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Electrochemical oxidation of adenine using platinum electrodes modified with carbon nanotubes

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HIGHLIGHTS

- Radio Frequency-catalytic Chemical Vapor Deposition was used for CNTs synthesis.
- The electro-catalytic characteristics of the carbon nanotubes were tested.
- MW and DW carbon nanotubes are more suitable for adenine electrochemical detection.

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ABSTRACT

Single- (SWNTs), double- (DWNTs), and multi-walled (MWNTs) carbon nanotubes were synthesized by controlled Radio Frequency-catalytic Chemical Vapor Deposition (RF-cCVD). Their morphological and structural characteristics were identified using Transmission Electron Microscopy (TEM/HRTEM) and X-ray powder diffraction (XRD). Next, three platinum electrodes with identical amounts of each nanotube material (denoted Pt-SW, Pt-DW, and Pt-MW) were modified in order to test the electro-catalytic characteristics of the carbon nanotubes and further used for the electrochemical oxidation of adenine. The signal recorded with the Pt-SW electrode was very poor, due to the predominantly semiconducting properties of these nanotubes. In contrast, the signal recorded with Pt-DW or Pt-MW was well-defined, with the peak potentials at 1.07 and 1.01 V vs Ag/AgCl, respectively. In both cases, the detection limit (DL) for adenine was found to be 3×10^{-6} M.

1. Introduction

Adenine is an important organic molecule found in nucleic acids, which participates in many biological processes. Abnormal changes in this purine base are related to deficiencies in the immune system; therefore, its concentration level is considered important for the diagnosis of cancer, disease progress, and therapy responses [1]. It is thus crucial to discover highly sensitive methodologies for the determination of this base in DNA.

Various approaches have been used to detect adenine: electrophoresis [2], flow injection chemiluminescence [3], and high performance liquid chromatography [4]. The latter two methods are highly selective and sensitive, but they are also time-consuming and costly. In contrast, electrochemical techniques are more attractive due to their low cost [5]. Direct oxidation of adenine at bare electrodes (metallic or glassy carbon) is difficult to achieve, due to its strong adsorption on the active area, thus leading to low sensitivity and selectivity [6]. For these reasons, several modified electrodes have been designed to detect adenine: ionic liquid–CNT/gold nanoparticle (AuNP) complex composite film-coated electrodes [7], MWNT–ionic liquid film-modified carbon paste electrodes [8], graphene–COOH modified glassy carbon electrodes [9], graphene-modified carbon ionic liquid electrodes [10], TiO_2–graphene nanocomposites [11], or graphene sheets having various amounts of gold nanoparticles embedded [12].

Carbon nanotubes (CNTs) were discovered in 1991 and have attracted significant scientific interest due to their unique structural morphologies as well as mechanical, chemical, and optoelectronic properties, which include a remarkably high tensile strength, excellent electrical conductivity, and good chemical stability [13]. These unique properties make CNTs an appropriate material for chemical and biological sensors [14], batteries [15], and nanoelectronic devices [16]. CNTs consist of sp^2 hybridized carbon atoms, arranged in a cylindrical nanostructure. Single-walled carbon nanotubes (SWNTs) exhibit excellent mechanical and thermal properties and are usually found in bundles composed of tens to hundreds of

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parallel tubes in contact with each other due to their high surface energies [17]. Double-walled carbon nanotubes (DWNTs), the simplest of the multi-walled nanotubes (MWNTs), combine the remarkable properties of SWNTs with the possibility of studying concentric intertube interactions with great precision [18]. MWNTs consist of several graphitic layers arranged as concentric cylinders. They have metallic conductivity and are thus suitable for the design of novel electrochemical sensors.

Here we present, for the first time to the best of our knowledge, a comparison between the electro-catalytic characteristics of all three types of carbon nanotubes: SWNTs, DWNTs, and MWNTs. We employed Linear Sweep Voltammetry (LCV) and Electrochemical Impedance Spectroscopy (EIS) to characterize the platinum electrodes modified with carbon nanotubes in the presence of an organic molecule, adenine.

2. Materials and methods

All reagents used for the experiments were of analytical grade or better. Pure adenine sulfate dihydrate powder was purchased from Tokyo Chemical Industry Co. Ltd., Japan. N,N-dimethylformamide (DMF) was purchased from Fluka-Germany and used for the dispersion of all types of carbon nanotubes. Phosphate buffer solution (PBS) pH 6 was prepared from a mixture of 0.2 M $NaHPO_4$ and 0.2 M Na_2HPO_4. Thereafter, a stock solution of 10^{-3} M adenine was prepared in this buffer for subsequent use in the preparation of lower concentration solutions (down to 10^{-6} M).

2.1. Synthesis of SWNTs, DWNTs, and MWNTs

SWNTs were synthesized by Radio Frequency-catalytic Chemical Vapor Deposition (RF-cCDV) over a novel catalytic system Fe:Mo/MgO obtained by co-precipitation, in a reactor with quartz walls that were water cooled, as previously described [19]. Briefly, the catalyst was dispersed in a graphite susceptor and then introduced into the middle of the reactor. The reactor was purged with Ar for 10 min; then the susceptor was heated to the calcination temperature (500 °C) for 10 min, followed by rapid heating (375 °C/min) to reach the reaction temperature (850 °C). When the reaction temperature was reached, in addition to the Ar flow, acetylene (3 mL/min) was introduced for 3 min (reaction time). Once the flow of acetylene was stopped, the reactor was allowed to cool to ambient temperature in Ar [19].

DWNTs were synthesized by RF-cCDV (cold-wall) from methane on a Fe:Mo/MgO catalyst, using a procedure similar to the one used for the synthesis of SWNTs, as described in detail in reference [20]. MWNTs were also synthesized by RF-cCVD from acetylene on a Fe:Co/$CaCO_3$ catalyst (at 720 °C) using the same method previously outlined [21].

2.2. Platinum electrodes modified with SWNTs, DWNTs, or MWNTs

Prior to modification with each type of carbon nanotube, three platinum electrodes having the same surface area (0.07 cm^2) were cleaned in 0.5 M H_2SO_4 solution by cyclic voltammetry (50 cycles from −0.25 to +1.6 V vs Ag/AgCl; 50 mV s^{-1}). Next, they were treated by ultrasound in ethanol and double-distilled water several times (3 min). Afterward, 20 μL from each colloidal suspension of nanotubes (SWNTs, DWNTs, or MWNTs) in DMF (0.5 mg/mL) was deposited onto the platinum substrates and dried at room temperature for about 5 h. The modified electrodes were further used to study the electrochemical oxidation of adenine. They were subsequently denoted as Pt-SW, Pt-MW, and Pt-DW.

2.3. Apparatus

Transmission Electron Microscopy (TEM) images were obtained by using a field emission JEM-2100F TEM (JEOL Inc.) equipped with a CCD camera. Carbon nanotube samples were solubilized in 2-propanol under sonication for 10 min. Further, several drops of the resulting solution were deposited onto the TEM grid and allowed to dry before the microscopy analysis [19].

X-ray powder diffraction (XRD) data were collected with a Bruker D8 Advance diffractometer in the 2θ=5–85° angular domain using CuKα_1 radiation (λ=1.5406 Å). A Ge(1 1 1) monochromator in the incident beam was used to eliminate the Kα_2 radiation and increase the resolution.

2.3.1. Electrochemical measurements

We performed Linear Sweep Voltammetry and Electrochemical Impedance Spectroscopy with an Autolab 302N Potentiostat/Galvanostat (Metrohm Autolab B.V., Utrecht, The Netherlands) connected with a three-electrode cell (the reference was an Ag/AgCl electrode). LCVs were recorded between 0 and +1.40 V/Ag (AgCl) at a scan rate of 50 mV s^{-1}. Using a small sinusoidal excitation signal (10 mV amplitude), EIS measurements were recorded over a frequency range of 0.1–10^5 Hz. The applied potential was +1.2 V vs Ag/AgCl. All experiments were carried out in a quiescent phosphate buffer solution having various concentrations of adenine (from 10^{-6} to 10^{-3} M). Data fitting was performed using Nova 1.8 Software (Metrohm Autolab B.V., Utrecht, The Netherlands).

3. Results and discussions

3.1. Morphological and structural characterization of carbon nanostructures

Fig. 1 reveals typical TEM images of SWNTs (a), DWNTs (b), and MWNTs (c). Due to van der Waals forces, SWNTs and DWNTs

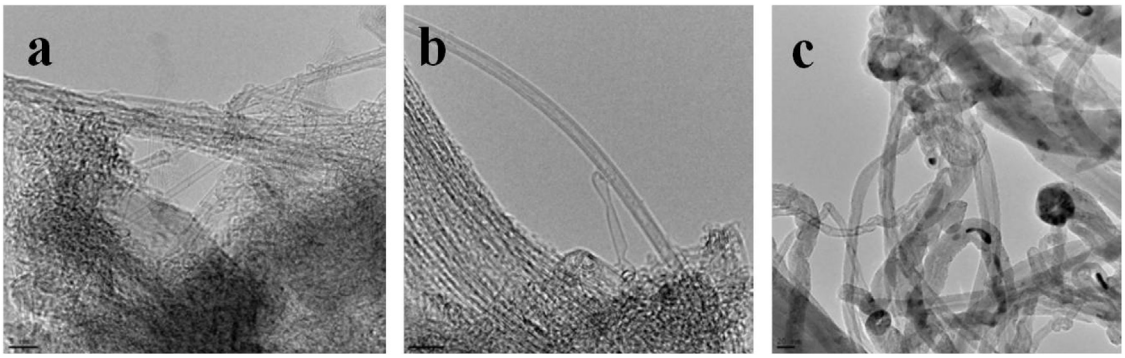

Fig. 1. TEM images of SWNTs (a) scale bar 5 nm; DWNTs (b) scale bar 5 nm; and MWNTs (c) scale bar 20 nm.