

Resonant electron tunneling through semiconducting nanocrystals in a symmetrical and an asymmetrical junction

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(Received 20 April 2000; revised manuscript received 26 June 2000)

We studied resonant electron tunneling through individual CdSe and CdS nanocrystals in two types of configuration. With nanocrystals electrodeposited on bare gold, the spectra show resonant tunneling via discrete unoccupied (CB region) and occupied levels (VB region) at positive and negative bias, respectively. In this asymmetrical configuration, the bias is only distributed across the tip/dot barrier; this allows one, in principle, to derive the electronic structure of nanocrystals from tunneling spectra. With colloidal nanocrystals covalently anchored to a gold substrate via hexane dithiol, tip-to-gold and gold-to-tip tunneling occurs via the same set of unoccupied levels.

There is a growing interest in the size-dependent electrical and optical properties of insulating nanocrystals.^{1,2} Scanning tunneling spectroscopy under cryogenic and ambient conditions has been used to study the electronic structure of nanocrystals with a large band gap (>1 eV), such as CdS,³ CdSe,⁴ and InAs.⁵ The current I through the substrate/dot/tip double-barrier tunnel junction (DBTJ) is measured as a function of the bias V (defined here as the Fermi level of the tip electrode minus the Fermi level of the substrate, $E_{F,tip} - E_{F,sub}$). Usually, tunneling spectra, i.e., plots of the differential conductance $\partial I/\partial V$ as a function of V , feature a wide region (1–3 eV) around zero bias in which $\partial I/\partial V$ is close to zero. A series of peaks on both sides of this region have been assigned to resonant tunneling between tip and substrate, via discrete unoccupied electron levels [conduction band] and occupied levels [valence band] of the quantum dot.

An important problem in the interpretation of the tunneling spectra is the distribution of the applied bias V over both barriers of the substrate/dot/tip junction. A straightforward interpretation is only possible if the bias is distributed in an *asymmetrical* way over the DBTJ; thus when the Fermi level of one of the electrodes (usually $E_{F,sub}$) has a constant position with respect to the energy levels in the dot, and the Fermi level of the other electrode ($E_{F,tip}$) scans through the energy range of interest with $\partial E_{F,tip}/\partial V \cong 1$. Datta *et al.* have discussed this topic in relation to tunneling spectroscopy with molecules covalently bound to the substrate.⁶ The problem has also been recognized in studies of the electronic structure of semiconducting quantum wells⁷ and quantum dots with a large band gap. For instance, Banin *et al.* reported that the tip should be retracted from the dot in order to ensure that the bias drops predominantly over the tip/dot junction.⁵ However, how resonant tunneling through quantum dots depends on the distribution of the applied bias across the substrate/dot/tip junction has not been systematically investigated.

We studied resonant electron tunneling through CdS and CdSe crystals of varying size in the nanometer range with two types of substrate/dot/tip configuration (Fig. 1); the distribution of the bias across the junction was systematically investigated by variation of the tip-to-dot distance. In the first type of configuration [Fig. 1(a)], CdS or CdSe nanocrystals were electrodeposited epitaxially on a bare gold substrate.^{3,4} It will be shown that the tunneling spectra reveal

the band gap and resonant tunneling through discrete unoccupied (positive bias) and occupied levels (negative bias) of the nanocrystal, independent of the tip-to-dot distance. This shows that the bias is distributed asymmetrically across this junction. The second type of configuration [Fig. 1(b)] is formed by covalent anchoring of colloidal CdS and CdSe nanocrystals to a self assembled monolayer of hexane dithiol or cyclohexylidene disulfide.⁸ The tunneling spectra depend strongly on the tip-to-dot distance; at sufficiently small distance, resonant tunneling at positive and negative bias occurs only via the discrete unoccupied levels of the nanocrystal.

Single epitaxially deposited quantum dots are obtained with the narrow size distribution at around 5 nm. With TEM it has been shown that the as deposited nanocrystals are not connected.⁹ CdSe and CdS nanocrystals with sizes between 1 and 10 nm could be obtained by a slight variation of the deposition conditions. Figure 2(b) shows quantum dots covalently anchored, in a sub-monolayer, at a gold/hexane dithiol SAM substrate. Tunneling spectroscopy, probing individual nanocrystals, is possible with both types of samples by positioning the tip above a dot that is somewhat isolated from the others.

Figure 3 shows tunneling spectra obtained with 10 nm-large CdSe dots electrodeposited on a gold substrate for three tip-to-dot distances. The bias range around $V=0$ in which

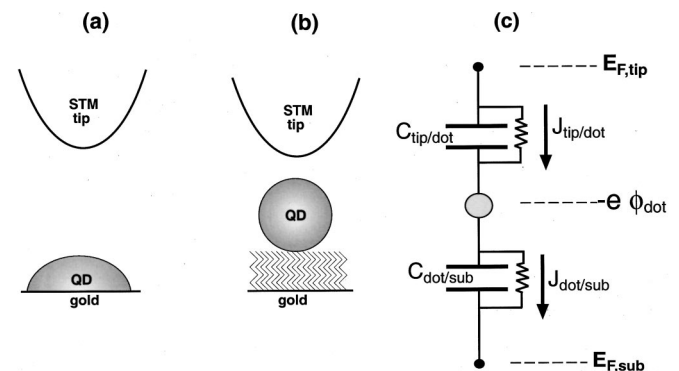


FIG. 1. Double-barrier tunnel junctions formed by a metal substrate, a semiconducting quantum dot (QD), and the tip of an STM. (a) A semiconducting nanocrystal is electrodeposited on bare gold. (b) A colloidal nanocrystal is covalently anchored on the gold substrate via an alkane dithiol self-assembled monolayer. (c) Electrical equivalent circuit corresponding to the double-barrier tunnel junction (see text). (In scheme a, the presented shape of the electrodeposited dot is not meant to be realistic.)

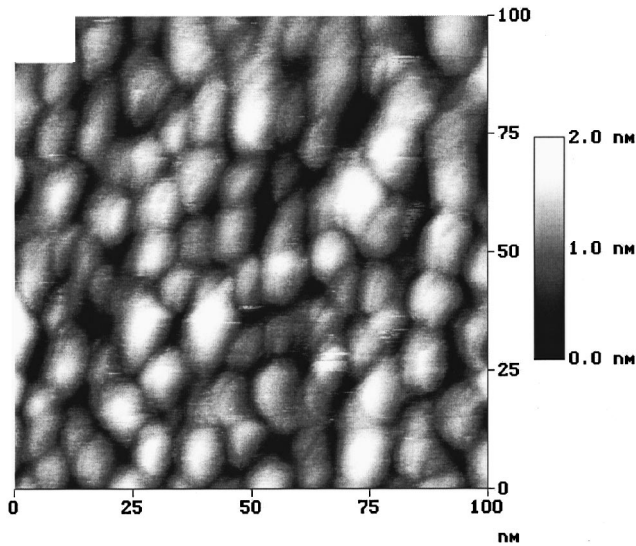


FIG. 2. STM image of CdSe colloids that are anchored on a gold substrate covered with a hexanedithiol SAM.

$\partial I/\partial V=0$ is about 1.8 eV wide, a value close to the band gap of macroscopic CdSe (1.84 eV). This agrees with the fact that a 10 nm-large CdSe dot has an electronic structure which is close to that of a macroscopic crystal. The essential features of the spectra *do not* change with the tip-to-dot distance. Very importantly, $\partial I/\partial V$ rises much slower with increasing negative bias ($E_{F,tip} < E_{F,sub}$) than with increasing positive bias. Similar results are obtained with electrodeposited CdS nanocrystals. The results obtained with electrochemically grown crystals of variable size will be discussed below.

Figure 4 presents tunneling spectra for CdSe colloidal nanocrystals (diameter of 3.2 nm, optical band gap of 2.3 eV) that are covalently anchored to a hexane dithiol SAM layer on the gold substrate. The shape of the spectra depends critically on the tip-to-dot distance, in contrast to those measured with the electrodeposited crystals. The spectra show a small region of low conductance. The width of this region

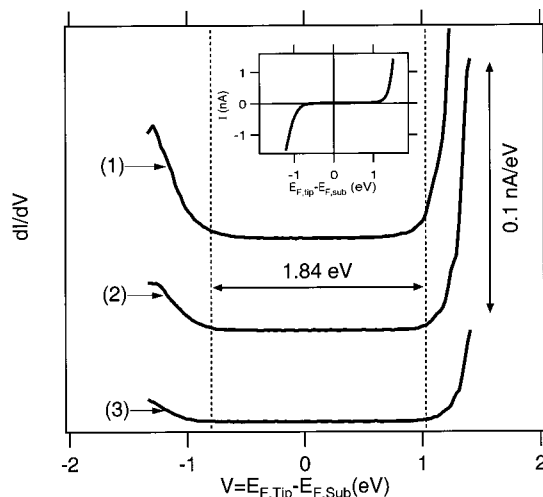


FIG. 3. Spectra of the differential conductance, dI/dV vs V , measured with CdSe nanocrystals (10 nm) that are electrochemically deposited on bare gold. Three different tip-to-dot distances are used, corresponding to the following settings: $V=1.2$ eV; (1) $I=1.0$ nA, (2) $I=0.1$ nA, and (3) $I=0.02$ nA. The insert shows a typical I vs V curve.

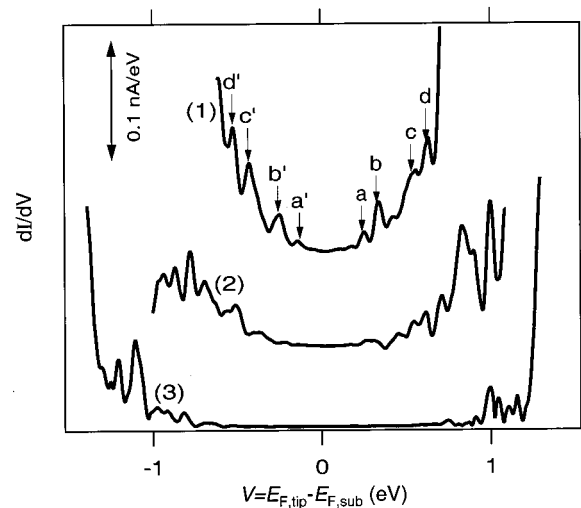


FIG. 4. Spectra of the differential conductance, dI/dV vs V , measured with colloidal CdSe nanocrystals ($d=3.2$ nm; optical bandgap 3.2 eV), which are covalently bound to gold via a hexanedithiol SAM. Three different tip-to-dot distances are used, corresponding to the following settings: $V=1.2$ eV, (1) $I=2.0$ nA, (2) $I=1.0$ nA, and (3) $I=0.2$ nA.

depends strongly on the tip-to-dot distance; it does not correspond to the band gap of the nanocrystal. Spectra obtained at a sufficiently small tip-to-dot distance suggest symmetry with respect to zero bias; curve 1, for instance, shows twin peaks (a, a'), (b, b'), and an equally steep slope of $\partial I/\partial V$ at positive and negative bias.

Figure 5 shows tunneling spectra obtained with electrodeposited CdSe nanocrystals, of varying size. The energy range with very small conductance increases from 1.8 eV for the 10 nm dots to 1.92 eV for dots of 5 nm in diameter, and 2.3 eV for dots of 2 nm in diameter. This illustrates the increase in the band gap with decreasing size of the dots. Despite the strong coupling of the dots to the metal, size-quantization of the electronic structure is clearly observed. Sharp peaks (width 50 meV), together with smaller satellites are found at positive bias. In the opposite bias region, the peaks are typically lower, and $\partial I/\partial V$ increases less steeply with increasing deviation from equilibrium. It should be remarked that tunneling spectra obtained with different nanocrystals (of a given size) show similar features, but are not completely identical. The peaks at positive bias ($E_{F,tip} > E_{F,sub}$) are due to tip-to-dot-to-substrate tunneling via discrete unoccupied levels. The peaks in the opposite bias region correspond to substrate-to-dot-to-tip tunneling via discrete occupied electron levels.

The distribution of the bias, $V=E_{F,tip}-E_{F,sub}$, over the two barriers of the junction is calculated by applying the laws of Kirchoff to the electrical equivalent scheme presented in Fig. 1(c); we assume that the quantum dot has a uniform potential φ_{dot} . The tip/dot and dot/substrate barriers are characterized by the capacitances $C_{tip/dot}$ and $C_{dot/sub}$, respectively. The currents $J_{tip/dot}$ and $J_{dot/sub}$ correspond to single electron tunneling. It is found that:

$$e\partial(\varphi_{dot}-\varphi_{tip}) = \frac{C_{dot/sub}}{C_{dot/sub}+C_{tip/dot}} \partial V + e \frac{\int (J_{dot/sub}-J_{tip/dot}) dt}{C_{dot/sub}+C_{tip/dot}}. \quad (1)$$

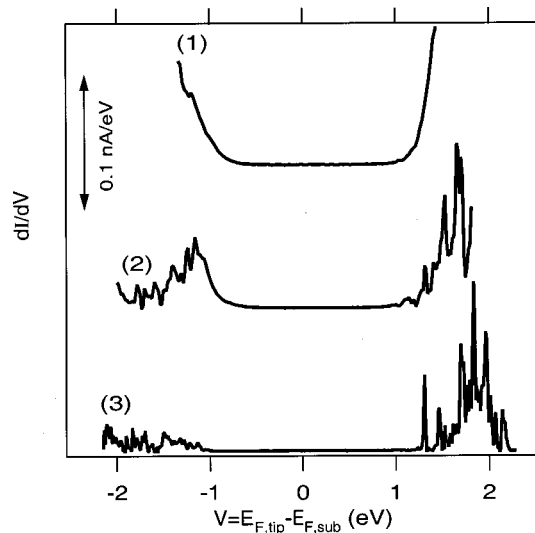


FIG. 5. Spectra of the differential conductance, dI/dV vs V , measured with electrodeposited CdSe nanocrystals. The setting is: $V=1.2$ eV; $I=0.1$ nA. The diameters of the crystals are (1) 10 nm, (2) 5 nm, and (3) 2 nm. The bandgap indicated by the spectra are (1) 1.73 eV, (2) 1.92 eV, and (3) 2.3 eV, respectively.

The second term on the right hand side accounts for the charging energy due to occupation of the nanocrystal with one or more additional electrons or holes.¹⁰ With an insulating nanocrystal, one can distinguish different contributions to the charging energy. A first electron (or hole) injected in the nanocrystal induces a polarization of the bonding electrons. The dielectric stabilization is limited by the small dimensions.¹¹ The charging energy paid for the first electron is called the polarization energy (denoted as E_e for the electron and E_h for the hole). When more electrons are injected into the nanocrystal, Coulomb interactions between the injected electrons forms another contribution to the charging energy.¹¹ These interactions depend on the dynamics of electron tunneling and relaxation in the particle¹² and will be discussed elsewhere in detail. If the semiconducting nanocrystal is in the ground state, i.e., does not contain an additional electron or hole, the distribution of the bias V over both barriers of the junction is determined by the first term on the right hand side. This holds in the bias range in which $\partial I/\partial V \cong 0$; by integration of Eq. (1) it is then found that $e(\varphi_{dot} - \varphi_{tip}) = V[C_{dot/sub}/(C_{dot/sub} + C_{tip/dot})]$. The spec-

tra obtained with electrodeposited CdSe and CdS nanocrystals can be explained by assuming that $C_{dot/sub} > C_{tip/dot}$ for all tip-to-dot distances that we have used. This is a reasonable assumption since the Au/CdSe interface consists, very probably, of an electrical double layer of molecular dimensions, with a large capacitance. It then holds that $e(\varphi_{dot} - \varphi_{tip}) \cong V$; a change of the bias results in an equal change of the tip Fermi level with respect to energy levels of the dot, while the Fermi level of the substrate remains unchanged. In this asymmetrical configuration, the tip Fermi level scans over the energy levels of the nanocrystal [see Figs. 6(a) and 6(b)]. The onset of $\partial I/\partial V > 0$ at positive bias corresponds to resonant tunneling from the tip-to-the-substrate via a discrete unoccupied level, see Fig. 6(a). The onset of $\partial I/\partial V > 0$ at negative bias indicates resonant tunneling from the substrate-to-the-tip via a discrete occupied level, see Fig. 6(b). In the latter case it is expected that the effective barrier height for tunneling is much larger. As a result, the differential conductance $\partial I/\partial V$ (and the height of the peaks in resonance) must be lower in the negative bias range. This is, indeed, observed with electrochemically grown CdS and CdSe nanocrystals (see Figs. 3 and 5). With such asymmetrical configurations it is possible, in principle, to derive from the spectra the band gap (the energy difference between LUMO and HOMO) and the level spacing in the conduction and valence bands.¹⁰

The spectra obtained with colloidal CdSe and CdS nanocrystals anchored at the substrate by hexane dithiol (Fig. 4) show that the bias is distributed over the two barriers of the junction, especially if the tip-to-dot distance is relatively small. The almost symmetrical spectra obtained with small tip-to-dot distances (curve 1) indicate resonant tunneling through the *same set* of electron levels at positive as well as at negative bias. Thus, the effective barrier height must be equal in both regions of bias. This agrees with our results which show that $\partial I/\partial V$ and the heights of the peaks are of equal magnitude in both bias regions, in sharp contrast to the case of nanocrystals electrodeposited on bare gold. The relatively high values of $\partial I/\partial V$ indicate that these levels are unoccupied levels in the energy region of the conduction band. It remains to be explained why the (symmetrical) pairs of resonances are observed so close to the point of zero bias. A possible explanation might be found in the electrostatic interaction between the crystal dipole of the dot with the image charges in the metal electrodes,¹³ which can lead to a

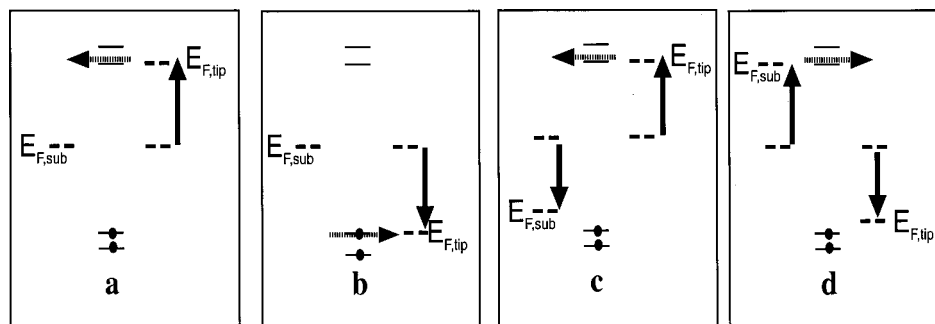


FIG. 6. Schematic representation of the discrete electron levels of a quantum dot with respect to the Fermi levels of the substrate and tip. (a,b) Asymmetrical configuration: the shift of the tip Fermi level (black arrow) with respect to the electron levels in the crystal correspond to the bias $V (=E_{F,tip} - E_{F,sub})$, tunneling occurs via unoccupied levels (a) and the occupied levels (b) at positive and negative bias, respectively. (c,d) Symmetrical configuration: The Fermi level of the tip and the substrate shift with respect to the electron levels in the crystal when a bias is applied; (c) positive bias: tip-to-substrate tunneling occurs mainly via the unoccupied levels; (d) negative bias: substrate-to-tip tunneling occurs via the same set of unoccupied levels.

lowering of the energy levels of the nanocrystal with respect to the Fermi level in both electrodes.

We conclude that the tip-to-dot distance is a critical parameter if tunneling spectroscopy is used to determine the electronic structure of colloidal nanocrystals. This is convincingly illustrated with the spectra shown in Fig. 7 obtained with 4.3 nm large colloidal CdSe nanocrystals at 4 K. Spectrum *a* features tunneling through discrete levels of the conduction band both at negative and positive bias. However, when the tip-to-dot distance is considerably increased [Fig. 7(b)], an asymmetrical spectrum is obtained. The conductance peaks at positive bias correspond to tunneling through the levels of the conduction band, whereas (the much lower) peaks at negative bias correspond to tunneling through levels of the valence band. The energy diagram of discrete electron levels which can be derived from such a spectrum will be discussed in detail elsewhere. Here, we report that the set of peaks observed at positive bias is very typical for this type of CdSe nanocrystals; the set is in fair agreement with the energy levels in a quantum box with cubic symmetry. The region of very low conductance is 2.5 eV. It corresponds to the band gap and the polarization energies of an electron and hole, $E_e + E_h$. From the optical absorption spectrum and the electron-hole attraction energy it follows that the band gap is 2.28 eV for these CdSe nanocrystals. We thus estimate that $E_e + E_h$ is 0.22 eV.

It is clear that the distribution of the bias over both barriers of a substrate/nanocrystal/tip configuration forms an essential element in the interpretation of tunneling spectra. We provide experimental results showing that the entire electronic structure of a nanocrystal can be studied conveniently by tunneling spectroscopy if the bias is distributed very asymmetrically over both barriers. This means that the essential features of the tunneling spectra must be independent of the tip-to-dot distance. In addition, the spectra in the negative and positive bias regions must reflect the difference in the

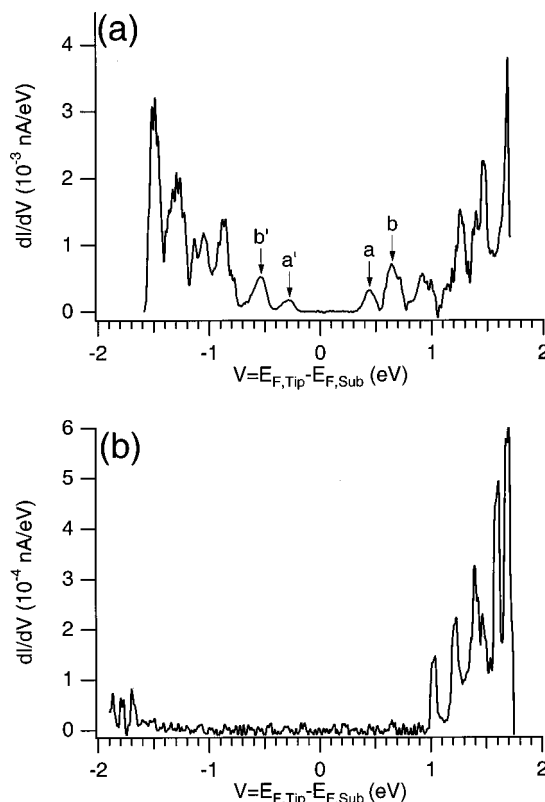


FIG. 7. Spectra of the differential conductance, dI/dV vs V , measured with colloidal CdSe nanocrystals (4.3 nm) on cyclohexyldenedisulfide-SAM on gold under vacuum at 4.2 K. The corresponding settings are: $V = 1.4$ eV (a) $I = 150$ pA, (b) $I = 5$ pA.

barrier height.

We wish to thank Professor L. Kouwenhoven [Department of Applied Physics, University of Delft] and Professor H. van Kempen [Department of Physics, University of Nijmegen] for their interest in this work.

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