SUPPLEMENTARY ONLINE MATERIAL

Compact polyelectrolyte hydrogels of gelatin and chondroitin sulfate as ion´s mobile media in sustainable all-solid state electrochemical devices

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CONTENT

Preparation and characterization of graphene oxide

1 g of graphite powder, 0.5 g of sodium nitrate and ~25 mL of concentrated H_2SO_4 were mixed and cooled to 0ºC, and the solution was maintained under vigorous stirring. Next, 3 g of $KMnO_4$ was added to the solution in stepwise manner so that the temperature was kept below 20ºC during the $KMnO_4$ addition steps. After the complete addition of $KMnO_4$ the temperature of the solution was slowly raised to 35ºC and maintained for 30 min. Next, 100 mL of deionized water was added to the solution. Subsequently, the temperature of the solution was increased to 98ºC during the addition of water and this temperature was maintained for 15 min. The solution was then mixed with 130 mL of warm water followed by addition of 10 mL of 3% H_2O_2. The solid as filtered, washed thoroughly with warm water and then with 10. wt% of aqueous HCl solution, followed by further washing with deionized water several times, and finally dried at 60 ºC under vacuum.

Powdered GO was evaluated by Raman spectroscopy, in the Microspectroscopy Laboratory of the Characterization Service in the Institute of Polymer Science & Technology (CSIC) using a Renishaw InVia Reflex Raman system (Renishaw plc., Wottonunder- Edge, U.K The Raman scattering was excited using an argon ion laser wavelength of 514.5 nm. All spectra were processed using Renishaw WiRE 3.4 software. Raman spectrum of GO clearly shows the typical G (sp^2 carbon network, 1598 cm^{-1}) and D (defects in the sp^2 lattice, 1352 cm^{-1}) modes, and the higher order 2D and G + D modes (Figure S1A).

It is widely known that GO dispersed very well in water. In this study, a solution of 1 mg/ml was drop casted on TEM grids for analysis. High resolution transmission electron microscopy (HRTEM) analysis of GO solutions was conducted at the Centro Nacional de Microscopía Electrónica, Madrid, Spain, with a JEOL JEM-2100 instrument (JEOL Ltd, Akishima, Tokyo, Japan), using a LaB6 filament, a lattice resolution of 0.25 nm and an acceleration voltage of 200 kV. TEM images suggest the presence of flakes of lateral dimensions in the order of microns (Figure S1B), and thickness ranging from monolayers to bilayers and few-layer (inset in Figure S1B).

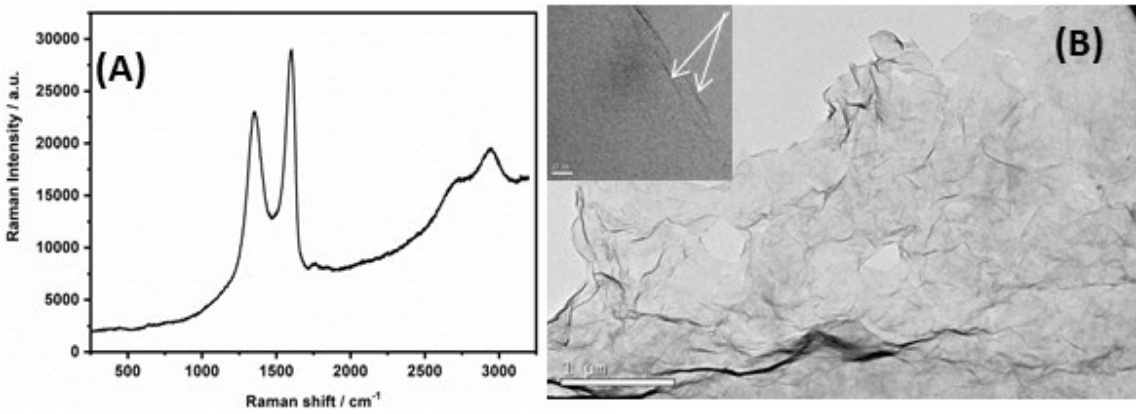

Figure S1. Characterization of GO employed in this work: a) Raman spectrum and b) transmission electron microscopy of drop-casted flakes. The inset represents a HRTEM image of the edges of the GO flakes (white arrows indicate the edges, in this case of a bilayer).

Study of the Z-potential of gelatin aqueous solutions

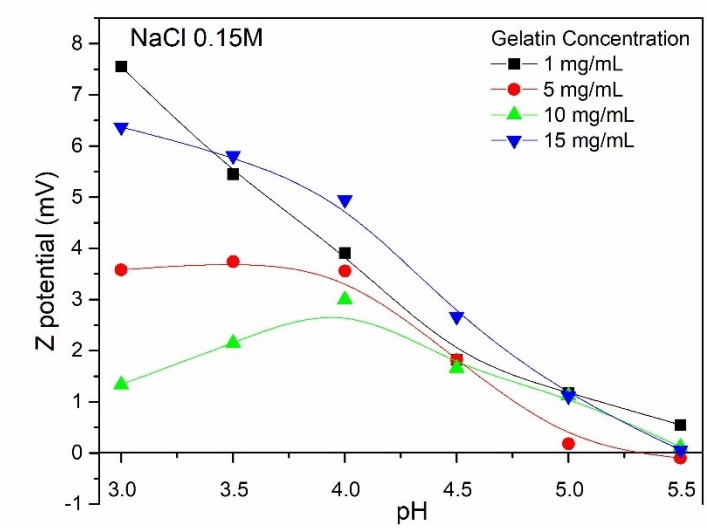

Figure S2. Representation of Z-potential as a function of pH for aqueous solutions of gelatin at different concentrations.

Precipitation test

The experiment was based on mixing directly (without any protocol) 10mL of Gelatin+ChS with the characteristics of the selected candidates. The results of the mixing can be observed in ***FigureS3***: every sample presented a precipitate that can be

Figure S3. Results from the precipitation study. A) From left to right: samples A, B, C and D. B) Detail on precipitate formation in sample D identified as the product of the interactions between ChS and gelatin.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra were carried out on lyophilized samples using a Perkin Elmer UATR TWO equipment. The employed resolution was 4 cm^{-1} and measurements were carried out in attenuated total reflectance modes (with ATR accessory) from 400 to 4000 cm^{-1}, performing 16 scans per sample. The ATR-FTIR spectrum corresponding to gelatin exhibit absorption bands at 3294 cm^{-1} (N–H stretching vibration), 2927 cm^{-1} (C–H stretching vibration), 1633 cm^{-1} (amide I, C=O stretching vibration), 1539 cm^{-1} (amide II, N–H bending vibration), and 1228 cm^{-1} (amide III, N–H bending vibration). The spectra of ChS exhibited peaks at 3350 cm^{-1} (–OH stretching vibration), 1030 cm^{-1} (C–O–C stretching vibration attributed to the saccharide structure), and 1220 cm^{-1} (S=O stretching vibration attributed to the negatively charged SO_4^{2-} groups of CS molecules). In addition, the bands at 1403 and 1365 cm^{-1} were due to the coupling of the C–O stretching vibration and O–H variable-angle vibration, indicating the existence of the free carboxyl group.

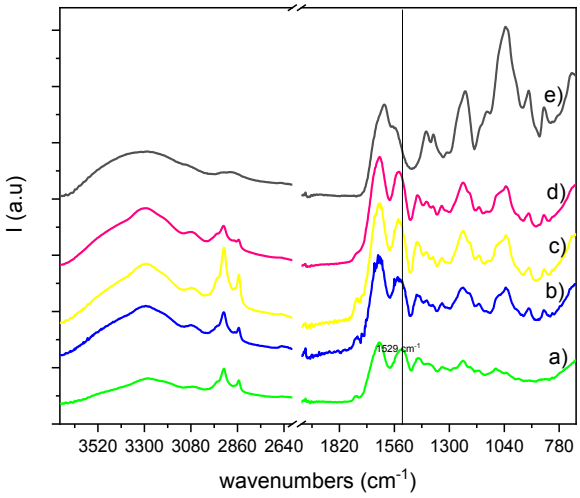

Figure S4. ATR-FTIR spectra corresponding to a) gelatin; b) sample A; c) sample B; d) sample D and e) ChS.

Scanning electron microscopy (SEM)

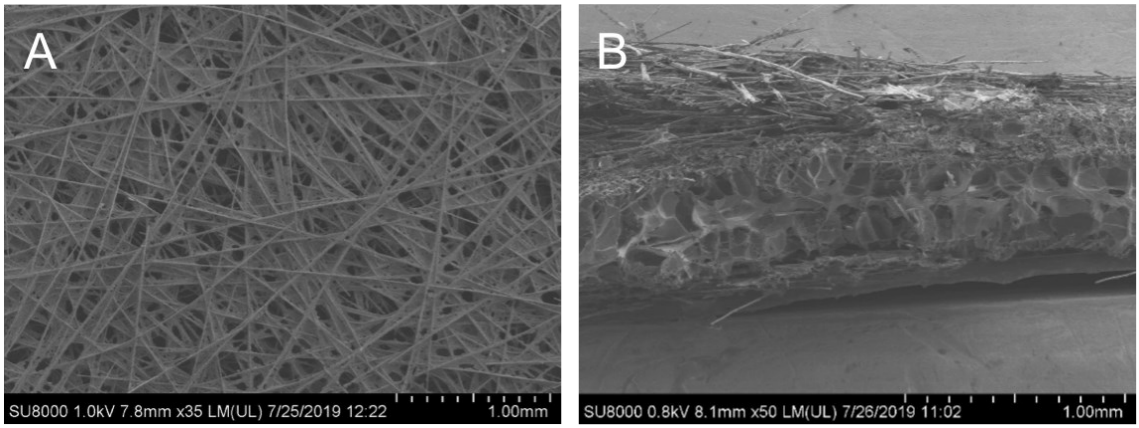

Figure S5. SEM images corresponding to the top (A) and cross-section (B) views of the CGDL material and the CGDL/biohydrogel/CGDL electrochemical cell respectively.

Study of the pore size and pore size distribution of the biohydrogel

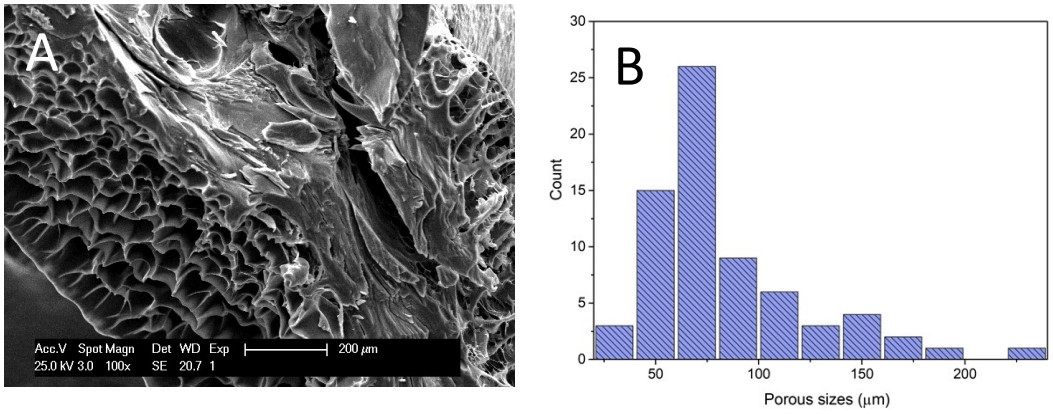

Figure S6. A.Representative SEM image corresponding to ChS-gelatin hydrogel. B. Analysis of the pore size distribution carried out with the software ImageJ.

Assembly of the electrochemical cell

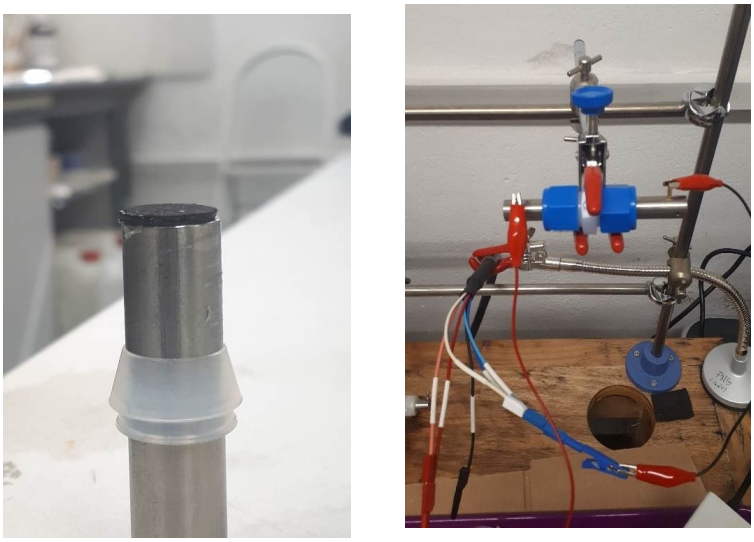

Figure S7. Left: Photograph corresponding to a CGDL/biohydrogel/CGDL electrochemical cell; Right: assembly of the electrochemical cell onto a Swagelok type cell with a symmetric configuration.

Cyclic voltammetry

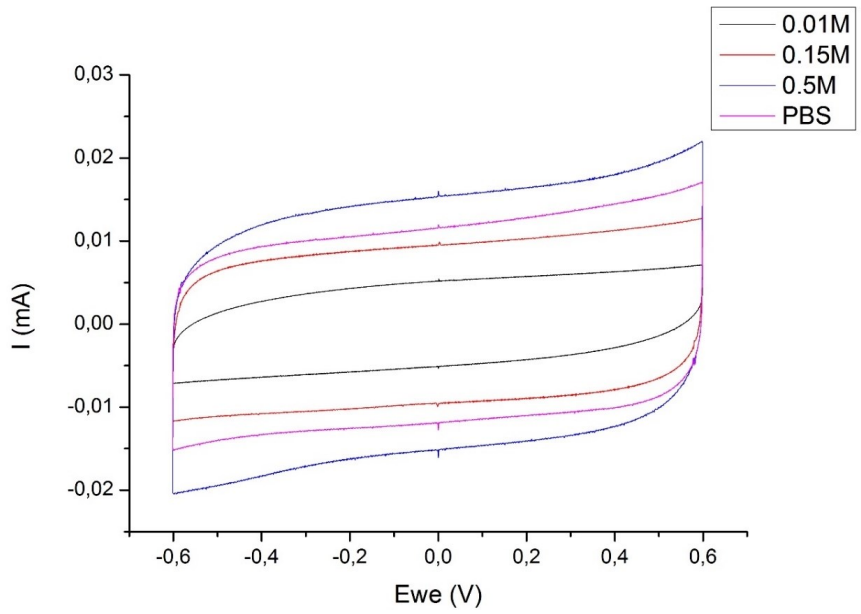

Figure S8. CVs of CGDL/biohydrogel/CGDL cell measured at 100 $mV.s^{-1}$ in a symmetric configuration.