



Electrocatalytic activity of multiwalled carbon nanotubes decorated by silver nanoparticles for the detection of halothane



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ABSTRACT

Commercially available multiwalled carbon nanotubes (CNTs) were decorated by size-controlled and stable silver nanoparticles (NPs) using a sol immobilisation technique. Silver nanoparticles were in some cases protected by polyvinyl-alcohol (PVA). These materials were used to prepare different glassy carbon modified electrodes, which were tested in the electrochemical reduction of the anaesthetic halothane in two different solvents: water and acetonitrile. A different behaviour in the two different solvents is observed: silver nanoparticles are essential for the electrocatalytic activity in water while CNT are useless; in acetonitrile silver and CNT present a similar catalytic behaviour. The best modified electrode was used for the electroanalytical detection of anaesthetic halothane in both solvents. The use of PVA protective polymer for silver NPs allows better electroanalytical performances due to the protection from oxidation, fouling products and interferents.

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1. Introduction

Since their discovery [1,2], carbon nanotubes (CNT) provided an interesting tool for researchers in many scientific and technological fields. From 2002, thanks to the work of Wang group [3], these compounds started to be used in electroanalysis because of their important peculiar properties. In particular, they permit the obtaining of low detection limits and enhanced sensitivities and they are resistant to surface fouling and passivation. Moreover, they often present some electrocatalytic properties towards certain analytes, which can provide an useful instrument also for enhancing selectivity.

Although the research in this field has greatly developed in the last decade by the work of many authoritative Groups in the world [4–11], the reasons of these important properties are still to be clarified [12]. In particular, the electrocatalytic performances of CNTs have to be searched in one or more of the following characteristics, also considering a possible cooperative effect: presence of edge-plane defects [13,14]; presence of metallic impurities (particularly iron) from the synthetic route, which are hardly eliminated by acid washing [5]; presence of carbonaceous impurities [15] or oxygen-containing groups [16]. Furthermore, also a possible change in the

diffusion mechanism from semi-infinite to thin-layer has also to be taken into account [17,18].

In 2006, Compton and co-workers demonstrated the electrocatalytic activity of multiwalled carbon nanotubes (MWCNT) in the reduction of the anaesthetic halothane as due to the presence of very low (0.1%) concentration of occluded copper nanoparticles [19]. The catalytic activity of copper and other metals towards halothane reduction is a certainty, as it is a certainty that silver behaves even better yielding to lower reduction potentials [20–22], although it presents some problems related particularly to its oxidizability.

In this context, the present research has focused the attention on the use of modified electrodes for the electrochemical reduction of anaesthetic halothane in two solvents (water and acetonitrile), with the aim of obtaining better results in terms of electrocatalytic effects and electroanalytical features (higher sensitivity, lower detection limits, better precision and accuracy). The electrodes were prepared by drop casting of previously prepared MWCNT decorated with silver nanoparticles (AgNPs). The materials were prepared in order to improve metal dispersion and stability. Therefore, we used the sol immobilisation technique which is known to provide a controlled size of metal nanoparticles and an improved stability and dispersion of them on a support during catalytic tests. The use of polymer protected AgNPs due to the presence of polyvinyl-alcohol (PVA) has also been evaluated.

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2. Experimental

2.1. Synthesis of AgNP decorated MWCNT

2.1.1. Sol immobilisation: Ag_{PVA}/CNTs catalyst preparation

Solid AgNO₃ (Ag: 0.047 mmol) and PVA (Ag/PVA = 1:1 wt/wt) solution were added to 50 ml of H₂O. After 3 min, 0.1 M NaBH₄ (Ag/NaBH₄ = 1:4 mol/mol) solution was added to the solution under vigorous magnetic stirring. A Ag(0) sol was immediately formed. Within few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilized by adding the support under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1 or 5 wt% (on the basis of quantitative loading of the metal on the support). The catalysts were filtered, washed on the filter and dried at 80 °C for 4 h.

2.1.2. Impregnation: Ag_{imp}/CNTs catalyst preparation:

Solid AgNO₃ (Ag: 0.047 mmol) were added to 50 ml of H₂O. After 5 min, the support has been added to the solution. After 4 h AgNO₃ was quantitative impregnated on the support. The solid has been filtered, washed and redispersed in 50 ml of water. After 3 min, 0.1 M NaBH₄ (Ag/NaBH₄ = 1:4 mol/mol) solution was added to the solution under vigorous magnetic stirring. The amount of support was calculated in order to obtain a final metal loading of 1 or 5 wt% (on the basis of quantitative loading of the metal on the support). The catalysts were filtered, washed on the filter and dried at 80 °C for 4 h.

2.2. Modified electrode preparation

For glassy carbon electrode modification, different dispersions of CNT-AgNP were prepared in dimethylformamide (DMF, the most suitable dispersing solvent according to [23]) in a concentration of 0.5 mg/mL. The dispersion was sonicated for 15 min and a single 20 µL drop was deposited on the surface of a glassy carbon (GC) electrode and finally dried at room temperature for 24 h before use.

A Kartell automatic pipette (2–20 µL range) was used for the drop-casting procedure.

The following five different modified electrodes were prepared:

- CNT: as received MWCNT from Baytubes[®], not treated.
- Ag_{imp}1%.CNT and Ag_{PVA}1%.CNT.
- Ag_{imp}5%.CNT and Ag_{PVA}5%.CNT.

2.3. Materials and methods

AgNO₃ of purity >99%, NaBH₄ of purity >96%, polyvinylalcohol (PVA) 87–89% hydrolysed (M.W. 13,000–23,000) from Aldrich were used. Commercial Baytubes[®] multiwalled carbon nanotubes, supplied from Bayer, have an average diameter of 10 ± 2 nm, a specific surface area of 288 m²/g and a micropore area of 40 m²/g [24]. These CNTs are also characterized by presenting some inorganic impurities, namely Co (0.78%), Mn (0.75%), Al (0.49%) and Mg (0.56%) [24]. Dimethylformamide (DMF, >99.5%) and acetonitrile (ACN, ≥99.9%) were from Fluka, Switzerland. Sodium hydroxide (>98%) and tetrabutylammonium perchlorate (≥99%, Sigma–Aldrich, Germany) were used as supporting electrolytes for water and acetonitrile, respectively. Halothane (≥99%) was purchased by Sigma–Aldrich, Germany. All reagents were used as received without further purification.

In the case of subsequent addition measurements by linear sweep voltammetry (LSV), a 0.1 M solution of halothane was prepared in acetonitrile, while, for additions in water a 0.1 M aqueous methanol solution of halothane was used.

Millipore milli-Q water (18 MΩ cm⁻¹) was used for the preparation of all the solutions and all the measurements were performed in a closed cell after careful degassing with nitrogen.

The electrochemical analyses were performed in a three electrode standard cell, using the glassy carbon GC (0.071 cm², Amel, Italy) modified electrode as working electrode, a saturated calomel electrode (SCE, Amel, Italy), as reference electrode and a platinum wire as counter electrode.

Voltammograms were registered using an Autolab PG-Stat 30 (EcoChemie B.V., The Netherlands) potentiostat/galvanostat, equipped with GPES (General Purpose Electrochemical System) software, version 4.9.

Cyclic and Linear Sweep Voltammograms were registered in the cathodic range at a scan rate of 0.2 V s⁻¹ with equilibration time of 5 s and a step potential of 5 mV.

The metal content was checked by ICP analysis of the filtrate or, alternatively, directly on the catalyst after the carbon was burned off, using a Jobin Yvon JY24 instrument. Morphology of the catalysts was characterized in a Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan imaging filter, GIF Tridiem.

UV–visible spectra of sols were performed on HP8452 and HP8453 Hewlett–Packard spectrophotometers in H₂O between 190 and 1200 nm, in a quartz cuvette.

3. Results and discussion

3.1. Characterization of AgNPs–CNTs

UV–vis characterization was performed on Ag colloid before immobilisation, confirming Ag reduction and the generation of Ag nanoparticles. All the catalysts have been investigated by TEM. Ag particles size is almost the same in all samples prepared by impregnation or sol immobilisation with a mean particle sizes ranging from 3.3 to 3.9 nm (Table 1). TEM image and particle distribution of Ag_{PVA}1%.CNT was reported as example (Fig. 1a). In all cases the dispersion of metal nanoparticles on the tubes is not completely homogeneous, and CNTs were found without metal nanoparticles. As this parameter could have an impact on the electrocatalytic properties of the materials, further studies needed to improve the metallic dispersion.

3.2. Electrocatalytic reduction of halothane

All the modified electrodes were tested in the electrochemical reduction of the anaesthetic halothane in the concentration range 10⁻³ to 10⁻² M, in two different solvents: water and acetonitrile with 0.1 M NaOH or 0.1 M TBAP as the supporting electrolytes, respectively. First of all, in acetonitrile, the use of the Ag–CNT modified electrodes permits to slightly widen the cathodic windows passing from the range 0/–2.5 and 0/–2.9 V (SCE) in the case of silver and GC, respectively, to the range 0/–3 V (SCE) for all the CNT modified electrodes, in presence or absence of silver.

The voltammetric patterns related to halothane reduction, shown in Fig. 1, are different for the two solvents.

In acetonitrile (Fig. 2A), all the CNTs and Ag–CNTs modified electrodes present an electrocatalytic well defined peak at ca. –1.55 V

Table 1
Statistical median and standard deviation of particle size analysis for Ag catalysts.

Catalyst	Statistical median (nm)	Standard deviations
Ag _{imp} 1%.CNT	3.5	1.0
Ag _{imp} 5%.CNT	3.9	1.4
Ag _{PVA} 1%.CNT	3.3	0.8
Ag _{PVA} 5%.CNT	3.6	1.1

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