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# Comparative Study on Polarization of DNA and CdSe Quantum Dots *

ZHOU Xing-Fei(周星飞)**, CUI Cheng-Yi(崔成毅), ZHANG Jin-Hai(张金海), LIU Jian-Hua(刘建华), LIU Jing-Song(刘京松)

*Department of Physics, Ningbo University, Ningbo 315211*

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*The polarizabilities of DNA in transverse direction and CdSe semiconductor quantum dots (QDs) deposited on mica surface are compared by means of electrostatic force microscopy (EFM). We observe clear EFM-phase shift over CdSe QDs, while no obvious signal on DNA is detected, suggesting that DNA molecules is an electrical insulator.*

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As a programmable and self-assembling polymer, DNA appears to be one of the most promising candidates for use in molecular electronics.[1−4] Motivated by this potential application, numerous studies on charge transport in DNA have been attempted.[5−9] However, the reported characteristics of DNA by direct conductance measurement vary from insulator, semiconductor to conductor possibly due to differences between measurement systems as well as experiment conditions.[4] In most of the measurements, contacts between DNA and electrodes strongly affect the efficiency of charge injection from the electrodes to DNA, thus the contacts could play a dominated influence on the experimental result.[10] Electrostatic force microscopy (EFM) is one of the powerful techniques that can be used to investigate the conductance of nanoscale samples without the electrical contacts.[11−13] It has been used successfully to study the polarizability of carbon nanotubes. In this Letter, we attempt to compare the polarizability of DNA and CdSe semiconductor quantum dots (QDs) by means of EFM. The basic idea of this work is to clear up the effects inducted by the electrical contacts and try to compare polarizability of DNA with CdSe QDs.

Lambda DNA solution (Sigma) with an original concentration of 400 ng/μl was diluted with TE buffer (100 mM NaCl, 10 mM Tris, and 10 mM EDTA, pH 8.0) to 10 ng/μl. A drop of 10 μl DNA solution was placed onto a $Ni^{3+}$ modified mica surface and then dispersed with molecular comb method.[14] Then sample was dried with a compressed nitrogen gas. After that, a drop of CdSe QD solution was droped on a DNA sample and incubated for several minutes, then rinsed with pure water gently and dried in flowing compressed nitrogen. EFM images were taken on a NanoScope IIIa SPM system using Ti-Pt coated tips (NSC12/Ti-Pt MicroMasch) with radius $R$ of about 30–50 nm and a typical spring constant of about 4.5 N/m. The AFM tip was oscillated at its resonant frquency. All images were collected at room temperature with controlled relative humidity around 35%.

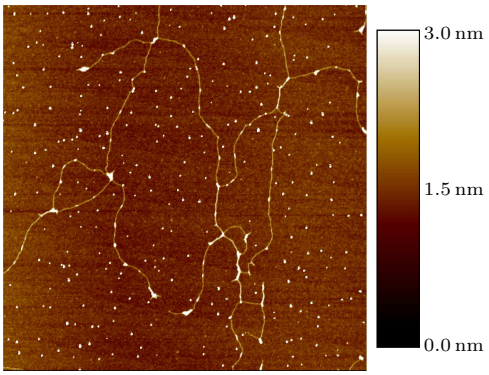



**Fig. 1.** High resolution AFM image of CdSe QDs and DNA molecules deposited on Mica surface. Scan Size: 5 μm × 5 μm.

EFM measures the variations of the electric field gradient above a sample.[12,15] It is based on dual-pass lift mode measurement. The main scan records the surface topographical data in the tapping mode. In the subsequent interleave scan, the tip is lifted and kept at a fixed height above the surface. During the interleave scan, A dc voltage is applied to the tip, and the cantilever is driven with the same frequency as in the main scan. EFM image records the phase of the cantilever oscillation as a function of tip position. If the cantilever is scanned at the lifted height $z$ above the surface and $C(z)$ is the capacitance of the tip-surface system, then $F(z)$ can be noted as[9,16]

$$F(z) = \frac{1}{2}\frac{dC(z)}{dz}(\Delta V)^2,$$

where $F(z)$ is the electrostatic force between the conductive tip and surface and $\Delta V$ is the bias applied on the AFM tip. When the tip scans on a local sample surface with different polarizabilities as compared

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**Email: zhouxingfei@nbu.edu.cn

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with those of the substrate background, the addition force gradient changes the resonant frequency of the cantilever and consequently leads to a phase shift. For small interaction, phase shift ($\delta\phi$) are given by[9,16]

$$\delta\phi \approx \frac{Q}{k}\frac{dF(z)}{dz},$$

where $Q$ is the cantilever quality factor and $k$ is the cantilever spring constant. Therefore, the relative electrostatic polarizability can be compared by phase mapping.

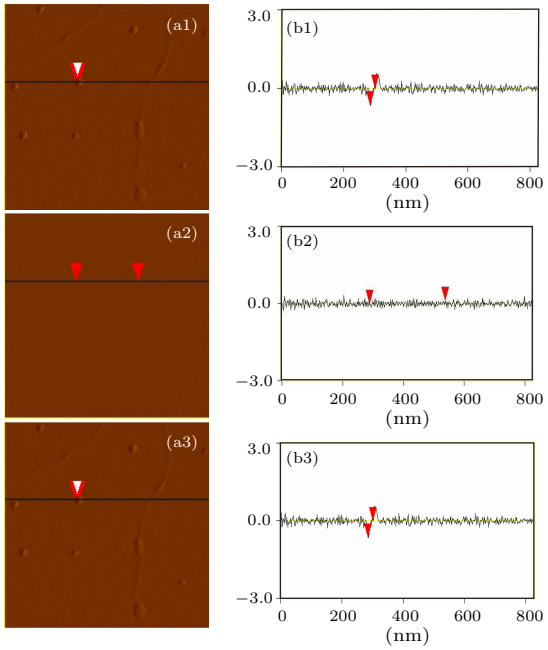



**Fig. 2.** Phase images of DNA molecules and CdSe QDs at different tip bias: +5 V(a1), 0 V(a2), −5 V(a3). Scan Size: 827 nm × 827 nm. (b1)–(b3) are corresponding section analysis.

Figure 1 shows the tapping mode AFM image of DNA and CdSe QDs. As we can seen from the images, DNA and CdSe QDs were well dispersed on surface and the apparent height of DNA and CdSe QDs was about 0.6–0.8 nm and 3–4 nm, respectively. The reduced height of DNA was mainly due to the tip compression during scanning as reported in our previous work.[17] Figure 2 shows the results of EFM-phase measurements on the DNA and CdSe QDs, obtained by applying separately a +5, 0 and −5 V dc bias to the tip with the lifted height about 30 nm. Figures 2(a1–a3) show the phase image corresponding to three different biases. Figures 2(b1–b3) illustrate the cross section analysis. When the bias was set to 0 V, there is no detectible signal over both DNA and CdSe QDs (Fig. 2(b2)), which means that the tip-sample distance was beyond the van der Waals interaction range. Figures 2(b1) and 2(b3) clearly shows the negatively phase shift (attractive force) on CdSe QDs when the tip was biased to +5 and −5 V. Unlike indium arsenide semiconductor nanowire attached on a tip, it could emit an electron beam in vacuum under external high voltage due to its ideal ohmic contacts. In our case, CdSe QDs were surrounded by some chemical to prevent its aggregation, thus we expect the EFM phase shift when tip was over CdSe QDs because of its larger dielectric constant compared with the surrounding air. It is worthwhile to point out that the height of QDS plays a negligible role in the EFM phase shift as indicated in Ref. [6]. The magnitude of phase shift on CdSe QDs is slightly different for the positive and negative bias. It is likely due to the local surface charges and defects or even due to inherent polarized charges in QDs.[18] Whatever the bias on tip was positive or negative, the phase shift was always negative, suggesting that it was polarization force instead of charger on QDs which contributed to the phase shift.[6] In contract the signal on DNA molecule was always at the noise level for the same bias, consistent with the previous report that DNA behavior is similar to an insulator.[4,19] However, under high humidity and high $Mg^{2+}$ concentration, EFM phase shift on DNA could be detectable (data not shown).

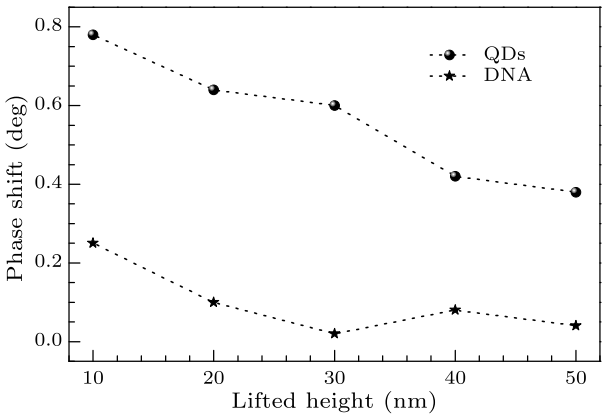



**Fig. 3.** Phase shift over DNA molecules and CdSe QDs at different lifted height.

To figure out the effect of surface defect and topography on phase shift on DNA and CdSe QDs, several different lifted heights were used in our experiment. Figure 3 shows the phase shift on DNA and CdSe QDs versus the scanning height. We can see that phase shift on QDs decreases nonlinearly with the increase of height, in agreement with the theoretical prediction.[5] For relative large scanning height ($h = 50$ nm), beyond the van der Waals interaction range, there was still observable signal on CdSe QDs, indicating that this interaction mainly comes from polarization force instead of van der Waals interaction. For DNA, we did not obtain any signal on phase shift for $h > 20$ nm. While at small lift height ($h = 10$ nm) there was a little un-uniform phase shift along the DNA chain (data not shown), because in this case the AFM tip was very close to the surface. As pointed out in Ref. [12], many factors such as stray capacitance, static charges and

surface topography could give rise to phase shift. We think that it is not appropriate to attribute this signal to polarization of DNA. When lifted height increases ($h > 20\,\text{nm}$), the phase shift on DNA almost vanishes.

In conclusion, EFM has been applied to characterize the polarization behavior of CdSe semiconductor QDs and DNA molecular in a transverse direction. The EFM-phase signal shows that QDs can be polarized by a biased AFM tip. Unlike CdSe QDs, we have failed to observe phase shift over DNA molecules deposited on mica surface, indicating its high insulator. Further experiment such as the effect of water and iron on measurement could potentially lead to a better understanding of DNA transverse polarizabilities.

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