

Supplementary Information

Atmospheric plasma deposition of bioinspired catechol-rich polymers: a promising route for the simple construction of redox-active thin films

*Abdelhafid Aqil,^a Farid Ouhib^a, Christophe Detrembleur^{*a} and Maryline Moreno-Couranjou^b*

Contents

- S1. Materials
- S2. Synthesis of 4-vinyl catechol
- S3. Atmospheric plasma deposition
- S4. Film characterizations
- S5. Electrochemical characterization
- S6. Figures and table.

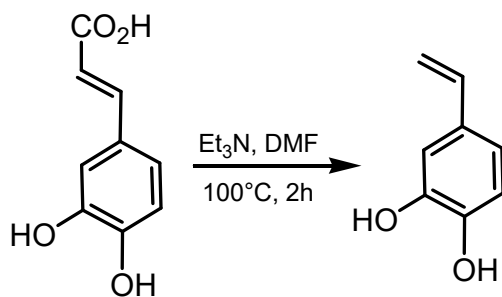
S1. Materials

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99%, ABCR), acetone and ethanol (VWR, technical grades) were used as received. Tetraethylene glycol dimethyl ether (tetraglyme $\geq 99\%$ -Aldrich), anhydrous ethyl methyl carbonate (EMC $\geq 98\%$ -Aldrich) and diethyl ether were dried using standard procedures, distilled, and stored under argon prior to use.

Silicon wafers (Siegert Wafer) and mirror polished 304-8ND stainless steel disks (SS, 2 cm diameter and 0.8 mm thickness, APERAM) and stainless steel disks (EQ-CR20 from MTI) were used as substrates for AFM, UV analyses and coin cell fabrication, respectively. All substrates were cleaned via two successive ultrasonic washings in acetone and ethanol during 5 min. and further dried under a nitrogen flux.

Prior plasma deposition, all substrates were cleaned and activated using a 95%/5% argon/oxygen plasma ignited by a 10 kHz sinusoidal electrical excitation (SOFTAL generator) operating at 1.6 W cm^{-2} in continuous mode during 3 s. This plasma pre-treatment step allowed the removing of organic impurities present at the surface of the substrates and ensured a good anchoring of the deposited film.

S2. Synthesis of 4-vinyl catechol



Caffeic acid (10 g, 55.5 mmol) was dissolved in DMF (25 mL). Triethylamine (15.38 mL, 111 mmol) was added to this solution, and then the mixture was heated to 100 °C under stirring. After 2 h, the reaction mixture was cooled to room temperature and the reaction mixture was concentrated by rotary evaporation to remove triethylamine. The residue was diluted with diethyl ether (100 mL) and washed with acidified water (pH = 3). The organic layer was dried over Mg₂SO₄ and then concentrated under vacuum (yield 68%, 5.13 g). To prevent its self-polymerization, 4-vinyl catechol was diluted at 7wt% in diethylether and stored under nitrogen atmosphere at -20 °C. ¹H NMR (ppm) : 8.9 (s, 2H), 6.7 (m, 3H), 6.51 (q, 1H), 5.46 (d, 1H) and 4.98 (d, 1H). NMR spectra were recorded on a Bruker instrument operating at 250 MHz.

S3. Atmospheric plasma deposition

Thin films were deposited using an open-air atmospheric pressure dielectric barrier discharge (AP DBD) process depicted in **Scheme 1**. The discharge was produced between two plane-parallel high voltage electrodes covered by alumina and a moving table used as substrate holder and ground electrode, thus generating a ~ 19 cm² plasma discharge area. The table speed and electrode gap were fixed adjusted at 10 mm s⁻¹ and 1 mm, respectively. The total process gas flow was fixed at 20 slm of argon (99.999%, Air Liquide). All experimental depositions have been carried out using a 10 kHz sinusoidal signal and a 1.6 W cm⁻² power density. The plasma t_{on} and t_{off} durations were fixed at 1 and 30 ms, respectively. The precursor solution composed

of vinyl catechol (7 wt%) in diethylether was nebulized using a OneNeb injector system (Agilent) and a syringe pump to control its flow delivery fixed at $50 \mu\text{L min}^{-1}$.

S4. Film characterizations

The film growth rates were determined from the coating thicknesses measured by ellipsometry (FS-1 model, Film sense), using a Cauchy function for fitting, divided by the synthesis process duration.

The 3D topographies were recorded in tapping mode at a scanning rate of 1 Hz with an atomic force microscope (AFM) MFP 3D Infinity (Asylum Research, Santa Clara, CA).

The optical absorbance of the films deposited on stainless-steel substrate was measured in the 200–800 nm range using a UV-Vis-NIR spectrophotometer (Perkin Elmer, Lambda 950) with a 150 mm diameter integrating sphere.

Fourier Transform Infra-Red (FT-IR) measurements were performed on a Bruker Hyperion 2000 IR microscope in Attenuated Total Reflectance mode. Spectra were acquired from 32 scans at a 4 cm^{-1} resolution.

XPS measurements were carried out on a Kratos Axis-Ultra DLD instrument, using a monochromated Al K α source (1486.6 eV) with a pass energy of 20 eV on a $700 \times 300 \mu\text{m}^2$ area. A charge neutralization system using electrons of few eV was used during the measurements. The curve fitting was performed with the commercial CasaXPS software (version 2.3.19).

Surface imaging analysis of the plasma thin films was determined by Secondary Ion Mass Spectroscopy (SIMS) technique. For this purpose, a Helium Ion Microscope (HIM) instrument (Orion Nanofab, ZEISS, Peabody, MA, USA) coupled with a mass spectrometer developed at Luxembourg Institute of Science and Technology, Luxembourg (LIST) was used. The analytical information were obtained by detection of the ions generated by using a 10 kV Ne $^+$

focused ion beam. The probe was in the range 20–40 nm in diameter, with an intensity of 3 pA. The SIMS observations were acquired in imaging mode with a raster size of 6 x 6 μm^2 , for a matrix of 512 x 512 pixels². The images were recorded simultaneously thanks to the multicollection system and the instrument was tuned for the detection of silver with a counting time of 2 ms per pixel.

S5. Electrochemical characterization

Electrochemical performance of the electrodes was evaluated in coin-type cells using lithium foil as a counter electrode, a pair of porous polypropylene (Celgard 2400) as a separator, and (1.5M) lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of tetraglyme (G4) and ethyl methyl carbonate (EMC) (G4:EMC = 1:2, v/v) as electrolyte. The working electrodes were prepared by atmospheric plasma deposition of active materials in stainless steel circular disc (12 mm). The thickness of the tested films is 66nm and 200nm, which corresponds to a number of cycles equal to 85 and 258, respectively. The coin cells were assembled in a high-purity argon filled glovebox (MBraun, O₂ < 0.1 ppm and H₂O < 0.1 ppm) to avoid any possible contamination by moisture and oxygen. Cyclic voltammogram (CV) and galvanostatic charge/discharge tests were measured using a BioLogic VSP300 electrochemical workstation. The voltage window was controlled in the range of 1.5-4.5 V vs. Li and the current densities were controlled from 0.1 to 5 A g⁻¹ during the galvanostatic tests.

S6. Figures and table.

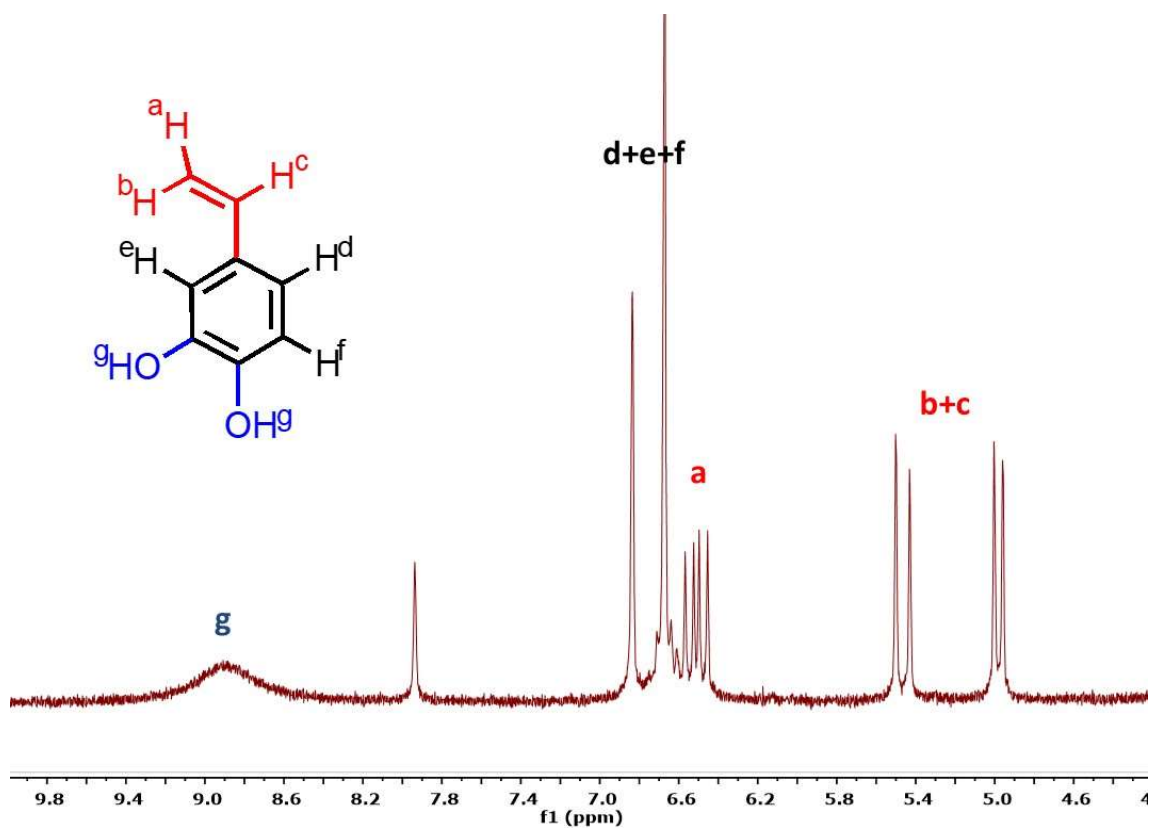


Figure S1: ¹H NMR spectrum of 4-vinyl catechol.

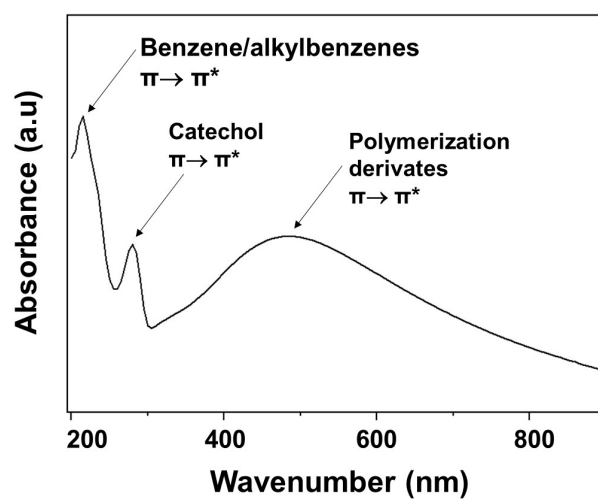


Figure S2: UV characterization of the plasma deposited catechol-rich film.

Table S1. XPS chemical composition, C1s and O1s deconvolutions of a plasma coating.

Peak	At. %	Atomic bond	BE (eV)	Area, %	Components, at. %
C1s	80	C-C/C-H / C=C	284.3	70.7	56.6
		C-O / catechol	285.9	29.3	23.4
O1s	20	O-H / catechol	532.8	100.0	20.0