Quantum regimes in long-range electron transport in an assembly of ZnO nanocrystals.

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In conventional photovoltaic solar cells, based on bulk semiconductors, absorption of a photon of energy ***h*ν** corresponds to the transition of an electron from the valence to the conduction band. The difference between the photon and band gap energy, i.e. E_g-$h\nu$ is lost by electron-phonon relaxation (heating). In order to reduce this loss, a number of solutions has been put forward; for instance the use of a number of different semiconductors in a tandem cell; or light absorbers consisting of units with a set of discrete electron levels, instead of bands. Colloidal nanocrystalline quantum dots, with their tunable atom-like energy levels, could be well suited for this purpose. It is required that the photogenerated electrons and holes occupying the different orbitals of the quantum dot do not relax to lower energies during their travel through the light absorbing layer. Thus, long-range transport of the photogenerated carriers is an important issue in future devices (including solar cells) based on quantum dots. The electronic properties of an assembly of quantum dots (a quantum dot solid) are determined by the coupling between the orbitals of individual quantum dot building blocks and the occupation of the orbitals with electrons (and/or holes).

We have studied the transport of ***electrons*** through an assembly of weakly coupled ZnO quantum dots. We have used an electrochemically-gated transistor (see Figure 1). The occupation of the electron orbitals is decided by the electrochemical potential of the ZnO assembly, which is controlled with respect to a reference electrode. The linear conductance of the assembly is measured between a source and drain electrode as a function of the number of electrons per ZnO quantum dot, which could be varied between 0 and 10.

The *capacitance* of the film during the injection of electrons reflects the sequential filling of the S and P atomic-like orbitals of the ZnO quantum dots. The *electron mobility*, derived from the source-drain conductance, shows a step-wise increase (staircase) as a function of the electron occupation per dot (see Figure 2). When the occupation number is below two, the mobility is 0.017 cm^2/Vs, while the mobility is increased to a constant value of 0.066 cm^2/Vs, for an occupation number between 2 and 8. We infer that transport occurs by tunneling between the S-orbitals of neighboring quantum dots at low occupation. The electron mobility becomes three times larger when the occupation number is between two and eight; tunneling now occurs between the P-orbitals. Long-range electron transport in an assembly of ZnO nanocrystals is thus critically determined by the quantum properties of the nanocrystalline building blocks.

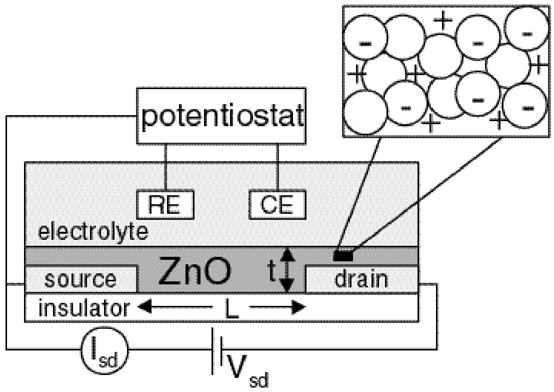

Figure 1: Schematic view of the electrochemically gated transistor with an assembly of ZnO quantum dots as active layer. The channel length (source-drain distance) is L (10μm), and the thickness of the conductive channel is denoted by t (~200nm). The electrochemical potential (and thus the electron density) of the active ZnO layer is controlled with respect to a Ag/AgCl reference electrode (RE) using a bipotentiostat; CE is a platinum counter electrode. The insert shows a detail of the active layer; the charge of the excess electrons in the quantum dots is counter-balanced by positive ions in the electrolyte, a 0.1 M phosphate buffer (pH=8), which permeates the layer. The conductance of the ZnO assembly at a given electron density is obtained by measurement of the source-drain current I_{sd} which is linearly dependent on the potential difference (1-10 mV) maintained between source and drain: $R^{-1}=I_{sd}/V_{sd}$.

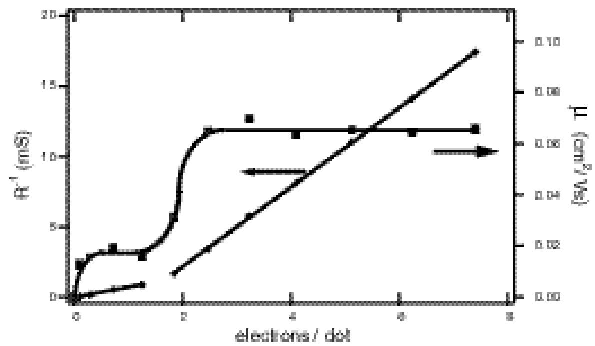

Figure 2: Transport properties of the ZnO quantum dot film. The source-drain conductance R^{-1} (circles) measured with an electrochemically gated ZnO quantum dot transistor (ZnO nanocrystals with an average diameter of 3.9 nm) and the corresponding electron mobility (squares) as a function of the average number of electrons per quantum dot $\langle \; \rangle$.