

Breaking and restoring a molecularly bridged metal|quantum dot junction

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Nanometer-sized insulating quantum dots (CdSe and ZnO) have been attached to a Au(111) substrate, using molecular bridges with thiol and carboxylate end functions. We demonstrate that the quantum dots can be probed by a scanning tunneling microscope at negative substrate bias. At positive bias, however, the gold–sulfur bond is broken and the quantum dots are transferred to the tip. Individual CdSe quantum dots can be picked up by the tip and displaced on the substrate in a controlled way. © 2002 American Institute of Physics. [DOI: 10.1063/1.1525396]

The chemical approach to nanostructured systems consists of a bottom-up construction of materials using chemical and physicochemical principles.¹ Typical building blocks are metal and insulating nanocrystals, which show striking optical and electrical properties.^{2,3} With bifunctional molecules that either link the colloids or bind the colloids to the substrate, these particles can be processed into nanodevices.^{4–6} An important element in this approach is the linking of colloidal nanocrystals to a conducting substrate. For instance, alkanedithiols have been used as molecular bridges to anchor gold nanocrystals and CdSe and InAs quantum dots to a substrate. In this way, the electronic properties of InAs and CdSe quantum dots could be measured by tunneling spectroscopy^{7,8} and the first transistor based on a single quantum dot was fabricated.⁵ Obviously, the stability of molecular bridges during electron transport is of paramount importance for electrical spectroscopy and applications of quantum dots in nanodevices.

In this letter, we report on the stability of gold|molecular bridge|quantum dot junctions under conditions of electron tunneling. We tested several dithiol molecules in combination with CdSe quantum dots and a thiol-carboxylate bridge in combination with uncapped ZnO quantum dots. We found that that molecular bridges [1,3-propanedithiol (PDT); 1,6-hexanedithiol (HDT), and 1,4-benzenedimethylthiol (BDMT), see Fig. 1] link the CdSe quantum dots to the gold substrate. However, when probing the quantum dots with a scanning tunneling microscope (STM) under ambient conditions, we discovered that the dithiol link only survives negative substrate potentials. If the substrate potential is raised above 250–500 mV, the quantum dots are transferred from the substrate to the tip. Uncapped ZnO quantum dots, linked to gold by 3-thiopropionic acid (see Fig. 1), are transferred to the tip at substrate potentials exceeding 500 mV as well. This yields evidence that this bridge failure is due to the Au–S bond. Clearly, this questions the use of molecular links based on this bond. However—in the case of semiconductor

quantum dots attached to Au(111)—it also opens the possibility of quantum dot manipulation using a STM. We demonstrate that, by using the potential-dependent linking properties of dithiols, individual quantum dots can be attached to the tip and distributed in a controlled way on the substrate.

The CdSe nanocrystals were synthesized at elevated temperature in a mixture of trioctylphosphine/trioctylphosphine oxide and hexadecylamine.⁹ The particles had a narrow size distribution with an average diameter of 3.5 nm. For the attachment, three routes were followed. First, a flame-annealed Au(111) surface was provided with a BDMT monolayer by immersion in a 10 mM solution of BDMT in ethanol for 30 min, followed by 12 h of annealing in ethanol at 60°. Monolayer formation was demonstrated by measuring the capacitance of the Au surface in 0.1 M NaClO₄; this decreased after treatment with BDMT from 18 to 2 $\mu\text{F cm}^{-2}$ at 0 V vs SCE. A submonolayer of CdSe quantum dots was formed by immersing the Au|BDMT sample in a 1 μM solution of CdSe quantum dots for 1–5 min (Fig. 1). Second, we dispersed a known amount of CdSe colloids (1 μM) in toluene and added ten molecules of HDT or PDT per quantum dot. In this case, a submonolayer of CdSe quantum dots was formed by immersing a Au sample in these solutions for 1–5 min. Third, a test sample was made by immersing a bare gold sample in a thiol free CdSe dispersion; this also yielded submonolayers of CdSe quantum dots on the gold surface.

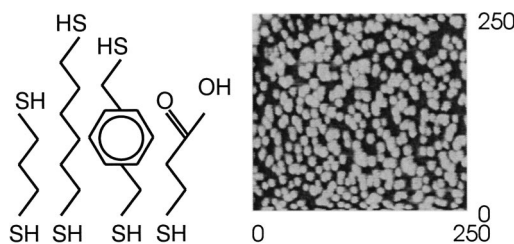


FIG. 1. Left. Representation of the different linker molecules used: (a) PDT, (b) HDT, (c) BDMT, and (d) 3-thiopropionic acid. Right. Atomic force microscopy image ($250 \times 250 \text{ nm}^2$) of a submonolayer of CdSe quantum dots attached to a Au(111) substrate by a BDMT monolayer.

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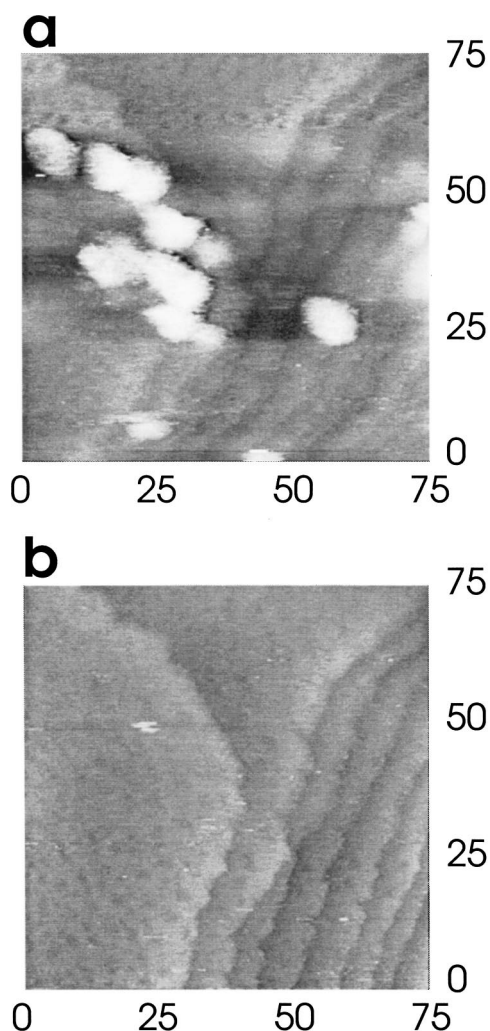


FIG. 2. (a) STM image of CdSe nanocrystals attached to a Au(111) substrate by HDT linker molecules. Bias potential: -250 mV. (b) STM image of the *same* spot on the substrate surface as in Fig. 2(A). Bias potential: $+500$ mV. Scaling in nanometers.

All gold|CdSe samples could be imaged by tapping mode atomic force microscopy (AFM). Although AFM indicated a density of quantum dots similar to that shown in Fig. 1, the CdSe nanocrystals attached to the gold by van der Waals forces only (method 3), could not be imaged by STM (only bare gold was seen). The layers of CdSe linked via dithiol molecules to a Au(111) surface could be imaged by STM at negative substrate potential. This is demonstrated by Fig. 2(a), which shows HDT-linked CdSe nanocrystals on a Au(111) surface imaged at -250 mV. The substrate potential could be decreased to -2000 mV, without affecting this result. However, if the substrate potential was raised above 500 mV, the quantum dots could not be observed. This is demonstrated by Fig. 2(b), which was obtained on the *same* spot of the gold surface as Fig. 2(a), at a substrate potential of $+500$ mV. At a potential of 250 mV, the quantum dots are partially removed from the substrate surface. Similar results were obtained with CdSe nanocrystals linked to the gold substrate with PDT or BDMT.

To understand what happens with these quantum dots, we made a series of three scans at the same spot on the surface of a sample with HDT-linked CdSe nanocrystals: a large area scan (200×200 nm) at negative bias potential

(-1000 mV), a small area scan (50×50 nm) at positive bias ($+1500$ mV) and again the large area at negative bias. As a result of the scanning at $+1500$ mV, a quantum dot free area of 50 by 50 nm is created in the center of the image. However, no additional quantum dots were found outside this area. Again, identical results were obtained in the case of linking via PDT or BDMT. We conclude that the CdSe quantum dots are not shunted by the STM tip but are transferred from the substrate to the tip.

A similar effect was found using uncapped ZnO quantum dots (3.3 nm in diameter)—made from zinc acetate and lithium hydroxide¹⁰—which were linked to Au(111) by a monolayer of 3-thiopropionic acid. In this case, linking is achieved by the thiol group binding to the gold and the carboxyl group binding to the ZnO.¹¹ A submonolayer of ZnO quantum dots could be formed by immersing the modified gold sample in the ZnO sol. Imaging of the ZnO nanocrystals was possible at negative bias potentials. Increasing the substrate potential to above 500 mV induced a transfer of the quantum dots from the substrate to the tip.

The transfer of semiconductor nanocrystals from the substrate to the tip can be seen as a two-step process: breaking of the link between the nanocrystal and transfer of the nanocrystal to the tip. A dielectric sphere in an inhomogeneous electric field moves towards the region of highest field strength.¹² This explains the transfer of the nanocrystal to the tip, since the highest field is found at the tip. The fact that we obtained similar results with CdSe quantum dots linked via several types of dithiol molecules and ZnO quantum dots linked via thiopropionic acid strongly suggests that the failure of the nanocrystal-substrate link is due to the breaking of the gold-sulfur bond. The strong asymmetry of the bond breaking can be explained as follows.¹³ Since the Au-S bond is closer to the substrate than to the tip, electrons entering this bond will have gained more energy by crossing the barrier when tunneling from the tip to the substrate (positive potential) than when tunneling from the substrate to the tip (negative potential). Hence, at positive potential, STM-induced excitations are possible at lower absolute values of the bias than at negative potential. The detailed mechanism of bond breaking remains unclear. Avouris and co-workers describe various STM-induced bond-breaking mechanisms:¹⁴ field induced desorption, electronic excitation, and vibrational excitation. In addition, alkanethiol monolayers can be desorbed from a gold surface by electrochemical reduction when the potential drop across the Au-S bond exceeds 600 mV.¹⁵ We found that the potential difference involved in the breaking of the Au-S bond is 500 mV or less. This makes field induced desorption and electronic excitation unlikely as bond-breaking mechanisms and it also questions the possibility of vibrational excitation since the desorption yield is relatively high ($>3 \times 10^{-9}$ quantum dots per electron, see later). Rather, this moderate threshold potential suggests a common origin of reductive desorption of alkanethiol monolayers and STM-induced desorption of the Au-S bond.

It is clear that the failure of the Au-S bond imposes a strong restriction on the bias range in which thiols and dithiols can be used as molecular linkers, although they have been used successfully in the past.^{5,7} However, as demonstrated by Fig. 3, it also opens the possibility of manipulating

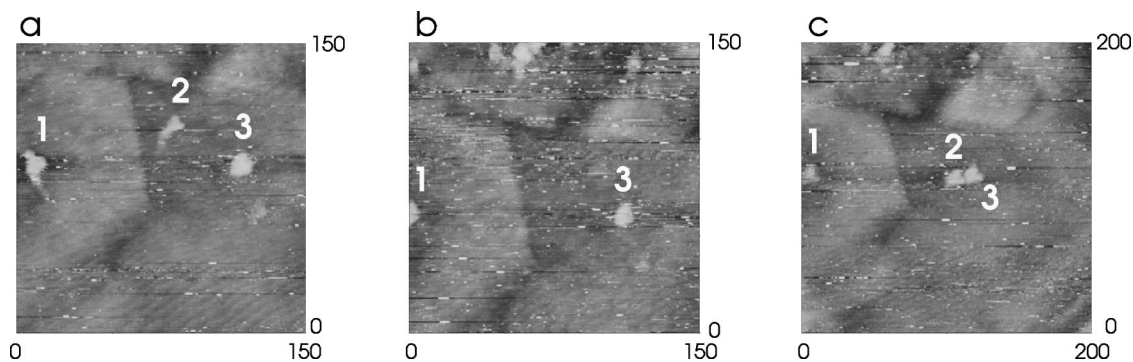


FIG. 3. (a) STM image of three CdSe nanocrystals attached to a Au(111) substrate. (b) Image of the same spot on the Au(111) surface after quantum dot 2 has been selectively transferred to the STM tip. (c) Image of the Au(111) surface after the quantum dot 2 has been redeposited on the substrate, to the left of quantum dot 3. All scans were obtained at -1500 mV. Scaling in nanometers.

individual quantum dots on a gold substrate. The left-hand figure [Fig. 3(a)] shows a scan at -1500 mV of a Au(111) surface ($I=10$ pA) on which three CdSe quantum dots—numbered 1–3—linked via HDT can be discerned. Subsequently, the STM tip was positioned above quantum dot 2 and the bias potential was raised to $+1500$ mV for 5 s. Afterwards, the sample surface was scanned again at -1500 mV. As demonstrated by Fig. 3(b), quantum dot 2 has been selectively transferred from the substrate to the tip and scanning occurs with this quantum dot on the tip. As a current of 10 pA, applied for 5 s suffices to desorb a quantum dot, the desorption yield is at least 3×10^{-9} quantum dots per electron. Afterwards, the STM tip was positioned to the left of nanocrystal 3 and the bias potential was further decreased to -3500 mV for 10 s. After raising to potential to -1500 mV again, a new scan of the surface shows that the nanocrystal 2 has been redeposited on the substrate [Fig. 3(c)]. Similar displacements have been realized using the BDMT and the PDT linked quantum dots. Controlled manipulation of quantum dots can be of value in the formation of quantum dot molecules from individual quantum dots and in the fabrication of nanotransistors based on a single quantum dot.

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