Electrical transport in onion-like carbon - PMMA nanocomposites

Claudio Grimaldi, 1 Egon Kecsenovity, 2 Maryam Majidian, 1 Vladimir L. Kuznetsov, 3 Arnaud Magrez, 1,4 and László Forró 1

1) Laboratory of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, Station 3, CH-1015 Lausanne, Switzerland
2) Department of Physical Chemistry and Materials Science, University of Szeged, Rakirich Square 1, Szeged H-6720, Hungary
3) Bóreskó Institute of Catalysis, SB RAS, Lavrentieva 5, Novosibirsk, 630090, Russia
4) Crystal Growth Facility, Ecole Polytechnique Fédérale de Lausanne, Station 3, CH-1015 Lausanne, Switzerland

We report electrical conductivity measurements of Polymethylmethacrylate filled by onion-like carbon particles with primary particle size of $\approx 5$ nm. We shown that the conductivity $\sigma$ is exceptionally high even at very low loadings, and that its low-temperature dependence follows a Coulomb gap regime at atmospheric pressure and an activated behavior at a pressure of 2 GPa. We interpret this finding in terms of the enhancement under the applied pressure of the effective dielectric permittivity within the aggregates of onion-like carbons, which improves the screening of the Coulomb interaction and reduces the optimal hopping distance of the electrons.

Onion-like carbon (OLC) nanostructures, also called carbon onions, are nanometric quasi-spherical particles consisting of multi-shell graphitic layers, obtained by the transformation of ultra-dispersed nano-diamonds through annealing above 1200 K [2]. When dispersed in polymeric host materials, the high electrical conductivity of OLC nanoparticles, as well as their lightweight and inert nature, are attractive properties for electromagnetic shielding applications, which can be controlled by tailoring the OLC cluster size and nano-diamond annealing temperature [2]. OLCs are interesting also for high power applications, due to their high charge-discharge rates, and for energy storage applications, as OLC particles act effectively as electrical double-layer micro-capacitors [2].

In addition to the properties specific to OLC particles, equally important factors influencing the performance of OLC-based composites are the quality and type of the OLCs dispersion in the host material, the operational temperature, and the response to external fields. Here, we report on our studies on the filler concentration, pressure, and temperature dependence of the electrical conductivity of OLC particles dispersed in Polymethylmethacrylate (PMMA). We show that OLC-PMMA composites display an exceptionally high value of the conductivity, with no sign of a percolative transition even for filler concentrations as low as 0.38% in volume fraction of the OLC particles. Even more strikingly, we find that the low-temperature conductivity crosses over from a Coulomb gap regime at atmospheric pressure to an activated behavior at a hydrostatic applied pressure of $P = 2$ GPa, regardless of the OLC concentrations considered. These results point to a non-trivial interplay between the morphology of the OLC aggregates in the polymer and the electron hopping processes between OLC nanoparticles.

The OLC nanoparticles were produced by the detonation method of precursor nanodiamonds, as described in Ref. [1]. The particles were extracted from the detonation soot by oxidative removal of non-diamond carbons using a hot mixture of acids. OLC materials were produced by annealing of nanodiamond powder in vacuum at 1650 °C for 3 h. As shown in TEM images of Figs. 1(a) and 1(b), the OLC particles were arranged in aggregates of nearly touching particles, and the primary particle size of the OLCs ranged from $\sim 4$ nm to $\sim 7$ nm. In the preparation of the OLC-PMMA composites, OLCs were first heat treated in a furnace at 400 °C for 2 hours, in order to eliminate the graphitic layers present between the onions and to functionalize their surface with oxygen-containing groups to improve the dispersion in the PMMA matrix. In the next step, isopropyl alcohol (IPA) was used for the pre-dispersion of the OLCs. A few drops of IPA (enough to wet the OLC powder) were added to the OLC powder and the suspension was sonicated in a bath for 1 hour. The PMMA solution was added immediately afterwards. The polymer-OLC mixture was stirred for 1 hour followed by probe sonication for 15 minutes. The obtained ink was deposited on a glass slide and baked on a hotplate at 100 °C for 30 minutes. The samples were kept at 50 °C overnight to assure the complete polymerization of the composite. We have prepared samples with OLC concentrations of $x = 0.5, 1, 2, 4$ wt% with respect to the weight of PMMA. The corresponding values of the OLC volume fraction are given by $\phi = x \rho_{\text{PMMA}} / (\rho_{\text{OLC}} + x \rho_{\text{PMMA}})$, where $\rho_{\text{PMMA}} = 1.18$ gm cm$^{-3}$ and $\rho_{\text{OLC}} = 2.25$ gm cm$^{-3}$ are the mass density values of the PMMA and OLC, respectively.

The conductivity, $\sigma$, of OLC-PMMA composites was measured using the standard 4 probe method. The golden wires were attached to the samples by means of a carbon paste. The typical dimensions of the samples were about $5 \text{ mm} \times 2 \text{ mm} \times 100 \text{ mm}$, however for each sample the geometrical factor was measured and applied.

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for conductivity measurement. The pressure dependence of $\sigma$ was measured under hydrostatic pressure up to 2 GPa in a piston cylinder cell, using Daphne oil 7373 as pressure transmitting medium.

TEM images of microtone slices of OLC-PMMA composites, Figs. 1(c) and 1(d), show that the agglomerates of OLC particles have average sizes of the order of 100 nm. The overall microstructure of the composite is therefore characterized by a strongly non-homogeneous distribution of the conducting OLC particles within the polymer, which gives rise to ramified regions that are rich in OLC particles interdispersed with regions of almost pure PMMA, Fig. 1(d). This kind of microstructure, which has been frequently observed in other carbon-based composites, favors hopping of electrons between closely separated OLC particles, promoting thus relatively high level of conductivity, $\sigma$, even at very small filler concentrations.

Enhanced conductivity is indeed measured also in our OLC-PMMA composites, which show values of $\sigma$ that can be even larger than the conductivity of polymers filled at similar loadings by carbon nanotubes or reduced graphene sheets, as shown in Fig. 3. Furthermore, the conductivity of OLC-PMMA decreases by just one order of magnitude as $\phi$ is reduced from $\approx 2\%$ ($x = 4\%$wt) to $\approx 0.25\%$ ($x = 0.5\%$wt), with no apparent sign of a percolation transition (see Supplementary Material). Figure 2 shows also that $\sigma$ under an applied hydrostatic pressure of $P = 2$ GPa is almost a factor 3 larger than the conductivity at atmospheric pressure. This behavior is consistent with an enhanced probability of tunneling between OLC particles promoted by the reduced interparticle separation under the applied pressure.

A more striking effect of the applied pressure is found in the low-temperature behavior of $\sigma$ shown in Fig. 3. While for all loadings and pressure values the conductivity at $T \lesssim 20$ K follows a stretched exponential behavior of the form

$$\sigma \propto \exp\left(-\left(\frac{T_0}{T}\right)^{\alpha}\right),$$  \hspace{1cm} (1)

the exponent $\alpha$ changes as a function of $P$. At atmospheric pressure the conductivity is well fitted by $\alpha \simeq 1/2$, Fig. 3(a), indicating a Coulomb gap regime in which hopping of electrons between nearest neighboring OLC particles is hindered by the Coulomb interaction. At a pressure of $P = 2$ GPa, instead, the low-temperature conductivity follows Eq. 1 with $\alpha \simeq 1$, Fig. 3(b), indicating an activated behavior. The change of the exponent from $\alpha \simeq 1/2$ to $\alpha \simeq 1$ as $P$ increases to 2 GPa is gradual, as shown in Fig. 3(c) for a sample with 2 %wt of OLC particles. Furthermore, the temperature parameter $T_0$ decreases as $P$ increases. In particular, $T_0$ is of several hundreds Kelvin at ambient pressure [with some dependence on the OLC concentration, Fig. 3(a)], while $T_0 \approx 20$ K at $P = 2$ GPa, with almost no effect of the filler loading.

To interpret the experimental results shown in Figs. 1 and 3 we express the conductance between a pair $i$ and $j$ of OLC particles as the product of probabilities for tunneling and thermal activation: $G_{ij} = G_0 \exp(-2(r_{ij} - D)/\xi - E_{ij}/K_BT)$, where $r_{ij}$ is the distance between the centers of two OLCs approximated by identical spherical conductors of diameter $D$, $\xi$ is the electron localization length, $K_B$ is the Boltzmann constant, and $E_{ij}$ is the energy difference for hopping between particles $i$ and $j$. By treating any OLC pair as immersed in an effective dielectric field developed by the PMMA and the other OLC

FIG. 1. TEM images of OLC powders, (a) and (b), and of OLC-PMMA with 1 wt% filler loading, (c) and (d). The images in (c) and (d) show that the dispersion of OLC particles in the PMMA matrix is characterized by aggregates of closely separated OLC fillers, giving rise to a locally nonhomogeneous microstructure.

FIG. 2. Room temperature electrical conductivity of OLC-PMMA composites (filled circles) as a function of the volume fraction $\phi$ of OLC fillers. The conductivity data for the carbon nanotubes (CNT) and reduced graphene oxides (RGO) dispersed in SU8 are taken from Refs. 7 and 8 respectively.
fillers, the energy difference becomes \( E_{ij} \simeq e^2 \tilde{C}_{ij}^{-1}/\tilde{\kappa} \), where \( e \) is the electron charge and \( \tilde{C} \) is the capacitance matrix of two spherical conductors embedded in the effective dielectric medium with permittivity \( \tilde{\kappa} \). Following Ref. [12] we find (see Supplementary Material):

\[
\tilde{C}_{ij}^{-1} \simeq \left\{ \begin{array}{ll} 1/r_{ij}, & r_{ij} \gg D \\ 1/(D \ln 2), & r_{ij} = D \end{array} \right., \quad (2)
\]

which can be more conveniently approximated by \( \tilde{C}_{ij}^{-1} \simeq (\delta_{ij} + D \ln 2)^{-1}, \)

where \( \delta_{ij} = r_{ij} - D \). In this way, the conductance between a pair of particles reduces to

\[
G(r_{ij}) \simeq G_0 \exp \left[ -\frac{2\delta_{ij}}{\xi} - \frac{e^2}{\tilde{\kappa}(\delta_{ij} + D \ln 2)K_BT} \right]. \quad (3)
\]

Since the composite conductivity \( \sigma \) is dominated by the highest pair conductances, and since these are most probably found within the OLC aggregates, we approximate \( \sigma \) by averaging \( G(r_{ij}) \) over particle pairs within the aggregates:

\[
\sigma \propto \sum_{i,j \in \text{aggregates}} G(r_{ij}) \propto \rho_{\text{aggr}} \int_D^{\infty} dr r^2 P(r)G(r), \quad (4)
\]

where \( \rho_{\text{aggr}} \) is the local number density of OLC particles in the aggregates and \( P(r) \) is the corresponding pair distribution function of particles. Similar to what is observed in other ramified aggregated structures like, for example, high-structured carbon-black composites [13-14] or some colloidal systems [15], we expect \( P(r) \) to follow for \( r > D \) a fractional power-law decay up to a distance, \( D_{\text{aggr}} \), of the order of the mean size of the aggregates. Here we make the assumption that at low temperatures \( P(r) \) has a much weaker \( r \)-dependence than \( G(r) \), so as to replace \( P(r) \) by a constant, \( \chi \), up to distances comparable to \( D_{\text{aggr}} \approx 100 \) nm:

\[
\sigma \propto \frac{\phi_{\text{aggr}} \chi}{D} \int_0^{D_{\text{aggr}}} d\delta \exp \left[ -\frac{2\delta}{\xi} - \frac{e^2}{\tilde{\kappa}(\delta + D \ln 2)K_BT} \right], \quad (5)
\]

where the local volume fraction within the region of aggregates, \( \phi_{\text{aggr}} = \pi \rho_{\text{aggr}}D^3/6, \) can be considerably larger than the macroscopic volume fraction \( \phi \), which explains the high conductivity values reported in Fig. 2.

At low temperatures the integral in Eq. (5) is dominated by the largest value of the integrand function. We obtain therefore that \( \sigma \) follows the Coulomb gap regime

\[
\sigma \propto e^{-\sqrt{T_{ES}/T}}, \quad T_{ES} = \frac{8e^2}{\xi K_BT}, \quad (6)
\]

when the optimal hopping distance that maximizes the integrand,

\[
\delta^* = \sqrt{\frac{\xi e^2}{2\xi K_BT} - D \ln 2}, \quad (7)
\]

is positive, while for \( \delta^* < 0 \) the conductivity follows an Arrhenius law:

\[
\sigma \propto e^{-T_A/T}, \quad T_A = \frac{e^2}{\xi K_BT \ln 2}, \quad (8)
\]

because in this case the integrand is a monotonous decreasing function of \( \delta \) in the range \((0, D_{\text{aggr}})\), and so its largest value is at \( \delta = 0 \).

Equations (6)-(8) suggest that in OLC-PMMA composites the cross-over of \( \sigma \) from the Coulomb gap regime to the activated behavior is related to the sign change of \( \delta^* \), from positive to negative, induced by the applied pressure. We claim that such sign change is possibly driven...
by the response of the effective permittivity to $P$. Indeed, since the OLC particles are essentially rigid with respect to the much softer PMMA matrix, at a given temperature the main effect of the pressure is that of enhancing the concentration of OLC particles, thus increasing $\tilde{\kappa}$. Larger values of $\tilde{\kappa}$ may in turn make $\delta^*$ smaller than its value at atmospheric pressure, or even negative.

To see if this mechanism is consistent with our experimental results, we first consider the Coulomb gap regime observed at the atmospheric pressure. The values of $T_0$ reported in Fig. 3(a) range from $\sim 300$ K to $\sim 700$ K as the OLC concentration is reduced. We take $T_0 \approx 500$ K as a representative value and we identify it with $T_{ES}$. From Eq. (6) we obtain $\xi\tilde{k}_0 \approx 270$ nm, where $\tilde{k}_0$ is the effective permittivity at atmospheric pressure. Since $\delta^*$ has to be positive to give rise to the Coulomb gap regime, we obtain from Eq. (7) $\xi > 4D \ln 2 \sqrt{T/T_{ES}}$. Using $D \approx 5$ nm and $T = 10$ K this condition leads to $\xi > 2$ nm and, consequently, $\tilde{k}_0 < 135$.

Let us now consider the conductivity at $P = 2$ GPa of Fig. 3(b), which follows an activated regime with $T_A \approx 20$ K. From Eq. (5) we get $\tilde{k}_1 = e^2 / T_A K_B D \ln 2 \approx 240$, where now $\tilde{k}_1$ is the value of $\tilde{k}$ at 2 GPa. Since an activated behavior comes into play only if $\delta^*$ is negative, for $T = 10$ K we obtain from Eq. (7) $\xi < 2(T/T_A)D \ln 2 \approx 3.5$ nm.

From the above analysis, therefore, we conclude that the two different regimes of $\sigma$ reported in Figs. 2(a) and 2(b) can be explained by the increase of the effective permittivity upon applied pressure, from less than about 135 at atmospheric pressure to about 240 at 2 GPa, assuming a localization length comprised between $\sim 2$ nm and $\sim 3.5$ nm. Although this range of $\xi$ values is quite realistic, an effective permittivity of order 100 appears to be far larger than that measured in other OLC composites at comparable filler loadings\cite{15,16}. It should be noted, however, that within the regions of the OLC aggregates, $\tilde{k}$ could largely exceed the macroscopic effective permittivity because of the enhanced local volume fraction of the conducting fillers\cite{15,16}. To see this, we adopt the cluster model of Ref. 15 and express the local permittivity in the aggregates as

$$\tilde{k} \simeq \kappa_0 \left( \frac{3\phi_c}{(2 - \phi_c)(\phi_c - \phi_{aggr})} \right),$$

where $\kappa_0 \approx 3$ is the permittivity of PMMA and $\phi_c$ is the critical packing fraction at which the effective polarization of the aggregate is one\cite{15,16}. Since we are considering aggregates of metallic spheres, $\phi_c$ can be identified as the minimal volume fraction such that a cluster of touching spheres spans the entire aggregate. Quite intuitively, Eq. (9) shows that large values of $\tilde{k}$ can be attained for $\phi_{aggr}$ sufficiently close to $\phi_c$, and that small variations of $\phi_{aggr}$ can induce significant changes in the effective permittivity. By identifying $\phi_c$ as the volume fraction of a random loose packing arrangement of spheres ($\approx 0.55$), we obtain from Eq. (9) that our estimate $\tilde{k} < 135$ obtained at atmospheric pressure is reproduced by $\phi_{aggr} < 0.534$. Furthermore, the relative change of the local permittivity under the application of 2 GPa, $(\tilde{k}_1 - \tilde{k}_0)/\tilde{k}_0 > 79 \%$, can be explained by a relative enhancement of only $\geq 2 \%$ in the local volume fraction of the aggregates.

In conclusion, we have reported conductivity measurements of OLC-PMMA composites as a function of volume fraction of OLC fillers, temperature and applied pressure up to 2 GPa. Our main finding is that the low-temperature of $\sigma$ can be changed from a Coulomb gap regime at atmospheric pressure to an activated behavior at 2 GPa. We interpret this feature by the increase of the effective permittivity upon the applied pressure, which reduces the optimal hopping distance at low temperatures.

See Supplementary Material for a percolation analysis of the conductivity data and a derivation of the interaction Coulomb term.

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I. ELECTRICAL TRANSPORT IN ONION-LIKE CARBON-PMMA - NANOCOMPOSITES: SUPPLEMENTARY MATERIAL

II. PERCOLATION ANALYSIS OF THE CONDUCTIVITY

In conductor-insulator composites it is often assumed that the conductivity follows a percolation behavior as a function of the conducting filler volume fraction $\phi$ characterized by the power-law behavior:

$$\sigma \simeq \sigma_0 (\phi - \phi_c)^t,$$  \hfill (S1)

where $\sigma_0$ is a conductivity prefactor, $\phi_c$ is the critical volume fraction of the conducting phase, and $t$ is the conductivity exponent. Equation (S1) follows from the assumption that electrical connections are established between conducting fillers (the OLC particles in our case) in such a way that the conductances between any two particles are either nonzero, when the relative particle separation is small enough, or zero when the particles are far apart. The bulk conductivity of the composite exceeds therefore the one of the matrix if there exists a macroscopic cluster of connected particles spanning the entire system, that is, if $\phi > \phi_c > 0$. Although the value of $\phi_c$ depends on the type of distribution of the conducting fillers, the value of the exponent is universal and is approximately equal to 2 in three dimensional systems.

Figure S1 shows the conductivity measured in our OLC-PMMA composites for different values of the hydrostatic pressure $P$. Although Eq. (S1) formally fits the measured $\sigma$ for all values of $P$, the resulting best fitting values for $\phi_c$ and $t$ reported in Table S1 are unphysical. We find indeed that not only the transport exponent $t$ is systematically larger or much larger than universal value $t \approx 2$ but, even more strikingly, that the percolation threshold $\phi_c$ is always negative. These results clearly indicate that percolation of the OLCs particles is inadequate in describing the conductivity of OLC-PMMA composites. This is confirmed by the low-temperature conductivity measurements reported in the main text, which show that $\sigma$ is proportional to $\exp[-(T_0/T)\alpha]$, a clear indication that $\sigma$ is governed by electron hopping processes between the OLC particles and that there is not a cut-off in the inter-particle conductances.

### Table S1. Values of $\phi_c$ and $t$ that best fit the measured conductivity of OLC-PMMA composites at room temperature.

| $P$ (Kbar) | $\phi_c$ (%) | $t$    |
|------------|--------------|--------|
| 0          | -0.6 ± 0.3   | 2.4 ± 0.6 |
| 5          | -1 ± 0.1     | 3.3 ± 0.2 |
| 10         | -1.3 ± 0.2   | 3.6 ± 0.4 |
| 15         | -1.4 ± 0.2   | 4.0 ± 0.3 |
| 20         | -2.0 ± 0.6   | 5 ± 1   |

III. DERIVATION OF THE INTERACTION TERM

We approximate the OLC particles by spherical conductors of identical diameter $D$. The energy difference for hopping between two particles $i$ and $j$ is $E_{ij} = e^2 C_{ij}^{-1}$, where $e$ is the electron charge and $C$ is the capacitance matrix for a system of conducting OLC particles embedded in the polymer. We assume that $E_{ij}$ can be approximated by the Coulomb interaction between two particles immersed in an effective dielectric field developed by the PMMA and the other OLC fillers. In this way write $E_{ij} = e^2 \tilde{C}^{-1} / \kappa$, where $\kappa$ is the effective permittivity and $

\tilde{C} = \begin{pmatrix} C_d & C_o \\ C_o & C_d \end{pmatrix}$ \hfill (S2)

is the capacitance matrix of two isolated conductor embedded in the effective dielectric. For distances $r_{ij}$ between the particle centers much larger than $D$ the diagonal and off-diagonal elements of $\tilde{C}$ reduce respectively to

$$C_d \simeq D/4 \left( \ln \sqrt{D/\delta_{ij} + \gamma} \right), \quad C_o \simeq -D/4 \left( \ln \frac{D}{2\delta_{ij} + \gamma} \right),$$ \hfill (S3)

where $\gamma \approx 0.5772$ is the Euler constant and $\delta_{ij} = r_{ij} - D$ is the distance between the surfaces of the two particles. From the inversion of Eq. (S2) and making use of the limiting values of $C_d$ and $C_o$ at $r_{ij} \gg D$ and $r_{ij} = D$ we obtain

$$\tilde{C}_{ij}^{-1} = -\frac{C_o}{C_d^2 - C_o^2} \simeq \begin{cases} 1/r_{ij}, & r_{ij} \gg D \\ 1/(D \ln 2), & r_{ij} = D \end{cases}$$ \hfill (S4)