Length-Dependent Dielectric Polarization in Metallic Single-Walled Carbon Nanotubes

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A major driving force behind the research of SWNT electronic properties is their potential in nanoelectronic applications. It has been predicted and experimentally verified that the electronic properties of metallic and semiconducting SWNTs are dependent on their diameter and chirality. With the increase in the density of integration, the length of SWNTs used in electronic devices is approaching submicrometer and nanometer scales. It is thus necessary to understand how the length affects the properties of SWNTs besides chirality and diameter. Here, we report that the dielectric response of metallic SWNTs decreases with length. Experimental investigation and numerical modeling determine that the apparent decrease in longitudinal dielectric polarization is due to higher defect density in shorter nanotubes.

Three motivations underlie the present study on the length dependence of SWNT dielectric properties. First, dielectric response of SWNTs heavily influences the behavior of electrons and holes in nanotubes, and thus, dielectric properties are critically important for device modeling in order to understand, for example, Schottky barriers in nanotube–metal contacts. With ever-decreasing device sizes in nanoelectronics, it becomes increasingly relevant to study how length, in addition to diameter and chirality, affects dielectric and electronic properties of SWNTs. Second, dielectric properties are the differentiating parameters in the separation of metallic and semiconducting SWNTs because different dielectric polarizabilities result in differentiating interaction forces between SWNTs and charges, dipole moments, or external fields, which has been conceived as the underlying mechanisms for nanotube separation methods such as ion-exchange chromatography, dielectrophoresis, and density gradient ultracentrifugation. Studying the length dependence of the nanotube dielectric response can thus elucidate whether the effectiveness of these methods is dependent on nanotube lengths. Third, the dielectric polarizability of SWNTs also affects the structure of molecules, ions, and polymers in the confined space inside of nanotubes and thus dictates the performance of SWNTs as nanofiltration channels. Understanding the length dependence of nanotube dielectrics helps to determine whether there exist optimal lengths for SWNTs used as ultimate nanopores in ultrafiltration membranes.

In contrast to the high level of attention in electrical transport and optical responses, investigations on SWNT dielectric properties are relatively few due to dielectric anisotropy and sample heterogeneity. Theoretical calculations agree that the transverse polarizability of SWNTs, \( \alpha_T \approx D^2 \), where \( D \) is the tube diameter, is independent of nanotube chirality. On the other hand, longitudinal polarizability, \( \alpha_L \approx 1/(E_g)^2 \), where \( E_g \) is the nanotube band gap, is drastically dependent on the chirality or electron type of the SWNT. Our recent electrostatic force microscopy (EFM) measurements of transverse and longitudinal dielectric polarizations at the individual nanotube level in the low-frequency range have verified these predictions. Here, we study the length dependence of SWNT dielectric properties in very low frequencies (\(~\text{kHz}\)) by using the single-tube EFM imaging technique.

The first evidence of length-dependent dielectric response came from a small ensemble EFM imaging experiment (Figure 1a and b). In a previous study, we identified the electronic type, namely, metallic or semiconducting, of EFM-imaged individual SWNTs by plotting their dielectric response against the diameter square (dielectric response versus \( D^2 \) plots). Metallic SWNTs have stronger dielectric response than their semiconducting counterparts of similar diameters, and thus, the two types of nanotubes form two “zones” separated with a gap in dielectric response versus \( D^2 \) plots. The assignment of electronic types has been verified with numerical modeling and single-tube resonance Raman imaging and spectroscopy. Interestingly, we found that it is necessary to discard data points from SWNTs shorter than 200 nm to obtain a dielectric response versus \( D^2 \) plot with good separation between the metallic and semiconducting zones (see Figure S1 in Supporting Information). Considering that the tube length is a dimension orthogonal to both dielectric response and diameter, we make dielectric response versus \( D^2 \) plots of tubes in increasing length ranges as shown in Figure 1c using the same data set. The disparity between metallic and semiconducting nanotubes, or the gap between the metallic and semiconducting zones, clearly widens as the tube length increases. For tubes shorter than 200 nm, the data points cluster, and the two zones cannot be distinguished. Since there is no evidence to support that either metallic or semiconducting SWNTs are more prone to breaking into small segments in solution processing or sample deposition, the length dependence does not undermine the qualification of dielectric response measurements as a metallic assay in mixture samples.
However, the apparent length dependence is interesting enough to be further studied. Figure 1c suggests pronounced length dependence for metallic nanotubes but less evident dependence for semiconducting nanotubes. These metallic tubes in the ensemble study may have different chirality. In order to confirm the length dependence of metallic tubes with the same chirality, single-nanotube cutting experiments were carried out on laser ablation SWNTs (for details of cutting experiments, see Supporting Information). Laser ablation SWNTs were chosen here for the possibility of getting a few micrometers long individual SWNTs on surfaces. Second, the absence of DNA coating simplifies data interpretation, and third, the surface deposition process for laser ablation SWNTs was used for scanning tunneling microscopy studies and is known to introduce the least defects possible to SWNTs. In our study, pristine SWNTs were first dispersed in 1,2-dichloroethane and then spin-cast on degenerate doped p-type Si wafers with 50 nm thick thermal oxide. Micrometers-long SWNTs were first imaged by a conductive tip with EFM and then cut into short pieces using sharp Si$_3$N$_4$ AFM tips in contact mode before imaging with EFM again. Figure 2a and b shows dielectric response images of a metallic SWNT before and after cutting. The dielectric response is clearly dependent on the length (nearly linear for lengths $< 1 \mu$m), and saturation is observed for tubes longer than $\sim 2 \mu$m (Figure 2e). On the other hand, the dielectric response from a semiconducting tube displays only moderate changes with length (Figure 2c and d). These observations corroborate the statistical data in Figure 1c and firmly establish the dependence of (especially metallic) SWNT dielectric response on nanotube length (more single-tube cutting data is given in Supporting Information Figures S2 and S3).

Since the quantum confinement of electronic states in SWNTs occurs on a length scale of several nanometers,$^{22,23}$ the observed length dependence must have a different origin. Considering the measurement setup, one possible explanation is that short nanotubes have a finite length that contributes to the overall dielectric force exerted on the EFM tip and thus may lead to smaller forces. Therefore, we compare the dielectric response at the middle and the end of a tube, as shown in Figure 3a. The topography and dielectric response images of a metallic tube of 1.8 nm in height are shown in Figure 3b and c. The end profiles in Figure 3d show a sharp ending at the height channel limited by the tip radius, but the dielectric channel displays a gradual change lasting $\sim 60$ nm at the tube end. Since the effect of finite tube length contributing to the dielectric force is limited to $\sim 60$ nm on one side, the full effect should be limited to double that length, $\sim 120$ nm. For tubes longer than 120 nm, the dielectric force shall saturate, and the saturation behavior

![Figure 1](image1.png)

**Figure 1.** (a and b) Topographical and dielectric response of ss-DNA-wrapped SWNT samples in EFM measurement. (c) Dielectric response versus $D^2$ plot for ss-DNA-wrapped SWNTs in different length ranges. Metallic and semiconducting nanotubes can be distinguished for tube lengths longer than 200 nm.

![Figure 2](image2.png)

**Figure 2.** (a and b) Topography and dielectric response images of a metallic tube before and after cutting. (c and d) Topography and dielectric response images of a semiconducting tube before and after cutting. White arrows indicate fragments from the cut tube. Scale bars are 500 nm. (e) Length-dependent dielectric response of the metallic (red) and semiconducting (blue) tubes shown in images (a)–(d). The error bars are the standard deviation of pixels along the tube length.
shall be the same for both metallic and semiconducting SWNTs, which clearly does not account for the observed results.

Another possible mechanism is that a critical length is required to completely screen the external field. SWNTs shorter than the screening length do not completely expel the field and will have higher potential and reduced dielectric response. If this assumption is true, metallic SWNTs would have stronger dielectric response at their ends than in the middle because the farther away the rest of the tube is from the tip, the larger the potential difference, and the great force there could be between the EFM tip and the tube. However, we observed that the dielectric signal is homogeneous all along the tube, except for at the weakened ends. A numerical model was built to calculate the dielectric forces between EFM tips and the middle section of metallic tubes (for details of numerical modeling, see Supporting Information). The results in Figure 4 show that the screening effect does result in a more obvious length dependence in metallic tubes than that in the semiconducting tube, but the saturation occurs at a length of ∼200 nm, much shorter than that observed in experiments.

We believe that the experimental results are explained by increased effective defect density in short metallic nanotubes. Under the Drude model, low-frequency dielectric response of metals is generally expressed as $\varepsilon' \approx \varepsilon_0(1 + i\sigma(\omega)) \approx i\sigma(\omega)$, in which $\varepsilon'$ is the complex dielectric constant, $\sigma$ is the conductivity, and $\omega$ is the angular frequency. The conductivity is $\sigma = (Ne^2\tau m)$, where $N$ is the electron density, $e$ is the electron charge, $m$ is the electron effective mass, and $\tau$ is the average time between collisions. In bulk metals, $\tau = (l/v_F)^{-1}$ is determined by $l$, the electron mean free path, and $v_F$, the electron Fermi velocity. Structural defects are generally rare in pristine carbon nanotubes and are mainly concentrated at the ends, which results in long mean free paths of hundreds of nanometers to several micrometers for electrons in metallic SWNTs at room temperature. Therefore, for metallic SWNTs shorter than this length, the defect density is substantially higher due to the ends, and the conductivity is reduced. This consequently lowers the dielectric response of the tube. More investigations are needed to clarify the length dependence in semiconducting SWNTs and the mechanisms thereof.

This study shows that the low-frequency dielectric response of SWNTs not only depends on their electronic types and diameter but also on their length. Metallic SWNTs show stronger length dependence than semiconducting SWNTs. We reason that the longitudinal dielectric polarization of metallic SWNTs is largely reduced by defects at tube ends in short tubes.

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**Supporting Information Available:** Descriptions of the methods, supporting figures, and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


