

TDK THESIS

Electronic properties of alkaline metal doped carbon nanotubes

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1 Introduction and motivation

The discovery of graphene in 2004 [1] led to a boost in various basic- and applied research fields due to its exceptional electronic, thermal and mechanical properties (Nobell prize 2010), it is widely believed that electronic circuits based on graphene may offer an outstanding solution for replacing silicon based technology, manufacturing lightweight flexible display screens, solar energy panels [2][3].

Beside graphene, diverse carbon nano-structures have been also investigated. For instance, fullerenes (0D carbon material and Nobel Prize in Chemistry 1996), 1D carbon nanotubes (CNTs), few layer graphene (FLG), graphene nano-ribbons (GNR)as a novel 2D material and graphite (3D carbon material). Their electronic properties vary from insulators through semiconductor and metallic (see Fig. 1) or even superconductor [4]. Although the mechanism responsible for charge carrier conduction differ from one another; in case of graphene the zero band gap is an intrinsic property, in CNTs it depends upon the chirality vector (edge geometry of the graphene sheet it is rolled from), in graphite it can be tuned with doping by either donor or acceptor atoms.



Figure 1: The electronic structure of different carbon nanostructures [5]

Among the above mentioned "carbon family" particularly interesting is the graphene nano-ribbon which is a thin strip (< 50nm) of graphene (Fig. 2). The reason why they are interesting lays in their electronic structure, which depends on the width of the GNRs and edge structure :zig-zag (saw-tooth pattern) or armchair pattern. DFT calculations and experiments show that armchair nanoribbons are semiconducting with an energy gap scaling with the inverse of the GNRs width [6], while zig-zag GNRs show metallic conduction independent of the width. GNRs showing semiconducting properties can be alternative to silicon in future electronics. For example field effect transistor operating at room temperature has been fabricated out of less then 10nm wide GNR [7], also the exceptional electronic and mechanical properties of GNRs make them a viable candidate to replace copper in integrated circuits interconnections [7].



Figure 2: AFM images of different types of GNRs and thier schematic structure [8]

A proven method to produce GNR is by exfoliation of the layers of *Multi Wall Carbon Nanotubes* (MWCNT), which can be realized by inter planar alkaline atom doping of MWCNT, that causes the carbon sheets to unzip of [9]. This procedure was reported in 2009, where MWCNTs were intercalated with lithium under ammonia liquid, and exfoliated with an acid treatment [10]. As a result the MWCNT unzip along its axis as seen in Fig. 3.



Figure 3: TEM image of a completly exfoliated MWCNT and a partially opened MWCNT (Fig. a.). Zoom of the partially opened (Fig. b.) [10]

For effective unzipping the tubes must be opened from the ends (uncapped), as the starting point of the unwrapping is the top (bottom) of the tube. Further more the nanotubes being uncapped enable the intercalation process Ref[10]. The mechanism which has been proposed for the exfoliation process is the following according to Cano *et al.*[10]: the intercalation expands the interlayer distance of MWCNT causing a stress that ruptures the walls, after acidic treatment and annealing the exfoliation is done and the graphitic sheets recrystallize see Fig. 4.

It was found that higher intercalation levels of MWCNT facilitates the exfolitation process as the nanotube is much easily unwrapped for higher degree of intercalation [10].



Figure 4: Suggested mechanism for unwrapping, dots represent the intercalated atoms [10]

To determine the effects of alkaline-intercalation in MWCNT Raman spectroscopy has proved to be a reliable technique as it already did for *Graphitic Intercalation Compunds* (GIC), where the intercalation level is determined by thermodynamically stable crystal structures with KCx stochiometry (x = 8, 24, 36, ...) socalled stages (stage 1, stage 2, stage 3,...)[11]. Each stage is assigned to a specific crystal order, where an intercalant layer is adjacent to several graphene sheets, whose number is determined by the stage index. Each stage phase can be assigned to a specific Raman response [12] [13]. Stage-1 GIC associated to the full intercalation level is particularly interesting, which is metallic compared to the semi-metallic pristine graphite and in case of potassium GIC (KC₈) it undergoes a metal-superconductor phase transition at $T_c = 0.138K$ [11][13], this superconductor behavior is not present in case of lithium stage-1 GIC (LiC₆). Stage-1 (KC₈) phase of potassium GIC can be determined from analysis of its Raman spectrum: it has a characteristic G-line response (assigned to in-plane vibrational modes of the carbon atoms), also new peaks appear compared to the pristine or higher stage cases.

Motivation

The main goal of this thesis is to study the possibility of preforming alkaline-atom intercalation between the walls of MWCNT and to determine the Raman response of such intercalation compounds, as no studies have been made so far in multi-walled carbon nanotubes. The possibility of staging could asset to future controlled exfoliation and nano-ribbons production. As mentioned before, complete/saturation intercalation level must be reached for MWCNT before the exfoliation process is applied, but the question arises: how do we know whether the MWCNT sample is completely intercalated or not? and which are the best conditions to promote a full/controlled intercalation mechanism in MWCNTs? and finally what is the crystal structure of such alkaline-atom doped MWC-NTs?

The experiments where done at the University of Vienna, Faculty of Physics at the Electronic properties of materials group led by Prof. Thomas Pichler. In my work I intercalated the socalled CO_x -MWCNT with potassium. CO_x -MWCNT were chosen for the following reason: for the possibility of future exfoliation procedures based on alkaline-atom intercalation, open (uncapped) nanotubes must be used, as it facilitates both intercalation and unwrapping process. Until recently pristine (closed) MWCNTs were used for such purpose, and uncapping them required prior chemical treatment [10], which leads to the damage of the final GNR structure. The situation is different in case of CO_x -MWCNT, where oxygen atoms are substituted for few cites instead of carbon atoms (hence the name CO_x); it was found that oxygen helps to keep open and stabilize the end of the MWCNT [14]. The steps of the synthesis of potassium (K) doped CO_x -MWCNT) is presented and the Raman response of such intercalated MWCNT (K@CO_x-MWCNT) is presented and compared to Raman the spectra of GIC, to identify the intercalation level and staging.

2 Spectroscopic technique

A large variety of spectroscopic techniques are available nowadays for the analysis of materials and chemicals. Among these is Raman spectroscopy, named after Sir C. V. Raman (Nobel Prize 1930) who discovered this technique [15]. Samples in this thesis were characterized by means of Raman spectroscopy, which is a non destructive optical method, applied in a wide range of scientific fields as physics, chemistry, biology. This technique relies on detecting the vibrational response of the specimen, and it is an outstanding tool when investigating such important properties as the purity, electronic and vibrational states of carbon nanostructures. The reason why Raman spectrosscopy is useful lies in the fact that carbon nanotstructures lack of the dipolemomentum due to the monoatomic construction, which makes Raman spectroscopy an alternative to infra red spectroscopy.

2.1 Raman scattering

Raman scattering is a type of inelastic photon scattering whose energy is transferred to or from the crystal due to the creation or decay of phonon modes in the solid (or vibration modes of molecules). The physical process underlying this effect is the following: a photon with arbitrary energy (in the visible or infra-red range) absorbed by an electron of the solid excites the electron to a virtual state, after which it relaxes by both emitting a phonon and a photon (Stokes Raman process), thus introducing a phonon to the solid, see Fig. 5. Relaxation of the electron can happen also by further absorbing a phonon while in the excited virtual state after which photon emission occurs, in the end a phonon mode is destroyed in the solid (Anti-Stokes Raman process) Fig. 5. By adjusting the incoming photon energy to match the transition energy of two real electronic states of the system, the probability of Stokes-Raman scattering can be enhanced by several moreder of magnitude (up to 10000x factor), which makes it possible to detect single molecules (resonance Raman scattering). For the purpose of this thesis, the resonance Raman stokes process will be used. For instance this type of scattering is highly applicable to carbon based nano-materials as graphene, and graphite, which highlights the use of resonance Raman spectroscopic studies for this thesis period.



Figure 5: Energy diagram of the possible scattering processes: Stokes process results in the emission of a phonon thus the scattered light is red-shifted. Anti-Stokes process results in the absorption of a phonon, thus the scattered photon is blue-shifted. Resonant stokes occurs when incoming photon energy matches that of an electronic transition. ω_i denotes the angular frequency of the incoming photon, while ω_f that of the phonon [5]

The governing equations of Stokes Raman scattering can be introduced by applying conservation of energy and momentum:

$$\begin{split} \hbar\omega_i &= \hbar\omega_s + \hbar\Omega\\ \hbar k_i &= \hbar k_s + \hbar q \end{split} \tag{1}$$

Where ω_i (k_i) is the angular frequency (wave number) of the incident-, ω_s (k_s) of the scattered photon, Ω (q) is the angular frequency (wavenumber) of the emitted phonon. Equations 1 yields a linear dispersion $p_{phonon} = cq$ where c is the speed of light, phonon modes must also obey their dispersion relation in the solid, so because the immense slope of the linear dispersion phonon modes only around the Γ point (q = 0) of the first Brillouin zone will be available for Raman scattering see Fig. 6. Conservation of energy and



Figure 6: phonon modes available for Raman scattering. Created phonons have impulse equivalent where the linear dispersion intersects the phonon dispersion

momentum is not enough to understand the Raman spectrum, as the scattering process must obey selection rules: a phonon modes is Raman active if the derivative of the polarizability with respect to the spatial coordinates is non zero around the equilibrium point [16].

If the Energy of the incident photon matches an optical transition in the solid, then it is possible to induce a coupling between electrons, and the induced phonons. The modeling of this phenomena involves the inverse of the energy difference between the phonon, and the transition in the electronic continuum. Thus, if the initial scattered level corresponds to an existing electronic level, a resonance effect will occur with a deformation of the absorption or emission band shape with subsequent increase of its intensity being called "Breit-Wigner-Fano effect" [17] characteristic in highly doped graphitic materials.

2.2 Fano resonance

When discussing interaction (scattering) processes in a quantum mechanical system with quantized eigenstates it is important to understand the characteristics of the transition amplitudes between two states of the system. If the system is prepared in an initial $|i\rangle$

ground state, than transition to a state $\langle \Psi_{E_o} |$ with energy E_0 due to interaction operator T is described by a total transition crossection of a Lorentzian taken admixtureform [17].

$$\langle \Psi_{E_0} | T | i \rangle \sim \frac{\Gamma/2}{(\Gamma/2)^2 + (E - E_o)^2}$$
 (2)

Where Γ is the full width at half maximum of the Lorentzian, as expected the transition amplitude has a resonant maximum at $E = E_o$. This kind of peak function describes the "usual" Raman peaks in the spectrum. The situation is qualitatively different if the final states interacts with a continuum of states. In this case the final state having energy E is the linear combination of one discrete state $|\varphi\rangle$ with energy E_{φ} and a continuum of states $|\psi_{E'}\rangle$ with energy E' leaving [17].

$$\Psi_E = a\varphi + \int dE' b_{E'} \psi_{E'} \tag{3}$$

U. Fano [17] showed that if the matrix element of the Hamiltonian between the continuum state and the discrete state is non zero $\langle \psi_{E'} | H | \varphi \rangle = V_{E'}$ and $\langle \psi_{E''} | H | \psi_{E'} \rangle = E' \delta(E'' - E')$ then the matrix element of a scattering operator T between $|i\rangle$ and $|\Psi_E\rangle$, Where P indicates the "principal value of":

$$\langle \Psi_E | T | i \rangle = \frac{1}{\pi V_E^*} \langle \phi | T | i \rangle \sin \Delta + \langle \psi_E | H | i \rangle \cos \Delta$$

$$\Delta = -\arctan \frac{\pi |V_E|^2}{E - (E_{\varphi} + F(E))}$$

$$\phi = \varphi + P \int dE' \frac{V_{E'}}{E - E'} \psi_{E'}$$

$$F(E) = P \int dE' \frac{V_{E'}}{E - E'}$$

$$(4)$$

According to equation 4 the resonance energy will be shifted to $E_{\varphi}+F(E)$, where F(E)describes the interaction between the discrete and continuum states by V_E . The transition amplitude to the state $\langle \Psi_E |$ arise as the interference of the amplitudes scattering to $\langle \psi_E |$ (direct or background scattering) and to $|\phi\rangle$ (resonant scattering) which is an admixture of the discrete state and continuum states. The strength of the interference is determined by the phase factor Δ which undergoes a π shift as we move around the shifted resonance $E_{\varphi} + F(E)$ during an interval of $|V_E|^2$ which describes the half width (life-time) of the resonance. This equation also tells us, that the scattering amplitude will be asymmetric , and will have a 0 value for a certain value of E.

The total scattering cross section σ will be described as a modified (asymmetric) Lorentzian called [17]:

$$\sigma = \frac{(1 + \frac{E - E_{res}}{q\Gamma/2})^2}{1 + (\frac{E - E_{res}}{\Gamma/2})^2}$$
(5)

The line shape describing scattering process with such cross section is called "Breit-Wigner-Fano" lineshape. Here q describes the asymmetry of the resonance and it is the ratio of the resonant scattering to the direct scattering

$$q = \frac{\langle \phi | T | i \rangle}{\pi V_E^* \langle \psi_E | T | i \rangle} \tag{6}$$

If q tends to infinity (ie. resonant scattering is dominant) than we will get back Eq. 2 describing the total cross section with a single lorentzian lineshape. In contrast if the interaction is strong between the discrete excitation and the continuum (leading to a small q), the peak will broaden in an asymmetric way, and will have a zero scattering amplitude for a specified energy near the peak (see Fig. 4). The BWF lineshape is important



Figure 7: BWF lineshape as function of the asymmetry parameter q. As q tends to infinity the line shape will resemble a Lorentz function [17]

when determining the Raman spectra and particularly G-line response of potassium doped MWCNT and GIC KC₈; In case of KC₈ the G-line response of the pristine graphite (which is described by a lorentzian lineshape) is split into two bands each of them being described by a BWF lineshape. The electron-phonon coupling responsible for superconductivity is directly related to the G-line phonon (which exhibit a BWF lineshape) frequency and line-width(Γ), as the Γ parameter changes it changes also the coupling responsible for superconductivity [12]. This type of the transformation of the G-line response was observed in the Raman spectrum when doping CO_x-MWCNT with potassium to the saturational level. The BWF lineshape of such intercalation compounds is due to the interaction of the phonon mode with a continuum of electronic states.

3 Setup and sample preparation

So far, the production of graphene nanoribbons has been performed by intercalating MWCNT with Li under a liquid ammonia solution [10]. This for instance do not enhance the full intercalation in the tubes, and the technique does not permit controllability in the number of layers. The same is the case by abrupt thermal expansion of MWNCTs [18], where no control of the number of layers exist, even if the sample is cleaner due to the absence of acid treatments. Therefore, a controlled intercalation technique for MWNTS must be developed in order to determine a staging sequence followed by an exfoliation technique which bring us graphene nanoribbons with different number of layers under a scalable method.

In this section I present the production and potassium intercalation of CO_x -MWCNT which can be fully intercalated as stage-1 in GICs for bulk production of controlled mono-, bi-, tri-, and few-layer graphene nanoribbons. These tubes were synthesized using a CVD technique explained in [14].

3.1 Gas phase intercalation

Potassium intercalation with CO_x -MWCNT was done by a modified type of two-zone vapour transport method: both the sample and the intercalant are placed in a closed tube but separated in space (two-zone) as seen in Fig. 8. The tube is heated to a temperature high enough to create a high saturation vapour-pressure, but not too high to damage or melt either the intercalant or the pristine sample. Due to the homogeneous temperature the intercalant vapour is evenly distributed in the volume of the tube, and intercalant atoms from the gase diffuses and intercalates with the host material.



Figure 8: schematic of two-zone vapour transport method

In case of alkaline-atom intercalation it is very important to have a high vacuum in the tube; as potassium is highly reactive with water and oxygen molecules. Even a small amount of water contamination (coming from uncleaned tube or sample), can inhibit the intercalation process. Also high vacuum level must be maintained after intercalation is done, as water molecules can deintercalate the sample [11].

For a complete intercalation the amount of the pristine sample and the intercalant must be chosen carefully, as too high amount of pristine sample may result in an insufficient intercalation level, too high intercalant amount can cause the intercalant vapour to condensate on the surface of the sample making it impossible to carry out measurements and characterize the sample. Also the geometrical structure of the pristine sample influences the intercalation quality, it was found out that smaller pieces of pristine sample promotes more uniform intercalation level among the sample and it promotes complete intercalation.

3.2 Sample preparation

The stages of sample preparation are depicted in Fig. 9. As a sample and intercalant container I chose a quartz tube that was cut, closed from one side, and narrowed in the middle with a torch. The narrowing is necessary to prevent direct contact of the pristine sample and the potassium ampule (see in gas-phase intercalation process) Fig. 8. To clean the quartz tube, I connected it to a turbo pump and pumped out the air to create a moderate vacuum. I annealed the quartz tube with a torch, so the water adsorbed on the wall of the quartz tube is eliminated, as it can cause a non complete intercalation.



Figure 9: Steps of sample preparation

In order to avoide interaction of air and pristine sample/potassium ampule, I worked in a glove box(*MBraun*), the quartz tube closed by a gauge valve (to keep vacuum level) was moved to the glove box Fig. 10 containing argon atmosphere, where it was opened and both pristine CO_x -MWCNT and prior prepared potassium ampules where inserted. Potassium ampules were made by heating up bulk potassium (99.95% purity Aldrich) for melting, and sucking couple of miligramms up in a long capillary tube, which was afterwards cut into smaller sections in order to be suitable for insertion in to the quartz tube.

After the pristine CO_x -MWCNT and the potassium ampule were inserted in the quartz tube, I connected it to a turbo pump seen in Fig. 11, where annealing was done again under dynamic vacuum in order to get rid from the argon atmosphere, and other contamination from the sample.



Figure 10: MBraun glove box used for preparation of the samples ready for intercalation process

After sufficient time of heat treatment, the quartz tube was cut and closed with a tourch. The applied quartz tubes has double walls, so when cut by a torch first the inner tube closes, after the outer wall closes and parts from the vacuum pump, this ensures that no air is introduced to the inner volume of the tube, thus the vacuum is maintained. After the quartz tube containing the pristine sample and the potassium ampule was prepared, I put it in a spiral metal wire, that had its two ends contacted to a power supply see Fig 12. By fine adjusting the current amplitude in the wire, with the help of a thermometer contacted to the surface of the wire, the intercalation temperature was set to the appropriate value.

After several days of intercalation the annealing was stopped and the the quartz tube containing the intercalated nanotubes (K@CO_x-MWCNT) were removed and ready for measurement. I note that several intercalation levels were recognized depending on the intercalation temperature, time, the quality of the prior cleaning of the quartz tubes and the sample and the purity of the potassium. Different intercalation levels were recognised based on the color of the K@CO_x-MWCNT which varied between yellow, red and pale blue see Fig 13. Note that in case of GIC these colors truly indicates semi stage-1, stage-2 and stage-3 GIC, thus considering that nanotubes has locally similar electronic structure as of graphite, there is a good chance that staging phases occurs in them upon intercalation. The change of color comes from the reflectance quality of the sample, by varying the intercalation level, the free charge carrier concentration also varies, that changes the plasma frequency, which is responsible for the reflectance of the sample, here in case of GIC the plasma frequency is found in the visible regime.



Figure 11: The applied vacuum turbo-pump



Figure 12: The applied intercalation setup. The sample was placed in the spiral wire, temperature was set by adjusting the electrical power and monitored by a thermometer contacted to the surface of the heating wire



Figure 13: prepared K@COx-MWCNT. The initial (pristine) black color of the sample turned to yellow after intercalation. This sample was found to be the most highly intercalated at saturational intercalation

3.3 Purpose built insitu Raman setup

Measurements were made by a modified state of the art commercial Horiba labRAM HR optical spectrometer. The modification of the spectrometer made it available for broadband measurements [19]. The optical path is shown in Fig. 15, a tunable Ar-Kr gas laser is used (Coherent Inc), that has several lines in the visible region, for my measurements I used 468nm, 514nm, and 532nm wave lengths. Filtered (Semrock 0.5 inch clean up filters in order to remove plasma lines of the laser) laser light is coupled to the spectrometer by a periscope system, where it passes through an attenuator in order to roughly adjust laser intensity, further light is guided to the sample by a beam splitter, and the microscope, equipped with an objective Olympus 50x/0.5, inf/0/NN26.5, yield about $1um^2$ spotsize in a confocal geometry. Scattered light passes through the same beam splitter are guided through a long-pass interference filter (Semrock Razor edge) to filter out Rayleigh scattered light (which saturates and damage the sensitive detector if unfiltered). After stray light filtering, Raman light enters the spectrograph where it is dispersed by eithre 1800 grooves/mm or 600 grooves/mm optical grating into the surface of a CCD photo detector Horiba Symphony 1024 pixels.



Figure 14: optical path of modified labRAM HR spectrometer [19]

Measurements were done with 5mW laser power and 532 nm laser. This gave a spectrum with reasonable signal to noise ratio without damaging the sample. High laser intensity was necessary as the thick quartz tube introduced sever optical aberration on the spot size of the laser beam, leading to the loss of Raman signal. When measuring with 468 nm and 514 nm, 0.5 mW laserpower was set (lower wavelength enhances sample damage). Spectra where acquired for 25 seconds integration time and 25 averaging, from $50 \ cm^{-1}$ to $3000 \ cm^{-1}$ Raman shifts.



Figure 15: labRAM Raman spectrometer used for my measurements [5]

4 Results and discussion

In this section the acquired Raman spectra of the pristine and prepared samples are discussed and the potassium doping effect on the spectrum is investigated. Raman response of the saturation intercalated sample is compared to those of GIC, as they resemble astonishing similarity. I revisit the mechanism underlying the Raman response of stage-1 GIC. Finally a mechanism for intercalation is proposed based on the Raman response obtained.

4.1 Raman response of pristine CO_x -MWCNT

For a start I acquired the Raman spectrum of pristine CO_x -MWCNT. For a valid comparison I measured the spectrum in two cases: one the pristine sample exposed to air, and two pristine sample enclosed in the quartz tube under vacuum conditions. Condition number 2 was measured after preparing the the quartz tube with the potassium ampule inside it, but before any intercalation process was preformed. The comparison of pristine in both conditions is necessary, to determine the Raman response of the quartz tube itself, which is co-added to every measurement, thus by measuring the pristine sample in air we can distinguish between true Raman response of the sample, and those of the quartz.

The Raman spectra of pristine CO_x -MWCNT can be seen in Fig. 16. Measurements were done with 514 nm and 568 nm laser lines. The Intensity of 514 nm laser line was 1 mW for both samples in air and in quartz tube. The 568 nm laser line was 1 mW for pristine in air and 5 mW for pristine in quartz tube, I increased the intensity in the latter case because the thick and round quartz wall degraded the quality of the focus on the sample and also it refracted the Raman light coming from the sample, which leads to a huge loss of Raman signal as seen Fig. 16 estimated to be a factor of 40x the loss was reduced to a factor of 8x when laser intensity was increased from 1 mW up to 5 mW (without thermal damage of the sample).

The Raman spectrum of Cox-MWCNT depicts the presence of 3 components (D, G, and 2D bands). The corresponding frequencies of each modes are: (defect)D-band (1358 cm^{-1}) coming from the imperfections and defects in the crystal structure, (graphitic) G-band (1582 cm^{-1}) coming from the tangential motion of carbon atoms and 2D-band (2708 cm^{-1}) at the double Raman shift of D-band. Additional peaks were observed in the Raman spectrum when measuring sample in quartz tube Fig. 16a. and b., these peaks were attributed to the quartz material, and confirmed to be located at 518 cm^{-1} 632 cm^{-1} 798 cm^{-1} 894 cm^{-1} 1085 cm^{-1} (5 peaks) for 568 nm laser line, and 506 cm^{-1} 632 cm^{-1} 880 cm^{-1} 1086 cm^{-1} (4 peaks) for 514 nm laser line. A strong fluorescent response was found in the Raman spectrum which was also attributed to the quartz, described by fitting a 5th order polynomial. The Raman response of the quartz and the CO_x-MWCNT were fitted with Lorentzian function as seen in. Eq. 5 ($q \rightarrow \infty$), the sum (cumulative) of the Raman peaks (red line) and the fluorescent baseline is also shown (blue line).

When Raman spectra of the intercalated samples were also fitted, the full width at half maximum (FWHM) and position of quartz peaks were taken from the pristine fitt



and fixed, only amplitude was free to change.

Figure 16: Raman spectra of pristine CO_x -MWCNT with two different laser lines, under vacuum and in air. Additional peaks appears in quartz tube (red dots) Fig. a. and b., which are attributed to the quartz. The spectrum is sitting on a strong fluorescent background (blue line) Fig. a. and b. It is also apparent that signal intensity is degraded in case of quartz tube. The spectrum is fitted with a 5th order polynomial for fluorescent background and Lorentzian functions for the quartz and sample response.

4.2 Raman response of K@CO_x-MWCNT



Figure 17: Raman response of K@CO_x-MWCNT. 1- pristine, 2- pale blue sample, 3red sample, 4- red sample in an other spot, 5- yellow sample. It can be seen that with increasing the intercalation level (from bottom to the top), the G-band of the pristine decreases (green square box) while a broadband and asymmetric intense peak appears (purple box). Also note that D (blue box) and 2D (orange box) bands decrease, while a new band appears at low Raman shift around 500 cm^{-1} (red box), characteristing in highly intercalated GICs

In Fig. 17/1 the archetipical spectrum of pristine CO_x -MWCNT is showed. After potassium intercalation of three different samples, sample No.1 turned to pale blue color with a spectrum depicted in Fig. 17/2. Fig. 17/3 and Fig. 17/4 Are the Raman response of sample No.2 that turned red. It was measured at two different spots of the surface, which resulted in a slightly different spectrum (indicating different intercalation level). Finally Fig. 17/5 is the Raman response of the third sample that turned yellow. Each spectrum was measured with the 568 nm laser line at the same intensity (5 mW) except for Fig. 17/3 which was measured at 514 nm with 0.5 mW.

It can be seen that for samples with different colors associated with increasing intercalation

level (see the following subsection), the G-band of the pristine sample decreases, while an asymmetric, intense and broadband appears near 1500 cm^{-1} Raman shift.

It is also apparent that both D-band and 2D band (1358 cm^{-1} and 2708 cm^{-1}) decreas, while for highly intercalated samples a new slightly asymmetric peak appears around 510 cm^{-1} .

To understand the Raman response of $K@CO_x$ -MWCNT, the Raman response of alkaline doped GIC must be revisited. Intercalation of potassium with graphite occurs according the staging phenomena, where the potassium atoms are found in a layer between a number of graphene layers. Stage-1 is the case where each potassium layer is separated by one graphene layer, stage-2 when separated by two graphene layers, and so on as depicted in Fig. 18.



Figure 18: staging in potassium doped GIC, potassium layers are bounded by 1, 2, 3, and so on graphene layers according to their stage index, thus the distance I_c of two potassium layers varies for each stage [11].

Raman spectra in case of potassium doped graphite drom [12] and [13] seen in figure 19 were reported. In stage-1 GICs the Broadband response of the G-band around 1500 cm^{-1} region is described by the superposition of two Breit-Wigner-Fano (BWF) lineshape(1547 cm^{-1} and $1510cm^{-1}$) that corresponds to vibrational modeds with E_{2g_1} and E_{2g_2} symmetry and a lorentzian (1563 cm^{-1}). E_{2g_1} and E_{2g_2} are vibrations of the graphite describing motions of the carbon atoms in the graphene plane (see Fig. 20).



Figure 19: Raman response of potassium GIC from [13]

The BWF line-shape arises due to the coupling and interference between a phonon mode and an electronic continuum [17], and it is a good indicator that charge transfer occurred between the host and the intercalant [11].



Figure 20: Vibration modes of graphite from [12]

In Fig. 19 it is also apparent that a new peak is present for stage-1/KC₈ around $500cm^{-1}$, which is named C_z mode and it is assigned to the out of plane vibration of graphite (with A_{2u} symmetry Fig. 20). The C_z vibrational mode corresponds to the **M** point of the graphene Brillouin zone and it is infrared active, this becomes Raman active for high intercalation level [13]. To better understand the C_z mode, one has to consider the crystal structure of KC₈ in the real and reciprocal space seen in Fig. 21.



Figure 21: The crystal structure (left), and first Brillouin one of KC_8 (right dashed) and graphene (right solid) with its high symmetry points. The K atoms are sited in the middle of the honeycomb structure of graphene, and are denoted by circles, graphene unit cell (left dashed) are depicted along side with KC_8 unit cell (left solid). [11]

The unit vectors of KC₈ are double of that of graphite, thus the Brillouin zone of KC₈ is half (Fig 21(right dashed)). The effect of K atoms on the phonon dispersion of graphite is regarded as perturbative effect, thus due to the shrink of the KC₈ Brillouin zone now graphite **M** point is equivalent with KC₈ Γ point and the dispersion curve is folded, thus graphitic phonon modes of **M** points are folded into Γ point, and can be detected with Raman spectroscopy (which detects $q \approx 0$ phonons), and this is why C_z modes appear for stage-1 GIC (KC₈), thus this phenomena only occurs for high intercalation level, and it is a strong indicator of stage-1 phase.



Figure 22: Comparison of the Raman response of saturational intercalation CO_x -MWCNT (yellow sample) and KC_8 (data of [13]). The similarity indicates similar intercalation mechanism and intercalant geometry

After understanding the origin of the different existing modes instage-1 GIC-s, we

can now return to the observed Raman respose of K@CO_x-MWCNT 17, which is very similar to the Raman response of KC₈ as it can be seen in Fig. 23. However as we are talking here about multiwalled carbon nanotubes and not graphite, we can not say that the Raman response corresponds to the same potassium concentration as in KC8, but we can certainly assign it to a semi empirical Stage-1 in COx-MWCNT. The similarity of the stage-1 and the highest intercalation level K@CO_x Raman response indicates a similar intercalation topology, and the BWF line of K@CO_x-MWCNT around 500cm⁻¹ can be directly assigned to the C_z mode of KC₈, which indicates that K atoms are placed between the walls of the CO_x-MWCNT host in a local KC₈ geometry and that is assigned to the stage-1 phase. From the previous assumption one can also infeer from the G-band response of CO_x-MWCNT a high charge transfer from the intercalant to the host (as in case of KC₈).

An appearance of staging phenomenon in alkaline intercalation of MWCNT could be understand due to the fact that MWCNT can be understood like a rolled up graphite thus the phonon dispersion is closely related to it, and can be derived by zone folding: first the discrete states in the reciprocal space that corresponds to the direction of the chirality vector of the nanotube are folded to the Brillouin zone of the graphene, second the folded dispersion relation are further folded in to the 1D Brillouin zone of the nanotube [20], this technique will transform the Raman active modes at the Γ point of the graphene to the Γ point of the nanotube Brillouin zone. Now if we consider CO_x -MWCNT as if it were rolled up from KC₈ sheets, the C_z , E_{2g_1} and E_{2g_2} modes of KC₈ would appear in the Raman response of CO_x -MWCNT, thus E_{2g_1} and E_{2g_2} modes of KC₈ that corresponded to graphite in-plane carbon atom motion will correspond to tangential directional motion in case of CO_x -MWCNT, and C_z that corresponded to out of plane motion will now correspond radial direction motion.

Detailed G-line analysis was carried out where lines corresponding to C_z , E_{2g_1} and E_{2g_2} modes were fitted with BWF lineshape of the form:

$$I(\omega) = I_0 \frac{(1 + \frac{\omega - \omega_{ph}}{q\Gamma/2})^2}{1 + (\frac{\omega - \omega_{ph}}{\Gamma/2})^2} + y_0$$
(7)

Fitted line	C_z	$E_{2g_{1}}$	E_{2g_2}	GD	D	2D
ω_{ph}	545.3	1472.2	1531	1582	1352.3	2683.6
q	-2.83	-0.92	-1.73	∞	∞	∞
Γ	27.65	136.7	71.41	33.2	75.57	114
I ₀	2.73	1.67	1.05	0.21	0.099	0.015

G and D lines were fitted with lorentzians (BWF lines where $q = \infty$).

5 Conclusions

Potassium intercalation compounds were obtained by using for the first time CO_x -MWCNT, which were chosen because of the uncapped ends of the tubes. The intercalation process was detailed step by step to explain from sample preparation to the



Figure 23: Comparison of the Raman response of stage-1 K@CO_x-MWCNT and pristine CO_x -MWCNT, spectra were acquired with 568nm laser line and 5mW laser power. Detailed G-line analysis is shown in panel b. from the highly intercalated sample by using BWF line shape and lorentzians

intercalation step itself. In the introduction part it was discussed that alkaline intercalation of MWCNT is important for production of GNR by exfoliation, also it was discussed that high intercalation level and open ended MWCNT are required for efficient exfoliation process. A mechanism relying on alkaline interlayer doping of MWCNT was suggested in the literature for the exfoliation process [10], but it was not supported by measurements. I showed that Raman spectroscopy is a powerful tool of such investigations, as it can clearly indicate saturated intercalation level of alkaline intercalated MWCNT. Raman response of K@CO_x-MWCNT was determined and compared to that of KC₈, this comparison suggests the presence staging phenomenon in MWCNT, and the highest intercalation level was associated to stage-1 phase, thus the interlayer structure of the intercalant is better understood and experimentally supported. The investigation processes in the future. After being achieved a controlled intercalation mechanism in COx-MWNT one can in principle look forward into the production of graphene nanoribbons.

6 References

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