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F. Delbecq, T. Kondo, S. Sugai, M. Bodelet, A. Mathon, et al.. A study for the production of a polysaccharide based hydrogel ink composites as binder for modification of carbon paper electrodes covered with PEDOT:PSS. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2021, 628, pp.127380. 10.1016/j.colsurfa.2021.127380 . hal-04392858

HAL Id: hal-04392858

<https://hal.science/hal-04392858>

Submitted on 22 Jul 2024

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A study for the production of a polysaccharide based hydrogel ink composites as binder for modification of carbon paper electrodes covered with PEDOT:PSS

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ABSTRACT

Flaxseed and guar gums were studied for their potential to produce in water stable viscous fluids loaded with poly(styrene sulfonate) PSSNa and poly(3,4-ethylenedioxythiophene) (PEDOT):PSS as hydrogels or viscous ink composite materials. In case of the composite hydrogels, their contents and mechanical behaviors were analyzed by FT-IR spectroscopy and rheology respectively. Once dried on a glassy carbon electrode, for a sample containing PEDOT:PSS, the morphology of the thin layer was observed by FE-SEM for monitoring the quality of the coating. Later, for further practical reasons, performant working electrodes were also prepared from these hydrogels simply by casting on a small piece of carbon paper. PEDOT electropolymerization were tried using a coating made of PSSNa in mixture with one of the polysaccharides. This step showed some difficulties due to the enhancement of the hydrophilic character of the carbon paper surface. Then, a definitive improvement of a direct electropolymerization of PEDOT was permitted by using another type of coating material always involving the previous guar gum-PSSNa composite reinforced with 4 wt % of exfoliated graphite powder in order to enhance both hydrophobicity and adhesion of the electropolymerized PEDOT. Finally, additional cyclic voltammetry experiences such as Electrochemical Impedance Spectroscopy were carried out to identify two of our most promising candidates of PEDOT:PSS based electroconductive materials.

Key-words: electroconductive polymer, composite hydrogels, printable electrode, cyclic voltammetry.

1. Introduction

Today, we assist to an emphasis on the preparation of structured composite materials consisting of renewable biosourced elements such as non-edible polysaccharide (cellulose, gums, chitosan) suitable to form hydrogels and incorporate carbonaceous nano-sized materials (nanotubes, graphene) or metallic and oxide nanoparticles, especially for various applications in the fields of sensors and solar cells [1].

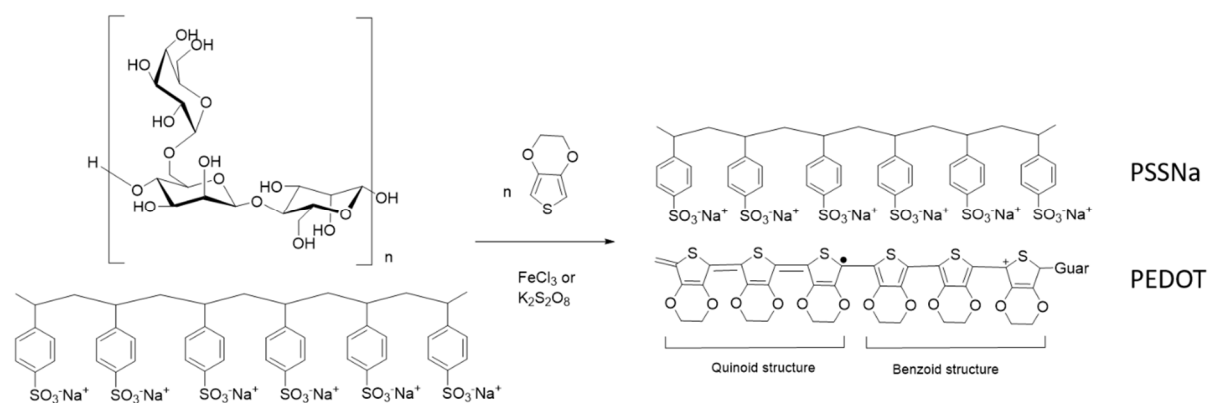
Polysaccharides from plants are often partially soluble in water and form viscous solution or gels at a minimum level of concentration. These viscous fluids are essentially based on physical bonds that cross-link the polymer chains to generate cavities able to entrap water or other aqueous solutions possibly loaded with various chemical species. Sometimes for specific applications, it is useful to produce strong hydrogels. Thus, chemists are able to create strong chemical and covalent bonds using highly toxic chemicals reagents such as dialdehydes or carbodiimides soluble in organic solvents or water to cross-link the polymer networks. Now, to respect most of the green chemistry principles, without the employ of any chemical additive, just by using biodegradable and eco-friendly polysaccharides, it is now conceivable to consider natural polysaccharides as biodegradable and biocompatible components of electronic composite materials. This kind of strategy could also permit specific applications in the field of biomedical research [2].

In this work, we focused on two different polysaccharides and compared them to reach our objective. The first one is the flaxseed gum obtained from the exudates of the plant seed wastes; its composition includes a complex mixture of acidic biopolymers composed mainly of glucose and xylose sub-units forming the main polymer backbone [3]. It could also incorporate in its structure other monosaccharides such as pentose (arabinose, rhamnose), galactose or other hexuronic acids found in slight amount. The second candidate is the guar gum, a branched biopolymer with a linear backbone including in its structure mannose sub-units decorated with a galactose residue at every second repeating unit forming the chain. Now, guar gum is known as a biopolymer that proved on many occasions its potential for exfoliating graphite into graphene sheets in water and for the stabilization of PEDOT inside the matrix of an ionogel [[4], [5]].

Recently, to form remarkable electroconductive nanocomposite materials, full organic conducting polymers (polyaniline (PANI), polypyrrole [[6], [7], [8], [9], [10], [11], [12]], polythiophene) were recognized for their good environmental stability, high conductivity, improved transparency and low oxidation potential. Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) expresses high stability and enough conductivity (10 S/cm) at an oxidized state [[13], [14], [15], [16]]. This is one of the most stable electroconductive polymer compared to polypyrrole (PPy); another polymer that shows conductivity values usually measured in a large window from 2 to 100 S/cm. By opposite, PEDOT has also the potential for enhancing the capacity performance of materials composing an electrode. However, when produced by typical methods such as emulsion polymerization or interfacial polymerization using a surfactant, starting from a liquid 3,4-ethylenedioxythiophene (EDOT) precursor, the resulting PEDOT is generated as an irregular amorphous material, the main cause of its reduced performance. Unfortunately, sole PEDOT is also an insoluble polymer [[17], [18]] and it is preferable to carry out the polymerization of EDOT in presence of a linear sulfonate polysaccharide [[19], [20], [21]] doubly employed as a doping agent through electronic interactions with the cationic oxidized PEDOT. Similar strategies could be carried out using polystyrene sulfonate (PSS or PSSna), a well-known and commercial water soluble polyelectrolyte [[22], [23]]. Thus, PEDOT:PSS system could be produced in water over the PSS template by oxidative chemical or electrochemical polymerization. By the way, these reactions often lead to the non-desired precipitation of insoluble dark-blue PEDOT:PSS aggregates, especially in an aqueous medium. Besides, a polysaccharide-PEDOT:PSS based nanocomposite should exhibit many remarkable properties, such as large specific surface area, high mechanical properties and enough biocompatibility keeping intact the electrochemical capacity of the entrapped synthetic conductive polymer able to modulate the original characteristics of the resulting water dispersion such as mechanical and rheological properties [[24], [25], [26], [27], [28], [29], [30], [31], [32]]. However, it exists in the literature several examples of strategies involving

synthetic polymers such as poly(acrylic acid) (PAA) or poly(vinyl alcohol) employed as binders [[33], [34], [35], [36]].

In this present work as reported in the scheme 1 for guar gum only, both stable flaxseed or guar gum/ PEDOT:PSS composite materials have been *in-situ* synthesized using a soft hydrogel template containing them with two different oxidizing agents as the polymerization initiators.



Scheme 1. Chemical procedure from the production of an hydrogel composite from guar gum loaded with a defined amount of PEDOT:PSS.

Among new types of electrodes reported in the literature, bare carbon paper is a material made of an interpenetrated network of carbon fibers of low hydrophilicity and relative poor surface area. Fundamentally, the fibers that compose carbon paper show a diameter of 7 μm in average and they are all connected by thinner membranes at the origin of a great number of interspaces between the fibers. Both structures are complementar and could work together to form a conductive network ready for various chemical or electrochemical modifications as reported in the Table 1.

Table 1. A short report of recent chemical modifications of carbon paper sheet for specific applications.

Modification	result	Application	Ref.
1. NaOH alkaline treatment	Oxidation and $-\text{OH}$ functionalization	Interlayer for lithium sulfur cell	37
2. Electropolymerization	PPy/ CO_3O_4	Supercapacitor	38
	PPy	Supercapacitor	39
	CNT/PPy	Phenolic treatment	40
	Br doped/ PEDOT	Hg ion detection	41
	P3MT-COOH/ glucose oxidase	Glucose fuel cell	42
3. Potassium dichromate oxidation	PANI		43
	$-\text{OH}/ \text{C}=\text{O}/ -\text{COOH}$ functionalizations ; PVA/ H_3PO_4 coating	Supercapacitor	44
4. Hydrothermal treatment $\text{H}_2\text{SO}_4/ \text{H}_2\text{O}_2$ (30 %)	PVA/ $\text{H}_3\text{PO}_4/ \text{PMo}_{12}$ coating	Supercapacitor	45

P3MT: Poly(3-methyl thiophene) ; CNT: carbone nanotube

In this present work, at each stage of our process, the air vacuum dried materials were characterized by FT-IR, UV spectroscopy, FE-SEM, and the PEDOT viscous aqueous dispersions by rheology. The gum/ PEDOT:PSS hydrogels were used to modify carbon paper (CP) electrodes simply by successive casting and drying steps. The incorporation of a slight amount of exfoliated graphite furnished a derived guar gum/graphite/PSSNa able to promote a better adhesion of electropolymerized PEDOT on the surface of the modified CP electrode [[46], [47],[48]]. In case of the EDOT electropolymerization, for every situation or template, the quality of the CP fiber coating was monitored by FE-SEM observation. In the same time, as the main conventional electroanalytical method, cyclic voltammetry (CV) permitted to evaluate the potentials of all altered CP electrodes.

2. Experimentals

2.1. Materials

Ethanol, poly(sodium-*p*-styrene sulfonate) with a molecular weight of 70000, 3,4-ethylenedioxythiophene 97 % (EDOT) and graphite powder were purchased from Acros Organics and Aldrich respectively. Potassium persulfate p.a. (KPS or $K_2S_2O_8$), Iron (III) chloride, reagent anhydrous powder 98% ($FeCl_3$) were also obtained from Acros Organics. Acetonitrile, dimethyl sulfoxide (DMSO), tetrabutylammonium tetrafluoroborate 99 % (TBATFB) and lithium perchlorate ($LiClO_4 \geq 95\%$) were purchase from Sigma Aldrich. Guar and Flaxseed gums were purchased from Sigma Aldrich and Xi'an Tian Guang Gyuan Biotechnology Co. Ltd (China) respectively. The carbon paper referenced as TGP-H-60 was obtained from Toray. Co., ltd (Japan).

2.2. Preparation of nanocomposite gum/PEDOT:PSS gel-like aqueous dispersion

To 2.0 mL of water were added a defined amount of gum (0.5-4.0 wt %). The resulted turbid dispersion was sonicated for 15-20 minutes until a viscous solution was formed. Then, another defined amount of PSSNa (0.08-0.24 g) was added to the solution and the resulted mixture was sonicated for more than 20 minutes. Later, the adequate mass of EDOT (0.05-0.15 g), calculated in function of the supposed sodium styrene sulfonate (SSNa) molar number of subunits constituting the PSSNa chains. It was added to the previous stable and homogeneous suspension. In the last step, the oxidation agent (0.04 g for KPS or 0.01 g for $FeCl_3$) was added to the mixture. In case of KPS, the viscous solution or hydrogel needed to be further heated at 80°C under argon atmosphere. For $FeCl_3$, the polymerization was only carried out at room temperature. All composites materials were obtained as a deep blue viscous fluid.

2.3. Fourier-Transform (FT-IR) Infrared Spectroscopy

FT-IR (ATR) of the dried samples were recorded on FT-IR 4000 Jasco in a range of 500 to 4000 cm^{-1} operated at 4 cm^{-1} resolution. FT-IR spectra of hydrogels and electropolymerized PEDOT coated carbon papers were measured using crushed samples by means of KBr method with the same apparatus.

2.4. UV spectroscopy

UV-Vis absorption spectra were recorded using a Jasco V550-Vis spectrophotometer using a sonicated water dispersion of the dark blue viscous fluid.

2.5. Field Emission Scanning Electron Microscopy (FE-SEM)

The observations were conducted using a Jeol JCM microscope with a small amount of a selected dried aerogel on a carbon coated Pd-Pt grid and dried again for 1 hour under reduced pressure. The morphology of each modified carbon paper electrodes was also controlled by the same manner.

2.6. Rheological measurements

For each significant sample, the viscosity measurement was carried out using a Physica MCR 301 from Anton Paar. It is a rotational rheometer equipped with a double gap measuring system able to regulate the temperature in a window from -40 to 200°C. The measurements were monitored by the Rheoplus software. All experiments were performed at 25°C and the viscoelastic behavior was checked for frequencies ranging from 0.1 to 10 Hz. Two replicates were performed for each sample. Thus, 0.5 g of a selected robust gel was uniformly laid between a disc and its corresponding cone forming the measuring system with 2.5 mm of diameter. The storage and loss modulus were plotted as a function of stress at 25°C. The viscoelasticity of each sample was characterized in terms of elastic modulus (G') and the loss modulus (G'').

2.7. Contact angle measurement and adhesion tests

A monolayer of dark blue native composite dispersion (or a re-dispersed dried gel in 30% ethanol aqueous solution produced by means of sonication for 3 hours) was first casted on a glass slide to form regular circle showing a diameter of 1.5 cm. Then, the samples were kept at room temperature in a desiccator. The sample slides were placed on the stage of a digital microscopic camera Kruss Dropshape Analysis System DSA 10 MK2. A drop of deionized water (10 μ L) was deposited on the surface of the sample layer using a syringe and a digital micro-photograph of the horizontal view of the water drop was taken briefly. The contact angle of each sample was determined from the photographs by the Logiciel Drop Shape Analysis. Similar experiments were performed to investigate the hydrophobic nature of each modified carbon paper electrode surfaces.

2.8. Preparation of guar gum/PSSNa/exfoliated graphite hydrogel composite

The exfoliation of graphite powder in water was realized as follow: 0.4 g of graphite, 0.4 g of a natural gum and 0.4 g of PSSNa were crushed together in a mortar and introduced in 18.8 mL of water followed by sonication for 1 hour. The material was obtained as a black hydrogel employed without further purification in the next stages of our study. The real production, the shape and the size of the expanded graphite sheets were observed using the Transmission Electron Microscopy (TEM). The contents of a diluted hydrogel composite containing 4 wt % of exfoliated graphite was observed by depositing a drop of a clear gray solution on a TEM grid (300 meshes Cu Grid) coated with a carbon film. The grid was dried under reduced pressure at room temperature overnight. All images were recorded using a Jeol JEM-2011 electron microscope operated on an accelerating voltage at 100 kV. For X-ray diffractions measurements, a fraction of the black crushed sample was also employed to obtain the XRD

pattern with a Rigaku Ultima IV diffractometer by using a graded elliptical side by side multilayer optics monochromated CuK α radiation equipped with a flat camera ($\lambda = 0,15$ nm, 40 Kv, 40 mA).

2.9. Electrochemical measurements and electropolymerization of EDOT on pristine or modified carbon paper electrodes

Cyclic voltammetry (CV) measurements of gum/PEDOT:PSS composite materials were conducted via a three electrode system on Metrohm autolab PGSTAT 204 monitored by the software NOVA. This procedure employed a saturated calomel electrode (SCE) and a platinum wire as the reference and the counter electrode respectively. Pristine and coated carbon paper of 10 mm long and 15 mm width were used as the working electrodes and the scan rate varied between 50 and 100 mV.s⁻¹. Thus, for the gum/PEDOT: PSS hydrogel composite, the dark fluids were deposited and dried covering a delimited area on the small carbon paper sheet. In case of dried solid composite materials, the powdered materials could be redispersed in 30 % ethanol-solution by sonication for 3 hours, and the same above procedure was also used to determine the conduction potential. Prior to each experiments, ferrocenium/ferrocene (Fc⁺/Fc) redox potential was measured for calibrating the reference electrode. For PEDOT:PSS composite systems coated on carbon paper, a 0.1 M LiClO₄ aqueous solution was used as the electrolyte and the CV curves were recorded at scan rates of 100 mV.s⁻¹ for a variation of potential found between -2.0 and + 2.0 V. Each experiment was repeated three times to ensure the reproducibility of the method. The PEDOT production by electropolymerization coating was carried out as follow: in 100 mL of acetonitrile were added 0.967 g (2.93 mmoles) of TBATFB. To the resulted 0.025 M electrolyte solution were also added 0.36 g (2.53 mmoles) of EDOT employed during the electropolymerization procedure/PEDOT coating, performed at 150 mV.s⁻¹ scan rates, in a range of potential from - 2.0 to + 1.2 V, directly on each simple gum/PSSNa coating or made of guar gum/PSSNa/exfoliated graphite deposited layer. Indeed, the experiment was realized on a delimited area of the carbon paper. A rapid control made by typical Nyquist plots of modified and selected CP electrodes was recorded in the frequency range of 1 Hz and 100 Hz using the same 0.1 M LiClO₄ aqueous solution as the electrolyte.

3. Results and discussion

3.1. Preparation and characterizations of gum/PEDOT:PSS hydrogel dispersions

In order to form a robust hydrogel template for the *in-situ* generation and stabilization of PEDOT macromolecules, the gum powders were first added to deionized water. For a concentration of 4 wt % the aqueous suspension remained as a viscous fluid state without apparent syneresis phenomenon. With a minimum of 4 wt % of concentration, flaxseed gum afforded also a robust and turbid gel in water with a pH value of 5 due to the acidic nature of its hexuronic acid subunits. Using guar gum at the same concentration, a white translucent and overall neutral gel was obtained in a remarkable short time after water addition. To promote the chemical production of a crystalline PEDOT, we tried to incorporate in both previous hydrogel networks a define amount of PSSNa as the polyelectrolyte able to ensure a supported linear polymerization of EDOT monomers. The results of the hydrogels preparations were done on the Figure 1.

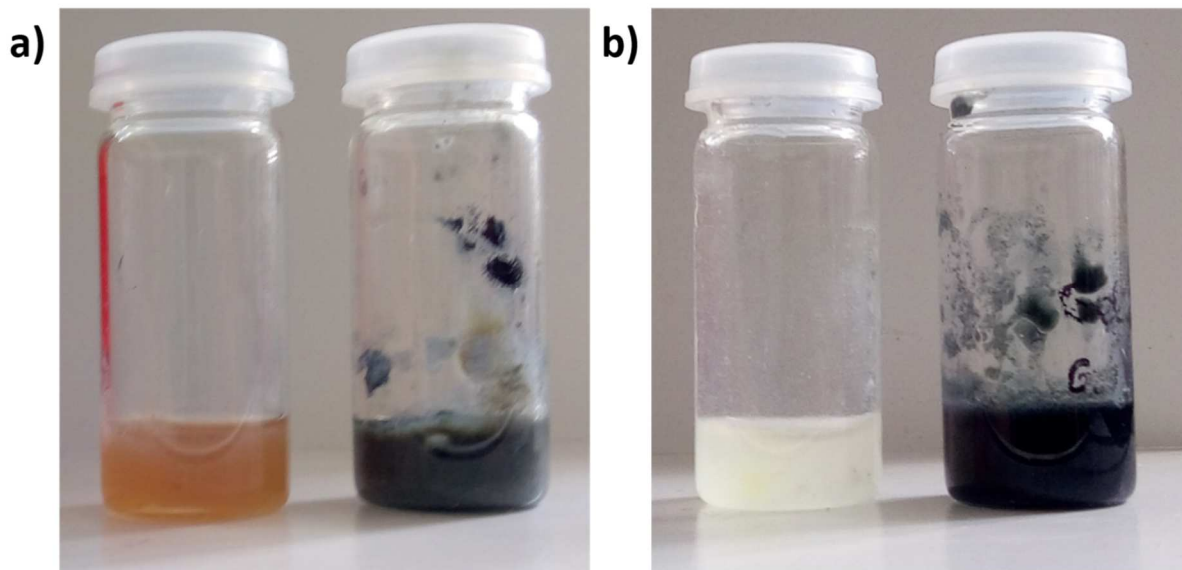


Fig. 1. Photographs of hydrogels samples, on each picture from left to right, hydrogel of 4 wt % gum mixed with 4 wt % of PSSNa and same hydrogel loaded with PEDOT: a) from flaxseed gum ; b) from guar gum.

The indirect and last role of gums was the partial replacement of PSSNa excess currently employed for developing composite materials. Usually, an excess of PSSNa shows a negative effect on the PEDOT electrochemical performances and some recent papers reported after the PEDOT chemical production, the employ of DMSO to remove a great part of PSSNa for restoring the PEDOT electroconductive capacity [50]. During the optimization for hydrogel production process, we increased progressively the concentration of PSSNa until it reached a maximum of 4 wt % before it begins to interfere with the polysaccharide inter-chains interactions. Beyond this concentration, the hydrogel networks was suspected to lose its normal porosity and could become unable to entrap more water.

In the next stage of the process, once PEDOT was introduced to the gum/PSSNa hydrogels, even sonicated for a long time, the liquid monomer formed an unmiscible phase located on the top of the hydrogels. But after addition of a slight amount of KPS or FeCl_3 to the flaxseed gum-based hydrogels, both solid and water-soluble initiators drag the monomer into the viscous medium and it began to diffuse homogeneously all the way to the bottom of the flask. Without stirring, the reaction produced EDOT oligomers and the green hydrogels turned into the desired deep blue viscous liquid. As depicted on the Figure 1, using KPS as the oxidizing agent, generally the formation of PEDOT takes two days leading to the formation of a characteristic dark blue composite hydrogel. With flaxseed gum, using KPS the blue hydrogel was obtained as a viscous fluid, however using FeCl_3 , the material was recovered as a more elastic hydrogel (result not shown here). It is possible to imagine further ionic interactions between Fe (II) or residual Fe(III) cations. Certainly, Fe cations could bind to gum or PSS in the hydrogel matrix through their carboxylate or sulfate pendant groups. By opposite in case of KPS, using guar gum, the dark-blue material was formed quickly as a strong gel with a pH around 7. Unfortunately, several weeks later even if we did not observe the formation of PEDOT aggregates in the medium, the guar gum based hydrogel has started to fluidize.

Then, the fourth types of hydrogels were casted and dried in vacuum on a glass slide to afford solid and regular membranes observable by electronic microscopy (FE-SEM) observations. The results are given in the following Figure 2.

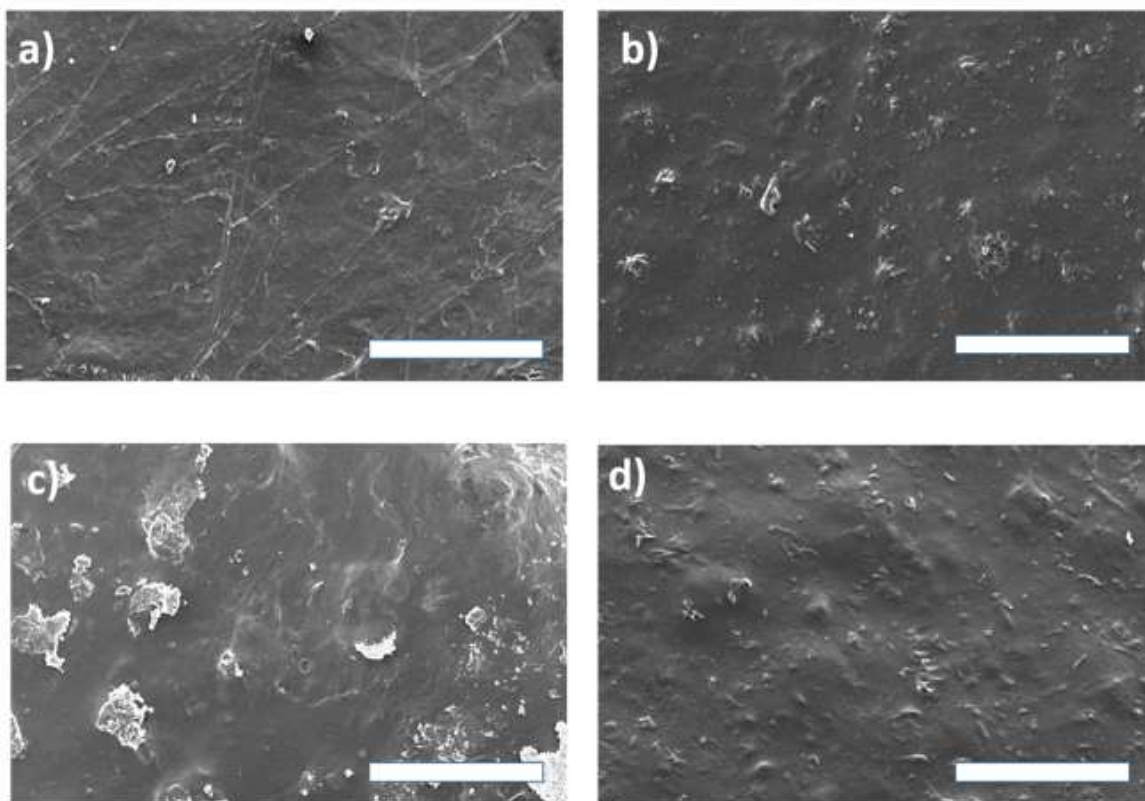


Fig. 2. FE-SEM images of surface morphologies from various hydrogels casted and dried on a glass side: a) from flaxseed gum/PSSNa ; b) from flaxseed gum/PEDOT:PSS ; c) from guar gum/PSSNa ; d) from guar gum/PEDOT:PSS. (The scale bars were set up at 400 μm).

On each photograph, the surface of the material appeared as a homogeneous membrane without apparent fracture. In the figures 2b and 2d, it is difficult to affirm the presence of PEDOT oligomers, however some kind of flower-like structures seemed to be hidden behind a thick layer of the gum/PSSNa mixture. Interestingly, when dehydrated by a freeze drying procedure, the flaxseed gum hydrogel shows a typical feature of a polymer-based aerogel networks displaying large cavities able to entrap a large volume of water. Compared to native flaxseed gum, 4 wt % of PSSNa started to improve its crystallinity character to the entire hydrogel networks without any loss of gelation ability. Unfortunately, in case of the FeCl_3 catalyzed polymerization, the networks of the resulted PEDOT enriched aerogel appeared more irregular, with a large amount of PEDOT granular shaped materials filling the cavities (results not shown here). Curiously, the same phenomenon was never observed with KPS, and the morphology of the formed composite aerogel was very well structured displaying polygonal structures. For all reasons, we abandoned the idea to employ FeCl_3 as the polymerization promoter and started to focus on KPS for the whole study.

3.2. FT-IR spectroscopy of dried material

All dried materials were studied by FT-IR spectroscopy to understand the interactions between the different elements of our composite materials. For the native flaxseed gum spectrum (see Figure S1, ESI), all typical bands of polysaccharide were found in the spectrum: a broad band at 3284 cm^{-1} characteristic of the $-\text{OH}$ stretch, a signal located at

2936 cm^{-1} attributed to the CH asymmetric stretch, another band at 1629 cm^{-1} for –OH bending vibration and 1412 cm^{-1} representative of C=O stretching vibration from carboxylic acid of the uronic acid sub-units. A strong signal at 1037 cm^{-1} representative of C-O stretching was also detected. For guar gum, despite the absence of carboxylic acid band, we obtained the same pattern with successive bands founds at 3421, 2922, 1653, and 1076 cm^{-1} . Once PSSNa was mixed in equal mass with one of the gums, its presence enlarge the signal at 1650 cm^{-1} and other appeared at 1496 and 1411 cm^{-1} on both spectra. The signals were relative to the skeletal vibration band of C=C in the aromatic rings. The vibration bands recorded between 1183 and 1037 cm^{-1} were also assigned to SO_3 asymmetric stretching vibration, which often appears as a broad band showing a shoulder. In case of flaxseed gum, when PEDOT was *in-situ* produced from EDOT using FeCl_3 or KPS the spectra were comparable. Curiously on the Figure 3, the spectra give the impression of keeping the =C-H bending vibration bands of the monomer and the =CH deforming bands at 3100 and 891 cm^{-1} , however when the dried materials was subjected to the higher temperature than monomer boiling point, both signals disappeared on the spectra of the Figures S2 and S3 of the ESI. If we come back on the FT-IR spectra of the Figure 3, only peaks located at 1366 and 1488 cm^{-1} that could be attributed respectively to the asymmetric stretching mode of C=C (quinoid) and C-C (benzenoid) between two successive rings. The bands located at 1185, 1129, and 1007 cm^{-1} are currently the mark of the C-O-C bending vibration in ethylene dioxy moieties. Besides, the bands at 676, 764, 831, and 934 cm^{-1} are the characteristic bands of C-S-C stretching vibrations in thiophene rings.

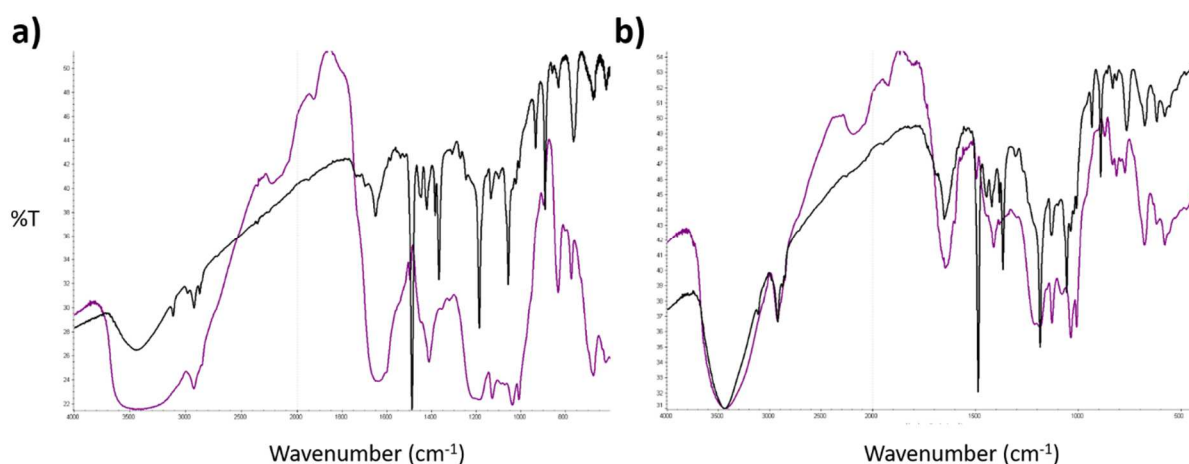


Fig. 3. FT-IR spectra of gum-PSSNa dried hydrogel (given in purple) and dried hydrogel composite containing PEDOT:PSS (given as black chart): a) for flaxseed gum ; b) for guar gum.

Some recent studies proved the relationship between the height ratio for two peaks located at 670 and 830 cm^{-1} and the polymerization degree of PEDOT. Herein, from integration of both IR bands, the signals are not equal and this result became the evidence of limited degree of polymerization inside the gel matrix [17]. Considering flaxseed and guar gum showing UV maximum absorption at 210 and 299 nm respectively, starting from the dark blue aerogel redispersed in water, it was difficult to detect the specific absorption peaks of EDOT generally observed at 230 and 260 nm also corresponding to the =C-H of the monomer or extremities of suspected small oligomers.

3.3. Viscoelastic behavior of the hydrogel composites

Except for hydrogels reinforced by the presence of Fe(III) cations, for all current flaxseed gum/PEDOT:PSS hydrogel composites, the material expressed a solid-like behavior just for frequencies inferior or equal to 1 Hz as demonstrated on the Figure 4. In fact, the material showed a behavior near to thixotropy and once the material was subjected to a mechanical stress, it could become a fluid easily printable, ideal for the modification of a solid electrode [49]. By opposite, the hydrogel incorporating iron cations inside its networks had a typical feature of gel with storage G' and loss modulus G'' almost parallel for all frequencies (see Figure S4 of the ESI). In case of guar gum/PEDOT:PSS hydrogels and compared to the previous flaxseed gum gel using KPS, as depicted on the Figure 4a, for the same range of frequencies, despite its gel-like aspect, the graphic response show unstable behavior during the experiments. However the viscous fluid was also easily casted on a flat surface like a glass slide or later on a piece of carbon paper.

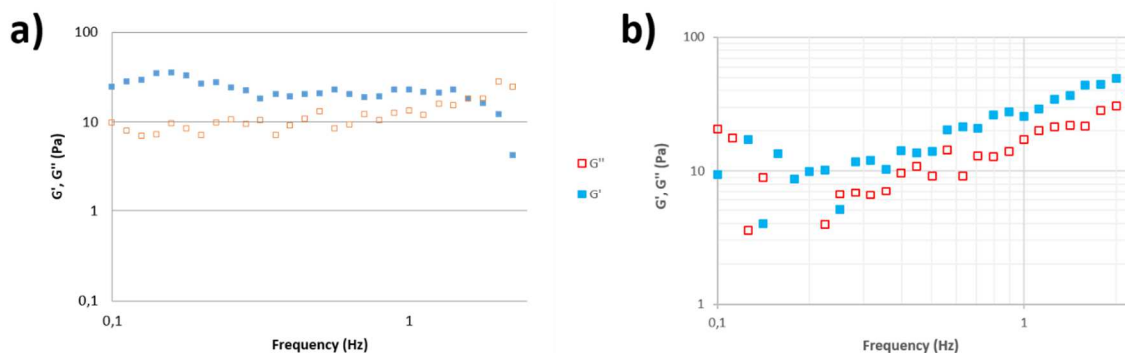


Fig. 4. Frequency dependence of the storage moduli (G') and loss moduli (G'') of: a) flaxseed gum/ PEDOT:PSS hydrogel ; b) guar gum/PEDOT:PSS hydrogel.

3.4. Identification of the best material to compose a modified working electrode

During the preparative experiences, each selected composite and dried material were introduced in 30 % aqueous ethanol solution and the resulted suspension was subjected to sonication for three hours to afford a dark blue paste suitable for being deposited and dried on a glassy carbon (GC) electrode. Despite our efforts, we were not able to reproduce the same procedure employing on this occasion the guar-based composite material. Then, 5-10 mL of Nafion ® solution was expected to act as an additional binder to complete the preparation of a modified electrode. In the first part of this study, a simple comparison between the electrochemical properties of various flaxseed gum-based materials produced using FeCl_3 or KPS was realized in 1M sulfuric acid (H_2SO_4) aqueous solution as the electrolyte. Interestingly, on the Figure 5a, in case of the composite material prepared with KPS, the CV showed an enlargement of 4V recorded for the plotted potential window and its curve shape was almost symmetric. Curiously, the potential window was larger than the results commonly encountered for simple PEDOT:PSS system with positive potential limit set at + 0.8V in average [17], evidence of PEDOT overoxidation. When each native sample of flaxseed gum/PEDOT: PSS were dried on a GC electrode, the potential window still remain unchanged in a voltage range evolving from -2.0 to + 1.8 V, but the electrical conductivity

remained constant with values closed to $2.25\text{-}2.36 \cdot 10^{-5}$ S/cm. Even all results were not given here, for the other samples prepared with FeCl_3 , the voltage range was comprised between values varying from -1.2 and $+1.2$ V. Besides, an unidentified cathodic current peak E_{red} was observed around -0.45 V. Regarding these results, we obtained another reason to pursue our investigation only with materials produced by using KPS as the main PEDOT polymerization initiator.

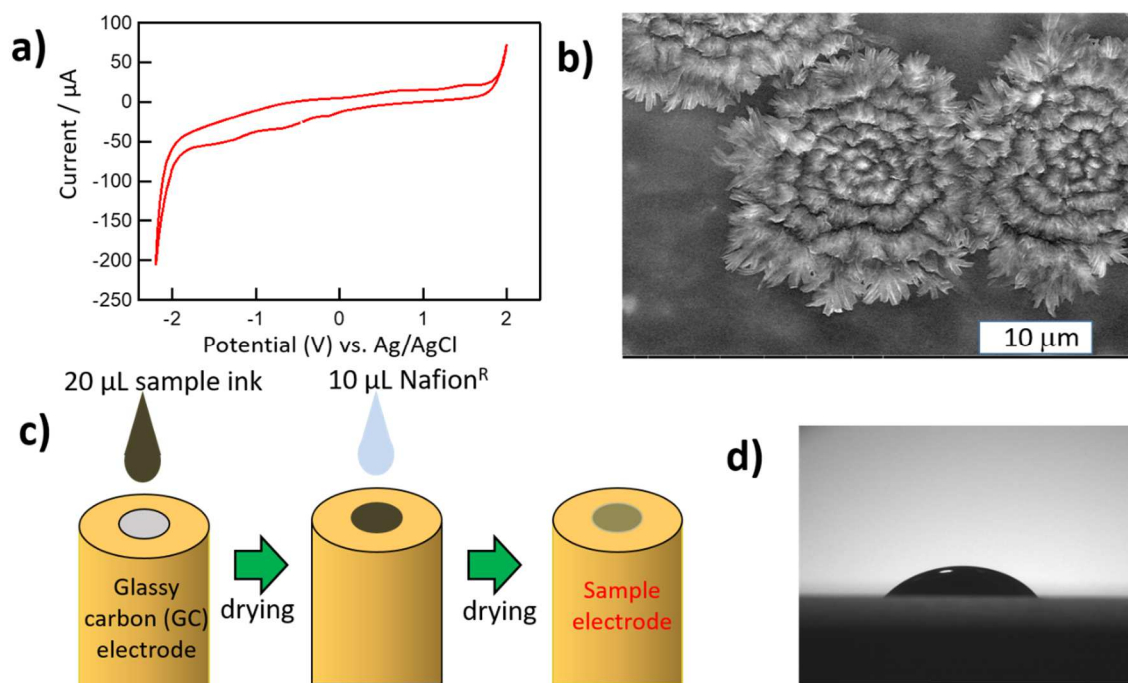


Fig. 5. a) Cyclic voltammogram of flaxseed gum/PEDOT:PSS recorded in a 1.0M H_2SO_4 solution ; b) FE-SEM observation of flaxseed gum/PEDOT:PSS ethanol dispersion on glassy surface ; c) Procedure for modification of GC electrode ; d) Water contact angle for electrode coated with dried flaxseed gum/PEDOT:PSS hydrogel.

On the Figure 5d, according to the sessile drop method, the homogeneous dried layer of our composite material expressed some wettability when placed in contact with deionized water with a contact angle of 36° . If we look at the FE-SEM observation from Figure 5b, the CV result could be connected to the particular flower-like crystalline morphology of the material and its localized hydrophobicity, especially if we consider the possible moderate EDOT conversion during the chemical synthesis of PEDOT, also proven by FT-IR analysis of the sample. In fact, the larger potential windows could be explained by the weakened hydrogen bonds between water and the surface of the modified electrode despite the existence of a Nafion-based coating, bearing in mind that hydrogels made with KPS were neutral viscous fluids. Unfortunately, we had to face a problem of reproducibility caused by the rapid detachment of the composite material lens from the GC surface.

3.5. Modifications of carbon paper surface by direct coating or electropolymerization on already modified electrodes

To remedy the adhesion problem of dried material we have chosen to use small pieces of carbon paper instead of the usual GC electrode, furthermore with Indium tin oxide (ITO) electrodes we have also encountered the same problem of coating detachment. As reported

on the Figure 6 and more exactly on the Figure 6b, the flaxseed gum/PEDOT: PSS composite material once produced was casted and dried on the surface of the CP. Herein, the solution was homogeneously deposited what resembles PEDOT deposited along the carbon fibers. On the picture 6c, in case of guar gum/PEDOT:PSS material, the product remained gathered in small groups on the exterior side of the CP and formed some kind of aggregates inside the apparent cavities. However, a simple exposure to DMSO [50] revealed by digging a non-uniform organization of the PEDOT granular species masked by the PSSNa layer. Thus, the electroconductive material was concentrated at the intersections of the carbon fibers. We have also to mention that employed small volume of DMSO turned into a blue and colored solution becoming the evidence of a non-desired PEDOT dissolution.

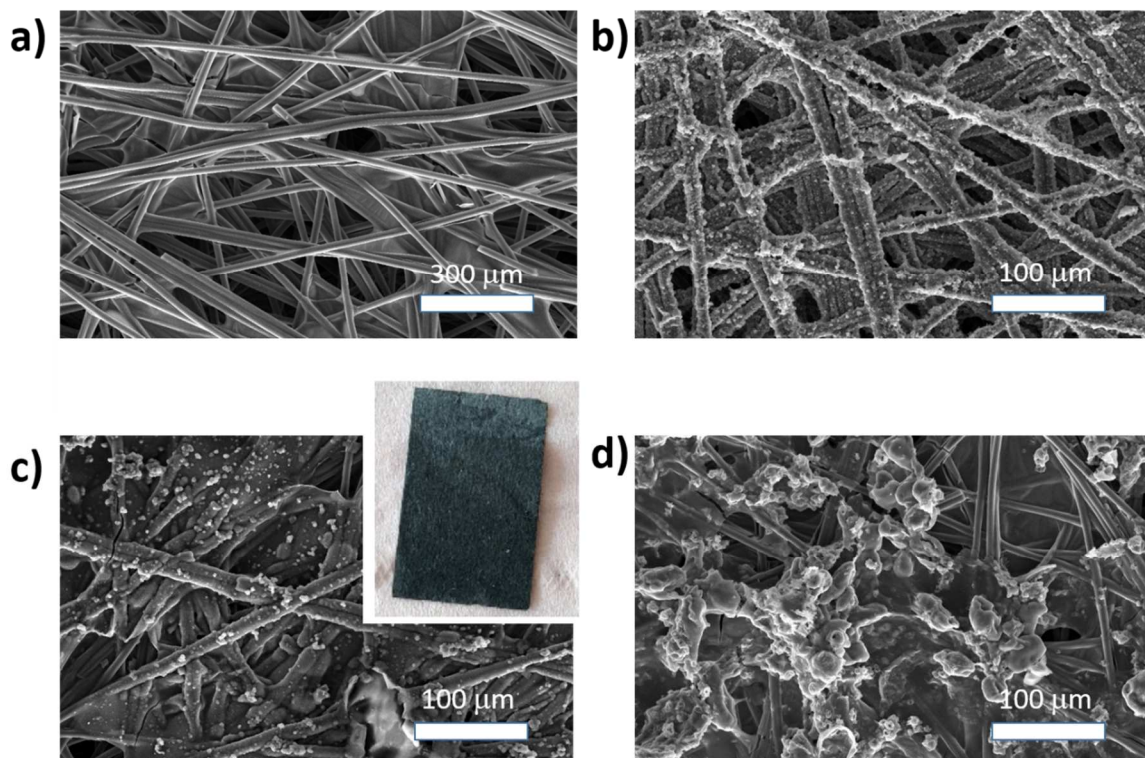


Fig. 6. FE-SEM pictures of surface observation of: a) Pristine CP; b) dried flaxseed gum/PEDOT:PSS casted on CP ; c) dried guar gum/PEDOT:PSS coated on CP (with picture of the corresponding modified CP); d) Result of DMSO digging of modified CP covered by guar gum/PEDOT:PSS.

In the Figure 7, the results of each corresponding CV were given to illustrate the differences between a pristine CP and all previous modified working electrodes. The cycling voltammograms were recorded by varying the initial and the final potential from -2.0 to +2.0 V in increments of 0.1 V at scan rates of 100 mV/S. On 7a, for the pristine CP, the CV measured in LiClO₄ 0.1 M aqueous solution showed a quasi-reversible process compared to the others CV of the same Figure 7. For all coated CP, during the experiments, the positive value of the potential window appeared to reach the overoxidation level of PEDOT ideal for high sensitive sensor applications in biological research fields [51]. Besides, it is also well known that capacitance of PEDOT coating decrease with extension of the positive limit of the electrode potential. On pictures 7b, 7c and 7d each electrode exhibited good or partial redox

activity with broad cathodic peaks respectively measured at -1.12, -0.82 and -0.9 V. Only the guar gum/PEDOT:PSS system shows a typical broad anodic peak at +0.35 V. However, in all cases, the potential windows was reduced compared to the initial measurement obtained from pristine CP. But the guar gum/PEDOT:PSS system is the sole material able to demonstrate a clear effective charge transfer with a half wave potential $E_{1/2}$ of 0.58 V. Furthermore, the DMSO dipping was apparently not recommended and the process is responsible of possible deactivation of the natural conductivity of the PEDOT enriched guar gum-based hydrogel deposited on a small piece of CP.

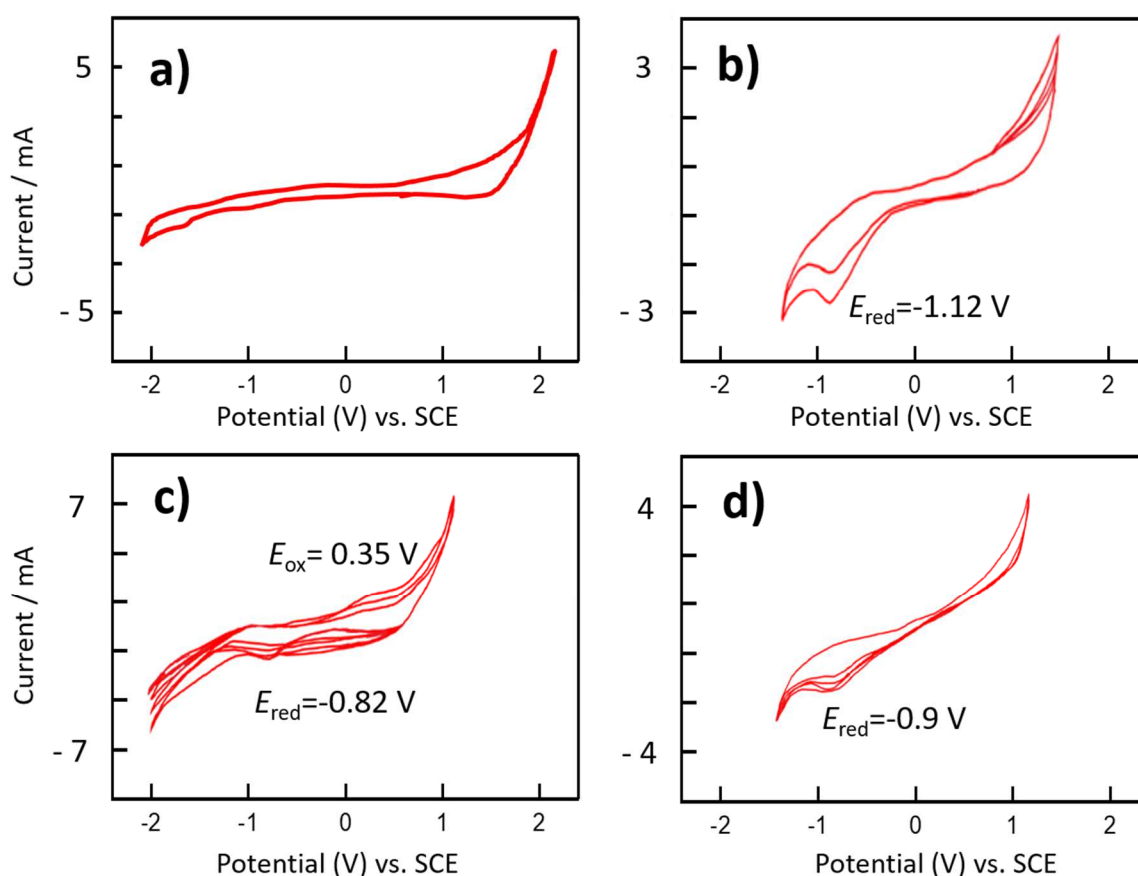


Fig. 7. Cyclic voltammograms recorded in 0.1 M LiClO_4 aqueous solutions for: a) pristine CP ; b) flaxseed gum/PEDOT:PSS modified CP ; c) guar gum/PEDOT:PSS modified CP ; d) guar gum/PEDOT:PSS modified CP exposed to DMSO dipping treatment.

On the other hand, we tried to produce PEDOT by electropolymerization using an optimized condition on CP electrode coated with a slight amount of dried guar gum/PSSNa hydrogel. Unfortunately, due to a lack of affinity for the more hydrophilic modified electrode of EDOT and overall that of its derived oligomer counterparts, proven by a simple test showing the preference of PEDOT for a nude pristine CP compared to the coated area. (see Figure S5 on the ESI). The same phenomenon was also observed for a CP surface coated with flaxseed gum/PSSNa layer. Considering this unattended and annoying result, we decided to incorporate another additional element in the guar gum/PSSNa hydrogel no other than a certain amount of exfoliated graphite first chosen for its strong hydrophobic character. Introduced at 4 wt % of concentration, on the picture 8a, the graphite was very well separated and dispersed inside the robust gel matrix. In order to determine the efficiency of

our exfoliation separation process, on the photograph 8b, we give the photography of a gray diluted sample. Despite our efforts, we were not in the capacity to obtain an exploitable UV-Vis spectrum easily observable in case of exfoliation processes involving PVP as wrapping agent.

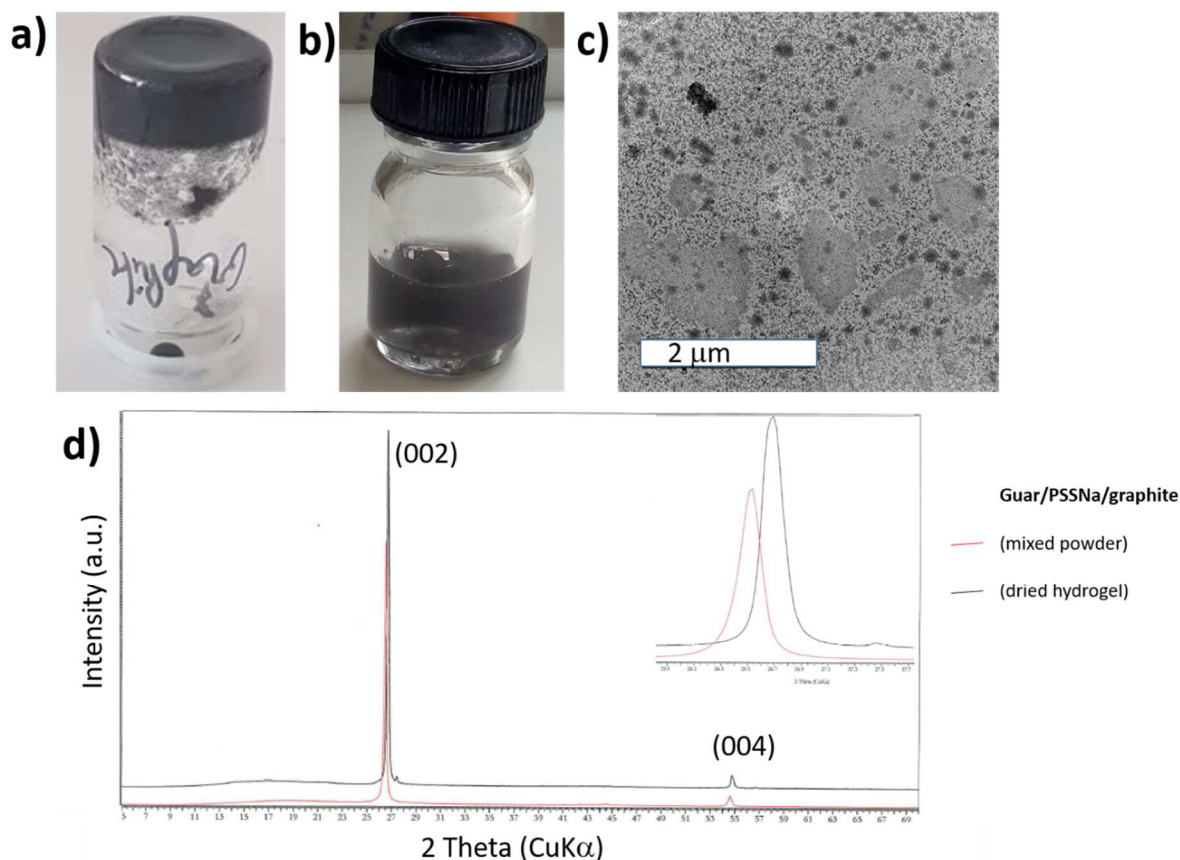


Fig. 8. a) Photograph of guar gum/PSSNa loaded with 4 wt % of exfoliated graphite ; b) picture of stable aqueous dispersion of graphite exfoliated with guar gum/PSSNa system ; c) TEM observation of expanded graphite ; d) XRD patterns of guar gum/PSSNa-exfoliated graphite.

However, the X-ray diffraction measurement could give us interesting informations about the efficiency of our exfoliation process. In case of a tripartite mixture (1:1:1) of guar gum, PSSNa and graphite, as reported on the Figure 8d, it is possible to see the characteristic diffraction peak (002) of an expanded graphite at 26.4° . Compared to a dried sample of guar gum/PSSNa/graphite hydrogel dispersion, the signal appeared as a less sharp signal. For the dried material, a larger and shaper peak is clearly visible at 26.4° , evidence of performant exfoliation. The material is currently obtained as a strong and robust band with the graphite sheets oriented along the two-dimensional network of polymer wrapping. Interestingly, the characteristic profiles of guar gum or PSSNa were not visible.

Thus like for a simple guar gum/PSSNa hydrogel, its hydrogel counterparts containing 4 wt % of exfoliated graphite was easily spreadable on a piece of pristine CP as displayed on the Figure 9c and the new working electrode was ready for an improved electropolymerization of EDOT [52]. At the opposite, when a carbon paper is directly coated with PEDOT under electropolymerization of the polymer, the material seems to cover the fibers all-around of the

whole length. But, according its corresponding CV pattern, (see ESI, Figure S6), the potential curve was completely reversible without the characteristic anodic and cathodic redox peaks of PEDOT respectively expected around +0.73 and -1.03 V.

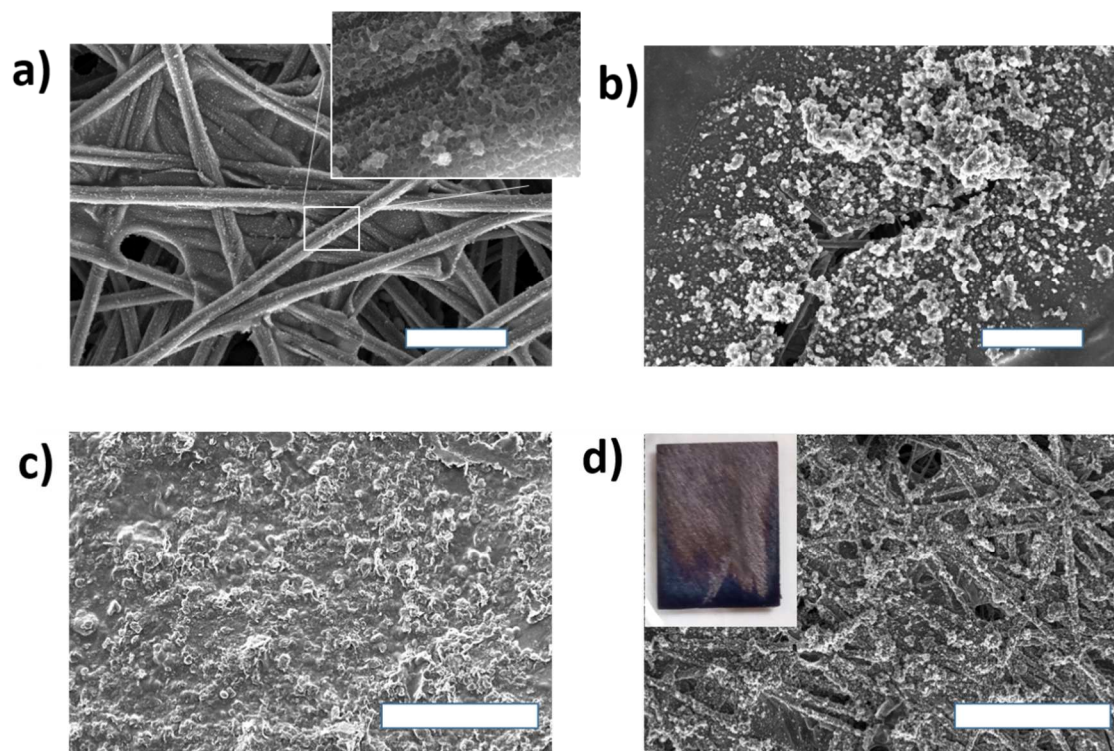


Fig. 9. Photographs of FE-SEM observation of: a) Direct EDOT electropolymerization on CP ; b) EDOT electropolymerized on CP coated with guar gum/PSSNa layer ; c) Guar gum/PSSNa/exfoliated graphite layer on CP ; d) EDOT electropolymerized on CP coated with Guar gum/PSSNa/exfoliated graphite (1:1:1) layer.

On the photograph 9b, it is possible to see the accumulation of electropolymerized PEDOT aggregates of granular shape on the periphery of a net fracture revealing the preview of carbon fibers behind the guar gum/PSSNa membrane. Finally, on the Figure 9d, a part of the CP coated electrode exhibited a high density of PEDOT granular species covering regularly the carbon fibers. Then, during the CV aided electropolymerization given as picture 10a, for a potential range set up from -2.0 to + 1.2 V, and after further scans, the CV curve gave one pair of redox of -0.8 and + 0.6 V coupled to another case of PEDOT overoxidation. The phenomenon could be associated to a loss of matter during the electropolymerization process. Herein the overoxidation is generated by a progressive delamination of the formed PEDOT layer [53] proven by the release of residuals product from the CP inside the cell. For this layer enriched with dispersed carbonaceous material, we observed a shift in the $E_{1/2}$ to higher potentials with a value of 0.7 V. Indeed, this result could suggest a need of potential increase to promote the oxidation of doped network by comparison with a simple guar gum/PSSNa layer.

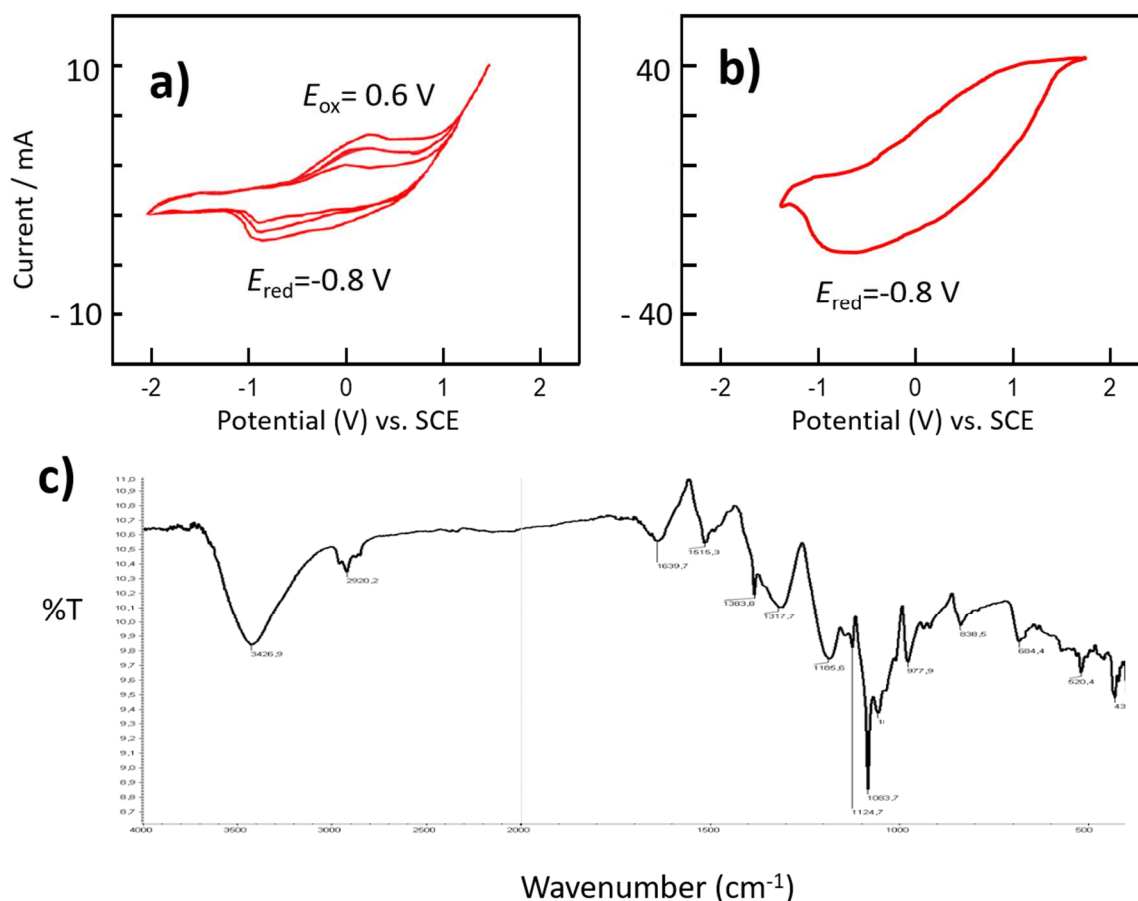


Fig. 10. a) Display of cyclic voltammogram recorded during the electrochemical deposition of PEDOT on a modified CP with a dried guar gum/PSSNa/graphite hydrogel in 0.1 M TBATFB acetonitrile solution ; b) cyclic voltammogram of electropolymerized PEDOT on modified CP with guar gum/PSSNa/graphite hydrogel in 0.1M LiClO₄ aqueous solution ; c) FT-IR spectrum of PEDOT electropolymerized on modified CP with guar gum/PSSNa/graphite.

On the image 10b, when immersed in a 0.1 M LiClO₄ aqueous solution, the CV curve of the previous modified CP electrode shows only a broad reduction peak starting around -0.6 V. In fact, it should be evidence of persistent porous structure inside the CP networks. Furthermore, if we consider the overoxidation of the electropolymerized polymer, even the plot of the curve approaches the ideal square shape often shown by a supercapacitor [[54], [55]], the response seems to remain insufficient for this kind of application. This result corroborates with the picture 9d of the modified CP. To affirm the elongation of PEDOT chain lengths, a FT-IR analysis of a crushed modified CP was carried out after the electropolymerization process. On the corresponding spectrum 10c, the characteristic peaks of PEDOT were found at their normal values of 1383 and 1515 cm⁻¹, but also at 684, 838 and 977 cm⁻¹. For the first time, the height ratio of peaks found at 684 and 838 cm⁻¹ are almost equal which is a good assessment for a higher polymerization degree of PEDOT. In addition, a large band observed at 1317 cm⁻¹ could confirm the partial oxidation of sulfur atom of thiophene rings into undesired sulfone moieties [56]

To validate our theories about the real nature of our modified electrodes, we proceed to simple and rapid EIS tests and focused only on two most promising materials, the handy coated CP with a guar gum/PEDOT:PSS ink and a CP recovered by PEDOT electropolymerized on guar gum/PSSNa/graphite layer. These experiments could also afford

more details about the interfacial behavior occurring on the surface of our modified CP electrodes [[57], [58]]. On the Figure S7 of the ESI, the results are given in the form of Nyquist plots often fitted later to a Randles equivalent circuit for a better understanding of the conducting behavior of the material. Generally, a Randles circuit could integrate the solution resistance (R_s), the charge transfer resistance (R_{ct}), a double layer capacitance (C_{dl}) and possibly a Warburg Impedance (Z_w). More exactly, R_s refers to the resistance between the solution of 0.1 M LiClO_4 and the electrochemical cell, R_{ct} refers to the electron transfer produced by a redox reaction at the modified CP electrodes and C_{dl} determines the capacitance obtained from the stored charge in the double layer region at the PEDOT:PSS composite interface. On the successive patterns of S7a and S7b Nyquist plots, both graphics show quite typical features of semi-circle in the middle frequencies representative of a charge transfer resistance at the working electrode and electrolyte interface. For both sample materials, there is no influence of Warburg impedance at the lower frequencies. This result could corroborate with the limited capacitance behavior of our CP electrode modified by means of overoxidized PEDOT. However, the incorporation of exfoliated graphite and an improved polymerization of EDOT could contribute to the improvement of the reversible electron transfer. In our opinion, these electrochemical properties are not definitive and could be significantly modulated by varying the proportion of each elements in hydrogels or with a different synthetic approach such as pH variation and by changing the reaction solvent in order to control PEDOT overoxidation [59].

4. Conclusion

For the first time, CP electrodes were chemically and electrochemically modified by a coated layer of PEDOT:PSS using flaxseed or guar gums as the binders. Using these strategies suitable for modifying the hydrophobic surfaces of carbon fibers, it seem possible to consider the design of a tailored PEDOT:PSS modified CP electrodes for various applications such as biomedical sensors by grafting enzymes or peptides. We could also imagine a utility as low impedance electrodes for nerve implants, or a constitutive element of an actuator on condition that the carbon paper could be made more flexible and resistant in a near future.

Acknowledgement

The writer of this article would like to thank his colleagues Dr A. Khelfa and Dr M. Koubaa for furnishing him the first flaxseed gum samples to define the preparative formulation of the gum-based composite inks prior to this study.

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A study for the production of a polysaccharide based hydrogel ink composites as binder for modification of carbon paper electrodes covered with PEDOT:PSS

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