



Nanocarbon electrode prepared from oppositely charged nanoparticles and nanotubes for low-potential thiocholine oxidation



Anna Celebanska^a, Marcin S. Filipiak^a, Adam Lesniewski^a, Elena Jubete^b,
Marcin Opallo^{a,*}

^a Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

^b IKACIDETEC, Sensors Unit, Materials Division, Parque tecnológico de San Sebastián, P^o Miramón 196, Donostia San Sebastian 20009, Spain

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ABSTRACT

Herein we report a modification of ITO electrode, by layer-by-layer deposition of positively charged carbon nanotubes and negatively charged carbon nanoparticles, its characterization and application. A correlation between the number of deposition steps and the thickness of the deposit was demonstrated. Positively charged ions: $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ were found to accumulate on the deposit, whereas no accumulation process was observed for the negatively charged redox probes: $\text{Fe}(\text{CN})_6^{3-/4-}$. Carbon nanoparticulate-nanotubular electrode exhibits catalytic properties towards oxygen reduction reaction and towards mediatorless thiocholine oxidation. Thiocholine oxidation peak potential was observed at 0.07 V vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{3\text{M}}$ electrode. A linear relationship between oxidation current and thiocholine concentration was observed for 30 - 2000 μM thiocholine. The detection limit of thiocholine is 25 μM ($\text{S/N} \geq 3$).

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1. Introduction

The layer-by-layer (LbL) technique does not require sophisticated instrumentation and allows to prepare mechanically stable film electrodes exhibiting good electrocatalytic properties. It has been extensively employed and developed since 1991 [1] and was mainly applied for the preparation of polymer films or for immobilization of nanostructures in polymer film, which were deposited on solid surfaces [1–3]. In these procedures, the electrostatic attraction between charged functional groups of polymers or between functional groups of polymers and nano-objects is employed for film formation. It has been also demonstrated that stable nanoparticulate films can be created by the LbL technique from oppositely charged functionalized nanoparticles without any linker molecules [4–7]. Such approach was also successful for preparation of entirely carbon nanotubular film [8].

Recently, it has been shown that commercially available hydrophilic carbon nanoparticles functionalized with negatively charged phenylsulfonate groups ($\text{CNPs}(-)$) are attractive electrode components, because of their electrocatalytic properties towards the oxidation of organic compounds [9–11]. They are perfectly suited [12] for the LbL technique because of their charged

functionalities. This allows for their immobilization on the electrode surface together with positively charged particles such as silicate submicroparticles [13–15], gold nanoparticles [16,17], carbon nanoparticles [10,18] or polymers with functional groups bearing positive charge [9,15,19,20]. Some of these electrodes exhibit electrocatalytic properties towards oxidation of biologically important molecules.

This report describes the preparation, characterization and application of an electrode, modified by the layer-by-layer technique, consisting of negatively charged carbon nanoparticles ($\text{CNPs}(-)$) and positively charged single-walled carbon nanotubes ($\text{CNTs}(+)$). LbL technique was earlier applied for the deposition of films consisting of functionalized carbon nanotubes and gold [21], Prussian Blue or TiS_2 nanoparticles [22]. Although preparation of film consisting of carbon nanotubes and carbon nanoparticles by low energy hydrocarbon ion deposition at 700 °C was already reported [23], its formation at mild conditions by the LbL is reported for the first time here. This work demonstrates that stable and homogenous films can be prepared by means of electrostatic interactions between single-walled carbon nanotubes wrapped with poly(diallyldimethylammonium) polymer (PDDA) with positively charged functionalities ($\text{CNTs}(+)$) and negatively charged carbon nanoparticles ($\text{CNPs}(-)$). The structure of these novel films is studied here with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Additionally, electrochemical properties such as capacitive current, ion accumulation and

* Corresponding author.

catalytic properties are also elucidated. Finally, the electrocatalytic properties of such films towards thiocholine (TC) oxidation were demonstrated.

TC is a product of enzymatic thiocholine ester hydrolysis catalysed by acetylcholinesterase (AChE) [24]. Its detection enables the monitoring of AChE activity [25]. This feature is commonly used in biosensors for pesticide detection [26,27]. TC oxidation on bulk electrodes occurs at relatively high potentials, but the deposition of nanomaterials significantly reduces TC oxidation overpotential [11,28–31]. Among other nanomaterials, electrophoretically deposited CNPs(–) [11], and CNTs films [30–33] (including LbL deposition) were applied for this purpose.

2. Experimental

2.1. Chemicals and materials

ITO coated glass (resistance 8–12 Ω /sq) was obtained from Delta Technologies, CNPs(–) (EMPEROR 2000), were kindly donated by Cabot Corp. Single-walled carbon nanotubes, SWCNT, were from Elicarb (UK), NaH_2PO_4 and Na_2HPO_4 were purchased from POCh. H_2SO_4 , NaOH were from Chempur and, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ from ABCR. $\text{K}_3\text{Fe}(\text{CN})_6$, acetylthiocholine chloride (ATCl), acetylcholinesterase (AChE) from electric eel, 5,5'-dithiobis-(2-nitrobenzoic acid) (DTNB), poly(diallyldimethyl-ammonium) chloride (PDDA) ($M_w < 100\,000$), acetonitrile, (ACN) (anhydrous, 99.8%), methanol, (MeOH) (CHROMASOLV[®], for HPLC, $\geq 99\%$) were acquired from Sigma-Aldrich. TC was enzymatically generated and its concentration was determined spectrophotometrically using Ellman's method [34]. Deionised water obtained from an ELIX system (Millipore) was used for the preparation of all aqueous solutions.

2.2. SWCNT modification

SWCNTs were modified with PDDA in order to introduce positively charged functionalities on their surface and to ensure good dispersion in water. First SWCNTs were refluxed in 2.6 M nitric acid for 2 h to remove impurities [35]. Next 75 mg SWCNTs were mixed with 2.45 ml of water and then 0.275 ml 35% PDDA solution was added. This mixture was left in an ultrasonic bath for 1 h and stirred mechanically for additional 15 h. The obtained CNT (+) were centrifuged, rinsed with water three times and finally diluted in 5 or 10 ml of water.

2.3. Film electrode preparation

First, the ITO plate was washed with ethanol and water in an ultrasonic bath for at least 15 minutes. Next, it was annealed at 500 °C for 30 min. Then ITO plate was immersed subsequently into CNTs(+) suspension in water (7.5 or 15 mg ml^{-1}) and CNPs(–) suspension in ACN (5 mg ml^{-1}). Every immersion step was followed by drying and immersion into the pure water or ACN, respectively. Electrodes were modified by one, three, six, nine, twelve and twenty four such double immersion and withdrawal

steps (n) and thus were named CNT-CNP(n). The electrode surface (0.2 cm^2) was masked with a scotch tape and electric contact was assured by using a piece of copper tape.

2.4. Instrumentation and cell

Cyclic voltammetry was performed with Autolab or μ Autolab III potentiostats (Metrohm Autolab) with dedicated software in a conventional three electrode cell. The bare or modified ITO or bare GC electrode (nLab d = 2 mm), platinum wire (d = 0.5 mm) and Ag|AgCl|KCl_{3M} were used as a working, counter and reference electrode respectively. All experiments were carried out at 25 °C. SEM analysis was performed using a FEI Nova NanoSEM 450. AFM images were obtained with a MultiMode AFM instrument using a Nanoscope V controller (Bruker) operating in tapping mode.

3. Results and discussion

3.1. Microscopic characterization

Optical images of the prepared electrodes (Fig. 1) show that the black colour intensity of the electrodes increases as a function of the number of immersion and withdrawal steps. This is in agreement with the larger amount of material being deposited due to electrostatic interactions between CNTs(+) and CNPs(–).

SEM images also reveal that the amount of nanomaterial is proportional to the number of immersions and withdrawal steps (n) (not shown). Given the example of CNT-CNP(6) electrodes it is clearly seen (Fig. 2a) that CNPs(–) form big, rugged clusters covered by tiny threads of CNTs(+). It is also visible that six immersion and withdrawal steps produce complete coverage of the ITO surface. The characteristic leaf like ITO surface structure is completely covered with carbon objects (Fig. 2a). As observed on the SEM images of the electrodes modified with the highest amount of carbon nanomaterials (CNT-CNP(12) and CNT-CNP(24) (Fig. S1)) cracks appeared in such cases. These cracks are most likely responsible for their mechanical instability (see below).

The AFM images of CNT-CNP(n) electrodes reveal bumpy, jagged surface (Fig. 2b). The images of the surface scratched by scalpel were used for the rough estimation of the film thickness. It was measured as the difference between the level of the film at five selected points (within 15 $\mu\text{m} \times 15 \mu\text{m}$ square) and the level of ITO substrate. This parameter ranges from 15 to 910 nm and clearly longer preparation procedure produces thicker films (Fig. 2c).

3.2. Electrochemical characterization

The CNT-CNP(n) ($1 \leq n \leq 6$) electrodes exhibit good mechanical stability. They keep their structure after 30 min sonication in water. The voltammetry performed in 0.1 M aqueous H_2SO_4 reveals a symmetric pair of peaks (Fig. 3), typical feature of carbon nanotubes electrodes in acidic medium resulting from protonation/deprotonation of functional groups such as quinone/hydroquinone [36,37]. Distinctly, the magnitude of these peak currents is

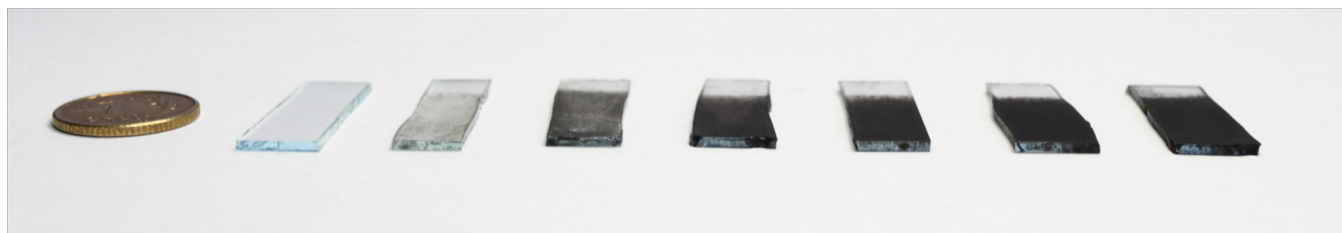


Fig. 1. Photo of ITO and CNT-CNP(n) electrodes where n = 0, 1, 3, 6, 9, 12 and 24 (from left to right) compared to 1 grosz (1/100 PLN) coin.

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