A Unified View on Nanoscale Packing,
Connectivity, and Conductivity of CNT Networks

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ABSTRACT

The design of functional structures from primary building blocks requires a thorough understanding of how size, shape, and particle-particle interactions steer the assembly process. Specifically, for electrically conductive networks build from carbon nanotubes (CNTs) combining macroscopic characterization and simulations shows that the achievable conductivity is mainly governed by CNT aspect ratio, length dispersity and attractive interactions. However, a direct link between the actual three-dimensional network topology that leads to the observed electrical conductivity has not been established yet due to a lack in nanoscale experimental approaches. Here we show experimentally for randomly packed (jammed) CNT networks that the CNT aspect ratio determines, as theoretically predicted, the contact number per CNT which in turn scales linearly with the resulting electrical conductivity of the CNT network. Furthermore, nanoscale packing density, contact areas, contact distribution in random and non-random configurations and least resistance pathways
are quantified. Our results illustrate how complex nanoscale networks can be imaged and quantified in three dimensions to understand and model their functional properties in a bottom-up fashion.

INTRODUCTION

Controlling the organization of primary building blocks into larger (dis)ordered structures with tunable (multi-)functional properties is a fundamental question in materials science and chemistry. It has been well established that geometrical and topological constraints of primary building blocks such as shape\(^1\) and size distribution,\(^2\) dictate the resulting packing density, orientation, co-ordination number and contact density in the final assembly.\(^3\) Furthermore, nanoscale interactions at the interfaces of metamaterials,\(^4\) composites,\(^5\) polymer blends\(^6\) or hybrid materials\(^7\) may be utilized to induce structural modifications that improve the functional performance, such as electrical conductivity,\(^8\) piezoresistivity\(^9\) and mechanical stability.\(^10\) For instance, attractive interactions between carbon nanotubes (CNTs) can result in inhomogeneous mesoscale networks with tunable electrical conductivity.\(^8b, 11\) To unravel the underlying design principles, quantitative information on the spatial distribution of CNTs are indispensable. However, there is a lack of experimental approaches to provide nanoscale structural information on densely packed CNT networks. Hence, quantitative three-dimensional (3D) analysis was so far limited to computer simulations, numerical methods,\(^12\) mesoscale structures\(^13\) or larger building blocks that can be resolved by X-ray tomographic techniques.\(^14\)

RESULTS AND DISCUSSIONS

Analysis of 3D CNT networks presents unique challenges as they are sensitive to the electron beam and have very low contrast, especially when imaging thick TEM specimens that are
required to analyze a representative volume of randomly ordered materials.\textsuperscript{[15]} To overcome these difficulties and to quantify the network topology, i.e., packing density, CNT-CNT contacts, and connectivity, which determine the final conductivity of the CNT network we employed electron tomography\textsuperscript{[16]} combined with model-based image analysis. Briefly, this method involves acquisition of (scanning) TEM tilt-series and reconstruction, followed by template matching to extract the centerline of the CNTs and associated information (such as local diameter), and reconstruction of CNTs using the best matched templates (see Figure 1 and SI section 2 and 3 for the detailed information).\textsuperscript{[17]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Quantitative electron tomography analysis. a) Representative STEM image of a CNT network. Bright white dots represent the gold markers used for alignment of the tilt-series prior to tomographic reconstruction. Scale bar is 500 nm; b) Orthogonal slices through the reconstructed tomogram; c) Volume rendered tube segments that are used for template matching with reconstructed tomogram; d) Centerline of the CNT network and the}
\end{figure}
spatially distributed CNT-CNT contacts (blue dots); e) Volume rendered reconstructed network with best matched tube segments. Volume: 2.6 μm x 2.4 μm x 700 nm.

In a first step, densely packed CNT networks denoted C1, C2, and C3 were prepared from CNTs population that has almost same diameter distributions but different polydisperse length distributions (hence, different average aspect ratio) skewed to shorter lengths – Figure S1. Representative annular dark-field (ADF) STEM images of the CNT assemblies are shown in Figure 2a. Quantitative electron tomography (QET) performed on these CNT assemblies provides the local diameter of CNTs, and contacts between CNTs present in the studied volume – Figure 2b.

Figure 2: a) Representative ADF-STEM images of the CNT networks (bright) illustrating their mesoscale topology. Scale bars are 500 nm; b) Volume rendered CNT networks illustrating the spatially distributed CNTs (grey) and contacts (blue). Vol: 1.35μm x 1.35 μm x 200 nm.
Based on QET data, we first studied the packing distribution and packing densities. The average nanoscale packing density $\phi$ asymptotically decreases with increasing average aspect ratio $\langle L\rangle/\langle D\rangle$ (Figure 3a and Figure 3b). The same behavior was also observed for macroscopic monodisperse rods\cite{18} and it was shown that the asymptotic decrease is a consequence of the excluded volume of the already deposited particle and scales to a constant. This relationship is expressed in the random contact model (RCM) as $\phi \langle L \rangle / \langle D \rangle \approx \langle C \rangle / 2$, for $\langle L \rangle / \langle D \rangle >> 1$, with $\langle C \rangle$ the average contact number per particle.\cite{18b} For populations of rods with length dispersity, packing densities higher than their monodisperse or bidisperse counterparts are found.\cite{19} Fitting our data with the RCM scaling relation leads to $\langle C \rangle \sim 7.2 \pm 2.9$, which although being lower than the experimental value $\langle C \rangle \sim 10$,\cite{18b} matches theoretical predictions for ideal packings of rods with high aspect ratio.\cite{20}

Next, from QET, the CNT-CNT contacts, i.e., their spatial distribution and position along individual CNTs was studied to quantify the nanoscale network connectivity. The proximity of CNT-CNT contacts in the network is described through the segment length (i.e. the distance between two contacts on the same CNT) distribution (Figure 3c). The observed broadening of the segment length (SL) distribution and shift towards longer SL with increasing average aspect ratio (C1 to C3) is expected.\cite{20d} Mean segment lengths $\langle l_s \rangle$ were determined (Figure 3d) and show a linear increase as a function of average aspect ratio. This change in $\langle l_s \rangle$ affects the mechanical stability and functional properties like electrical conductivity that are distinct to each network. Our results for $\langle l_s \rangle$ are somewhat lower than theoretically predicted although the prediction is within the error of measurement. The lower than expected average segment length and average packing density is due to the presence of inhomogeneities (e.g., CNT aggregates and voids as seen in Figure 2a) and the fact that we used cross-sections thinner than the average CNT length which may contribute to the somewhat lower than predicted $\langle l_s \rangle$ value as well. From the CNT length distribution and $\langle l_s \rangle$,
the average number of contacts per CNT is estimated as (see SI, section 4) $\langle C \rangle = 6.2$, 7.7, and 9.2 for C1, C2, and C3, respectively (Figure 3e and Figure 3f). While this first of its kind independent measurement of $\langle C \rangle$ at the nanoscale is consistent with theoretical results for rods of high aspect ratio,[20] it evidences nonetheless that the coordination number of our CNT networks is non-invariant. This can be attributed to the combination of shape, size, and tortuosity,[2b] attractive interactions,[8b] and viscosity and frictional dependencies[21] that arrest the nanoscale system before ideal packing is achieved, thus resulting in an increase of the excluded volume and affects the value of $\langle C \rangle$ (See SI section 5).[22]

Figure 3: a) Packing density distribution of CNT networks; b) Average packing density $\varphi$ plotted as a function of average aspect ratio $\langle L \rangle/\langle D \rangle$. Blue data represents the packing behavior of macroscopic monodisperse particles and the fit given by RCM with average number of contacts per particle approaching $\langle C \rangle \sim 10$ at large aspect ratios.[18b] Red data represents the packing behavior of our CNT networks and the fit given by RCM with $\langle C \rangle \sim 7.2 \pm 2.9$; c) Segment length distribution of CNT networks; d) Mean segment length $\langle l_s \rangle$ plotted as a function of average aspect ratio $\langle L \rangle/\langle D \rangle$. Blue line represents the estimated $\langle l_s \rangle$ for our CNT
networks estimated according to Pan's model;[20d] e) Estimated average number of contacts per CNT \( \langle C \rangle \) measured from \( \langle l_s \rangle \) and initial length distribution of CNTs; f) Distribution of estimated number of contacts per CNT measured from \( \langle l_s \rangle \) and initial length distribution of CNTs. Red line represents \( \langle C \rangle \).

As mentioned above, changes in \( \langle C \rangle \) will have a significant effect on the resulting electrical conductivity of the networks which were further analyzed using the effective medium approximation in combination with 4-point conductivity measurements. A systematic increase of the measured conductivity from C_1 to C_3 was observed (Figures S8 and S10), indicating a predominant effect on the electrical transport of the average contact number per particle. An analysis based on the effective medium approximation shows that the conductivity varies linearly with \( \langle C \rangle \) (see SI section 6), supporting thus our conclusion that the variation of \( \langle C \rangle \) is indeed the cause of the observed increase in conductivity with increasing aspect ratio.[23]

To get more insight into the transport properties of the networks, we modelled electrical conductivity in a bottom-up fashion based on above analysis in combination with estimates of the contact areas (see SI section 3.3) by QET. Electrical conduction in CNT networks is controlled by the conductivity of the CNTs themselves and their contacts. If we assume that that the resistance of the CNTs is negligible as compared to the resistance of the CNT-CNT contacts,[24] the number of contacts \( N_c \) and the contact resistance (inversely proportional to the CNT-CNT contact area \( A_c \))[25] dictate the conductivity.[26] This leads to a network of perfect conductors (CNTs) connected by Ohmic resistors \( R_c \) (CNT-CNT contacts) for which Kirchoff’s laws directly apply (see SI section 3.4).

In calculating the electrical resistance of the imaged networks, we applied a current of 1 \( \mu \)A between two terminal nodes of the network along the x-axis (see SI section 3.4). As shown in
Figure 4a and Figure S9a, the calculated voltage gradually drops across the network as the current pass through several resistors (CNT-CNT contacts). The voltage difference between the two terminal points decreases in going from C1 to C3 (Figure 4a), and it scales with the total number of contacts $N_c$ (Figure 4b). In any (disordered) network, the electrical conduction takes place primarily along the least resistant (LR) pathways. Hence, between any 2 arbitrary points of the network tracking the voltage drop and the number of contacts is required to find LR pathways. We measured all possible end-to-end LR pathways along the $x$-axis of the imaged network and show the total number of CNT-CNT contacts in Figure 4c (and their terminal voltage in Figure S9b). First, we sorted the terminal nodes of the CNT based on their position in both ends of the $x$-axis, followed by a matrix plot of connected ends. Second, if there is no possible connection between 2 nodes on opposite sides, then it is removed from the analysis (see SI section 3.5 for further details).

As expected, C1 shows the highest total number of CNT-CNT contacts (Figure 4c). Surprisingly, C3 shows a slightly larger number of CNT-CNT contacts in LR pathways than C2, which is a result of local network inhomogeneities and/or statistics. To visualize these differences, among all the LR pathways the global minimum is highlighted in Figure 4d and the corresponding voltage drop at CNT-CNT contacts is shown in Figure 4e. In C1, at the start, the voltage drop was negligible compared to C2; however, at later stages a steep voltage drop resulting from significantly reduced contact areas $A_c$ are observed (See SI Figure S9c for $A_c$ distribution). The lower voltage drop for C3 results from increased contact areas along the LR pathway. This direct influence of reducing $A_c$ (in C1) and increasing $N_c$ compensated by increased $A_c$ (in C3) on the LR pathways changes the connectivity and conductivity locally. The subtle effects of local inhomogeneities increase when analyzing 2 distinct local microstructures in a highly inhomogeneous network, referred to as C4 (See SI section 8 for the detailed analysis). In terms of effective medium approximation, these variations in $A_c$ and
$N_c$ led by inhomogeneous packing (caused by the assembly behavior, processing, and fabrication) represent the effective term $\chi$ that changes $\langle C \rangle$ locally (also see SI section 9 for orientation ordering that affects $\langle C \rangle$). Therefore, the local conductivity $\sigma_0$ (See SI, section 6) and the effective medium conductivity $\bar{\sigma}$ are determined by the average morphology of the entire network. Hence, if the network contains many highly conductive regions due to inhomogenously packed local microstructures, the average conductivity and connectivity can be drastically improved as observed in several cases.\textsuperscript{[11b, 27]}

Figure 4: Electrical conductivity and connectivity analysis of CNT networks. a) Illustration and distribution of voltages (in V) at CNT-CNT contacts across C1, C2, and C3 when an arbitrary current (we chose 1 $\mu$A) is applied between two end points on the x-axis of the network. The resistance at contacts $R_c$ (ranges between $10^1 \Omega$ and $10^5 \Omega$ – see SI section 3.4)
were classified based on the CNT-CNT contact area $A_c$ measured between the CNTs. Color bar represents the corresponding voltage drop (in V); b) Total number of CNT-CNT contacts in CNT networks; c) Probability distribution of CNT-CNT contact number found along all possible end-to-end least resistant pathways in x-axis; d) Visualization of the global minimum LR pathway in networks; e) Voltage drop along global minimum LR pathway plotted as a function of contact number.

CONCLUSIONS

In summary, for the first time QET was employed to obtain a unified experimental view on nanoscale packing, connectivity and conductivity of CNT networks. We highlight the effects of varying CNT length and dispersity on the resulting packing density and show that they can be modelled close to their macroscopic monodisperse counterparts, i.e., with the effective medium approximation. We utilize connectivity data ($l_s$, $N_c$, $A_c$) to determine the electrical conduction pathway to explain differences in functional performance. Finally, we show how inhomogeneities in the network can lead to the formation of highly conductive networks. We expect that QET will be essential to obtain fundamental insight into nanoscale packing phenomena and in future may allow us to tune the synthesis/fabrication of materials by designing the assembly behavior into the initial polydispersity and interactions of the building blocks to achieve improved functional properties.

METHODS

Detailed experimental details are given in the Supporting Information.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

KEYWORDS


REFERENCES


Carbon nanotube networks are imaged quantitatively in three dimensions to experimentally assess the effects of nanoscale packing density, contact distribution in random and non-random configurations. This allows to establish a direct link between network topology and its electrical properties as a function of CNT aspect ratio and length polydispersity in a bottom-up fashion.

**Keyword:** Quantitative Electron Tomography.