Electrochemistry Communications 48 (2014) 69–72

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

1,3-Dioxolane: A green solvent for the preparation of carbon nanotube-modified electrodes

R. Moscoso [a], J. Carbajo [b], J.A. Squella [a,*]

[a] Laboratorio de Bioelectroquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile
[b] Departamento de Ingeniería Química, Química Física y Química Orgánica, Facultad de Ciencias Experimentales, Universidad de Huelva, Huelva, Spain

ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 19 August 2014
Accepted 19 August 2014
Available online 27 August 2014

Keywords:
MWCNT
MWCNT dispersion
1,3-Dioxolane
Modified electrode

ABSTRACT

One of the main challenges associated with the handling of carbon nanotubes (CNTs) for modifying electrodes is the production of adequate dispersions. We report the first example in which 1,3-dioxolane was used to produce dispersions of multiwalled carbon nanotubes (MWCNTs) to modify glassy carbon electrodes (GCE). The films of MWCNTs obtained after evaporation were characterised by scanning electron microscopy (SEM) and adsorptive stripping voltammetry (ASV). 1,3-Dioxolane, a green solvent that is nontoxic, odourless and environmentally friendly, produces nanotube dispersions that leaves no residue on the resulting electrode when it evaporates.

1. Introduction

In electroanalysis and many other fields, one of the main problems encountered when handling carbon nanotubes (CNTs) is the CNTs low capacity to form dispersions. Consequently, many investigations have been focused to resolve this issue. There are several approaches to improving the handling of nanotubes by the introduction of functional groups on the walls of CNTs or the attachment of molecules that give the nanotubes a hydrophilic character, making them compatible with certain solvents [1–12].

The methods for functionalising CNTs are divided into three main types [13,14]: covalent bonding [15–18],physical adsorption to the surface [19,20] and miscellaneous methods in which CNTs are incorporated into modified films [21–24].

However, these methods lack the ability to control the degree of functionalisation [25–27], are incapable of generating reproducible surfaces in the modification of electrodes, involve tedious procedures, are very time-consuming and involve reactions that are destructive to the structure of CNTs.

The most frequently used method for easily and quickly preparing modified electrodes consists of placing microlitres of a suspension of CNTs on a glassy carbon electrode (GCE) and then evaporating the solvent. However, this method depends on the ability of the solvent to disperse CNTs to obtain a reproducible aliquot to deposit on the GCE. Therefore, in the process of developing a modified electrode, the dispersion of CNTs is a key factor because of its effect on the amount of CNTs that are deposited on a GCE, on the homogeneity of the CNT films that are obtained and consequently on the reproducibility of the resulting electrodes.

The literature [12] reveals many solvents, dispersants and surfactants that are used to modify single-and multi-walled CNTs (SWCNTs and MWCNTs, respectively), such as H_2O, EtOH, DMSO, CH_3CN, $CHCl_3$, THF, toluene, 1,2-dichlorobenzene (o-DCB), 1-methylnaphthalene, *N,N*-dimethylformamide (DMF). Practical requirements for a suitable dispersing agent for preparing modified electrodes include rapid evaporation and nontoxicity due to the release of the solvent to the environment in the drying stage. As the solvents found in the literature do not simultaneously possess these characteristics, we were motivated to study 1,3-dioxolane as a new solvent for dispersing CNT.

1,3-Dioxolane is nontoxic, odourless, easy to evaporate and environmentally friendly. There are no publications concerning the use of 1,3-dioxolane as a dispersing agent for CNTs; in fact, the majority of publications have only mentioned the use of 1,3-dioxolane as a solvent for the preparation of batteries and capacitors. The studies described are based on the use of surfactants or long-term processes of covalent modification to form good dispersions [8,28–33].

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were carried out in a conventional three-electrode cell. Voltammetric curves were recorded on a CHI 900 (CH Instruments Inc., USA) instrument. We used a GCE measuring 3 mm in diameter (Model CHI104, CH Instruments) as the working

* Corresponding author.
E-mail address: asquella@ciq.uchile.cl (J.A. Squella).

http://dx.doi.org/10.1016/j.elecom.2014.08.019
1388-2481/

electrode. A platinum wire (BASiMW-1032) and an Ag/AgCl/NaCl electrode (0.3 M) (BASi MF-2052) were used as the auxiliary and reference electrodes, respectively. All potentials are referred to the Ag/AgCl reference electrode.

MWCNTs not oxidised (1.5 μm in length and 10 nm in diameter) were obtained from Dropsens S.L., Spain. The CNTs were used without further modification.

All voltammetric experiments were performed after bubbling N_2 into the test cell for 10 min before each run. The temperature was held constant at 25 ± 0.1 °C.

We used a 0.1 M Britton-Robinson buffer, pH 2, as the aqueous medium.

Nitrendipine, >95% (NTD) (*RS*)-ethyl-methyl-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate was obtained from SIGMA ALDRICH.CAS 39562-70-4.

All other reagents were of analytical grade.

Stock solutions of NTD were prepared at a constant concentration of 2×10^{-2} M in ethanol. The working solutions were prepared by diluting the stock solution with 0.1 M Britton–Robinson buffer, pH 2, to obtain solutions with a final concentration of 0.05 mM NTD.

2.2. Preparation of MWCNT suspensions and modified GCEs

Before each modification, the GCE was cleaned by polishing with 0.3 μm and 0.05 μm alumina and then was washed thoroughly with water. The MWCNTs were dispersed in a solvent by sonicating for 5 min. The sonication procedure was repeated three times. The MWCNTs were immobilised by casting 5 μl of the MWCNT dispersion on the GCE. Then the modified electrodes were obtained by drying the dispersion depending on the solvent.

To evaluate the effect of the solvent on the dispersions, we tested polar and apolar solvents including: water (H_2O), 1,2-dichlorobenzene (o-DCB), 1,2-dichlorobenzene-ethanol (o-DCB/ethanol, 1:1), 2-methyl tetrahydrofuran (MeTHF), N,N-dimetilformamide (DMF) and 1,3-dioxolane.

2.3. Adsorptive stripping voltammetry

The voltammetric determination of NTD was carried out after the accumulation of NTD on the GCE modified with MWCNTs (CNTGCE) with agitation at 250 rpm in a 0.1 M buffer Britton–Robinson, pH 2, solution containing 0.05 mM NTD. The optimum accumulation time was 4 min, and no potential was applied during this step, yielding the modified electrode NTD-CNTGCE. After NTD was adsorbed on the modified electrode, the potential was scanned between −0.1 V and −0.5 V vs. Ag/AgCl to register the voltammetric curve.

2.4. Scanning electron microscopy (SEM)

For SEM measurements, glassy carbon discs (TED Pella brand, INC (N 16524)) measuring 12.7 mm in diameter were used. The discs were previously polished with suspensions of alumina particles measuring 0.05 and 0.1 mm in diameter. The morphology of the modified electrode was investigated by SEM using an Inspect Scanning Electron Microscope F-50 operated at 20 kV.

3. Results and discussion

The dispersant used to prepare the modified electrode was evaluated by adsorptive stripping linear voltammetry using the well-known 4-electron, 4-proton reduction [34] of the nitro aromatic drug NTD to form the corresponding hydroxylamine derivative. Fig. 1A shows the voltammetric signal of the reduction of 0.05 mM NTD in Britton–Robinson buffer, pH 2, on modified electrodes using different dispersants. All of the dispersants produced adequate voltammetric signals, but that obtained using 1,3-dioxolane demonstrated the highest limiting current.

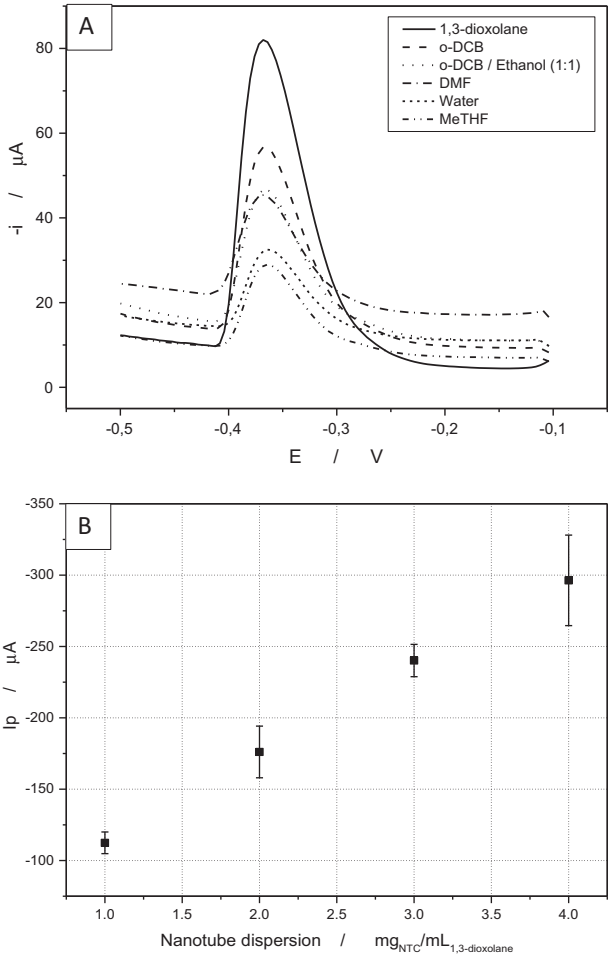

Fig. 1. A) Reduction peak obtained from a voltammogram of 0.05 mM NTD in buffer Britton–Robinson, pH 2, on modified electrodes fabricated using different MWCNT dispersions. B) Peak currents obtained from a voltammogram of 0.05 mM NTD in buffer Britton–Robinson, pH 2, on modified electrodes fabricated using different concentrations of MWCNT dispersions in 1,3-dioxolane. We used eight electrodes for each concentration.

To verify the voltammetric behaviour of each of the above mentioned dispersants, we obtained calibration curves for the analysis of NTD with modified electrodes. In all cases, we obtained linear relations between the peak current of the nitro group reduction and the NTD concentrations. Table 1 presents the analytical parameters obtained with the electrodes produced with different dispersing agents.

Using the voltammetric response for 0.05 mM nitrendipine in Britton–Robinson buffer, pH 2, we also studied the effect of the CNT concentration in the dispersion with 1,3-dioxolane. We used concentrations ranging between 1 and 4 mg of MWCNTs per ml of 1,3-dioxolane. The optimal dispersion was obtained at 3 mg/ml. Dispersions higher than 3 mg/ml produced little homogeneous dispersions generating a

Table 1
Analytical parameters obtained with electrodes produced with different dispersing agents.

Dispersant	CV (%)	Detection limit (LOD) (μM)	Quantification limit (LOQ) (μM)
H_2O	5.18	0.070	0.235
MeTHF	6.14	0.083	0.278
1,2-DiChlobz.	4.43	0.008	0.028
DMF	4.89	0.053	0.201
1,2-DiChlobz/EtOH (1:1)	4.21	0.127	0.426
1,3-Dioxolane.	3.81	0.012	0.039

loss of the homogeneity of the CNT films that are obtained and consequently on the reproducibility of the resulting electrodes (Fig. 1B).

Another very important factor affecting the electrochemical signal in this type of reaction is the accumulation time. The accumulation time corresponds to the period during which a modified electrode remains immersed in solution, with agitation, without any applied potential and before the voltammetric run is performed. During this period, the MWCNTs act as an adsorbent for the electroactive compound, allowing for its encapsulation. We selected an optimal accumulation time of 4 min, corresponding to 75% of the current obtained between 8 and 10 min of accumulation.

Fig. 2A shows SEM image of the naked GCE and Fig. 2B displays an SEM image of the GCE modified with the MWCNT–1,3-dioxolane dispersion at 50,000 × magnification. The image reveals that MWCNTs were well distributed on the electrode surface. The MWCNTs were very well packed, with randomly aligned tubes, which formed pockets of surfaces under various conditions. The NTD was encapsulated in these pockets, allowing for its accumulation and thus yielding the voltammetric signal.

The MWCNT dispersions in 1,3-dioxolane allow us to fabricate electrodes that, unlike those prepared with dispersions formed in water or other dispersants, can be submitted to a washing process without losing the layer of nanotubes deposited on the modified electrode surface. This feature allows for the reuse of the same electrode for different measurements and for the removal of compounds from the electrode surface without losing the surface's nanostructure. Moreover, this procedure eliminates the need to prepare an electrode for each measurement, thus eliminating the risk of obtaining different active surfaces between electrodes. Electrode regeneration can be achieved as follows: 1. The electrode is washed with 1 ml of DMF; 2. Then, the electrode is washed with 1 ml of acetonitrile to remove the DMF; 3. The electrode is then washed with 1 ml of ethanol. 4. Finally, the electrode is flushed with Britton–Robinson buffer. The electrode is immersed in each solvent for approximately 10 s with agitation. After this procedure, the electrode can be used again without the CNTs peeling off of the GCE, as is often the case with electrodes prepared with aqueous CNT dispersions. This methodology allows for the same electrode to be used many times. Indeed, we obtained a coefficient of variation of 4.5% for the reproducibility of seven consecutive measurements after performing the regeneration procedure.

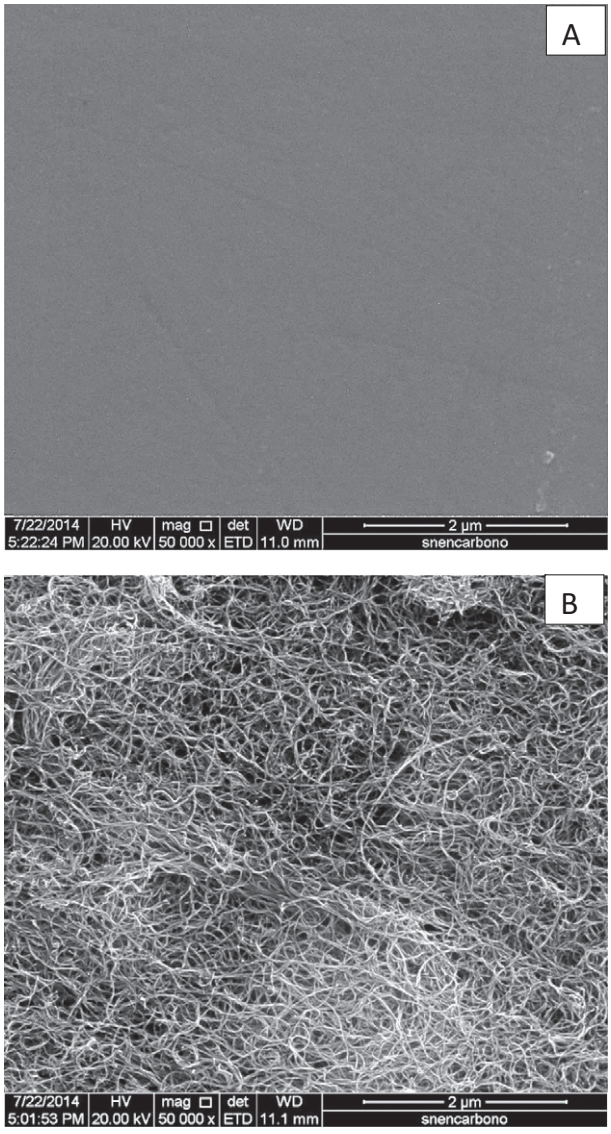

Fig. 2. SEM image obtained for a naked GCE (A) and with MWCNTs dispersed in 1,3-dioxolane on a GCE (B). Magnification: 50,000 ×.

4. Conclusions

1,3-Dioxolane presents multiple comparative advantages over other dispersants in the preparation of modified electrodes. 1,3-Dioxolane nanotube dispersions support an adequate amount of nanotubes. The electrodes formed thereof are easy to prepare because the dispersions dry rapidly on the electrode, without requiring the use of a drying oven. Moreover, MWCNTs exhibit improved adhesion to the electrodes, allowing an electrode to be reused after following a specified washing procedure.

From the perspective of green chemistry, 1,3-dioxolane can be considered a green solvent because it is nontoxic, odourless, and environmentally friendly. 1,3-Dioxolane produces nanotube dispersions that leave no residue on electrodes when it evaporates (unlike surfactants such as Nafion or SDS).

Acknowledgements

The authors are grateful to FONDECYT (grant no. 1130160) for their support of this work.

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