Zero Bias Anomaly in an Individual Suspended Electrospun Nanofiber

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Abstract. We report observing a double broad Kondo-like zero bias conductance peak at low temperatures in individual suspended electrospun nanofibers Poly(methyl methacrylate)-multiwalled carbon nanotubes. This anomalous behavior is suppressed at higher temperatures. We attribute this to the existence of correlated double impurity system inside the nanofiber. From the results we calculate a Kondo-like temperature for the nanofiber to be \(\sim 31.7-34K\).

1. Introduction

Mesoscopic devices offer a venue for observing fundamental many-body phenomena. One of the many phenomena encountered is the zero bias anomaly at low temperature where the devices presents unusual tunneling behavior. While Coulomb blockade is a first order tunneling process, and does not allow tunneling when states are not aligned, higher order processes allow tunneling through virtual intermediate states. One such higher order process is the Kondo effect\textsuperscript{[1]}. The Kondo effect is realized in quantum dot device which consists of a small electronic island connected by tunnel barriers to extended leads. For this kind of device with a localized unpaired spin embedded between metal leads, it is possible to observe signatures of Kondo effect in its conduction properties. Kondo physics incorporates the growth of correlated state comprising the local spin interacting with spins of conduction electrons of the leads. In devices as noted above, the result is enhanced transmission, manifested by a zero bias peak in the conductance. Kondo effect was observed in carbon nanotubes\textsuperscript{[2; 3]}, fullerenes\textsuperscript{[4]}, graphene\textsuperscript{[5]}, single molecule transistors containing metal ions\textsuperscript{[6]} and semiconductor quantum dots\textsuperscript{[7]} to name a few and has been on the focus of many papers\textsuperscript{[2; 4; 8–15]}. So far this was not observed in nanofibers.

In this Letter, we present an early experimental data of a double peak zero bias anomaly resembling Kondo behavior in an individual nanofiber. This is done through transport spectroscopy over ultra long (\(\sim 100\mu m\)) individual suspended electrospun nanofiber Poly(methyl methacrylate)-multiwalled carbon nanotubes. We discuss the adaptability of the Kondo model and calculate the Kondo-like temperature associated with this kind of behavior\textsuperscript{[16]}. This system
is of importance since it presents an unusual correlated two impurity electron system observed only few times albeit in much lower temperatures.

2. Experimental
For the fabrication of a substrate with trenches, we used 100mm ⟨100⟩ wafers with one polished side. A cleaning process was performed using H₂SO₄+H₂O₂. This was followed by a photolithography process with a resist thickness of 1.5µm. The trenches were etched using deep silicon etching followed by resist stripping and another cycle of H₂SO₄+H₂O₂ cleaning. For the insulation of the substrate, a 600nm thick SiOₓ layer was deposited on the wafer using wet oxidation at 1000°C. For the production of the nanofibers a 0.6g of MWCNTs (From Bayer-Baytubes C150) was dispersed in 60g of dimethyl acetamide (DMAC, Carl Roth, GMbH) with 1g of hydroxypropyl cellulose (HPC) (from Aldrich Mw 100.000) by ultra-sonicator for 30 minutes. 3g of PMMA (from Aldrich Mw 996.000) were dissolved in 30g of acetone. DMAC and acetone were used without any additional purification. For dispersion tip sonicator Sonopuls HD3100, Bandelin GmbH, equipped with a cup horn operating at 10kHz and 100W output power was used. Components were mixed and dispersed by ultra-sonicator for additional 30 minutes. Nanofibers were electrospun over a substrate Si/SiOₓ using Yflow®2.2.D-300 lab-scale electrospinning unit with single-nozzle electrospinning (Yflow Sistemas y Desarrollos S.L) with an injector-collector distance of 15 cm, an applied voltage of +9.5/-8.0kV, and a flow rate of 2ml/h. Candidate nanofibers suspended over trenches were located using an optical microscope and afterward were connected through direct bonding of Aluminum wires onto the nanofibers. We determined the diameter of the nanofibers with atomic force microscopy imaging was performed with Park XE150 in tapping mode. We performed electrical measurements with a Keithley 4200 – SCS and an Oxford closed cycle cryostat with 2-probe in Helium ambiance.

![Image](image_url)

**Figure 1.** A typical transmission electron microscopy image of the nanofiber. The MWCNTs are aligned as a chain inside the nanofiber. Along this chain defects and impurities, marked with black arrows accumulate creating quantum dots.

3. Results
As Fig. 2(a) shows, the conductance drops gradually in dependence to the temperature. This type of behavior was recorded in various devices[18] [19] and also shows up in all of our devices. For highly resistive devices as the temperatures drop the conductance is suppressed in the zero bias regime and a Kondo-like peaks begin to rise sharply until saturation at lower temperatures[20]. It is noteworthy that we notice a resolved double peak as Fig. 2(a) shows. This kind of behavior has also been reported in the past[8] [12]. As Fig. 2(b) shows, it is roughly Lorentzian in shape and becomes narrower and higher in lower temperatures. The extracted maxima and full width at half maximum (FWHM) values from Fig. 2(b) through a fit for Lorentzian are presented at Fig. 3 in dependence with temperature. Fig. 3(a) and Fig. 3(b)
Figure 2. 2(a) Temperature dependence of the conductance in log scale. The conductance is suppressed close to zero bias while in low temperature a Kondo-like double peak appears. In the inset it is possible to see the interplay between the normal conduction and the emergent zero bias anomaly. 2(b) A close-up of the temperature dependence of the main Kondo-like feature. It can be noticed that normal conductance in higher voltages is suppressed as the temperature drops while a zero bias sharp peaks appear. Under 40K the Kondo-like peaks cannot be traced due to suppression of conduction. In the inset, in low temperatures, the Zero bias anomaly is shifted between forward and reverse sweeps but does not change its location in different temperatures. The secondary lower peak is absorbed by noise and cannot be noticed until reaching lower temperature. The differential conductance of all graphs was obtained through numerical differentiation and using Savitzky-Golay smoothing in an effort to reduce the noise at the cost of the bias voltage resolution.

are a fit of the Kondo model (continuous line) according to Eq. 1 and Eq. 2 respectively to the data (Black points).

4. Discussion
Crystallographic defects affect multiwalled carbon nonotubes (MWCNTs) electrical and thermal properties. Usually the result is lowered electrical conductivity which is related with reduced mean free path and thermal conductivity which is related with increased relaxation rate of the phonons through the defective region of the MWCNTs. Ultrasonification through the electrospinning process of the nanofiber creates defects over the MWCNTs as Fig. 1 shows. As our nanofiber is rich with impurities and defects- it is reasonable to believe that for highly resistive devices, at low temperatures, along the conduction nanochain we can get a quantum dot. In MWCNTs and carbon based materials in general, defects of single monoatomic vacancies induce magnetic properties. This is reflected in our results through a Kondo-like zero bias peak we observe in Fig. This Zero-bias peak is Lorentzian in shape, grows narrower and higher as we lower the temperature. Therefore, we assign this to the Kondo effect which is associated to logarithmic increase in the peak maximum conductance toward lower temperatures. We analyze the results in a similar manner. We adapt Lorentzians to the zero-bias peaks and plotted the extracted values for maximum conductance $G_{\text{max}}$ and peak width -full width at half maximum (FWHM) as a function of the temperature according to these equations, respectively,

$$G_{\text{max}}(T) = G_{C} + G_{0}(1 + (2^{1/3} - 1)(T/T_{K})^{2})^{-s},$$

(1)
Figure 3. (a) Temperature dependence maximum conductance at Zero bias with $G_{max}$ collected from Fig. 2(b). The data (Black points) is fitted to the Kondo model (continuous line) according to Eq. 1 resulting with $T_K = 34.1K$. (b) Temperature dependence with FWHM collected from Fig. 2(b) through FWHM Lorentzian fits performed on each of the zero-bias peaks. The data (Black points) is fitted with the Kondo model (continuous line) according to Eq. 2 resulting with $T_K = 31.7K$

$$\Lambda_{FWHM} = g_0\sqrt{(\pi k_B T)^2 + 2(k_B T)^2},$$

where $T_K$ is Kondo temperature, $G_0$ is the conductance range, $s = 0.22$ is the spin parameter for carbon nanotubes (0.22 for spin 1/2, the simplest case[28]) $G_C$ is an offset value and $g_0$ is a dimensionless parameter. Both fits yield a similar result for the critical temperature which indicates the validity of the Kondo model in this case.

In Kondo phenomena the width of the localized state, $\Gamma$ is the sum of the level widths due to the couplings $\Gamma_S, \Gamma_D$ of the localized state to the source and drain, respectively. An asymmetric source-drain coupling ($\Gamma_S \gg \Gamma_D$) results in high Kondo temperature (set by $\Gamma$) and a low total conductance (limited by $\Gamma_D$). This is identical to the case we observe in this system - low conductance with high Kondo-like temperature. From the inset of Fig. 2(a) it is possible to notice that there is an apparent interplay between the emergent zero bias anomaly and the conductance staircase[29]. As the first order process of conductance staircase trails off, the zero bias peaks rise. The conductance staircase is not symmetrical which again is a signature of asymmetrical coupling to the leads. This is also exemplified from the inset to 2(b) where we notice a shift between the forward and the reverse sweeps.

We find that the saturation value of the conductance is lower than the expected conductance quantum. This has been reported in the past[6]. We attribute this to poor transmission in the leads and over the nanochain of conduction($\Gamma_S \gg \Gamma_D$ or vice versa), insufficient local thermalization or insufficient Kondo screening. This seems plausible since the zero bias peaks and the conductance in high voltage are of the same magnitude. At temperatures 40K and lower, it is impossible to spot the zero bias peak due to noise. It is conceivable that in lower temperatures the nanochain of conduction is hampered by insufficient local thermalization. This again may be the result of lowered total conductance. As can be noticed, the peaks are broadened. FWHM is in the size of $\sim 330meV$ at 110K. While normally the energy gaps in MWCNTs are relatively small ($< 100meV$), a substantial amount of defects can raise it. We also notice a split in the zero bias peak or a broad side band. This was observed recently for single walled carbon nanotubes[30], quantum point contacts[31] as well as in other devices. It was explained as two-
impurity Kondo effect with coupled spins. We believe that this is also a demonstration of similar behavior as Fig. 2 shows. Two impurity sites with unequal coupling strength $\Gamma$ to the adjacent leads results with asymmetric double-peak zero bias anomaly. with the minimum conductance between the two peaks roughly at zero bias voltage. This result was observed earlier albeit in microkelvin temperatures[31]. The coupling strength remains to be tested in future experiments.

5. Summary
To summarize, we have shown a double Kondo-like effect in an individual nanofiber performing as quantum dot. This situation is associated with a two-impurity Kondo effect. We calculated a Kondo-like temperature of $\sim 31.7 – 34K$ for the nanofiber for the main feature. Connecting a nanofiber consisting multilawled carbon nanotubes aligned in series widens the scope of possibilities to investigate different regimes in the mesoscopic electron transport. Further experimental work will be needed to unambiguously support this picture.

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