

SENSORS BASED ON MULTI-WALLED CARBON NANOTUBES

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Abstract

Sensors based on multi-walled carbon nanotubes (MWCNTs) were produced on oxidized silicon substrate by means of chemical vapor deposition (CVD) technique using as carbon source either acetonitrile (ACN) or benzene (BZ) and their electrochemical response towards simultaneous oxidation of ascorbic acid (AA) and uric acid (UA) was investigated. The MWCNT-ACN film exhibits high sensitivity and fast electrochemical response towards AA and UA while the electro-catalytic ability of MWCNT-BZ film towards the investigated redox systems is limited. The enhanced electrochemical performance of MWCNT-ACN film can be probably attributed to the unique structure and the improved electrochemical properties of the nanotubes of this particular film that are strongly related to their high nitrogen doping level.

1 Introduction

Biosensors based on nanomaterials have received considerable attention the last years since they are extremely reactive, sensitive, selective, and permit the rapid and accurate in-vitro analysis of biomolecules. In the medical diagnostics area, nanotechnology-based biosensors can be used to replace more costly and tedious laboratory methods for monitoring the blood of patients for proteins, chemicals, and pathogens [1]. Among other numerous applications, multi-walled carbon nanotubes (MWCNTs) were widely used as electrode materials in sensing technology since they exhibit many desirable effects, specifically they have high electrochemically accessible area, high electrical conductivity, and useful mechanical properties. Furthermore, it was recognized that MWCNTs improve the electro-catalytic properties and decrease the over-potential of electro-active substances, and therefore amplify the reaction rate, the sensitivity, the stability, and the reproducibility of sensors response. Consequently, advanced electrochemical techniques in conjunction with micro electrodes consisting of MWCNTs were extensively used in biological studies for analysis of compounds of great importance [2].

Our research activities were involved currently in the development of MWCNT-based sensors and in their application for the electrochemical analysis of electro-active compounds [3-6]. In the present article we extend our research interest into application of MWCNT-based sensors for the electrochemical determination of biomolecules. Specifically, the aim of the present research work is the investigation of the electrochemical response of novel MWCNT-based sensors towards the simultaneous oxidation of ascorbic acid (AA) and uric acid (UA). For the electrochemical studies the cyclic voltammetry (CV), differential pulse voltammetry (DPV),

and electrochemical impedance spectroscopy (EIS) techniques were applied. The findings are very promising and reveal that a rapid and sensitive MWCNT-based biosensor for the simultaneous analytical determination of UA and AA was produced [7].

2 Materials and testing methods

2.1 Materials

L(+)-Ascorbic acid (99.7 %) and uric acid (≥ 98 %) were purchased from Merck and Fluka, respectively, and were used as received without any further purification. All measurements were carried out by using phosphate buffer (pH=7). The aqueous buffer solutions were prepared immediately prior the electrochemical experiments by using double-distilled water.

2.2 Apparatus and procedures

CV, DPV, and EIS curves were recorded using a computer-controlled system Zahner/IM6/6EX and analyzed by means of Thales software (version 4.15). The measurements were carried out using a three-electrode cell configuration. The working electrode used was MWCNT-based film and the counter electrode was Pt plate. All potentials were recorded relative to Ag/AgCl (KCl sat.) reference electrode. A three-compartment electrochemical cell designed to minimize the distances between the electrodes with a total volume of 20 ml was used for all measurements. Before each measurement the measured solution was purged with high purity argon to eliminate interference from dissolved oxygen. All measurements were carried out at the room temperature (21°C).

Scanning electron micrographs (SEM) of MWCNT-based films were obtained on FEI/Philips (model XL30 ESEM) computer-controlled scanning electron microscope with an accelerating voltage of 10 kV, while transmission electron micrographs (TEM) were recorded on TECNAI/Philips (model 20 S-TWIN) transmission electron microscope.

2.3 Production of MWCNT-based films

Vertically aligned MWCNTs (outer diameter ~ 50 nm) were selectively synthesized on oxidized porous silicon wafer in a furnace at 900°C by means of chemical vapor deposition (CVD) technique using ferrocene (FeCp_2) as catalyst and ACN and BZ as carbon source. The silicon wafer (1.0 cm²) had thickness of 525 (± 25) μm and it was fully covered with a SiO_2 -coating of about 1.7 μm thickness. The FeCp_2 solution (1% w/w) was introduced to the furnace through a syringe with a flow rate of 0.2 ml·min⁻¹. The synthesis process was performed using argon as carrier gas. In order to construct the MWCNT-working electrode for the electrochemical measurements, the MWCNT-based film produced by means of CVD technique was connected to platinum wire by using silver conducting coating. Once the silver coating was dried (after 24 hours), the silver conducting part of the electrode was fully covered with varnish protective coating. The scheme of CVD apparatus and experimental details concerning the method that was followed are reported in previous published article [8].

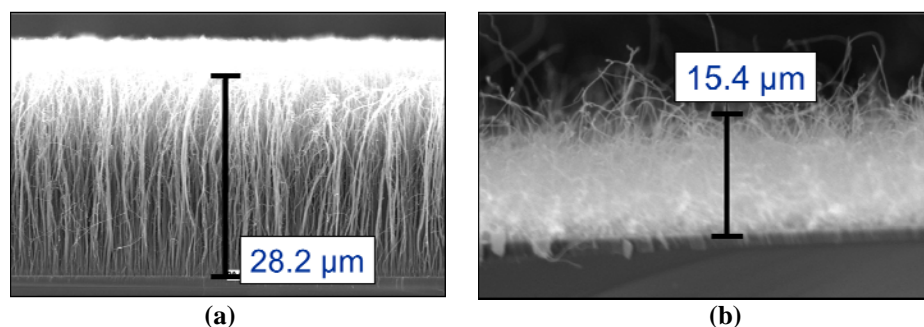


Figure 1. SEM micrographs of MWCNT-ACN (a) and MWCNT-BZ (b) films.

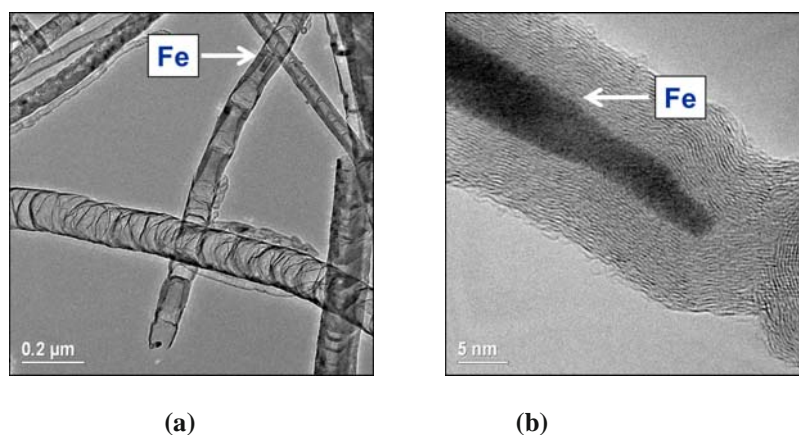


Figure 2. TEM micrographs of MWCNT-ACN (a) and MWCNT-BZ (b) films.

3 Results and discussion

3.1 SEM and TEM analysis

The surfaces of the synthesized MWCNT-based films were characterized by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Representative SEM and TEM micrographs are shown in Figures 1 and 2. The low magnification SEM images demonstrate the uniformity of the surface of both MWCNT-based films. Furthermore, high magnification SEM images reveal that the packing organization, and thus, the degree of arrangement of aligned MWCNTs are modified by varying the carbon source material. Namely, the SEM images reveal that when ACN is used as carbon precursor the packing organization of aligned MWCNTs is rather enhanced (Figure 1a), while the MWCNTs arrangement becomes quite worse, when BZ is used as carbon source material (Figure 1b). This observation can be attributed to structure differences of the synthesized MWCNTs, namely according to the obtained TEM images, MWCNT-ACN have the so-called bamboo-shaped structure (Figure 2a). Specifically, the TEM images demonstrate that without any doubt MWCNT-ACN are bamboo-shaped and N-doped and therefore they are less tangled compared to MWCNT-BZ, which seems to be rather knotted (Figure 2b) [8-10].

3.2 Electrochemical studies on MWCNT-based films

The oxidation of AA and UA was probed on MWCNT-BZ and MWCNT-ACN films. The findings reveal that the MWCNT-ACN film exhibits excellent electrochemical response towards UA and AA and consequently it can be considered as rapid biosensor for their simultaneous analytical determination. In contrast to MWCNT-ACN, the MWCNT-BZ film reveals limited electrochemical response towards UA and AA. The better response of MWCNT-ACN can be explained with the drop of overpotential of AA that occurs at this particular electrode. Namely, on MWCNT-ACN the overpotential of AA decreases for about 450 mV from that required on traditional electrodes (Figure 3a). The benefit of the decrease of overpotential of AA on MWCNT-ACN is very important, since it leads to great separation between the electrochemical waves of AA and UA and permits, thus, the determination of one substance in the presence of the other. As it can be clearly seen in the CV curve shown in Figure 3b the oxidation of UA occurs at a potential of about 450 mV more anodic compared to that of AA resulting to a noticeable separation of the oxidation waves of the investigated biomolecules [7].

Electrochemical experiments for various AA/UA binary mixtures reveal that AA and UA can be simultaneously detected at MWCNT-ACN even if one substance is in excess. As it can be

seen in representative CVs shown in Figure 4a, independently on their concentration ratios, the oxidation of AA on MWCNT-ACN is not influenced by the presence of UA and likewise the oxidation of UA is not influenced by the presence of AA. Consequently, it can be suggested that AA and UA can be simultaneously analyzed on MWCNT-ACN. It is amazing that very low detection limits were determined for MWCNT-ACN towards AA (0.97 μM) and UA (0.54 μM) [7].

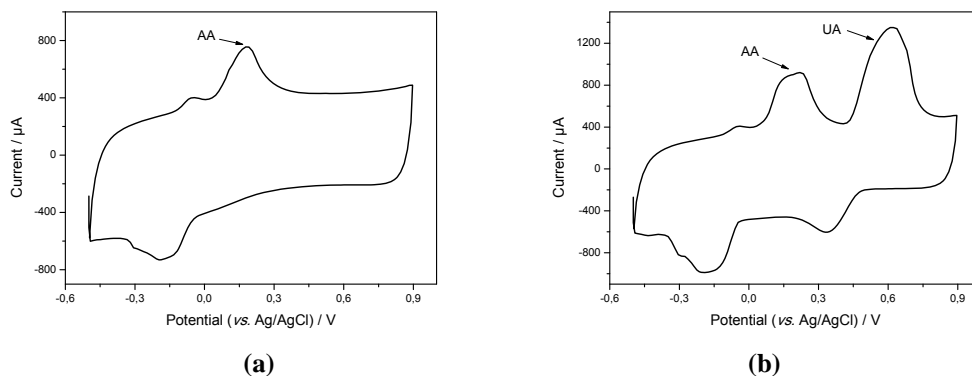


Figure 3. CVs recorded for AA (a) and AA/UA (1:1) mixture (b) on MWCNT-ACN.

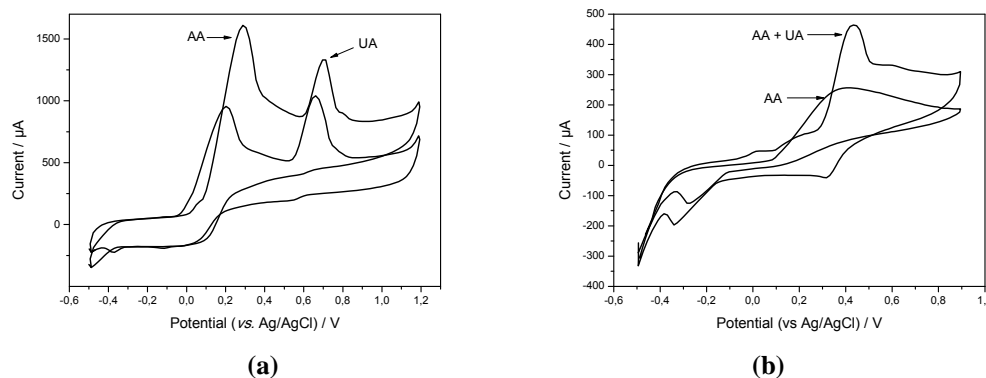


Figure 4. (a) CVs recorded for AA/UA (10:1 and 20:1) mixtures on MWCNT-ACN; (b) CVs recorded for AA and AA/UA (1:1) mixture on MWCNT-BZ.

In contrast to the promising findings obtained on MWCNT-ACN film totally different electrochemistry results were attained on MWCNT-BZ film. Namely, the oxidation of AA on MWCNT-BZ film occurs at a potential that is about 264 mV more anodic compared to that measured on MWCNT-ACN film (Figure 4b). The findings demonstrate that MWCNT-BZ does not favor the decrease of the oxidation overpotential of AA. Thus, the overlapped oxidation waves of AA and UA observed on MWCNT-BZ can be attributed to the huge oxidation overpotential of AA that is measured on this particular film. According to the findings it can be concluded that MWCNT-BZ prevents the parallel determination of AA and UA substances [7].

The ability of AA and UA to be oxidized simultaneously on MWCNT-ACN can be probably attributed to the unique structural and the improved electro-catalytic properties of the nanotubes of this particular film that are strongly correlated to their high nitrogen doping level. Specifically, it is well known that the bamboo-shaped nanotubes have enhanced electronic properties compared to the un-doped pristine nanotubes. The findings clearly demonstrate that the novel fabricated MWCNT-ACN electrochemical sensor can be successfully used for facile, selective, rapid and precise simultaneous determination of AA and UA. Future research work will be focused on modification of fabricated MWCNT-based sensors for the improvement of their electrochemical response and their reactivity.

4 Conclusions

MWCNT-BZ and MWCNT-ACN films were fabricated by means of CVD with decomposition of BZ and ACN, respectively, and used for the simultaneous electrochemical oxidation of AA and UA. On MWCNT-ACN both AA and UA can be simultaneously oxidized and determined since the electrochemical peak of one compound is not influenced by the presence of the other. The findings reveal that the MWCNT-ACN film improves the electrochemical oxidation of UA and AA and resolves their overlapping oxidation peaks. The well-defined separation of about 400 mV of oxidation waves of AA and UA is mainly attributed to the significant decrease of the overpotential of AA at this particular electrode. The detection limit of AA and UA on MWCNT-ACN film was determined to be 9.67 μM and 5.41 μM , respectively. In contrast to MWCNT-ACN, the film produced with decomposition of BZ does not favor the decrease of anodic overpotential of AA, and consequently, it prevents the parallel determination of AA and UA substances. The findings exhibit that the doping of MWCNTs plays an important role for their electrochemical performance.

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