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Bridging the Junction: Electrical Conductivity of Carbon Nanotube Networks

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ABSTRACT: Carbon nanotube (CNT) films have excellent conductivity and suitable flexibility for chemical sensing and touch screen devices. Understanding the pathways of charge transport within the network is crucial to develop new functional materials and improve existing devices. Here, we study the electrical conductivity of networks of CNTs containing Group 11 metals (Au, Ag, and Cu), s-p metals (K, Ca, and Al), AuCl₃, AuCl₄, and Cl using quantum mechanical methods and semiclassical Boltzmann transport theory. The conductivity is characterized along the nanotubes and across the intersecting junction. The conductivity is much weaker across the junction than along the nanotubes and could be strengthened in all directions using dopants. The largest



increase in conductivity is induced by Al along the nanotubes and by Cu across the intersection [389-fold and 14-fold relative to the pristine (8,0) network, respectively]. Additionally, Ag dopants activate charge transport along the semiconducting nanotube in heterogeneous networks of mixed metal and semiconducting nanotubes. The conductivity along the semiconducting nanotube increased 781-fold. This activation removes the bottleneck of charge transport along the semiconducting nanotubes within the network of mixed chiralities. Small amounts of dopants within nanotube networks drastically change the directional conductivity and provide new pathways for charge transport for applications such as chemical sensing or touch screens.

INTRODUCTION

Carbon-based materials are promising materials for a range of applications. Carbon nanotubes (CNTs) and graphene have large electrical conductivity and suitable flexibility for use in applications such as chemical sensing or touch screens.^{1–3} Charge transport along CNTs has been exploited in nanotubes wrapped in polymers⁴ or decorated with Pd for H₂ detection.⁵ However, a more complete molecular-level understanding of the electrical transport would improve functionalization and better interpretation of degradation mechanisms.

Electrical transport through a CNT film involves electronic and morphological aspects such as the nanotube length, bundling, alignment, and number of intersection regions (junctions).^{6–16} Granular information from percolation theory or charge carrier transport models has highlighted the importance of nanotube junctions to the total conductivity of a network.¹⁷ However, standard percolation theory lacks the electronic structure information of the nanotubes. Computational studies based on density-functional theory (DFT) have revealed how the overall conductivity and electronic structure of a CNT network are changed by analytes or dopants such as H_{22}^{18} nitrogen oxides,^{19,20} gold chlorides,^{21,22} halogens,²³ and transition metals.²⁴ DFT methods predict significant variation in the electronic transport and reactivity of different configurations of N-substituted nanotubes.²⁵⁻²⁷ Enhanced conductivity and improved sheet resistance have been measured experimentally in films containing Cl anions²⁸ or doped with Cr.²⁹ Furthermore, atomic force microscopy measurements

have supported the importance of the tube crossing region in the total electrical transport through a network. $^{30-32}$

In this manuscript, we investigate CNT networks doped with atomic and molecular dopants using DFT and semiclassical Boltzmann transport theory. First the effect of nanotube junction angle is demonstrated on junctions with two-dimensional periodicity. The junctions are made periodic in the third direction, which enables calculation of the conductivity across the junction in pristine networks. The effects of dopants on the electronic structure and the anisotropy of electrical conductivity of the network are examined. Charge transport within CNT thin films with heterogeneous chirality is expected to be limited by the semiconducting tubes. The focus is on homogeneous networks of (8,0) nanotubes and other chiralities [semiconducting (16,0) and metallic (9,0) nanotubes], and mixed networks are also considered.

Computational Details. All calculations presented in this work are performed with CRYSTAL17.³³ Junctions of two CNTs were constructed and made periodic in two dimensions (Figure 1). Networks of CNTs were constructed with periodicity in three dimensions. The atomic positions and

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Figure 1. Carbon nanotubes as (A) junction with two-dimensional periodicity viewed laterally and top-down. The nanotube intersection angle is θ . A network of nanotubes with three-dimensional periodicity either (B) pristine or (C) doped with Ag atoms. There is one dopant atom per nanotube. The nanotubes have (8,0) chirality.

lattice constants of the junctions and networks were relaxed to their minimum energy geometric conformation without any symmetry constraints. The junctions were relaxed from starting geometries with intersection angle, θ , equal to 90, 75, or 45°. The repeating unit along the nanotubes was about 1.7 nm long for the structures with initial intersection angle of 90 or 75°. To accommodate the larger overlap at smaller θ , the nanotubes and unit cell were elongated to 3.4 nm in the junction and network with initial intersection angle of 45°. The focus of the manuscript is on nanotubes with (8,0) chirality. Additionally, (9,0) or (16,0)networks and mixed networks consisting of one (8,0) and one (9,0) nanotube were investigated. Unless otherwise specified, the dopants were oriented at the center of the intersection and unrestrained during optimization. All systems belong to the triclinic P1 space group and are overall neutral. The optimized structures are provided in the Supporting Information.

We applied the PBE0 hybrid density functional method with 25% Hartree–Fock and 75% PBE exchange^{34,35} and utilized an all-electron, Gaussian-type basis sets based on the molecular Karlsruhe basis sets.³⁶ All basis sets are listed in the Supporting Information. Spin polarization was taken into account in all pristine and doped (8,0) networks due to the open-shell nature of some of the dopants. The (9,0) networks were calculated without spin polarization. The reciprocal space was sampled using a Monkhorst–Pack-type $2 \times 2 \times 2$ k-point mesh. The calculations were carried out with Coulomb and exchange integral tolerance factors (TOLINTEG) set to tight values of 8, 8, 8, 8, and 16.

Since our main aim was to characterize the qualitative trends in electrical conductivity resulting from doped CNT networks, van der Waals effects were not considered, and the conductivities are analyzed relative to pristine cases. The electrical conductivity, σ , at temperature, *T*, equal 300 K was obtained using Boltzmann transport theory as implemented in CRYSTAL17.³⁷ The transport coefficient was solved within the constant relaxation time and rigid band approximations such that

$$[\sigma]_{\rm qr}(\mu, T) = e^2 \int dE \left(-\frac{\partial f_0(\mu, T)}{\partial E} \right) \Xi_{\rm qr}(E)$$
(1)

where the energy was *E*, Fermi-Dirac distribution was f_0 , Fermi level was μ , and the transport coefficients, $\Xi_{qr}(E)$, are defined as

$$\Xi_{\rm qr}(E) = \tau \sum_{\mathbf{k}} \frac{1}{N_{\mathbf{k}}} \frac{1}{V} \sum_{i,j} v_{i,q}(\mathbf{k}) v_{j,r}(\mathbf{k}) \delta(E - E_i(\mathbf{k}))$$
(2)

 $v_{i,q}$ was the velocity of the *i*th band along q, N_k is the number of k-points over the cell volume, V, and the lifetime, τ , was 1 fs for all studied systems. The conductivity is shown as the summation of the α and β spin states. The reciprocal space paths for the electronic band structures of the networks were obtained from the SeeK-path service.³⁸ The density of states and electrical conductivities were obtained with dense k-point mesh, and details are provided in the Supporting Information.

RESULTS AND DISCUSSION

Pristine Junctions: Two-Dimensional Periodicity. The minimum energy geometry of two intersecting (8,0) nanotubes was identified from three starting intersection angles: 90, 75, and 45°. The final optimized intersection angles were 88, 65, and 37°. The minimum C–C atomic separation across the junction was 3.3–3.4 Å. This distance is approximately equal to the separation between sheets in graphite obtained using PBE0 (3.35 Å).

The band gap was 1.50, 1.49, and 1.49 eV for the (8,0) nanotubes intersecting at 88, 65, and 37°, respectively. This was consistent with the band gap of an individual (8,0) CNT (1.50 eV). The electrical conductivity is large along the CNTs due to the delocalized π -electron system (Figure 2). The conductivity is calculated along the Cartesian axes (x, y) rather than the unit cell axes (a, b). While the magnitude of conductivity is nearly identical along x and y in the 88° junction, it is asymmetric for the 65 and 37° junctions. The Cartesian and unit cell axes are nearly coincident in the 88° junction. At other intersection angles, the conductivity is larger along the Cartesian axis with an aligned tube. The average of the conductivities along *x* and *y* in the 65° junction is approximately equal to the 88° junction. This is not the case for the 37° junction. The band structures validate that the asymmetry of the electrical conductivity is due to the rotation of the Cartesian axis with respect to the unit cell axis (Figure 3). The band velocity is large and symmetric along the Γ -X and Γ -Y directions regardless of the intersection angle.



Figure 2. Electrical conductivity and density of states of junctions of pristine (8,0) CNT intersecting at (A) 90, (B) 65, and (C) 37°. σ_{xx} and σ_{yy} are the conductivities along the *x* and *y* Cartesian axes, respectively. The system is periodic in two dimensions. The energy is reported relative to the Fermi level.

The 37° junction has band folding due to the supercell. The local conductivity minima occur when the bands are flat such as at -0.5 and -1.5 eV. These are Van Hove singularities, which have local maxima in the density of states and have previously been noted for CNT systems.²⁰

Pristine Networks: Three-Dimensional Periodicity. The electrical conductivity in the previous sub-section was restricted to the nanotube plane due to the two-dimensional periodicity of the junctions. To calculate the charge transport properties between nanotubes with finite intersection area, the periodicity is expanded. The primitive cell lattice constants and band gaps of pristine networks of homogeneous (8,0), (16,0), or (9,0) nanotubes, and networks having a mixture of (8,0) and (9,0) nanotubes, are shown in Table 1. The (8,0) network was

Table 1. Intersection Angle (θ) and Band Gap of Pristine Carbon Nanotube Networks

	starting $\theta\left(^\circ\right)$	optimized θ (°)	gap (eV)
(8,0)	90	89.4	1.46
(8,0)	75	57.2	1.47
(8,0)	45	39.2	1.49
(9,0)	90	90.1	0.23
mixed (8,0)/(9,0)	90	95.8	0.24
(16,0)	90	87.2	0.81

optimized with an intersection angle, θ , of either 89, 57, or 39°. The distance between nanotubes across the junction was 3.2 Å for the 89 and 39° networks and 3.3 Å for the 57° network, as estimated from the tube diameter and cell length. Due to curvature of the nanotubes, the junction distance is smaller than the interlayer distance in graphite at the same level of theory (3.35 Å). This was also found in pristine networks of nanotubes having different chiralities. The junction distance was 3.3 Å for the (16,0) network, 2.9 Å for the (9,0) network, and 3.0 Å for the mixed (8,0)/(9,0) network. The small variation is likely related to the distinct curvatures and changes in the unit cell shape.

The intersection angle did not significantly change the band gap of (8,0) networks. As expected, networks of different chiral tubes had vastly different band gaps. The (16,0) network was semiconducting with narrower band gap (0.81 eV). The band gap was narrowest in networks containing (9,0) tubes, either exclusively or as a mixture. A small but finite gap was expected from metallic nanotubes, ^{39,40} which indicates the metallic nature of the network.

Similar to the two-dimensional junctions, charge is easily transported along the tubes in pristine networks due to the delocalized π -electron system. Furthermore, the three-dimensional periodicity enables the calculation of the electrical conductivity across the junction. Although methods such as Green's function²⁴ and hopping mechanisms⁴¹ can improve the quantitative conductivity predictions, our focus is on the qualitative trends in the conductivity of doped networks at the Fermi level accessible using semiclassical Boltzmann transport theory. Pristine networks are studied here first to establish a baseline for the doped nanotube networks. The directional conductivities of the (8,0) network intersecting at 89° are shown in Figure 4A. The conductivity is much weaker across the intersection than along the tubes (see the inset). This is consistent with the previous literature^{24,31,42,43} and suggests that intersections are the bottleneck of electrical conductivity in pristine networks. The disparate properties are apparent in the band velocity near the Fermi level (Figure 4B). The bands are highly dispersive and have large overlap regions along $\Gamma - Y$ and



Figure 3. Band structures of two (8,0) nanotubes intersecting at (A) 88, (B) 65, and (C) 37°. The energy is reported relative to the Fermi level.

Article



Figure 4. (A) Electrical conductivity of a three-dimensional network of pristine (8,0) CNTs intersecting at 89°. σ_{yy} and σ_{zz} are the conductivities along the *y* and *z* Cartesian axes, i.e., the nanotubes. The relatively small conductivity across the junction (σ_{xx}) is shown in the inset. (B) Band structure and density of states of the same network. (C) Projected charge density of the topmost valence band (no. 768), which is colored in blue in (B). The isovalue is $3 \times 10^{-4} a_0^{-3}$, and the blue isosurface is a visualization artifact due to the edge of the unit cell. The occupancy of this band is 2.00 electrons ($\alpha + \beta = 2.00$ and $\alpha - \beta = 0.00$). The energy is reported relative to the Fermi level.

 $\Gamma-Z$ (the direction of the nanotube axis). The band dispersion is much lower along $\Gamma-X$ (across the junction). The delocalized π electron system along the nanotubes is further illustrated by the charge density of the topmost valence band, as shown in Figure 4C. Similar effects are observed in the pristine (8,0) networks intersecting at 57 and 39° (Figure S1).

Consistent with (8,0) networks, networks of other chiralities have markedly weaker conductivity across the junction compared to along the tubes (Figure S2). The electrical conductivity at the Fermi level is 159-fold weaker across the junction of the (9,0) network than that along the nanotubes. The bottleneck at the Fermi level is worse (794-fold) in a mixed

Table 2. Lattice Constant across Junction (a), CNT
Intersection Angle (θ), and Cell Volume (V) of Doped (8,0)
CNT Networks

	a (Å)	θ (°)	$V(Å^3)$
pristine (8,0)	19.1	89.4	5473
K	23.0	86.6	6406
Ca	21.7	88.6	6233
Al	20.8	104.4	5293
Cu	21.3	85.4	6096
Ag	22.2	77.7	6216
Au	22.1	71.4	6017
AuCl ₃	25.3	90.0	7259
AuCl ₄	25.8	90.0	7344
Cl	24.1	79.5	6682

Table 3. Binding Energy Per Dopant in (8,0) CNT Networks

binding energy per dopant (kJ/mol)
-538
-711
-210
-212
-211
-215
-107
-207
-227



Figure 5. Band structure of the (8,0) CNT network doped with (A) K and (B) Ca. There is one dopant atom per nanotube. The energy is reported relative to the Fermi level.

Table 4. Electrical Conductivity of Pristine and Doped (8,0) CNT Networks at the Fermi Level Reported Relative to the Pristine (8,0) Network Intersecting at 89° [14 S/m across the Junction (σ_{junc}) and 5360 S/m in the Plane of the Tubes (σ_{plane})]

	gap^{a} (eV)	$\sigma^*_{ ext{junc}}$	$\sigma^*_{ m plane}$
pristine (89°)	1.46	1.0	1.0
pristine (57°)	1.47	14.3	1.0
pristine (39°)	1.49	0.7	1.2
K	N-type	63.0	12.7
Ca	N-type	49.7	4.8
Al	N-type	388.7	5.4
Cu	N-type	6.1	13.9
Ag	N-type	5.7	13.7
Au	N-type	55.0	9.8
AuCl ₃	P-type	0.5	5.5
AuCl ₄	P-type	17.4	6.6
Cl	0.50	2.6	0.8

^{*a*}N-type means that the pseudogap lies below the Fermi level, and P-type means that it lies above the Fermi level.



Figure 6. (A) Electrical conductivity of a (8,0) CNT network doped with Al. σ_{yy} and σ_{zz} are the conductivities along the *y* and *z* Cartesian axes, i.e., the nanotubes. The relatively small conductivity across the junction (σ_{xx}) is shown in the inset. (B) Band structure of the same network. (C) Charge density of the top valence band (no. 781) which is colored blue in (B). The isovalue is $3 \times 10^{-4} a_0^{-3}$, and the blue isosurface is a visualization artifact due to the edge of the unit cell. There is one dopant atom per nanotube. The energy is reported relative to the Fermi level.

Figure 7. Electrical conductivity and density of states of (8,0) CNT networks doped with (A) Ag, (B) Au, and (C) AuCl₃. The relatively small conductivity across the junction (σ_{xx}) is off-scale. There is one dopant per nanotube. The energy is reported relative to the Fermi level.

network containing semiconducting (8,0) and metallic (9,0) nanotubes. Notably, the conductivity of a mixed network is largest along the metallic tube. The charge density of the topmost valence band is more pronounced along the metallic tube. The asymmetric charge transport is validated by the projected density of states in which the states of the semiconducting tube straddle the Fermi level. The mixed network is discussed in more detail in comparison to the doped mixed network.

Networks of other semiconducting nanotubes have electronic properties that qualitatively resemble the (8,0) network. For example, the (16,0) network has highly dispersive bands at the band edge albeit a smaller band gap (0.81 eV, Figure S3).

Doped Networks: Three-Dimensional Periodicity. Networks containing experimentally relevant dopants, including Au, AuCl₃, and AuCl₄, 28,44 were examined. To analyze the additional trends, the dopants were expanded to other Group 11 metals, s-p metals (K, Ca, and Al), and Cl. The neutral dopants were at the center of the junction (Figure 1C), and the primitive cell lattice constants of the doped (8,0) networks are shown in Table 2. The metal dopants donate electrons to the nanotubes, leading to geometric changes. The changes upon the addition of dopants are predominantly to the intersection angle, θ , and the cell length across the junction, a. Molecules or dopants with relatively large ionic radii, such as K or Au, form relatively long bonds with the nanotube than dopants having smaller ionic radii, such as Al. For example, the lattice expands from Al < Ca < K, in accordance with their ionic radii. 45 The AuCl_4 dopants have the longest junction separation due to the size of the molecule. The length across the junction is slightly smaller in networks doped

Figure 8. (A) Electrical conductivity and density of states and (B) band structure of a (8,0) nanotube network doped with Cl. The relatively small conductivity across the junction (σ_{xx}) are off-scale. There is one dopant atom per nanotube. The energy is reported relative to the Fermi level.

Table 5. Electrical Conductivity of Pristine and Doped Nanotube Networks Containing Metallic Tubes at the Fermi Level Reported Relative to the Pristine (8,0) Network Intersecting at 89° [14 S/m across the Junction (σ_{junc}) and 2680 S/m along the Tube (σ_{tubeA} , σ_{tubeB})]

	$\operatorname{gap}^{a}\left(\mathrm{eV}\right)$	$\sigma_{ m junc}$	$\sigma_{ m tubeA}$	$\sigma_{ m tubeB}$
pristine (9,0)	0.23	6.7	2.8	2.8
pristine, mixed (8,0)/(9,0)	0.24	1.5	3.1	< 0.01
Ag-doped(9,0)	N-type	48.2	12.7	13.0
Ag-doped mixed (8,0)/(9,0)	N-type	0.3	9.1	6.2
^{<i>a</i>} N-type means that the pseu	dogap lies be	low the	Fermi lev	el.

with Au than Ag. This may be due to electronegativity of the dopant. Au and Ag are relatively similar in size, but Au has a larger ionization energies or electronegativity⁴⁶ which makes it less willing to donate electrons to the nanotubes. As will be discussed later, the Cl-doped network is a special case because Cl forms a chemical bond with only one of the nanotubes.

The interactions between the dopants and the nanotubes are energetically favorable, and the binding energies are provided in Table 3. The binding energy per dopant is calculated using $(E_{doped} - E_{pristine} - 2E_{dopant})/2$ where $E_{pristine}$, E_{doped} , and E_{dopant} are the energies of the pristine and doped networks and the isolated dopants, respectively. The d metals are situated adjacent to a C–C bond of each nanotube, which leads to the local coordination with four neighboring C atoms. K and Al shift to the edge of the junction, and the open geometry around the dopant leads to a skewed lattice network. Ca is coordinated in a metallocene-like manner.

The nature of the bonding between the dopant and the nanotube influences the electronic properties of the doped networks. The networks may become N-type or P-type systems according to the electron affinity of the dopant. For example, the 4 s electrons of K and Ca are donated to the nanotubes creating an N-type conducting system with a pseudogap below the Fermi level (Figure 5). Similar to the pristine networks, the bands have high and symmetric dispersion along $\Gamma-Y$ and $\Gamma-Z$ with large overlap between states. The additional electrons from the dopants raise the Fermi level higher. Intriguingly, the α and β spin states of the Ca-doped network are delocalized on a particular nanotube.

While the electrical conductivity is calculated as a function of the energy, the focus is on the junction and in-plane conductivities at the Fermi level. Doping shifts the Fermi level into the dispersive band edges which facilitates charge transport. The conductivities are reported relative to the pristine (8,0)network intersecting at 89° , as listed in Table 4. The in-plane conductivity is the average along the *y* and *z* axes. Most of the dopants considered here enhanced the electron flow both along the tubes and across the junction. The largest improvements in the plane of the tubes were for Cu (13.9-fold) and Ag (13.7fold).

The Al-doped network, another N-type network, has the largest calculated conductivity across the junction. The network is a metallic conductor with partially filled states at the Fermi level. The Al dopant extends the electron density across the junction without strongly disrupting the delocalization along the tubes (Figure 6). This leads to significantly more dispersive bands along Γ -X compared with the pristine network. The bridged electron density across the junction was validated by visualizing the charge density of band no. 781 (colored blue in the band structure). The band's occupancy is 1.58 electrons ($\alpha + \beta = 1.58$, $\alpha - \beta = 0.00$). Notably, the skewing of the network lattice and nanotube intersection angle lead to a more compact cell volume than the pristine network.

The junction conductivity of the network doped with Au is better than Ag (Figure 7A,B), which is consistent with its higher electronegativity. The directional conductivities of the Cu- and Ag-doped networks are similar.

The networks become P-type when containing electronwithdrawing dopants, such as AuCl₃ and AuCl₄. Similar to the N-type networks, the charge transport increases along the tubes. This occurs due to the lowering of the Fermi level into the highly dispersive states at the valence band edge (Figure S4). The network doped with AuCl₃ has smaller conductivity across the junction than the pristine network (Figure 7C). Its band dispersion along Γ -X is low, and the charge density does not extend across the junction. Interestingly, the conductivity of AuCl₄ is comparatively larger than that in AuCl₃ despite the similar band dispersion. The charge is transported more easily between the bands in AuCl₄ due to their higher degree of overlap at the Fermi level. AuCl₄ typically exists in an anionic form [AuCl₄][¬], and so it has a strong electron-withdrawing capacity as part of the network.

The conductivities along the tubes are symmetric with the exception of the networks containing Cl (see the Supporting Information for details). The anisotropy in the Cl-doped networks was due to the covalent bonding of the dopants only with the tube along the *y*-axis. The bonding is apparent from the unequal distances between the Cl and adjacent tubes (1.89 and 3.5 Å). The conductivity is larger along the *y*-nanotube than the

Figure 9. Electrical conductivity of (A) pristine and (B) Ag-doped networks containing mixtures of (8,0) and (9,0) nanotubes. σ_{xx} and σ_{zz} are the conductivities along the *x* and *z* Cartesian axes, i.e., the nanotubes. The relatively small conductivities, including across the junction (σ_{yy}), are shown in the inset. Band structure and density of states of (C) pristine and (D) Ag-doped networks containing mixtures of (8,0) and (9,0) nanotubes. There is one dopant atom per nanotube. The energy is reported relative to the Fermi level.

z-nanotube (Figure 8). The directional bonding is further validated by the asymmetric band dispersion.

Charge is transported more easily in pristine networks containing metallic nanotubes than the (8,0) nanotubes (Table 5). Interestingly, doping the network of mixed (9,0)and (8,0) nanotubes activates the charge transport along the semiconducting tube. The electrical conductivity along the semiconducting tube improves by 781-fold when doped with Ag (Figure 9). The drastic change is due to the orbital mixing between the dopant and the intersecting nanotubes. The localized Ag states mix with delocalized π -electron system of the (8,0) nanotube and become occupied with electrons. The overlapping bands at the Fermi level in the doped system have high dispersion along the tubes (X and Z). The rearrangement of states is validated by the projected density of states. The band edges in the pristine network are predominately from the metallic nanotube, and the states with density on the semiconducting nanotube straddle the Fermi level. However after the N-type doping, the pseudogap conducting band edge has density on both the metallic and semiconducting nanotubes. This rearrangement improves the charge transport along both nanotubes in the mixed network.

The doping effects in the networks of other homogeneous chiralities are similar to the homogeneous (8,0) networks. The magnitude of the conductivity enhancement in the networks of metallic (9,0) nanotubes doped with Ag [7.2-fold across the junction and 4.6-fold along the tubes relative to the pristine

(9,0) network] is approximately the same as in the (8,0) nanotube network. Further details about the directional conductivities of doped networks of different chiralities are reported in the Supporting Information.

The effect of the dopant position was investigated by fully relaxing the atomic positions and lattice of a network doped with a single dopant atom. The dopant was initially situated at the center of the intersection or shifted along one of the nanotubes by either 5 or 8 Å. The dopant initially situated 5 Å away from the intersection shifted back to the intersection in the minimum energy conformation (Figure S5). The dopant did not relocate when initially situated 8 Å away from the intersection, and the minimum energy conformation was 98 kJ/mol less energetically favorable than that at the intersection for Ag and 104 kJ/mol less energetically favorable for Au. Exceptionally, there is only one dopant per two nanotubes, and it is a closed shell calculation.

CONCLUSIONS

The electrical conductivity of pristine and doped CNT networks was studied using quantum mechanical methods and semiclassical Boltzmann transport theory. The conductivity was calculated along the CNTs and across the intersections of the three-dimensionally periodic networks. The charge transport was smaller across the junction than that along the nanotubes. Furthermore, the charge transport in networks of homogeneous and heterogeneous mixtures of chiralities was larger along metallic nanotubes than semiconducting ones. This suggests

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that semiconducting nanotubes are the bottleneck of charge transport within CNT films.

The electrical conductivity of nanotube networks containing experimentally relevant dopants, including Au, AuCl₃, and AuCl₄, Group 11 metals, s–p metals (K, Ca, and Al), and Cl were examined. The dopants are most energetically favorable at the intersections of the tubes. The electronic structure and charge transport through the nanotube network are altered, and doping can increase the conductivity along nanotubes and across their intersections. The largest increase in conductivity along the nanotubes of a homogeneous (8,0) network was induced by Al dopants (389-fold relative to the pristine network). Cu dopants had the largest increase conductivity across the intersection (14fold). Delocalization of the α and β spin states along a particular nanotube of the Ca-doped network suggests the possibility of spintronics effects in CNT films. The precise changes depend on the bonding and chemical properties of the dopant.

Our results show that doping activates charge transport in heterogeneous networks of mixed metal and semiconducting nanotubes. The conductivity along the semiconducting nanotube increased 781-fold after doping the heterogeneous network with Ag. The qualitative improvements demonstrate that incorporation of small amounts of atomic dopants within CNT networks could remove bottlenecks and provide new pathways for charge transport for applications such as chemical sensing or touch screens.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03904.

Lattice parameters, basis set information, computational details, pristine (8,0) networks at other intersection angles, networks doped with gold chlorides, and other networks of other chiral nanotubes (PDF)

Optimized structures of three-dimensional networks in the CIF format (ZIP)

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Notes

The authors declare no competing financial interest.

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