

CRITICAL REVIEW



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Powering the future: application of cellulose-based materials for supercapacitors

Maria M. Pérez-Madrugal,^{*a,b} Miquel G. Edo^{a,b} and Carlos Alemán^{*a,b}

In recent years, significant research has aimed at developing environmentally friendly supercapacitors by introducing biopolymeric materials, such as polysaccharides or proteins. In addition to the sustainability and recyclability of such novel energy storage devices, these polymers also provide flexibility, lightweight nature and stable cycling performance, which are of tremendous importance for applications related to wearable electronics. Among the different sustainable natural polymers, cellulose deserves special consideration since it is the most abundant and is extensively recycled. Consequently, research on electrically active cellulose-based supercapacitors has noticeably increased since 2012, which makes this review on the field timely. Specifically, recent advances in preparing high performance cellulose supercapacitors are summarized. Moreover, the key roles of cellulose in improving the specific capacitance and cycling stability of cellulose-based devices are compiled to offer important fundamental guidelines for designing the next generation of all-cellulose energy storage devices that are to come. Finally, challenges and perspectives in this exciting area of study are also discussed.

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^aDepartament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal 647, Barcelona E-08028, Spain

^bCenter for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain.

E-mail: m.mar.perez@upc.edu, carlos.aleman@upc.edu

Introduction

In the last decade, energy and environment related topics have been recognized as major challenges for human beings. The rapid development of consumer electronic devices with very



Maria M. Pérez-Madrugal

Maria M. Pérez-Madrugal received her BSc degree in Chemical Engineering (2010) and her MSc degree in Polymers and Biopolymers (2011) from the Universitat Politècnica de Catalunya (UPC, Barcelona, Spain). In 2010, she joined the “Innovation in Materials and Molecular Engineering” (IMEM) group in the Chemical Engineering Department (UPC), where she conducted her PhD under the supervision of Prof. Carlos Alemán and

Dr Elaine Armelin and graduated in 2015. Her research focused on combining conducting polymers (CPs) with conventional polymers to obtain biointerfaces at the nanoscale for different bioapplications. After a post-doctoral year in the IMEM group working on supercapacitor devices based on CPs and hydrogels, she has just joined the Dove Research Group (University of Warwick, UK) as a Marie-Curie Researcher Fellow for developing polycarbonate-based hydrogels as scaffolds for load-bearing soft tissue regeneration.



Miquel G. Edo

Miquel G. Edo received his BSc degree in Physics Engineering (2016) at the Universitat Politècnica de Catalunya (UPC), Barcelona, Spain. In 2016, he joined the “Innovation in Materials and Molecular Engineering” (IMEM) group in the Chemical Engineering Department at UPC. Under the supervision of Prof. Carlos Alemán and Dr Maria M. Pérez-Madrugal, he conducted his final degree project and graduated in

2016. His research focused on developing supercapacitors combining conducting polymers (CPs) with organic materials (hydrogels, cellulose etc.) to obtain new fully sustainable and applicative devices. Currently, he is a scholar member in the IMEM group for improving cellulose-based supercapacitors' features with commercial aspirations.

different and varied functionalities (e.g. roll-up displays, smart mobile devices, and implantable biosensors) has motivated a huge amount of research to improve the performance, flexibility, and/or environmental friendliness of energy storage devices.^{1–6} These devices are classified into capacitors, electrochemical capacitors (ECs), batteries, and fuel cells depending on their power and energy densities.

Supercapacitors (also termed electrochemical double-layer ECs) are high capacity ECs with the ability to be charged and discharged very quickly with little degradation after an increasing number of charge–discharge cycles. Because of these properties, supercapacitors bridge the gap between conventional ECs and rechargeable batteries. Each supercapacitor cell consists of two electrodes, a separator, and an electrolyte. The two electrodes are often electrically connected to their terminals *via* a metallic collector.

Recently, polymeric materials for supercapacitor applications have received much attention because of their beneficial properties, such as flexibility, lightweight nature, and stable cycling performance.⁷ Additionally, replacement of heavy metals by redox active polymers in battery electrodes is highly attractive with regard to recyclability and sustainability.⁸ Although a large number of polymers have been employed as redox active materials in energy storage devices,^{9–12} electroactive conducting polymers (ECPs) render promising electrodes in supercapacitors due to their cost-effectiveness, lightweight nature, flexibility, and high charge/discharge rate.^{13–15}

Powering the future, the employment of organic polymeric materials for the fabrication of energy storage devices has been extended to biopolymers. The properties of these materials offer challenging opportunities in the development of renewable, sustainable, cheap and scalable charge storage devices. For example, chitin and chitosan, which are linear

polysaccharides abundant in the biosphere, have been used in the fabrication of solid state proton-conducting polymer batteries.¹⁶ Other naturally occurring polysaccharides, such as alginate and pectin, have been used for the development of new bioelectrodes,^{17,18} while sodium alginate, κ -carrageenan and chitosan hydrogels have recently been employed as supporting electrolyte in semi-solid organic batteries.¹⁹ Moreover, DNA²⁰ and proteins, for example, gelatin²¹ and lysozyme,²² have been used to fabricate supercapacitors.

Among biopolymers, natural polysaccharides are being developed as alternatives to synthetic materials for electrochemical devices. Indeed, the most abundant and sustainable natural polymer is cellulose. This linear polysaccharide, which was discovered by Anselme Payen in 1838, is an important structural component of the primary cell wall of green plants. Cellulose, which is odourless, biodegradable, hydrophilic, and water insoluble, derives from the condensation of D-glucose units through $\beta(1\rightarrow4)$ glycosidic bonds (Scheme 1) and is organized in fibrous arrangements. Cellulose fibres exhibit high aspect ratios, high surface area, high porosity, excellent mechanical properties, excellent flexibility, and the ability to bind to other conductive materials, enabling extensive application in flexible energy-storage devices.^{23,24}

Although the interest in designing electrically active cellulose-based devices for energy storage applications started with the new century, as a review by Nyholm *et al.*²⁵ evidenced in 2011, research in the field has noticeably increased since 2012. This is reflected in Fig. 1a, which displays the number of papers published from 2000 to 2016 that defined “cellulose” and “supercapacitor” as keywords. Even though there was a progressive increase from 2007 to 2014, the number of papers published in this field has grown considerably during the last three years (2014–2016). The number of citations of such published papers reveals similar features (Fig. 1b), thus evidencing the fast expansion of this exciting research area.

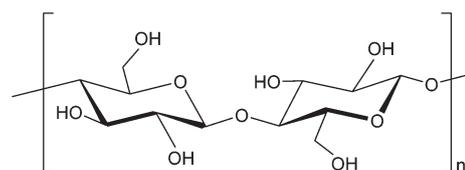
Accordingly, in this review, we discuss very recent and important advances regarding the use of cellulose in supercapacitors with promising high performance. This discussion has been divided into four sections according to the roles played by cellulose in the fabricated devices. More specifically, cellulose has been employed as: (i) a lightweight mechanical substrate that imparts flexibility and strength to electrochemically and electrically active materials, for example, carbon nanotubes (CNTs), graphene, and ECPs; (ii) a natural template to be coated with other electrochemically active electrode materials or to be transformed into other carbon species through pyrolytic processes; (iii) a separator membrane



Carlos Alemán

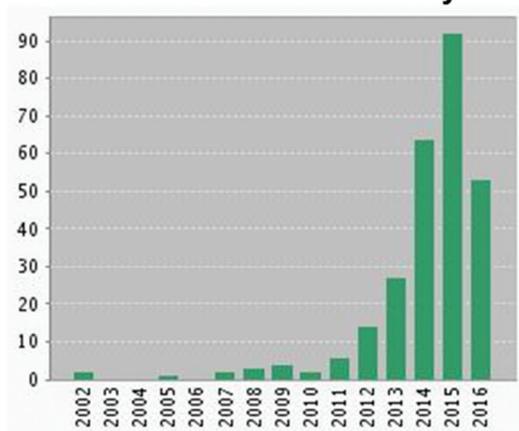
Carlos Alemán graduated in Chemistry from the University of Barcelona (Spain). He received his Ph.D. from the Polytechnic University of Catalonia (UPC) in 1994, where he was promoted to the position of Full Professor of Physical Chemistry. He was a postdoctoral researcher at the ETH in Zürich (Switzerland) and a visiting professor at the Università di Napoli Federico II (Italy), University of Twente (Holland) and Universidade

Federal do Rio Grande do Sul (Brazil). Since 2003, he has been the leader of the “Innovation in Materials and Molecular Engineering” (IMEM) group in the Chemical Engineering Department and in the Centre for Research in Nano-Engineering. His main research interests focus on conducting polymers and biopolymers with biomedical and technological (energy) applications.



Scheme 1

(a) Published items in each year



(b) Citations in each year

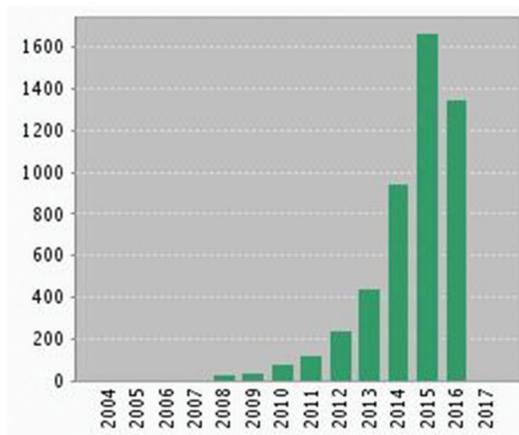


Fig. 1 Evolution of (a) the number of papers published every year in the field of cellulose-based supercapacitors and (b) the number of citations of such papers. The search was carried out using the Web of Science (Thompson Reuters) combining *cellulose* and *supercapacitors* as keywords.

between supercapacitor electrodes; and (iv) a material that facilitates the absorption of electrolytes acting as an electrolyte reservoir or even as a part of the electrolyte itself. Besides, special emphasis has been placed on relating the fabrication of cellulose-based supercapacitors to green chemistry. Thus, in spite of this biopolymer being extracted from renewable natural sources, green chemical processes must fulfil some important conditions, for example, preventing pollution at the molecular level using safe solvents and reactants, reducing the negative impacts, on human health and the environment, of chemical products and reactions, increasing energy efficiency by avoiding high temperatures and pressures when possible, and avoiding chemical derivatives that use additional reagents and generate waste. All the studies cited in sections (i), (ii) and

(iv) have been summarized in three tables to facilitate their comparison (Tables 1–3).

(i) Cellulose as a support for mechanical reinforcement

Flexible display devices require lightweight, bendable and high performance supercapacitor electrodes. To this end, cellulose-based materials have been widely used as simple structural scaffolds for depositing active conducting materials.^{26–28} This case, which is the most frequent, is based on the fact that the good mechanical properties of this polysaccharide confer mechanical strength and/or flexibility to the electrode, even though other interesting properties, such as transparency, chemical stability, and lightweight, can also be indirectly obtained. Table 1 summarizes the main characteristics of the supercapacitors based on cellulose acting as a mechanical reinforcement that are described below.

In a pioneering study, Cui and co-workers²⁹ fabricated supercapacitors and lithium ion batteries using simple commercial paper sheets that were coated with aqueous CNT ink with sodium dodecylbenzenesulfonate (SDBS) as a surfactant. Because paper absorbs water easily and binds to CNTs, the fabrication process was based on a simple Meyer rod coating process (*i.e.* the ink is deposited onto the paper as it passes over the bath roller), enhancing the main principles of green chemistry (*i.e.* avoid or at least reduce the consumption of organic solvents and use low-energy consumption processes avoiding high temperature and/or pressure). The resulting conductive paper exhibited not only flexibility but also excellent mechanical strength. Interestingly, supercapacitors based on CNT-conductive paper showed a specific capacitance of 200 F g⁻¹ and stable cycling life over 40 000 cycles.²⁹ Later, the same group coated single-walled CNTs (SWCNTs) onto cotton fibres (fabrics) to obtain a highly electrically conductive interconnecting network.³⁰ Supercapacitors composed of such electrodes (SWCNTs-coated cotton as the active material and the current collector, and Li₂SO₄ as the electrolyte) had excellent cycling performance (good capacity retention after 35 000 cycles) and a specific capacitance of 70–80 F g⁻¹.³⁰ Due to these properties, the integration of cotton/SWCNT electrodes into wearable electronics was proposed.

Indeed, everyday textiles, which are flexible and porous, represent an interesting option to prepare flexible electrodes. In general, the fabrication processes here described, which resemble those used in the textile industry, stand out because of their simplicity, scalability and frequent use of green chemistry tools. For instance, by an extremely easy “dipping and drying” process, where the cellulose textile is coated with aqueous SWCNTs ink followed by drying in an oven at 120 °C for 10 min, the resulting conductive electrodes have outstanding flexibility and stretchability, excellent conductivity (125 S cm⁻¹), and high areal capacitance when assembled into supercapacitors (0.48 F cm⁻²).³¹ Besides, after electrodepositing MnO₂ onto the SWCNT coated textile fibers,

Table 1 Summary of the most important characteristics (*i.e.* preparation method, properties provided by cellulose, gravimetric and areal – if available – SC) of supercapacitors in which cellulose is used as a support for mechanical reinforcement

Cellulose-based system	Preparation method	Properties provided by cellulose Gravimetric SC; areal SC	Ref.
CNT-conductive paper	Coating of commercial paper with an aqueous CNT ink	Low cost, flexibility and mechanical strength 200 F g ⁻¹	29
SWCNT-conductive cotton	A cotton sheet was dipped into a SWCNT ink, which coated the textile immediately	Flexibility, wearable ability and mechanical strength 70–80 F g ⁻¹	30
SWCNTs ink/cellulose textile	Coating by “dipping and drying” followed by drying in oven at 120 °C (10 min)	Flexibility, stretchability, and excellent conductivity (125 S cm ⁻¹) 0.48 F cm ⁻²	31
Cotton cloth/GNS composite	“Brush-coating” and drying process using a cotton cloth piece and a stable GO suspension as ink, followed by annealing at 300 °C under an argon atmosphere	Flexibility, light-weight, mechanical strength 82 F g ⁻¹	32
CNT-conductive paper	Coating CNTs on office papers by a “drop-dry” method	Flexibility 135 F g ⁻¹	33
GO/cellulose tissue	Graphene sheets, which are produced by oxidizing a graphene aerogel with hydrogen peroxide. The oxidized graphene suspension is mixed with cellulose to render a graphene–cellulose composite by vacuum filtration	Very open structure; high ion-transport rates 54–80 mF cm ⁻²	34
Cellulose graphene	Drawn with a graphite rod on standard printing paper	Flexibility, lightweight nature, and porosity 12–23 F g ⁻¹ ; 2.3 mF cm ⁻²	35
Cellulose/graphite/Ni/MnO ₂	Graphite drawn on a cellulose paper and subsequent coating by electrodeposition of Ni and MnO ₂ layers	Flexibility and lightweight nature 680 F g ⁻¹ ; 175 mF cm ⁻²	36
Paper/CNT/MnO ₂	Paper coated with CNTs dispersed in water and a MnO ₂ layer electrochemically deposited on the top	Flexibility, robustness and low-cost 540 F g ⁻¹	40
MFC/MWCNT	Chemically modified MWCNTs mixed with a water dispersion of MFCs	Mechanical strength and flexibility 155 mF cm ⁻²	41
CNF/SWCNT non-woven macrofiber mats	Controlled extrusion of a CNF/SWCNT dispersion and drying under restricted conditions	Flexibility, mechanical strength, porosity and hydrophilicity 3.3 mF cm ⁻²	42
Oxidised carbon nanohybrids/commercial cellulose membrane	Filtering a water dispersion of oxidised carbon nanohybrids, which were derived from MWCNTs through the cellulose membrane	Flexibility 75 mF cm ⁻²	43
Electrically conductive paper made of CFs coated with GNSs	Papermaking process consisting of dispersing chemically synthesized GNS into a cellulose pulp, followed by infiltration	Flexibility, mechanical tough and resistance against mechanical scratching 252 F g ⁻¹	44
CF-GNS paper	3D interwoven structure of GNSs and CFs obtained through a dispersion	Flexibility 120 F g ⁻¹ ; 81 mF cm ⁻²	45
Cross-linked Ni(OH) ₂ –CFs composite covered with graphene	One-pot hydrothermal synthesis of the composite one graphene coated CFs	3D substrate for graphene coating 2276 F g ⁻¹	46
CNF/RGO/MWCNT	Freeze-drying of an aqueous dispersion of CNFs, GONSS and MWCNT, followed by subsequent thermal reduction of GONSS <i>in situ</i>	Flexibility, porosity and electrolyte absorption properties 252 F g ⁻¹ ; 216 mF cm ⁻²	47
CNF aerogel with Ag particles coated with PANi nanoparticles	<i>In situ</i> deposition of Ag particles on CNF aerogel and subsequent electrochemical coating of Ag particles with PANi	Flexibility and porosity 176 mF cm ⁻²	48
BNC coated with CNTs	An ink is fabricated by dispersing DWCNTs with sodium dodecylbenzenesulfonate surfactant in deionized water. Then, the ink is poured onto BNC paper	Flexibility, mechanical strength and chemical stability 50 F g ⁻¹	52
Cellulose paper/RGO	Successive application of papermaking and flash-reduction processes to a single-layer GO and recycled pulp mixture	Flexibility, recyclability and mass-productibility 212 F g ⁻¹ ; 24 mF cm ⁻²	53
Cellulose/PPy aerogel composite	Surface modification of a cellulose scaffold using a template-polymerization method	Flexibility and structured porosity 392–308 F g ⁻¹	54
Paper/PPy	“Soaking” of common printing paper in a Py monomer solution and subsequent immersion in a ferric chloride solution containing hydrochloric acid to polymerize PPy onto the paper substrate	Flexibility 370 F g ⁻¹ ; 42 mF cm ⁻²	55
Cellulose/PPy	<i>In situ</i> oxidative polymerization of Py in a cellulose–water dispersion after adding oxidants	Flexibility and lightweight nature ~120 F g ⁻¹	56
Cellulose/PPy	<i>In situ</i> oxidative polymerization of Py in a cellulose–water dispersion after adding oxidants	Mechanical strength and high surface area 32 F g ⁻¹ or 38 F g ⁻¹ (210 mF cm ⁻²) depending on the charging process	58, 59
NC/PPy	Cellulose/PPy composite reinforced with 8 μm-thick chopped carbon filaments	Mechanical strength 60–70 F g ⁻¹ ; 480 mF cm ⁻²	60

Table 1 (Contd.)

Cellulose-based system	Preparation method	Properties provided by cellulose Gravimetric SC; areal SC	Ref.
CNCs/PPy nanocomposites	Electrochemical co-deposition of chemically modified CNCs and Py monomers	Mechanical strength and porosity 240 F g ⁻¹	61, 63
CNCs/PPy nanocomposites	Grafting of carboxylic acid groups on CNCs to enhance the adsorption of Py monomers, followed by <i>in situ</i> chemical polymerization of the latter	Mechanical strength and lightweight nature ~250 F g ⁻¹	64
CNCs/PVP/PPy	Chemical polymerization of PPy on PVP coated CNCs	Mechanical strength and lightweight nature 339 F g ⁻¹	65
Cotton/MWCNT/PPy	Cotton/MWCNT by the “dip and dry” method followed by potentiostatic deposition of PPy	Flexibility and mechanical strength 535 F g ⁻¹	66
NC/PPy/GONS composite	<i>In situ</i> polymerization of PPy on a NC/GONS composite	Flexibility, mechanical properties and interacting ability 244 F g ⁻¹	67
Cotton/activated carbon	Activated carbon impregnated into cotton fabrics using screen printing	Flexibility, porosity and mechanical strength 85 F g ⁻¹ ; 430 mF cm ⁻²	68
BC/PPy composite	<i>In situ</i> chemical polymerization of PPy onto dispersed BC nanofibers	Porosity 316 F g ⁻¹	71
3D network of BC/GO/PPy	Chemically polymerized PPy onto a BC/GO composite made by dispersing BC nanofibers on the surface of GO	Provide mechanical stability. Formation of 3D conduction paths 556 F g ⁻¹ ; 278 F cm ⁻³	72, 73
BC nanofibers/PPy	PPy nanoparticles were homogeneously coated onto TEMPO-oxidized BC nanofibers (TOBC) through chemical polymerization	High porosity 153 F g ⁻¹	74
BC/PPy nanofibers/MWCNT	Vacuum-filtering of a suspension of BC/PPy nanofibers, which were prepared by <i>in situ</i> polymerization of Py adsorbed onto BC, and functionalized MWCNTs	Flexibility and mechanical strength 590 mF cm ⁻²	75
BC/PPy composite	Immersion of BC membranes in a Py solution for subsequent <i>in situ</i> polymerization of the monomer in the swollen membrane	Flexibility 459 F g ⁻¹	76
Cotton fabrics/PPy composite	Immersion of cotton fabrics in a Py aqueous solution with lignosulfonate for subsequent <i>in situ</i> polymerization of the monomer	Flexibility and wearability 304 F g ⁻¹	77 and 78
BC/PAni composite	<i>In situ</i> chemical polymerization of PAni onto dispersed BC nanofibers	Flexibility and porosity 273 F g ⁻¹	79
3D network of CNF/MWCNT/PAni	Chemically polymerized PAni using an aerogel-like 3D CNFs/MWCNTs substrate with aniline adsorbed at the surface and inside	Improvement of the flexibility and mechanical strength of the film electrode. Formation of 3D conduction paths 250 F g ⁻¹	80
Paper/Au/PAni composite	PVA coating of a paper made of cellulose fibres and subsequent deposition of a layer of evaporated gold. PAni is electrodeposited on top	Flexibility, lightweight nature and porosity 560 F g ⁻¹	81
Regenerated cellulose/PAni composite	<i>In situ</i> chemical polymerization of PAni in native cellulose (cotton linter pulp)	Mechanical strength and porosity 160 F g ⁻¹	82
PAni nanowires onto nylon-6/CA thin film	Chemically polymerized PPy onto mats of electrospun nylon-6 nanofibers infiltrated with CA	Reinforced nylon fibres 400 F g ⁻¹	83
SWCNTs and PAni nanoribbons wrapped around interconnected cellulose fibre	Dip-adsorption polymerization: coating of macroporous cellulose fibres with SWCNTs, followed by infiltration and <i>in situ</i> polymerization of aniline	Flexibility and mechanical integrity upon repeated fold-unfold 533 F g ⁻¹ ; 33 mF cm ⁻²	84
PAni/exfoliated graphite/cellulose/silver nanoparticles	Aniline is <i>in situ</i> polymerized in the presence of exfoliated graphite, cellulose and silver nitrate. The resulting nanocomposite is vacuum-filtered to obtain a free-standing thin film	Flexibility and consistency 240 F g ⁻¹ ; 3840 F cm ⁻²	85
Conductive PEDOT paper	Polymerization at the interface of two immiscible liquids on a cellulose paper	Flexibility 115 F g ⁻¹ ; 115 mF cm ⁻²	89
Integrated SWCNT-paper device	SWCNT ink printed with Meyer rods coated onto single sheets of commercial paper pre-treated with PVDF	Lightweight nature and mechanical strength 33 F g ⁻¹	124

the areal capacitance of these devices experienced a 24-fold increase. Similarly, flexible electrodes were prepared *via* a “brush-coating and drying” process using everyday cotton cloth as the platform and a stable graphene oxide (GO) suspension as the ink.³² Thus, after transforming the system into a cotton cloth/graphene nanosheet (GNS) composite by anneal-

ing at 300 °C under an argon atmosphere, it exhibited good electrical conductivity, outstanding flexibility, and strong adhesion between GNSs and cotton fibres. Then, these cotton cloth/GNS electrodes were easily assembled into a home-made symmetric supercapacitor with cylindrical format (Fig. 2) that showed a specific capacitance of 82 F g⁻¹, varying only 6.2%

Table 2 Summary of the most important characteristics (*i.e.* preparation method, properties provided by cellulose, gravimetric and areal – if available – SC) of supercapacitors in which cellulose is used as a mechanical inert template or a renewable carbon source

Cellulose-based system	Preparation method	Properties provided by cellulose Gravimetric SC; areal SC	Ref.
CMC/PPy nanocomposite	<i>In situ</i> chemical polymerization of PPy using CMC nanospheres as a template	Protection of the backbone of the PPy layer in charge-discharge processes 180 F g ⁻¹	90
Interconnected PPy and NC/PPy fibres	Synthesis of PPy fibres and NC/PPy using NC fibres as template followed by mixing and subsequent filtration	Mechanical integrity and high surface area 36 F g ⁻¹ (154 mF cm ⁻²)	93
Nitrogen-functionalized carbon nanofibers	Electrospinning of acetate cellulose, deacetylation of electrospun cellulose acetate nanofibers, and PPy polymerization	Template to prepare a raw material with 3D structure 236 F g ⁻¹ (1045 F g ⁻¹ with Ni(OH) ₂)	94
Carbonaceous composite derived from DWCNTs	Carbonization of cellulose fibers impregnated with DWCNTs	Sustainable raw material as a precursor of carbon nanofibers 163 F g ⁻¹	95
Carbonaceous composite derived from MWCNTs	Carbonization of cellulose fibers impregnated with MWCNTs	Sustainable raw material as a precursor of carbon nanofibers 241 F g ⁻¹	95
Ultramicroporous carbonaceous material	Cotton cellulose carbonised and activated using atomically dispersed potassium and heating at 800 °C	Sustainable raw material as a precursor of a carbonaceous amorphous material 130 F g ⁻¹	96
Carbon nanofibers activated with MWCNTs	Electrospinning of CA/MWCNTs, deacetylation and carbonization at 1000 °C	Precursor of carbon nanofibers 145 F g ⁻¹	97
Carbonized CA nanofibers	Partially hydrolyzed CA electrospun nanofibers are carbonized in N ₂ flow at 1000 °C and activated in CO ₂ at 850 °C	Precursor of inter-bonded carbon nanofibers 241 F g ⁻¹	98
CNFs/AC paper-like films	CNFs were mixed with traditional activated AC and heated at 800 °C to produce paper-like films	Raw material AC particles increase the maximum power density values	99
Ramie-based ACHF	One-step activation of natural hollow ramie fibres under ZnCl ₂ impregnation and pyrolysis at 650 °C. The resulting samples were washed with HCl, rinsed in distilled water to neutral, filtered and dried to obtain the ACHF	Natural biomaterial 287 F g ⁻¹	100
Heteroatom-doped carbon material	Hydrothermal treatment of <i>Broussonetia papyrifera</i> stem bark in the presence of KOH followed by simultaneous pyrolysis and KOH activation	Raw material for the fabrication of a material with a porous and localized graphitic structure 320 F g ⁻¹	101
Interconnected carbon nanosheets	Hydrothermal treatment of hemp bast fibre followed by KOH impregnation and carbonization	Raw material for the fabrication of graphitic nanosheets 110–144 F g ⁻¹	102
Oxygen-rich activated carbon	Acidification, pyrolysis under nitrogen flow and activation with KO of animal cellulose from crab shell wastes	Raw material for the fabrication of porous and oxygen-rich activated structures 281 F g ⁻¹	103
Meso-microporous activated carbon	Template-assisted synthetic method and chemical activation using renewable cellulose and biowaste lignosulphonate as the precursors	Raw material for the fabrication of activated structures with micro- and mesopores 286 F g ⁻¹	105
Nanoporous carbon nanosheets	Soaking citrus peels in a 30 wt% KOH aqueous solution (30 min) and drying at 80 °C (36 h) in presence of potassium ions	Sustainable raw material as a carbon precursor 110 F g ⁻¹	106
Carbonised cotton pulp	Pre-treatment at 600 °C to eliminate volatile components and graphitisation at 1000 °C	Abundant biomass raw material 107 F g ⁻¹	107
ACT/MnO ₂	Application of a traditional dipping, drying and curing process to cotton T-shirt textiles and subsequent electrochemical deposition of MnO ₂	Raw material for the fabrication of porous supporting backbones with high surface area 120 F g ⁻¹	108
Activated nanosized carbon	Pyrolysis of BC at 950 °C and subsequent activation with CO ₂	Raw material for the fabrication of nanosized carbon 42 F g ⁻¹	109
Carbon nanofibers/Ni ₃ S ₂ composite	BC transformed in carbon nanofibers using a pyrolytic treatment under a flowing N ₂ atmosphere and subsequent loading of Ni ₃ S ₂ nanoparticles	Raw material for the fabrication of porous 3D carbon nanofiber networks 69 F g ⁻¹	110
Carbon nanofibers-bridged porous carbon nanosheets	Heat-treatment under a nitrogen atmosphere of a BC and potassium citrate mixture	Raw material for the formation of carbon nanofibers 261 F g ⁻¹	111
Nitrogen and phosphorous co-doped carbon nanowires	Impregnation of NH ₄ H ₂ PO ₄ into BC pellicles and carbonization under a NH ₃ atmosphere at 800 °C	Renewable raw material as a precursor of carbon nanowires 258 F g ⁻¹	112
Nitrogen-doped BC nanofibers	PAni coated bacterial cellulose (BC) was carbonized in a one-step process at 700 °C for 2 h under an Ar atmosphere	3D bio-template 1950 F g ⁻¹	113

Table 2 (Contd.)

Cellulose-based system	Preparation method	Properties provided by cellulose Gravimetric SC; areal SC	Ref.
BC-based supercapacitor	Activated pyrolysed BC as the electrode combined with a BC/H ₃ PO ₄ gel electrolyte	Eco-friendly and sustainable energy storage device 242 F g ⁻¹ (289 mF cm ⁻²)	114
Carbon aerogel	Formation of cellulose aerogels after purification of bagasse from sugarcane. Pyrolysis of cellulose aerogels at 800 °C under nitrogen flow and activation with KOH	Raw material of porous carbon 142 F g ⁻¹	115
Nitrogen-doped graphene onto carbonized cellulose fibres	Mixing of cotton and urea and subsequent annealing to form functional aerogels in controlled shape, followed by a pyrolysis process	Raw material 108 F g ⁻¹	116
Hierarchical porous nitrogen-doped carbon aerogel	After dissolving, gelling and freeze-drying the cellulose, a carbonization process was applied under a NH ₃ atmosphere at 800 °C	Renewable and low-cost raw material as a precursor of carbon aerogels 225 F g ⁻¹	117 and 118

Table 3 Summary of the most important characteristics (*i.e.* preparation method, properties provided by cellulose, gravimetric and areal – if available – SC) of supercapacitors in which cellulose plays a role as electrolyte

Cellulose-based system	Preparation method	Properties provided by cellulose Gravimetric SC; areal SC	Ref.
CF/CNT/MnO ₂ /CNT	Two dip-coating of CNTs separated by electrodeposition of MnO ₂	Porosity and electrolyte reservoir 327 F g ⁻¹	128
CNF/RGO aerogel	Transformation of a CNF/RGO hydrogel, which was prepared by acidifying an aqueous solution of CNFs, GONSs and VC-Na, into an aerogel by supercritical CO ₂ drying	Electrolyte nanoreservoir and nanospacer, hydrophilicity and flexibility 207 F g ⁻¹ ; 158 mF cm ⁻²	129
CNF/MWCNT aerogel	Supercritical CO ₂ drying of CNF/MWCNT aerogels derived from the hydrogels resulting from a CNF/MWCNT suspension	Electrolyte nanoreservoir, dispersant and nanospacer 178 F g ⁻¹	130
CF/PPy	<i>In situ</i> polymerization of Py adsorbed onto CFs extracted from waste paper	Electrolyte transfer medium, spacer and mechanical strength 51 F g ⁻¹	132
CF/graphene/PPy	<i>In situ</i> polymerization of Py adsorbed onto a CF/graphene composite prepared using CFs extracted from waste paper	Electrolyte reservoir, electrolyte transfer medium, spacer and mechanical strength 243 F g ⁻¹	133
MC ion gels	Codissolution of PYR ₁₄ TFSI and MC in <i>N,N</i> -dimethylformamide, which after heating and subsequent cooling forms a gel	Strong and solid polymer electrolyte A capacitance of 2 μF cm ⁻² ; high ambient ionic conductivities (>1 × 10 ⁻³ S cm ⁻¹),	133
CAP	Hydrolysis of cellulose using acetic acid and propionic acid	Fabrication of a solid polymer electrolyte combining CAP, H ₃ PO ₄ and PEG 64 F g ⁻¹	134

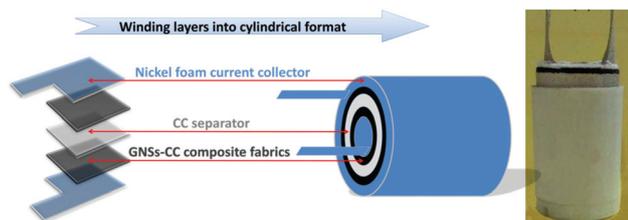


Fig. 2 Schematic diagram (left) and photograph (right) of the cylindrical symmetric supercapacitor obtained by assembling cotton cloth/GNS pieces as electrodes and pure cotton cloth as a separator. CC refers to cotton cloth. Adapted from ref. 32.

after 1500 consecutive redox cycles,³² which is in good agreement with the values reported by Cui *et al.*³⁰ using less energy.

Another simple strategy to obtain flexible supercapacitors with cellulose as a mechanical reinforcement consists of coating paper with conductive materials. Hence, Kang *et al.*

fabricated all-solid state flexible supercapacitors by coating CNTs onto office papers – the “drop-dry” method – and using ionic-liquid-based gel electrolytes (*i.e.* fumed silica nanoparticles were mixed with an ionic liquid, 1-ethyl-3-methylimidazolium). Although the supercapacitor showed excellent stability and flexibility, the specific capacitance of the electrode being 135 F g⁻¹,³³ this approach represented a step back in terms of green chemistry in which the use of ionic liquids is highly controversial due to their unsafe synthesis.

Recently, graphene sheets, which were produced by oxidizing a graphene aerogel with hydrogen peroxide, a potentially green and environmentally-friendly oxidant because it releases only water as by-product, were deposited over a common porous cellulose tissue to render free-standing and flexible composites with enhanced robustness.³⁴ The closely interconnected and porous 3D graphene architectures, which consisted of two types of holey graphene units (*i.e.* wrinkled graphene sheets and graphene nanoscrolls), produce a very open structure that provides easy access to the electrolyte, thereby

guaranteeing high ion-transport rates and, consequently, remarkable capacitive performance ($54\text{--}80\text{ mF cm}^{-2}$). Moreover, drawing graphite on cellulose paper also results in flexible and lightweight supercapacitors.³⁵ Although this solvent-free deposition technique represents a low cost, eco-friendly, highly scalable, and versatile fabrication method for integrated paper-based energy devices, the resulting gravimetric capacitance was very low (*i.e.* $12\text{--}23\text{ F g}^{-1}$ depending on the paper) in comparison with other cellulose-based devices.³⁶ Specifically, multi-layered paper/graphite/Ni/MnO₂ electrodes were prepared by sequentially coating a graphite layer (drawn), a Ni layer (electrodeposited), and a MnO₂ nanosheet (electrodeposited) onto ordinary cellulose paper.³⁶ Besides, the capacitance of this electrode (680 F g^{-1}) was significantly higher than those reported for hierarchical MnO₂ structures (315 F g^{-1}),³⁷ MnO₂ nanotube/nanofibers (461 F g^{-1}),³⁸ and MnO₂-CNT sponges (240 F g^{-1}).³⁹ Accordingly, assembled symmetric and green supercapacitors, which were prepared using a filter paper as the separator and sodium carboxymethyl cellulose (CMC) gel as the solid state electrolyte, exhibited excellent flexibility and mechanical properties, thus allowing bending to different angles and twisting, in addition to exhibiting good capacitive behaviour (specific capacitance of $\sim 10\text{ F g}^{-1}$) and stability (*i.e.* less than 4% loss of the capacitance after 6000 cycles between 0.8 and 1.2 V).³⁶

In another study, MnO₂ was electrochemically deposited onto papers which had previously been coated with CNT through the “drop-by-drop” method.⁴⁰ Flexible paper/CNT/MnO₂ supercapacitors, which were tested using Na₂SO₄ as the electrolyte, showed a specific capacitance of 540 F g^{-1} , even though in this case the cycling stability was not tested.⁴⁰

Cellulose fibres (CFs), either nano- or microfibrillated, impart flexibility and mechanical strength to the electrode, thus acting as an adequate skeleton material. Based on these features, Deng and co-workers⁴¹ prepared electrode sheets combining microfibrillated cellulose (MFC, water slurry) with chemically modified MWCNTs (*i.e.* -COOH groups were introduced through an oxidation reaction). The tensile strength and modulus of the resulting MFC/MWCNT sheets, which contained 48 wt% of MWCNTs, were 1 and 123 MPa, respectively, evidencing that these electrodes behave as strong paper. In addition, although the specific areal capacitance of symmetric supercapacitors constructed using MFC/MWCNT electrodes depended on the thickness of the sheets increasing from 31 mF cm^{-2} (0.19 mm) to 155 mF cm^{-2} (1.08 mm),⁴¹ the capacitance remained almost constant under bending at different curvatures.

Furthermore, CNF/SWCNT microfiber mats, which were prepared by extruding a CNF/SWCNT suspension in an ethanol coagulation bath and drying under restricted conditions,⁴² showed a porous structure with SWCNTs preferentially oriented along the extrusion direction, thus favouring electron transport along the axial direction of the microfiber. When used as electrode materials and charge collectors, symmetric supercapacitors show a capacitance of only 3.29 mF cm^{-2} , one order of magnitude lower than that in the

previous study for the thinnest electrode.⁴¹ However, the system retained 97% and 96% of that value after 5000 charge-discharge cycles and 1500 bending cycles, respectively, demonstrating not only long-term cycling stability but also excellent flexibility without loss of electrochemical performance.⁴² In contrast, functionalized MWCNTs were assembled with cellulose membranes as free-standing flexible electrodes that rendered solid state symmetric supercapacitors with higher areal capacitance (75 mF cm^{-2}) and excellent cycling stability.⁴³

In another example, CFs were coated with GNSs by a simple paper-making process (Fig. 3a) forming a continuous network through a bridge of interconnected CFs at a relatively low GNS concentration (3.2 wt%).⁴⁴ The resulting flexible conductive paper, which was also mechanically tough and resistant against liquid attack and mechanical scratching (Fig. 3b), exhibited a capacity of 252 F g^{-1} . Likewise, a three-dimensional interwoven structure of GNSs and CFs showed a gravimetric capacitance of 120 F g^{-1} , retaining >99% capacitance over 5000 charge-discharge cycles.⁴⁵ The capacitance of the corresponding supercapacitor was 68 F g^{-1} under highly flexible conditions.⁴⁵

Following a simple hydrothermal route, Zhang and co-workers⁴⁶ developed vertical cross-linked Ni(OH)₂-graphene composite networks using CFs that exclusively acted as the support for the graphene coating. The composite presented an extremely high mass capacitance (2276 F g^{-1}), good rate capability, and excellent cycling stability.

In addition to the flexibility displayed by CFs, the extremely high porosity and excellent electrolyte absorption properties displayed by cellulose nanofiber (CNF)-based aerogels were exploited to fabricate free-standing, lightweight, all-solid-state flexible supercapacitors.⁴⁷ Hence, extremely highly porous CNF/reduced graphene oxide (RGO)/MWCNT electrodes (Fig. 3c), which were obtained using the process described in Fig. 3d, exhibited a specific capacitance of 252 F g^{-1} and an excellent cyclic stability, with more than 99.5% specific capacitance retained after 1000 charge-discharge cycles.⁴⁷ Deng and co-workers⁴⁸ deposited Ag particles on CNF aerogels to provide fast electron transportation channels, and polyaniline (PANI) nanoparticles were deposited on the surface of Ag particles to achieve high capacitive performance. The areal specific capacitance of as-fabricated supercapacitors, which retain electrochemical properties when they are bent, reached 176 mF cm^{-2} .

Moreover, due to its characteristic features, bacterial nanocellulose (BNC) represents an alternative to plant-derived cellulose as the reinforcing element when preparing electrode paper for supercapacitor applications.⁴⁹ It is worth mentioning that, despite its biosynthetic origin, production of BNC is farther from main green chemistry principles than cellulose, which is directly extracted from nature. BNC has high purity and crystallinity, and therefore BNC-based papers have higher mechanical strength and chemical stability than regular cellulose papers (*i.e.* in general, BNC and regular CFs are 20–100 nm and $\sim 100\text{ }\mu\text{m}$, respectively).^{50,51} Because of this, Kim and co-workers⁵² prepared all-solid state flexible supercapacitors combining BNC with double-walled CNTs

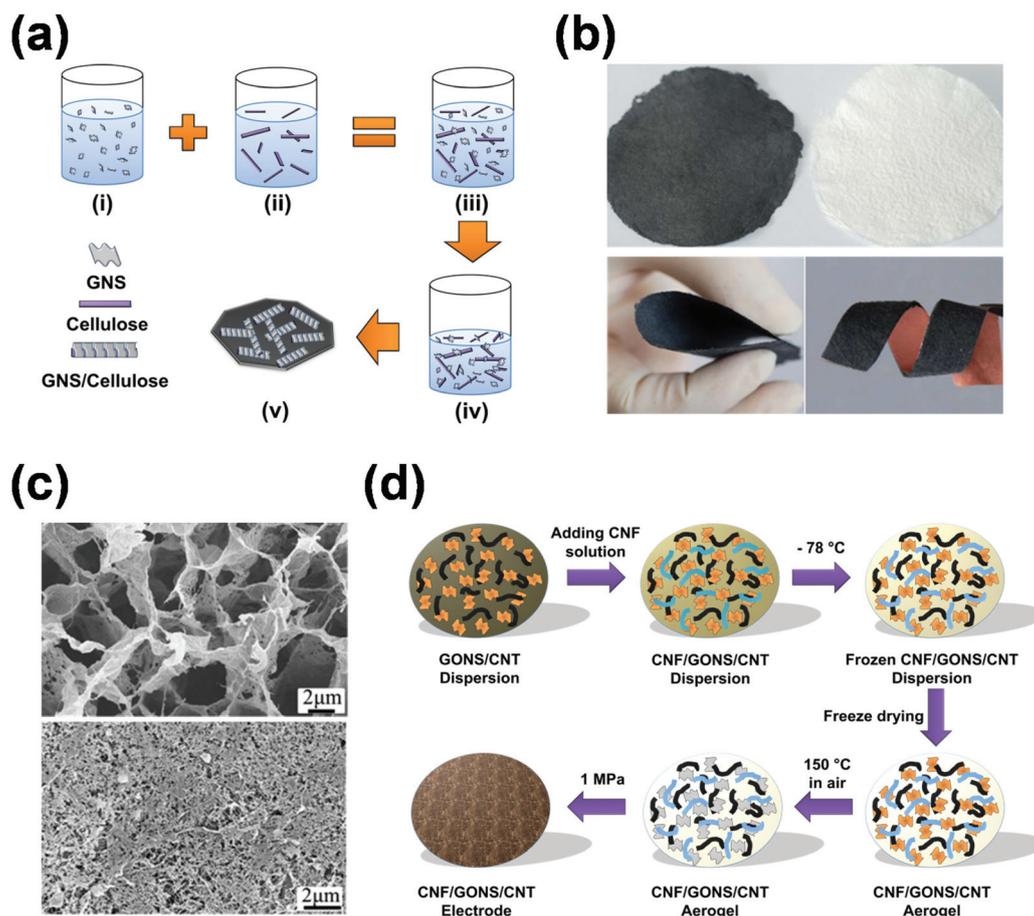


Fig. 3 (a) Scheme of the process for the fabrication of conductive paper using cellulose fibres and GNSs: dispersion of GNSs in water (i) and mixing with cellulose pulp (ii) to form a homogeneous GNS and cellulose dispersion (iii), followed by infiltration to induce the deposition of GNSs onto cellulose fibres (iv), resulting in the formation of GNS-coated interconnected cellulose composite paper (v). (b) Photographs of the GNS/cellulose composite paper (black) and a pure cellulose paper (white) as a comparison (top); the bent composite paper, showing the flexibility of the paper (bottom left); a flexible supercapacitor made with a composite paper adhered to a copper foil as the electrical conductor (bottom right). Taken from ref. 44. (c) SEM images of the cryofractured surface of a CNF/RGO/MWCNT aerogel (top) and a compressed film of the same aerogel (bottom). Taken from ref. 47. (d) Schematic diagram of the fabrication process of CNF/RGO/MWCNT electrodes. CNT refers to MWCNT.

(DWCNTs) and triblock copolymer ion gels as electrolytes. These BNC-containing supercapacitors showed a specific capacitance of 50 F g^{-1} , as well as an excellent cyclability with a reduction of only $<0.5\%$ of the specific capacitance after 5000 charge–discharge cycles.⁵²

Although cellulose-based materials are environmentally friendly, the chemical processes involved during their manufacture represent a threat towards the environment. Therefore, designing green energy storage devices not only has included the use of cellulose as a raw material, but also has tried to minimize the impact of its production. In this regard, Koga and co-workers⁵³ successfully transformed recycled waste pulp-fibres and single-layer GO sheets into a cellulose paper/RGO composite using a combination of a scalable papermaking process and flash reduction techniques (Fig. 4). The room-temperature, additive-free, and millisecond-time scale reduction of GO was achieved *in situ* in the composite by high-intensity pulsed light irradiation. This RGO/cellulose paper

composite electrode, which exhibited a specific capacitance of 177 F g^{-1} , was successfully applied for preparing an all-paper based flexible supercapacitor that provided a capacitance of 212 F g^{-1} .⁵³

Even though nanostructured carbon materials (*i.e.* CNTs or graphene) bind easily to cellulose to produce highly conductive electrodes, ECPs have satisfactorily been used to increase the specific capacitance of cellulose-based electrodes by Faradic reactions. Within this context, flexible and porous structured cellulose/polypyrrole (PPy) electrodes integrating the mechanical merits of cellulose with the conductivity of PPy have been prepared using several green technologies.^{54–67} For instance, a template polymerization method was carried out to produce cellulose/PPy flexible electrodes that, when assembled into a supercapacitor, showed a specific capacitance of about $308\text{--}392 \text{ F g}^{-1}$ and high stability during charge–discharge cycles.⁵⁴ On the other, PPy-coated paper was obtained by using a simple and low-cost “soaking and polymerization” method.⁵⁵

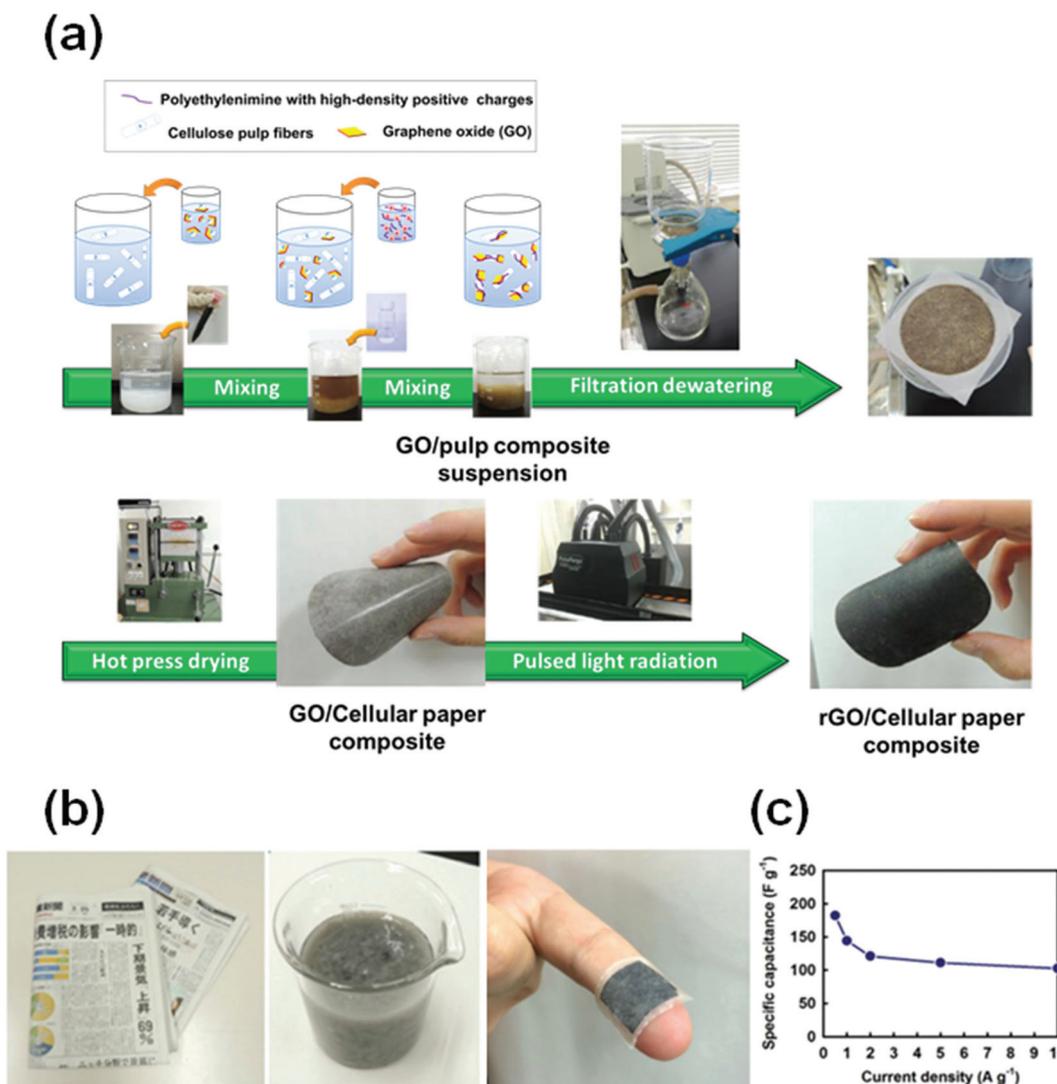


Fig. 4 (a) Preparation of the composite derived from single layer GO and recycled cellulose pulp fibres by papermaking and successive flash-reduction processes. Adapted from ref. 53. (b) Optical images of Japanese newspapers (left) and an aqueous suspension of their recycled waste pulps (middle) used to prepare all paper-based flexible supercapacitors (right). Taken from ref. 53. (c) Specific capacitance versus current density for the rGO/cellulose paper electrodes prepared using recycled waste pulps. Taken from ref. 53.

The resulting paper/PPy composite displayed high electrical conductivity (15 S cm^{-1}) and specific capacitance (370 F g^{-1}) values; exhibited high mechanical flexibility; and retained 76% of its initial capacitance after 10 000 cycles.⁵³

Interestingly, in 2014, Tammela *et al.*⁵⁶ evaluated the influence of the electrode thickness on the performance of symmetric charge storage devices fabricated using cellulose/PPy. These composites were prepared by mixing pyrrole (Py) monomer and the rest of the reagents required for the *in situ* polymerization in a water dispersion of *Cladophora* cellulose. The specific capacitance of the cellulose/PPy electrodes was $\sim 120 \text{ F g}^{-1}$, while the cell capacitance ranged from 39 to 43 F g^{-1} for the thinnest (800 μm) and thickest (1600 μm) electrodes, respectively. Since the gravimetric capacitance was practically unaffected by the electrode thickness, the authors

assumed that the active material was utilized to the same extent in all cases. This was further supported by the fact that the charge capacity of thick electrode devices was two times larger than that of devices containing thinner electrodes. Consequently, devices with higher charge capacities and area specific capacitances were obtained by increasing the thickness of the composite electrodes.⁵⁶ It is worth noting that, almost a decade ago, a similar procedure was used by Nyström *et al.*⁵⁷ to fabricate ultra-fast all-polymer paper based batteries. However, although the systems were limited in terms of delivered cell potential with respect to Li-ion batteries, the capacitance of the corresponding symmetric supercapacitors (32 F g^{-1}) only decreased 0.7% during 4000 galvanostatic cycles.⁵⁸ Besides, when charging was performed using the potential step method rather than the conventional constant

current charging, the cell capacitance of this symmetric device increased to 38 F g^{-1} .⁵⁹ Interestingly, symmetric supercapacitors prepared using electrodes made of *Cladophora* nanocellulose (NC) reinforced with $8 \mu\text{m}$ -thick chopped carbon filaments reached cell capacitances of $60\text{--}70 \text{ F g}^{-1}$, no loss of capacitance being detected during charging–discharging over 1500 cycles.⁶⁰ It should be noted that NC, which can be extracted from various plant resources through mechanical and chemical ways, with its nanoscale dimensions, highly crystalline nature and the ability to form hydrogen bonds resulting in strong and stable networks, provides a very suitable material for sustainable applications requiring mechanical integrity and flexibility.

A completely different approach based on electrochemical co-deposition was followed to prepare cellulose nanocrystals (CNC) and PPy-containing nanocomposites.⁶¹ Interestingly, CNCs were incorporated as the counterion during the electro-deposition, resulting in highly porous nanocomposites.

Accordingly, the capacitance of CNC/PPy electrodes (336 F g^{-1}), which was even higher than that of PPy doped with Cl^- (258 F g^{-1}), was attributed to such a porosity.⁶¹ More recently, the same authors observed similar features when applying this technology to PANi and poly(3,4-ethylenedioxythiophene) (PEDOT).⁶² Concretely, the specific capacitances of CNC/PAni and PAni were 488 and 358 F g^{-1} , respectively, while those of CNC/PEDOT and PEDOT were 69 and 58 F g^{-1} , respectively. Under potential cycling, the durability of CNC/PAni and PEDOT was slightly better than that of PAni and CNC/PEDOT, respectively. Besides, symmetric supercapacitor using CNC/PPy electrodes showed not only a high capacity (240 F g^{-1}), but also excellent stability (*i.e.* 47% of the initial capacitance was retained after 50 000 charge–discharge cycles).⁶³

Likewise, CNC/PPy electrodes with outstanding supercapacitor behaviour (250 F g^{-1}) were developed by following a smart protocol (Fig. 5a).⁶⁴ Specifically, carboxylic acid groups were grafted onto CNCs *via* a 2,2,6,6-tetramethyl-1-piperidinyloxy

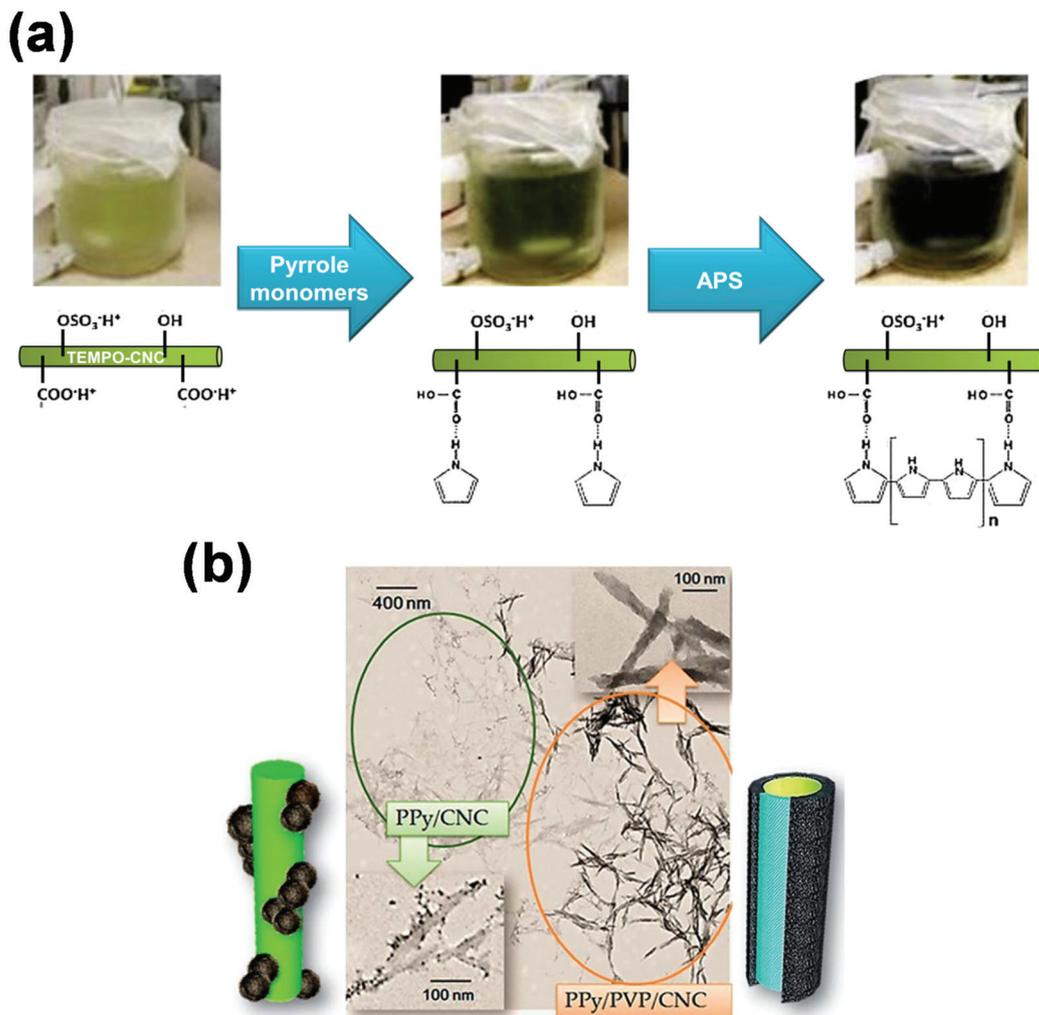


Fig. 5 (a) *In situ* chemical polymerization of CNCs/PPy nanostructures and colour change of the reacting solution during the polymerization process. Adapted from ref. 64. (b) PPy polymerization in the presence of equal amounts of pristine CNCs and PVP/CNCs with a cartoon illustrating the two drastically different morphologies of the end products. Taken from ref. 65.

(TEMPO)-mediated oxidation providing strong hydrogen bonding to enhance the adsorption of Py monomers. Later, *in situ* chemical polymerization of Py was further performed on a single high aspect ratio CNC. The high mechanical strength and good dispersability of CNCs resulted in a nanotemplate that controlled the deposition and growth of the polymeric layer, improving the electrochemical properties and processibility of PPy. Unfortunately, this strategy did not prevent the formation of PPy particles and irregular PPy coatings. Hence, to overcome such a limitation, the surface of CNCs was modified through physical adsorption of poly(*N*-vinylpyrrolidone) (PVP).⁶⁵ PVP altered the hydrophilic surface of CNCs to promote the favourable growth of hydrophobic PPy and, in addition, behaved as a steric stabilizer to prevent PPy-coated hybrid nanoparticles from further aggregation (Fig. 5b). As a result, the capacitance of CNCs/PVP/PPy increased to 339 F g⁻¹,⁶⁵ which represents an increment of ~35% with respect to the value displayed by composites prepared following the previous strategy.⁶⁴ Besides, the specific capacitance loss was lower than 9% and 13% after 1000 and 2000 charge–discharge cycles, respectively.

Flexible cellulose-based/PPy electrodes for high-performance supercapacitors have also been prepared by using either cotton⁶⁶ or NC⁶⁷ as reinforcement material. Thus, MWCNT-coated cotton electrodes with potentiostatically deposited PPy exhibited a good electrochemical performance with a specific capacitance of 535 F g⁻¹.⁶⁶ The latter value is significantly higher than that of flexible textile electrodes previously fabricated by Gogotsi and co-workers using nontoxic electrolytes, common cotton textiles employed in the apparel industry, and inexpensive but highly capacitive activated carbons (average specific capacitance of 85 F g⁻¹).⁶⁸ On the other hand, after combining NC with a small amount of graphene oxide nanosheets (GONSs) as a reinforcing and structure directing additive (5.8 wt%), PPy was polymerized *in situ* to render self-

standing, binder-free, dense, and flexible paper-based electrodes.⁶⁷ As reflected in Fig. 6, the success of this strategy relied on the ability of NC fibres, which contain abundant functional groups, to form inter- and intramolecular hydrogen bonds providing strong interaction between the components of the composite. Moreover, NC also prevented the re-stacking of GONSs.^{69,70} When used in an aqueous symmetric charge storage device, the specific gravimetric capacitance of NC/PPy/GONS electrodes was 244 F g⁻¹, and their capacitance retention higher than 85% over 16 000 charge–discharge cycles.⁶⁷ Besides, the impressive flexibility and mechanical robustness of NC/PPy/GONS electrode are displayed in Fig. 6.

Furthermore, there are plenty of studies in the literature that take advantage of the characteristics (*i.e.* 3D reticulate structure, high chemical purity, porosity and specific surface area, high hydrophilicity, and water-holding capability⁴⁹) of bacterial cellulose (BC) to produce BC/PPy nanocomposites with high capacitance performance.^{71–76} BC is secreted by bacterial cells from the genus *Acetobacter* in the form of entangled nanoribbons that are typically 70–150 μm wide and several micrometres long. The 3D network of nanoribbons exhibits high strength, elasticity and conformability, which show that such a green biologically produced material provides mechanical robustness. In 2013, Tang and co-workers⁷¹ prepared core-sheath structured nanocomposites by wrapping a homogeneous layer of PPy around previously dispersed BC nanofibers *via in situ* polymerization of self-assembled Py. The influence of the reaction parameters (*i.e.* mass and molar ratios of the BC, Py and the different oxidant agents and solvents) on the electrical conductivity of the BC/PPy nanocomposite was systematically investigated. The optimized electrical conductivity of BC/PPy, 77 S cm⁻¹, gave a sixty-fold increase with respect to pure PPy (~1.2 S cm⁻¹), which was attributed to the better doping and more porous structure of the nanocomposite. Therefore, BC/PPy nanocomposites exhibi-

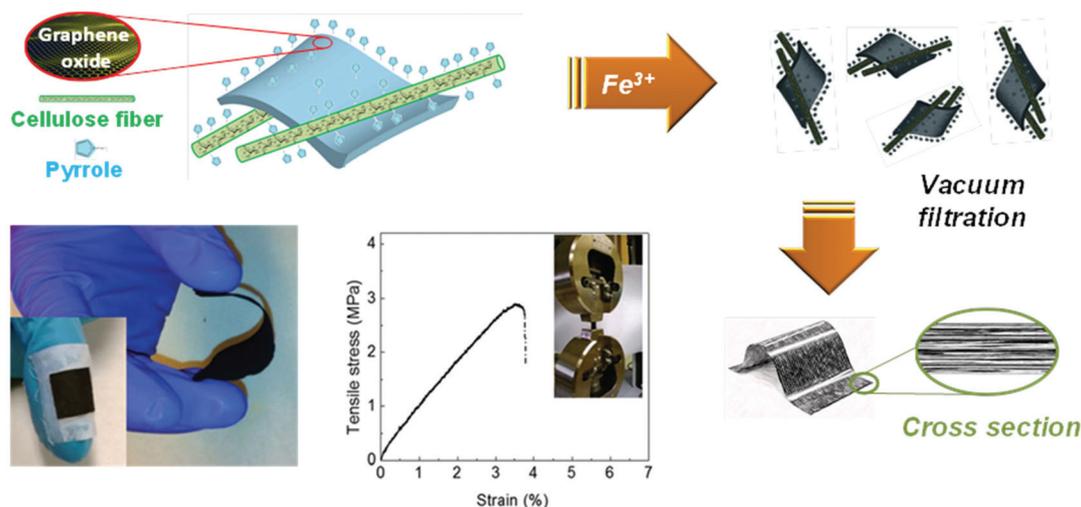


Fig. 6 Schematic illustration of the preparation and structure of NC/PPy/GONS electrodes. Digital photograph and strain–stress curve show the flexibility and robustness of this electrode, respectively. Taken from ref. 67.

ted specific capacitances of 316 F g^{-1} in a supercapacitor assembly, revealing great potential for practical application. Later, in 2015, the same group used the same synthetic strategy for wrapping PPy onto a previously developed hybrid made of BC nanofibers and GO.^{72,73} The coating of PPy on the BC/GO skeleton removed the perverse influence of the oxygen containing groups previously observed on GO.⁷³ Indeed, the as prepared BC/GO/PPy composites showed the highest electrical conductivity (1320 S m^{-1}) and the largest volumetric capacitance (278 F cm^{-3}) ever shown by carbon-based electrodes. However, despite these remarkable advantages, the main roles of BC were only the formation of 3D conduction paths and the enhancement of the mechanical stability.⁷² In a more recent study, PPy nanoparticles were homogeneously coated onto TEMPO-oxidized BC nanofibers (TOBC) through chemical polymerization to render films with high porosity ($101 \text{ m}^2 \text{ g}^{-1}$) and electrical conductivity (6.63 S cm^{-1}).⁷⁴ When assembled as electrodes in supercapacitor cells, the system showed a specific cell capacitance of 153 F g^{-1} and an exceptionally good cyclic stability (93% of retention after 1000 charge/discharge cycles).

Moreover, highly conductive paper electrodes of BC/PPy nanofibers in combination with MWCNTs were fabricated through a simple and environmentally friendly vacuum-filtering method, avoiding the use of other reagents.⁷⁵ Without the assistance of binders, conductive additives or any additional current collectors, the resulting BC/PPy nanofibers/MWCNT hybrid films were easily assembled into symmetric supercapacitors that offered large areal capacitances (590 mF cm^{-2}) and excellent cycling stability (94.5% retention after 5000 cycles),⁷⁵ benefiting from the high conductivity and hierarchical porous structure of the electrode.

Finally, not only BC nanofibers, but also membranes have been applied to reinforce the mechanical integrity of PPy. Indeed, BC/PPy flexible electrodes with an electrical conductivity and a discharge capacity of 3.9 S cm^{-1} and 459 F g^{-1} , respectively, were prepared after the immersion of BC membranes in a Py aqueous solution, and the subsequent *in situ* oxidative polymerization by gently adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (oxidant agent) to the swollen membranes.⁷⁶ Nevertheless, the cycling stability of such relatively simple composites was poor for practical applications: the discharge capacity decreased $\sim 30\%$ after 50 cycles only. Following a similar strategy, the same group prepared cotton fabrics coated with lignosulfonate-doped PPy.⁷⁷ In this case, the fabrics were previously immersed in an aqueous solution containing Py and lignosulfonate, and FeCl_3 initiated the *in situ* chemical polymerization.⁷⁸ These aqueous-mediated coated fabrics, which had high specific capacitance (304 F g^{-1}) and good cycling performance, can be used in flexible and wearable supercapacitors.⁷⁸

The strategy described above for preparing core-sheath structured BC/PPy nanocomposites⁷² was also employed to prepare BC/PAni.⁷⁹ More specifically, dispersed aniline was self-assembled onto BC with the assistance of dimethylformamide, and subsequently polymerized *in situ* with ammonium peroxide sulphate and HCl as doping agents. However, the electrical conductivity and specific capacitance

exhibited by BC/PAni (5.1 S cm^{-1} and 273 F g^{-1} , respectively) were lower than the outstanding properties exhibited by BC/PPy.⁷¹ Following another approach,⁸⁰ foldable, flexible, light-weight aerogel-like 3D electrodes were obtained by adsorption and *in situ* chemical polymerization of aniline on the surface and interior of a substrate where CNFs and multi-walled CNTs (MWCNTs) intertwine with each other randomly (Fig. 7a). Cyclic voltammograms and galvanostatic charge-discharge curves (Fig. 7b) proved that the very low pseudocapacitance of the CNF/MWCNT substrate increased noticeably (*i.e.* from 50 to 250 F g^{-1}) after polymerizing aniline.⁸⁰

Other methodologies to obtain PAni-based flexible supercapacitors have been proposed.^{81–85} Yuan *et al.*⁸¹ used paper as substrates. Specifically, cellulose fibres contained in common printing papers were coated with a thin layer of PVA, and then an 80 nm thick gold film was evaporated onto the treated

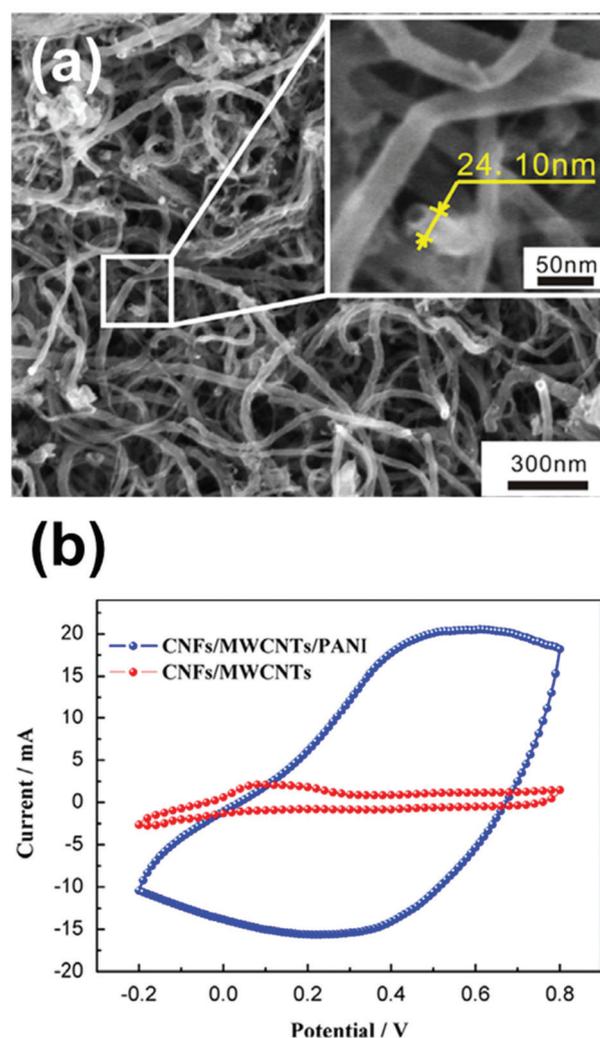


Fig. 7 (a) SEM micrograph of CNF/MWCNT substrate and (b) comparison of the cyclic voltammograms recorded at 10 mV s^{-1} before and after polymerizing the adsorbed aniline (CNFs/MWCNTs and CNFs/MWCNTs/PAni, respectively). Taken from ref. 80.

paper. The resulting conductive paper, which was lightweight and highly flexible, preserved the porous structure, facilitating the electrodeposition of fibrous PANi networks. The paper/Au/PAni device exhibited a capacitance of 560 F g^{-1} and a very high cyclability.⁸¹ More recently, conductive cellulose/PAni films with excellent mechanical properties were prepared by *in situ* polymerization of aniline monomers in regenerated cellulose films derived from native cellulose (*i.e.* cotton linter pulp).⁸² In the swollen state, these films had a porous structure, comprised of nanofibrils, that allowed the efficient penetration of aniline monomers and initiator. Nevertheless, even under the optimized reaction conditions, the electrical conductivity (0.06 S cm^{-1}) and specific capacitance (160 F g^{-1}) of the resulting cellulose/PAni composite were still lower than those reached by other systems previously discussed.^{79–81} Finally, nylon nanofibers-reinforced cellulose acetate (CA) films were used as substrate to build up PANi conductive layers *via in situ* polymerization.⁸³ These electrodes exhibited a capacitance and a transmittance of up 400 F g^{-1} and 40%, respectively.⁸³ A similar strategy was followed by Ge *et al.*,⁸⁴ who coated macroporous CFs with SWCNTs, followed by infiltration of aniline and *in situ* polymerization of PANi nanoribbons. The interpenetrating networks of CFs, SWCNTs, and PANi nanoribbons were folded–unfolded repeatedly up to 1000 times without mechanical failure and maintaining electrochemical stability (*i.e.* the material conductivity remained constant during repeated folding).⁸⁴ In a very recent study, flexible films of PANi, tissue wiper-cellulose, exfoliated graphite and silver nanoparticles were used as electrodes in supercapacitors for wearable electronics.⁸⁵ Cellulose was the backbone and the source of the flexibility and the consistency of the composite film, which exhibited a SC of 240 F g^{-1} and excellent cyclic stability after optimizing the weight ratios of different components. It should be noted that, in general, the fabrication of nanocomposites derived from cellulose derivatives, including BC, and PANi, does not apply sustainable chemistry principles in terms of solvents (as is the case for PPy). Thus, the preparation of PANi is frequently carried out using organic solvents, while PPy-containing nanocomposites are obtained in aqueous environments.^{76–78}

Before concluding this section, a brief discussion is presented on PEDOT-based flexible electrodes for supercapacitor applications. This CP is among the most successful ECPs due to its excellent electrochemical and thermal properties, high conductivity, good environmental stability in its doped state, mechanical flexibility, relative ease of preparation, and fast doping–undoping process.^{86–88} In a very recent study, Kurungot and co-workers⁸⁹ prepared highly conducting and robust PEDOT-paper using an amazing synthetic approach: surfactant-free interfacial polymerization at the interface of two immiscible liquids (Fig. 8). This procedure resulted in flexible PEDOT films with highly ordered polymer chains and enhanced doping level. The specific capacitance of supercapacitors prepared using such a PEDOT-paper and polyvinyl alcohol– H_2SO_4 as the solid electrolyte was 115 F g^{-1} . Furthermore, these flexible devices were stable during charge–

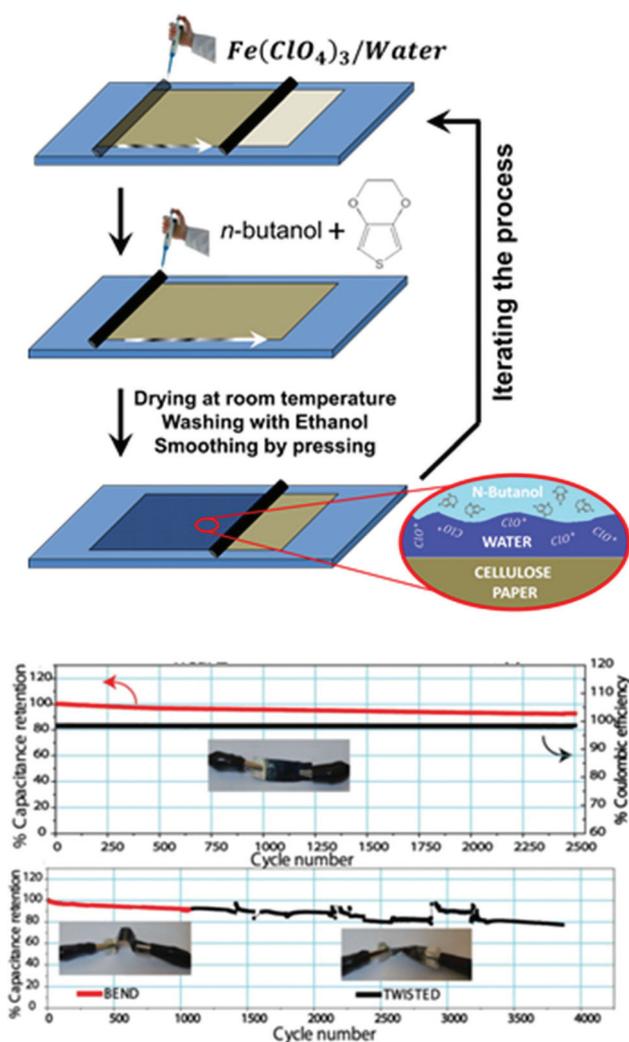


Fig. 8 Schematic representation of the synthetic strategy for PEDOT-paper preparation (top) and profiles illustrating the cycling stability data of PEDOT-paper (bottom). Adapted and taken from ref. 89.

discharge cycling under twisted and bending conditions over more than 3800 cycles (Fig. 8).

In all applications described in this section, cellulose plays the role of a passive component in the electrochemical supercapacitor's performance. However, it is worth nothing that, in general, cellulose-based mechanical reinforcements do not influence negatively the electrochemical properties of the electrically active components, bringing closer smart energy storage technologies and green chemistry. Thus, cellulose-based electrodes can be easily fabricated using techniques known from the paper industry (*e.g.* roll-to-roll), facilitating an economical large-scale production. However, the most important advantage is to encourage ecological companies aimed to cellulose insulation against enterprises oriented towards the production of chemicals. Within this context, it should be emphasized that cellulose insulation has one of the highest levels of recycled content in industry. Furthermore, cellulose

insulation, which frequently is locally produced, is not an energy-consuming process.

(ii) Cellulose as a mechanically inert template or a renewable carbon source

As cellulose is the largest renewable natural carbon source on earth, it has been employed not only as the precursor (raw material) of activated carbon for supercapacitors, but also as template for the synthesis of electrodes using template-assisted polymerization processes. In both cases, the main objective of these uses is to convert this low-value biomass and biowaste into a high-value commercial product. It is worth noting that many applications discussed in this sub-section are those in which the mechanical properties of cellulose are ignored, the use of this biopolymer being frequently motivated by its low-cost, abundance and natural origin. Table 2 summarizes the main characteristics of the supercapacitors described below.

In general, among the green chemical approaches in the synthesis of nanostructured materials for energy storage applications, the use of natural materials as templates, green solvent as primary solvents and the simplification of the synthesis procedure deserves special mention. Within this context, simple template-assisted polymerization processes combined with cellulose nanostructures as green templates have been used to fabricate supercapacitors. Xu and Zhang⁹⁰

used sodium CMC, a polysaccharide bearing a number of $-\text{CH}_2\text{COO}^- \text{Na}^+$ groups, for such a purpose. More specifically, CMC nanospheres with a diameter of ~ 100 nm were used to adsorb Py, and subsequently obtain PPy by *in situ* chemical polymerization (Fig. 9a). Although CMC nanospheres did not provide any mechanical benefit in terms of strength and/or flexibility, authors justified this choice by the good properties of CMC as a stabilizer in preparing nanocomposites,^{91,92} the low cost and green (*i.e.* non-toxic) character of this template compared with others made of CNTs or transition metal oxides, and the protection imparted to the backbone of the PPy layer during charge–discharge processes. Indeed, CMC/PPy electrodes showed a specific capacitance of 180 F g^{-1} and adequate cycling stability (*i.e.* 80% of the capacitance after 200 charge–discharge cycles). In another example, instead of CMC nanospheres, NC fibres were used as a template to obtain PPy fibres.⁹³ The most important advantages of this strategy, which is illustrated in Fig. 9b, were: (i) no polymer binders or carbon additives were required to ensure high electrical conductivity and mechanical integrity of the electrodes; (ii) the inclusion of the intertwined PPy nanofibres yielded electrodes with higher weight fractions of PPy (*i.e.* up to 90%) compared to composites containing only PPy coated NC; (iii) both PPy nanofibres and PPy-coated NC fibres contributed to the charge storage capacity (the cell capacitance was 36 F g^{-1}); and (iv) the intertwined PPy nanofibres may facilitate electron transport by interconnecting PPy-coated NC fibres.⁹³

Cellulose NFs have been used not only as template, but also as the carbon precursor to obtain carbonized fibres mats that

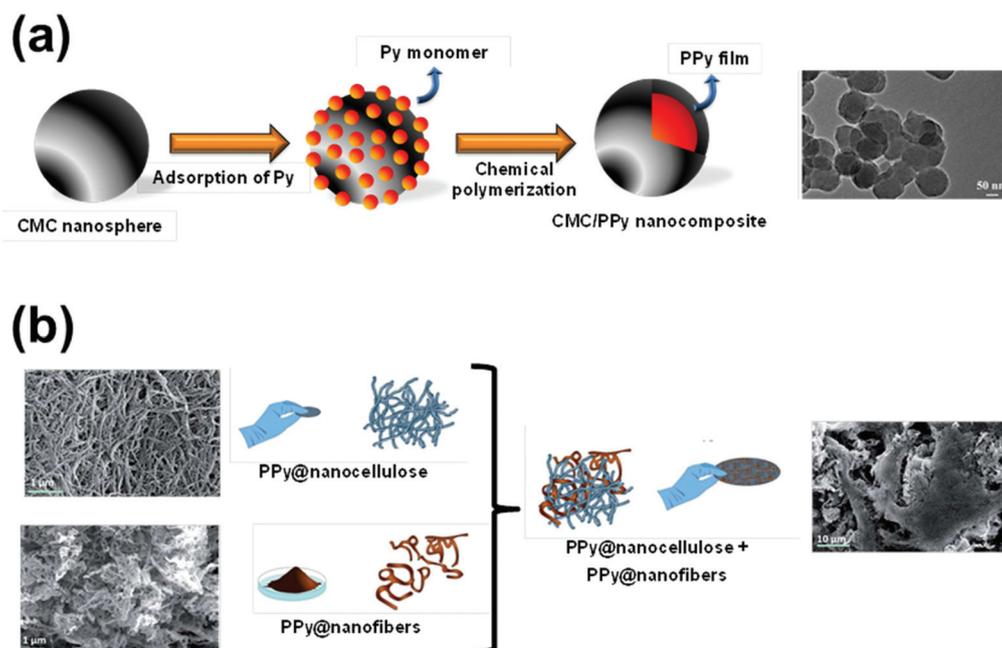


Fig. 9 (a) Scheme illustrating the fabrication of CMC/PPy nanocomposites using CMC nanospheres as a polymerization template. A TEM image of CMC/PPy, which has been taken from ref. 90, is also displayed. (b) Schematic representation of the preparation of free-standing binder free electrodes in which PPy nanofibres are integrated into a matrix made of NC/PPy. NC fibres were used as the template for the chemical polymerization of Py. Taken and adapted from ref. 93.

act as the storing charge electrode through electric double-layer capacitance. For example, carbonizing PPy-coated CNFs rendered supercapacitor electrodes with a specific capacitance of 236 F g^{-1} , this value increasing to 1045 F g^{-1} when the carbonized material was combined with Ni(OH)_2 .⁹⁴ The supercapacitor retained 84% of the specific capacitance after 5000 cycles of consecutive oxidation–reduction cycles.⁹⁴ Similarly, carbonization of fibrillar cellulose impregnated with CNTs resulted in a composite electrode of carbon nanofibers (diameter: 50–250 nm) with a specific capacitance of 163 F g^{-1} (ref. 95) that increased to 241 F g^{-1} when DWCNTs were replaced with MWCNTs during the impregnation process.⁹⁵ Thus, although attached CNTs increase the surface area in both cases, the greater adsorption of MWCNTs provoked not only higher surface area, but also enhanced electrical conductivity (*i.e.* 98.2 S cm^{-1} and 85.3 S cm^{-1} for MWCNTs and DWCNTs, respectively). Ultraporos carbonized materials, which display a large number of sub-nanometer pores, have recently been obtained by a controlled *in situ* carbonization–activation process of cotton cellulose with atomically dispersed potassium.⁹⁶ The resulting carbonized material exhibits an amorphous carbon structure composed of several nanometre-scale hexagonal carbon fragments, in which ultramicropores able to store remarkably high charge are developed. The symmetric supercapacitors achieve a specific capacitance of 130 F g^{-1} and a capacitance retention value of $\sim 90\%$ after 10 000 cycles.⁹⁶

In another case, in addition to enhancing the electrical conductivity of carbon nanofibers, MWCNTs reduced the activation energy of the oxidative stabilization of cellulose, thus increasing the crystallite size and structural order.⁹⁷ Specifically, MWCNT/cellulose composite nanofibers, which were prepared by electrospinning a CA/MWCNT blend solution followed by deacetylation to regenerate the CA into cellulose (carbon activation took place by carbonizing the composite at $1000 \text{ }^\circ\text{C}$), exhibited a cell capacitance of 145 F g^{-1} and a capacitance loss of 6% after 1000 charge–discharge cycles when used as the electrodes of symmetric supercapacitors.⁹⁷ However, although the addition of CNTs to the electrode material results in an excellent supercapacitor performance, their high production cost limits their application in the large scale. Likewise, following a facile one-step strategy, inter-bonded carbon nanofibers are obtained from partially hydrolysed CA electrospun nanofibers (carbonized in N_2 flow at $1000 \text{ }^\circ\text{C}$ and activated in CO_2 at $850 \text{ }^\circ\text{C}$). The inter-fibre connection is responsible for the considerable improvement in the electrode electrochemical performance: a specific capacitance of 241.4 F g^{-1} while maintaining high cycling stability (negligible 0.1% capacitance reduction after 10 000 cycles).

Furthermore, it is known that the large amount of surface functionalities shown by CNFs is able to strongly interact with activated carbon (AC), resulting in a network of carbonized CNFs with markedly better electron transport efficiency than AC particles.⁹⁹ Considering this, mechanically delaminated CNFs were mixed with traditional activated AC, most of which is produced from renewable biowaste, such as dead trees,

bamboo, and coconut shells, and heated at $800 \text{ }^\circ\text{C}$ to produce paper-like films with significantly higher capacitance than bare activated carbon, especially at high current densities, and excellent stability (over 92% capacitance retention after 10 000 cycles).⁹⁹ Also, activated carbon hollow fibres (ACHFs) with high specific surface area were prepared from hollow ramie fibres by one-step activation at different ZnCl_2 concentrations.¹⁰⁰ The impregnated ramie fibres were pyrolyzed at $650 \text{ }^\circ\text{C}$ under nitrogen flow. Interestingly, the structural development of ACHFs was found to greatly depend on ZnCl_2 concentrations, which not only can swell and dissolve cellulose but also can serve as the skeleton of newborn pores. As the supercapacitor electrode, the ACHFs exhibited a maximum capacity of 287 F g^{-1} and a high stability with more than 93% retention after 1000 cycles.¹⁰⁰

Hence, the evolution towards a more sustainable energy storage technology requires using biomass-derived carbon materials as electrodes and cellulose is indeed an excellent source of that. This line of actuation has attracted a lot of attention in recent years. In 2015, *Broussonetia papyrifera* stem bark was used as a raw material for the synthesis of nitrogen-doped porous carbon species for supercapacitor electrodes.¹⁰¹ After hydrothermal treatment of the stem bark in a KOH solution, the resulting material was subjected to simultaneous pyrolysis and KOH activation. The produced heteroatom-doped carbon material exhibited a porous texture (average pore size of 3.8 nm) with partial graphitic structure. These electrodes exhibited a specific capacitance of 320 F g^{-1} together with excellent cycling stability,¹⁰¹ which were attributed to the synergistic effect of the heteroatom-doped species. Considering the worldwide abundance and recyclability of *Broussonetia papyrifera*, a very resistant flowering plant native to Asia but introduced in parts of Europe, United States, and Africa, these results suggest the potential application of this strategy for the large-scale production of biomass-derived electrodes. In another example, Wang *et al.*¹⁰² combined the unique complex multi-layered structure of hemp bast fibre precursor with hydrothermal treatment, KOH activation, and carbonization at $700\text{--}800 \text{ }^\circ\text{C}$ to achieve carbon nanosheets with micro- and mesoporosity, specific capacitance in the range of $110\text{--}144 \text{ F g}^{-1}$, and excellent cycling stability (8% capacitance reduction after 1000 cycles).¹⁰²

Following these two approaches,^{101,102} Gao *et al.*¹⁰³ prepared oxygen-rich activated carbon using animal cellulose from crab shell wastes as a raw material. This activated carbon, which was achieved by combining different processes that included carbonization and KOH activation,¹⁰⁴ displayed high surface area, large pore volume, and high surface oxygen content (18.5%). Besides, the corresponding supercapacitor electrodes exhibited a specific capacitance of 281 F g^{-1} , even though their stability against charge–discharge processes was not tested.¹⁰³ Furthermore, cellulose and biowaste ligno-sulphonate led to meso-microporous activated carbon electrodes that, when assembled in KOH aqueous electrolyte, showed a specific capacitance of 286 F g^{-1} .¹⁰⁵ Specifically, increasing the micropore volume improved the specific capacitance of the

carbon electrode, whereas increasing the mesopore volume enhanced the rate capability. Finally, Kim *et al.*¹⁰⁶ simply soaked citrus peels, which are mainly composed of cellulose, hemicellulose, lignin and pectin (*i.e.* good carbon precursors), in a 30 wt% KOH aqueous solution for 30 min, dried at 80 °C for 36 h, and finally pyrolyzed at 800 °C for 2 h under a nitrogen atmosphere. Heating in the presence of K⁺ transformed the waste from citrus fruits into nanoporous carbon nanosheets containing numerous redox-active heteroatoms (*i.e.* nitrogen and oxygen). Hence, pseudocapacitors based on a symmetric electrode configuration exhibited a specific capacitance of 110 F g⁻¹ and a capacitance retention of 64% after 100 000 cycles.¹⁰⁶

Carbonized cotton pulp at 1000 °C showed a capacitance of 107 F g⁻¹ and excellent stability for 2000 cycles.¹⁰⁷ These good properties were attributed to the low surface contamination and high surface area of the resulting carbon fibre structure achieved using a two-step carbonisation process: (i) pre-carbonization of the cotton pulp at 600 °C; (ii) graphitisation at 1000 °C. Although the pre-treatment and the graphitisation steps apparently preserved the long fibres of unmodified cotton pulp, carbonised cotton pulp fibres are slimmer and have increased number density (Fig. 10). Moreover, cotton

T-shirt textiles were transformed into highly conductive and flexible activated carbon textiles (ACTs) through a three-step process:¹⁰⁸ (i) traditional dipping with 1 M NaF solution; (ii) drying at 120 °C for 3 h in a pre-heated oven; and (iii) curing the dried textiles at 800–1000 °C. The electrochemical performance of the resulting porous ACTs was enhanced after electrochemical deposition of nanostructured pseudo-capacitive MnO₂, which adopted nanoflower architectures: the specific capacitance of the asymmetric supercapacitor was 120 F g⁻¹, the loss of capacitance after 1000 cycles being only 2.5%.¹⁰⁸ These good properties were attributed to: (1) the highly conductive ACTs backbone with a high surface area that provided an excellent interfacial contact between ACT microfibers and MnO₂; (2) the nanoflower architecture of MnO₂ shortened the diffusion paths of electrolyte ions during fast charge/discharge processes; and (3) the high surface area of the ACT negative electrode facilitated the electrolytic ion transport, enhancing the energy and power density values.

A completely different approximation was applied by Bismark and co-workers,¹⁰⁹ who produced activated carbon material with a graphitic structure by pyrolyzing BC in dense paper form at 950 °C and activating the resulting carbonaceous material with CO₂. The electric double layer capacitance of the activated carbon was 42 F g⁻¹ in K₂SO₄ electrolyte solution, being proposed as a potential new active material for supercapacitors.¹⁰⁹ Besides, Ni₃S₂ nanoparticles grown on the surface of carbon nanofibers derived from BC¹¹⁰ resulted in an asymmetric supercapacitor with a similar electrochemical response: a high specific capacitance (69 F g⁻¹) and good cyclic stability after 2500 cycles (97% of retention). The carbonization of a mixture of BC and potassium citrate (K₃C₆H₅O₇) produced a 3D-integrated porous carbon architecture with high specific surface.¹¹¹ Again, not only was the latter compound used as a carbon precursor for the formation of porous carbon nanosheets, but also provided potassium as a chemical activating agent during heat-treatment under a flowing nitrogen atmosphere. As a consequence, this composite displayed a specific capacitance of 261 F g⁻¹ and an outstanding cycling stability of 97.6% after 10 000 cycles.¹¹¹ Nitrogen and phosphorus co-doped carbon nanowires, which were prepared by impregnating NH₄H₂PO₄ into BC pellicles followed by carbonization in a NH₃ atmosphere at 800 °C,¹¹² showed a specific capacitance of 258 F g⁻¹ and an excellent cycling stability (*i.e.* 98% retention of specific capacitance after 30 000 cycles).¹¹² Similarly, PANi coated bacterial cellulose (BC) was carbonized (one-step process at 700 °C for 2 h under an Ar atmosphere) to render nitrogen-doped BC nanofibers exhibiting excellent capacitive performance (1949.5 F g⁻¹) and cycling stability (74.4% after 5000 cycles), as well as acting as a 3D bio-template for depositing an ultrathin Ni-Co layered double hydroxide nanosheet.¹¹³

In a very recent study, an all-biomaterial-originated film supercapacitor was constructed using activated pyrolysed BC as the electrode material and a biobased BC/H₃PO₄ gel electrolyte, which exhibits much higher ion mobility than the fossil fuel based PVA/H₃PO₄ gel electrolyte.¹¹⁴ Although the all-

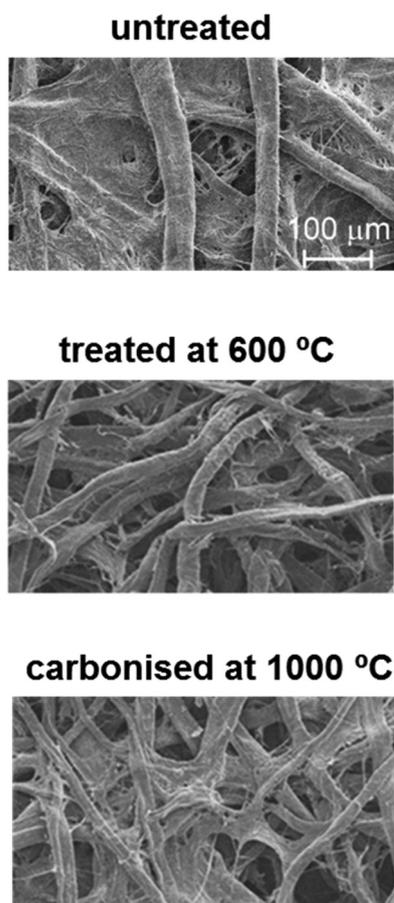


Fig. 10 SEM images of untreated cotton pulp (top), and treated at 600 °C (center) and 1000 °C (bottom). The scale for all these images is the same (left). Taken from ref. 107.

biomaterial supercapacitor displayed an excellent specific area capacitance of 289 mF cm^{-2} , the capacitance retention was very low (66.7% after 100 cycles only). In spite of this limitation, the concept of eco-friendly all-biomaterial supercapacitors will be of great importance in the coming years because of the increasingly serious environmental problems.

Finally, porous carbon aerogels derived from cellulose have also been prepared as supercapacitor electrodes. Aerogels are solid materials with very low densities and high thermal specific surface areas. For that, bagasse, the waste product from sugarcane that mainly contains cellulose derivatives, was employed as a raw material (Fig. 11a).¹¹⁵ The activated carbon aerogels, which exhibited hierarchical macro-, meso- and micro-porous structures, were employed as electrodes in solid

state symmetric supercapacitors (KOH/PVA as the solid electrolyte) revealing a specific capacitance of 142 F g^{-1} and a capacitance retention of 94% after 5000 charge–discharge cycles. Similarly, raw cotton was converted into functional aerogels containing a significant amount of nitrogen-doped graphene sheets grafted on cellulose fibres.¹¹⁶ For this purpose, an entanglement of cotton was immersed in an aqueous urea solution, a porous structure being then obtained by freeze-drying. Urea was used not only as a molecular template to form graphene, but also as the nitrogen source for doping, whereas cotton microfibrils acted as the carbon source to grow nitrogen-doped mushroom-like graphene sheets through a thermal condensation method at high temperature. The specific capacitance of symmetric supercapacitors constructed

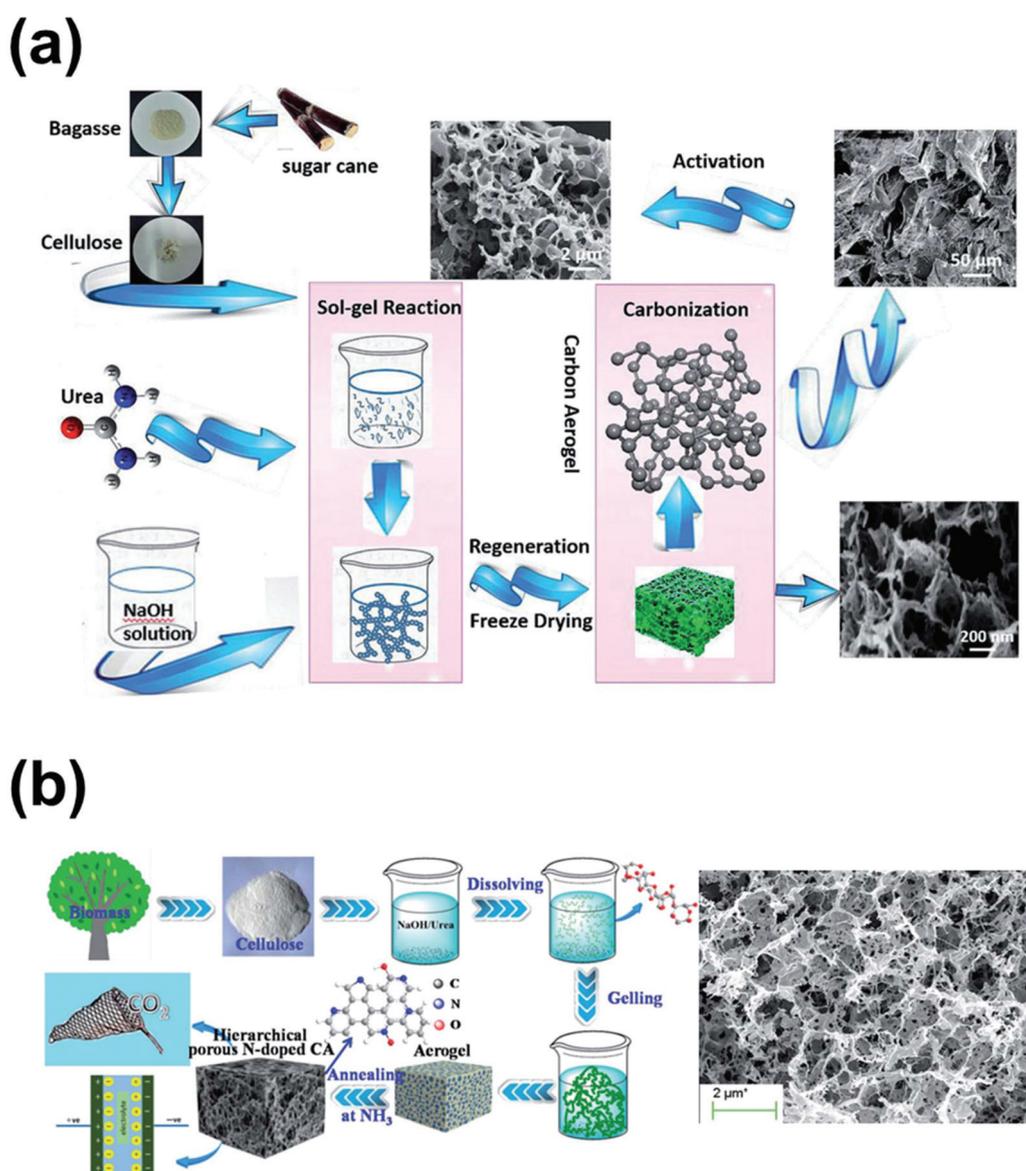


Fig. 11 (a) Schematic of the fabrication of highly porous bagasse-derived carbon aerogels with hierarchical pore structure. Taken from ref. 115. (b) Illustration of the preparation and SEM micrograph of the hierarchical porous nitrogen-doped carbon aerogel. Adapted from ref. 117.

using such aerogel electrodes and KOH as electrolyte was 108 F g^{-1} .¹¹⁶ After 10 000 charge–discharge cycles, the capacitance retention was only 64%. This relatively reduced cycling stability was attributed to the effects from doped heteroatoms.¹¹⁵ Nitrogen-doped carbon aerogels with hierarchical porosity (*i.e.* with multi-scale pores) were prepared by a dissolving–gelling process followed by carbonization in a NH_3 atmosphere at $800 \text{ }^\circ\text{C}$ (Fig. 11b).^{117,118} In addition to a capacitance of 225 F g^{-1} , these carbon aerogels displayed an excellent cycling life (6% loss after 5000 cycles) as well as an exceptional CO_2 adsorption capacity (4.99 mmol g^{-1}). These combined abilities, which were attributed to the formation of interconnected macropores and micropores (Fig. 11b), revealed the system to be a multifunctional material with great potential for applications in CO_2 capture and energy storage.

Carbonaceous hydrogels and aerogels with a 3D porous structure, which were prepared by simple one-pot hydrothermal reactions, have shown a tremendous potential as scaffolds for the fabrication of 3D composite materials for their application in energy storage. For example, Xu and co-workers¹¹⁹ prepared electrodes by embedding Fe_3O_4 nanoparticles in a template made of carbonaceous nanofibers and nanospheres that was prepared using watermelon as a carbon source. On the other hand, nanofibrillated cellulose, a rapidly emerging class of bio-friendly nanomaterials that offers tremendous possibilities for the aqueous self-assembly of a range of advanced micro- and nano-structures, has been used to fabricate aerogels functionalized by rapid layer-by-layer assembly.¹²⁰ Although these aerogels exhibited high charge storage, they have not been configured as supercapacitors yet.

On the other hand, from the perspective of green technologies, carbonization and pyrolysis processes present serious drawbacks because of the very high temperature requirements (up to $1000 \text{ }^\circ\text{C}$). However, in recent years, other, but less exploited, approaches have been reported to reduce the energy consumption. For example, Yushin and co-workers¹²¹ transformed cellulose into porous carbon by hydrothermal carbonization (HTC). As opposed to processes such as carbonization or pyrolysis, HTC uses heated water (at temperatures around $200 \text{ }^\circ\text{C}$ and at an elevated pressure) to transform the biomass employing more efficiently the energetic potential. This process, also known as “wet pyrolysis”, offers a huge potential for char production to a range of non-traditional renewable and plentiful agriculture residues and municipal wastes.^{122,123} Furthermore, HTC can be completed to obtain activated carbons *via* a chemical activation with KOH similar to that described above.¹²² The capacitance of the hydrothermally carbonized cellulose electrodes was 236 F g^{-1} ,¹²¹ even though they were not assembled in supercapacitors.

(iii) Cellulose as a separator

In supercapacitor devices, the separator has to fulfil two functions: (i) it must provide electronic insulation between electrodes of opposite polarization to avoid short circuits; and (ii) it

must favour high ionic conduction/mobility from the electrolyte towards the electrode surface. Although currently most of the separators used in commercial supercapacitors are based on polymers [*e.g.* polypropylene, polyethylene, Teflon®, polyvinylidene fluoride (PVDF) and polyvinyl chloride (PVC)], glass, and cellulose derivatives, we have included in this section those systems where cellulose is both employed to fabricate the separator and the electrodes. Therefore, most of the works cited have already been described in the previous sections, but now the focus is placed on the separator. In addition, we have illustrated the use of cellulose as a separator in supercapacitors made of textile nanostructures (*i.e.* polyester), which are oriented towards wearable electronics.

Deng and co-worker⁴¹ combined MFC/MWCNT electrodes with MFC separator sheets to fabricate symmetric supercapacitors. Specifically, separator sheets were made with a solid electrolyte of polyethylene oxide (PEO)/LiCl that was uniformly distributed among MFC networks forming a film support. The addition of MFC networks greatly improved the mechanical properties of PEO/LiCl; their porous structure provided enough passages for ion movement; and their insulating nature prevented electric contact between the MFC/MWCNT electrode sheets.

While an all-paper symmetric supercapacitor was successfully prepared by using two cellulose paper/RGO electrodes and one piece of paper as a separator⁵³ (the main advantage of this green supercapacitor was that both the electrodes and the separator were based on recycled cellulose from newspapers), pure cotton cloth was employed as a separator in the cylindrical symmetric supercapacitor displayed in Fig. 2. Cotton cloth/GNS pieces were used as positive and negative electrodes, and nickel foam as a current collector.³² This rechargeable energy storage device was designed to be light-weight, cheap, and portable.

As mentioned before, Tammela *et al.*⁵⁶ used a varying number of filter paper sheets (0.15 mm thick and pore size 12–15 μm) soaked in 1.0 M NaNO_3 electrolyte as the separator of cellulose/PPy electrodes in symmetric energy storage devices. Thus, the separator thickness was controlled through the number of paper sheets. Authors found that the cell resistance was unaffected by the electrode thickness, whereas it increased linearly with the thickness of the separator. This dependence probably originates from the electrolyte resistance in the pores of the separator sheets (*i.e.* the tortuosity of the cellulose-based filter paper sheets). From these results it was concluded that the electrode should be as thin as possible to reduce the cell resistance.⁵⁶

The all-biomaterial supercapacitor recently developed by Zhi and co-workers¹¹⁴ combined 3D BC-derived electrodes with a novel BC-based gel electrolyte. The BC/ H_3PO_4 gel is dielectric, flexible and semi-transparent. Interestingly, the volume capacitance of such a supercapacitor decreased from 35.5 F cm^{-3} to 23.6 F cm^{-3} when the BC/ H_3PO_4 separator was replaced by PVA/ H_3PO_4 . In spite of this, the applicability of BC/ H_3PO_4 was limited by the evaporation of aqueous electrolyte, which retarded the ion movement and increased the resistance of the whole device.

A fully integrated printed supercapacitor was prepared on a commercial paper substrate using SWCNT ink.¹²⁴ The paper surface was pre-treated with PVDF to produce a thin layer without large holes but this still allowed the transport of electrolytes through the paper. After this, the SWCNT ink was coated using the Meyer rod method on both sides of the PVDF-treated paper. The most striking characteristic of this extremely simple device is that the SWCNT coatings behave as both the electrodes and the current collectors, whereas the paper acted as both the substrate and the separator. The specific capacitance of such a lightweight paper-based supercapacitor was 33 F g^{-1} (Table 1), the loss of capacitance after 2500 charge–discharge cycles being very small.¹²⁴

Although the use of filter paper as a simple separator in inorganic supercapacitors is relatively frequent, some studies deserve special mention because the applications of those devices were intimately related to conventional applications of cellulose-containing materials. For example, Cui and co-workers¹²⁵ reported a structure where MnO_2 nanoflowers were electrodeposited onto CNT-wrapped polyester fibres. Supercapacitors prepared using this conductive textile, which could be considered as an extension of a previously reported conductive paper,²⁹ were assembled using paper sheets as separators. Thus, polyester fibres and paper low-cost materials were essential to propose these elements as promising large-scale wearable devices for energy storage.^{69,126}

In summary, in the last few years there have been promising reports on paper-/cellulose-based materials being applied to fabricate both electrodes and separators for supercapacitors, in which their rough and porous surface has proved a strong advantage where both high surface area and electrolyte absorption are demanded. Recyclability and biodegradability are significant benefits considering that the cost of waste management and the impact on the environment could be considerably low.

(iv) Cellulose's role as an electrolyte

In addition to the two electrodes separated by an ion-permeable separator, supercapacitors also require an electrolyte (*i.e.* a mixture of positive and negative ions dissolved in a solvent, such as water) that connects them ionically. When the supercapacitor is polarized, an electric double-layer emerges at the interface between the electrode (electronic layer) and the electrolyte (opposite polarity layer from dissolved ions). Moreover, pseudocapacitance appears when the electrode material is able to store electrical charge by reversible faradaic redox reactions. In this specific case, electron charge-transfer occurs between the electrolyte and the electrode, and intercalation or electrosorption processes take place with ions permeating the double-layer and being adsorbed. Although the charge storage ability depends primarily on the electrode conductivity, porosity, size, and surface shape, capacitance is also affected by the ion movement speed in the electrolyte towards the double-layer. Furthermore, an excellent electrolyte perform-

ance is based on optimized working voltages, non-toxicity, low corrosion, and safety.¹²⁷ All these requirements are fulfilled by cellulose, as discussed in the previous section, representing a green alternative to conventional materials currently used to fabricate supercapacitors. Table 3 summarizes the most relevant trends of cellulose-containing supercapacitors discussed in this section.

Gui *et al.*¹²⁸ focused on the electrolyte absorption properties of CFs as a potential substrate in energy storage devices. More specifically, these authors considered that natural CFs behave like a cell wall that takes up the electrolyte from bulk electrolyte baths. Electrolytes are then transported *via* the pores through the CF matrix to the energy-active material. In this way, the mesoporous channels inside the CFs act as an extra ion diffusion pathway for charge–discharge processes. On the basis of these assumptions, different hybrid electrodes were prepared even though the best ion diffusion and electrochemical properties were obtained for CF/CNT/ MnO_2 /CNT electrodes prepared by dip-coating (Fig. 12). This system exhibited dual ion diffusion and electron transfer pathways demonstrating superior supercapacitive performance (*i.e.* specific capacitance of 327 F g^{-1} and excellent cyclic stability, retaining 85% of the capacitance up to 50 000 cycles). Hence, these results highlight the merits of the mesoporous CFs as substrate for supercapacitor electrodes: the water-swelling effect of cellulose fibres induce absorption of the electrolyte, whereas their mesoporous internal structure provides channels for ions to diffuse towards the electrochemical energy storage material.

Flexible CNFs were also selected as aqueous electrolyte nanoreservoirs, nanopacers, and hierarchical nanostructure makers of graphene-based electrode materials.¹²⁹ Specifically, CNF/RGO hydrogels, which were prepared by acidizing a homogeneous solution of CNFs and GONSs with hydrochloric acid vapour, were transformed into aerogels by supercritical CO_2 drying. Within this context, it should be emphasized that the use of carbon dioxide is often promoted as a green solvent, and its use in this role has permeated throughout the chemical and materials research communities. Specific green-properties of supercritical CO_2 are non-flammability, relatively low toxicity and relatively low reactivity. In addition, unlike water, the supercritical regime of CO_2 is readily accessible, given its critical temperature of only 304 K. The outstanding properties of these novel CNF/RGO hybrid aerogels (*i.e.* capacitance of 207 F g^{-1} and excellent cyclic stability) were ascribed to (i) the excellent re-swell performance of the electrode in aqueous electrolyte, which was induced by the hydrophilic CNFs, and (ii) to the effective prevention of graphene nanosheets aggregation.¹²⁹ By following a similar approach, the same group reported CNF/MWCNT hybrid aerogels where hydrophilic 1D CNFs were used as environmentally friendly aqueous electrolyte nanoreservoirs that effectively reduced the electrolyte ion transport distance in the aerogel 3D porous network.¹³⁰ In addition, 1D CNFs acted as a steady dispersant of MWCNTs and nanopacers. Hence, when CNF/MWCNT hybrid aerogel films were assembled as the electrode material

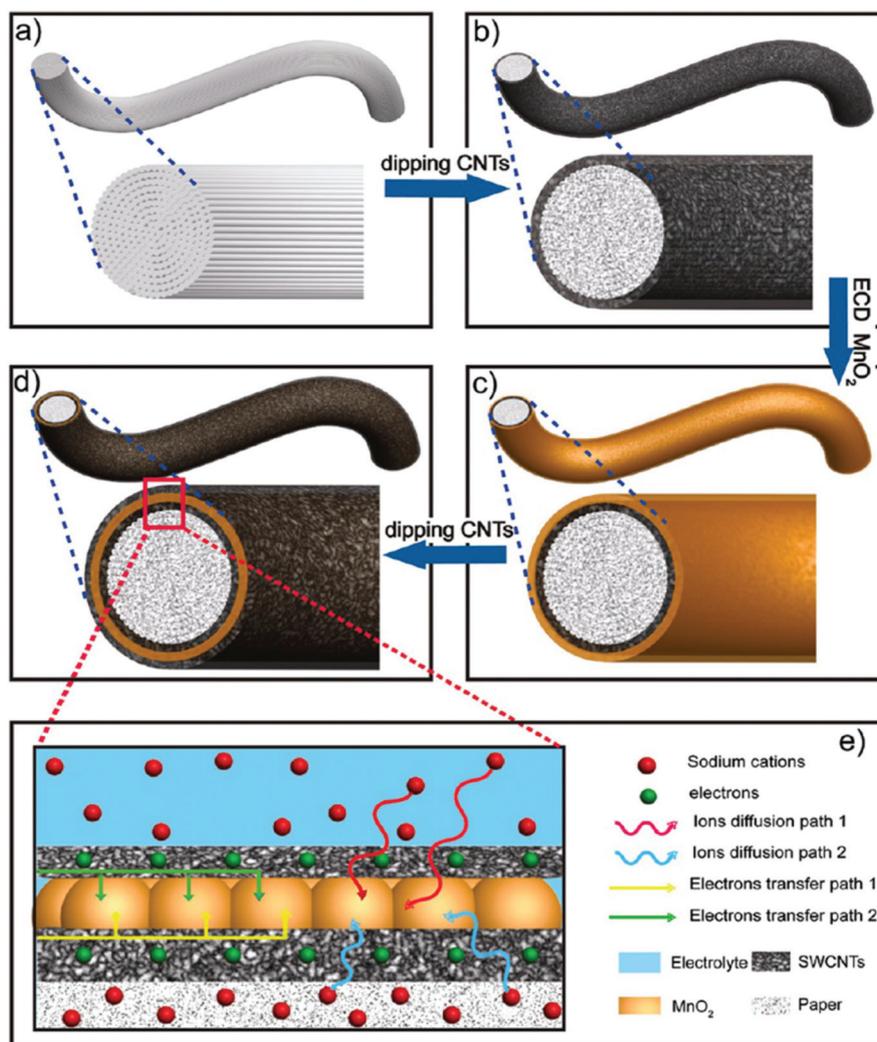


Fig. 12 Schematic illustration of the synthetic process of CF/CNT/MnO₂/CNT electrodes and graphics showing the dual electron charge transfer and ion diffusion paths in this electrode configuration: (a) single CF; (b) CNT dip-coating; (c) electrodeposition of MnO₂; (d) second CNT dip-coating; (e) magnification of the square area highlighted in (iv) to illustrate the dual electron charge transfer and ion diffusion paths in the CF/CNT/MnO₂/CNT configuration. Taken from ref. 128.

and charge collector, these all solid-state flexible supercapacitors exhibited high specific capacitance (178 F g⁻¹) and excellent electrochemical stability under different bending angles and even after withstanding 100 bending cycles, which was attributed to the properties provided by CNFs.¹³⁰ Thus, CNFs exploited the full potential of MWCNTs by preventing their aggregation, enhanced the re-wettability of the mesopores with aqueous electrolytes, and improved the utilization efficiency of the mesopores.

Pushparaj *et al.*¹³¹ opened a new concept by integrating into a single unit the multiple basic components of supercapacitors (*i.e.* the electrode, the separator, and the electrolyte) with the specific electrochemical and interfacial properties required to build such energy storage devices. Therefore, they concluded that nanoporous cellulose papers embedded with aligned MWCNTs satisfy the requirements of such basic components. Indeed, the porosity of cellulose combined with its

inherent flexibility provided the characteristics of an unprecedented integrated design for a variety of compact devices.

The extraction of CFs from waste papers and their subsequent application in supercapacitor electrode design was presented as a cost effective route for developing energy storage devices with improved performance.¹³² CF/PPy and CF/graphene/PPy electrodes were prepared by *in situ* polymerization of adsorbed Py (Fig. 13). The specific capacitance of CF/PPy and CF/graphene/PPy (51 and 243 F g⁻¹, respectively) was found to be significantly higher than that of PPy and graphene/PPy (16 and 89 F g⁻¹, respectively).¹³² Hence, adding CFs significantly enhanced the electrochemical properties of the electrode materials, in addition to their mechanical stability. Most importantly, the incorporation of CFs enhanced the electrolyte accessibility in both composites: not only CFs separated graphene sheets, which acted as a barrier to the hydrogen bonding tendency of cellulose molecules, but also

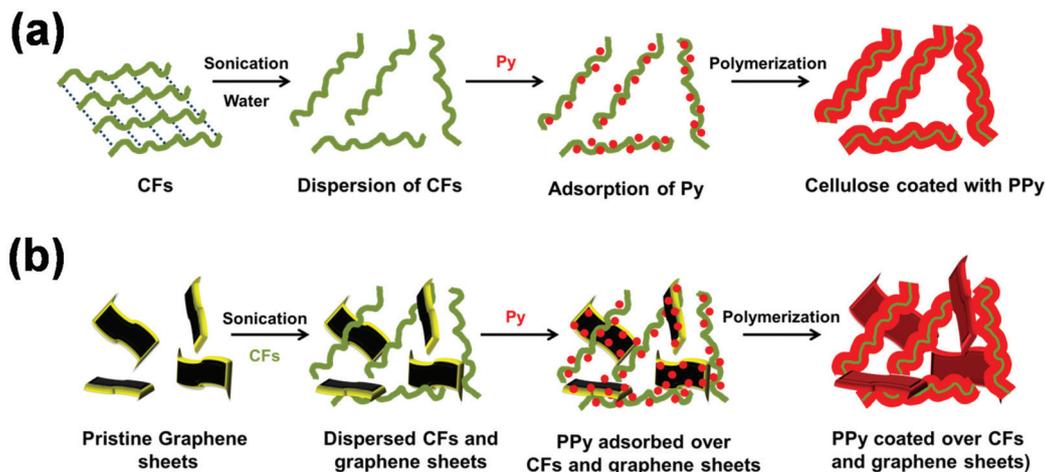


Fig. 13 Schematic representation of the (a) CF/PPy and (b) CF/graphene/PPy electrodes formation using CFs extracted from waste paper.

behaved as an electrolyte reservoir and a transfer medium in CF/graphene/PPy electrodes. Besides, these CFs' abilities were also related to the excellent cyclic stability of the system (94% retention of specific capacitance after 2000 charge–discharge cycles).

From another perspective, strong and solid polymer electrolyte ion gels composed of methyl cellulose fibres, which were prepared using low viscosity solvents, show high ambient ionic conductivities ($>10^{-3} \text{ S cm}^{-1}$), high capacitance ($2 \mu\text{F cm}^{-2}$), a wide voltage stability window (5.6 V) and excellent mechanical properties. Nevertheless, although their application in electrochemical supercapacitors was not tested, this line of actuation that is being widely under consideration for ion gels (and ionic liquids) can potentially provide high potential stability windows and improve the electrochemical stability of electrodes.¹³³

Finally, a new approach and application of cellulose was recently reported by Sudhakar *et al.*¹³⁴ These authors prepared an eco-friendly and transparent solid polymer electrolyte (SPE) based on cellulose acetate propionate (CAP), H_3PO_4 , and poly(ethylene glycol) (PEG), which acted as a plasticizer. CAP is obtained by hydrolysis of cellulose using acetic acid and propionic acid, and it is typically developed for coating applications. The performance of this cellulose-containing SPE was evaluated by fabricating a thin and compact supercapacitor that revealed a specific capacitance of 64 F g^{-1} and a stability of 96% at 1000 cycles. The electrode material for such a supercapacitor was prepared by mixing AC derived from areca fibres with a binder to form a slurry. Then, this slurry was screen print coated onto stainless steel electrodes.

Perspectives and conclusions

This review comprehensively explores recent advances in developing high performance energy storage devices based on cellulose. Specifically, its main objective is to present an overview

of the fabrication approaches followed to incorporate cellulose as a component in supercapacitors. Regarding the charge storage response, comparison between the described systems is established in terms of the displayed specific capacitance as well as cycling stability. Hence, an important effort is made to understand the role played by this polysaccharide and its related properties on such parameters.

But, why has the interest in cellulose for designing future supercapacitors grown so strongly during the last years? Within the context of energy storage devices, electrochemical supercapacitors have emerged as a promising option that is able to display high energy density values, thus improving the reported values for conventional capacitors, fast charging–discharging times, and long-lasting cycling stability. In addition to these properties, our daily routine, which relies on consumable electronics with advanced functionalities, has led research towards novel and bendable electrodes. Furthermore, the growing concern about sustainable development demands implementing greener energy technologies. If all these conditions are combined, the next generation of supercapacitors is being conceptualized to fulfill the following aspects: excellent functionality, flexibility, environmental friendliness and, if possible, affordability. Hence, as it has been highlighted in this review, cellulose materials (*e.g.* commercial paper products, cellulose fibres, cotton, bacterial cellulose and biomass-derived cellulose) have properties that result in final devices perfectly matching the abovementioned requirements, which explains the large amount of recent studies devoted to this exciting field of study. Above all, the abundance and low cost of cellulose allows for simple and scalable preparation processes that reduce the final economic cost of the prototype.

Besides, cellulose stands out for its versatility and adapting nature when introduced in the supercapacitor system. For example, most of the methodological strategies that apply cellulose as a flexible mechanical reinforcement element in supercapacitor electrodes are straightforward and cheap. Basically, they rely on combining commercial sources

of cellulose or derivatives with electroactive materials by approaches that resemble those already in use in the textile industry (e.g. brushing, coating, pouring, soaking, immersing, dipping, drawing, screen printing and filtering). Thus, during the preparation of the electrode, carbon-derived materials (*i.e.* CNTs, graphite, GNS, GO) end up being introduced into the cellulose system, whereas CPs (*i.e.* PPy, PANi or PEDOT) are generally polymerized *in situ* or electrochemically deposited. As a result, specific capacitance values range between ~ 20 and $\sim 700 \text{ F g}^{-1}$, 2276 F g^{-1} being the highest value reported in this review. In fact, an enhanced performance is obtained for the combined system in comparison with the electroactive material alone.

From a practical point of view, the mechanical stability imparted by cellulose not only results in flexible and bendable electrodes for advanced applications, but also increases the ability of such electrodes to withstand the structural changes (expansion and contraction movements) taking place during consecutive charging–discharging, thus enhancing the cycling stability of the device and, consequently, its long-term use. However, there is still some space for improvement in this area. For example, one of the aspects to be explored is related to the overoxidation process that affects CPs at high positive potentials, which is related to poor cycling stability performances. Despite this, the performance of cellulose-based supercapacitors portrays them as potentially competitive products in comparison with non-sustainable energy storage devices.

The concept of cellulose as the largest renewable carbon source for preparing activated carbon electrodes has also attracted a lot of attention. Thus, research on preparing biomass-derived carbon materials has included a wide range of varied sources: cellulose fibres, acetate cellulose, animal cellulose (from crab shells), BC (fibres and pellicles), stem bark, hemp bast fibres, renewable cellulose and biowaste lignosulphonate, cotton products (T-shirt pieces, pulp, or a mixture of cotton and urea), citrus peels, bagasse from sugarcane, and ramie fibres. In this case, preparation methods, which are based on pyrolytic treatments where cellulose is thermochemically decomposed at high temperatures (from $650 \text{ }^\circ\text{C}$ up to $1000 \text{ }^\circ\text{C}$) under a N_2 or NH_3 atmosphere, require more steps (after cellulose carbonization, an activation process is applied, either using CO_2 or KOH) and are more demanding energetically. However, despite these drawbacks, cellulose becomes an attractive renewable carbon source to prepare supercapacitor electrodes that display high specific capacitance values ($42\text{--}320 \text{ F g}^{-1}$) and excellent cycling stability.

Some general remarks on the synergy between the cellulose morphology and the electroactive material should also be discussed. It is well known that the charge storage ability of supercapacitors is directly affected by the electrode conductivity, porosity, size, and surface shape. As has been reflected in this review, the porous network formed in cellulose fibres contributes to improve SC values. Likewise, even though designing aerogels increases the complexity of the process, their extremely high porosity and conduction paths are respon-

sible for excellent SC values and adequate cycling response. For example, in meso-microporous activated carbon electrodes, the SC and rate capability increase with the micropore and mesopore volumes, respectively. Moreover, properly dispersed CNCs and CNFs effectively prevent CNTs or graphene nanosheets from aggregating, which results in supercapacitors with exceptional properties.

BC deserves a brief mention apart. Indeed, this cellulose derivative embraces a long list of advantages, such as 3D reticulate structure, high chemical purity, ample porosity and specific surface area, high hydrophilicity, and water-holding capability; this makes most of the studies exploiting this cellulose source outstanding (specific capacitance values as high as 556 F g^{-1}).

Cellulose's role in the remaining two parts of any supercapacitor cell, namely the separator membrane and the electrolyte, is also worth noting. Regarding the former, designs as plain and manageable as commercial paper, filter paper sheets or cotton cloths, or slightly more complex, such as MFC or BC gels, effectively accomplish the separating function and even improve the mechanical properties of the device as well as provide a porous structure favouring ion conduction. On the other hand, the electrolyte absorption properties of cellulose indicate its crucial contribution to promoting ion movement and diffusion from the bulk electrolyte to the electrode material by providing extra ion pathways, thus enhancing the overall supercapacitive performance. Research on this specific area (*i.e.* cellulose as electrolyte nanoreservoirs and nanospacers) is still scarce, but the results obtained so far encourage additional efforts.

It should be noted that currently available commercial supercapacitor cells based on organic electrolytes and carbonaceous electrodes exhibit specific capacitances lower than 200 F g^{-1} , while the capacitance retention extends to several thousands of cycles (*i.e.* from 2000 to 10 000).^{135,136} Similar, or even higher, performances have been reported in the last few years for some cellulose-based supercapacitors (Tables 1–3). Accordingly, the environmental advantages associated with the use of cellulose-based green materials are not affected by a reduction in the performance of the resulting energy storage device. Consequently, future perspectives for all-cellulose based supercapacitor devices are exciting and technically challenging. Significant advances have been achieved by optimizing the fabrication processes towards more simple and straightforward strategies, while the performances of the electrodes have been improved by controlling their morphology and composition. In the majority of investigations, attention is focused on the specific capacitance and energy and power densities, even though the performance of a supercapacitor device should also be analysed by considering other determining factors, such as maximum voltage, leakage current, equivalent series resistance, or self-discharging response. Therefore, it is mandatory to explore the feasibility of cellulose-containing energy storage devices from all these points of view to fully ensure their correct performance. Similarly, the potential application of cellulose hydrogels as electrodes (if made con-

ductive) or the electrolyte in all-solid supercapacitors awaits further development.

Moreover, it seems of major importance to gain a better understanding of events occurring at the electrode–electrolyte interface. For such purposes, computer molecular dynamics simulations represent a potent tool to clarify some of these questions. For instance, the mechanisms of self-discharging or overoxidation processes that affect CPs remain still unknown. Another interesting consideration learnt from this review deals with designing multifunctional energy storage devices to be applied, for example, in motor vehicles where hybrid systems (capacitor/battery/fuel) power the engine. Actually, even though few studies exploit this facet, the introduction of cellulose-based supercapacitors able to store charge in addition to capture CO₂ would represent a huge innovation in the field of green energy technologies.

Finally, not only is cellulose the most abundant polymer, but also the most extensively recycled. Indeed, sustainable cellulose recycling shows a two-fold repercussion regarding cellulose-based supercapacitors. On the one hand, as it has been evidenced in some of the studies described above, high-quality recycled cellulose pulp and fibres (from newspapers, for instance) can be transformed into strong and flexible electrodes with excellent capacitive performance, and therefore this perspective also requires deep thought. On the other hand, disposal of cellulose-containing parts from energy storage devices is environmentally respectful when introduced into the paper recycling infrastructure.

Within the context of this section, it should be noted that paper/cellulose-based composite materials have been used to fabricate not only supercapacitors but also other kinds of energy storage devices. In particular, the successful implementation of cellulose-based materials in Li-ion batteries^{137,138} and fuel cells^{139,140} is particularly attractive since, together with supercapacitors, these devices hold the promise of effective solutions for a more sustainable future regarding energy storage devices. In addition to this, similarly to what happens with supercapacitors, intensive efforts are underway to develop Li-ion batteries and fuel cells by using renewable resources and water (as solvent) to reduce the environmental impact, and to simplify the fabrication processes to lower costs.^{141–143} However, as the distinctive characteristics and electrochemical performance of the materials used to fabricate Li-ion batteries and fuel cells are frequently different from those of supercapacitors, the former devices have not been explicitly included in the present review.

In summary, to meet the global energy challenge that we are facing, green and forward-thinking strategies are expected to sustain research initiatives, and cellulose and its derivatives will undoubtedly play a decisive role in this difficult task.

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