



Comparing sensitivities of differently oriented multi-walled carbon nanotubes integrated on silicon wafer for electrochemical biosensors

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ARTICLE INFO

Article history:

Received 28 April 2011

Received in revised form 12 July 2011

Accepted 27 July 2011

Available online 3 August 2011

Keywords:

Multi-walled carbon nanotubes

Chemical vapor deposition

Cyclic voltammetry

Wettability

Potassium ferricyanide

Hydrogen peroxide

Electrochemical biosensors

ABSTRACT

In this study, we report on multi-walled carbon nanotubes fabricated on silicon substrate with four different orientations via chemical vapor deposition. It is well-known that chemical treatments improve the nanotube electrochemical reactivity by creating edge-like defects on their exposed sidewalls. Before use, we performed an acid treatment on carbon nanotubes. To prove the effect of the treatment on these nanostructured electrodes, contact angles were measured. Then, sensitivities and detection limits were evaluated performing cyclic voltammetry. Two target molecules were used: potassium ferricyanide, an inorganic electroactive molecule, and hydrogen peroxide that is a product of reactions catalyzed by many enzymes, such as oxidases and peroxidases. Carbon nanotubes with tilted tips become hydrophilic after the treatment showing a contact angle of $22^\circ \pm 2^\circ$. This kind of electrode has shown also the best electrochemical performance. Sensitivity and detection limit values are $110.0 \pm 0.5 \mu\text{A}/(\text{mM cm}^2)$ and $8 \mu\text{M}$ for potassium ferricyanide solutions and $16.4 \pm 0.1 \mu\text{A}/(\text{mM cm}^2)$ and $24 \mu\text{M}$ using hydrogen peroxide as target compound. Considering the results of wettability and voltammetric measurements, nanotubes with tilted tips-based electrodes are found to be the most promising for future biosensing applications.

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1. Introduction

Since their discovery, *carbon nanotubes* (CNTs) have attracted considerable interest in many different fields due to their good electric, chemical and mechanical properties [1]. CNTs include two types of structures. *Single-walled carbon nanotubes* (SWCNTs) are cylindrical graphite sheets capped by hemispherical ends with typical diameter of 1–2 nm [2], whereas *multi-walled carbon nanotubes* (MWCNTs) comprise several to tens of concentric cylinders of the respective graphitic shells separated by a distance of approximately 0.34 nm [2]. SWCNTs can be metallic, semi-conductors, or small band gap semiconductors depending on their diameter and chirality. MWCNTs, which behave as metallic conductors are good candidates for different electrochemical applications [2].

The improvement in the active surface area [3], their capability to facilitate redox reactions of many compounds [4], the increase in the sensitivity from millimolar [5] to micromolar ranges [6] advocate to the use of nanotubes as key building blocks to fabricate

electrodes. In particular, electrochemical biosensing for medical purposes is one of the most promising application of MWCNTs [7].

The electrochemical performance of CNT-based electrodes depends on many factors, such as the synthesis method [8], treatment [9], binding with the substrate [7,10], orientation of tubes and type of target compounds [11]. Most of the literature on CNTs is based on the assumption that tips are responsible for their electrochemical activity. The role of the CNT sidewall is presently under investigation [12]. However, recent studies demonstrate a large contribution from the sidewalls in case of randomly oriented CNTs [13]. Moreover, treatments generate alterations on CNT sidewalls changing their electrochemical properties [12,14].

In this paper, we describe a method to produce MWCNTs onto a silicon wafer via *chemical vapor deposition* (CVD). We selected ferrocene as the catalyst material and commercial camphor as the carbon source. Images from *field emission scanning microscopy* (FE-SEM) show nanotubes with four types of orientation with respect to the substrate. In order to create edge-like defects on nanotube sidewalls and to improve CNT electrocatalytic activity, the nanostructured electrodes were treated with sulfuric acid. The electrochemical properties, sensitivity and detection limit, were investigated by using *cyclic voltammetry* (CV). Potassium ferricyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) and hydrogen peroxide (H_2O_2) were chosen as target molecules. The first compound was selected for the well-defined response at carbon materials, the latter for its significant importance in the biomedical field.

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Table 1
Growth parameters.

	Substrate temperature [°C]	Rotational velocity [r/min]	Ferrocene flow time [min]	Camphor flow time [min]
Horizontal	925	12	10	10
Vertical/pillars	850	12	3 (N ₂ flow)	10
Tilted tips	775	40	3 (N ₂ flow)	7 (N ₂ flow)

2. Experimental procedure

2.1. Synthesis of carbon nanotubes

We grew MWCNTs directly onto silicon wafer (Si-mat, Germany) with a diameter of 10.16 cm via CVD. We used commercial camphor as the carbon precursor, because the 3D structure of this material helps the formation of nanotube rings [15]. Ferrocene (98% purity in weight, Aldrich) was the organometallic chemical compound acting as both a catalyst and a carbon source. It creates iron atoms that agglomerate in clusters on which the CNTs grow. We utilized a reactor consisting of a furnace (Kenosistec, Milan, Italy) fed with only two evaporation chambers where the precursors were heated. The silicon substrate was located on a graphite plate in a deposition chamber (IONVACPROCESS SRL, Rome, Italy) and was heated up at the desired temperature (700–925 °C). Different nanostructured electrodes were obtained. Selected parameters for each growth are listed in Table 1.

- *Islands of horizontally/randomly oriented MWCNTs*, hereinafter called *horizontal CNTs*. The substrate was heated at 925 °C. Ferrocene and camphor were contemporary introduced in the deposition chamber by only their evaporation pressure for 10 min. The substrate holder rotated at 12 r/min and, after the deposition, it was kept at 925 °C for 30 min before cooling to room temperature.
- *Densely packed vertical MWCNTs and pillars of double-bedded MWCNTs*, hereinafter called *vertical CNTs* and *pillars of CNTs*, respectively. The substrate was kept at 850 °C and its holder rotated at 12 r/min. Ferrocene was introduced by a laminar flow of nitrogen (0.83 cm³/s) for 3 min and contemporary camphor with no carrier gas for 10 min. After the deposition, the substrate was immediately cooled to room temperature in inert atmosphere. In different regions we detected various kinds of CNTs. The two types of orientations correspond to different positions onto the Si-wafer.
- *Vertically aligned MWCNTs with oriented tilted tips*, hereinafter called *CNTs with tilted tips*. The substrate was kept at 775 °C with a rotational velocity of 40 r/min. Ferrocene was introduced in the deposition chamber for 3 min and, then, camphor for 7 min both with carrier gas. The substrate was cooled to room temperature inside the chamber in inert atmosphere immediately after the deposition.

2.2. Chemicals and materials

We prepared all solutions using 0.01 M Phosphate Buffer Saline (PBS, Sigma) at pH 7.4. We treated pristine MWCNTs in 6 M H₂SO₄ (Sigma, 95–98% vol) solution for 6 h [16]. We utilized potassium ferricyanide in the form of powder and hydrogen peroxide (30% vol) from Sigma.

2.3. FE-SEM and contact angle

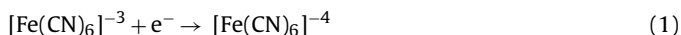
We used a SUPRA™ 40 (ZEISS) to acquire FE-SEM images with a nominal resolution of 1.5 nm at 10 kV. We measured contact angles using PBS drops (20 μl) cast onto the surface of MWCNT-based electrodes either before and after the treatment. The images were

acquired with a digital camera. For each sample, we averaged five measurements from five different images.

2.4. Electrochemical apparatus

We performed CV using Versastat 3 potentiostat (Princeton Applied Technologies) with a standard three electrode configuration. A platinum wire served as counter electrode, while we chose a wire in Ag/AgCl saturated with KCl (3 M) as reference electrode (Roschi Rohde and Schwarz AG, Switzerland). We used acid treated MWCNTs on silicon substrate as working electrode. All experiments were carried out under aerobic conditions at room temperature.

Voltammograms were recorded using different K₄Fe(CN)₆ concentrations (from 0 to 25 mM by steps of 5 mM) at scan rates in the range 25–200 mV/s. K₄Fe(CN)₆ was chosen because it is a redox analyte widely used in electrochemistry. The redox reaction at +300 mV is:



The cathodic peak currents (I_{pc}) were taken from the baseline of the voltammogram [17,18]. The baseline current was determined by a linear fit of the voltammogram where no electrochemical analyte activity was observed. For a reversible reaction at standard temperature the expected peak current, I_p , can be computed referring to the Randles-Sevcik equation [17,18]

$$I_p = 2.69 \times 10^2 AD^{1/2} n^{3/2} \nu^{1/2} C, \quad (2)$$

where A is the surface area of the electrode, D is the diffusion coefficient of the analyte, n is the number of electrons transferred in the redox reaction, ν is the scan rate and C is the bulk analyte concentration. Based on expression (2), sensitivity (S) per electrode area was computed from the angular coefficient of the straight line obtained by plotting the current density versus the analyte concentration at a scan rate of 100 mV/s [7]. We define the smallest detectable current signal as the mean square root deviation of the voltammogram line with no electrochemical analyte activity. Detection limit was computed as three times the signal-to-noise ratio according to the expression $3\delta i/S$ where δi is the average standard error relative to the measurements performed for different target concentrations [19].

CV was also evaluated using solutions with different H₂O₂ concentrations for its importance in biosensing. H₂O₂ was selected since it is the product of reaction based on oxidases [13]. A potential of +650 mV causes the oxidation of hydrogen peroxide, according to the reaction



Using hydrogen peroxide as target, we varied the concentrations from 0 to 50 mM by steps of 10 mM at a scan rate of 100 mV/s. We also performed CVs in 30 mM of H₂O₂ solutions with scan rates in the range 25–200 mV/s.

3. Results and discussion

3.1. Morphological characterization

Fig. 1 depicts FE-SEM images of MWCNTs directly grown on silicon wafer. The diameter of the tubes is not uniform ranging

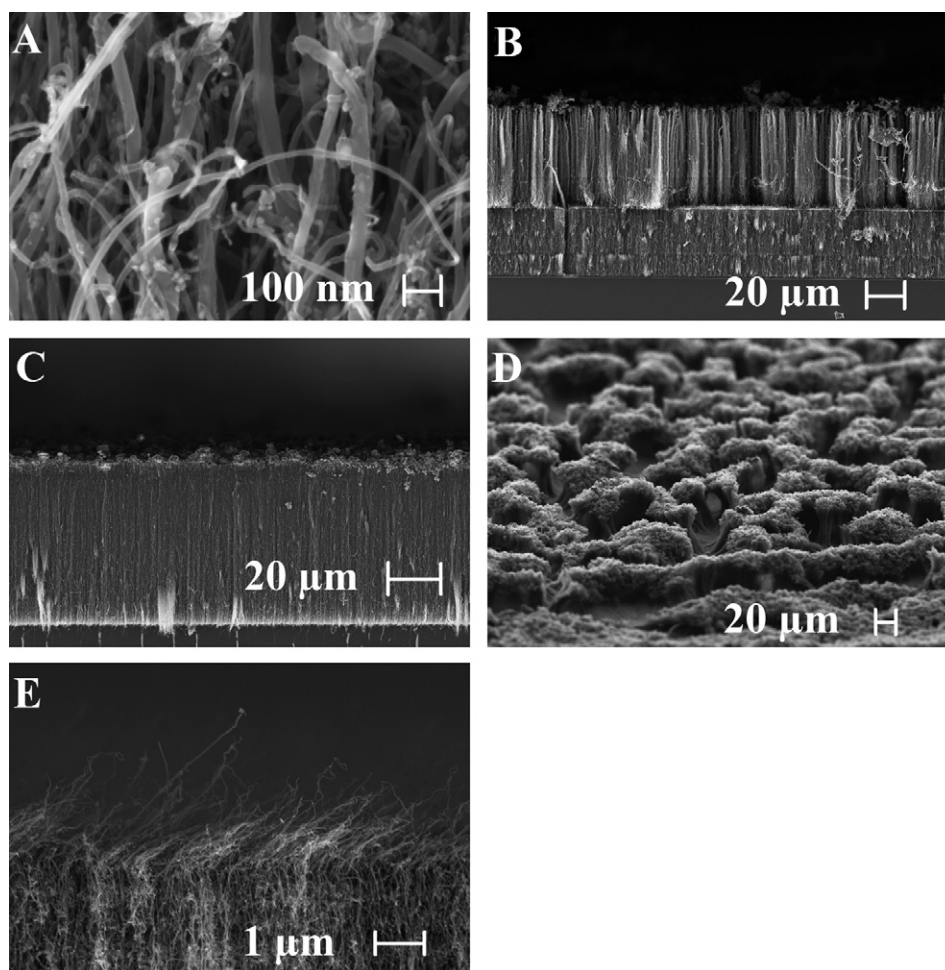


Fig. 1. FE-SEM images of CNT diameters (A), pillars of CNTs (B), vertical (C) and horizontal (D) CNTs and CNTs with tilted tips (E).

from 5 to 100 nm (see Fig. 1(A)). In Fig. 1(B), we observe pillars of vertically aligned double-bedded nanotubes and in Fig. 1(C) a “carpet” of vertically oriented MWCNTs that exposes only the CNT edge ends (length 60–100 μm). Fig. 1(D) shows aggregates of CNTs with exposed sidewalls separated by areas of more horizontally/randomly oriented ones. Finally, Fig. 1(E) shows a FE-SEM image of nanotubes with oriented tilted tips. Note that, in this case, the density of the vertical nanotubes (length 20–30 μm) is higher than that of tilted tips (few μm in length). The average inclination of the tubes in respect to the substrate is of 30°. Considering horizontal CNTs, pillars of CNTs and CNTs with tilted tips both tips and sidewalls are wet by the electrolyte during measurements.

3.2. Contact angle measurements

Pristine MWCNTs show a hydrophobic behavior which is explained by the size and the intrinsic disorder of the tubes [20]. To investigate the effect of treatment on multiple oriented MWCNTs, we measured contact angles. Vertical CNTs maintain a characteristic hydrophobicity (average contact angle: 107°), while CNTs with tilted tips become hydrophilic after the acid treatment (average contact angle: 22°). As a result of the activation, contact angle values for horizontal CNTs and pillars of CNTs result of 62° and 96°, respectively. Accordingly, it is clear that acid treatment improves the CNT wettability acting on the sidewalls (see Table 2). The significant decrease in the contact angle in case of CNTs with tilted tips is due to the larger exposition of the sidewalls to the acid solution. Indeed, in the top layer tip-containing, the tube density

is lower than the above layer as we can observe from Fig. 1(E). On the other hand, the well-packing of the vertical aligned nanotubes prevents the acid action. The lower density of the CNTs organized in pillars enables a slight wall modification. Considering the system with CNTs clusters, the treatment is allowed only on the areas with horizontally/randomly oriented tubes. A schematic explanation of the acid activation for the four system of nanotubes is shown in Fig. 2. Since greater hydrophilicity is required to integrate biomacromolecules, treated nanotubes with exposed walls could be the most suitable for bio-applications.

3.3. Electrochemical characterization with potassium ferricyanide

Fig. 3 shows cyclic voltammograms obtained using $K_4Fe(CN)_6$ as target. Horizontal CNTs show a cyclic voltammogram more sigmoidal in shape similarly to a nano-electrode ensemble (see Fig. 1(D) with CNTs aggregates). More well-defined peaks result from the other nanostructured electrodes more similarly to a macro-electrode electrochemical behavior. The cyclic voltammetry

Table 2
Contact angle measurements before and after the acid treatment.

	Before	After
Vertical	109° ± 2°	107° ± 4°
Tilted tips	101° ± 7°	22° ± 2°
Horizontal	108° ± 6°	62° ± 5°
Pillars	102° ± 7°	96° ± 5°

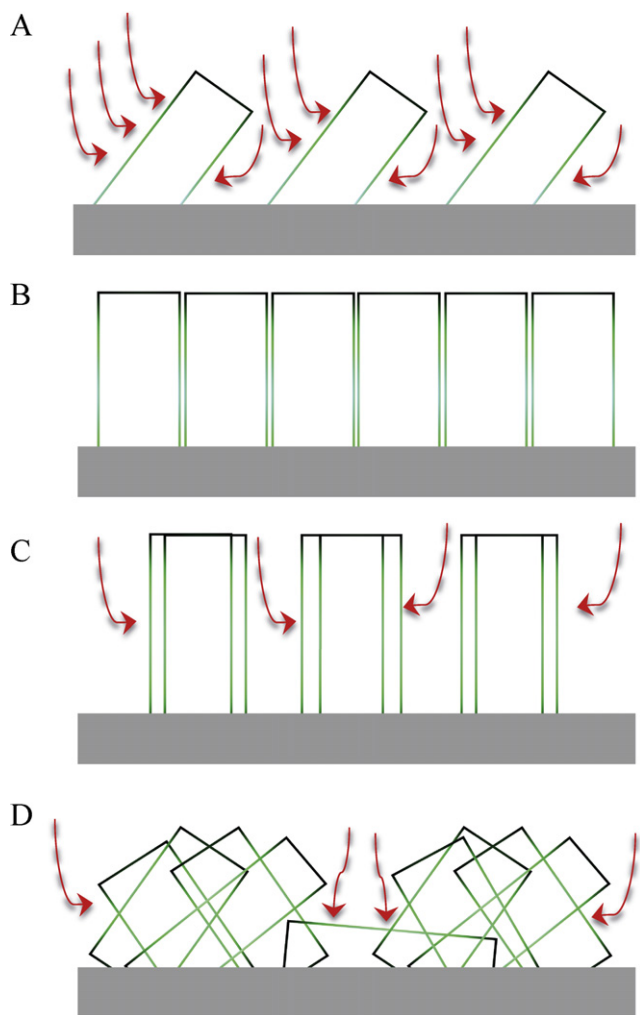


Fig. 2. A schematic representation of the sidewall alteration during acid treatment in case of CNTs with tilted tips (A), vertical CNTs (B), pillars of CNTs (C) and horizontal CNTs (D).

is also investigated at scan rates ranging from 25 mV/s to 200 mV/s. Fig. 4 shows voltammograms obtained at various scan rates in case of pillars of MWCNTs. For all the investigated electrodes, the variation of the peak currents with the square root of the scan rate

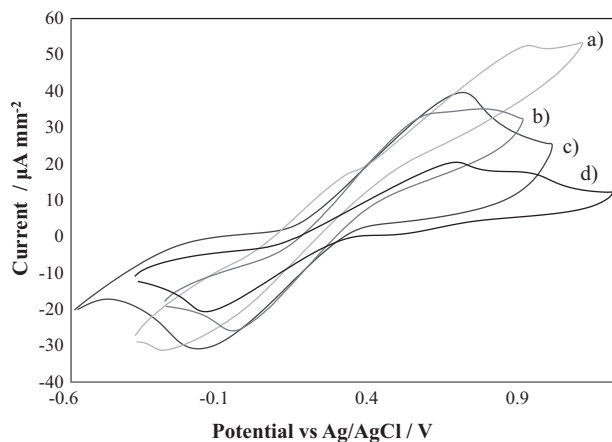


Fig. 3. Voltammograms obtained with horizontal (a) and vertical CNTs (b), pillars of CNTs (c) and CNTs with tilted tips (d). $K_4Fe(CN)_6$ concentration: 25 mM. Scan rate: 100 mV/s.

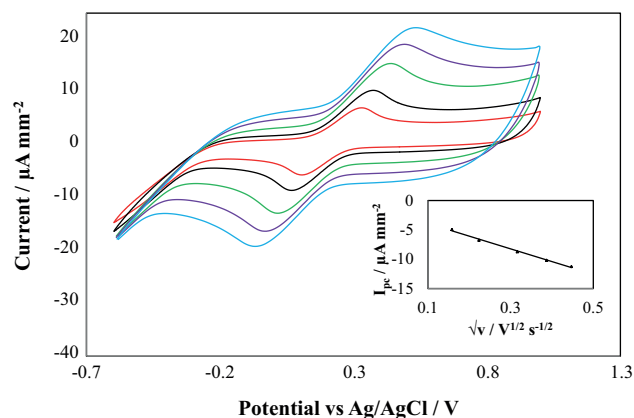


Fig. 4. Cyclic voltammograms obtained using pillars of CNTs showing the effect of the scan rate on the electrochemistry of $K_4Fe(CN)_6$ (5 mM in 0.01 M PBS solutions; scan rates of 25, 50, 100, 150 and 200 mV/s). The shows the cathodic peak currents as a function of the square root of the scan rates.

was found to be linear (inset Fig. 4) and the peak-to-peak separation expands gradually. The absolute values of the anodic and cathodic peak currents are found to be almost equal and the peak-to-peak separation ΔE_p was large, which means an high electrode resistance (see Table 3) [21].

We computed sensitivity and detection limit in reference to cathodic peaks of voltammograms obtained for different $K_4Fe(CN)_6$ concentrations (see example in Fig. 5(A)). A calibration curve is shown in Fig. 5(B). CNTs with tilted tips show the highest sensitivity

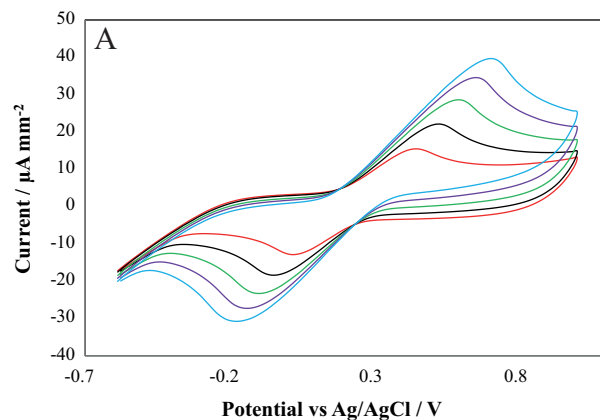


Fig. 5. Voltammograms obtained for 5, 10, 15, 20 and 25 mM of $K_4Fe(CN)_6$ concentrations at pillars of CNTs (A) and relative calibration curve in reference to cathodic peaks (B).

Table 3

Anodic E_{pa} and cathodic E_{pc} peak potentials, peak-to-peak separation ΔE_p , half-wave potentials $E_{1/2}$ and peak current ratio I_{pc}/I_{pa} for the redox couple $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ ($\text{K}_4\text{Fe}(\text{CN})_6$ concentration: 5 mM; scan rate: 100 mV/s).

	E_{pa} [mV]	E_{pc} [mV]	ΔE_p [mV]	$E_{1/2}$ [mV]	I_{pc}/I_{pa}
Vertical	397	67	330	232	0.9
Tilted tips	300	134	166	217	0.8
Horizontal	467	25	442	246	1
Pillars	441	16	425	228	0.8

Table 4

Electrochemical sensing parameters computed using multiple oriented MWCNTs for $\text{K}_4\text{Fe}(\text{CN})_6$ and H_2O_2 solutions.

	Sensitivity [$\mu\text{A}/(\text{mM cm}^2)$]	Detection limit [μM]
$\text{K}_4\text{Fe}(\text{CN})_6$		
Vertical	71.5 ± 0.3	28.233 ± 0.003
Tilted tips	110.0 ± 0.5	8.3095 ± 0.0001
Horizontal	62.8 ± 0.3	78.56 ± 0.03
Pillars	101.5 ± 0.5	51.57 ± 0.01
H_2O_2		
Vertical	10.08 ± 0.04	252.4 ± 0.1
Tilted tips	16.4 ± 0.1	23.9872 ± 0.0001
Horizontal	1.81 ± 0.01	1534 ± 2
Pillars	3.26 ± 0.02	1623 ± 3

approximately twice higher than the value obtained with horizontal CNTs ($110.0 \pm 0.5 \mu\text{A}/(\text{mM cm}^2)$ and $62.8 \pm 0.3 \mu\text{A}/(\text{mM cm}^2)$, respectively). The detection limit for vertical CNTs and pillars of nanotubes is almost the same. We obtained the highest detection limit using horizontal CNTs ($79 \mu\text{M}$). On the contrary, the lowest

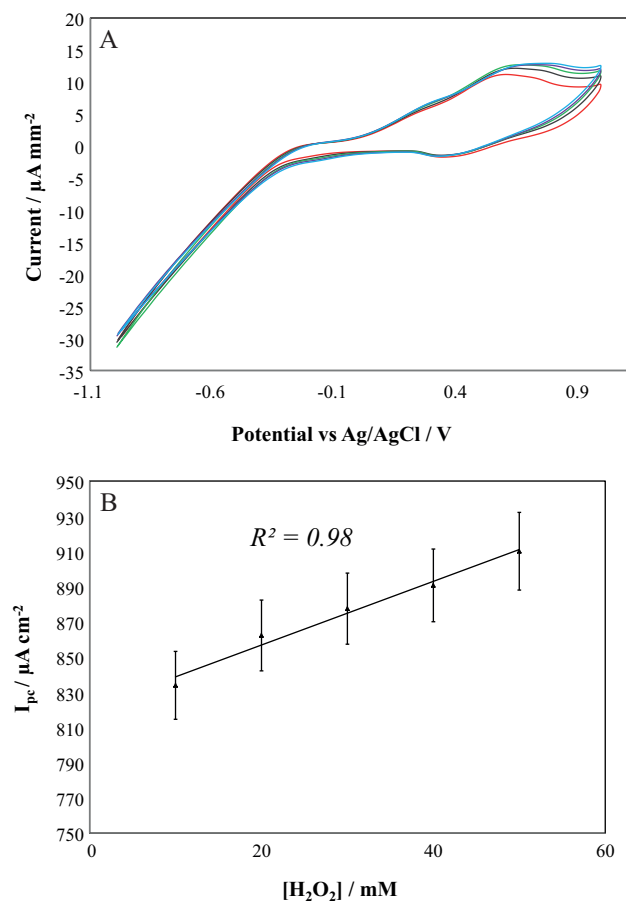


Fig. 6. Voltammograms obtained for 10, 20, 30, 40 and 50 mM of H_2O_2 concentrations at horizontal CNTs (A) and relative calibration curve (B).

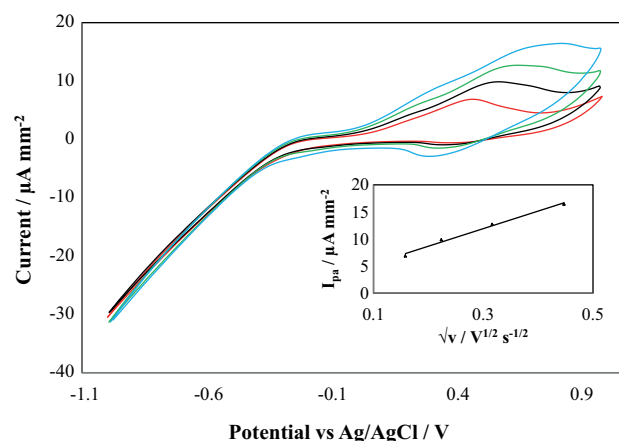


Fig. 7. Cyclic voltammograms obtained using horizontal CNTs showing the effect of the scan rate on the electrochemistry of H_2O_2 (30 mM in 0.01 M PBS solutions; scan rates of 25, 50, 100 and 200 mV/s). The inset shows the anodic peak currents as a function of the square root of the scan rates.

value corresponds to CNTs with tilted tips that is equal to $8 \mu\text{M}$. Table 4 reports sensing values for $\text{K}_4\text{Fe}(\text{CN})_6$ at different electrode interfaces.

3.4. Detection of hydrogen peroxide

We also used H_2O_2 as analyte because it is a product of reactions catalyzed by many enzymes [13]. This molecule is not as electroactive as the potassium ferricyanide. Indeed, only less well-shaped anodic peak currents appear in CVs (see Fig. 6(A)) [22]. In addition, with this compound, the CV curves were registered at various scan rates. An increase of the peak currents was found as the scan rate increased (inset of Fig. 7) and the anodic potential becomes more positive as shown in Fig. 7. Voltammograms obtained for different H_2O_2 concentrations at horizontal CNTs are shown in Fig. 6(A). The related calibration curve is reported in Fig. 6(B). Also with this molecule, we obtained the highest sensitivity and the lowest detection limit using CNTs with tilted tips equal to $16.4 \pm 0.1 \mu\text{A}/(\text{mM cm}^2)$ and $24 \mu\text{M}$, respectively. Lower sensitivities and higher detection limits were measured for the other nanostructured electrodes as shown in Table 4.

The different results obtained with the two probes are due to the specific electrochemical sensitivity of potassium ferricyanide and hydrogen peroxide to various surface electrode states [11].

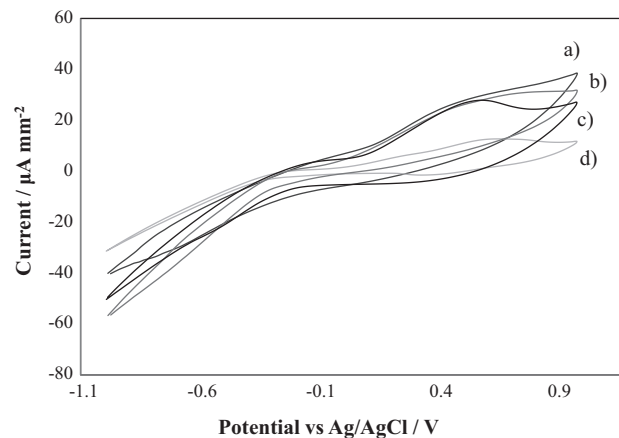


Fig. 8. Voltammograms obtained with pillars of CNTs (a), vertical CNTs (b), CNTs with tilted tips (c) and horizontal CNTs (d). H_2O_2 concentration: 30 mM. Scan rate: 100 mV/s.

Nonetheless, in both cases, vertical CNTs with tilted tips show the highest sensitivity and the lowest limit of detection.

Cyclic voltammograms measured using the four nanostructured electrodes in 0.01 PBS solution and containing 30 mM of H₂O₂ are shown in Fig. 8. For vertical CNTs, the hydrogen peroxide electrooxidation is observed at 718 mV. Values of potential peaks for pillars of nanotubes and horizontal CNTs appear at 593 mV and 633 mV, respectively. The accelerated electron transfer reaction at CNTs with oriented tilted tips allows the detection of hydrogen peroxide at the lowest potential (570 mV) and, consequently, at the lowest energy cost. Moreover, it is well-shaped if compared with the oxidation peaks obtained using the other types of electrodes (see Fig. 8).

4. Conclusion

This study reports the preparation and the characterization of a new type of CNT-based electrode. We obtained multiple oriented MWCNTs via CVD onto silicon substrates. In CNT-based bioelectrochemistry, two important factors should be emphasized: CNT reactivity, which increases with the introduction of topological defects, and the nanotube wettability by the solvent/electrolyte medium. Taking into account of these two points, we used acid treatment to facilitate electron transfer and also to decrease the well-known CNT hydrophobicity. The considerable change of wettability on CNTs with more exposed sidewalls confirms the assumption that acid treatment causes a predominant change on sidewalls [23].

The most interesting properties for sensing applications, namely sensitivity and detection limit, were investigated by CV. By using potassium ferricyanide and hydrogen peroxide solutions, CNTs with tilted tips show the best electrochemical behavior. This result is due to the electroactivity contribution of both edge-plane-graphite-like open ends and defects sites. The lowest sensitivity and the highest detection limit found using horizontally/randomly oriented CNTs are due to the lowest exposition of the tips and the lowest density of the active sites.

Interestingly, electrochemical responses at the electrode surface depend on the type of target. We demonstrated that the introduction of wall defects influences more nanotube–potassium ferricyanide interaction rather than the interaction between MWCNTs and hydrogen peroxide. Nonetheless, CNTs with tilted tips resulted in the most effective electrode to detect both the targets. In addition to providing the best electrocatalytic activity in terms of sensitivity and limit of detection, the last nanostructure offers the lowest oxidation potential of hydrogen peroxide. Considering also the large increase in wettability, we can argue that CNTs with tilted tips are the most suitable for an efficient immobilization of oxidases producing hydrogen peroxide in order to develop amperometric biosensors.

The chance to increase the reactivity of CNTs by varying both pretreatments and the CNT tilt with respect to the electrode substrate offers the opportunity to fabricate biodevices with promising target-selective electroanalytical performance. Moreover, the CNT nanometer size favors the fabrication of miniaturized transducers also usable for real-time in vivo measurements.

Acknowledgments

The authors would like to thank Giuseppe Dino Albini for the useful discussion on the electrochemical properties of differently oriented carbon nanotubes and Salvatore Guastella to acquire FE-SEM images. The research has been supported by the i-IronIC project. The i-IronIC project was financed with a grant from the Swiss Nano-Tera.ch initiative and evaluated by the Swiss National

Science Foundation. This work was also partially supported by LATEMAR, Centre of Excellence funded by the Italian Ministry for Education, University and Research.

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Biographies

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