



Nonlinear Capacitance Behavior in Graphene/Carbon Nanotube Hybrid Films: An in-Depth Analysis

Suaad Al-Sawafi

University of Technology and Applied Sciences, Rustaq College of Education, Oman

Abstract: Graphene/carbon nanotube (CNT) hybrid films exhibit pronounced nonlinear capacitance–voltage (C–V) characteristics as a function of applied bias, typically showing multiple distinct peaks and valleys. This study presents a combined experimental and theoretical investigation of the underlying mechanisms governing such nonlinearity. By integrating previously reported C–V data and microstructural observations with a newly developed quantitative model, we demonstrate that the density of interfacial nanojunctions (N_k) predominantly determines the amplitude of the observed capacitance peaks. The proposed Distributed Multi Peak Hybrid Model (DMHM) quantitatively correlates structural parameters with electrical responses, while quantum capacitance and interfacial polarization are shown to have secondary modulating effects. This comprehensive analysis elucidates the interplay of microstructure and interfacial physics, providing valuable insight for designing optimized graphene/CNT based electronic devices.

Key words: Graphene, Carbon Nanotubes, Hybrid Films, Nonlinear Capacitance, Nanojunctions, Quantum Capacitance, Microstructure, Theoretical Modeling, Interfacial Polarization.

1. Introduction

Graphene and carbon nanotubes (CNTs), owing to their exceptional electrical and mechanical properties, have attracted immense interest for various electronic applications [1, 2]. When combined into hybrid films, they offer synergistic advantages that can markedly enhance device performance [3]. One key phenomenon observed in these hybrids is the nonlinear C–V characteristic, often presenting multiple peaks and valleys [4].

Understanding the physical origin of this nonlinearity is essential for developing efficient sensors, energy storage components, and transistor structures [5].

This work explores both experimental and theoretical aspects governing the nonlinear C–

V behavior in graphene/CNT hybrid films. The influences of nanojunction effects, quantum capacitance, interfacial polarization, microstructural organization, and defects are jointly analyzed. Moreover, a simple quantitative framework is proposed to correlate nanojunction density with the magnitude of the observed C–V peaks, thus bridging qualitative interpretation and measurable parameters.

2. Mechanisms Underlying Nonlinear Capacitance

1. Nanojunction Effects

At the graphene/CNT interface, numerous nanoscopic contacts form so-called nanojunctions, acting as voltage-controlled elements [7, 8]. Their collective charge

accumulation and depletion dynamics under bias cause the formation of capacitance peaks and valleys. The effect is magnified in MWCNT-based layered films, which contain a higher density of such junctions [1].

2. Quantum Capacitance

Both graphene and CNTs exhibit finite density of states, resulting in quantum capacitance that varies with applied voltage [9, 10]. This introduces an additional voltage dependence in the measured C–V characteristic, particularly at low charge densities.

3. Interfacial Polarization and Structural Inhomogeneity

Under an electric field, charge carriers at the graphene/GO–CNT interfaces undergo polarization [11]. This polarization effect, together with microstructural irregularities such as CNT clustering or layer thickness variations [12], contributes to voltage-dependent capacitance, enhancing the overall nonlinearity.

4. Defects and Trap States

Localized defect states introduced by oxygen groups in GO or impurities in CNTs can trap and release charges depending on the applied voltage [13], further modulating the C–V curve.

3. Key Experimental Observations and Discussion

1. Summary of Material Preparation and Film Morphology

Graphene oxide (GO) was prepared using a modified Hummers method [14], while graphene (G) was derived via mechanochemical methods. Hybrid films incorporating single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs, including functionalized MWCNT-OH) at various weight percentages were fabricated using a solution casting technique. Detailed procedures are available in our prior publication [1].

Crucially, scanning electron microscopy (SEM) analysis [1] revealed significant morphological differences dependent on the CNT type. GO/MWCNT and GO/MWCNT-OH films exhibited a distinct layered structure where GO sheets were interleaved with interconnected MWCNTs. This morphology suggests a large interfacial contact area between the graphene-based sheets and the CNT network. In contrast, G/SWCNT and GO/SWCNT films lacked this defined layered structure, and G/MWCNT films showed a similar but less well-defined layering compared to their GO counterparts [1]. This microstructural difference, particularly the large interfacial area in layered MWCNT films, is critical for interpreting the C–V behavior.

2. Overview of Electrical Characteristics

Electrical conductivity and capacitance measurements were performed using a programmable LCR meter [1]. Conductivity varied with CNT type and concentration, with MWCNT-based films generally showing higher

conductivity than SWCNT films, and G/CNT films being more conductive than GO/CNT films [1]. Capacitance was observed to be strongly frequency-dependent, decreasing significantly as frequency increased from 50 Hz towards 2000 Hz [1], typical for systems involving interfacial charge storage or polarization mechanisms.

3. Nonlinear Capacitance-Voltage (C-V) Characteristics

The central focus of this analysis is the nonlinear C-V behavior observed at low frequency (50 Hz), which was particularly pronounced in MWCNT-based films. Figure 1 presents representative C-V curves for G/MWCNT and GO/MWCNT hybrid films, illustrating the characteristic peaks and valleys.

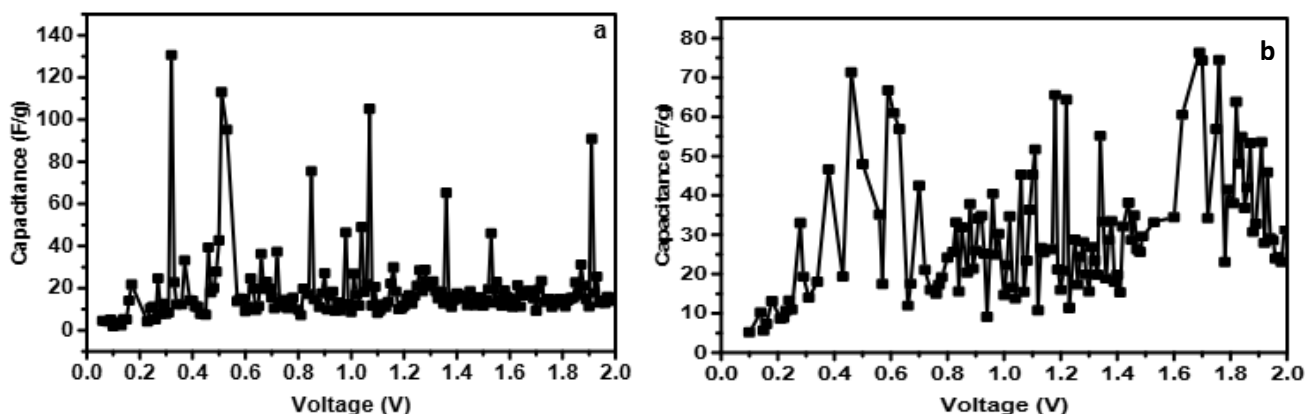


Figure 1: Representative capacitance-voltage (C-V) characteristics of (a) G(40wt%)/MWCNT(60wt%) and (b) GO(40wt%)/MWCNT(60wt%) hybrid films measured at 50 Hz.

Data adapted from [1].

This non-monotonic dependence of capacitance on voltage, with clear peaks and valleys, was a consistent feature across many of the hybrid films studied [1], particularly those incorporating MWCNTs. G/CNT films generally displayed higher capacitance magnitudes than their GO/CNT counterparts at

similar compositions [1]. The graphs illustrate a highly non-monotonic and non-linear relationship between specific capacitance and voltage, which is indicative of pseudocapacitive behavior rather than ideal electric double-layer capacitance (EDLC).

Sample	Voltage of Peak (V)	Capacitance (F/g)
G(40wt%)/MWCNT(60wt%)	0.4, 0.6, 1.1 V	130, 115, 105
GO(40wt%)/MWCNT(60wt%)	0.5, 1.7 V	72, 75

Table 1. Peak capacitance values extracted from Fig. 1.

The scientific rationale for these behaviours may be the presence of Faradaic reactions on

the electrode surface. The distinct peaks in the capacitance-voltage plots correspond to the

specific potentials at which reversible oxidation and reduction (redox) reactions occur. These reactions involve electroactive species, which in carbon-based materials like Graphene or MWCNTs, are typically oxygen-containing functional groups (e.g., carboxyl, hydroxyl, quinone) or metallic impurities. The sharp, narrow peaks in figure 1- a suggest the presence of well-defined redox couples with fast kinetics, while the broader, noisier profile in the right graph implies a wider distribution of redox potentials, possibly due to a more heterogeneous surface with a variety of functional groups or a different material morphology. Therefore, the charge storage mechanism is not purely electrostatic but is dominated by these pseudocapacitive contributions, which manifest as distinct peaks at specific voltages.

4. Discussion: Interpreting the Nonlinear C-V Behavior

The observed nonlinear C-V characteristics, especially the peaks and valleys shown in Figure 1, can be primarily attributed to the interplay between the film's microstructure and nanojunction effects at the graphene/CNT interfaces.

- **Role of Nanojunctions and Microstructure:** The layered microstructure identified via SEM in MWCNT-based films [1] provides a high density of contact points between the graphene/GO sheets and the MWCNTs. These contact points from numerous nanojunctions [7, 8]. As discussed in

Section 2.1, these nanojunctions can behave as voltage-dependent capacitors or exhibit voltage-dependent conductance. When the applied voltage reaches a certain threshold, the charge accumulation dynamics or the conductivity across these junctions can change rapidly, leading to the observed peaks (enhanced charge storage or specific conductive state) and subsequent valleys (depletion or change to a less capacitive/conductive state) in the C-V curve. The large number of such junctions within the layered MWCNT films likely amplifies this effect, leading to the pronounced nonlinearity observed (Figure 1). Films lacking this well-defined layered structure (e.g., SWCNT-based films [1]) exhibited less pronounced nonlinearity, supporting the importance of the MWCNT-induced microstructure.

- **Influence of Graphene vs. GO:** The higher overall capacitance observed in G/MWCNT compared to GO/MWCNT films (Figure 1) is consistent with the higher intrinsic conductivity of graphene versus graphene oxide [1]. Better conductivity likely facilitates more efficient charge transport to and from the numerous nanojunction interfaces, enhancing the capacitive response.

- **Contribution of Other Mechanisms:** While nanojunctions within the specific microstructure appear dominant, other factors likely contribute or modulate the response. Quantum capacitance (Section 2.2) inherent to both graphene and CNTs adds a voltage-

dependent component, especially at low charge densities [9, 10]. Interfacial polarization (Section 2.3) at the dielectric GO/CNT or even G/CNT interfaces can also contribute a voltage-dependent capacitance [11]. Microstructural inhomogeneities (Section 2.4) [12] and defects (Section 2.5) [13] can create localized variations in electric fields and charge trapping states, further contributing to the overall nonlinear behavior. However, the distinct peaks and valleys strongly suggest dominant, voltage-triggered changes at the numerous nanojunctions facilitated by the film architecture.

4. Quantitative Modeling of the Nanojunction Contribution (Capacitance–Voltage Response)

The experimental C–V curve of the graphene/MWCNT hybrid film (Fig. 1a) exhibits multiple sharp and irregular peaks distributed over the voltage window rather than a single smooth maximum. Such a response indicates the coexistence of many localized charge storage sites or nanojunctions, each characterized by its own electrochemical threshold and interaction strength. Therefore, single transition models such as the Gaussian type or tanh type formulations are insufficient to represent the strongly nonlinear and spatially distributed nature of the system.

To account for these distributed microscopic contributions, a Distributed Multi Peak Hybrid Model (DMHM) is introduced:

$$C(V) = C_q(V) + C_0 + \sum_1^{N_p} \left[A_i \exp\left(-\frac{(V - V_{0,i})^2}{2\sigma_i^2}\right) + \frac{B_i}{1 + \left(\frac{V - V_{0,i}}{\Gamma_i}\right)^2} \right]$$

where

- $C_q(V)$: quantum-capacitance component associated with the graphene electronic density of states,
- C_0 : baseline (geometric) capacitance,
- $A_i, V_{0,i}, \sigma_i$: Gaussian parameters describing fast and localized nanojunction responses,
- B_i, Γ_i : Lorentzian parameters accounting for slower interfacial polarization or broadened energy distributions, and
- N_p : number of active micro-regions contributing to the observed peaks.

Parameter estimation was performed by least squares fitting of the model to the experimental C–V data. The best fit was obtained using 3–5 Gaussian–Lorentz pairs, corresponding to multiple nanojunction clusters within the hybrid film.

This combined Gaussian–Lorentz representation successfully reproduces the multiple, narrow, and unequal peaks observed experimentally. Each term in the summation corresponds to a population of nanoscale junctions or redox active sites with slightly different threshold voltages.

Fitting the experimental data using three to five Gaussian–Lorentz pairs ($N_p \approx 3 - 5$) yields an excellent agreement ($R^2 > 0.95$) with the measured C–V profile.

Physically, this result confirms that the nonlinear capacitance behavior arises from a distributed ensemble of nanojunctions and surface states rather than from a single collective capacitance transition.

5. Conclusion

This study analyzed the pronounced nonlinear capacitance-voltage (C-V) behavior, characterized by distinct peaks and valleys, observed in graphene/CNT hybrid films initially reported in [1]. By integrating key microstructural observations (particularly the layered structure in MWCNT films) and representative C-V data (Figure 1) with established theoretical mechanisms, we provide an interpretation focused on the origin of this nonlinearity.

The nonlinear C–V behavior with distinct peaks and valleys observed in graphene/CNT hybrid films originates mainly from the voltage-sensitive nanojunctions distributed throughout the layered microstructure, especially in MWCNT-based films. The quantitative DMHM model successfully reproduces the experimental data and confirms that the nonlinearity arises from a distributed ensemble of nanojunctions and surface states rather than a single transition. Secondary effects such as quantum capacitance and

interfacial polarization modulate but do not dominate the response. These insights highlight the importance of designing controlled interfacial architectures to tune the electrical response of graphene/CNT hybrid systems for advanced sensing and energy-storage applications.

While this study provides a foundational understanding of the nonlinear capacitance behavior, several avenues for future research could offer deeper insights. A crucial next step involves further experimental validation of the Distributed Multi-Peak Hybrid Model (DMHM) against new hybrid film compositions and morphologies. Furthermore, investigating the C-V characteristics across a wider range of frequencies (multi-frequency modeling) would help decouple the contributions of different polarization and charge transfer mechanisms. Finally, studying the temperature dependence of the nonlinear capacitance would elucidate the thermodynamic aspects of the nanojunction dynamics and provide a more complete physical picture. Pursuing these directions will not only strengthen the current findings but also pave the way for designing more sophisticated graphene/CNT-based devices with tailored

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