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From banana stem to conductive paper: A capacitive electrode and gas sensor

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ABSTRACT

A capacitive, conductive and methanol sensor composite have been prepared by a simple process of acid hydrolysis, using potential cellulose source extracted from a residue of banana stem. The material was hydrolyzed with sulphuric acid in the presence of carboxylated multiwalled carbon nanotubes (MWCNTs) to promoted chemical interaction among cellulose and carbon surface. With these material was prepared a paper film used to design an electrode. The cellulose/MWCNT composite was investigated using x-ray diffraction, nuclear magnetic resonance, infrared spectroscopy, transmission electron microscopy and size measurement. The electrical properties were evaluated by cyclic voltammetry, impedance spectroscopy, charge/discharge testing and simulation in an equivalent circuit. The gas sensor property was evaluated by an experimental apparatus, measuring the electric current front exposure the electrode to different concentrations of methanol in different temperatures. The cellulose/MWCNT electrode displays a strong dependence of a scan rate and potential range in capacitive properties. The chemical interaction archived between MWCNT and cellulose is relevant to develop a flexible cellulose composite, with specific capacitance of 3,08 mF/cm^2 as functional nanotube integration. The flexible electrode developed in this study would be the ideal matrix to anchorage sensitive molecules and particles on specific applications like biosensor or electronic device.

1. Introduction

The waste of natural resources is an environmental concern that intensifies each decade. Thus, studies about the zero waste of matter and energy of materials increase every day. Recycling and reuse are routes used to reduce the amount of raw materials wasted. An example of it is banana, one of the most consumed fruit in the world that results in the generation of organic residues (peel and stem) which are usually discarded in landfills. However, it is possible to use these residue as raw material to obtain lignocellulosic materials and more valuable product [1,2]. This kind of material can be used in the exploitation of bio-energy waste by biochemical or thermochemical processes or can be utilized as a reinforcing agent in biodegradable composites [3]. Encountered in at least one-third of the world's vegetable matter, cellulose is the most abundant natural polymer, composed of thousands of D-glucose monomers linked by glycosidic linkages. Cellulose presents peculiar properties as biocompatibility, biodegradability, low cytotoxicity, and in addition, it is renewable and has a low cost [4,5]. Cellulose can be processed by many techniques to obtain different products, such as microcrystalline cellulose and nanocellulose, a material with potential applications that is being widely researched. Recently, the mainly process used to obtain this material is through acid hydrolysis, enzymatic hydrolysis or high energy milling [5,6]. Cellulose and its derivatives are being applied successfully in countless composite materials as reporter in literature: supercapacitors made by bacterial nanocellulose and carbon nanotube (CNT) [7]; humidity sensors with cotton linters and CNT [8]; actuators where multi-walled carbon nanotubes (MWCNT) was covalently bonded to cellulose [9]; transistors with single-walled carbon nanotubes (SWCNT) that was covalently grafted to cellulose fibrils in a regenerated cellulose film [10]; and conductive paper

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made throw a simple mixture of A4 paper waste with CNT [11]. Applications cited above used cellulose as a matrix to which are attached different CNTs. The degree of interaction between these materials determine the properties of the final composite. Composites with strong interaction are only obtained through complex processes that involve exchange of solvent, and reactions of conversion of MWCNT in imidazolide-MWCNT [12]. These processes are very efficient however complex and expensive due to the use of non-ecofriendly solvents and reagents. Therefore, the main goal of the present study is to obtain a cellulose/MWCNT composite by a simple acid hydrolysis with sulphuric acid of bleached cellulose from banana stem in the presence of the carboxylated multi-walled carbon nanotubes (MWCNT-COOH). During this process the cellulose chains are broken by H^+, which also acts as a catalyst to promote interactions between the functional groups of cellulose and MWCNT-COOH. The process also reduces the cellulose size and is based on acid hydrolysis reactions of lignocellulosic materials and esterification of cellulose by heating, stirring and ultrasonication [6,13,14]. Banana was used as source of cellulose because it represents 40% of world trade fruit [15], has a high rate of production, is produced annually, and only 12% by weight of the plant is consumed [1]. This cause large volume of residue that can be used to generate products and reduce environmental impact caused by waste, the large availability of banana waste provides almost zero cost. In addition, banana stem has low lignin content, which facilitates the delignification process, therefore, the cellulose extracted from this source has numerous advantages in relation to wood fiber source [16]. On the other hand, the stem was also selected as a source of cellulose based on experimental observation of studies performed in our research group, that indicated that the stem is rich in cellulose (a potential bio-based materials) with a lower content of fatty, which facilitates and increases the yield of the process.

2. Experimental

2.1. Materials

Banana stems were removed from *Musa sapientum* collected in the restaurant of the Federal University of Pelotas. This genre is grown in Midwest region of Brazil. The banana stem previously studied showed a higher yield in the obtainment of cellulose due to the fact that stem has higher fiber content. The MWCNT used present D × L 6–9 nm × 5 μm >95% carbon, and were purchased from Sigma-Aldrich Co. (St. Lous, USA). All other reagents were purchased from Synth (São Paulo, Brazil), all of analytical grade and used without any further purification.

2.2. Preparation of cellulose fibers

In order to obtain cellulose fiber, the banana stems were washed with distilled water and then cut into parts of 1 cm, which were placed in a vertical autoclave (Phoenix Brand, model AV-18) during 2 h at 127 °C with pressure of 1,5 kgf/cm^2. The autoclaved stems were then macerated and washed with distilled water. This crude fiber was then delignified and bleached in three stages to remove lignin, hemicellulose and pectin. The first stage of the process is an alkali extraction using a 1.8 M NaOH solution (1:20 w/v) during 90 min at 120 °C. The second stages consist of a reaction with 0.2 M $NaClO_2$ solution (1:20 w/v) in pH 4 achieved with acetic acid, during 120 min at 75 °C. Finally, a treatment with 3 M H_2O_2 solution (1:10 w/v) at pH 11 achieved with NaOH during 150 min. After each step the fibers were washed with distilled water until pH 7, dried at 50 °C and stored in a desiccator [17].

2.3. Carboxylation of carbon nanotubes

Controlled CNT carboxylation was performed according to the methodology of Goyanes [18], where a commercial MWCNT (Sigma Aldrich) was treated with a 3:1 vol solution of H_2SO_4/HNO_3 in 1:1 w/v proportion. The reaction was conducted in an ultrasonic bath (which has a nominal frequency of 40 kHz with power of 135 W) during 120 min at 30 °C. The solution was cooled in an ice bath and neutralized with NH_4OH until pH 7. The nanotubes were then washed several times and dried in an oven during 24 h at 50 °C.

2.4. Preparation of cellulose/MWCNT composite

The preparation of the composites was carried out in four stages: (1) 200 mg of MWCNT-COOH was dispersed in 100 mL of distilled water in an ultrasonic (nominal frequency of 20 kHz with power of 500W) at 25 °C during 30 min; (2) In some flasks, the dispersed MWCNT-COOH solution were added in four different aliquots, 0 mL, 5 mL, 25 mL and 50 mL, according to the following percentage by weight in relation to 1 g of cellulose corresponding to 0%, 1%, 5% and 10% of MWCNT-COOH. In each flask distilled water was added until complete a volume of 60 mL, then 1 g of bleached banana stem cellulose was added under stir. Afterwards, 10.2 M H_2SO_4 solution (1:10 w/v) was slowly added. The solution was kept under stirring during 4 h at 80 °C. (3) In sequence the flask was placed in an ultrasound bath (frequency of 40 kHz with power of 135 W) at 75 °C during 4 h. (4) The final solution was centrifuged and washed four times with distilled water and then filtered and washed until pH 7 was reached. The neutral composite was kept in water with a concentration of 25 g/L.

2.5. Paper electrode design

Fig. 1 shows the assembly of the electrode performed with the paper composite. To control the thickness, the paper was prepared through drying 15 mL of the composite solution in a 25 mL petri dish at 25 °C, a simple casting technique. Once dried, an adhesive membrane of cellulose acetate (3 M) is taped on one side and then, in the other side an electric contact is placed at one end and insulated with ethoxylated bisphenol-A glycol dimethacrylate (Bis-EMA) to ensure that only a conductive face is exposed and the electrolyte does not wet the electrical contact as shown in the electrode in scheme (Fig. 1).

2.6. Structural characterization

Particle size was measured in a nanosizer (Malvern Nano-ZS90), refractive index for cellulose was considered at 1.49, and for water 1.33. Measurements were performed in a plastic cuvette at 25 °C in a 1 g/L of composite water suspension, performing 3 records of 50 scans at each sample. A Bruker Alpha-P FT-IR Spectrometer equipped with an universal attenuated total reflectance accessory with internal reflection diamond crystal lens was used to provide the spectra. The spectrum of each sample were recorded with 64 scans in the range of 4000–700 cm^{-1} taken at a resolution of 8 cm^{-1}, in transmittance mode. Diffraction profiles were collected by a Shimadzu diffractometer, model XRD6000. The diffracted intensity of CuKα radiation (0.154 nm, 40 kV and 30 mA) was measured in a 2θ range between 10° and 30°. Crystallinity index (%Cr) was calculated from the X-ray diffraction patterns by Segal method [19] using Eq. (1), where $I_{(200)}$ is the height of the crystalline peak and $I_{(am)}$ is the minimum for amorphous material.

$$\%Cr = \frac{I_{(200)}}{\left(I_{(200)} + I_{(am)}\right)} 100 \quad (1)$$