"Green" Electrodes for Supercapacitors Fabricated by One-step Visible Direct Laser Writing of Cork Natural Substrates

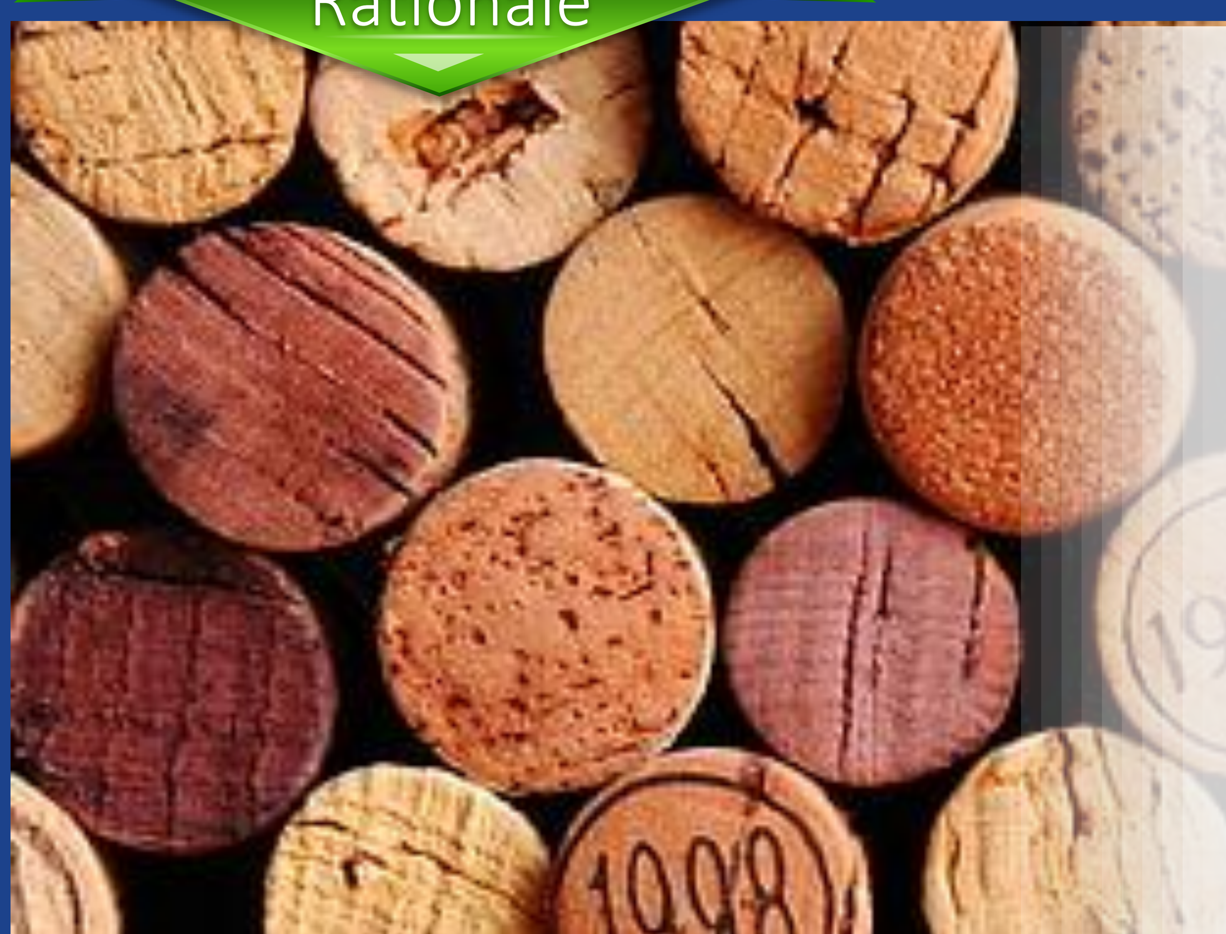
Alessandra Imbrogno[1], Jahidul Islam[1] and Daniela Iacopino[1]

[1]Tyndall National Institute, University College Cork, Cork, Ireland

Tyndall National Institute
Institiúid Náisiúnta

Science Foundation Ireland For what's next

Rationale



Motivation

To address the challenge of incorporate biodegradable materials and sustainable production routes in order to ensure sustainability in the electronic device sector is paramount to:

- ✓ Replace the traditional substrates with natural, biodegradable ones
- ✓ Develop novel green, versatile, low cost and scalable fabrication routes with low footprint impact

Impact

The introduction of the laser-writing technique on cork substrates for the fabrication of electrodes for supercapacitors allows:

- ✓ Production cost reduction for the fabrication of electrodes
- ✓ Reduction of non recyclable waste at the end of life of the device
- ✓ Reduction of carbon footprint impact during the fabrication of electrodes.
- ✓ Possibility to obtain materials with tailored properties

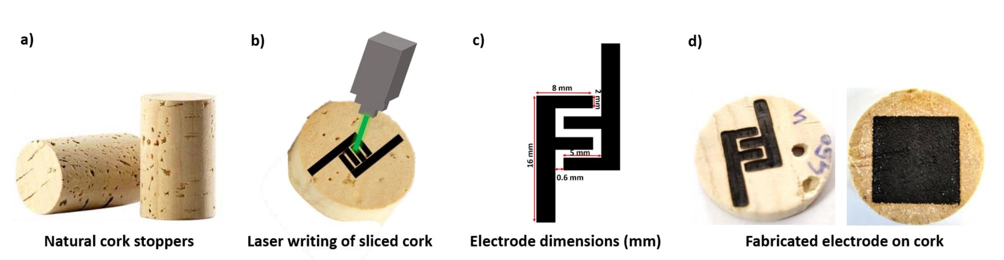
Keywords: green electrochemistry; biodegradable supercapacitors; laser-writing technique;

Introduction

The energy crisis is one of the major challenges affecting globally every aspect of people's lives. The growth of the high tech devices market is currently facing an increasing demand for novel and more environment-friendly technologies to address the decrease of traditional fossil-based resources and to reduce the environmental footprint associated to technology production both in terms of fabrication and precursor materials. Thus, the development of novel and more environment-friendly technologies that ideally use renewable, low cost and Earth-abundant resources as well as mild production routes is of paramount importance for future environmental sustainability.

In this context, carbon-based natural materials derived from abundant and renewable sources possess properties such as biodegradability and potential cost-effectiveness, which makes them promising for future "green" electronics applications.

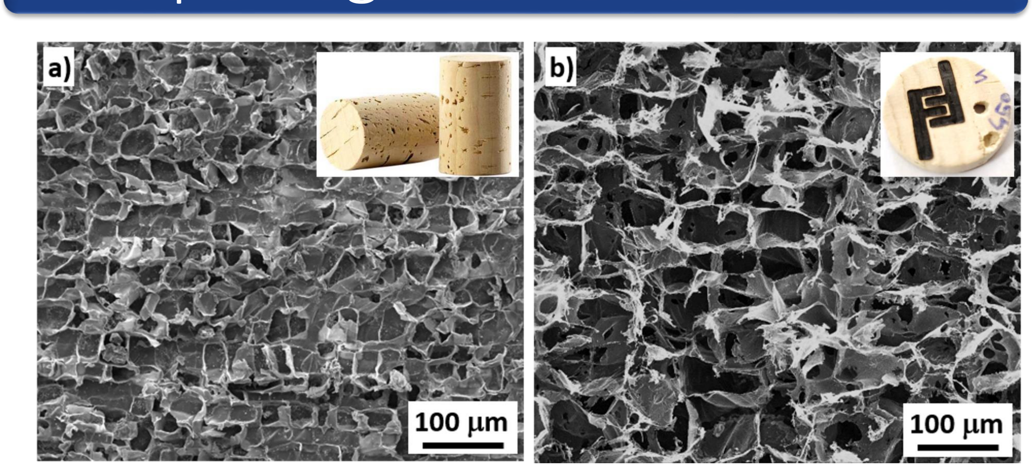
Materials & Methods



Schematic of laser-written cork electrodes preparation

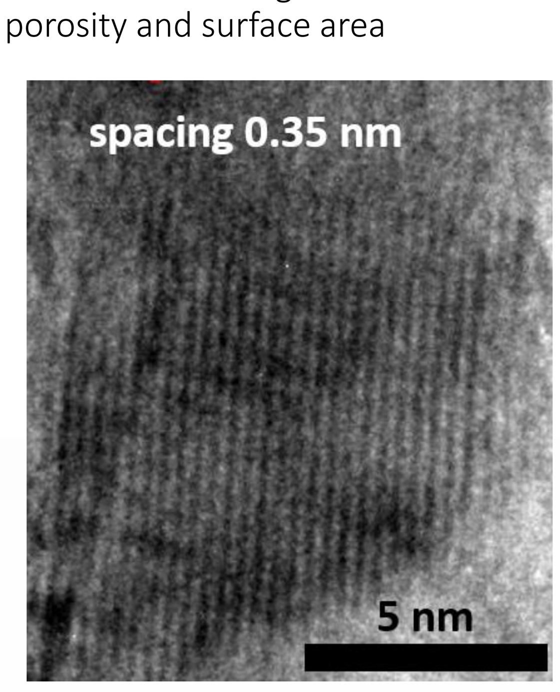
Graphitic carbon structures were fabricated by laser irradiation with a KKmoon Compact Automatic Desktop Laser Engraving Machine equipped with a laser with wavelength of 450 nm and power of 3 W.

Morphological Characterization



SEM top view of (a) pristine and (b) laser-written cork..

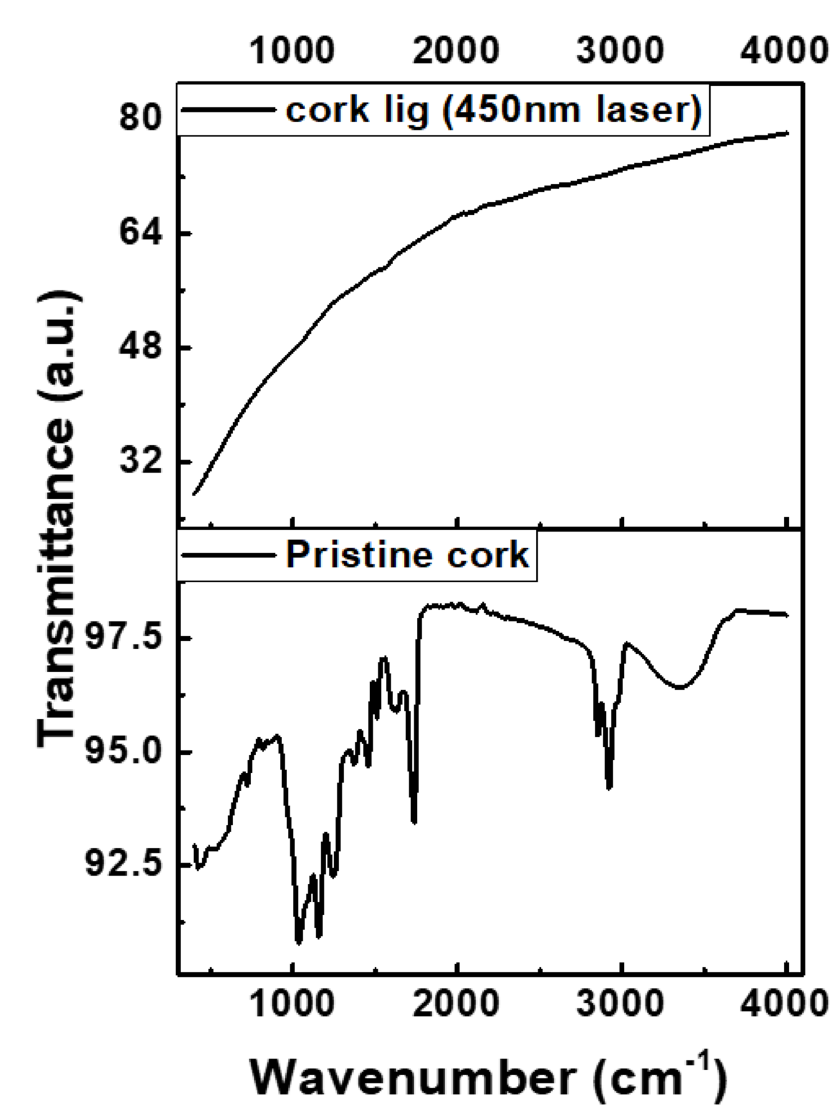
The pristine cork stopper (a) displayed a homogeneous tissue of thin walled cells regularly arranged in an alveolar structure, analogous to that of a honeycomb. cork cells However, following laser graphitization an extended rougher pattern emerged (b) while still maintaining an ordered honeycomb structure, cells displayed thin micro-flaked walls and hollows stacked in an extended interconnected large 3D network arrangement showing high porosity and surface area



HR-TEM of laser-written cork..

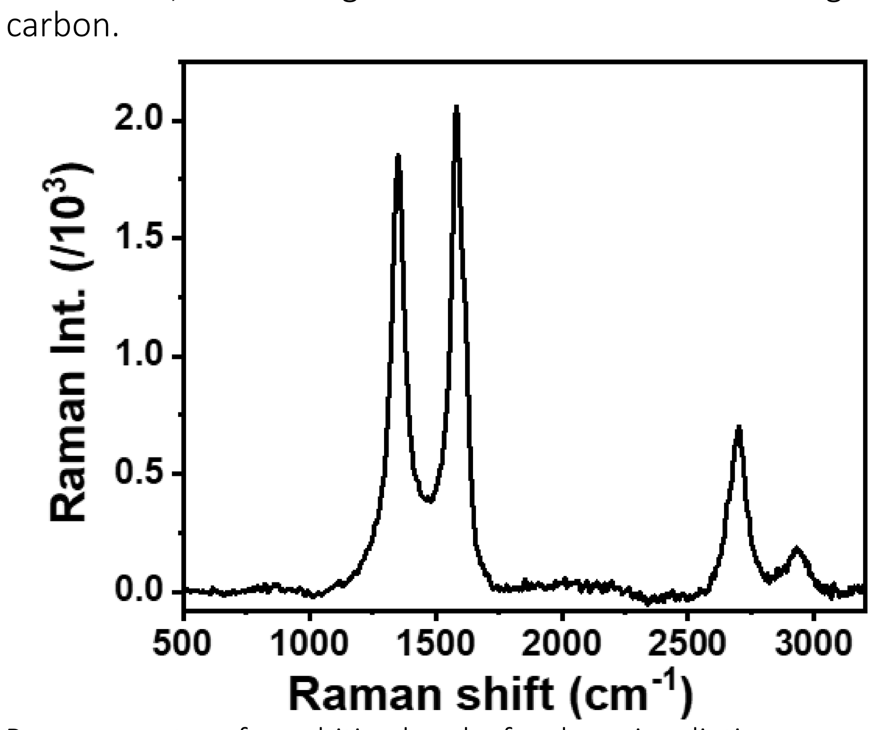
The high resolution TEM permitted to observe the formation of a crystalline structure with d-spacing of 3.5 Å that is typical of graphene obtained through laser-scribing process from lignine-rich materials

Chemical Characterization



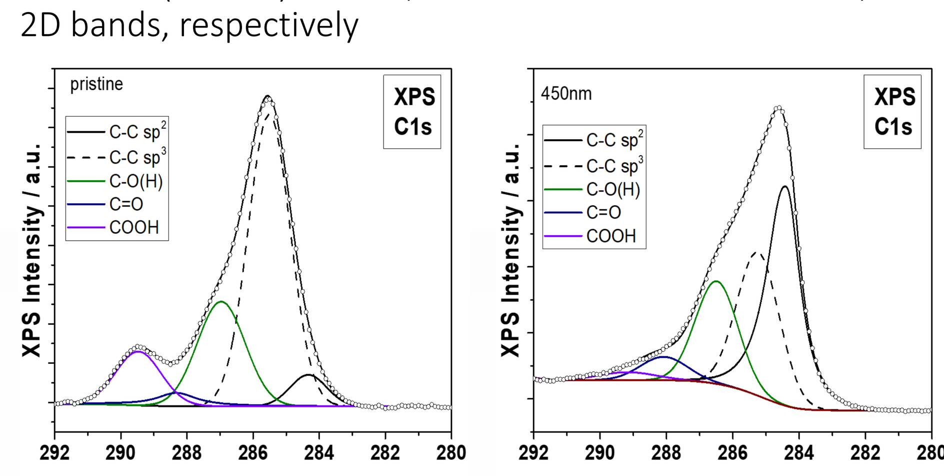
FTIR spectrum of laser-written graphitic carbon structure (upper) and pristine cork (lower)

The typical FTIR spectrum of pristine cork showed the presence of well-defined peaks that were associated with the presence of suberin(2920, 2851, and 1739 cm^{-1}), guaiacyl-type lignin (1510, 853, and 820 cm^{-1}), polysaccharides 1099 and 1037 cm^{-1}) and extractives (1607 and 1460–1300 cm^{-1}). After the laser engraving process, the FTIR spectrum appeared featureless, confirming the conversion of cork into graphitic carbon.



Raman spectra of graphitised cork after laser irradiation.

The Raman spectrum of the cork-graphitic carbon area was characterized by three main bands (D, G, 2D) indicating the formation of a graphite-like carbon morphology. All bands could be fitted by a single Lorentzian peak with full-width-at-half-max (FWHM) of 73.1, 65.9 and 73.4 cm^{-1} for the D, G and 2D bands, respectively

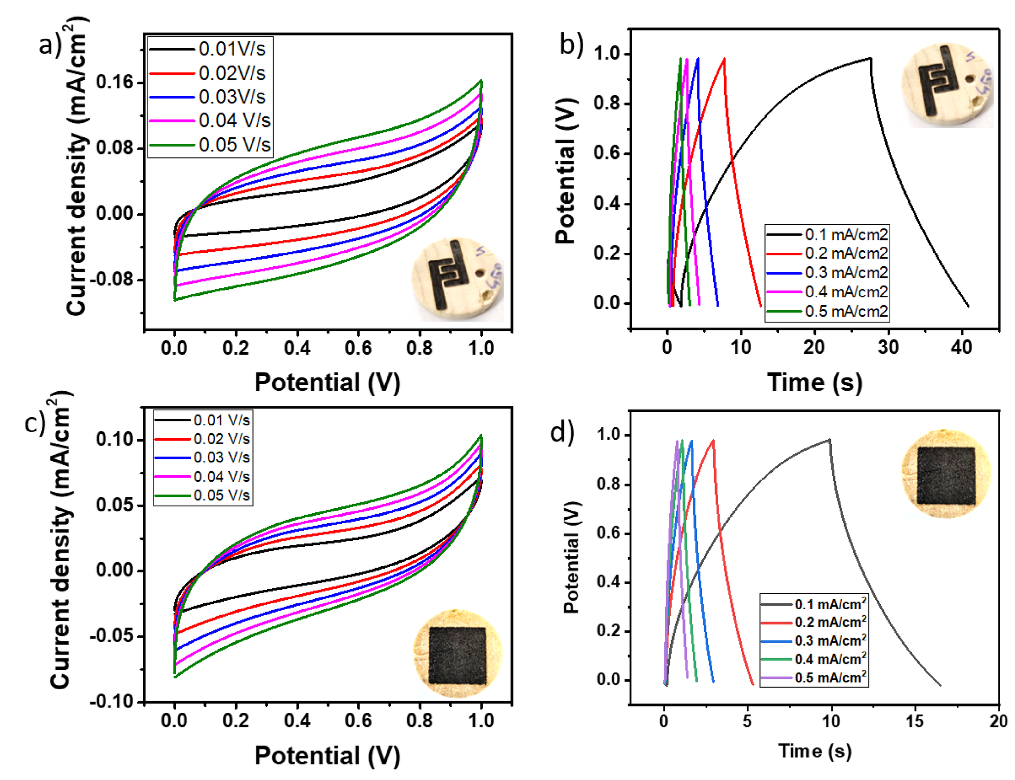


XPS spectra of pristine (left) and of laser-written (right) cork.

The XPS iC peaks of pristine and graphitized cork were deconvoluted into five components (the main C-C sp2 and C-C sp3 carbon bonds, C-O(H) epoxides and hydroxides, C=O carbonyl groups, and COOH carboxyl groups).

Supercapacitive behaviour

The supercapacitive behavior of fabricated interdigitated electrodes was electrochemically tested in a two-electrode configuration (interdigitated, or sandwiched squares) by drop casting PVA/H2SO4 electrolyte on the electrodes.

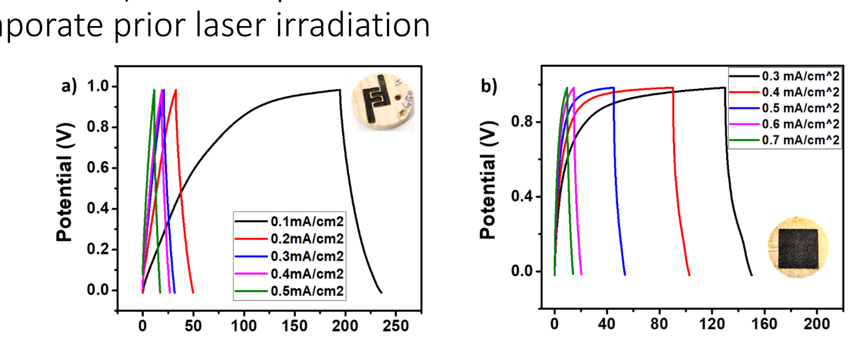


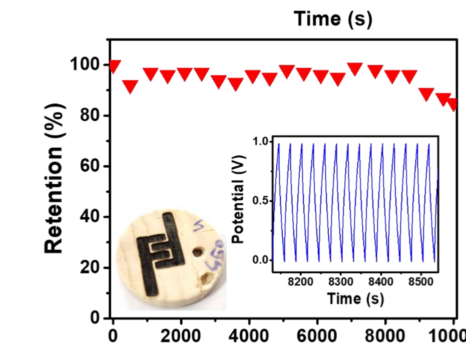
Cyclic voltammetry (a, c) and galvanostatic charge-discharge (b, d) performed on interdigitated and sandwiched squares respectively.

Cyclic voltammetry showed a pseudo-rectangular shape commonly associated with a good capacitive behavior., which is furthermore confirmed by the Galvanostatic charge-discharge curves: all curves displayed a nearly triangular shape, another indication of good capacitive behavior. The specific areal capacitance was calculated from the discharge curves of the galvanostatic charge-discharge measurements at 0,1 mA/cm^2 was found 1.56 mF/cm^2. for the interdigitated electrodes, and of 0.2 mF/cm^2 for the sandwiched square design.

Doping with Boron and retention

In order to improve the electrochemical performance a doping strategies was adopted, whereby an aqueous solution of H3BO4 (2.5% w:w) was deposited on the cork substrate and left evaporate prior laser irradiation





Design	Doping	Capacitance (mF/cm^2)
Squares sandwich electrodes	No doping	0.2
	With Boron	1.8
Interdigitated electrodes	No doping	1.6
	With Boron	4.7

Retention over 10000 cycles of galvanostatic charge-discharge.

The calculated specific areal capacitance was as high as 4.7 mF/cm^2 which shows an increase of about 200% compared to the un-doped electrode for the interdigitate configuration, while the square sandwich reached 1.8 mF/cm^2 which is an order of magnitude more than the un-doped one. The stability over time of the interdigitated graphitic carbon electrodes doped with boron was tested over 10000 cycles of galvanostatic charge–discharge (inset). The material showed an excellent stability over time with only a 15% loss of capacity.

Acknowledgements

The research is supported in part by a research grant from Science Foundation Ireland (SFI) and is co-funded under the European Regional Development Fund under Grant Number 13/RC/2077 , Grant Number 16/RC/3918, and Grant Number 16/RC/3835.