SUPPLEMENTARY INFORMATION

Electron counting spectroscopy of CdSe quantum dots

Mariusz Zdrojek , Maria Jose Esplandiu, Amelia Barreiro and Adrian Bachtold

1. Electron counting spectroscopy

We here discuss the electron transfer mechanism in the device [R1]. Figure S1a shows the electrochemical potential of the carbon nanotube, the quantum dot and the gate. The gap in the dot corresponds to the addition energy, which is the energy needed to add one extra electron onto the dot. In addition, the scheme displays a thick barrier between the dot and the gate to emphasize that electrons do not tunnel through it. When the gate voltage V_g is swept, the electrochemical potential of the CdSe dot μ_{CdSe} changes as $\mu_{CdSe} = eV_g C_{CdSe-gate} /(C_{CdSe-gate} + C_{CdSe-NT})$ with $C_{CdSe-gate}$ the dot-gate capacitance and $C_{CdSe-NT}$ the dot-nanotube capacitance (Fig. S1b). When an empty level of the dot matches the electrochemical potential of the tube, an electron is transferred onto the dot (Fig. S1c). This shifts the electrostatic potential of the dot by the charging energy (Fig. S1d), which changes the charge density in the nanotube ρ_{tube} and therefore its conductance.

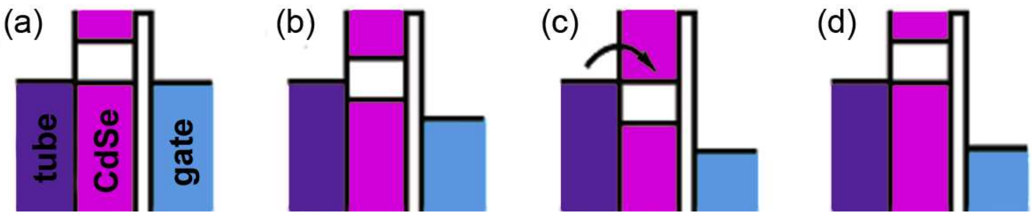

Fig. S1 Schematics of the potentials in the nanotube, the CdSe quantum dot and the gate. In this figure, the addition energy equals to the charging energy.

2. Determination of the charging energy and the averaged level spacing

The gate voltage shift V_g^{shift} can be evaluated assuming that it corresponds to the gate voltage for which $\rho_{tube}(N) = \rho_{tube}(N+1)$ with N the electron number in the quantum dot [R2]. Since $C_{CdSe-NT} >> C_{CdSe-gate}$, it reads

$$eV_g^{shift} = \frac{C_{CdSe-NT}}{C_{NT-gate} + C_{CdSe-gate}}\left(E_c + \Delta E\right) \qquad \text{(E1)}$$

where e is the electron charge, $C_{NT-gate}$ is the nanotube-gate capacitance, and ΔE is the level spacing. The charging energy is given by

$$E_c = e^2 / C_{CdSe-NT} \qquad \text{(E2)}$$

The separation in gate voltage between two electron transfers is

$$eV_g^{jump} = \frac{C_{CdSe-NT}}{C_{CdSe-gate}}\left(E_c + \Delta E\right) \qquad \text{(E3)}$$

Note that the electron-transfer events are stochastic processes [R1]. Indeed, the V_g value for which a shift occurs in $G_{tube}(V_g)$ measurements changes for different V_g sweeps. For this reason, V_g^{shift} is more straightforward to analyse than V_g^{jump} and we look at the statistical aspects of V_g^{shift} and not V_g^{jump} in Fig. 4. We get from equations (E1) and (E3)

$$\frac{< V_g^{jump} >}{< V_g^{shift} >} = \frac{C_{NT-gate} + C_{CdSe-gate}}{C_{CdSe-gate}} \qquad \text{(E4)}$$

Finally, V_g^{gap} the gap in the gate voltage in Fig. 3 is related to the energy gap of the semiconducting quantum dot $E_g \approx 2$ eV by:

$$eV_g^{gap} = \frac{C_{CdSe-NT}}{C_{CdSe-gate}} E_g \qquad \text{(E5).}$$

We have $< V_g^{shift} >$ = 114 meV, $< V_g^{jump} >$ = 156 meV, and V_g^{gap} = 14 eV for sample A. In addition, the fit of the bimodal Wigner distribution to the shape of the distribution in Fig. 4c gives $C_{CdSe-NT} /(C_{NT-gate} + C_{CdSe-gate})E_c$ = 86 meV and $C_{CdSe-NT} /(C_{NT-gate} + C_{CdSe-gate}) < \Delta E >$ = 68 meV. Using equations E2, E4, and E5, we get α=3.7, E_c = 23 meV and $<\Delta E>$ = 18 meV. We apply the same analysis to sample B and obtain E_c = 19 meV and $<\Delta E>$ = 15 meV. For purposes of comparison, Klein *et al.* obtained E_c = 14 meV and ΔE ~ 15 meV for a CdSe quantum dot contacted to two gold electrodes [R3]. These values are quite close to the ones we have found.

We notice that the above analysis is expected to provide only a rough estimate for E_c and ΔE. Indeed, the model assumes that it is possible to obtain the same charge density in the nanotube by adding an electron to the quantum dot or sweeping V_g (by the amount V_g^{shift}). However, the model does not take into account the fact that the electrostatic potential profile along the nanotube may be different depending upon whether an electron is added or V_g is swept. This can somewhat affect V_g^{shift}.

3. Spectrum distribution for electrons and holes

Figure S2 shows that the V_g^{shift} distributions for the electron and hole states are quite similar. This is rather surprising, since $<\Delta E>$ of electrons is expected to be different at first sight from that of holes. Indeed, the effective mass of electrons is $0.13m_0$ and that of holes is $0.45m_0$ with m_0 the electron mass. However, the electric field experienced by the quantum dot is huge and can modify the electronic states dramatically [R4,R5]. The electric field E_r can be estimated by considering a coaxial cable, $E_r = \frac{V_g}{r \ln(b/a)}$ with b=1µm the tube-gate distance and a=0.5 nm the tube radius. We obtain E_r = 13 V/nm for r=0.5 nm and V_g=50 V.

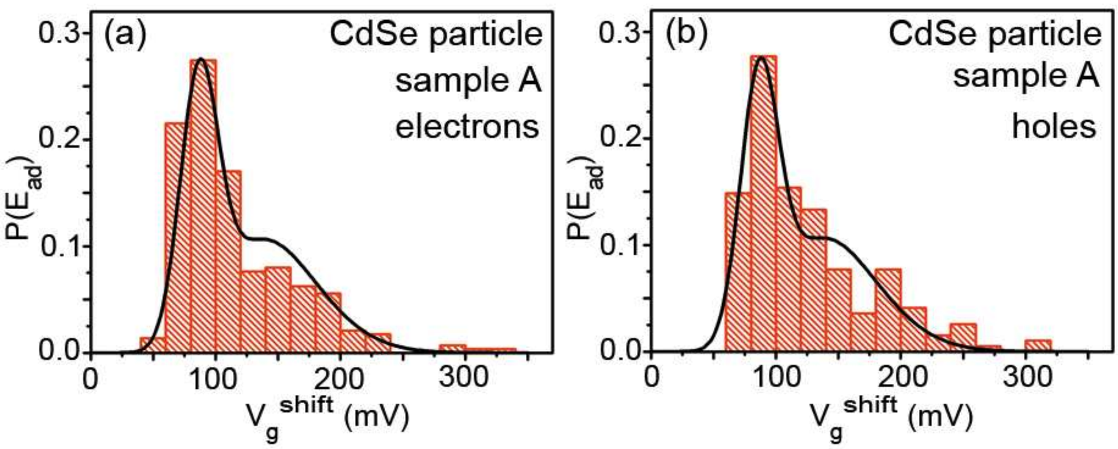

Fig. S2 Spectrum distribution of V_g^{shift} for a CdSe quantum dot (sample A). **a**, Spectrum distribution for electron states. **b,** Spectrum distribution for hole states.

4. Counting electrons tunneling out from the quantum dot when increasing V_g

One of the important findings in our experiment is the ability to add many electrons to the quantum dot by increasing V_g. The question is whether some of the electrons tunnel out of the dot back onto the tube during the V_g sweep. Such question can be answered by looking at the direction of the $G_{tube}(V_g)$ shifts. An electron tunneling out of (into) the dot into (out of) the tube causes the $G_{tube}(V_g)$ curve to shift to the left (right). Figure S3 shows that the number of electrons tunnelling out of the dot is very low (about 2% of the overall number of shifts). In addition, the probability of an electron tunneling out increases at large positive V_g values. This can be attributed to the intense electric field at the dot-nanotube interface, which lowers the tunnel barrier.

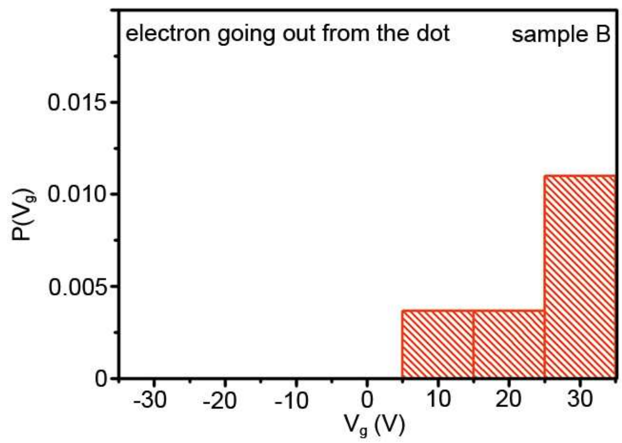

Fig. S3 Histogram of electrons tunneling out of the dot as a function of the gate voltage. The histogram is normalized with respect to the total number of tunnel events.

References

[R1] A. Gruneis, M.J. Esplandiu, D. Garcia-Sanchez, A. Bachtold, Nano Lett. **7**, 3766 (2007).

[R2] K. Yano *et al.*, Proc. IEEE **87**, 633-651 (1999).

[R3] D. L. Klein *et al.,* Nature **389,** 699 (1997).

[R4] K. Chang, J.-B. Xia, J. Appl. Phys. **84**, 1454 (1998).

[R5] E. Menendez-Proupin, C. Trallero-Giner, Phys. Rev. **B** 69, 125336 (2004).