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Tuning the electrical transport properties of double-walled carbon nanotubes by semiconductor and semi-metal filling

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Manipulating the electrical properties of carbon nanotubes through semi-metal or semiconductor filling is of paramount importance in the realization of nano-electronic devices based on one dimensional composite materials. From low temperature electrical conductivity measurements of a network, of empty and filled double-walled carbon nanotubes (DWNT's), we report a transition in electrical transport features from hopping to weakly activated conduction by HgTe filling and also semi-metallic conduction in selenium (Se) filled DWNT's. Magneto-resistance (MR) studies of the filled DWNT's show suppression of the hopping conduction and a signature of 3D weak localization for Se@DWNT's at low temperatures and high magnetic fields. These results are discussed on the basis of strength of interaction between the filler material and the inner-walls of the host DWNT's, which enhances the electronic density of states (DOS) in the material as well as the change in the property of the filler material due to constrained encapsulation.

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I. INTRODUCTION

Filling of carbon nanotubes (CNT's) with metals or other materials has become an interesting research direction pursued by a large number of groups in the past decade.[1–5] This is because constrained encapsulation of certain materials, e.g. Se or HgTe, has been shown to modify the electrical properties of the host or foreign material, respectively.[6,7] Theoretical calculations have suggested that the conversion of semiconducting CNT's to metallic ones due to the introduction of '*p*' states from the filler element into CNT's bandgap.[6] Other studies have also suggested hybridization of the CNT's π states and filler element resulting in a slight change of the diameter.[8] It is important to understand the coupling between CNT's and the fillers to establish the specific change in the transport of this composite material. For example, encapsulation of an electron donor in metallic SWNT's enhances the electrical conductivity of the composite material[9] and titanium filling reduces the conductivity of SWNT's.[10]

Double-walled carbon nanotubes (DWNT's) are interesting materials in their own right, because they are in essence SWNT's with an outer shell, which can serve as a protection of inner shell. Their properties and morphology are very close to those of SWNT's[11] with an added advantage over SWNT's in some applications, such as nano-capacitors. This is because of the concentric cylindrical graphene sheets and relatively wider diameter of DWNT's compared to SWNT's that implies more capacity of filling. While there has been significant theoretical work in interpreting the transport of semiconductor filled DWNT's,[6,7,12] direct experimental proof of superior electrical transport has not been firmly established. One of the challenges has been the difficulty in synthesizing high quality DWNT's.[13] Semiconductor filling of nanotubes, particularly with Se and HgTe, is of immense interest because they exhibit photoconductive properties, which can be exploited in photovoltaic applications. Therefore, encapsulation of Se or HgTe in DWNT's is expected to combine the properties of both DWNT's and one dimensional Se and HgTe nanowires. Recent studies on the temperature dependence of Raman scattering in filled DWNT's have shown that van der Waals interactions between the host and the filling material are stronger for Se@DWNT's and weaker for HgTe@DWNT's samples.[14] Incorporation of HgTe in SWNT's was reported to transform it from the semi-metallic to semiconducting phase depending on the tube diameter.[7] Furthermore, *ab initio* calculations have predicted an increase in conductivity of SWNT's by Se filling,[6] which motivated us to extend the work to filled DWNT's through detailed transport measurements at low temperatures and high fields. In this study, we intend to determine the effect of semi-metal/semiconductor nanomaterials within the core of DWNT's on the transport of the composite materials. The significance of the interactions between the filling material and the carbon at the walls of tubes is investigated. Based on low temperature and magneto-resistance (MR) measurements we establish the modified electrical properties of DWNT's filled with Se and

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HgTe, which may find applications in various fields ranging from electrical interconnections in nano-electronics to nano-probes and optoelectronic sensors.[15,16]

II. EXPERIMENTAL WORK

DWNT's were prepared by catalytic chemical vapor deposition through the decomposition of a H_2-CH_4 mixture over an MgO based catalyst and the filling of the tubes was accomplished using a capillary technique. The amount of the filler material was estimated from high resolution transmission electron microscope studies given in Ref 14. Further details on the synthesis, filling and purification are given elsewhere.[14,17,18] The electrical transport measurements were performed by contacting a 5 μm thick film made of bundles of DWNT's deposited on a highly insulating fused quartz substrate with area $\sim$ 0.12 cm^2 over a temperature range of 300 K down to 2 K in the presence of 0 T to 12 T magnetic fields in a fully automated cryostat (Cryogenic Ltd, UK). A current of 10 μA was sourced from a Keithly 2400 and the voltage was measured using a Keithly 2182 A nano-voltmeter using the van der Pauw configuration.

III. RESULTS AND DISCUSSIONS

A. Electrical conductivity

Figure 1(a) shows Arrhenius plots for the filled and unfilled samples. It is evident from Fig. 1(a) and the inset that filling changes the transport properties of DWNT's as indicated by the weak temperature dependence of the conductance (G) of filled samples compared to unfilled DWNT's. Further analysis shows that Mott 3D variable range hopping (VRH) expressed by $G(T) = G_0\ exp\ [-(T_0/T)^{1/4}]$,[19] is the dominant conduction mechanism in the empty DWNT's between 2.1 K and 35 K mostly due to the disordered nature of the network (see Fig. 1(b)). The hopping characteristic temperature $T_o = 6.86$ K for unfilled DWNTs is found to be smaller than $\sim$15.8 K, the reported value for empty SWNT's.[20,21]

For HgTe filled DWNT's, the conductivity follows the Mott VRH mechanism only below 7 K (Fig. 1(b)). However, a very weakly activated behavior in the temperature range 10 K to 30 K becomes predominant (Fig. 1(a)). This suggests a semiconducting or semi-metallic nature of the composite material depending on the conductivity activation energy (E_{act}). Using the Arrhenius equation $G(T) = G_0\ exp(-E_{act}/kT)$ and Fig. 1(a) the value of $E_{act} \sim 1$ meV was derived for the HgTe filled samples. Such a small energy gap can be expected in semi-metallic CNT's whose diameter is slightly greater than 1 nm[22] and also reported in thick films of SWNT's network.[23]

We attempt to find the best possible explanation to improve the transport features in the filled DWNT's either by (i) altering the property of the filler or (ii) changing the DOS of the filled tubes by enhancing the interaction of the filler to the inner wall. Previous studies have suggested that

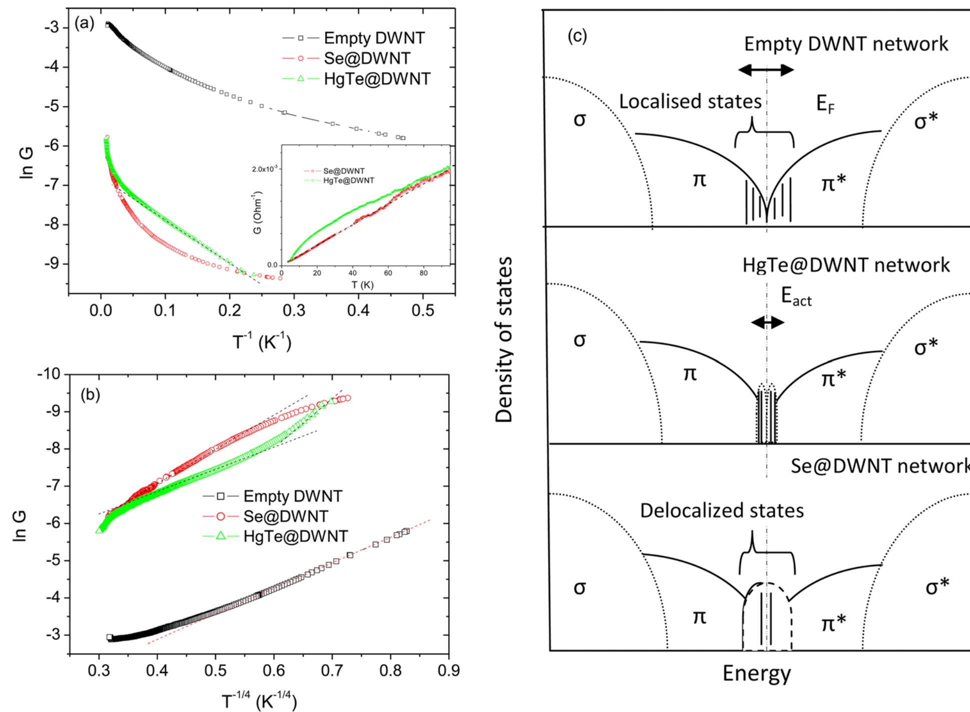

FIG. 1. (Color online) (a) Arrhenius plot (ln G *vs* T^{-1}) graph to investigate activated conduction mechanism in empty, Se and HgTe filled DWNT's. The linear behavior of the HgTe@DWNT samples in the temperature range (10 K to 30 K) indicates the significance of activated mechanisms. Inset: The temperature dependence of the conductance for Se and HgTe filled DWNT's. The linear $G(T)$ behavior shown by the Se@DWNT's samples suggests WL mechanism below the Debye temperature. The dashed line shows the linear fit to data. (b) ln G *vs* $T^{-1/4}$ graph to investigate Mott 3 D-VRH in empty, Se and HgTe filled DWNT's. A linear fit indicates the applicability of the model for the given temperature range. The dotted lines are to guide the eyes. (c) Schematic diagram of change of electronic properties showing the π and σ bands for the network of empty and filled DWNT's, which is similar to disordered materials. The electrical conductivity is governed by the density of localized states (marked as hatched lines) for empty DWNT's. Filling with HgTe reduces the density of localized states resulting in an activated conduction. Se filling further reduces the localized states and introduces delocalized states because of the stronger interaction between the host and filler material. The change of density of the delocalized states at the Fermi level plays an important role in the electrical transport of these materials.

HgTe confined in DWNT's is in amorphous or crystalline (sphalerite) phase, which can show a transition to 1D crystalline form depending on the diameter of the tube.[7] The DWNT's presently investigated have a large inner diameter distribution ranging from 0.5–2.5 nm and therefore, the possibility of the suggested conversion could be high. However, we believe that this conversion can be detected only from an isolated HgTe@DWNT or a few tubes unlike the network of entangled DWNT's, studied presently. Therefore, the small apparent energy gap implies that the observed activated mechanism in the HgTe@DWNT's sample is due to semi-metallic CNT's (averaged ensemble) and not crystalline HgTe for which a larger energy gap would be expected.[24]

To understand the strength of interactions between the filler and the inner wall of DWNT's, Raman studies were performed[14] which, showed weak interaction for HgTe@DWNT's, compared to Se@DWNT's. This result suggests that HgTe should have less effect on the host material than Se.[14] Nonetheless, our results indicate that, although the interaction between HgTe and DWNT's is weak, it is sufficient to modify the net electron transport of the DWNT network perhaps due to charge transfer between the two resulting in altering the bandgap of the DWNT's (see Fig. 1(c)). Overall, the present results show that transport through the 3D network of HgTe@DWNT's is more prevalent than transport through 1D crystalline HgTe nanowires. The schematic diagram in Fig. 1(c) illustrates the possible effect of filler elements on the band energy of the DWNT's network which includes disorder effects. Due to the presence of a large density of localized states at the Fermi energy level (E_F), hopping conduction dominates at low temperatures. The rapid decrease of electrical conductivity below $\sim$7 K suggests the presence of localized states near to E_F (Fig. 1(c)). As the temperature rises, the thermally activated electrons can overcome the localized states and can be transferred between delocalized states, which presents an activated conduction process shown in Fig. 1(a).

The VRH plot for Se@DWNT's shows a deviation from linearity, which indicates the presence of few localized states only very close to E_F. The change of conductivity with T at low temperatures is weak, which suggests the presence of delocalized states in the vicinity of E_F (Fig. 1(a) to 1(c)). As a result, the Se filled DWNT's show a linear *G versus T* behavior (Fig. 1(a), inset) in the temperature range 9 K to 80 K. For Se@DWNT's, the density of delocalized states is much higher than the other two samples so that at intermediate temperatures, the conductivity is governed by these states where the electrons can maintain phase coherence over a certain time. Such behavior has previously been observed in boron doped SWNT's[25] and metallic alloys where localization effects are considered.[26] The temperature dependence of the electrical conductivity (σ_l) due to the effect of localization is expressed as:

$$\sigma_l(T) = e^2/\left[\pi^2 \hbar L_i(T)\right]. \tag{1}$$

Here, the inelastic diffusion length is given by $L_i(T) = (l_e\, l_i/2)^{0.5}$, with l_e and l_i representing the elastic and inelastic mean free path, respectively. This expression gives two temperature dependences depending on whether the temperature is below or above one third of the Debye temperature i.e. $\sigma_l \propto T$ for $T < \Theta_D/3$ or $\sigma_l \propto T^{0.5}$ for $T > \Theta_D/3$. The temperature dependence of the conductivity in different regimes arises due to the T^{-2} dependence of the inelastic mean free path below $\Theta_D/3$, instead of the usual T^{-3} dependence because the requirement for momentum conservation is relaxed in amorphous metals.[26]

Like HgTe@DWNT's, the change of transport in Se@DWNT's may be explained by two effects, e.g. the change of structure of one-dimensional Se or change of the band energy of the DWNT's due to interactions between the filler and the host. We note that several reports have suggested Se is encapsulated in the amorphous phase for relatively wide CNT's.[7,14,27] This amorphous Se plays a crucial role in the conduction as it possibly introduces significant inelastic scattering. The linearity of *G versus T* graph (Fig. 1(a), inset) confirms the dominant effect of 3D weak localization (WL) with a T^{-2} dependence of the inelastic mean free path at temperatures below $\Theta_D/3$. The value for Θ_D was estimated to be $\sim$50 K in MWNT's and $\sim$466 K for bulk amorphous Se.[28,29] With the decrease of particle size, Θ_D reduces in nano-crystalline (15 nm) Se to approximately 156 K.[30] These temperatures suggest that Θ_D below or close to 150 K for the Se and DWNT composite should be expected and hence a linear $G(T)$ behavior, below 150 K or 51 K if we consider $\Theta_D = 466$ K or 156 K, respectively. This is in agreement with our results showing a linear $G(T)$ behavior below 51 K in Se@DWNTs samples. These results prove that the interactions between Se and DWNT's are sufficiently strong, as predicted earlier,[14] resulting in a drastic change of the transport properties of the composite.

Furthermore, Se filling in semi-conducting CNT's has been shown to convert them into semi-metallic CNT's provided the diameter is within a given range.[6] Since the present samples investigated have a wide diameter distribution, the metallic behavior observed in the Se@DWNT's samples is justified on the basis that new states from Se are introduced into the pseudo bandgap regions of DWNT's (see Fig. 1(c)). The stronger interaction between the Se and inner walls of the DWNT's may result in a significant reduction of the density localized states around the Fermi energy. This mechanism explains the experimental observation of semi-metallic conduction instead of hopping for Se@DWNT's samples, which, however, requires further analysis. It is interesting to note that filling of DWNT's either by HgTe or Se does not create any extra defect states, which explains the very small contribution of hopping transport to the total conductivity.

B. Magneto-resistance

The zero field transport mechanisms can be confirmed through MR (defined as $(R_B - R_0)/R_0$) measurements, which show positive MR for all samples at 4 K (Fig. 2(a)), which could be due to the presence of localized states yielding a hopping transport. However, an interplay of two mechanisms, i.e. electron orbital wavefunction shrinkage and quantum interference (i.e. weak localization), in the hopping regime produce positive MR and negative MR, respectively

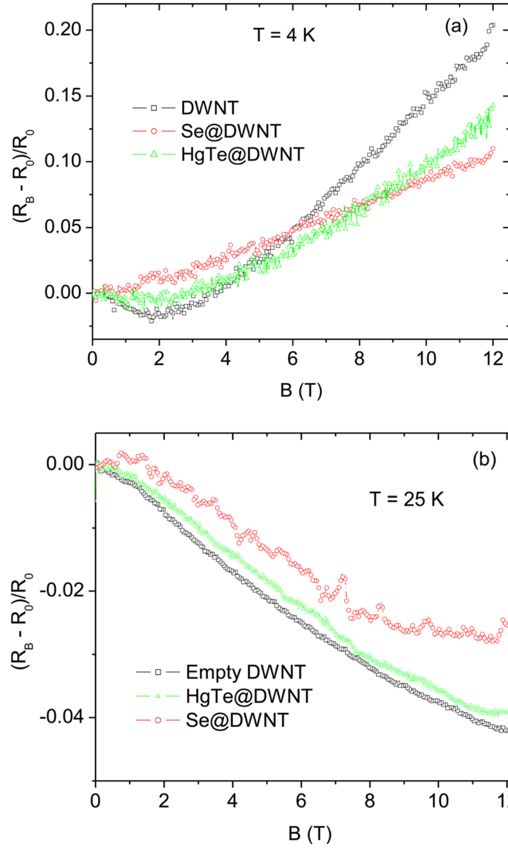

FIG. 2. (Color online) (a) MR vs B graph measured at 4 K for the empty, Se and HgTe filled DWNT samples. (b) MR vs B measured at 25 K for empty, Se and HgTe filled DWNT samples.

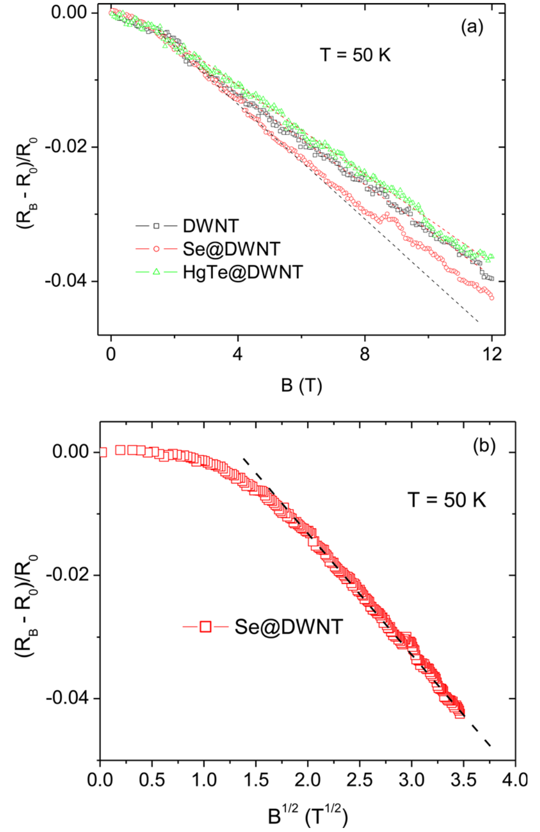

FIG. 3. (Color online) (a) MR vs B graph measured at 50 K for empty, Se and HgTe filled DWNT samples. (b) MR vs $B^{1/2}$ for the Se@DWNT sample. The dotted lines are to guide the eyes.

(Figs. 2(a), 2(b), and 3(a)). Electron orbital wavefunction shrinkage results in reduction of the hopping probability, increasing resistance and resulting in positive MR[31] (see (Fig. 2(a)). On the other hand, negative MR due quantum interference is characterized by a linear field dependence in the hopping regime[32] (see Fig. 2(b)). These two competing mechanisms explain the small upturns of MR at high fields and high temperatures shown in Fig. 2(b). However, at higher temperatures, i.e., 25 K and 50 K, the negative MR trend for HgTe@DWNT's appears to be almost similar to the empty DWNT. Figure 3(a) shows a linear negative MR (for empty and HgTe@DWNT's), a characteristic of quantum interference in the hopping regime. These observations indicate that the wave function shrinkage is prevalent at very low temperatures and high fields while the quantum interference dominates at high temperatures and low fields. The results also show the reduction of hopping transport in HgTe@DWNT's that supports the observation of activated conduction in these materials at low temperatures (Fig. 1(a)).

The positive MR Se@DWNT's at 4 K is characteristic of wave function shrinkage in the hopping regime. As the temperature increases above 10 K (as observed from the $G(T)$ data), a transition from hopping to WL occurs, which results in the negative MR with a $B^{1/2}$ dependence (Fig. 3(b)). Overall, there is a weaker field dependence of Se@DWNT's at 4 K and 25 K compared to the empty and HgTe filled DWNT, indicative of the enhanced metallic nature of the Se filled samples. Furthermore, the Se filled samples show a significant deviation from linear MR at high fields suggesting that hopping is not a dominant mechanism, in agreement with the zero field conductance versus temperature results. The suggested WL effects are characterized with the inelastic mean free path with T^{-2} dependence due to the amorphous Se in CNT's, which tend to enhance inelastic scattering as explained earlier.

IV. CONCLUSIONS

Delocalized metallic conduction can be observed in single isolated nanotubes or highly aligned nanotubes having very low degree of defects. A network formed by nanotube bundles generally shows the variable range hopping due to the high density of localized states near the Fermi level. The present analysis shows that the introduction of few states near the Fermi level due to the presence of foreign elements in the core of CNT's may result in an increase or reduction of the density of localized states depending on the structural phase and electro- negativity of the filler. This modifies the transport mechanism of nanotube network but does not necessarily translate to an improvement in the conductivity of the network. As such, there should be an in-depth study to establish the most dominant mechanism for the change of transport in filled tubes. However, we have shown experimentally that some of the previous theoretical predictions[6,7,12] on the change of electrical transport by Se and HgTe filling can be confirmed.

Doping of nanotubes by noble gases was found to be inefficient. In this report we attempted a different method of tuning the electrical transport in a nanotube network i.e. filling of tubes by semimetals and semiconductors. The filling of tubes could have degraded the quality of the material through the introduction of a large amount of disorder resulting namely in VRH conduction in the filled tubes. However, from low temperature conductivity and MR studies, we have shown that approximately 50% filling of DWNT by HgTe or Se results in a significant modification of the electrical transport properties which change from hopping to semi-metallic conduction. The relatively stronger van der vaals interaction between Se and the host material, shown from Raman studies might explain why Se filling enhances metallic behavior compared to HgTe in which the metallic behavior is not so pronounced. Indeed, the relationship between the tube-filler interaction and the change of conductivity needs to be studied further. A linear conductance versus temperature dependence in selenium filled DWNT's is due to WL effects with T^{-2} dependence of the inelastic mean path below Θ_D because of the amorphous nature of selenium in wider CNT's which results in significant inelastic scattering. From these measurements, the modified transport property of the filled DWNT's is established although the conductivity of filled materials is lower than the unfilled samples perhaps due to the low density of new states from the filler. The chemical stability of CNT's, photovoltaic properties of HgTe and Se and modified electrical conduction in the composite material raises hopes for new applications in nano-electronic devices.

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