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Press-transfer optically transparent electrodes fabricated from commercial single-walled carbon nanotubes

J. Garoz-Ruiz, S. Palmero, D. Ibañez, A. Heras, A. Colina *

Department of Chemistry, Universidad de Burgos, Pza. Misael Bañuelos s/n, E-09001 Burgos, Spain

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ABSTRACT

A simple method for the fabrication of optically transparent electrodes (OTE) from commercial single-walled carbon nanotubes (SWCNT) is presented. We disperse SWCNT in organic solvents, avoiding surfactants. Films obtained by filtering are transferred to non-conductive polymer substrates only by pressure, avoiding the chemical removing of the filter. The electro-optical properties of the electrodes have been studied and optimized using an experimental design strategy, concluding that both properties depend on the total mass of SWCNT transferred to the support. In general, well-interconnected SWCNT networks yield little differences in the electrochemical behavior. However, it has been observed that electrodes with a high mass of SWCNT produce significant changes in the voltammograms, obtaining unexpected ratios between the anodic and cathodic peak currents. SWCNT-OTE have been used to study the electropolymerization of aniline.

1. Introduction

SWCNT play an important role in electrochemistry because of their remarkable electrical properties [1–3], being used in very different applications [1–4]. SWCNT electrodes show important advantages with respect to other classical electrode materials [5–8]. For example, electrochromic properties of poly(3,4-ethylenedioxythiophene) and tungsten oxide films improve considerably when SWCNT films are used instead of Sn-doped In_2O_3 (ITO) as the transparent conductive layer [6]. In addition, SWCNT films exhibit a wider potential window than ITO and are more resistant to acids [5]. ITO conductivity is lower on polyethylene terephthalate than on glass and ITO cracks are observed after repeated bending or strain [5]. SWCNT have been demonstrated very useful in electrochemical measurements due to the large active electrode surface, the enhanced electron transfer or the electrocatalytic properties [7,8]. Particularly, SWCNT have extensively been used in electrochemical biosensing studies because biomolecules are easily integrated with SWCNT [9].

The fabrication of optically transparent SWCNT films has been achieved using different approaches [10–19]. In some cases, a transparent conductor is used as support [12], in other cases, non-conductor supports are used but SWCNT dispersions are prepared with a surfactant that has to be removed after the transference of the films to the support [15,16]. When the SWCNT film is transferred from a filter, it has to be dissolved by a chemical reaction and the film has to be washed to remove any degradation product [13–16]. Our group developed a press-transfer method using SWCNT collected directly from the CVD reactor [18]. The main challenge of our previous approach is that it is not usual to have a CVD reactor in the laboratory. Here, we have developed a methodology as simple as the previous one, but using commercial nanotubes.

Using the same type of filters that we used for the collection of SWCNT from the reactor, we were not capable of transferring the SWCNT films without chemical removing of the filter. Initially, we used surfactants to obtain good SWCNT dispersions that had to be removed after the transference to the support.

After trying very different approaches, we have developed a simple fabrication methodology using dispersions in organic solvents, avoiding surfactants. The proposed methodology allows us to transfer the films to non-conductive polymer substrates only by pressure. Next, the filter is mechanically removed, in a very simple way, by pulling it out using tweezers. In this work, we present a thorough description of the fabrication methodology and the optimization process performed with the aim of obtaining films with the best properties for spectroelectrochemical purposes.

2. Material and methods

2.1. Reagents

1,2-Dichloroethane, DCE, (Fluka), ferrocenemethanol, (Sigma-Aldrich), aniline (Sigma-Aldrich), H_2SO_4 (Acros Organics) and KCl (Merck) were used as received. All chemicals were analytical grade. Aqueous solutions were prepared using high-quality water (Milli-Q gradient A10 system, Millipore).

SWCNT (Sigma-Aldrich), 175 μm thick polyethylene terephthalate, PET, (HiFi Industrial Film), hydrophilic polytetrafluoroethylene (PTFE)

* Corresponding author. Tel.: +34 947258817; fax: +34 947258831.
E-mail address: acolina@ubu.es (A. Colina).

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filters, pore size 0.1 μm (JVWP01300, Millipore Omnipore), silver conductive paint (Electrolube) and epoxy protective overcoat (242-SB de ESL Europe) were used to produce the SWCNT-OTE.

2.2. Instrumentation

All electrochemical experiments were carried out at room temperature using a potentiostat/galvanostat CHI900 (CH Instruments). A standard three-electrode cell was used in all the experiments, consisting of a SWCNT-OTE as working electrode, a Au wire as auxiliary electrode and a homemade Ag/AgCl/KCl (3 M) as reference electrode.

Spectroelectrochemical setup has been previously described elsewhere [20].

Transmittance was measured using a S2000 spectrometer (Ocean Optics). The light beam, supplied by a halogen light source (HL-2000, Ocean Optics), was conducted to and collected from the spectroscopic cell qpod2e (Quantum Northwest) by 200 μm optical fibers (Ocean Optics).

SWCNT solutions were dispersed using a CY-500 ultrasonic generator (Optic ivymen System). For safety considerations, all handling and processing were performed carefully, particularly when DCE is used.

2.3. Electrodes fabrication

In this work we have fabricated electrodes using nanotubes from different manufacturers. As a proof of concept, we have selected SWCNT from Sigma-Aldrich to show our methodology but it has been successfully used with other types of SWCNT, and even with modified carbon nanotubes. We neither add any surfactant nor functionalize the SWCNT in the dispersion to produce the SWCNT-OTE, that is to say, we do not modify the SWCNT prior to the fabrication. Our methodology takes place in six consecutive steps: (1) we disperse 1.5 mg of SWCNT in 100 mL of DCE, as stock solution, being the homogenization a fundamental step. In order to obtain homogeneous films we use a tip-sonicator using a power of 250 W for 15 min; then we reduce the power to 100 W and the dispersion is sonicated again for 15 min. (2) We prepare dispersions of different SWCNT concentrations from the stock dispersion. Each one was homogenized again for 15 min at 100 W. (3) Once we obtain a good dispersion, without any SWCNT agglomeration, the desired volume of the dispersion is filtered under vacuum using a hydrophilic PTFE filter. Next, the film is dried at room temperature for 5 min. It is noteworthy that for a good transfer, filters should not be in contact with the air for more than 10 min. From our experience, interaction between SWCNT and PTFE is dependent on time, implying a bad transfer for longer times. (4) Using a laboratory hydraulic press, carbon nanotubes collected on the filter was transferred by pressure to a sheet of PET applying 20 ± 1 tons for 60 s. A much lower pressure was enough to transfer the film but we use 20 tons to ensure always a good transference. PET sheets have been previously washed with deionised water and dried. The separation of the filter is performed slowly and carefully pulling it out with tweezers so that the transfer of the SWCNT to the polymeric support provides a very homogeneous film with an area of 3.14 cm^2. (5) Electrical contacts were made using conductive silver paint, creating a small line from the origin of the SWCNT to the end of PET. The silver paint is dried in an oven at 75 °C for 45 min. (6) After further cooling, conductive silver paint is tested and it is electrically isolated using insulating paint. Finally, the electrode is inserted into the oven at 75 °C for 120 min.

3. Results and discussion

Our first experiments demonstrated that SWCNT film could be transferred to PET supports with very high reproducibility using commercial SWCNT. Concentration and volume filtered of SWCNT dispersions were the two factors studied to obtain more information about the electro-optical properties of the electrodes and to produce optimal OTEs. SWCNT concentration is important because of the difficulty in obtaining highly homogeneous solutions. The study of the volume filtered is also important to understand whether it influences on the homogeneity of the films and, therefore, on the electro-optical properties of the film.

Transparency and conductivity of the electrodes depend on the SWCNT concentration and the volume filtered. Therefore, it is essential to optimize these parameters to produce highly conductive electrodes with maximum transparency to be used as OTE in spectroelectrochemistry.

Optical transparency of the electrode was evaluated by measuring transmittance at 550 nm. Evaluation of the conductivity of the SWCNT-OTE was performed by measuring the voltammetric reversibility of a redox couple with a high standard rate constant, taking into account that the electrodes will be used for spectroelectrochemistry. In our case we have selected ferrocenemethanol, measuring the difference of potential between the anodic and cathodic peak (ΔEp) from cyclic voltammograms. Potential was scanned between -0.20 and $+0.60$ V at 0.01 Vs^{-1} in a 0.60 mM ferrocenemethanol and 0.10 M KCl solution. Charge transfer rate does not depend on the redox pair but on the electrical resistance of the electrode that makes the electrochemical process slow.

Fabrication of the electrodes is relatively costly from the experimental point of view, thus, it is very important to optimize the resources. For this reason a strategy of experimental design was used to optimize both volume filtered and SWCNT concentration in only 11 experiments. We performed a design consisting of a central two-level factorial plus additional star points used to model curvature with respect to each factor. The concentration range was limited to 0.0025–0.0130 mg/mL and the volume filtered was limited to 0.75–3.00 mL.

Analysis of the design indicated that the two factors, SWCNT concentration and volume filtered, and their interactions were significant. Fig. 1A shows the two superimposed response surfaces obtained for the two variables that provide the optimum concentration and volume filtered. The best conductivity is obtained at the higher values of the factors and the best transparency at the lower values of the factors, as could be expected. As the response changes in the diagonal of the experimental space, we can conclude that the total mass of SWCNT transferred to the electrode is the most influential factor on the responses.

Fig. 1B shows the logarithmic relationship of the transmittance with respect to the mass of SWCNT. A linear relationship of absorbance *vs.* mass of SWCNT is obtained, indicating that we can control the electrode transparency. When the mass of nanotubes is less than 0.03 mg of SWCNT, the relationship is perfectly linear ($R^2 = 0.996$), which leads us to conclude that very high concentrations and volumes filtered do not provide acceptable optical results.

Fig. 1B also shows ΔEp *vs.* the mass of SWCNT. As can be seen, the percolation effect is observed. When a good SWCNT network is formed, ΔEp is substantially constant. Mass values lower than 0.0022 mg of SWCNT electrodes leads to worse electrical properties, as can be deduced from the significant high value of ΔEp.

Although good electrical results should be expected when large amounts of nanotubes are used, an unexpected behavior is obtained. In principle, transmittance and ΔEp seem to be sufficient to explain the behavior of these electrodes, but voltammetric responses contain much more information. Fig. 1C shows the voltammograms of ferrocenemethanol registered using two electrodes prepared with different SWCNT mass. As can be seen, the ratio between the intensity of the anodic and cathodic peaks (ip_{ox}/ip_{red}) does not show the expected value for ferrocenemethanol ($ip_{ox}/ip_{red} = 1$) in the experiment with high mass of nanotubes, presenting an ideal behavior at low mass of SWNCT.

To evaluate the influence of the mass of SWCNT on ip_{ox}/ip_{red}, a concentration of 0.005 mg/mL of SWCNT was fixed and the volume