

This is a pre-peer reviewed version of the manuscript published in:

Electrochimica Acta, 2014, Volume 129, Pages 171-176

(DOI: 10.1016/j.electacta.2014.02.094)

**Dynamic Raman Spectroelectrochemistry of Single Walled Carbon
Nanotubes modified electrodes using a Langmuir-Shaefer method.**

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Abstract

Raman spectroelectrochemistry is a fundamental technique to characterize single walled carbon nanotube (SWCNT) films. In this work, we have performed the study of SWCNT films transferred to a glassy carbon electrode using a Langmuir-Shaefer method. Langmuir balance has allowed us to control the characteristics of the film that can be easily transferred to the electrode support. Time-resolved Raman spectroelectrochemistry experiments at scan rates between 20 and 400 mV s⁻¹ were done in two different solvents, water and acetonitrile. Spectroscopic results indicate that electron transfer of

carbon nanotubes is a very fast process. The electrochemical process is reversible in acetonitrile and, on the contrary, nanotubes are degraded when the characterization is performed in water being the degradation independent on the scan rate.

Keywords: Spectroelectrochemistry; Electrochemistry; Raman spectroscopy; Langmuir balance; Single walled carbon nanotube.

1.- Introduction

Carbon nanotubes (CNT) are one of the most promising materials for electrochemical purposes. Their exceptional mechanic, electric, electronic and thermal properties give them a great number of potential applications in different fields [1–8]. Raman spectroelectrochemistry is a multiresponse technique that obtains simultaneously an electrochemical and a spectroscopy signal, providing information about both the oxidation-reduction process and the vibrational structure of CNT films [9–16]. Therefore, this technique could be considered as one of the best for characterization and understanding of carbon nanotube films [17–23]. There are two dominant Raman signatures in the Raman spectrum that distinguish a single wall carbon nanotube (SWCNT) from other forms of carbon: the tangential vibrational modes of SWCNT (G-band) and the symmetric in-phase displacements of all carbon atoms in the SWCNT along the radial direction (radial breathing mode). Others important features are the D-band, which arise due to a double resonance process in which excited electrons are scattered by defects and the G'-band (overtone of D mode) owing to high

frequency two phonon mode. The unique optical properties of SWCNTs are due to quantum confinement of their electronic states (van Hove singularities) [10].

Usually, Raman spectroelectrochemistry takes long integration times to obtain each spectrum. However, for some chemical systems it is possible to obtain informative spectra in shorter integration times, allowing us to work in a real dynamic regime.

The development of rational processing techniques for carbon nanotubes is crucial for their technological applications and further understanding of their fundamental properties. In addition, the realization of uniform thin films with controlled nanostructures is important prerequisite for a number of optical and electric characterization techniques. Film formation can be performed by different techniques: spin coating, chemical vapour deposition (CVD), sputtering, Langmuir method, etc. Uniform films with good conductive properties can be formed by Langmuir techniques [24–33]. Moreover, these bottom-up techniques are very useful to control the properties (thickness, porosity, etc) of the films more than any other one. Furthermore, Langmuir-Schaefer method has the advantage that films can be transferred easily to a number of different substrates.

In the present work we have prepared SWCNTs films on glassy carbon (GC) electrodes using a method based on Langmuir balance and we have selected Dynamic Raman Spectroelectrochemistry to explain the behaviour of these films during the oxidation and reduction processes.

2. Experimental section

2.1 Chemicals

Chloroform, CHCl_3 , for HPLC, stabilized with ethanol and 1,2-dichloroethane (1,2-DCE) HPLC grade, were obtained from Acros Organics. SWCNTs produced by CVD, purified more than 80% with a diameter of 2 nm and several microns in length were obtained from Dropsens S.L. Lithium perchlorate 3-hydrate, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ was purchased from Panreac and acetonitrile for HPLC, isocratic grade was obtained from ProLabo. All compounds were used as received without further purification. Aqueous solutions were prepared using high-quality water (MilliQ gradient A10 system, Millipore, Bedford, MA). For safety considerations, all handling and processing were performed carefully, particularly when 1,2-DCE is used.

2.2 Instrumentation

All electrochemical measurements were carried out with a PGSTAT20 potentiostat (Eco Chemie B.V.) in three-electrode arrangement using a SWCNT/Glassy Carbon (GC) working electrode, a Pt wire counter electrode and a homemade Ag/AgCl reference electrode.

Raman spectra were obtained with a Confocal Raman Voyage (BWTEK). A laser wavelength of 532 nm with a power of 5 mW was employed to obtain the spectra, using a 20X objective. The spectral resolution was 3.8 cm^{-1} . The spectrometer was connected to a computer that recorded spectra continuously at set time intervals and for set integration times.

Synchronization between potentiostat and Confocal Raman microscope was performed using a trigger and several hardware and software changes

were made in the instrumentation to obtain a real-time Raman signal during the electrochemical experiments.

SWCNT films were examined with a Zeiss Ultra Plus field-emission scanning electron microscope (FE-SEM).

2.3 Preparation of SWCNT films

The formation of SWCNT films begins with the preparation of the liquid-air interface. SWCNT can be considered amphiphilic compounds because the carbon structure of the tubes is hydrophobic and most of the defects are hydrophilic. SWCNT were dispersed using a tip sonicator in a mixture of 1,2-DCE and chloroform. A controlled volume of the SWCNT dispersion was slowly dropped onto the aqueous liquid surface using a microsyringe. The aqueous sub-phase was thermostated at 30 °C. Fifteen minutes must be taken to get the evaporation of the mixture of organic solvents. When the interface air-liquid was ready the polytetrafluoroethylene (PTFE) barriers were moved at low step rates reducing the space in such a way that the SWCNT were packed till the films are prepared to be transferred.

SWCNT transference to the GC electrode was performed by using the Langmuir-Schaefer method more useful for small surfaces like a commercial electrode. Thus, deposition was done by dipping the GC electrode substrate horizontally through the floating SWCNT. A SWCNT film was formed by one or several Langmuir films deposited onto the GC surface by horizontal dipping the electrode from the gas phase toward the liquid phase. The films obtained can be organized in several multilayer structures. This approach allows us to use any solid commercial electrode to deposit the SWCNT film.

Several isotherms were done changing work conditions. Temperature, SWCNTs solution concentration, solvent mixtures and compression rate are key factors to obtain reproducible films. For example, very low concentrations of SWCNTs produced many islands on the film. The optimal conditions to obtain good films were: 30 °C of temperature, 0.016 mg mL⁻¹ SWCNT in a mixture 8:2

of 1,2-DCE:CHCl₃, 1.25 mL slowly dropped onto the water surface and the barriers moved at a compression rate of 5 mm min⁻¹. Fig. 1 shows the surface pressure–area isotherm using these conditions. Actual trough area was used as the abscissa instead of area per molecule because SWCNTs are a mixture of tubes with different lengths and diameters. In gas phase the slope is zero, i.e., SWCNTs are sufficiently dispersed so there is no interaction between them. From 125 cm² onwards, as the area decrease, a continuous increase of the pressure is observed because of the compression of the SWCNTs. The isotherm was characterized by a steep rise during the surface pressure range of 10–50 mN m⁻¹, at area values lower than 17 cm² corresponding to the solid phase, when the SWCNTs are further packaged. In this isotherm, it is not observed negative changes in the slope because despite the slowly sweep of the barriers (5 mm min⁻¹) there is not a true ordered packaging due to the shape and flexibility of the nanotubes. The SWCNTs are arranged forming islands that are rearranged up to the islands are interconnected. Inset in Fig. 1 shows the FE-SEM image of a SWCNT film obtained after transferring 3 SWCNT layers to a silicon substrate maintaining the surface pressure at 40 mN m⁻¹. As can be seen, SWCNTs were densely packed and cover uniformly the silicon surface.

3. Results and discussion

Raman spectroscopy is one of the best methods to characterize SWCNTs due to the resonant enhancement of the Raman signal. The main components of the SWCNT's spectra are the radial breathing mode (RBM) which gives diameter information, the disorder induced mode (D), the high frequency two phonon mode (G', overtone of D mode) and the tangential

displacement mode (G). The most intense band is the corresponding to the tangential displacement mode that was selected to illustrate our dynamic experiments.

The G-band evolution during a cyclic voltammetry for a SWCNT film is shown in Fig. 2. The potential was scanned from 0 V to +1.20 V and -1.20 V at 20 mV s⁻¹ in a LiClO₄ 0.2 mol dm⁻³ acetonitrile solution. The integration time was 1.910 s.

Both, oxidation (p-doping) and reduction (n-doping) of SWCNTs, lead to a decrease of G-band intensity. These changes in Raman intensity are related to the depleted/filled of the Van Hove singularities (VHs) in the SWCNTs electronic density states. G-band bleaching is connected to changes of the resonance condition [11]. Moreover, an up-shifting of the G-band is observed for anodic charging. There are two important effects that influence the position of the G mode: the phonon renormalization effect and changes in the spring force constant of C-C bonds [13]. While the phonon renormalization effect causes a wavenumber up-shifting for both positive and negative doping, the change of the spring force constant causes a wavenumber down-shifting for negative doping and a wavenumber up-shifting for positive doping. Hence, for positive charging only up-shifting of the G mode is expected, when the nanotubes are oxidized and they lose electrons of the vibrational levels. Consequently, the bond is shortened and becomes more rigid, increasing the vibration frequency. However, for negative doping both effects are competing with each other and in some cases, as the one shown in Fig 2.b, both effects are compensated and no shifting is observed. Furthermore, the interaction between nanotubes cannot be forgotten and it could also play an important role.

We have performed experiments at scan rates between 20 and 400 mV s⁻¹, not typically used in Raman spectroelectrochemistry. If we want to know the behaviour of the film for higher scan rates, a decrease of the integration time is needed. For example with 400 mV s⁻¹, the experiment lasts 12 seconds, so if the integration time was the same than in the case of the experiment at 20 mV s⁻¹, (Fig. 2) we could register only 6 spectra, clearly insufficient to understand the whole process. Dynamic Raman Spectroelectrochemistry allows us to use integration times as shorter as only 0.096 s, obtaining similar results at 400 mV s⁻¹ (Fig 3.a and 3.b) to the shown in Fig. 2 at 20 mV s⁻¹. In the experiment at 400 mV s⁻¹, the bleaching and the wavenumber up-shifting of the G-band during the oxidation is observed, while for the cathodic charging only the bleaching is observed. Therefore, as could be expected, the electrochemical doping/de-doping of the film is a very fast process, being potential dependent and independent on the scan rate. This conclusion cannot be extracted only from the voltammetric signal that is clearly affected by the non-faradaic component and does not provide information on the faradaic process related to the oxidation and reduction of the SWCNT.

Fig 3.c shows the evolution of the maximum intensity of the G-band with the potential. The oxidation and the reduction are not completely symmetric processes. This asymmetry can be ascribed to the density of states for the π band that is bigger than for the π^* band [9]. This fact shows that the filling of the states with electrons is more difficult than the depleting process.

Solvent is an important factor to be considered in the stability of the doping/de-doping of the SWCNT films. If we obtain Raman spectra of the films at different applied potentials without dynamic information, it is possible to think

that oxidation and reduction are similar processes in acetonitrile and water (dots in Fig. 4). However, Dynamic Raman spectroelectrochemistry shows the different G-band behaviour in the two solvents.

In acetonitrile solution (Fig. 4.a), carbon nanotubes reduction begins when the experiment has just started being observed a simultaneous decrease of Raman intensity reaching a minimum at -1.20 V. When the potential return to 0.00 V, Raman intensity recovers its initial value decreasing again when the nanotubes are oxidized reaching a lower value than during the reduction scan. Finally, carbon nanotubes recover an almost similar intensity to the initial one at the end of the experiment. On the other hand, when the same experiment is performed in water (Fig. 4.b) nanotubes reduction does not begin when the experiment starts, being necessary to reach a lower potential (approximately -0.50 V) to induce the reduction of the SWCNT film. The same behaviour occurs when the nanotubes are oxidized (beginning at around +0.50 V). The higher applied overpotential to transfer electrons in water could be related to the high hydrophobicity of the film. Moreover, final intensity after the whole potential cycle is much lower than the initial one, demonstrating that SWCNTs are not stable under these experimental conditions. Probably, the anodic polarization can produce defects by oxidation of the carbon network or even the film can be broken when it is illuminated by a laser light [18,34]. The degradation of the SWCNTs films also explains the deeper asymmetry observed between the cathodic and anodic scan when the experiment is performed in water than in acetonitrile.

Dynamic Raman spectroelectrochemistry not only provides qualitative information but also quantitative information. As an example, it has been

calculated the SWCNT film degradation during anodic charging in water. The degradation percentage (%D) has been calculated using the initial intensity value ($I_{initial}$), the final one (I_{final}) and the minimum value obtained during the anodic process (I_{anodic}) using the following equation:

$$\%D = \frac{I_{final} - I_{anodic}}{I_{initial} - I_{anodic}}$$

Table 1 shows data for the degradation percentage as a function of the scan rate. As can be seen there is no effect with the scan rate, %D values change between 36-46 % which means that the degradation depends on the potential but not on the time that the film is at this potential.

4. Conclusions

Langmuir balance is a very useful method to prepare SWCNTs films. It provides several advantages that make it a really interesting technique for this purpose.

We have shown that Dynamic Raman spectroelectrochemistry is a powerful technique to study dynamic chemical systems, like carbon nanotubes oxidation and reduction. These processes are not symmetric, the G-band intensity decreases in the two cases but only during the oxidation there is a shifting to higher frequencies. The redox behaviour of these films depends strongly on the solvent used to perform the voltammetric experiments but not on the scan rate at which they are carried out. We have demonstrated that the oxidation/reduction of the films is not equal in water than in acetonitrile solution. The difference of the process can be easily observed using Dynamic Raman

spectroelectrochemistry that also provide information on the degradation process in water.

Acknowledgments

Support from Junta de Castilla y León (GR71, BU349-U13) and the Ministerio de Economía y Competitividad (CTQ2010-17127). D.I. is gratefully for his FPI-MICINN agreement of the Ministerio de Economía y Competitividad. We thank Dr. Virginia Ruiz for her help in obtaining the SEM images.

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Figure Captions

Figure 1. Carbon nanotubes isotherm using a temperature of 30°C, a solution concentration of 0.016 mg mL⁻¹, and a volume injected of 1.250 mL, being the step rate 5 mm min⁻¹. Inset: FE-SEM image of 3 SWCNT layers transferred to a Si substrate.

Figure 2. G-band evolution of a SWCNT film at different potentials during (a) the anodic and (b) the cathodic sweep in a voltammetric experiment. The potential was scanned between +1.20 V and -1.20 V at 20 mV s⁻¹, starting potential 0.00 V in the cathodic direction, in a 0.20 mol dm⁻³ LiClO₄ acetonitrile solution. Integration time: 1.910 s.

Figure 3.. G-band evolution of a SWCNT film at different potentials during (a) the anodic and (b) the cathodic scan in a cyclic voltammetric experiment. (c) Raman intensity at 1590 cm⁻¹ vs. potential. The potential was scanned between +1.20 V and -1.20 V at 400 mV s⁻¹, starting potential 0.00 V in the cathodic direction, in a 0.20 mol dm⁻³ LiClO₄ acetonitrile solution. Integration time: 0.096 s.

Figure 4. Evolution of the normalized Raman intensity at 1590 cm⁻¹ vs. potential. The potential was scanned between +1.20 V and -1.20 V at 80 mV s⁻¹, starting potential 0.00 V in the cathodic direction, in a 0.20 mol dm⁻³ LiClO₄ in a) acetonitrile and b) water. Integration time: 0.480 ms. Dots represent intensity at 1590 cm⁻¹ at different potentials between -1.20 V and +1.20 V recorded at different applied potentials without dynamic information.

Fig3a

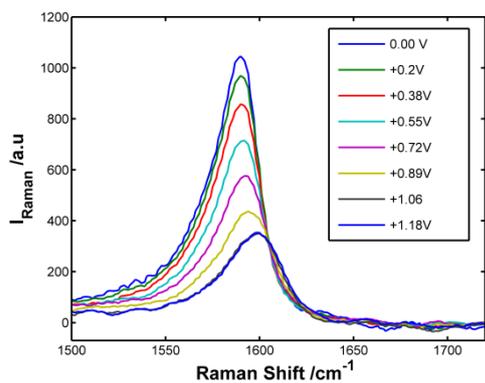


Fig3b

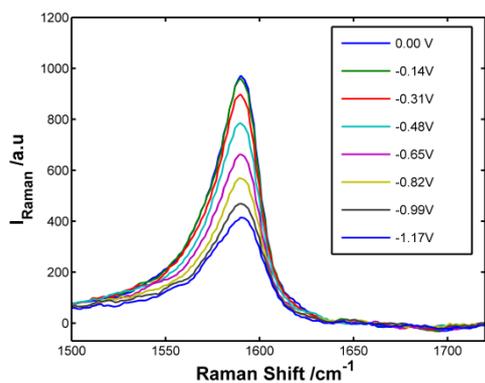


Fig3c

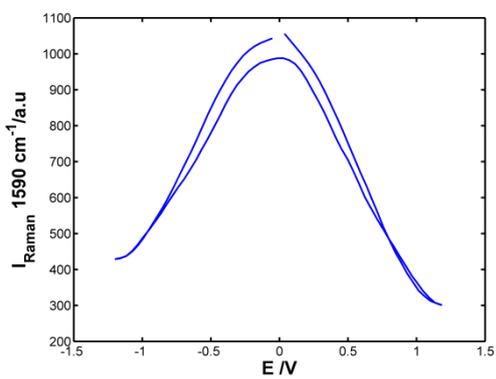


Fig4a

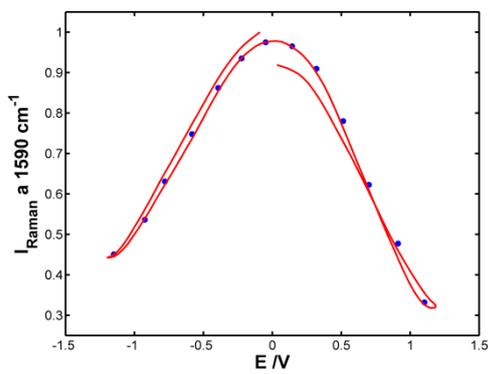


Fig4b

