



Short communication

Multi-walled carbon nanotubes/graphene nanoribbons hybrid materials with superior electrochemical performance



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ABSTRACT

Graphene nanoribbons (GNRs) were synthesized by oxidation of arc discharge multi-walled carbon nanotubes (MWCNTs) in concentrated H₂SO₄ using KMnO₄ as oxidizing agent at different times from 15 to 120 min. One of the GNR samples was further electrochemically and chemically reduced. The material obtained after 15 min of oxidation time (GNR₀₁₅) was a hybrid material containing MWCNTs, partially unzipped GNRs-MWCNTs and fully unzipped GNRs, and it demonstrated a superior electrochemical performance. This material presented the highest heterogeneous charge transfer constant and sensitivity towards H₂O₂ reduction. These properties are due to the balance between the content of unzipped MWCNTs, C_{sp2} carbon structure and oxygen moieties. GNR₀₁₅, thus reveals as a promising platform for further applications in electrochemical sensing.

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1. Introduction

Graphene is a hot topic in materials science. In the last years, several papers have been focused on the preparation and applications of graphene nanoribbons (GNRs) using Tour's method, consisting in the longitudinal unzipping of multi-walled carbon nanotubes (MWCNTs) [1,2]. Electrochemistry of graphene (in all its forms) [3] and CNTs [4] has been widely studied. Metal content [5], available electrochemical area [6], oxygen moieties/edge chemistry [7], and functionalization [8] have demonstrated to have a great influence on the electrochemical properties of carbon nanomaterials, and all of them must be considered to gain a fruitful insight.

Graphene-CNT hybrids have been revealed as promising materials in electrochemical applications [9,10]. Synergic effects between both materials have been reported [10], although this synergy, is not observed by other authors [11]. The preparation of graphene-CNT hybrids is usually performed using a high-cost and time-consuming method involving several steps, i.e. graphene oxide synthesis, reduction, and mixing of graphene oxide, reduced graphene oxide and CNTs to obtain material's best performance [10]. Another approach to obtain the graphene-CNT hybrid material is using MWCNTs as carbon source. The procedure starts with MWCNTs and ends in GNRs, having in the middle several GNR-MWCNT hybrid materials with different characteristics. Controlling the reaction conditions [9], a material with optimal electrochemical properties should be obtained.

The objective of the work is to synthesize electroactive MWCNT-based nanomaterials for the development of efficient electrochemical (bio)sensors. The significance of the work is that we have determined with an exhaustive structural and electrochemical characterization, that a hybrid nanomaterial with low oxidation degree and having an optimal balance of conductive C_{sp2} and electroactive oxygen groups, presents an excellent electrochemical performance. This nanomaterial was prepared by a low-cost and simple methodology.

2. Experimental

2.1. Material synthesis

GNRs were synthesized using Tour's method [1,2]. Briefly, 150 mg of arc-discharge MWCNTs [12] were dispersed by ultrasonication in 150 mL of concentrated H₂SO₄. Afterwards, the dispersion was heated up to 65 °C and 750 mg of KMnO₄ were added. The different materials were prepared by heating the dispersion for 15 (GNR₀₁₅), 30 (GNR₀₃₀), 60 (GNR₀₆₀), 90 (GNR₀₉₀), 100 (GNR₁₀₀) and 120 (GNR₁₂₀) min.

A portion of GNR₁₂₀ was reduced using N₂H₄ (GNR_{120-N2H4}), following a protocol previously described [2].

2.2. Electrode preparation

The materials were dispersed in 1.0% of NH₄OH solution to obtain a dispersion of 1.0 mg/mL. The GCE was polished with alumina slurries of 0.30 and 0.05 μm. Afterwards, they were modified by drop coating with 10 μL of the dispersions, evaporating the solvent at room temperature.

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GCEs modified with untreated MWCNTs (GNR₀₀₀) were also used as control.

2.3. Apparatus

X-ray diffraction (XRD) was done with a Bruker D8 Advance Series 2 instrument, Transmission Electron Microscopy (TEM) images were obtained with a INCA 200 X-Sight, (Oxford Instruments) microscope. X-ray photoelectron spectroscopy (XPS) was carried out on a ESCAPUS Omicron. Direct oxygen determinations were carried out with a Thermo Flash 1112 analyzer. Electrochemical experiments were performed with Epsilon (BAS), Autolab 128N and TEQ-04 potentiostats. Scanning Electronic Microscopy (FE-SEM) images were obtained with a Field Emission Gun Scanning Electron Microscopy (FE-SEM Zeiss, ΣIGMA model). BET area was determined with a Micromeritics ASAP 2020 analyzer, using N₂ adsorption isotherm at 77 K, with degasification at 150 °C for 300 min.

2.4. Electrochemical procedure

A 0.010 M phosphate buffer solution pH 7.40 containing 0.100 M NaCl was the supporting electrolyte. A platinum wire and Ag/AgCl, 3 M KCl were used as counter and reference electrodes, respectively.

Amperometry was carried out by applying the desired potential and allowing the transient current to reach steady-state prior to the addition of the analyte. Heterogeneous electron transfer rate constants (k_0) were calculated according to the Nicholson method [13] from cyclic voltammograms of 2.0×10^{-3} M K₃Fe(CN)₆ performed by scanning the potential between -0.200 and 0.400 V. Electroactive areas were calculated by chronocoulometry [14] using 1.0×10^{-3} M hydroquinone, by applying 0.400 V for 5 s.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed with an Autolab128N at -0.100 V, between 10 kHz and 10 mHz, with $\Delta E = 10$ mV using 5.0×10^{-2} M H₂O₂. The impedance spectra were analyzed using the Z-view program.

Electrochemical measurements were performed in deoxygenated solutions. Charge–discharge curves were recorded using a current of $1.0 \text{ A} \cdot \text{g}^{-1}$. Some samples were also electrochemically reduced (GNR_{XXX-ER}) by scanning the potential from 0.800 to -2.000 V at $0.100 \text{ V} \cdot \text{s}^{-1}$ (1 cycle). All measurements were performed at room temperature.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows TEM micrographs for different GNR samples. GNR₀₀₀ (Fig. 1A) consists of long graphitized MWCNTs with good distribution of lengths and diameters, along with graphitic impurities. In GNR₀₁₅ (Fig. 1B), it is possible to observe a heterogeneous material, containing oxidized, unopened MWCNTs, and MWCNTs with different degrees of unzipping. Large graphene sheets and anisotropic GNRs can be observed for GNR₁₀₀, (Fig. 1C), demonstrating that, at higher reaction times, the sample contains mostly unzipped MWCNTs, with some unopened MWCNTs. In the case of GNR_{100-ER} (Fig. 1D), individual and entangled GNRs, together with large graphitic sheets, are evident.

XRD spectrum (Fig. 1E) for GNR₀₀₀ shows a very strong peak at 26° , indicating a well-defined sp² structure, with large domains. As the reaction proceeds, this peak decreases, and a new peak appears at $\sim 10^\circ$, due to the formation of oxygen moieties during the oxidation step. This peak reaches a maximum for the GNR₁₀₀ sample, in agreement with the elemental analysis results (Table 1). The peak at $2\theta = 26^\circ$ is observed at all reaction times, indicating the existence of remaining MWCNTs. To estimate the quantity of remaining MWCNTs, a tentative approximation, as far as we know not

previously used before, has been carried out by considering a parameter, defined by us as *graphitic fraction*

$$\text{Graphitic fraction} = \frac{A_{10}}{(A_{10} + A_{26})}$$

being A_{10} the area at $2\theta = 10^\circ$ and A_{26} the area at $2\theta = 26^\circ$. Considering that A_{10} comes from GNRs, and A_{26} comes from the remaining MWCNTs. It is not a quantitative method, but it is a valid approach as much as A_{10} is correlated to the quantity of oxidized material and A_{26} is correlated to the quantity of remaining MWCNTs. Oxygen content, determined directly by elemental analysis (Table 1) increases with oxidation time until reaching the maximum for GNR₁₀₀, indicating overoxidation at GNR₁₂₀. The highest BET surface area (Table 1) was obtained at GNR_{120-N2H4}, while for the other hybrid samples the area increases, in general terms, with the oxidation time.

The Csp2 atomic percentage, as determined by C1s XPS, decreases when the oxidation degree increases (25.7% GNR₀₁₅, 15.8% GNR₀₃₀, 1.9% GNR₁₂₀, 22.8% GNR_{120-N2H4}), while carbonyl/quinone groups decrease as seen by O1s XPS (17.9% GNR₀₁₅, 9.0% GNR₀₃₀, 0.0% GNR₁₂₀, 24.2% GNR_{120-N2H4}). On the other hand, carboxylic groups increase with the oxidation degree (3.8% GNR₀₁₅ and GNR₀₃₀, 63.8% GNR₁₂₀, 18.1% GNR_{120-N2H4}). GNR₀₁₅ has the highest content of Csp2 and carbonyl/quinone groups and the lowest content of carboxylic groups.

The chemical reduction of GNR120 restores part of the C-sp2 structure and carbonyl/quinone groups and decreases the electrically insulating carboxylic group content that does not reach the low content determined for GNR₀₁₅ sample. SEM micrographs of deposited electrodes show a higher stacking of layers for GNR_{120-N2H4} (Fig. 1G) than for GNR₀₁₅ (Fig. 1F).

3.2. Electrochemical characterization

The highest capacity, determined by galvanostatic experiments, was obtained for GNR₀₁₅, followed by reduced materials (Table 1). The highest electroactive areas were also obtained for GNR₀₁₅ (Table 1). CVs in supporting electrolyte (not shown) follow the same trend as capacity and electroactive area measurements. Although higher BET areas should lead to higher capacities and electroactive areas, there is a considerable stacking in GNR_{120-N2H4} sample observed by FE-SEM. Furthermore, the content of conductive Csp2, oxygen, and electroactive carbonyl-quinone groups in GNR₀₁₅, results in a higher capacity and electroactive area.

To evaluate if the electrochemical response of the materials is only due to their electroactive area or there is also an improvement in charge transfer, amperometric experiments were performed using H₂O₂ as redox marker. A sensitive and fast amperometric response was obtained at -0.100 V for successive additions of 5.0×10^{-4} M H₂O₂. Fig. 2A shows the calibration plots for the different modified GCEs. The highest sensitivity was obtained for GCE/GNR₀₁₅, (0.85 ± 0.07) $\mu\text{A} \cdot \text{mM}^{-1}$. The sensitivity reaches a value 87 times higher than the one obtained for GCE/GNR₀₀₀, 3 times higher than the one obtained for GCE/GNR_{120-N2H4} and 4 times higher than the one obtained for GCE/GNR_{120-ER}, demonstrating the advantages of this sample on the reduction of H₂O₂. The extremely low activity observed for GCE/GNR₀₀₀ discards the presence of electrocatalytic metals on the starting material [15,16]. GCE/GNR₀₁₅ presents the best compromise between unzipped MWCNTs, C-sp2 and electrochemically active carbonyl/quinone groups, thus showing the best electrochemical performance.

For better comprehension of its electrochemical behavior, the system was evaluated by EIS (Fig. 2B). The model proposed considers that the surface consists of different regions, covered and uncovered, which can act in parallel. Electron transfer occurs on the covered regions as well as on the macroscopic uncovered zones. In the equivalent circuit (Fig. 2B) the electrolyte resistance (R_s) is in series with the charge transfer resistance (R_{ct}), which is in parallel with the double layer

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