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Comparison of unusual carbon-based working electrodes for electrochemiluminescence sensors

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ABSTRACT

In this work, unconventional carbon-based materials were investigated for use in electrochemiluminescence (ECL) working electrodes. Precursors such as bamboo, pistachio shells, kevlar® fibers and camphor were differently treated and used as working electrodes in ECL experiments. After a proper process they were assembled as electrodes and tested in an electrochemical cell. Comparison among them and with a commercial glassy carbon electrode (GCE) shows a very good response for all of them thus demonstrating their potential use as disposable low-cost electrodes for early detection electrochemical analysis.

1. Introduction

Recently, there is tremendous interest into green, renewable and possibly low-cost bioresources or waste-reuse as an alternative way to produce efficient and disposable sensing elements for different kind of sensors. Decentralization of diagnostic exams from hospital laboratories directly to the patient's home was a focus of researchers for many years and is a key component in the current medicine innovation [4,31]. In addition, with the advent of Internet-of-Things (IoT), there is an increasing trend to realize small and connected medical devices for any kind of uses [3,5,12]. Among these, point-of-care devices (POC) for qualitative analysis for consumer market have attracted much interest due to the high impact on the people's perception of healthiness [14,18]. Such technology would enable the patient to routinely and remotely monitor their disease progression and treatment effectiveness remotely [26]. Principal requirements for POC biosensor devices are price, dimension and ease-of-use. Surprisingly, accuracy is not a key factor as one could expect because the ultimate goal of such devices is to give an approximate value (glucose test) [16] rather than a yes-or-no answer (pregnancy test) [15,23] that, in any case, will be analyzed in depth with laboratory equipment. Among all the sensing mechanisms used by POC devices, electrochemical detection is by far the most exploited due to its simplicity and sensitivity. It does not require expensive detectors because the measurement is accomplished only by means of three electrodes and it can reach extreme sensitivity [7-9,29]. Electrochemiluminescence (ECL) is a powerful electrochemical technique that combines high sensitivity with low cost and reduced size instrumentation [6,13,32]. Solid electrodes based on carbon are currently widely used in electrochemistry and in ECL, due to their superior stability, broad potential window, low background current, rich surface chemistry, chemical inertness, and suitability for various sensing and detection applications [2,30]. Although their manufacturing process is cheap as compared to their non-carbon-based counterparts, in some cases they require carefully controlled process conditions as in the case of Glassy Carbon Electrodes (GCE) [1] or expensive instrumentation like in the case of Boron-Doped Diamond (BDD) electrodes [11].

Biochar is a recalcitrant carbonaceous product obtained from the pyrolysis of biomasses and other biogenic wastes [22,28]. The final product is strongly dependent on the pyrolysis's temperature that influences its yield and its properties. In fact, low pyrolysis temperatures lead to a higher yield, low resistivity and a good cation-exchange capacity. On the other hand, high pyrolysis temperatures

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lead to an activated biochar with a great extent of aromatic carbon, high alkalinity and to an extended microporosity with a consequent high surface area [25].

Under these premises, we tested and compared different materials based on carbon (usually wastes) for their use in ECL tests in order to find the ideal candidate to be the future sensing material for next generation of low-cost ECL biosensing devices [19].

2. Experimental

2.1. Chemicals

Solution used in the experiments was 50 ml of $Ru(bpy)_3^{2+}$, with a concentration of 10^{-4} M and 60 μl of tripropilammine (TPA) dissolved in 50 ml of phosphate buffer solution (PBS) with 10^{-1} molar concentration (pH 7.5). The ruthenium complex used as an electrochemiluminescent label was purchased by Cyanagen S.r.l. The PBS was prepared by dissolving 13.6 mg of KH_2PO_4 with 871 mg of K_2HPO_4 in 50 ml of deionized water. Both TPA and phosphates were purchased by Sigma-Aldrich. All deionized water used in the experiments was obtained from a Milli-Q water purification system. All measurements were carried out at room temperature.

2.2. Instrumentation

Cyclic voltammetry (CV) curves were obtained with a custom potentiostat and related software while ECL detections were carried out by appling a −800 V to power a photomultiplier tube (PMT) purchased from Hamamatsu Photonics. A glassy carbon (1 mm in diameter) was used as a benchmark to compare the performance of our electrodes. A high-purity (99.99%) silver wire purchased by Advent Research Material was used as reference electrode. It was necessary to remove the oxide on its surface before its use. This was accomplished by dipping the wire in 0.1 M HNO_3 for a few seconds. The wire was rinsed with deionized water prior to use in subsequent steps: the anodic AgCl coating [35]. The freshly cleaned silver wire was chloridized by placing it in a compartmentalized cell containing 1 M KCl and by applying 0.4 $mAcm^2$ current for 30 min. The coated wire was washed and soaked for 1 day in deionized water. A gold wire was used as counter electrode.

The x-ray photoelectron spectroscopy (XPS) was conducted on a Physical Electronics XPS Instrument Model 5700, operated via monochromatic Al-Ka X-ray source (1486.6 eV) at 350 W. The data analysis was conducted on MultipakTM software and the Shirley background subtraction routine had been applied throughout.

Field Emission Scanning Electron Microscope (FESEM), a Zeiss Supra 40 connected to an Energy Dispersive X-ray Spectroscopy (EDS-Oxford Inca Energy 450) was used to observe the electrodes.

TGA was conducted on a TGA/SDTA 851 Mettler Toledo V4.01, 25–1000° C with the ramp rate of 10 °C/min in air (50 ml/min) and argon (40 ml /min).

2.3. Electrodes fabrication

2.3.1. Bamboo

About 5 mm height bamboo cylinders with a diameter of approximately 2.4 mm were inserted in an oven and pyrolyzed for 1 h at 850°C in an argon flux. After the process the sticks resulted slightly deformed along their length, 1 mm in diameter and a weight loss of about 70% [24].

2.3.2. Pistachio

The Pistachio Nut Shells were initially dried at 120°C for 24 h in order to remove moisture. They were then crushed into smaller pieces using mortar and pestle. Carbonization was subsequently performed by heating the shells at 500°C for 2 h inside a Chemical Vapor Deposition (CVD) chamber in an argon atmosphere at a pressure of 0.1 bar. The char obtained was then ball milled for 72 h and finally activated[20]. Two step activation process comprised (i) impregnating the carbonized material with potassium hydroxide (KOH) at 1:1 and then (ii) annealed it for 1 h at 900°C in the presence of Argon at 0.1 bar. The resulting material was used to make the pellets of 3 mm in diameter by applying a force of 4.9 kN with the help of pelleting machine.

2.3.3. Kevlar

Carbonization of Kevlar fibers was done in a pyrolysis unit. Carbonization was performed by heating the fibers at 800°C for 1 h in Argon (50 ml/min). The carbonized Kevlar Fibers were used to make the working electrode.

2.3.4. CNT

CNTs were fabricated by CVD using a gas mixture evaporated from a catalyst powder (Ferrocene) and a solid carbon source (Camphor) [17]. CNTs were grown on lightly doped p-type Si substrates (resistivity $40 \div 100\ \Omega \cdot cm$), previously patterned by optical lithography. A Ti (5 nm) / Cu (100 nm) bi-layer was in fact deposited using thermal evaporation under high vacuum conditions ($\sim 10^{-7}$ mbar), with Ti acting as adhesion layer. A lift-off procedure allowed pattern definition, selectively removing the metal layer from specific areas. Patterned substrates were necessary for a selective growth as CNTs grow only on uncoated parts, that is of circular shape. CVD deposition was ran at 850°C in a quartz tube (100 cm in length, 4.5 cm in diameter) hosted in an horizontal furnace [21]. The gas mixture obtained by the co-evaporation of the reagents (camphor-ferrocene mixture in a 20:1 ratio) was inserted in the reaction chamber, where the patterned Si substrate was housed, with a constant nitrogen flux (approximately 420 ml/min). The process started with a pure nitrogen flow, to get rid of residual air inside the reaction chamber, while the temperature was increased up to 850°C. Next, the gas flow of the reagents was released in the chamber. Inside the furnace, the high temperature caused the pyrolysis of the gases with consequent deposition of the carbon species and the catalyst on the metal-free circular spots of the substrate. After a a defined reaction time the desired height of the cylinders were obtained with a growth rate of about 0.5 μm/s, the furnace was then switched off and cooled down. At the end of the process the substrate was covered by a field of vertical and uniform CNTs pillars organized in rows.

2.3.5. Common procedure

The following procedure is common to all the material used because the macroscopic output of the processes were in all cases a sort of carbonized cylinder. In fact, resulting electrodes were first electrically contacted from one side and then encapsulated in epoxy resin by leaving free the non-wired surface. All samples were treated in HNO_3 1 M for 1 h for cleaning purposes and with the final aim to have a clean surface after its construction procedure. At this stage each electrode was ready to be characterized and used as working electrode. Final electrodes geometry is shown in Fig. 1 and it is the same for all kind of electrodes fabricated.

3. Results and discussion

3.1. Electrodes characterization

3.1.1. Bamboo

Fig. 2a shows the SEM image of a pyrolyzed bamboo stick after the acid treatment. The surface presented areas with high density of holes as well as areas with low density of holes. Hole diameters varied between hundreds of nanometer to tenths of micrometer. We speculate that these holes are a key factor in determining the