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Electrical conductivity behavior of wet spun graphene fiber

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In this paper, we report the conductivity behavior in the insulating phase at zero magnetic field. We have theoretically investigated the temperature dependence of the electrical conductivity of wet spun graphene fiber and its composites. The temperature dependence of electronic conduction follows the law $\sigma \sim \exp(E_0/E)^m$. Indeed, the electronic conduction is dominated by the coexistence of two regimes: Efros–Shklovskii variable range hopping mechanism where $m = 1/2$ and the activated mechanism where $m = 1$. By using two different methods: the numerical method based on the calculation of the percentage deviation Dev (%) and the conductance curve derivative analysis method which is based on the logarithmic derivative function $W = d\ln\sigma/d\ln E$, we have found the exponent m is close to 1.

Keywords: graphene, Electrical conductivity, Variable range hopping conduction.

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Graphene fiber, a recently discovered member of the carbon fiber family, has potential applications in a variety of technology areas, from energy storage to structural components, electronics and optics, electromagnetics, thermal conductor and thermal management. Several theories and models try to explain the electronic transport phenomena in two-dimensional systems and especially the behavior of the electrical conductivity. In this context, two models can be evoked to explain this behavior: a model of thermally activated transport linked to the existence of a gap in the band structure and a model of transport by electron hopping to nearest neighbors between localized electronic states [1–4].

The theory of electron hopping to the nearest neighbor, called Variable Range Hopping (VRH), seems to be more adapted to describe the system. The VRH model does not take into account the electronic interactions, which are negligible at sufficiently high temperatures. On the other hand, at low temperature, these effects can no longer be neglected: this is the Efros–Shklovskii (ES-VRH) model [3,5,6]. In 2D, when the hopping probability is maximized, the conductivity in the VRH conduction regime takes the functional form [7,8]:

$$\sigma(T) = \sigma_0 \exp\left(-(E_0/E)^m\right), \qquad (1)$$

where σ_0 is a pre-factor that can be temperature dependent or independent and $m = 1/3$ for the Mott-VRH regime. At lower temperature or low charge concentration, electron repulsion localizes the electron wave functions more. The conduction is decreased: it is the VRH regime of Efros–Shklovskii (ES-VRH) characterized by the exponent $m = 1/2$. At higher temperatures, it is the activated regime where $m = 1$. In this work, we reanalyzed the data obtained by Fourhouri et al [9]. We study the electronic transport mechanisms governing the behavior of the electrical conductivity of the samples: graphene fiber, graphene/PEDOT, graphene/CNT and graphene/PEDOT/CNT composite fibers.

In Fig. 1, *a*, we plot the electrical conductivity as a function of energy $E = k_B T$ where k_B is Boltzmann's constant and T is the temperature. The adjustments of the conductivity curves show that:

For $T < 50$ K, the conductivity follows the empirical law $\sigma(E) = \sigma_0 + \sigma_1 \exp(-\frac{E}{E_0})$, where σ_0 and σ_1 are temperature-dependent prefactors and can be determined by extrapolating the curves to zero $\sigma(0) = \sigma_0 + \sigma_1$ [6].

For $T > 50$ K, the conductivity follows the VRH law: $\sigma(E) = \sigma_0 \exp\left(-\left(\frac{E_0}{E}\right)^m\right)$ with temperature dependent prefactor [10,11] and $E_0 = \frac{C\beta}{4\pi\varepsilon l}$ is the Efros–Shklovskii characteristic energy [12]: l is the localization length and $\varepsilon = \varepsilon_0\varepsilon_r$ the dielectric permittivity of the material. In 2D, $\beta = 13.8$ and $C = 6.1$ [13].

According to Mott's law, the density of states $N(E)$ is constant around the Fermi level. However, Efros and Shklovskii have shown that, due to carrier interactions, the density of states $N(E)$ must cancel out at the Fermi level according to a law [12]:

$$N_c(E) = \frac{\frac{d}{\pi}(4\pi\varepsilon_0\varepsilon_r)^d}{e^{2d}}|E - E_F|^{d-1}, \qquad (2)$$

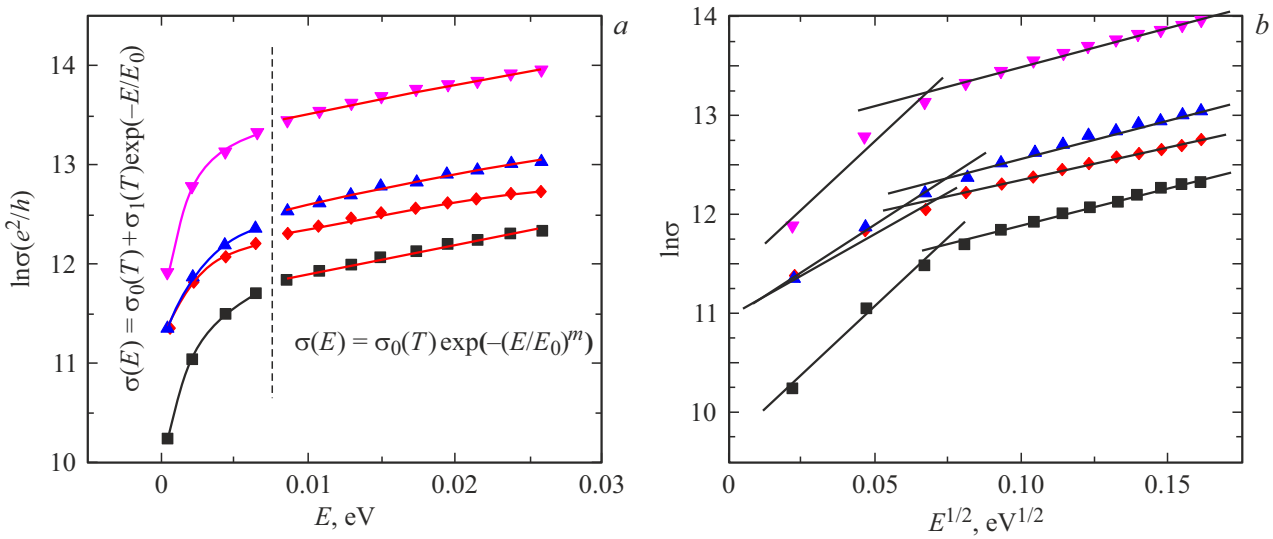

Figure 1. *a* — electrical conductivity versus energy for different samples (from highest to lowest curve): *A* — Grahene fiber, *B* — Graphene/CNT, *C* — Graphene/PEDOT, *D* — Graphene/PEDOT/CNT; *b* — electrical conductivity as a function of the square root of *E* for the different samples (from highest to lowest curve): *A* — Grahene fiber, *B* — Graphene/CNT, *C* — Graphene/PEDOT, *D* — Graphene/PEDOT/CNT.

where E_F is the Fermi level and d is the dimensionality of the material.

In 2D, the expression for the density of state becomes: $N_c(E) \propto |E - E_F|$ and only cancels at a single point, creating a soft gap that plays an important role in the observed behaviour of electrical conductivity. This soft gap is due to the long range of interactions between electrons. Finally, it can be noted that a hard gap at the Fermi level resulting from the cancellation of the density of states over a range of energies leads to an activated or $m = 1$ type of conduction. This mechanism has been suggested to interpret certain experiments.

In the VRH mechanism, charge carriers are trapped in localized energy states and tunneling can be induced by temperature and/or the applied electric field. In addition, for this mechanism, significant resistance is contributed by barriers separating localized carrier states. The characteristic conductivity can be described by:

$$\sigma_0 = e^2 N(E_F) R^2 \nu_{ph}, \tag{3}$$

where R is the hopping distance, e is the elementary charge, E_F is the Fermi level and $\nu_{ph} \sim 10^{13}$ Hz is the phonon frequency for conductive polymers. Electronic conduction can be achieved by the transition of carriers between localized states, which are tunneling assisted by phonons where electron hopping is accompanied by phonon emission. The plot of logarithm of the conductivity $\sigma(E)$ for the different samples at $T > 50$ K as a function of E^{-m} shows an almost linear dependence. Based on the intercept and gradient, the parameters E_0 and σ_0 can be determined. However, these parameters can be better estimated using two different methods: the conductance curve derivative analysis method and the numerical percentage deviation method.

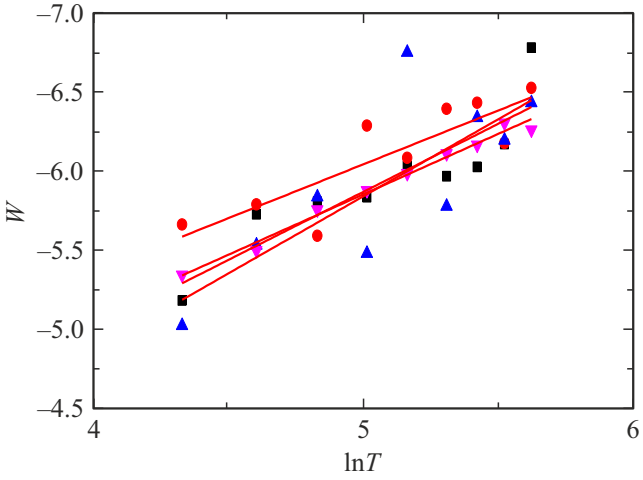

Figure 2. Variation of the function $W(T)$ and their fits for the different samples at $T > 50$ K.

To test the validity of the VRH law, we began by plotting the curves in Fig. 1, *b*, which follow the $ln\sigma \propto E^{1/2}$ law with two different temperature-dependent prefactors. We also found linear curves as a function of $E^{1/3}$ and E^1. So it is difficult to choose the dominant mechanism among these three mechanisms. To try to overcome this difficulty, we used (the conductance curve derivative analysis method), indeed, from Eq. 1 we define the function $\delta(T)$ as follows: [8,10]:

$$\delta(T) = -\frac{d\left(\ln[\sigma(T)]\right)}{d\ln T} = m\left(\frac{E_0}{E}\right)^m. \tag{4}$$

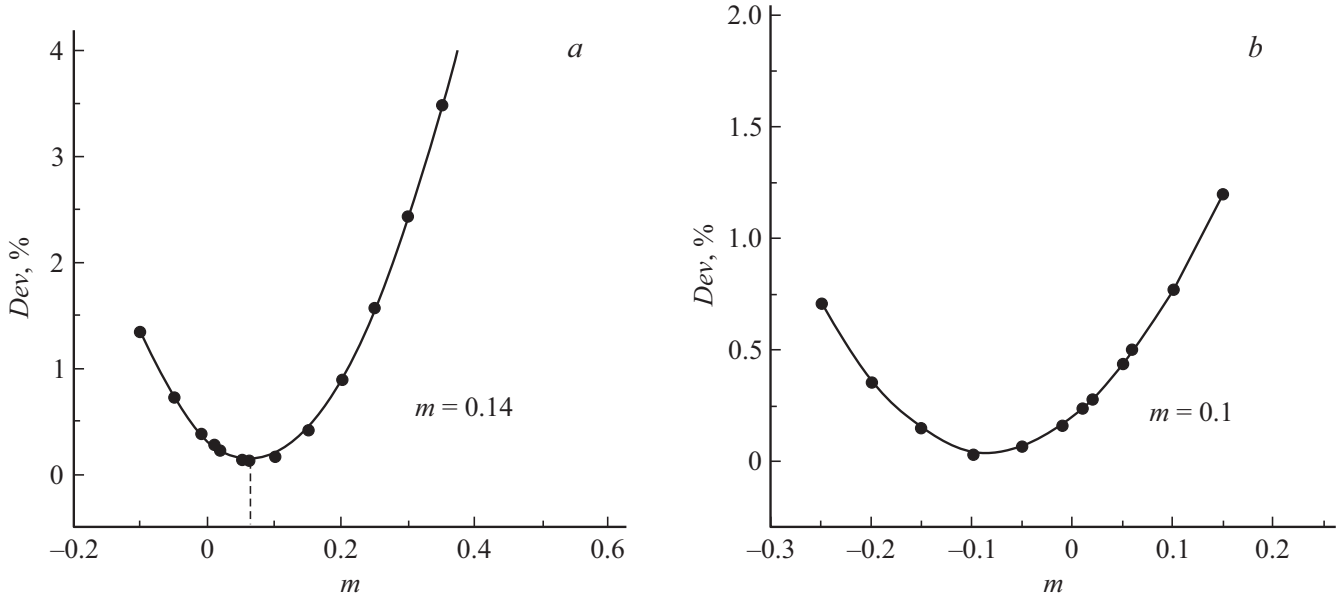

Figure 3. *a* — percentage deviation Dev versus exponent m for grahene fiber sample at $T > 50$ K; *b* — percentage deviation Dev versus exponent m for graphene/PEDOT sample at $T > 50$ K.

It then comes:

$$W(T) = \ln[\delta(T)] = \ln m + m \ln E_0 - m \ln T = A - m \ln T. \quad (5)$$

We can determine m by the slope $m = \frac{d(\ln[\delta(T)])}{d \ln T}$ from Fig. 2. The values of m are found to tend to 1 as shown in Table 1 which implies the transition from the ES-VRH to the activated regime. At $T < 50$ K, the hopping laws are not valid and the conductivity has an undetermined behaviour. The curves are not characteristic of an insulator, but of a metal. At high temperatures, the observed behavior of the activated law can be interpreted by the opening of a hard gap at the Fermi level due to the interaction between the electrons. This gap can in particular characterize the formation of a Wigner crystal-like electronic phase, for which a simply activated law is indeed expected. The activated regime can also be due to percolation-type electronic transport. Indeed, when the system is made up of metal islands separated by insulating zones, the transport of carriers is ensured by activated hops from one island to another. We continue our investigation by testing the numerical percentage deviation method Dev (%) to extract the slope m that corresponds to the minimum deviation. This method consists in varying the value of m and fitting the experimental curves to the law $\sigma(T) = \sigma_0 \exp\left(-(E_0/E)^m\right)$ with σ_0 and E_0 as adjustable parameters. The best value of m is obtained by minimising the percentage deviation. In other words, the method of percentage deviation Dev (%) consists of evaluating the deviation between the measured values σ_i and the value of

Table 1. The values of the slope m extracted from the linear fits (A — Grahene fiber, B — Graphene/CNT, C — Graphene/PEDOT, D — Graphene/PEDOT/CNT)

Sample	m value
A	0.86
B	0.68
C	0.97
D	0.76

the linear regressions (lineair fits of σ) [14–18]:

$$Dev(\%) = \left[\frac{1}{p}\sum_{i=1}^{i=p} \frac{100}{\sigma_i}\left(\sigma_0 \exp\left(-\left(\frac{E_0}{E}\right)^m\right) - \sigma_i\right)\right]^{1/2}, \quad (6)$$

where p being the number of experimental points.

In Fig. 3 we plot Dev (%) against the exponent m in Eq. (5) for several values of temperature. The results obtained are shown in Table 2. The values of m found using the latter method are closer to the Mott mechanism (Mott-VRH). The results obtained by the different methods show that for $T > 50$ K there is coexistence of the three regimes of electronic transport in the studied samples: Mott-VRH, ES-VRH and the activated regime with the dominance of the last two regimes. We also noticed that the electronic transport is characterized by a crossover from ES-VRH to the activated regime for high temperatures. The universal behavior of the conductivity remains valid for higher temperatures. In this high temperature range no deviation of the data from the theoretical curve is noted. The temperature of the transition from a high temperature nearest-neighbor hopping regime to a low

Table 2. The values of the slope m extracted from the percentage deviation (*A* — Grahene fiber, *B* — Graphene/CNT, *C* — Graphene/PEDOT, *D* — Graphene/PEDOT/CNT)

Sample	*m* value
A	0.14
B	−0.1
C	−0.1
D	−0.1

temperature variable range hopping regime corresponds to the point where the average hopping distance calculated in the variable range hopping regime is equal to the distance between nearest neighbors [13]. In the variable range hopping theory, the average hopping distance is evaluated by:

$$r_m(T) = l\left(\frac{T_{\mathrm{ES}}}{T}\right)^{1/2}, \qquad (7)$$

where l is he localization length and T_{ES} is the Efros−Shklovskii's charcteristic temperature. The hop length determines the transition between the two regimes $m = 1$ and 1/2.

The temperature dependence of the electronic conduction of wet spun graphene fiber and its composites follows the empirical law $\sigma(E) = \sigma_0 + \sigma_1 \exp\left(-\frac{E}{E_0}\right)$ for $T < 50\,\mathrm{K}$ and the law $\sigma \sim \exp\left(-(E_0/E)^m\right)$ for $T > 50\,\mathrm{K}$ where the electronic conduction is dominated by the coexistence of two regimes: Efros−Shklovskii variable range hopping mechanism (ES-VRH) where $m = 1/2$ and the activated mechanism where $m = 1$.

Conflict of interest

The authors declare that they have no conflict of interest.

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