Electrochimica Acta 129 (2014) 171–176

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Dynamic Raman Spectroelectrochemistry of Single Walled Carbon Nanotubes modified electrodes using a Langmuir-Schaefer method

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ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form 10 February 2014
Accepted 17 February 2014
Available online 3 March 2014

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

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-Schaefer 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.

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 SWCNT are due to quantum confinement of their electronic states (van Hove singularities) [10].

Rapid switching of the doping state of SWCNT has been previously studied using NIR spectroelectrochemistry [24] even at scan rates as high as 1000 mV s^{-1} [25].

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 at scan rates as fast as 400 mV s^{-1}. SWCNT films formed by Langmuir-Schaefer are very thin, allowing us to observe the rapid switching of the doping state of SWCNT at fast scan rates.

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 [26–35]. 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 SWCNT films on glassy carbon (GC) electrodes using a method based on Langmuir balance and we have selected Dynamic Raman Spectroelectrochemistry

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http://dx.doi.org/10.1016/j.electacta.2014.02.094
0013-4686/

to explain the behaviour of these films during the oxidation and reduction processes.

2. Experimental

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. SWCNT 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, $LiClO_4.3H_2O$ 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

KSV 2000 Minitrough (fabricated by KSV Instruments Ltd) was used for the study of Langmuir films and the deposition of Langmuir-Schaefer with an effective film area of 273 cm^2 (364×75 mm).

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.

Dynamic 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.

Raman spectra, using a 785 nm laser, were obtained with a R3000 Low-Resolution Raman Spectrometer (Raman Systems).

Vis/NIR spectrum was recorded using a combination of two spectrometers, a QE65000 (Ocean Optics) and a NIRQuest (Ocean Optics). The light beam, supplied by an Avalight DH-S halogen light source (Avantes), was conducted to the cell by a 600 μm optical fiber (Avantes) and collected by a 600 μm bifurcated optical fiber.

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 subphase 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.

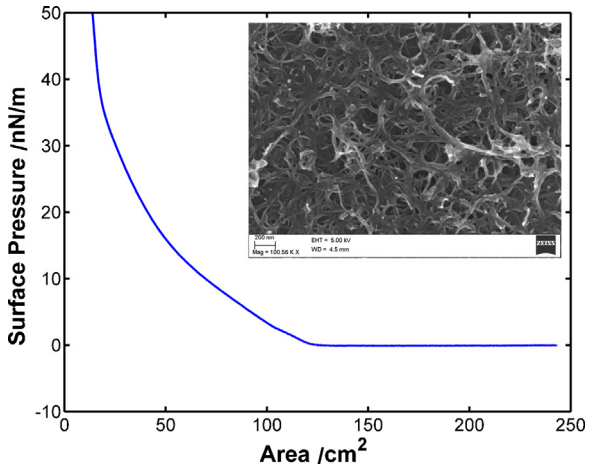

Fig. 1. Carbon nanotubes isotherm using a temperature of 30 °C, a solution concentration of 0.016 mg mL^{-1}, and a volume injected of 1.250 mL, being the step rate 5 mm min^{-1}. Inset: FE-SEM image of 3 SWCNT layers transferred to a Si substrate.

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, SWCNT solution concentration, solvent mixtures and compression rate are key factors to obtain reproducible films. For example, very low concentrations of SWCNT 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:$CHCl_3$, 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 SWCNT are a mixture of tubes with different lengths and diameters. In gas phase the slope is zero, i.e, SWCNT are sufficiently dispersed so there is no interaction between them. From 125 cm^2 onwards, as the area decrease, a continuous increase of the pressure is observed because of the compression of the SWCNT. 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 cm^2 corresponding to the solid phase, when the SWCNT 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 SWCNT 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, SWCNT were densely packed and cover uniformly the silicon surface.

3. Results and discussion

Raman spectroscopy is one of the best methods to characterize SWCNT due to the resonant enhancement of the Raman signal. Fig. 2 shows a Raman spectrum of a film obtained after transferring 3 SWCNT layers to a GC substrate. The main components of the spectrum are: the radial breathing mode (RBM), the disorder induced