrier transport has been observed in molecular crystals [22], self-assembled super-lattices of gold [23] and cobalt [24] nanocrystals, and assemblies of CdSe quantum dots [10]. The thermal activation energy obtained from the temperature dependence of the conductance varied between 10 and 200 meV depending on the system studied. The results are com-
Figure 3.13: The source-drain conductance of an assembly of ZnO quantum dots (average diameter of the quantum dots is 4.3 nm) permeated with propylene carbonate (Fig. 3.13A) or with ethanol (Fig. 3.13B) as a function of $1/k_B T$. The plots are obtained with different accumulation potentials and thus different electron occupation in the quantum dots. Fig. 3.13A: $\langle n \rangle$ is 1.2 (●), 1.5 (■), 1.8 (▲), 2.2 (▼) and 3.0 (◆) respectively. Fig. 3.13B: $\langle n \rangle$ is 0.8 (●), 1.2 (■), 1.7 (▲), 2.0 (▼), and 3.5 (◆) respectively.
3.4. Conclusions

Monitored in terms of the orthodox Coulomb-blockade model in which the thermal activation energy found in the conductance is assigned to the electrical charging energy, $e^2/C$, needed to add an electron to a molecule, a metallic nanocrystal or a semiconductor quantum dot in the assembly. The conductance of a ZnO quantum-dot assembly permeated with water is independent of the temperature (5-35°C) showing that, in this case, the electric charging energy is smaller than $k_BT$. It also shows that the energy mismatch between the $S$ type conduction 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 thermal activation of electron transport. Thus, the strong temperature-dependence of the conductance of ZnO nanocrystal assemblies reported here must be assigned to the electric charging energy; i.e. the Coulomb-blockade effect. The electric charging energy is close to 100 meV for films permeated with ethanol or propylene carbonate, independent of the nature of the charge-compensating positive ions used in the film.

It is not entirely clear why the electric charging energy is much smaller if the film is permeated with water: the dielectric constants of the solvents are not very different. We conjecture that charge screening by protons chemisorbed on the surface of the ZnO nanocrystals or even intercalated in the ZnO lattice may lead to a very effective screening of the charge of the electrons. Our results suggest that the electric charging energy increases slightly with increasing electron occupation of the ZnO quantum dots. This is in contrast to the standard, i.e. constant capacitance model. Microscopic models which account both for dielectric polarization and electron-electron repulsion may be helpful in understanding such details [3].

3.4 Conclusions

We have used an electrochemically gated transistor to study the storage and transport of electrons in an assembly of ZnO quantum dots permeated with a PC or ethanol solution and we compared the results with those obtained in an aqueous solution in Chapter 2. The differential capacitance of the films shows the subsequent filling of the $S$ and $P$ orbitals of the ZnO quantum dots. Optical measurements show that localization of electrons in surface states between the HOMO and LUMO is not important.

The distribution in the size of the dots leads to an overlap between the $S$ and $P$ density-of-states. The electron-electron Coulomb repulsion in films permeated with an aqueous electrolyte is very small ($\leq k_BT$), but is much larger in propylene carbonate and ethanol (100-200 meV). As a result, less electrons per quantum
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dot can be injected in the films permeated with propylene carbonate and ethanol. From the low-temperature measurements we found a thermal activation energy of 80-120 meV. These values correspond quite well to the Coulomb repulsion of 100-200 meV found in the charging experiments.

The electron mobility measured as a function of the electron occupation per quantum dot in water shows that there are two quantum regimes in the long-range transport of electrons. In the first regime transport occurs by tunnelling from dot to dot via the $S$ orbitals, in the second regime tunnelling occurs via the $P$ orbitals. In propylene carbonate and ethanol, mixed tunnelling regimes are observed, due to the fact that the strong Coulomb repulsion energy masks the effects of quantum confinement.

It is shown that the quantum properties of individual nanocrystals in an assembly define the characteristics of long-range electron transport. The screening of the charge of the electrons depends strongly on the choice of the liquid permeating the porous assembly. On the basis of this work it would be interesting to investigate the role of the permeating electrolyte solution in more detail.

References


References


