Storage and long-range electron transport of conduction electrons in an electrochemically gated assembly of ZnO quantumdots.

The effects of quantum confinement, Coulomb charging and disorder.

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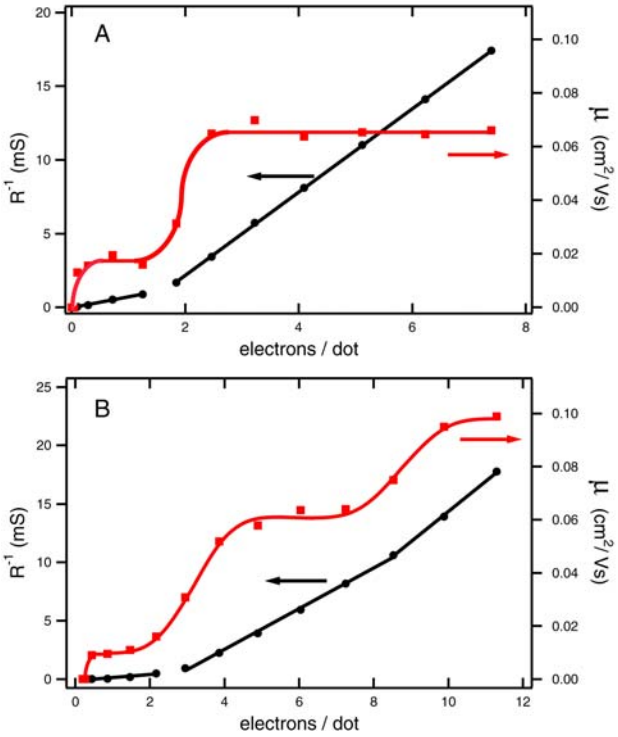
Colloidal semiconducting nanocrystals have attracted much scientific interest in the last decade. Such nanocrystals possess a set of discrete electron and hole energy levels, and a HOMO-LUMO band gap which depends on the size and shape of the nanocrystal. The optical and electrical properties of ensembles of colloidal nanocrystalline quantum dots[1] and single quantum dots[2] has been studied extensively.

Quantum dots can be assembled into quantum dot solids[3]. The optical and electrical properties of quantum dot solids will be determined by the atom-like orbitals of the nanocrystal building blocks and their electronic coupling, and Coulomb repulsion and disorder effects. Although these effects have been considered in some detail in theoretical work[4], experimental research in this field has just started.

An essential requirement in the research on quantum dot solids or assemblies is the control of the number of electrons per quantum dot i.e. the electron number N. This can be done, in principle, by using a gate electrode. In a field effect transistor, there is a two-dimensional charged layer in the active material[5]. The charge densities obtained in such a way are, however, relatively low, resulting in no more then one electron per quantum dot. In contrast, in porous quantum dot assemblies the charge of the conduction electrons can be compensated by positive ions in the electrolyte solution which is permeated in the quantum dot assembly. In such a way, the entire quantum dot assembly can be homogeneously charged with electrons, and the average number of electrons per quantum dot $\langle N \rangle$ can be as high as ten. This method of charge control is called *electrochemical gating*.

We have studied storage and transport of electrons in an assembly of ZnO nanocrystals (3-5 nm) using a transistor-type set-up with an electrochemical gate[6]. The average electron number $\langle N \rangle$ is controlled by the electrochemical potential of the assembly. Depending on the size of the ZnO nanocrystals and the electrolyte solution we could reversibly store between one and ten electrons in the atom-like S and P conduction orbitals of the ZnO quantum dots. Electrochemical reactions do not occur under these conditions. With optical experiments we showed that charge storage in surface band gap states is not important. Long-range transport in the ZnO assembly was studied by measuring the linear conductance between a source and drain electrode for varying $\langle N \rangle$. From these results, the electron mobility, the most fundamental transport parameter, could be obtained. The results with a ZnO quantum dot assembly, consisting of nanocrystals with a diameter of 3.9 nm (A), and 4.2 nm(B), permeated with an *aqueous* solution are shown in the Figure.



The mobility shows a constant value in the regime $0 < \langle N \rangle < 2$, in the second regime $2 < \langle N \rangle < 8$, a second regime is found with a constant mobility which is 3.5 times larger. In the first regime, only the atom-like S-orbitals are occupied, and the mobility reflects electron transport by tunneling events between the S-orbitals of adjacent quantum dots. In the second regime, transport occurs by tunneling via the P-orbitals. Transport was not affected by the temperature which indicates that the Coulomb charging energy was smaller than **kT**.

The results obtained with a propylene carbonate electrolyte solution permeating the quantum dot solid shows that the charging energy for injecting an electron in a quantum dot is about 200 meV, much higher than in aqueous solution. This has important consequences for the storage of electrons and the long-range transport.

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