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Electrochemical synthesis and characterization of carbon nanotube/modified polypyrrole hybrids using a cavity microelectrode

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ABSTRACT

A cavity microelectrode (CME) was used to perform an electrochemical synthesis of hybrid materials made of carbon nanotubes (CNTs) and conducting polymers. The confinement of the CME is used to produce a uniform nanometric coating of an electronically conducting polymer such as poly(*N*-methylpyrrole) (Pmpy) on multiwalled carbon nanotubes. The CME also allows easy characterization of the presence of the polymer layer on the surface of the CNTs by cyclic voltammetry. Transmission electron microscopy allowed us to measure the thickness and confirm the homogeneity of the Pmpy coating around the CNTs. Finally Raman spectroscopy brings additional information on the electrogenerated hybrid materials.

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1. Introduction

Hybrid materials constituted from CNTs and electronically conducting polymer (ECP) have been extensively studied these last years, mainly because of their wide potential applications, from supercapacitors to biochips, including gas sensors [1–5]. In most cases, the effective electrical conductivity of the hybrid is enhanced compared to the conductivity of the conducting polymer alone, but is lower than the conductivity of CNTs [6,7]. Our motivation for the present research started with the necessity to address the three following issues. The first one concerns the need to reduce electrical contact resistance between CNTs (used as fillers) in a thermoplastic or thermoset polymer matrix [8]. Secondly, we are interested in improving the mechanical properties of the CNT/polymer matrix interface [9]. The last issue is justified by achieving a biocompatibility of the CNTs (because of

their eventual toxicity). In this work, we focused on Pmpy as an example of stable electroactive layer for nanotubes [10].

Most of CNT/ECP hybrids are synthesized by using conventional chemical oxidative polymerization techniques, especially for CNT/polypyrrole hybrids, as used for the elaboration of ECPs for about 25 years [11]. However, the generation of hybrids with stable and controlled structure, such as “core-shell” ones, requires an adequate dispersion of the CNTs in the synthesis medium. This was obtained mainly by the micro or miniemulsion polymerization or the use of surfactants [12–15]. Another way to generate well defined structures of CNT/polypyrrole hybrids is the application of radiations [16]. Besides chemical polymerization approaches, electrochemical routes are often applied to obtain ECPs, but much less frequently in the case of CNT/ECP hybrids [17–19]. However, electropolymerization presents several advantages over oxidative chemical methods, among which a better

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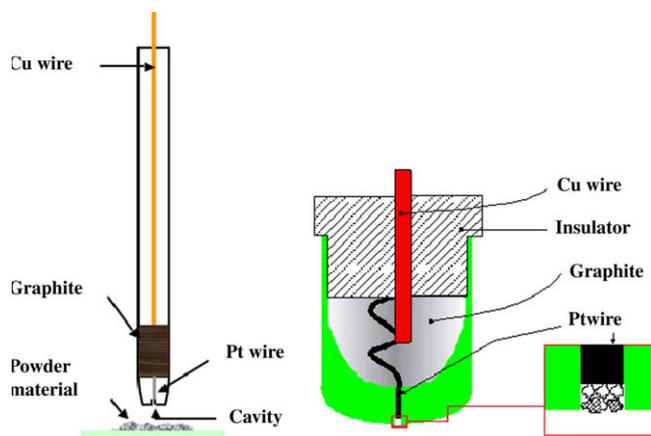


Fig. 1 – Scheme of the cavity microelectrode used for electropolymerization.

control of the thickness of the electrodeposited layer through the injected charge and the absence of purification steps after the synthesis. A challenge is to limit the electropolymerization outside the CNTs resulting in a disordered incorporation of the CNTs in the ECP matrix, which often occurs when starting from a dispersion of the CNTs in the monomer containing electrolyte solution. Controlled structure hybrids can be obtained for example when performing the electrodeposition on a well-aligned CNT array [18,20] or by using a surfactant as the supporting electrolyte to favor the electropolymerization on the CNT surface [19]. Recently an electrochemically induced deposition method of the CNTs on ITO electrode was described [21], which constitutes an interesting way to confine the CNTs on the location where electropolymerization takes place. We propose here an alternative solution to this issue by using the CME sketched in Fig. 1. This electrode was first described by Cha et al. [22] and later developed on the one hand by Vivier for conducting polymers [23,24], battery materials [25] and on the other hand by Qiu et al. [26] for molten salt applications. It is especially designed to deal with small amounts of materials, but the main interest in our case comes from the confinement of the CNTs in a very small volume close to the electrode surface, thus favouring the polymer deposition on the CNT surface, while this is much more difficult to achieve with conventional millimeter-size electrode. This makes it possible to avoid the use of surfactants, which may influence the properties of the electrogenerated hybrid material. Moreover, thanks to pulse electrochemical techniques, very thin layers of conducting polymers can be coated homogeneously onto the surface of CNTs in a one-step easy method that could be successfully scaled up to continuous coating processes.

2. Experimental

2.1. Materials

The CNTs used in the present work have been obtained by chemical vapor deposition. A mixture of xylene, C_8H_{10} (as carbon source) and ferrocene, $Fe(C_5H_5)_2$ (as catalyst source) with concentration of (0.1 g mL^{-1}) was injected into a reactor at

750°C , during about 10 min. The CNT growth was performed on a SiO_2 substrate. Field-emission scanning electron microscopy (FESEM) reveals a carpet of aligned and clean multi-walled carbon nanotubes (MWCNTs) obtained using this method (Fig. 2). *N*-methylpyrrole monomer with purity 98% and lithium perchlorate salt ($LiClO_4$) were purchased from Aldrich.

2.2. Electrochemistry

Raw MWCNT carpets are disaggregated by a mortar and pestle. This preliminary phase promotes the CNT dispersion in the CME. Then, using the CME as a pestle, CNTs are inserted into the cavity (dimensions: ca. 15 by $30 \mu\text{m}$). The electrochemical measurements were performed using an EGG Princeton Applied Research PAR273 Potentiostat/Galvanostat electrochemical workstation, with a three-electrode cell at room temperature. Hence, the CME was involved as the working electrode in an aqueous solution of lithium perchlorate (0.5 M); a platine wire and an $Ag/AgCl$ wire were used as the counter and reference electrodes, respectively. The presence of CNTs within the CME is confirmed by the cyclic voltammograms in Fig. 3a. Afterwards, the monomer (*N*-methylpyrrole) was injected into the solution (concentration 10^{-2} M). Electropolymerization was achieved following two procedures. In the first one, we carried out classical cyclic voltammetry methods (1 cycle from 0 to $+1.2 \text{ V}$ with a scan rate of 100 mV s^{-1}) and in the second one, we applied an electrochemical pulse (0 to $+1.2 \text{ V}$ for 0.5 s). Then, the electrochemical features of the Pmpy coating are identified by substituting the solution containing the monomer by a pure electrolyte solution and applying 1 cycle from -0.6 to $+0.6 \text{ V}$ with a scan rate of 50 mV s^{-1} (Fig. 3b). Ultimately, the hybrids are collected by sonication in tetrahydrofuran (THF) for 20 min at

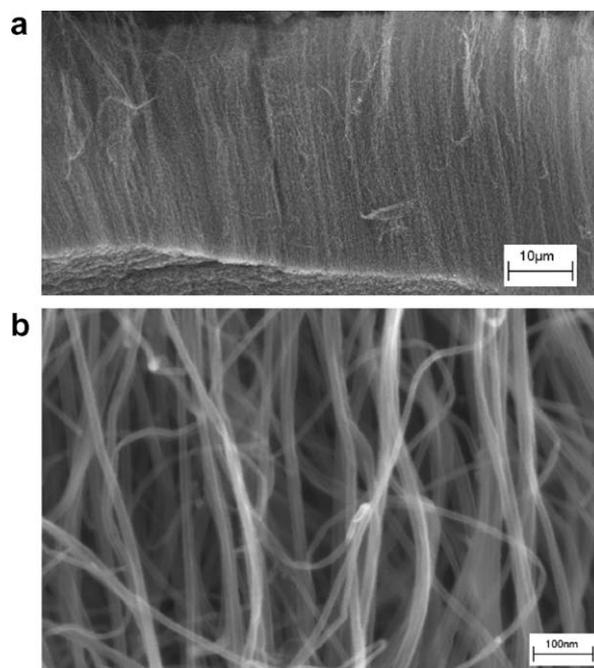


Fig. 2 – FESEM images of pristine CNT carpet: (a) low magnification and (b) high magnification.

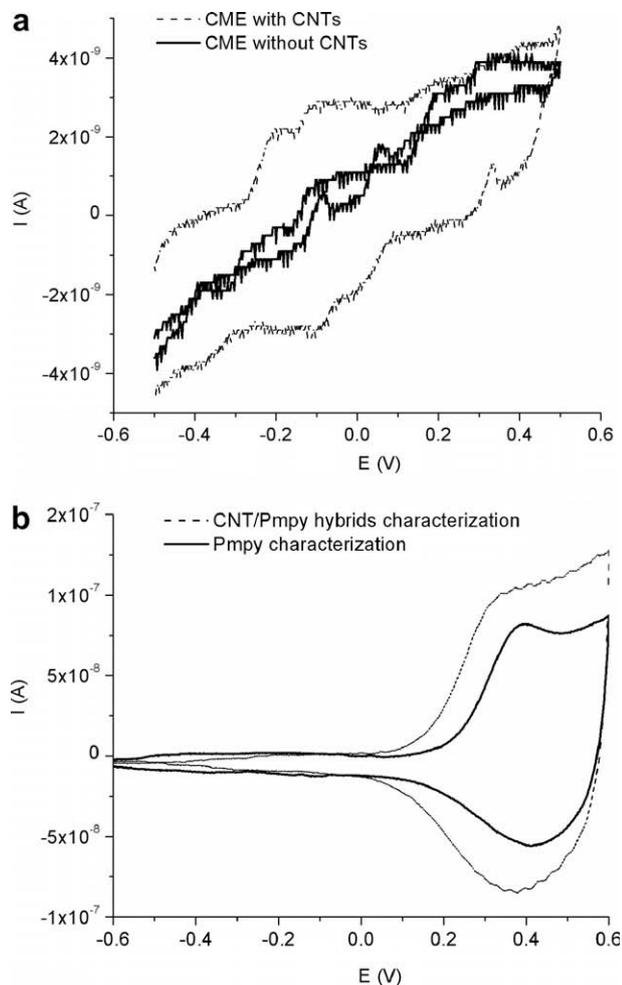


Fig. 3 – (a) Cyclic voltammograms showing residual currents in the electrolyte solution without monomer (scan rate: 100 mV s^{-1}). (b) Cyclic voltammograms of the CNT/Pmpy hybrids and Pmpy characterizations (scan rate: 50 mV s^{-1}).

45 kHz. Observations and analyses are carried out by evaporating a droplet of the hybrids suspending in the previous solution onto a copper grid (with randomly perforated carbon tape) (Agar Scientific).

2.3. Other characterization

Pristine CNT carpets were observed using FESEM (LEO 1530 Gemini operated at 5 kV). The morphology and the structure of the CNT/Pmpy hybrids were analyzed with Transmission electron microscopy (TEM) (FEI Tecnai G2). In situ Raman spectroscopy was performed using a microspectrometer Labram, Jobin Yvon with a resolution: 1 cm^{-1} .

3. Results and discussion

3.1. Electrochemistry

The electrochemical features of the CNT/Pmpy hybrid are displayed in Fig. 3. Fig. 3a shows the residual currents recorded without monomer, respectively, in presence and absence of

CNTs. The increase of the electroactive area results in a slightly higher current when CNTs are introduced in the CME. Once the electropolymerisation performed, the electroactivity of the electrogenerated polymer appears on the cyclic voltammograms of Fig. 3b, recorded after substituting the monomer containing solution by a pure electrolyte one. The comparison with cyclic voltammogram of pure Pmpy powder synthesized under similar conditions in the CME but without CNTs shows very similar features: in particular the peak potential for the redox process converting the polymer from the neutral reduced form into the conducting oxidized one is almost the same (ca. 0.38 vs. 0.4 V). This shows that the conjugation length in the Pmpy layer in the hybrid is not altered by the presence of CNTs compared to pure Pmpy. The reversibility of the doping process is also fully maintained in the hybrid. The cyclic voltammogram of Pmpy electrosynthesized on a conventional Pt electrode and cycled in the CME also exhibits the same features, demonstrating that the use of the CME for electropolymerization has no influence on the polymer electroactivity.

The doping level δ of the ECP can be estimated from the following equation, assuming an electropolymerization yield of 100%

$$\delta = \frac{2Q_r}{Q_s - Q_r} \quad (1)$$

where Q_r ($Q_r = 490 \text{ nC}$) and Q_s ($Q_s = 4.5 \text{ } \mu\text{C}$) correspond to the redox and synthesis charges, respectively [11]. In our case, δ has a value about 0.25 which is in accordance with usual values for doped polypyrrole.

As the volume of the cavity is about $1.6 \times 10^{-8} \text{ cm}^3$, this implies a material mass (CNTs) of approximately 15 ng assuming a volume filling rate of 50%. Knowing the average dimensions of the CNTs (average diameter: 15 nm and average length: 45 μm) and their density (1.87 g cm^{-3}), we can evaluate the corresponding area of the CNTs inserted into the CME to be roughly equal to ca. 2 mm^2 . Therefore, if we neglect the side-wall surface of the cavity non-in contact with the CNTs, we can estimate the value of the synthesis charge to ca. $200 \text{ } \mu\text{C cm}^{-2}$. In general, the thickness of a polypyrrole coating on the surface of an electrode is related to the synthesis charge Q_s and the surface of the electrode A , as follows [11]:

$$l_{/\mu\text{m}} \cong 4 \left(\frac{Q_s}{A} \right)_{/\text{cc m}^{-2}} \quad (2)$$

which leads to a thickness of ca. 0.8 nm. This value is certainly much lower than the actual thickness. Indeed, the area has been overestimated by ignoring the non connected nanotubes as well as those within entanglements. Nevertheless, the order of magnitude of the coating thickness is nanometric, as confirmed by electron microscopy.

3.2. TEM

TEM images of the produced hybrids (Fig. 4) show clearly the location of the Pmpy coating on the CNT walls. The average thickness of the amorphous polymer layer is 1.5 nm. We can mention that the coating thickness is slightly higher at the edge and at some irregular areas (if any) of the CNT, probably

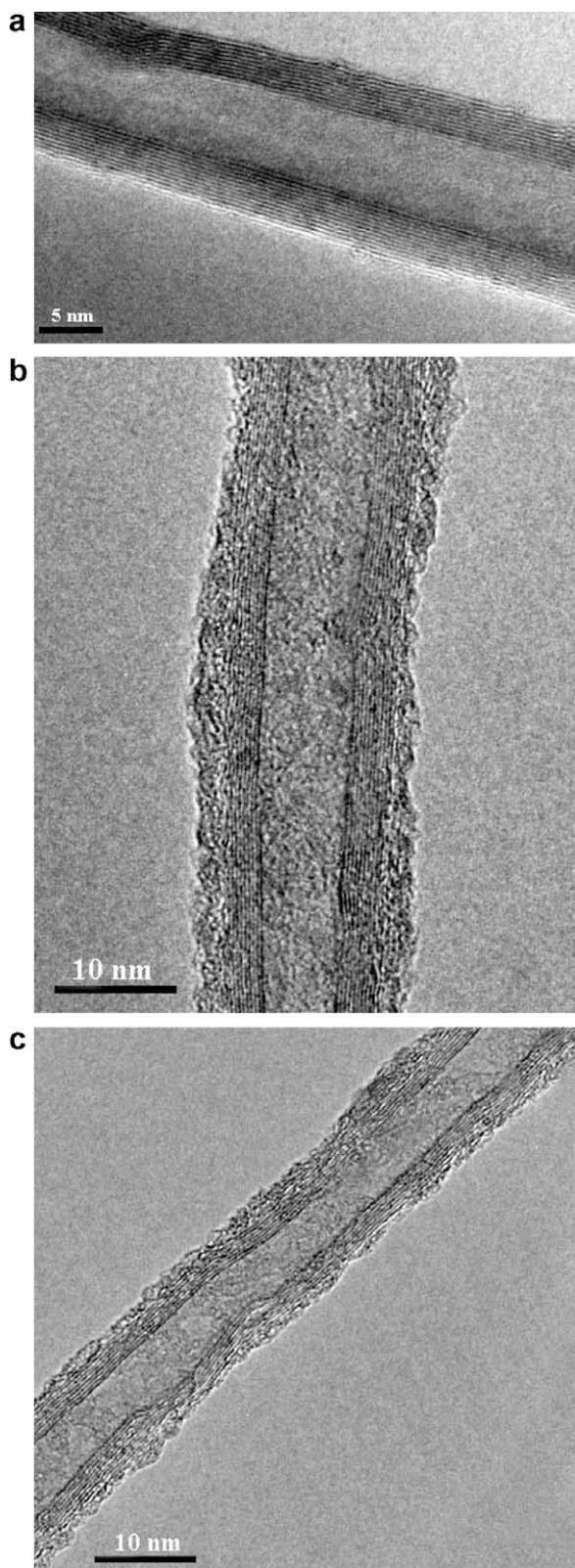


Fig. 4 – TEM images of a pristine MWCNT (a), two crossing CNT/Pmpy hybrids obtained by electropolymerization: 0.5 s pulse (b) and cyclic voltammetry (c).

because these edges or defects promote higher current areas for electropolymerization and thus act as favored nucleation

sites. A detailed analysis of the TEM images shows a significant difference in the structure of the Pmpy film depending on the synthesis method employed. In comparison with cyclic voltammetry, the pulse technique has shown its ability to improve the regularity and homogeneity of the coating. Such results demonstrate the ability of the CME to produce reliable and very thin coatings of ECP on CNTs.

3.3. Raman spectroscopy

Fig. 5 shows the Raman spectra of the different materials studied in this work. The MWCNTs are identified by their two characteristic peaks: the D band (disordered sp^3 band) at around 1350 cm^{-1} , and the G band (atomic motions in the graphene plane) at around 1580 cm^{-1} (Fig. 5a).

The spectra obtained for CNT/Pmpy hybrids (synthesized by cyclic voltammetry and potential pulse) are in accordance with previous works [15,27]. Especially, the broad peaks due to the CNT graphene sheets (D and G modes, see Fig. 5a) are hidden in presence of the coating layer (see Fig. 5b–c). Independently on the synthesis method, the spectra reveal specific peaks due to CNT/Pmpy hybrids. The C=C backbone stretching is observed at 1580 cm^{-1} , and the antisymmetrical C–H in-plane deformation at 1210 cm^{-1} (it is shifted to 1400 cm^{-1} in the case of cyclic voltammetry). The symmetrical C–H in-plane deformation is represented by the peak at 1065 cm^{-1} . We assume that the peak at 970 cm^{-1} corresponds to the quinoidic polaronic structure, associated with the polymer doping. The broad bands below 900 cm^{-1} are due to diffusion of silica of the glass substrate around the electrode.

In the meantime, we have also reproduced the spectra corresponding to pristine Pmpy prepared electrochemically in aqueous LiClO_4 . In this latter case, we note the presence of peaks at 1370 cm^{-1} (ring stretching) and 1580 cm^{-1} (C=C backbone stretching). Peaks recorded at 1000 and 1150 cm^{-1} are characteristic of C–H in-plane deformation. A peak at 680 cm^{-1} can be assigned to the symmetric stretching mode of ClO_4^- dopants.

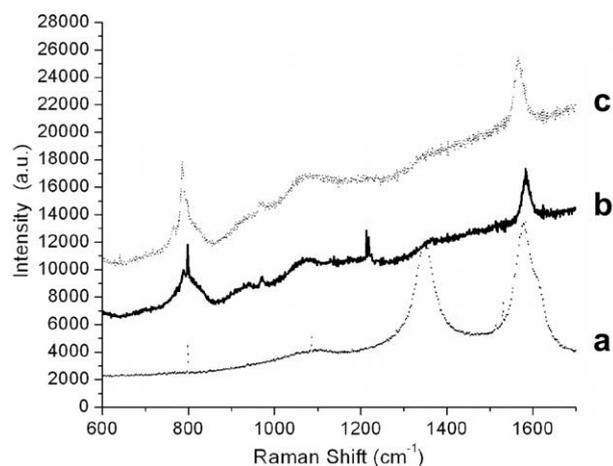


Fig. 5 – Raman spectroscopy of pristine MWCNTs (a), CNT/Pmpy hybrids obtained using two different methods: pulse for 0.5 s (b) and cyclic voltammetry (c).

4. Conclusions

A simple method is reported for coating the surface of CNTs with thin layer of conducting polymer (poly *N*-methylpyrrole) by electropolymerization using a CME. This electrode provides appropriate confinement allowing localization of the polymer coating at the CNT surface, without any additive (surfactant). The results reveal the production of high-quality CNT/Pmpy hybrids with uniform coverage of the nanotube. Moreover, this work shows an innovative way to modify precisely the surface of CNTs and especially those with small diameters, whereas previous studies used mainly large diameter CNTs. To overcome the problem of the small amounts of material obtained with such a method, we are currently developing a new experimental setup based on the same concept, but likely to produce larger amounts of similar hybrids to reinforce conventional polymer matrix.

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