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Synthesis of an organic conductive porous material using starch aerogels as template for chronic invasive electrodes

Ricardo Starbird [a,*], Carlos A. García-González [b], Irina Smirnova [b], Wolfgang H. Krautschneider [c], Wolfgang Bauhofer [a]

[a] Institute of Optical and Electronic Materials, Hamburg University of Technology, Hamburg, 21073, Germany
[b] Institute of Thermal Separation Processes, Hamburg University of Technology, Hamburg, 21073, Germany
[c] Institute of Nanoelectronics, Hamburg University of Technology, Hamburg, Germany

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ABSTRACT

We report the development of an organic conducting mesoporous material, as coat for invasive electrodes, by a novel methodology based on the use of starch aerogel as template. The poly(3,4-ethylenedioxythiophene) (PEDOT) aerogel was synthesized by polymerization of 3,4-ethylenedioxythiophene within a saturated starch aerogel with iron (III) p-toluenesulfonate (oxidizing agent) and subsequent removal of the polysaccharide template, followed by supercritical CO_2 drying. The chemical structure and oxidation state of the resulting material were studied by Raman spectroscopy. The morphology and surface properties of the obtained nanoporous material were investigated by scanning electron microscopy (SEM), micro computed tomography (μCT) and nitrogen adsorption–desorption techniques. The composition and thermal behaviour were evaluated by energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA) respectively. A preliminary biocompatibility test verified the non-cytotoxic effects of the PEDOT aerogel. The large surface area and wide pore size distribution of the PEDOT conductive aerogel, along with its electrical properties, enable it to be used as extracellular matrix scaffold for biomedical applications.

1. Introduction

Long-term invasive electrodes require low electrochemical impedance and biocompatibility [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT), as coating layer on invasive electrodes, is used for electrical stimulation of nerve cells and recording of brain impulses since this polymer provides lower impedance (Z) and higher charge injection (Q_{inj}) than bare metal electrodes [2–5]. These electrochemical properties of the PEDOT and its simple processability can be applied to a broad range of applications [6,7]. Besides, cytocompatible scaffolds are recommended to improve the biological response [8], because those materials emulate the topological and microstructural characteristics of the extracellular matrix. Extracellular scaffolds require properties such as a high degree of porosity, high surface-volume ratio, high degree of pore interconnectivity and appropriate pore size [8]. PEDOT aerogel as extracellular scaffold is thereby a strategy to improve the biological and electrical properties of the invasive electrode interface.

Aerogels are highly porous solid nanomaterials with unique characteristics, such as extremely low densities, large open pores and high inner surface areas that provide interesting physical properties [9,10]. They can be prepared from molecular precursors of inorganic and organic origin by sol–gel processing and subsequently by supercritical fluid drying to remove the solvents in the wet gels [7,10–14]. Templating has been traditionally used as a processing technique for the engineering of materials with controlled structure and morphology. The use of aerogels as a template gives the possibility to fabricate tailor-made nanostructured materials.

Starch aerogel microspheres in the range of 200–400 μm, obtained after supercritical drying of emulsion-templated starch gels, are promising templates for new materials in the biomedical field [13,15]. Microspherical starch aerogel template system has previously been used by Tang et al. as a negative template for the preparation of 3D-interconnected TiO_2 monoliths with hierarchical meso- and macroporosity [16]. The aerogel template was then removed via thermal treatment to decompose the starch [16]. Therefore, this approach was restricted to the preparation of monolithic materials with higher thermal stability than the template. In this work, a breakthrough technique using aerogel templating for thermally sensitive materials in the form of microspheres is herein developed.

We proposed the use of starch aerogels as a positive template for PEDOT aerogels due to its high interaction with heavy metals. Carbohydrates (e.g. starch) and derivatives form metal ion complexes with high interaction between the oxygen donor atoms present in the carbohydrates and the metal ions [18]. Iron (III) salts (Fig. 1a) are commonly used in the polymerization of 3,4-ethylenedioxythiophene (EDOT) as oxidizing agent, so that iron (III) salts can oxidise EDOT onto the aerogel surface [19]. Although, the anion in the iron (III) salt does not participate

* Corresponding author at: Eissendorfer strasse 38, 21073, Hamburg, Germany.
E-mail address: ricardo.starbird@tu-harburg.de (R. Starbird).

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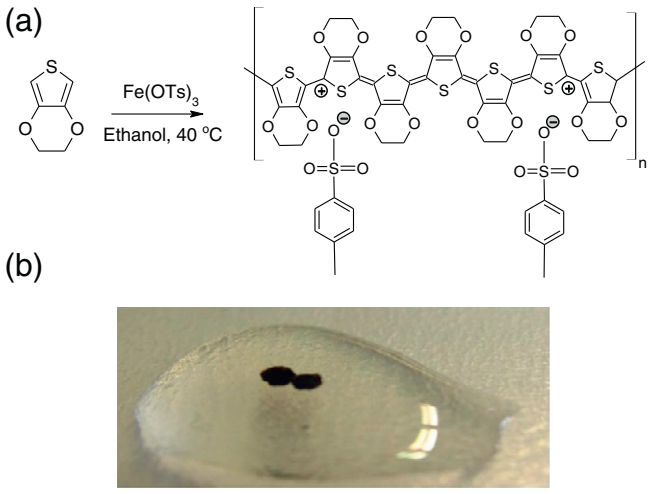

Fig. 1. (a) Chemical polymerisation of 3,4-ethylenedioxythiophene (adapted from [17]), the doped structure of PEDOT (bipolaron) enables the electronic and ionic conductivity. (b) The PEDOT aerogel in DMSO demonstrates the structural cohesion of the resulting material.

in the reaction, it influences the composition of the PEDOT polymer complex [20]. Hence, iron (III) p-toluenesulfonate ($Fe(OTs)_3$) is selected as an oxidizing agent because it is a common and well-established method in the PEDOT oxidation [21–23]. Moreover, an increase in the doping level as well as conductivity of the PEDOT were reported when p-toluenesulfonate was utilized as counterion in alcoholic media, compared with other organic solvents [21,22].

Zhang et al. first reported the emulsion template synthesis of PEDOT aerogels [7,11]. The authors attributed the absence of previous reports on the organic conducting aerogels to the difficulty in obtaining the conductive organic sol–gel during the aerogel preparation [7]. Our methodology overcomes the above-mentioned problem, since a well-studied material regarding sol–gel chemistry (i.e. starch) is used to prepare the aerogel template with defined properties. In this manner, it is feasible to avoid the conductive organic gelation step and it is possible to control the properties of the final material through the nanostructured starch template. The conductive PEDOT aerogel preserves the highly porous characteristics of the starch aerogel template, due to the high interactions with the template during the reaction (Fig. 1b). Previously, Abidian et al. [24,25] reported a significant improvement in the electrical and biocompatible properties of chronic neural microelectrode when nanostructured conductive polymers were used as interface. The inherent electrical properties of the PEDOT, along with the porous morphology acquired by the template structuration, endow the PEDOT aerogel with proper characteristics to improve the biological and electrical properties of the electrode interface. The potential application of this material is discussed in the development of invasive electrodes in biomedical science.

2. Experimental section

2.1. Materials

3,4-Ethylenedioxythiophene (EDOT) and iron (III) p-toluenesulfonate hexahydrate $Fe(OTs)_3 \cdot 6H_2O$ (yellow powder) were purchased from Sigma–Aldrich Company Ltd. Ethanol (99.8% purity), dimethylsulfoxide (DMSO) and acetonitrile analytical-grade solvents were purchased from Carl Roth Company. Native corn starch (Starch Amylo N-460) was provided by Roquette. Vegetable (canola) oil was obtained from domestic shops. CO_2 (>99.9 mol% purity) was supplied by AGA Gas GmbH. All chemicals were used without further purification. The mouse fibroblast cell line NIH-3T3 was obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ).

2.2. Template preparation

Starch aerogel (SA) microspheres were prepared according to the literature [14]. Briefly, oil:starch solution emulsions were prepared by mixing a 15% (w/w) corn starch dispersion in water with the corresponding amount of vegetable oil to get a 2:1 volume phase ratio. The resulting emulsion was then heated up to 120 °C and pressurized at 0.1–0.2 MPa in a closed stirred autoclave (Berghof RHS 295 at 300 rpm). After 20 min, the pressure of the autoclave was released and the temperature of the emulsion lowered up to 45 °C using an ice bath (cooling rate: 3 °C/min) under agitation (marine type; d = 40 mm; stirring: 1400 rpm). After centrifugation, particles were separated from the oil phase, soaked in ethanol and placed in the refrigerator (4 °C) for retrogradation for 48 h. After retrogradation, starch particles were transferred to a fresh ethanol solution (i.e., second solvent exchange). Finally, the resulting starch alcogels were dried by extraction of the solvent with a continuous flow (2–4 Nl/min) of supercritical carbon dioxide ($scCO_2$) during 4 h at 40 °C and 11.0–12.0 MPa.

2.3. EDOT polymerization

PEDOT aerogel (PA) was prepared adding *ca.* 40 mg. of aerogel starch spheres to 250 μL of one saturated solution of iron (III) p-toluenesulfonate in ethanol. Ultrasonic stirring was used until the starch spheres were deposited in the bottom of the vial. The starch spheres acquired a yellowish appearance and this composite (SFeA) was stored for 24 h in solution and then washed with 10 mL of ethanol. Subsequently, 0.50 mmol of EDOT was dissolved in 750 μL of ethanol and added to the SFeA. This mixture was left to stand for 24 h at 40 °C. In these conditions a material with a constant blue colour was produced. The obtained starch PEDOT aerogel (SPA) was washed again with 1 mL of ethanol at least 5 times. Alternatively, in an attempt to study the effect of the template during the synthesis, a sample of PEDOT was prepared in the absence of the starch template using the same procedure as described above.

The obtained starch PEDOT aerogel was washed with DMSO in order to remove the starch template. The process was repeated until no white precipitate was observed, when few drops of acetonitrile were added to the DMSO. Finally, the PEDOT aerogel was washed and stored in acetonitrile (*ca.* 500 μL). The resulting material was dried by extraction of the acetonitrile with a continuous flow of supercritical carbon dioxide ($scCO_2$).

2.4. Aerogel characterization

PEDOT particles, starch aerogels and composites were studied by scanning electron microscopy (SEM). Starch aerogels and composites were characterizated by energy dispersive spectroscopy (EDS), thermal gravimetric analysis (TGA), Raman spectroscopy, N_2 adsorption–desorption analysis and helium pycnometry. The final microstructure of the PEDOT aerogel was studied by micro computed tomography (μCT). SEM was conducted in a ZEISS Supra 35 field-emission-gun scanning electron microscope at 5–10 kV and samples for SEM were prepared by cutting some pieces of the resulting PEDOT-starch aerogels and placing them onto carbon adhesive tape. Energy dispersive spectroscopy (EDS) was executed at 20 kV using an Oxford SDD detector. TGA measurements were performed in a Shimadzu TGA-50 Thermogravimetric Analyzer. Each sample was heated at 10 °C/min of heating rate in a nitrogen atmosphere up to 600 °C. Prior to thermal treatment, the samples were dried in a vacuum oven at 80 °C for 24 h. Raman spectra were obtained and recorded with one excitation line from the visible range (633 nm) using a multichannel Jobin-Yvon HR800