Comment on "Electrostatics of Individual Single-Walled Carbon Nanotubes Investigated by Electrostatic Force Microscopy"

In a recent Letter [1], Paillet *et al.* have addressed the issue of electrostatics of single-walled carbon nanotubes (SWCNTs) based on electric force microscopy (EFM). The apex of an EFM cantilever was used to inject charges in SWCNTs deposited on a thin insulating layer, followed by EFM detection to map the sample surface charges. Paillet *et al.* have estimated a nanotube linear charge density of 1 electron per nanometer for a SWCNT of 2.5 nm in diameter for an injection voltage $V_{\mathrm{inj}} = -3.5$ V.

The purpose of this Comment is to show that the experimental data of Ref. [1] provide no clear evidence of charge storage in the SWCNTs but likely also correspond to charging in the silicon dioxide thin layer along the SWCNTs. Oxide charging can indeed predominate over the SWCNT charging, and we dissociate both effects here. This questions the charge density given in Ref. [1] and its agreement with a classical capacitance model.

EFM experiments have been hereafter performed on multiwalled carbon nanotubes (MWCNTs) and SWCNTs deposited on a 200 nm thermal silicon dioxide layer. We report in Figs. 1(a) and 1(b) the EFM data of a MWCNT (height 15 ± 0.2 nm, length $\simeq 1.7$ μm) and in Figs. 1(c) and 1(d) a SWCNT (3 ± 0.2 nm, length $\simeq 14$ μm) acquired with $V_{\mathrm{EFM}} = -3$ V and lift heights $z_0 = 80$ and 60 nm. The negative EFM frequency shifts prior to charging are capacitive footprints of the nanotube topography [2].

After charging (with $V_{\mathrm{inj}} = -6$ V for 2 min), the EFM signal of the MWCNT exhibits a pronounced positive frequency shift [see Fig. 1(a)] predominating over the capacitive signal and corresponding to a negative stored charge. A first evidence for charge storage in the MWCNT is given by the occurrence of an abrupt discharge while scanning with the grounded tip, as reported in Ref. [2]. This is confirmed by the EFM signal after discharge exhibiting the capacitive frequency dip typical of the uncharged MWCNT, however, surrounded by negative charges trapped on the oxide surface [2] which appear as a bright halo along the MWCNT in Fig. 1(b). Finally, the MWCNT charging is observed from its height in topography images (16.5 nm after charging, 15 nm after the discharge) as a result of electrostatic image forces [3].

Similar experiments have been performed on the SWCNT. Immediately after charging, the nanotube height raises to 4.8 nm and falls to 3.5 nm within 5 min, indicating that the SWCNT also undergoes a discharge, though not abrupt here. The discharge is demonstrated by comparison of the EFM data of two consecutive scans (of 20 min durations) acquired after charging and showing the resurgence of the SWCNT capacitive frequency dip after the discharge [see Fig. 1(c)]. This proves that some charge has indeed been injected in the SWCNT, but, in contrast with MWCNTs, it represents only a small fraction of the trapped oxide charge which here dominates EFM images after charging [see Fig. 1(d)].

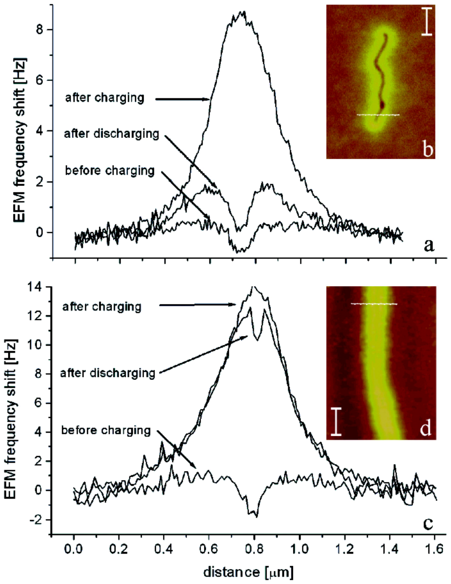

FIG. 1 (color online). (a) EFM signals ($V_{\mathrm{EFM}} = -3$ V) recorded across a 15 nm-diameter MWCNT [see horizontal line in (b)] before charging, after charging ($V_{\mathrm{inj}} = -6$ V for 2 min), and after the MWCNT discharge. (b) EFM image of the discharged MWCNT. The scale bar is 500 nm. (c) Similar EFM signals acquired on a 3.0 nm-diameter SWCNT. (d) EFM image of the discharged SWCNT. The scale bar is 300 nm.

In conclusion, the EFM images of Ref. [1] do not bring clear evidence of charge storage in SWCNTs. Since the issue of oxide charging is essential for electronic applications such as transistor or memory devices based on SWCNTs, complementary experiments are actually required to establish the charge densities of Ref. [1].

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