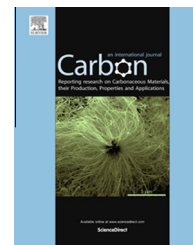


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Iodine monochloride as a powerful enhancer of electrical conductivity of carbon nanotube wires

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ABSTRACT

We report a new method to modify electrical properties of carbon nanotubes (CNTs). Single-, double- and multi-wall CNTs were subjected to treatment with a polar interhalogen compound, i.e. iodine monochloride (ICl) for 8 h at room temperature or briefly at 350 °C to assess kinetics and thermodynamics of the reactions. The results showed a powerful p-doping, which enabled us to decrease electrical resistance of the material by more than 60% eventually reaching specific conductivity of 1.24 S m² g⁻¹. Functionalization of CNTs with halogen atoms resulted in evident changes to the material microstructure and composition. To illustrate viability of this technique for manufacturing highly conductive wires, we have produced an ICl-doped CNT-based USB cable. The tests unequivocally revealed that the cable could be successfully used for power or data transmission on the verge of USB 2.0 capabilities.

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1. Introduction

Carbon nanotubes (CNTs) have shown remarkable potential in the field of electrical engineering [1,2]. Due to the unique features such as lack of electromigration [3], negligible skin effect [4] and ballistic conduction [5], CNTs can in theory outperform copper and achieve three orders of magnitude higher current densities [1]. Moreover, they are highly tunable as control of diameter and chirality can directly steer the electronic character of the sample in predominantly metallic or semiconductive direction [6]. The other approach is based on employing physical or chemical doping agents, which affect the band structure of CNTs, and thus their electrical conductivity. CNTs have an amphoteric electrical nature and both p-dopants, e.g. strong mineral acids (H₂SO₄, HNO₃

[7]), halogens (Cl₂ [8], Br₂ [9], I₂ [10]), Au³⁺ [11], or n-dopants, e.g. alkali metals (Li [12], K [9], etc.), amine-based compounds (hydrazine [13]) or polymers (polyethyleneimine [14]) can be utilized to modulate their electrical properties.

By now, a particular attention has been focused on halogens because of their high reactivity, which can readily influence electronic structure of CNTs. The least complicated treatments employed halogen atom carriers, e.g. SOCl₂ [15] or PBr₃ [16] that easily eject them onto CNTs to which they become chemically bound or physisorbed. Moreover, to facilitate the reactions with Cl_{2(g)} or Br_{2(l)}, these processes were often assisted by plasma [17,18], high-temperature treatment [19] or irradiation with microwaves [20]. Alternatively, halogens were deposited by more sophisticated methods such as electrolytic functionalization [21] or ball milling of CNTs in

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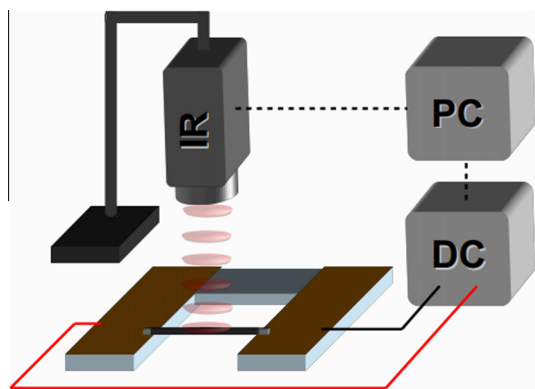


Fig. 1 – Experimental setup for ICl-treatment of CNWs between room temperature and 350 °C. DC (power supply) and IR (pyrometer) measured and recorded electrical properties and temperature, respectively, on a PC. (A color version of this figure can be viewed online.)

chlorine atmosphere [22]. Because of its high vapor pressure, iodine can be delivered by sublimation-deposition [10], but attempts have also been carried out to treat CNTs in molten iodine [23,24] or subject oxidized CNTs to Hunsdiecker reaction [25].

Here, for the first time, we perform a comprehensive survey of how an interhalogen compound, iodine monochloride (ICl), affects the electronic properties of carbon nanotube wires (CNWs) – individually composed of CNTs with a various number of walls. Partially ionized (ca. 1%, and thus poor conductor by itself) ICl with a specific conductivity of just ca. $2.58 \times 10^{-9} \text{ S m}^2 \text{ g}^{-1}$ (at room temperature) [26] carries both

electron-rich chlorine anion and electron-deficient iodine cation, both of which can interact with the material on contrary to *e.g.* SOCl_2 in which thionyl group remains the unused vector only to deliver halogen atoms. Moreover, ICl upon hydrolysis releases hydrochloric acid [27] known to have beneficial effects on electrical properties of CNWs [28]. Single-wall CNTs (SWCNTs), double-wall CNTs (DWCNTs) and multi-wall CNTs (MWCNTs) were engaged to compare how this doping agent interplays with CNTs upon a simple dripping of 1 droplet (15 μL) onto CNWs. The above depicted variety of CNTs was subjected to two types of treatment: overnight (8 h) exposure to ICl at room temperature and a brief self-heating by Joule effect [29] up to 350 °C in the presence of ICl. As a consequence, we have observed a powerful enhancement of electrical conductivity of CNWs with significant changes to the material microstructure and composition. CNWs reached specific conductivity as high as $1.24 \text{ S m}^2 \text{ g}^{-1}$. It is important to note that the benefits of ICl use we present are not limited to CNWs, but can be extended to other carbon nanostructures with graphene being the most immediate choice. Finally, to illustrate the electrical capabilities of as-doped CNWs, we manufactured the first USB cable made of CNTs. To prove its durability and high conductivity, we successfully used it as a lead to an external hard-drive, whilst we have been composing this manuscript on it. Moreover, operation in a power transmission mode allowed us to charge a mobile phone.

2. Experimental

CNWs were directly spun from a CVD furnace [30] and mounted on custom-designed sample holders (Fig. 1). 10 cm

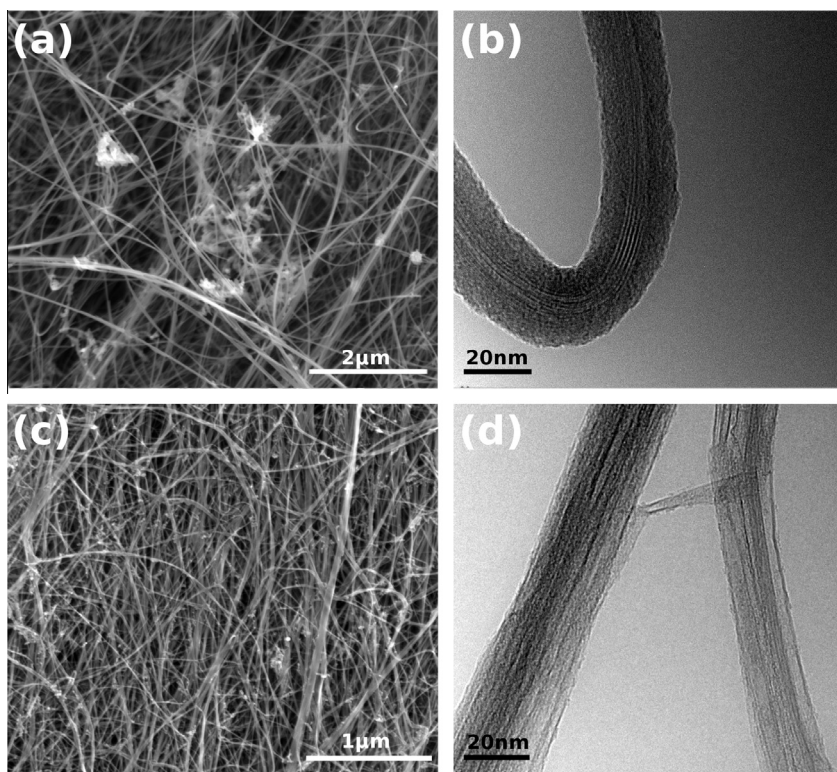


Fig. 2 – (a,c) Scanning and (b,d) transmission electron micrographs of (top) SWCNT- and (bottom) DWCNTs-based CNWs.

long specimens were suspended between two quartz microscope slides covered with Cu tape electrical terminals. To assure good mechanical and electrical connection between Cu and CNWs, Ag conductive paste was applied at the interface and dried in the ambient overnight. Then, the samples were connected to a PC-controlled DC power supply and their initial two-point electrical resistance was recorded. Furthermore, we deposited ICl (reagent grade, >95%; Sigma-Aldrich, UK) onto the CNWs and electrical resistance was recorded for 8 h at room temperature (indicated as overnight). In a parallel experiment, we also resistively heated ICl-doped CNWs briefly up to 350 °C at which the sample burned at one point (indicated as ‘to breaking point’) to observe change in material microstructure. Finally, we made a USB cable from four doped DWCNT wires insulated with heat-shrink sleeves. More details regarding preparation of the CNWs or USB cable and their characterization can be found in the [Supporting Information](#) file.

3. Results and discussion

We selected three different sorts of CNTs to study how they would respond to the ICl treatment. Electron microscopy imaging confirmed the predominance of SWCNTs (Fig. 2a, b), DWCNTs (Fig. 2c, d) and MWCNTs (Figs. S1a, b). In all of the cases, one could notice the presence of amorphous carbonaceous impurities, in particular on SWCNTs bundles. CNTs had an average outer diameter of 2.0 ± 0.5 (SWCNTs), 7.2 ± 5.7 (DWCNTs) and 25.1 ± 6.5 (MWCNTs) nm as measured by TEM on 100 randomly selected CNTs. Impurities present in the SWCNT sample and poor graphitization of walls constituting MWCNTs translated into a relatively high D/G ratio of intensity of D-mode to G-mode to be 0.80 and 0.59 (Fig. S2), respectively. On the other hand, due to high crystallinity of DWCNTs, its D/G ratio was as low as 0.07. Radial-breathing modes (RBMs) gradually disappeared from SWCNTs to MWCNTs (Fig. S2) as expected (detailed analysis of this feature is described later in text).

Fig. 3 shows how electrical resistance changed over time when ICl was deposited onto CNWs. In the case of SWCNTs (Fig. 3a), we observed a continuous decrease in resistance from 85% (when the measurement was started after 5 s from ICl droplet application) to 40% of the initial resistance in the end (after 8 h of treatment at room temperature). Looking behind again to Fig. 2b, TEM images show that SWCNT were bundled up and covered with an amorphous layer of carbonaceous deposits, which acted as a diffusion barrier. After the initial rapid decrease in resistance, we observed an asymptotic behavior and the final drop of resistance by subsequent 15% was spread over 7 h as the dopant permeated into the material. Conversely, the action of ICl on DWCNTs afforded firstly 17% of the initial resistance and then it started to rise eventually reaching 43% of the starting value. DWCNTs were not wrapped by the amorphous layers, and thus intercalation of liquid ICl therein was stronger and took place much faster. Furthermore, when we consider flow resistance of relatively viscous ICl (comparable to that of blood, 3.74 cP at 35 °C [26]) into bundles of SWCNTs or DWCNTs (of almost four fold larger diameter), migration of ICl into the grooves

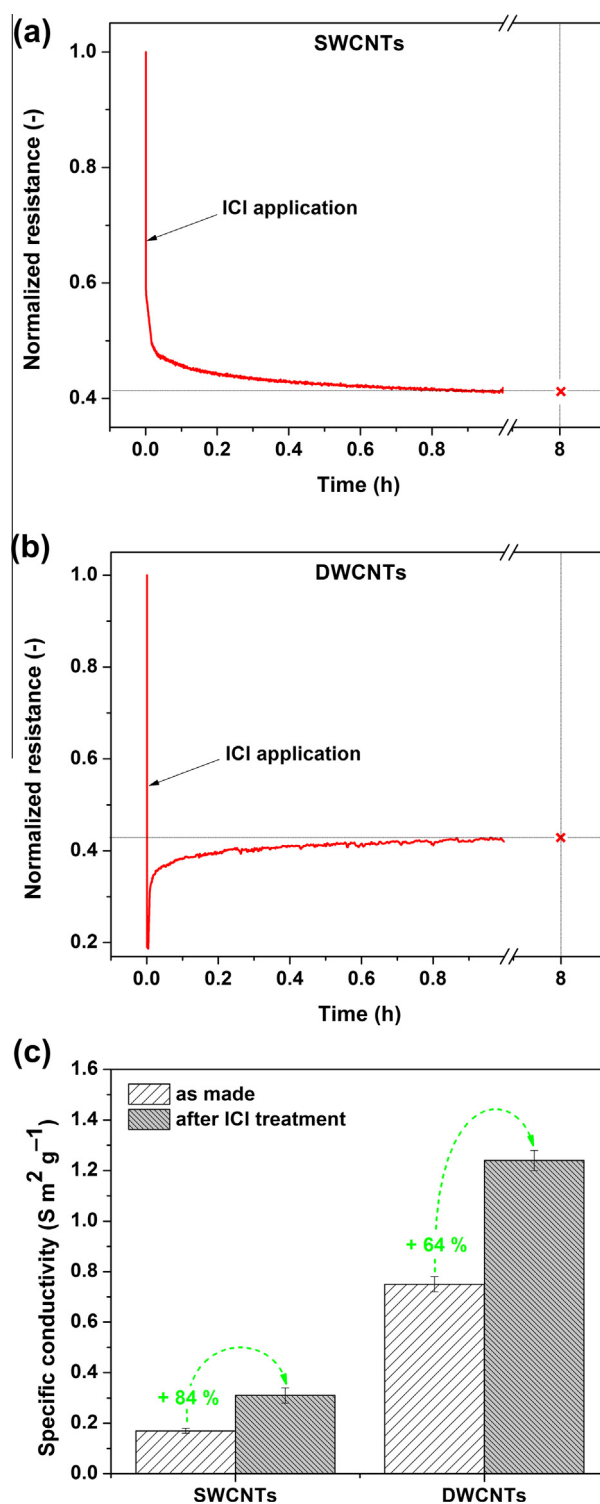


Fig. 3 – Changes in the electrical resistance (normalized to as made CNWs) of (a) SWCNTs and (b) DWCNTs in the course of overnight exposure to ICl at room temperature. (c) specific conductivity of SWCNTs and DWCNTs before and after overnight ICl-treatment at room temperature. (A color version of this figure can be viewed online.)

between individual CNTs plays a major role. The number and small size of interstitial space between individual

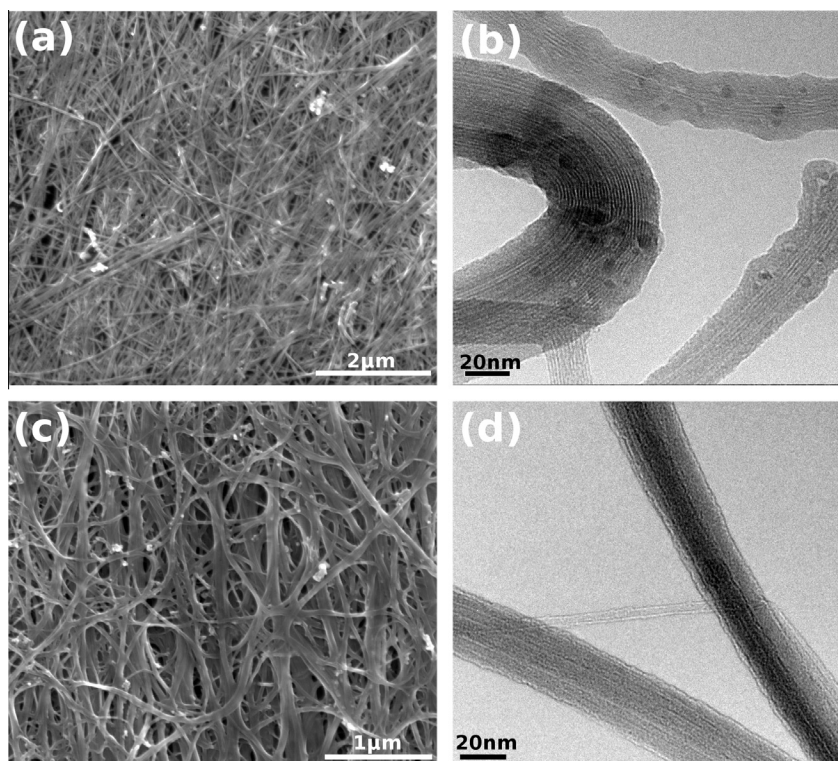


Fig. 4 – (a,c) Scanning and (b,d) transmission electron micrographs of (top) SWCNT- and (bottom) DWCNTs-based CNWs after overnight exposure to ICl at room temperature.

SWCNTs hinders the access of doping agent, what is more substantial than in the case of DWCNTs. Then, because of a high vapor pressure (52 hPa at 30 °C [31]), partial evaporation of surplus ICl continued from within the CNWs and the resistance increased. At last, MWCNTs were tested and they showed a minor improvement, in terms of conductivity wherein mere 10% reduction was observed (Fig. S3). Electronic structure of only the most outer and inner shell MWCNTs could be affected as van der Waals diameter of iodine is too bulky [32] to penetrate the interplanar cavity between graphitic planes [10,33]. Moreover, MWCNTs we used were of a considerable large outer diameter. CNTs with small diameters (SWCNT in particular) have larger pyramidalization of the honeycomb lattice, what renders a severe mismatch between π -orbitals due to the curvature effects [34]. As a consequence, such CNTs are more reactive and interact with electrophilic species such as I^+ with more ease. ICl is a powerful iodinating agent and has been successfully used for aromatic electrophilic halogenation of benzene ring, *e.g.* in tyrosine to yield diiodotyrosine [35].

Nascent C–I bonds on CNTs effectively increase the number of holes and hence improve electrical conductivity of CNWs [36,37]. In addition, inner diameter of all three types of CNTs we used could allow for the formation of polyiodide chains I_n^- inside [23,38] as all of them were wider than 0.398 nm [32]. These linear structures were found to contribute to p-doping [38]. Finally, the presence of Cl^- or ICl_2^- (from auto-dissociation of ICl [39]) further contributes to the observed strong p-doping as reported by Kim et al. [40]. The only up-to-date publication on interaction between CNTs and ICl

indicated strong changes at the Fermi level after the treatment [41], which stays in accordance with the electrical properties of ICl treated CNT macroassemblies reported here for the first time.

Measurements of specific conductivity of CNWs made of SWCNT and DWCNT (Fig. 3c) showed an overall improvement to the electrical properties after the overnight ICl treatment by 84% and 64%, respectively. Although addition of dopant may add to the weight of CNWs, and thus have a negative impact on the specific conductivity, the benefits in terms of conductivity are not overpowered here and increase in the specific conductivity is observed in both cases. Furthermore, SWCNTs had a lower weight gain than adulterated SWCNTs (0.75 S m² g^{−1} for DWCNTs and 0.17 S m² g^{−1} for SWCNTs). Moreover, we observed a similar decrease to the diameter of CNWs for both SWCNTs and DWCNTs, reduced by about two thirds after the treatment, what indicates strong densification action of ICl on CNTs (Table S1). Finally, the highest specific conductivity we observed was for ICl-treated DWCNTs reaching 1.24 S m² g^{−1} (Fig. 3c). To put it into a perspective, the recorded value is in the same order of magnitude as specific conductivity of iron (1.27 S m² g^{−1}) or highly pure

CNT fibers comprising over 90% of metallic nanotubes also produced by direct-spinning from CVD ($2.00 \text{ S m}^2 \text{ g}^{-1}$ [42,43]).

It has to be noted that the enhancement of the electrical conductivity could not have been achieved by simple improvement of the quality of CNTs using, for instance, thermal annealing. In a parallel study, CNWs were annealed up to 500°C under vacuum to remove contamination from CNTs, but in fact, we have observed deterioration of the electrical properties (53% increase in electrical resistivity [44]). Although removal of adulterants may in theory improve the contact between individual CNTs and their bundles, it also creates additional voids within the material. The effect of junction resistance under these conditions overpowers potential benefits from improved transport of carriers between individual CNTs.

Electron microscopy revealed a significant improvement to the packing density after the treatment (Fig. 4). This is most evident in the images of CNW cross-sections (Fig. S4), where in we see how the most of the voids filled up with air (Fig. 2) were eliminated and the material became more homogeneous (which is coherent with densification of the material shown in Table S1). As a macroscopic consequence, CNWs became rigid as it was much more difficult to cut ICl-treated specimens out from CNWs than those as-made for characterization. From the electrical properties point of view, a shorter distance between individual CNTs and their bundles adds to the improvement in conductivity due to diminished number of electrical junctions and simple geometrical decrease in the junctions' length [45].

Raman spectroscopy manifested the successful action of ICl on CNWs. The first apparent feature is a shift of G band towards larger wavenumbers caused by p-doping [41,46]. Overnight treatments resulted in 5 cm^{-1} shifts (SWCNTs, DWCNTs; Fig. 5), whereas for CNWs treated to the burning point the shift was equal to 3 cm^{-1} . Prolonged exposure to ICl at room temperature resulted in functionalization of the material with halogens (responsible for the D/G increase) and removal of low-molecular weight adulterants on the surface [47] (responsible for the D/G decrease). SWCNT-based CNWs had D/G ratio as high as 0.80 indicating the abundance of these species, which upon reaction with halogens became more volatile as generally expected for the halogenated molecular fragments. SWCNTs functionalization taking place competitively to removal of these halogenated compounds resulted in a net decrease of D/G ratio to 0.38. In case of DWCNTs, we begun with highly crystalline and pure material ($D/G = 0.07$), and thus functionalization itself was the main force giving eventually $D/G = 0.32$ after the overnight treatment. Finally, in both cases we observed lower D/G ratios after bringing CNWs up to 350°C , as related to the samples treated overnight. At elevated temperatures, halides start to purify the material and etch through amorphous contaminations and the most defected CNTs [19,48]. Then, under these conditions thermally-assisted evaporation of halogenated fragments could occur. D/G of SWCNTs decreased from 0.80 (as-made) to 0.12 (after high-temperature treatment) because of relatively high content of adulterants in the starting material. They are expected to be the primary site of chemical attack due to the labile nature of disordered functional groups as compared to largely inert network of sp^2 -hybridized carbon

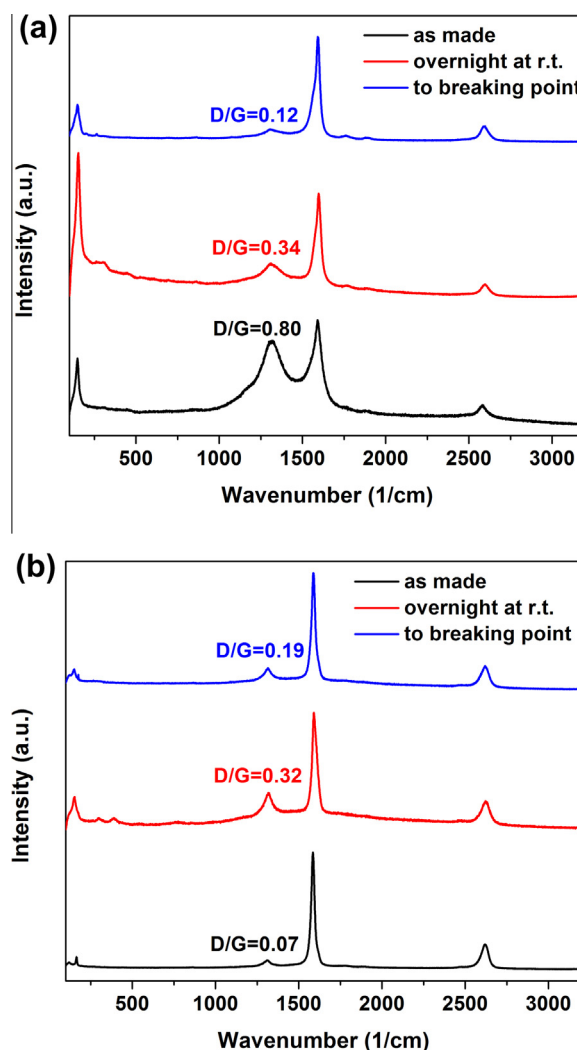


Fig. 5 – Raman spectra of (a) SWCNTs and (b) DWCNTs before and after ICl-treatments. 780 nm laser was employed. (A color version of this figure can be viewed online.)

atoms in CNTs. The elevated temperature caused the reaction with ICl to take place faster and to a larger extent. D/G of DWCNTs, on the other hand, increased from 0.07 (as-made) to 0.19 (after high-temperature treatment). The as-made material was virtually free of contaminations, and thus functionalization proceeded on the most defective CNTs.

Acquisition of Raman spectra with a blue laser ($\lambda = 488 \text{ nm}$; Figs. S5, S6) gave the same trends, but corresponding D/G ratios were lower, what is coherent with the observation that irradiation with higher energy laser gives less rich and intense spectral response [49,50]. In our case, RBMs of DWCNTs were less pronounced at $\lambda = 488 \text{ nm}$ to this extent that we refrained from their deconvolution into individual Lorentzian peaks. SWCNTs however, manifested as three broad peaks with maxima at 101, 133 and 160 cm^{-1} corresponding to 2.52, 1.85, 1.46 nm diameters [50]. In addition, deconvolution of RBMs observed at $\lambda = 488 \text{ nm}$ (Figs. S7, S8) for SWCNTs ($117, 148 \text{ cm}^{-1} \rightarrow 2.13, 1.65 \text{ nm}$) and DWCNTs ($119, 161 \text{ cm}^{-1} \rightarrow 2.1, 1.5 \text{ nm}$), also gave diameters that stay within the distribution observed in TEM. According to the Kataura plot we

prepared, both metallic and semiconductive populations of CNTs were present in the as-made samples (Fig. S9). What regards changes after the ICl treatments, intensity of lower wavenumber RBMs in DWCNTs (coming from the outer walls) fades away, what is indicative of their functionalization (Figs. S6, S8) [51]. In a similar fashion, signal from larger diameter SWCNTs was slightly silenced and small diameter fraction was more evident in the Raman spectra (Figs. S5, S7). Interestingly, we observed evolution of SWCNTs G^- side feature to the G-band (Fig. S5), whose Lorentzian shape is usually attributed to a considerably semiconductive character of CNTs [50,52,53]. Ghosh et al. noted a similar effect, wherein ICl was sufficiently potent to convert metallic CNTs into semiconductive due to changes in the Density of States (DOS) near Fermi level [41]. Among a selection of a surveyed halogen compounds, ICl was proved to be the one with the highest electron affinity, and thus it has a very strong p-doping influence on metallic CNTs in particular. Metallic CNTs are often considered as more reactive than their semiconductive counterparts due to their higher DOS near the Fermi level and lower ionization potential [54].

Analysis of the composition of CNW surface confirmed introduction of chlorine and iodine into the CNW structure (Fig. 6). Less Cl and I atoms were incorporated into SWCNTs than into DWCNTs (consistent with the observed weight gain,

Table S1), due to the fact that dopant infiltration into SWCNT and DWCNT bundles is limited by flow resistance as explained before. Moreover, we applied the same amount of ICl onto them and whilst it was penetrating the carbonaceous coating of SWCNTs and was lost in parallel by evaporation/sublimation, in the case of DWCNTs it filled up the voids instantaneously. Lastly, a substantial part of ICl was consumed in a variety of reactions with SWCNTs contaminants (e.g. addition of ICl to unsaturated bonds or iodination of aromatic moieties via electrophilic substitution) that decreased D/G from 0.80 to 0.34. Interestingly, in both SWCNTs and DWCNTs the oxygen content rose after the treatment with ICl (SWCNT: 2.8 \rightarrow 7.5 at., DWCNTs: 5.6 \rightarrow 13.2 at.). Halogen groups on aliphatic carbon atoms are well-known for being good leaving groups [55], and thus moisture in the ambient may cause their substitution for hydroxyl group coming from water vapor, what recovers aliphatic oligoalcohols present in the as made material [47]. Moreover, halogen moieties on aromatic carbon atoms can undergo nucleophilic addition–elimination S_NAr substitution, in which phenolic moieties are formed [56], and thus the oxygen content increases (co-formed HCl in the hydrolysis of ICl [27] catalyzes the reaction).

To illustrate the viability of CNWs as power and data transfer leads, we made a USB cable based on them. An external

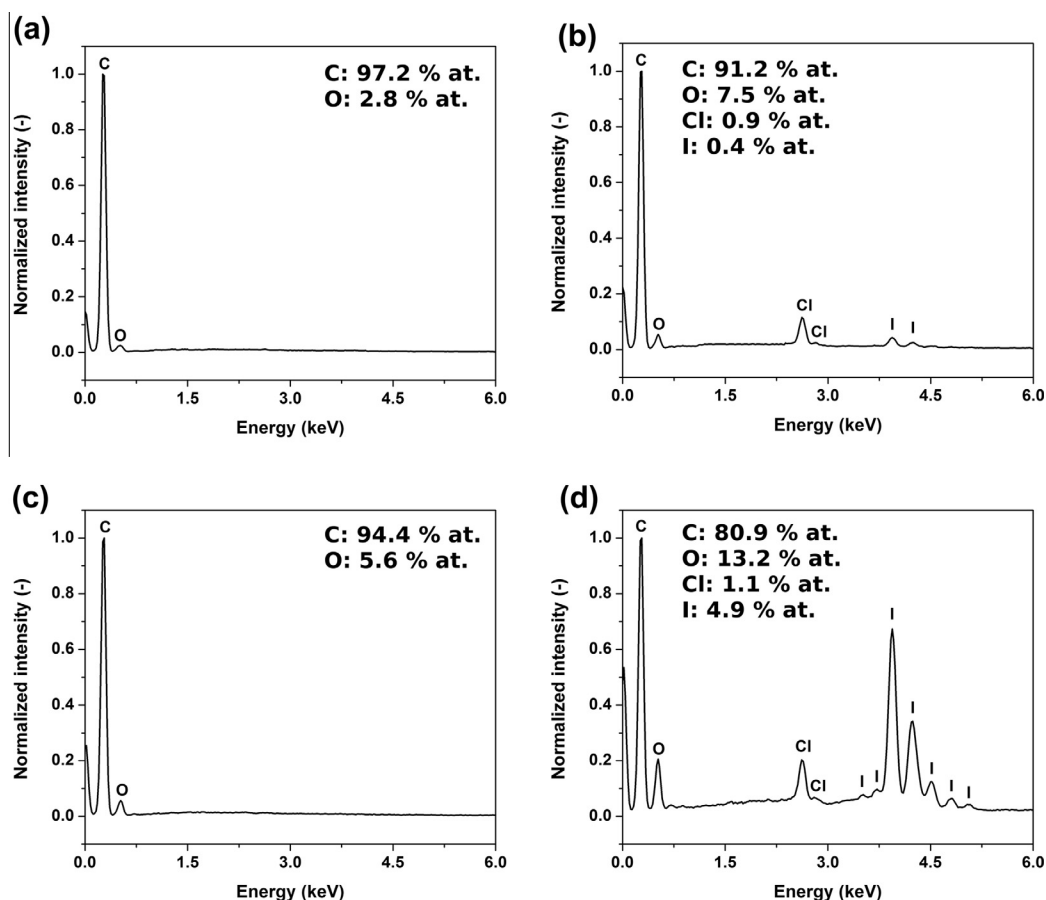


Fig. 6 – EDX patterns of (a,b) SWCNTs and (c,d) DWCNTs before and after overnight ICl treatment at room temperature, respectively.

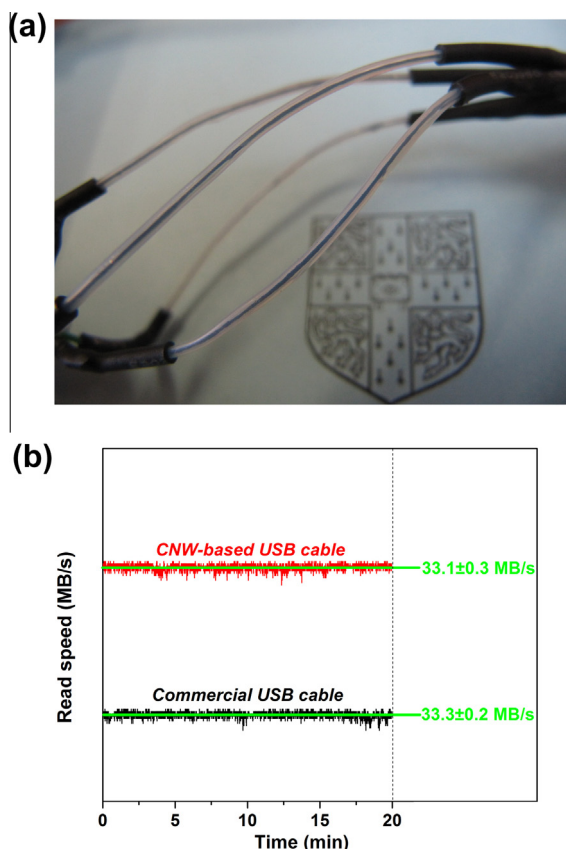


Fig. 7 – (a) A close-up image of USB cable comprised of four insulated CNWs doped with ICl, (b) Comparison of read speeds of commercial and CNW-based USB cables. (A color version of this figure can be viewed online.)

hard-drive was connected to a PC using CNW-based and regular Al-Cu USB cable of equal length and cables' performance was compared in terms of data transfer. Results (Fig. 7) showed that CNWs achieved alike average read speeds with no transmission errors. In both cases practically full effective throughput of USB 2.0 protocol ($\sim 35 \text{ MB s}^{-1}$) was attained. In addition, we charged a cell-phone using both USB cables. Operation in power transmission mode was equally efficient as there was no difference between time spans of bringing the battery from discharged state to full capacity regardless of the USB cable we employed (CNW: 211 min, commercial: 207 min). CNWs proved to be efficient, light-weight and low-cost replacements of traditional wiring.

4. Conclusions

SWCNTs, DWCNTs and MWCNTs all reacted with ICl, with varying extents, to which electrical resistance was diminished. As expected, the least affected were MWCNTs due to the fact that iodine can interact with the inside and outside of the material and CNT walls in between do not interact with the dopant. What regards the efficacy of treatment on few-wall CNTs, it depends on the diameter and extent of presence of contaminants in the sample among other factors. Although SWCNTs are supposed to be the most prone to doping, the

sample we used was incompletely graphitized on the surface of particular CNT bundles and thus diffusion limited the access of the doping agent to the core of bundles. On the other hand, crystalline DWCNTs of an almost four times larger diameter readily absorbed ICl and initially 80% drop in electrical resistance was observed until surplus of chemically- or physically-unbound ICl evaporated. Moreover, the highest specific conductivity, $1.24 \text{ S m}^2 \text{ g}^{-1}$ that we observed was for the ICl-treated DWCNTs. Since ICl enabled detection of strongly p-doped semiconductive CNTs (as evidenced by Raman spectroscopy), we believe that the proposed treatment methodology would also be beneficial to improve electrical properties of other carbon nanostructures such as graphene. Successful operation of ICl-doped USB cable almost at the limit of USB 2.0 illustrates viability of this doping strategy and brings us one step closer towards replacing traditional conductors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.02.058>.

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