

Crystalline Graphene Nanoribbons with Atomically Smooth Edges via a Novel Physico-Chemical Route

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I. INTRODUCTION

Abstract—A novel physico-chemical route to produce few layer graphene nanoribbons with atomically smooth edges is reported, via acid treatment ($H_2SO_4:HNO_3$) followed by characteristic thermal shock processes involving extremely cold substances. Samples were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy. This method demonstrates the importance of having the nanotubes open ended for an efficient uniform unzipping along the nanotube axis. The average dimensions of these nanoribbons are approximately ca. 210 nm wide and consist of few layers, as observed by transmission electron microscopy. The produced nanoribbons exhibit different chiralities, as observed by high resolution transmission electron microscopy. This method is able to provide graphene nanoribbons with atomically smooth edges which could be used in various applications including sensors, gas adsorption materials, composite fillers, among others.

Keywords—Carbon nanoribbons, carbon nanotubes, unzipping.

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WITH the discovery of graphene and, promptly, graphene nanoribbons (GNRs) there have been new frontiers for carbon science. Graphene is very interesting due to its extraordinary electrical [1], thermal [2] and mechanical properties [3], which may lead to many applications in electronic devices, sensors and composites [4]. GNRs may be synthesized by mechanical cleavage followed by lithography, etching, chemical stripping and chemical vapor deposition [4]-[8]. Recently, methods have been developed able to produce atomically smooth edges within GNRs. Some of these methods apply a bottom-up approach by intermolecular coupling of monomers resulting in nanoribbons of several nanometers in length [9]. Other methods have used the top-bottom approach via sonication of mildly oxidized MWNTs [10],[11] and hydrogenation of SWNT [12]. Unfortunately these methods have reported low yield of nanoribbons from the starting material, require non-facile or time consuming procedures. In addition, the majority of the previous methods used to unzip nanotubes create many structural defects and large volumes of chemical waste products caused by the strong acid treatments. Therefore, alternative routes to produce large quantities of graphene nanoribbons with atomically sharp edges need to be implemented. In this work a novel and environmentally friendly method to synthesize few-layer GNRs is reported, using multi-walled carbon nanotubes (synthesized with ethanol and toluene) (CO_x -MWNTs) as starting material, by unzipping [13] them abruptly via a thermal shock process involving extremely cold substances, here the presence of some structural defects (e.g. uncapped tubes and vacancies) aid the process.

II. METHODOLOGY

The synthesis of pristine CO_x -MWNTs (CO_x -P) was performed by chemical vapor deposition (CVD). The CVD was performed in an argon inert atmosphere carrying a nebulized solution, containing 5% by wt. of Ferrocene ($FeCp_2$), 2.4 % of ethanol and the rest of toluene (C_7H_8), with a flow of 2.5 lt/min at 825 ° C [14]. The acid treatment was performed by adding 200 mg of CO_x -P in 30 ml of a solution of $H_2SO_4:HNO_3$ (3:1) and sonicated for 6 hours. After sonication the resulting solution was filtered and washed with deionized water and dried. Subsequently, the acid treated CO_x -MWNT material (CO_x -A) was kept in a recipient with a very cold substance followed by abrupt heating. The exfoliated samples of CO_x -MWNT are labelled as CO_x -F.

Powder samples ($\text{CO}_x\text{-P}$, $\text{CO}_x\text{-A}$, $\text{CO}_x\text{-F}$) were characterized by scanning electron microscopy (SEM) (FEI Helios 600 Nanolab), Raman spectroscopy (HORIBA T6400, 633 nm and Reinshaw in Via Raman microscope, 514 and 785 nm), X-Ray powder diffraction (Bruker D8 DISCOVER with GADDS, with Cu-K α radiation, $k = 1.54 \text{ \AA}$). The powders were also dispersed ultrasonically in isopropanol in order to carry out transmission electron microscopy (TEM) studies (Cs-corrector (2) equipped HR-TEM, JEM2100, JEOL, Japan). Powder samples (1 mg) were analyzed by thermal gravimetric analysis (Rigaku Thermo Plus TG8120) with a flow of air (300 cc/min) and a heating ramp of $10 \text{ }^\circ\text{C/min}$. Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS) using a (Axis-Ultra, Kratos, UK).

III. RESULTS

Fig. 1a depicts an SEM image of pristine $\text{CO}_x\text{-MWNT}$ ($\text{CO}_x\text{-P}$), and Figure 1b shows mild-acid treated $\text{CO}_x\text{-MWNT}$ ($\text{CO}_x\text{-A}$) with open nanotube tips. Furthermore, the $\text{CO}_x\text{-A}$ material exposed to the thermal shock reveals different unzipped structures (see Figure 1 c-e) such as: partially unzipped $\text{CO}_x\text{-MWNTs}$, curved nanoribbons and completely flat nanoribbons. From the observed structures, 12% were unzipped, within these unzipped structures 45% were partially unzipped, and 55% were completely flat nanoribbons. The average diameter of the $\text{CO}_x\text{-P}$ was 74 nm, whereas the nanoribbons were 210 nm wide. The nanoribbons did not exhibit a hollow core under TEM, typically observed for $\text{CO}_x\text{-MWNT}$, confirming the unzipping of the carbon nanotubes (see Figure 2 a - c). Surprisingly, HRTEM images reveal atomically smooth edges of the nanoribbons. Here the nanoribbons exhibit different chiralities, where each layer has a different twist angle (see Figure 2 d - i). These kinds of edges have only been observed in graphitic nanoribbons that were Joule heated/irradiated under a HRTEM [8]-[10]. In the X-ray diffraction the interlayer spacings for the carbon structures are *ca.* 3.43 \AA , 3.40 \AA and 3.39 \AA for the pristine, acid treated ($\text{CO}_x\text{-A}$) and nanoribbon ($\text{CO}_x\text{-F}$) samples, respectively, along with the presence of iron carbide from the catalyst (see Figure 3 a). The Raman spectroscopy showed that all samples exhibit the D-band (*ca.* 1554 cm^{-1}), G-band (*ca.* 1583 cm^{-1}), and G^2 -band (*ca.* 2650 cm^{-1}), a shoulder next to the G-band arises in the $\text{CO}_x\text{-F}$ sample and corresponds to the D'-band (see Figure 3 b). This D' band at 1620 cm^{-1} in the Raman spectrum of $\text{CO}_x\text{-F}$ sample originates from a large amount of edge sites, indicating the formation of nanoribbons through the efficient unzipping of MWNTs. There is an increase in disorder during each stage of the method, shown by the variation in the $I_{D'}/I_G$ ratio (the integrated intensity of the band divided by the integrated intensity of the G band)

from 0.59 to 0.90 for $\text{CO}_x\text{-P}$ and $\text{CO}_x\text{-A}$, respectively, and then to 0.94 for the $\text{CO}_x\text{-F}$ sample.

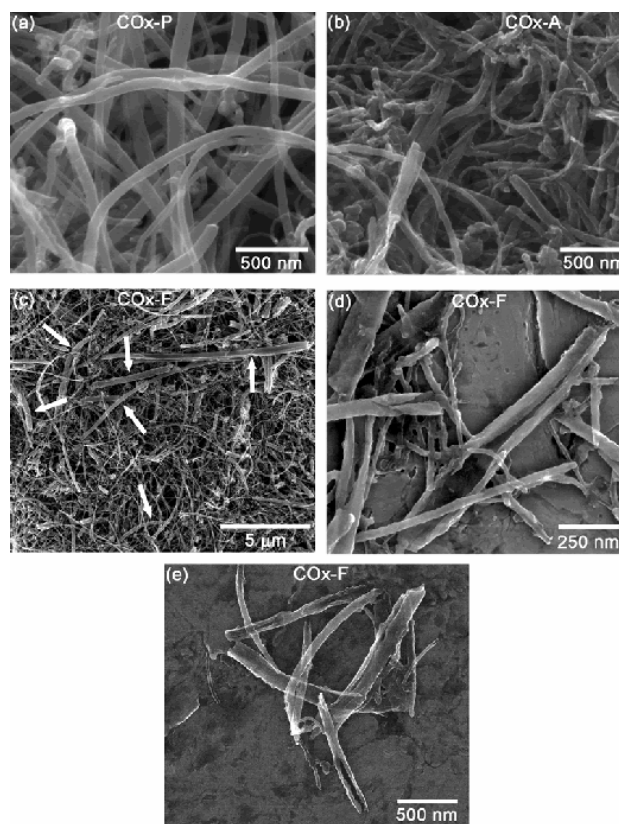


Fig. 1 SEM images of (a) $\text{CO}_x\text{-MWNT}$ pristine, (b) acid treated $\text{CO}_x\text{-MWNT}$ and (c)-(e) unzipped sample. Arrows indicate the unzipped structures

From the XPS measurements observation of the carbon C 1s peak (see Figure 4) there was an sp^2 binding decreases from 87% to 67% for the $\text{CO}_x\text{-A}$, and then when they are unzipped it decreases to 50%, due to the bare edges of the nanoribbons. Also, there is an increase of the shoulder corresponding to C-O/epoxy, carbonyl and carboxyl groups. From the intensity and width of the oxidation peaks it is observed that the material is not heavily oxidized as graphene oxide and graphene oxide nanoribbons [14]-[17]. When analyzing the N 1s region, the NO_x and substitutional binding is present, caused by the adsorption or intercalation of nitric acid within the carbon nanotubes, the intercalation of acids in carbon materials has been previously observed by other groups [18]-[20], furthermore when the sample is unzipped a pyridinic peak arises which may be caused by the bare edges that exhibit binding with the remaining nitric acid.

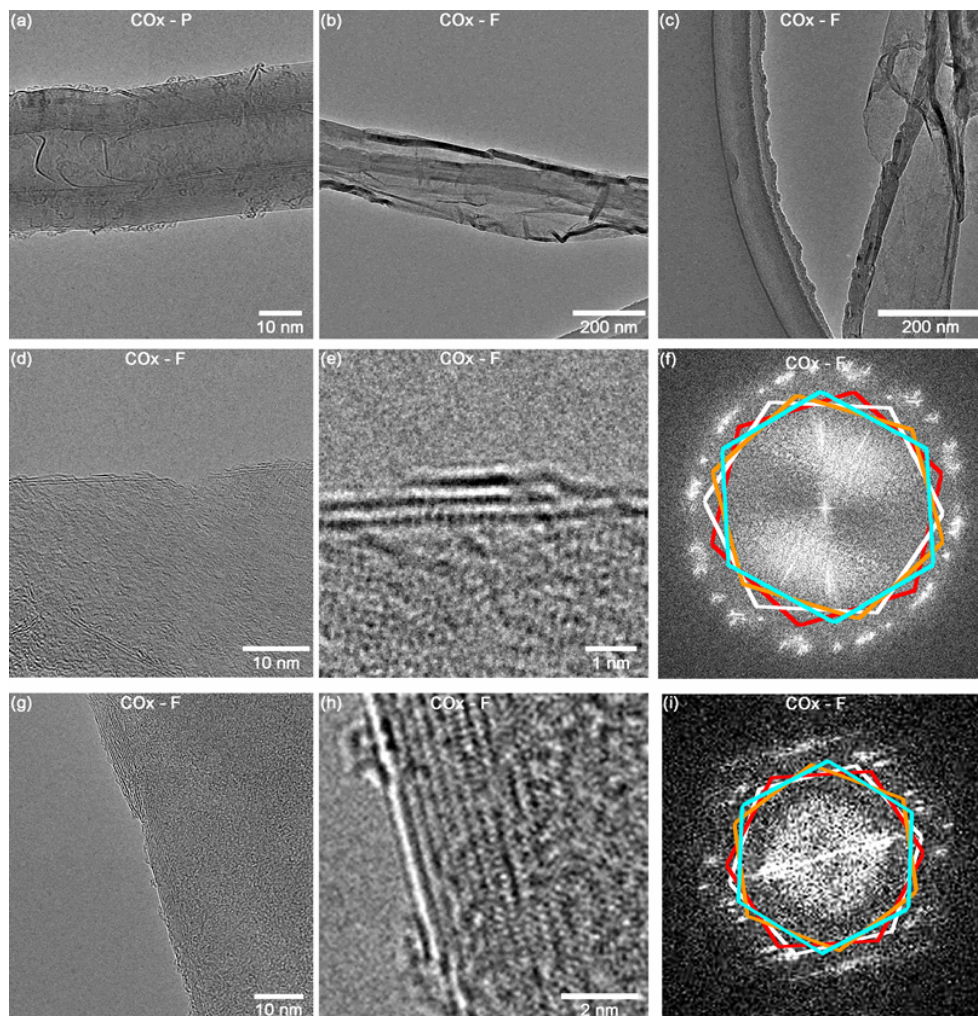


Fig. 2 HRTEM images and their corresponding fast Fourier transformations (FFT) of unzipped CO_x -MWNTs. Low magnification images of (a) pristine MWNT and (b), (c) GNRS. (d), (e), (g), (h) The high magnification images reveal the presence of atomically smooth edges of NRs, (f), (i) from their respective FFT it is evident that the graphene layers are twisted

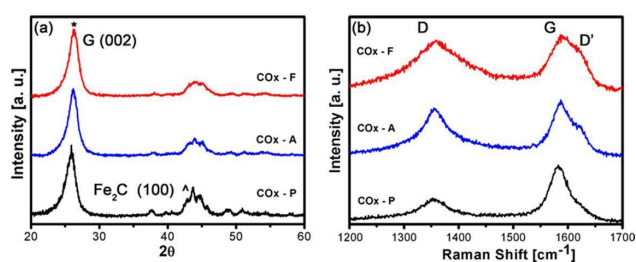


Fig. 3 (a) X-ray diffraction patterns of pristine (CO_x -P), acid treated (CO_x -A) and unzipped (CO_x -F) CO_x -MWNT. (*) represents the graphite (002) planes, (^) indicates iron carbide (Fe_3C). (b) Raman spectra (514 nm) of pristine (CO_x -P), acid treated (CO_x -A), unzipped CO_x (CO_x -F)

From the thermo gravimetric analysis (TGA) in air the samples exhibit different thermal decomposition temperatures (see Figure 5a). In the derivative of TGA (DTGA) of CO_x -P there is one single peak centered at 575 °C. After the acid treatment (CO_x -A) this peak splits in two: one located at 445 °C and the other at 595 °C, this clearly indicates the presence of two kinds of reactive materials; open-ended nanotubes and closed nanotubes (see Figure 5b). Regarding the nanoribbon samples (CO_x -F) there clearly are two independent peaks located at 390 °C and 585 °C, the first peak may correspond to nanoribbons with bare edges that exhibit higher reactivity and the other peak corresponds to CO_x -MWNT that were not completely unzipped.

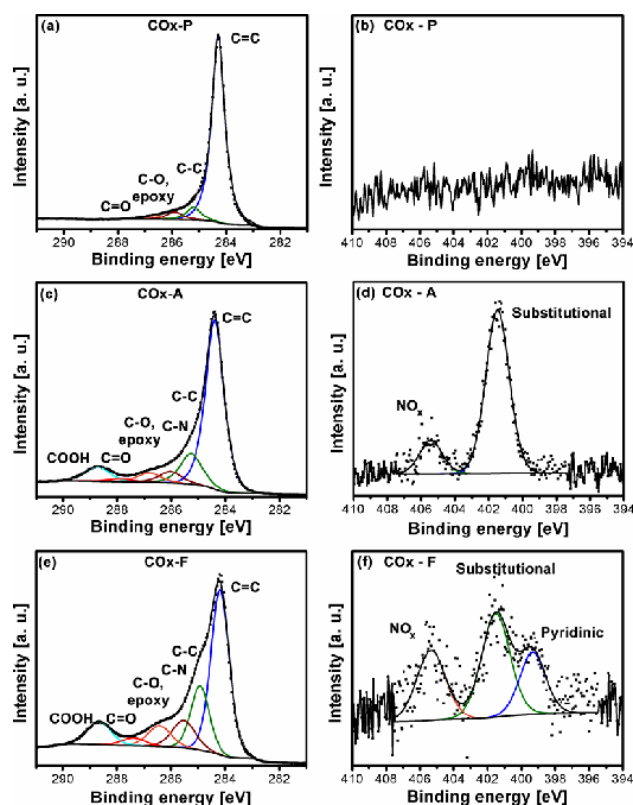


Fig. 4 X-ray photoelectron spectroscopy of unzipped (a), (b) pristine ($\text{CO}_x\text{-P}$), (c), (d) acid treated ($\text{CO}_x\text{-A}$) and (e), (f) unzipped ($\text{CO}_x\text{-F}$). The C 1s region is depicted on the left column whereas the N 1s binding energy appears on the right hand column

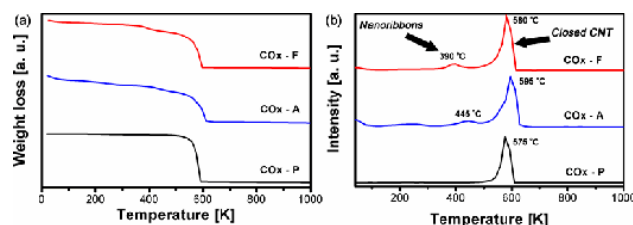


Fig. 5 (a) Thermogravimetric analysis of unzipped $\text{CO}_x\text{-MWNT}$ and (b) derivative of the weight loss vs. temperature. The analysis was carried out using 1 mg of sample in air at a heating rate of $10^\circ\text{C}/\text{min}$

Experiments without acid treatment did not show unzipping of the MWNTs, thus proving that the presence of defects such as oxidation and/or vacancies aid the unzipping process.

IV. CONCLUSION

An efficient, inexpensive and green method capable of producing crystalline few-layer graphene nanoribbons has been developed. The characterization of all the samples has lead to the following mechanism of unzipping. The mild acid treatment removes the nanotube caps, creates structural defects on the outer walls and shortens the nanotubes. The cold substance was then infiltrated within the hollow cores of the MWNTs due to capillary condensation, and with the rapid

change in temperature it abruptly expanded causing an atomically smooth unzipping. The produced nanoribbons are mildly oxidized with a good degree of crystallinity. The crystallinity is reflected in the observation of perfect armchair and zig-zag edges. In addition, it was clear that the edges of nanoribbons would increase reactivity, as shown by TGA.

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