ACCOUNTS of chemical research

Article

Cite This: Acc. Chem. Res. XXXX, XXX, XXX−XXX

pubs.acs.org/accounts

Nanocellulose toward Advanced Energy Storage Devices: Structure and Electrochemistry

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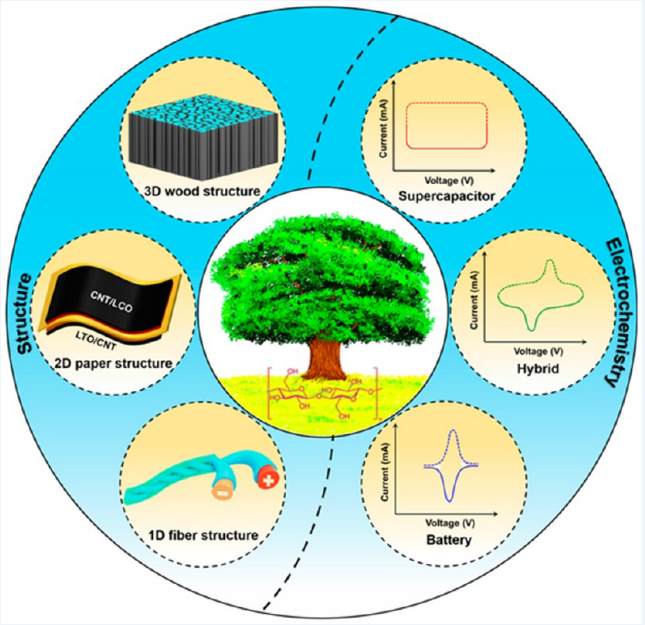
CONSPECTUS: Cellulose is the most abundant biopolymer on Earth and has long been used as a sustainable building block of conventional paper. Note that nanocellulose accounts for nearly 40% of wood's weight and can be extracted using well-developed methods. Due to its appealing mechanical and electrochemical properties, including high specific modulus (~100 GPa/(g/cm^3)), excellent stability in most solvents, and stability over a wide electrochemical window, nanocellulose has been widely used as a separator, electrolyte, binder, and substrate material for energy storage. Additionally, nanocellulose-derived carbon materials have also drawn increasing scientific interest in sustainable energy storage due to their low-cost and raw-material abundance, high conductivity, and rational electrochemical performance. The inexpensive and environmentally friendly nature of nanocellulose and its derivatives as well as simple fabrication techniques make nanocellulose-based energy storage devices promising candidates for the future of "green" and renewable electronics. For nanocellulose-based energy storage, structure engineering and design play a vital role in achieving desired electrochemical properties and performances. Thus, it is important to identify suitable structure and design engineering strategies and to better understand their relationship.



In this Account, we review recent developments in nanocellulose-based energy storage. Due to the limited space, we will mainly focus on structure design and engineering strategies in macrofiber, paper, and three-dimensional (3D) structured electrochemical energy storage (EES) devices and highlight progress made in our group. We first present the structure and properties of nanocellulose, with a particular discussion of nanocellulose from wood materials. We then go on to discuss studies on nanocellulose-based macrofiber, paper, and 3D wood- and other aerogel-based EES devices. Within this discussion, we highlight the use of natural nanocellulose as a flexible substrate for a macrofiber supercapacitor and an excellent electrolyte reservoir for a breathable textile lithium−oxygen battery. Paper batteries and supercapacitors using nanocellulose as a green dispersant, nanocellulose-based paper as a flexible substrate, and nanocellulose as separator and electrolyte are also examined. We highlight recent progress on wood-based batteries and supercapacitors, focusing on the advantages of wood materials for energy storage, the structure design and engineering strategies, and their microstructure and electrochemical properties. We discuss the influence of structure (particularly pores) on the electrochemical performance of the energy storage devices. By taking advantage of the straight, nature-made channels in wood materials, ultrathick, highly loaded, and low-tortuosity energy storage devices are demonstrated. Finally, we offer concluding remarks on the challenges and directions of future research in the field of nanocellulose-based energy storage devices.

1. INTRODUCTION

The development of modern society has fueled growing demand for energy. Electrochemical energy storage (EES) techniques, including rechargeable batteries, supercapacitors, and hybrid capacitors as power sources for portable electronic devices and electric vehicles have gained tremendous attention in the past three decades due to their high energy density, long lifespan, and safety.[1] The pursuit of higher performance has driven an unremitting interest in materials and structural engineering.[2,3] The past decade has witnessed a significant enhancement of EES energy density and cycling life.[4] Besides high performance, material cost, resource abundance, safety, and environmental friendliness have been raised as major challenges for next-generation affordable and sustainable energy storage devices,[5,6] requiring extraordinary technological and materials progress.

Received: August 2, 2018

DOI: 10.1021/acs.accounts.8b00391
Acc. Chem. Res. XXXX, XXX, XXX−XXX

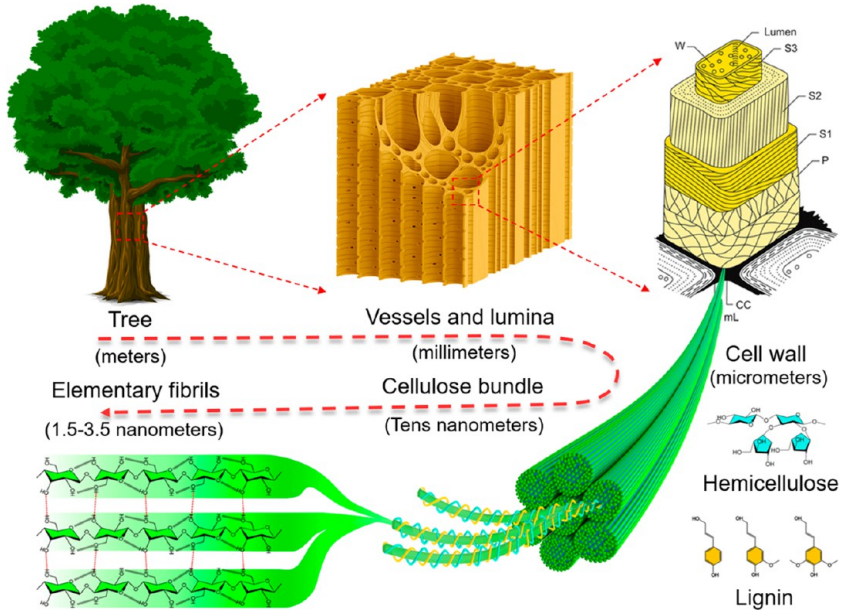


Figure 1. Graphical illustration of the hierarchical structure of wood, from macroscopic to molecular scale. Tree image is adapted from ref 10. Copyright 2017 American Chemical Society. The cell wall comprised of multilayers is adapted with permission from ref 11. Copyright 2006 Springer Nature.

Recently, nanocellulose and its derivatives have emerged as one of the most attractive candidates for components used in EES devices. As the most abundant natural biopolymer on earth, cellulose can be extracted from diverse plants, algae, and other organisms on an industrial scale.[7] The unique and appealing mechanical and electrochemical properties make nanocellulose highly attractive in EES for diverse components, including separators, electrolytes, binders, and substrate materials. Besides, via simple carbonization, nanocellulose-derived carbon materials can be made highly electrically conductive and have been widely used as electrode materials or current collectors in sustainable energy storage. The inexpensive and environmentally friendly nature of nanocellulose and its derivatives, as well as its simple fabrication techniques, positions nanocellulose-based energy storage devices as promising candidates for next-generation "green" and renewable electronics.[6,8,9]

In this Account, we aim to summarize recent progress made in diverse structure design and engineering of nanocellulose-based energy storage, especially from our research group. We will highlight structure design strategies of nanocellulose-based EES devices with macrofiber structures, with new insights on nanocellulose as an excellent electrolyte reservoir. We will then discuss paper batteries and supercapacitors, which demonstrate excellent flexibility and diverse fabrication strategies by using nanocellulose as a substrate for battery and supercapacitor electrodes, as well as for electrolytes and separators. Next, three-dimensional (3D) wood-based and other aerogel-based batteries and supercapacitors will be reviewed, which demonstrate some of the highest reported areal capacities but have their own unique set of challenges and solutions. Lastly, concluding remarks on the challenges and directions of future research in the field of nanocellulose-based EES devices will be offered, albeit briefly due to the limited space.

2. NANOCELLULOSE PRODUCED FROM WOOD AND OTHER PLANTS

Cellulose nanofibers can be synthesized from diverse biomasses, including tall plants, agricultural byproducts, algae, and bacteria during their growth process.[8] Many strategies have been developed to produce nanocellulose from plant cell walls, algae, and other organisms since the disintegration of cellulose pulp into cellulose nanofibers in 1980s, including top-down methods like acid hydrolysis and mechanical nanofibrillation and bottom-up methods like solvent dissolution and bacterial synthesis of bacterial cellulose (BC).[9] Commonly, cellulose nanofibers can be classified into three categories, cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and BC, according to their morphology and source materials. NFCs and CNCs are generally produced from high plants, whereas BCs are high aspect ratio nanofibrils produced by bacteria. NFCs have both long lengths and high aspect ratios but relatively low crystallinity (with both amorphous regions and crystalline regions), while CNCs exhibit shorter lengths, lower aspect ratios, and high crystallinity, mainly ascribed to the distinct intensity of fabrication methods.

A tree is a typical high plant with a unique cellular hierarchical structure with abundant vessels and lumina (10–80 μm) aligned in the tree-growth direction (Figure 1).[10] Wood cell walls are composed of middle lamellae, as well as primary and secondary cell walls, with the latter being further divided into three layers, namely, S1, S2, and S3 (Figure 1).[11] Cellulose (~40–50 wt %), hemicellulose (~20–35 wt %), and lignin (~20–30 wt %) form the main components of the cell wall, intertwining with each other and contributing to the good mechanical properties of wood.[12] Cellulose bundles with diameters of several tens of nanometers can be further divided into nanocellulose fibers with diameters ranging from 5 to 20 nm. At a finer scale, elementary fibrils of 1.5–3.5 nm can be found in the nanocellulose fiber, acting as the elementary building blocks of the hierarchical cellulose fibers. At the

DOI: 10.1021/acs.accounts.8b00391
Acc. Chem. Res. XXXX, XXX, XXX–XXX

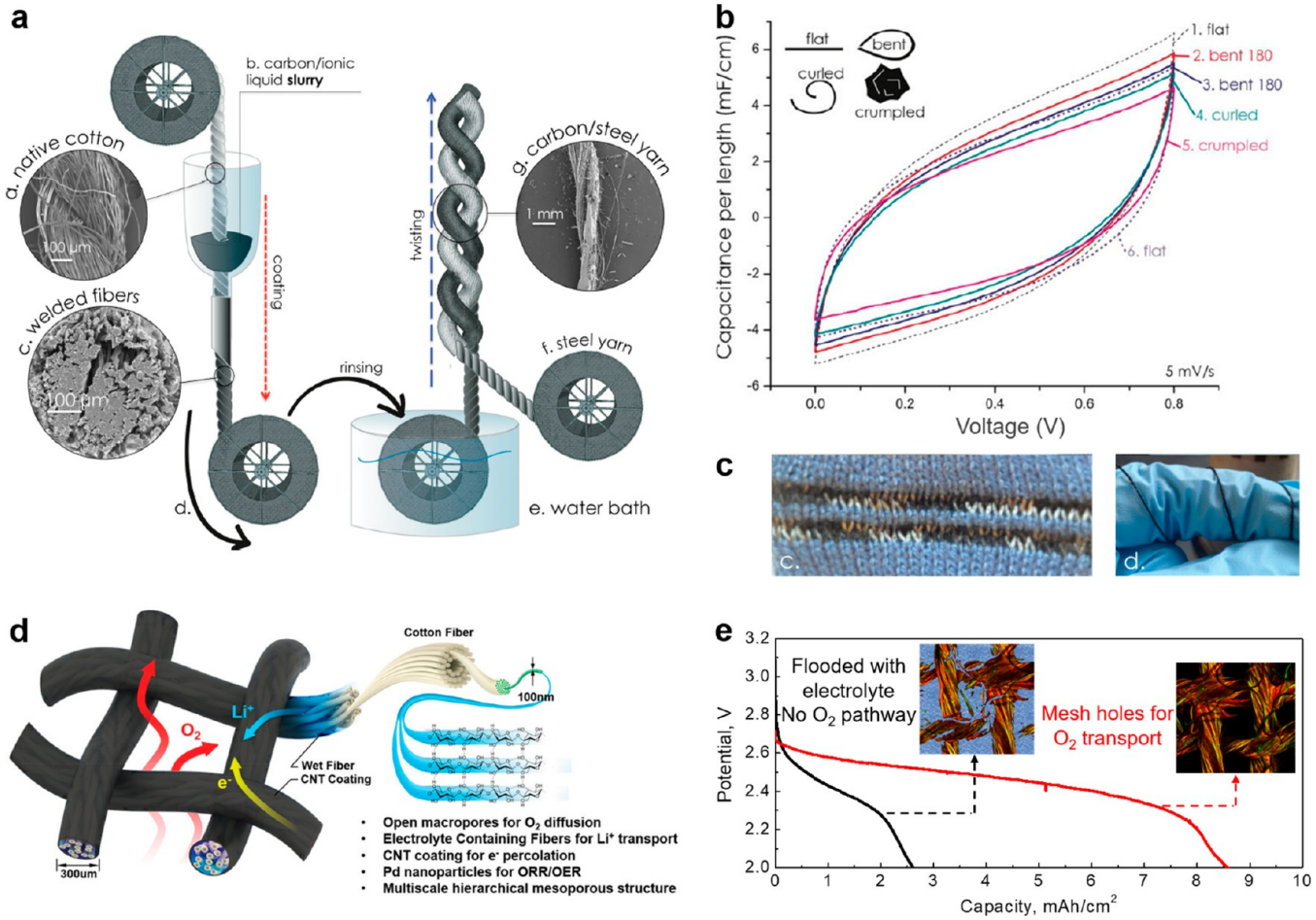


Figure 2. (a–c) Nanocellulose-based macrofiber supercapacitor: (a) fabricating process; (b) charge–discharge curves of device tested in different bent, curved, and crumpled states; (c) photo images showing its flexibility. Adapted from ref 20. Copyright 2015 WILEY-VCH. (d,e) Nanocellulose-based textile as breathable air cathode for Li–O_2 batteries: (d) illustration of the breathable cellulose fiber-based air cathode; (e) discharge curves. Adapted with permission from ref 21. Copyright 2018 WILEY-VCH.

molecular level, repeated units of D-glucose assemble through covalent bonding and intra- and interchain hydrogen bonding, forming the linear and stiff cellulose chain.[6]

The unique chemical structure of nanocellulose contributes to an array of advanced mechanical and electrochemical properties that are attractive for various EES applications,[7–9,13–18] including (1) high aspect ratio along with good mechanical properties making nanocellulose highly attractive for flexible energy storage, (2) the abundant hydroxyl groups on the reactive surfaces enabling a variety of hybridization possibilities with diverse active materials to construct nanocellulose-based composite electrodes and separators, (3) the good thermal and structure stability and wettability in various electrolytes over a wide potential window positioning it as a competitive candidate for EES applications, and (4) the high aspect ratio, high carbon content, and easy modification making it an excellent source material for fabricating diverse carbon electrodes with high surface area and tunable microstructure, pore structure, and doping structure.

3. STRUCTURAL DESIGN AND ENGINEERING IN NANOCELLULOSE-BASED MACROFIBER EES DEVICES

The high aspect ratio and mechanical robustness of nanocellulose makes it highly attractive for constructing macrofiber, paper, and 3D bulk EES devices. One-dimensional fibers in particular demonstrate excellent flexibility, allowing them to be incorporated into textiles and suggesting promising strategies toward portable and wearable electronics.[19] Nanocellulose also demonstrates excellent electrolyte absorption capability. These combined merits position nanocellulose as an excellent candidate for macrofiber-based EES devices.

3.1. One-Dimensional Nanocellulose Macrofiber as a Flexible Substrate

Macroscopic fiber assembled from cellulose nanofibers possesses good mechanical robustness, flexibility, and abundant pores in the nanocellulose network that are available for active material loading, making it ideal as a strong and flexible substrate for 1D energy storage devices. Gogotsi et al. report a natural cellulose fiber welded yarn embedded with porous carbon materials for wearable supercapacitors.[20] In this work, cellulose yarns are converted to supercapacitors through a natural fiber welding process that uses controlled amounts of ionic liquids and molecular cosolvents to selectively swell and

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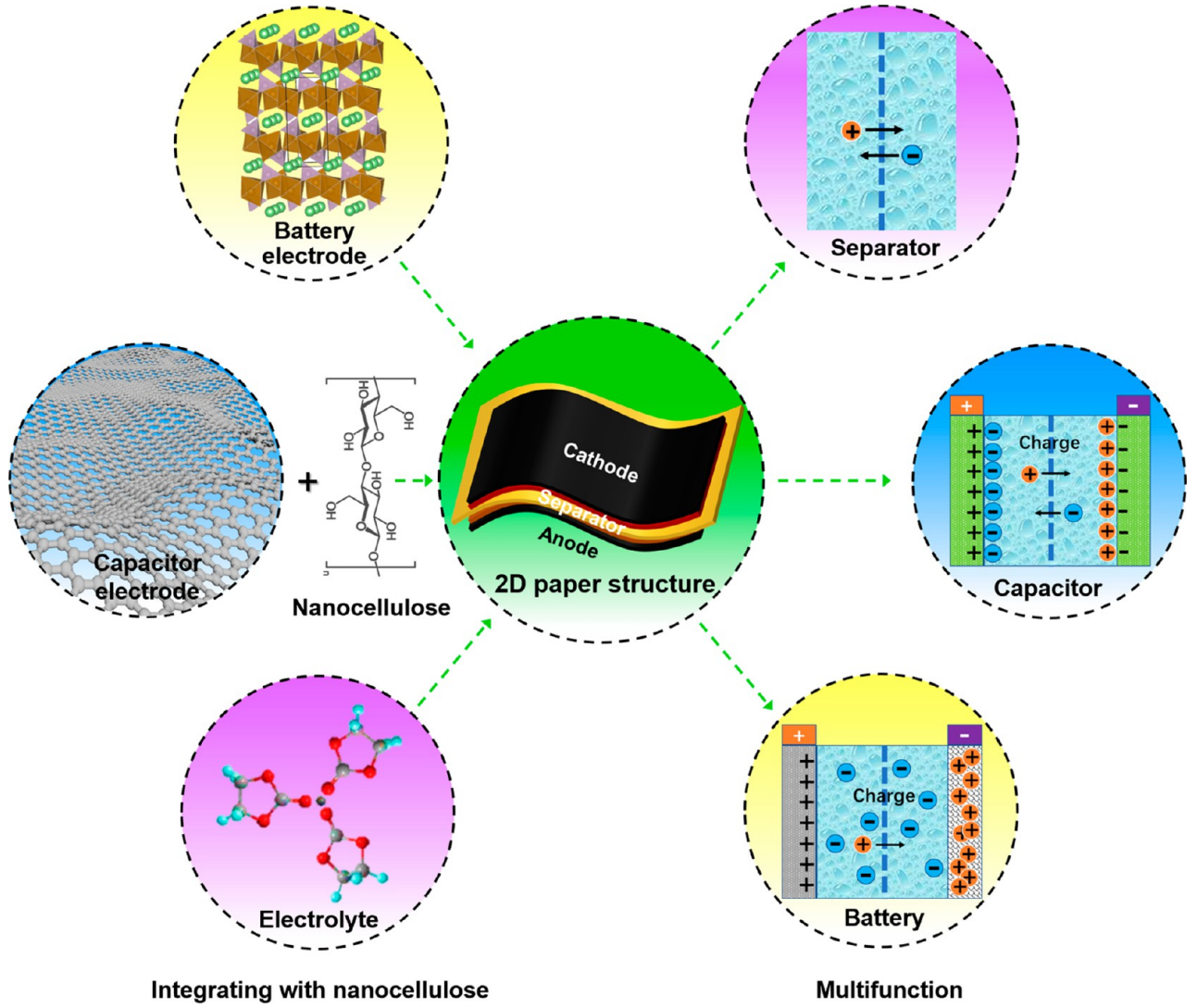

Figure 3. Multifunction of nanocellulose in paper EES devices, including as substrate materials for batteries, supercapacitors, and separators when integrated with battery electrodes, capacitor electrodes, and electrolyte, respectively.

mobilize biopolymers in fibrous materials for functional modification (Figure 2a). In this manner, functional materials (e.g., nanocarbons) can be incorporated into natural fibers to generate hybrid macroscopic fiber electrodes, which demonstrate both high capacitance (up to 37 mF cm^{-1}) and flexibility (Figure 2b) and can be incorporated into commercial textiles for wearable applications (Figure 2c). Despite its excellent flexibility and low cost, the mass loading per length is still relatively low (less than 1 mg cm^{-1}), which needs further improvements by structure engineering, especially pore structure design.

3.2. One-Dimensional Nanocellulose Macrofiber as Electrolyte Reservoir

To explore new functions of nanocellulose fiber, the Hu group has contributed a brilliant strategy by constructing breathable structure with decoupled electrolyte and oxygen gas pathways for Li-oxygen batteries using carbon nanotube (CNT)-coated nanocellulose macrofiber-based textile (cotton textile) as a flexible substrate and electrolyte reservoir (Figure 2d).[21] The macropores act as passages for oxygen gas transport, while the nanocellulose bundles (macroscopic fibers) with abundant nanopores provide pathways for electrolyte/ion transport. Both pathways combined in one structure enable the noncompetitive transport of Li^+ ions and oxygen gas, representing a smart solution to the long-standing issue of competition between electrolyte (ions) and oxygen gas in Li-oxygen battery systems. Benefiting from such decoupled pathway design, the CNT-coated textile cathode demonstrates a high areal capacity of 8.6 mAh cm^{-2}, which is ~3-times higher than its counterpart with a flooded structure (Figure 2e) and surpasses most reported values as well. The decoupled pathway structural design enabled by the robust, flexible, and electrolyte absorptive nanocellulose fiber network can be extended to other facilities involving reactions on multiple phase interlayers.

Other than Li-oxygen batteries, nanocellulose macrofiber-based textiles have also demonstrated great potential in constructing flexible supercapacitors and lithium-ion batteries.[22,23] The past decade has witnessed fast growth in this field due to its real promise for commercially viable wearable devices. One major concern for nanocellulose macrofiber-based textile devices is their long-term stability against water given that washability is a critical property for textile applications. Another challenge is the scalable fabrication of

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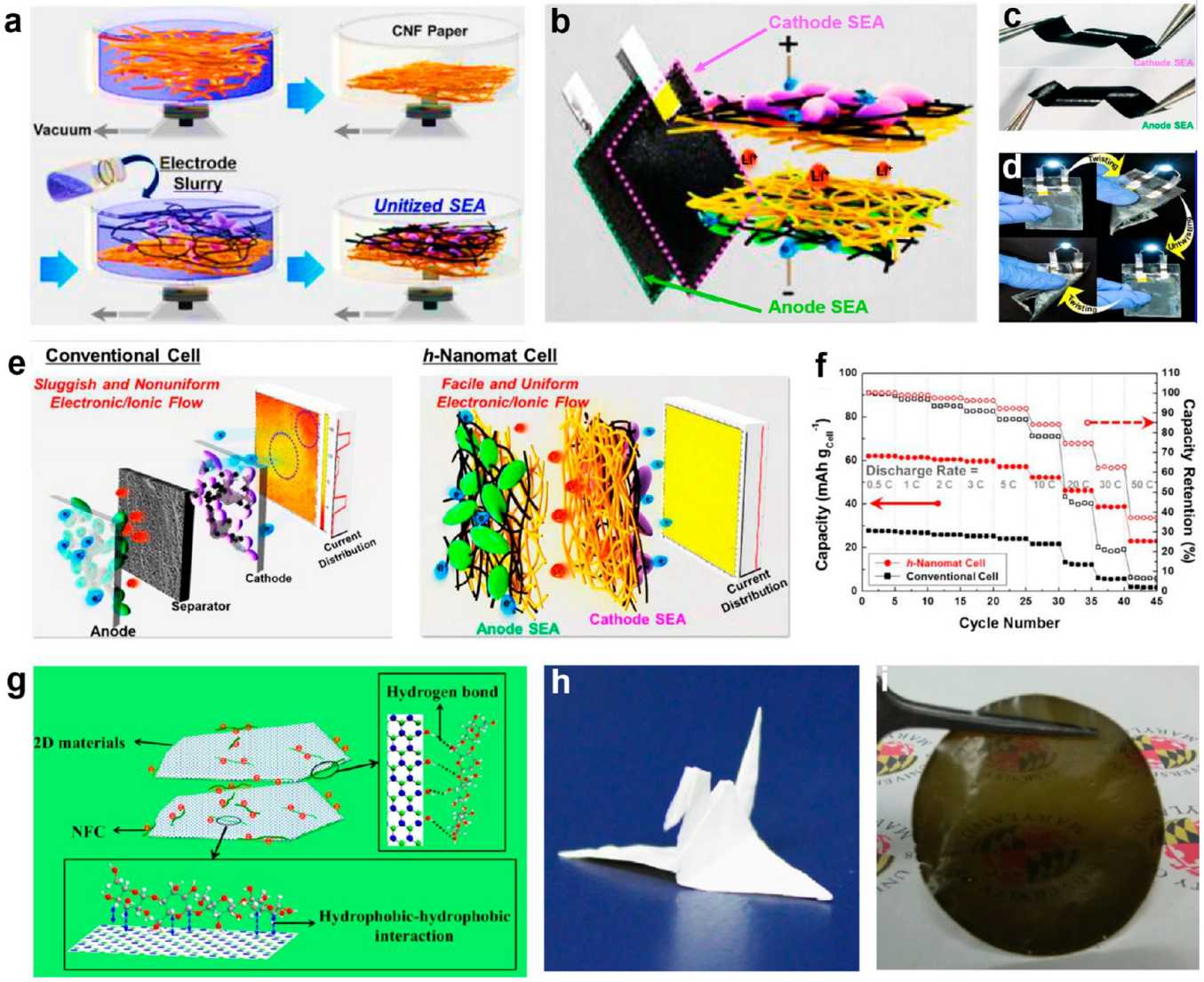

Figure 4. (a–f) Nanocellulose-based paper (mat) battery: (a) fabrication process; (b) structure of the mat battery; (c) digital images of the anode and cathode; (d) digital images of the assembled pouch cell with good flexibility; (e) structural comparison between conventional and *h*-nanomat cells; (f) lithium storage performance of the conventional and *h*-nanomat cells. Adapted from ref 25. Copyright 2014 American Chemical Society. (g–i) Nanocellulose as a green dispersant for paper electrodes in sodium ion batteries: (g) interaction between nanocellulose and 2D materials; (h) origami crane made from the strong, flexible BN film; (i) digital image of the MoS_2 film. Adapted with permission from ref 28. Copyright 2015 Elsevier.

materials and devices for real-world implications of this technique, which, however, is generally absent in literature of this field.

4. STRUCTURAL DESIGN IN NANOCELLULOSE-BASED PAPER EES DEVICES

Paper-based batteries and supercapacitors have been regarded as an interesting and significant group of flexible EES devices, which are attracting intensive attention from both industry and academia.[24] Paper constructed from cellulose is a commodity ubiquitous in our daily lives and can be produced at large scale and low cost by the paper industry. Due to its unique hierarchically porous structure and rough yet absorptive surface properties, diverse electrochemical active materials (e.g., battery electrode and supercapacitor electrode materials) and electrolyte can be facilely incorporated with the paper structure, demonstrating excellent accommodating capability (Figure 3).

4.1. Nanocellulose as Substrate Materials for Paper Batteries

The accommodation of diverse functional materials endows the cellulose paper with multiple functions depending on the incorporated materials. By incorporating battery electrode materials into cellulose paper, paper batteries with good performance, high flexibility, and low cost can be achieved. Lee's group has devoted tremendous efforts to developing paper batteries using nanocellulose as substrate materials.[25−27] For example, the authors demonstrated a novel heterolayered nanomat (*h*-nanomat) structure design strategy for fabricating paper batteries.[25] In this design, both the anode and cathode can be facilely fabricated by filtering electrode slurry using nanocellulose. Meanwhile, the separator (bottom layer of the film without electrode slurry) can be integrated with the film electrode during the filtration process (Figure 4a). The *h*-nanomat cell with good flexibility can be achieved by putting the cathode and anode films together with the integrated

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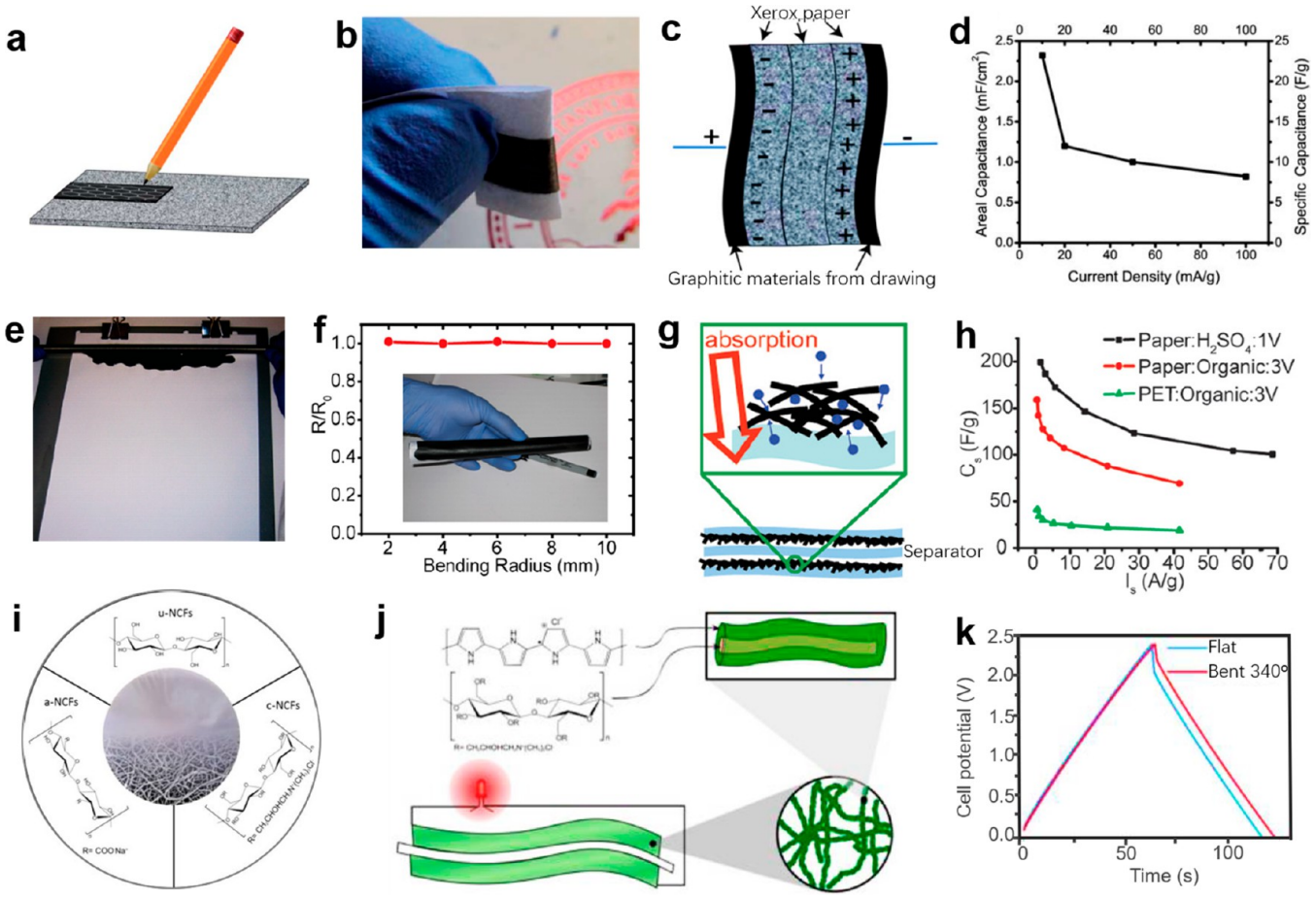

Figure 5. (a–d) Paper supercapacitor fabricated by direct pencil drawing: (a) pencil drawing process on Xerox paper; (b) digital image of the paper electrode; (d) areal and gravimetric capacitances at different current densities. Adapted with permission from ref 29. Copyright 2011 Royal Society of Chemistry. (e–h) Direct printing of conductive ink on commercial paper for supercapacitor application: (e) direct printing of CNTs on commercial paper; (f) sheet resistance changes after bending the conductive paper at different radii; (g) illustration of the all-paper supercapacitor; (h) gravimetric capacitances. Adapted with permission from ref 30. Copyright 2009 National Academy of Sciences of the USA. (i–k) Paper supercapacitor based on conductive polymer coated nanocellulose: (i) molecular structure of unmodified and modified NFCs; (j) illustration of the conductive polymer coated nanocellulose; (k) charge–discharge curves of three paper supercapacitors connected in series. Adapted with permission from ref 31. Copyright 2015 American Chemical Society.

separator layers from both electrodes facing each other (Figure 4b–d). Another benefit of the integrated nanomat structure design is that a much more uniform current distribution is achieved than that in conventional cells, which contributes to the substantially higher capacities (~60 vs ~30 mAh g_{cell}^{-1} at 0.5 C, Figure 4e,f).

In addition to simple mixing and infiltration methods, our group has contributed another effective strategy by using nanocellulose as a green dispersant to exfoliate two-dimensional (2D) materials, such as boron nitride (BN) and molybdenum disulfide (MoS_2).[28] Nanocellulose contains both hydrophilic functional groups and hydrophobic C–H moieties, which enables the hydrophobic sites to interact with the hydrophobic plane of 2D materials, while the hydrophilic hydroxyl groups link with the defective edges of the 2D material flakes through hydrogen bonding (Figure 4g). Nanocellulose-BN and nanocellulose-MoS_2 films fabricated by filtering the dispersions demonstrate excellent flexibility and foldability (Figure 4h,i). The nanocellulose-MoS_2 film with CNTs exhibits both excellent mechanical robustness and electrochemical performance (147 mAh g^{-1} at 10 mA g^{-1}) as a sodium-ion battery anode.

In the pursuit of higher energy density, thick electrode design with high mass loading has been regarded as an attractive direction by reducing the fraction of nonactive materials in the device. Although conventional cellulose-based paper EES devices demonstrate good flexibility, they are often characterized by low energy density due to the large volumetric ratio of cellulose, which limits the mass loading of the paper electrode. To solve this issue, Lee et al. developed a heteronet architecture with large thickness (thus high mass loading) and abundant hierarchical pores for ion and electron transport without sacrificing its flexibility.[27]

4.2. Nanocellulose as Substrate Materials for Paper Supercapacitors

A supercapacitor is another type of EES device that is characterized by high power and long cycling life. Flexible supercapacitors based on paper structures are attractive for portable and wearable electronics, particularly as cellulose paper features attractive structural configuration (porous, with good stability and mechanical properties), natural abundance, and low cost, making it a promising substrate material.[24] We have reported several pioneering works on paper supercapacitors made by coating various conductive carbon

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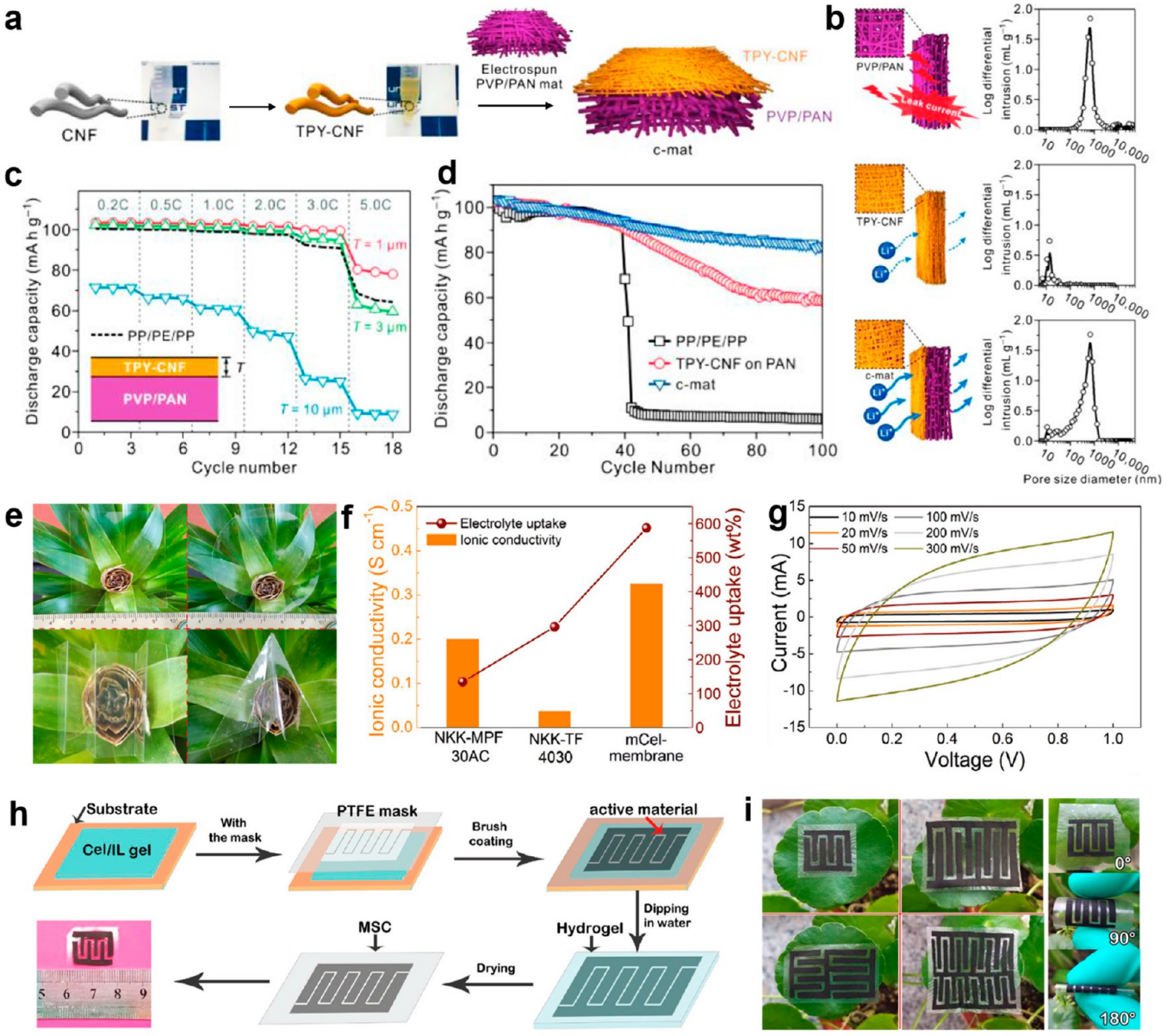

Figure 6. (a–d) Functionalized nanocellulose-integrated heterolayered nanomats as battery separators: (a) illustration of the fabrication process; (b) schematic and pore size distribution of the PVP/PAN electrospun mat, TPY-CNF, and TPY-CNF on PVP/PAN (c-mat); (c,d) rate and cycling performance. Adapted with permission from ref 37. Copyright 2016 American Chemical Society. (e–i) Flexible paper supercapacitor based on an ionic liquid regenerated nanocellulose mesoporous membrane separator (electrolyte): (e,f) digital images and ionic conductivity of the membrane; (g) cyclic voltammetry curves of the mCel-membrane-based MSC; (h,i) schematic diagram of the preparation process and digital images of MSCs with different configuration patterns. Adapted with permission from ref 38. Copyright 2017 WILEY-VCH.

materials (e.g., graphite, CNT ink) onto cellulose-based commercial paper.[29,30] In the first example, we directly draw patterns on Xerox paper using pencil to construct a paper supercapacitor, which demonstrates both good flexibility and high areal capacitance of 2.3 mF cm^{-2} at 20 mA g^{-1} (Figure 5a–d).[29] In another example, regular A4 printing paper was used as a flexible substrate that was directly coated with CNT ink to construct a paper supercapacitor (Figure 5e).[30] After CNT coating, the paper becomes highly conductive with good stability (Figure 5f). A symmetric supercapacitor setup was used to demonstrate the high capacitance, in both aqueous and organic electrolyte, greatly surpassing its counterpart using poly(ethylene terephthalate) as a substrate (Figure 5g,h).

Using a similar strategy, various carbonaceous materials, including active carbon, graphene, conductive polymers (e.g., polypyrrole and polyaniline), and metal oxides (e.g., MnO_2, V_2O_5) have been incorporated with paper to fabricate flexible supercapacitors via direct printing, filtration, surface coating, and conformal coating.[31−34] Among these approaches, conformal coating ensures the strong integration between active materials and the cellulose paper throughout the entire structure, thus enabling better mechanical robustness and stability and higher mass loading. Wang et al. first introduced quaternary amine groups on the surface of nanocellulose to prepare cationic nanocellulose (c-NFC) surface charges (Figure 5i,j).[31] After conformally coating pyrrole on the c-NFC substrate via *in situ* polymerization, the composite paper electrode delivered both high normalized gravimetric (127 F g^{-1}) and volumetric (122 F cm^{-3}) capacitances at 300 mA cm^{-2}, representing one of the best results for paper

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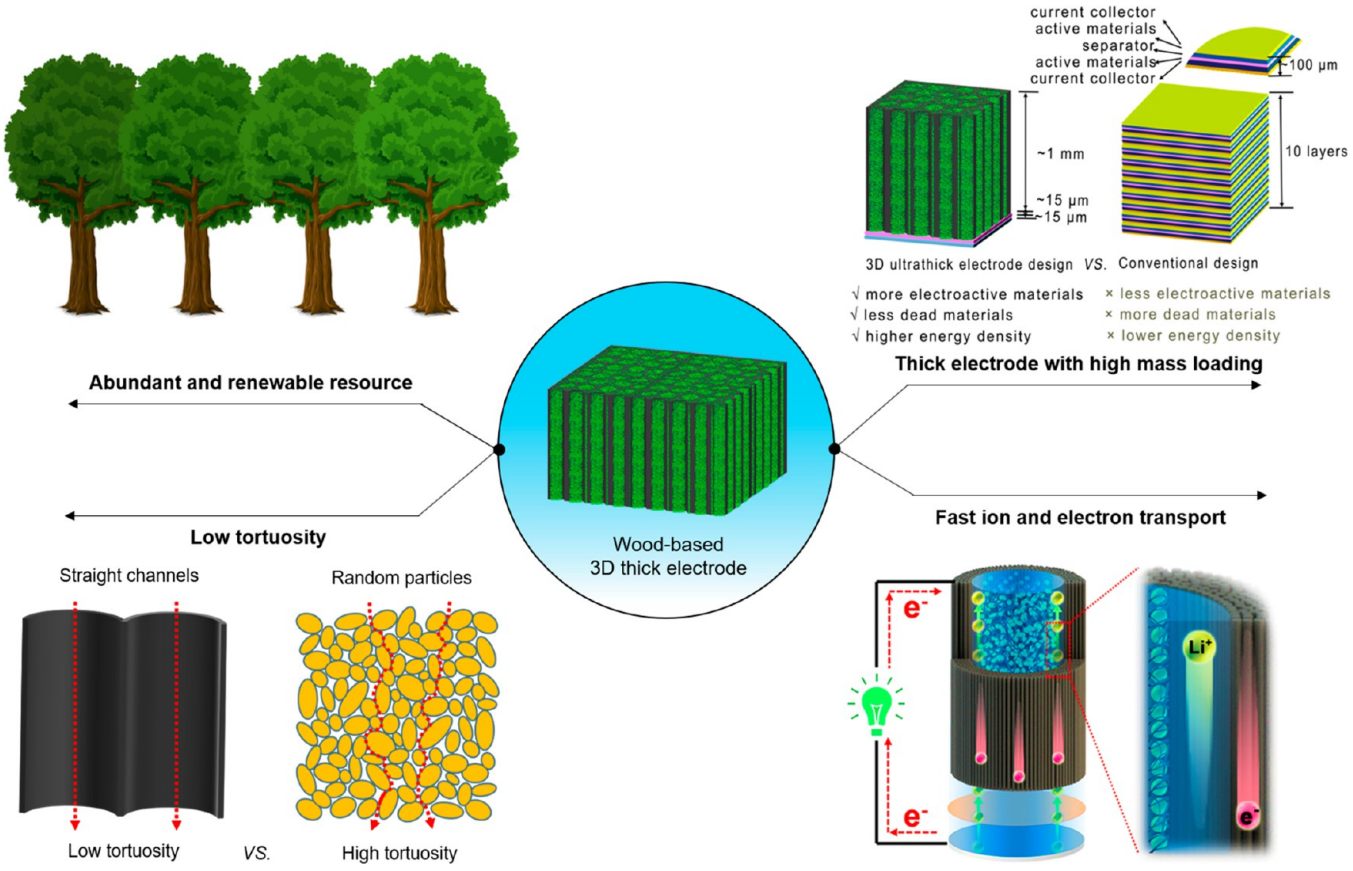

Figure 7. Advantages of 3D wood-based energy storage, including the abundant and renewable resource of trees, thick electrodes with high mass loading, straight channels with low tortuosity, and fast ion or electron transport. Adapted with permission from ref 44. Copyright 2017 WILEY-VCH.

supercapacitors.[24] A symmetric supercapacitor assembled from two such composite paper electrodes exhibited high volumetric energy and power density (3.1 mWh cm^{-3} and 3 W cm^{-3}) and excellent flexibility (Figure 5k).

4.3. Nanocellulose as a Separator for Paper EES Devices

Nanocellulose has also been used as separator by accommodating certain electrolytes. The native properties of nanocellulose (i.e., low cost, outstanding mechanical strength and flexibility, and high dimensional, thermal, and chemical stability) can meet the key requirements for an ideal polymer electrolyte separator. In some early studies, cellulose-based membranes (especially cellulose acetate, methyl cellulose, and cellulose-based composites) were used as separators in energy storage devices, but with unsatisfactory performance due to the low porosity and insufficient electrolyte wettability.[35] It has been suggested that high porosity is desirable in separator design to ensure good electrolyte retention and enhanced ionic conductivity.[36−38] Following this guidance, Lee et al. have recently demonstrated a nanoporous cellulose separator with a bilayer nanomat structure that features high porosity.[37] In this work, a terpyridine (TPY)-functionalized cellulose nanofibril (CNF) nanoporous thin mat was fabricated as the top layer and a thick electrospun polyvinylpyrrolidone (PVP)/polyacrylonitrile (PAN) macroporous mat served as the support layer, forming the unique bilayer hierarchical/asymmetric porous structure to balance leakage current and ion transport rate (Figure 6a,b). Consequently, a substantial improvement in the high-temperature cycling performance of cells was realized utilizing this unique nanocellulose-based separator design (Figure 6c,d).

Most recently, Zhao et al. developed a mesoporous cellulose (m-Cel) membrane with good mechanical flexibility and foldability, high electrolyte uptake capability (nearly 600%), and high ionic conductivity (~0.33 S cm^{-1}) via an ionic liquid dissolution-regeneration strategy (Figure 6e and 6f).[38] More attractively, active material ink can be directly printed on the m-Cel membrane soaked with 6 M KOH solution, resulting in a highly flexible and integrated microsupercapacitor (MSC) with high capacitances at different current rates (Figure 6g−i). This innovative work further highlights the importance of high porosity in cellulose-based polymer electrolyte separator design for the rapid and continuous flow of ions back and forth between the electrodes.

Despite the great progress achieved in nanocellulose-based paper EES devices, continuous efforts are needed to address current challenges, including (1) cheap material and device manufacturing process that can be easily scaled up, (2) stable and highly conductive solid-state electrolyte to improve the energy density and safety of the devices for practical applications, and (3) advanced integration techniques to make highly integrated, flexible, and multifunctional paper-based devices. With addressing these remaining challenges, ubiquitous applications of flexible nanocellulose-based paper EES devices with low cost and high energy density in portable electronic devices are anticipated in the near future.

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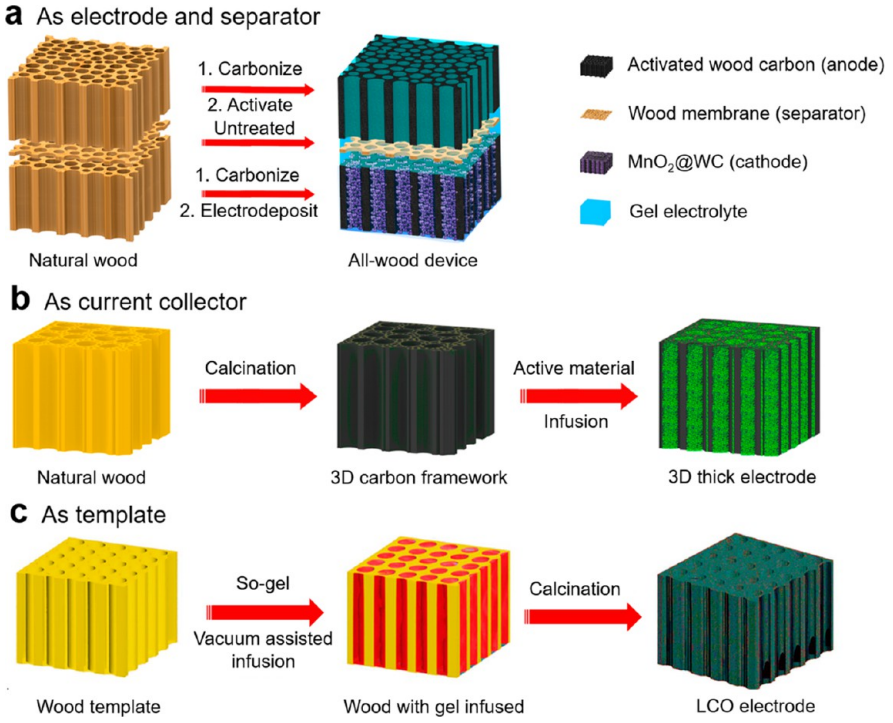

Figure 8. Construction strategies of wood-based energy storage devices. (a) Wood and wood-derived carbon as separator and electrode material, respectively. Adapted from ref 43. Copyright 2017 Royal Society of Chemistry. (b) Wood-derived carbon as a 3D current collector. (c) Wood as a sacrificial template for constructing a 3D thick electrode. Panels b and c adapted with permission from refs 44 and ref 45. Copyright 2017 and 2018 WILEY-VCH.

5. STRUCTURAL DESIGN IN NANOCELLULOSE-BASED THREE-DIMENSIONAL EES DEVICES

Recently, nanocellulose-based 3D EES devices demonstrate great potential in improving the energy density on the device level. For example, a BC-derived carbon nanofiber (CNF) aerogel with large thickness, high porosity, large surface area, and controllable doping structure was shown to be an excellent electrode and scaffold material for EES devices.[39] Other than 3D aerogel structure, wood and its derivatives have recently emerged as a novel and attractive group of components for 3D EES devices.[40−45] Various strategies have been demonstrated for constructing wood-based structures and devices for batteries and supercapacitors, with both large thickness and high mass loading.

5.1. Advantages of Three-Dimensional Wood-Based Energy Storage

The advantages of wood-based materials for energy storage include its large thickness and mass loading beyond the limits of traditional electrodes, straight channels with low tortuosity, and rich pathways for the fast transport of ions and electrons, in addition to being an abundant and renewable resource (Figure 7). Substantially different from the traditional bottom-up approach using extracted nanocellulose as building blocks to construct targeted cellulose-based materials, the fabrication of a 3D wood-based electrode generally involves top-down processes, which allows the intrinsic unique structure of wood, featuring multiple aligned channels (i.e., vessels and lumina), to be well retained. In this way, the advantages of wood structure for energy storage can be fully utilized.

5.2. Construction Strategies for Three-Dimensional Wood-Based EES Devices

In terms of developing various types of energy storage devices by directly engineering the natural wood structure, the Hu and Yu groups have made an array of contributions.[41−45] The construction strategies of wood-based energy storage devices can be divided into three types (Figure 8): (1) directly using wood and its carbonaceous derivatives as separators and electrode active materials; (2) carbonizing the wood membrane to act as a 3D current collector, enabling various kinds of electrode active materials to be infiltrated or coated into the pores (channels); (3) using wood as a self-sacrificial template to fabricate 3D electrodes that replicate the unique multichanneled structure of wood. The diversity of these construction strategies enables the fabrication of various wood-based electrodes and devices with multiple functions, which helps extend the scope of applications in the field of energy storage.

5.3. Structure and Electrochemical Performance of Three-Dimensional Wood-Based EES Devices

Wood structures are naturally rich in vertically aligned channels that demonstrate strong mechanical robustness that can be well preserved even after high-temperature carbonization, which at the same time imparts the wood carbon with high electrical conductivity. These structural characteristics along with the facile fabrication make wood carbon an ideal 3D current collector, particularly for thick electrode design. We demonstrated that a variety of electrode materials, including lithium ion phosphate (LFP), sulfur, lithium metal, and sodium metal can be incorporated with the 3D wood carbon to construct ultrathick (up to millimeter) and highly loaded (up to 60 mg cm^{-2}) electrodes with multiple functionalities.

DOI: 10.1021/acs.accounts.8b00391
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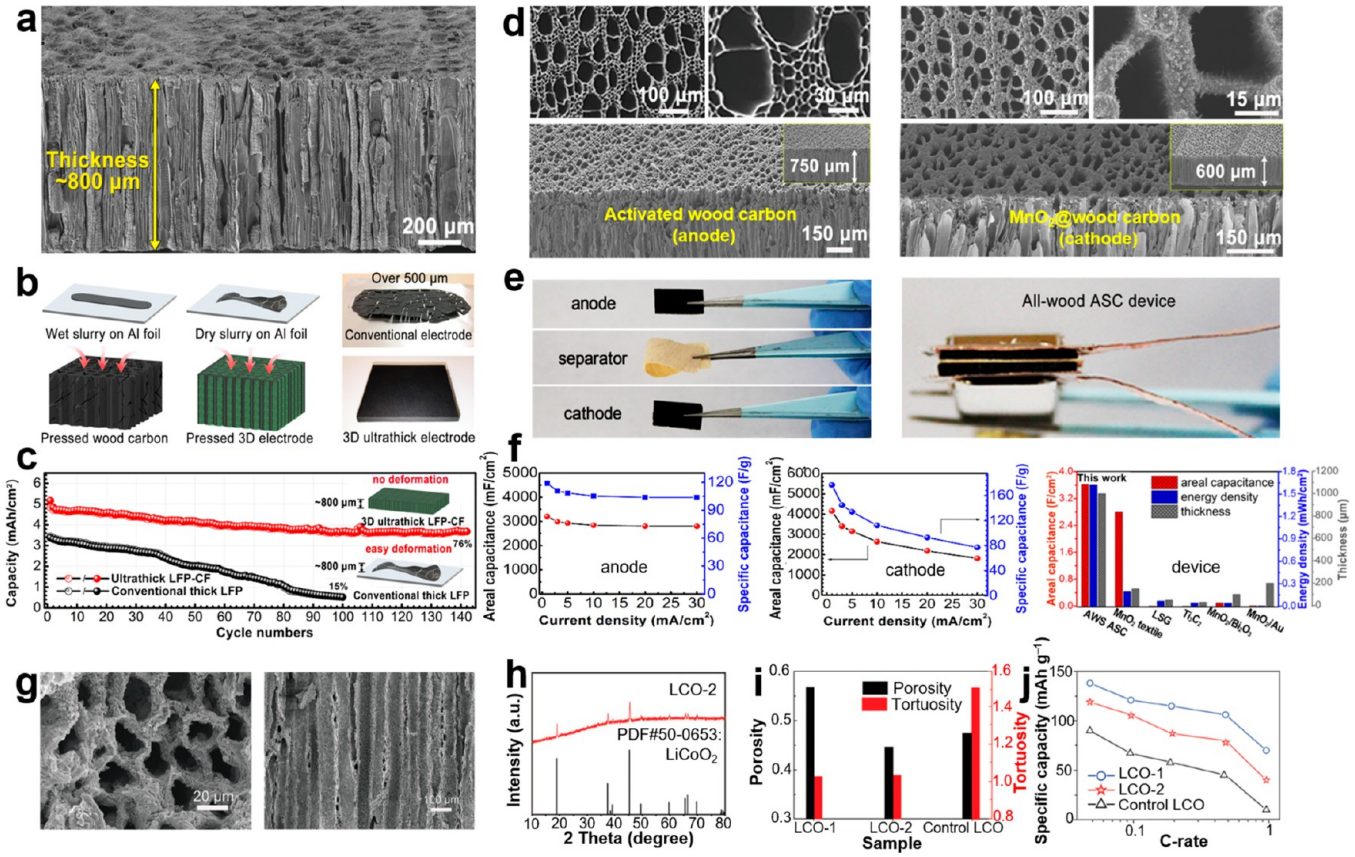

Figure 9. (a–c) Wood carbon as a 3D current collector: (a) a 3D electrode by infiltrating LFP slurry into the channels of the wood carbon; (b) low deformability of the 3D electrode compared with a conventional thick electrode; (c) cycling performance. Adapted with permission from ref 44. Copyright 2017 WILEY-VCH. (d–f) All-wood supercapacitor: (d) morphologies of the activated wood carbon anode and MnO_2@WC cathode; (e) digital images of the anode, separator, cathode, and all-wood supercapacitor; (f) electrochemical performance of anode, cathode, and the all-wood device. Adapted with permission from ref 43. Copyright 2017 Royal Society of Chemistry. (g–j) Wood-templated ultrathick bulk battery electrodes: (g,h) scanning electron microscopy images and X-ray diffraction pattern of LCO electrodes; (i) porosity and tortuosity of different LCO samples; (j) rate performance of various LCO electrodes. Panels g–j adapted with permission from ref 45. Copyright 2018 WILEY-VCH.

For example, we developed an ultrathick (~800 μm) 3D LFP/wood carbon framework (LFP-CF) cathode by infiltrating LFP slurry into the channels of the carbon framework (Figure 9a).[44] The 3D electrode demonstrates better mechanical stability and cycling performance than conventional thick electrodes made by slurry coating method (Figure 9b,c).

Additionally, wood and its derivatives can also be used as electrode or separator components in energy storage devices. Chen et al. developed an interesting and innovative all-wood asymmetrical supercapacitor with its major components (cathode, anode, and separator) all derived from a piece of wood.[43] Wood carbon activated by CO_2 can be directly used as an anode, while wood carbon deposited with MnO_2 can serve as the cathode, and a thin natural wood membrane can act as the separator (Figure 9d,e). Due to their low tortuosity, large thickness, high mass loading, and conductivity, both anode and cathode exhibited record-high areal capacitance. When these components were assembled into an all-wood asymmetrical supercapacitor, a high capacitance of 3.6 F cm^{-2} can be achieved based on device level, representing one of the highest values ever reported (Figure 9f).

Wood also has demonstrated value as a sacrificial template material. Most recently, Yu and co-workers reported a wood-inspired thick electrode design that used natural wood as a template.[45] In this work, 3D ultrathick lithium cobalt oxide (LCO) electrode replicating the multichanneled structure of wood was fabricated, which demonstrated a low tortuosity and high capacities at various current rates (Figure 9g–j).

Although wood-based EES devices demonstrate high electrochemical performance, especially with ultrahigh mass loading for thick electrode design, several challenges remain and need further exploration: (1) the scalability is limited by the size of the wood slice; (2) macrosized pores are undesired in some devices; (3) the mechanical robustness of carbonized wood is still relatively low compared with commercial Cu or Al foil current collectors. Further material and structural engineering, such as new wood cutting process, pore size engineering, and hybridization design are desirable for addressing these issues.

6. CONCLUSIONS

In this Account, we surveyed recent developments in nanocellulose-based energy storage with a focus on macrofiber, paper, and 3D structured EES devices. Nanocellulose exhibits great potential as a flexible and robust 1D substrate that can serve as an excellent electrolyte reservoir and mechanical buffer. Incorporating electrode materials with cellulose-based paper by direct printing, infiltration, surface coating, or conformal bulk coating provides a simple yet effective strategy for producing high performance flexible paper electrodes. Progress has also been made on optimizing the pore structure

DOI: 10.1021/acs.accounts.8b00391
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of cellulose-based separators for enhanced electrolyte uptake, ionic conductivity, and mechanical robustness. Three-dimensional wood structures as rising stars have demonstrated unique advantages, featuring large thickness and enabling high mass loading beyond the limit of their traditional counterparts. Additionally, such structures demonstrate a low tortuosity of close to 1 and rich pathways for ion and electron transport, opening a new direction toward ultrathick and highly loaded electrode and device design.

In conclusion, significant progress has been made in the past few years for nanocellulose-based energy storage, but it is still in the growing stage. In the short term, nanocellulose-based macrofiber and paper devices may be the best choice for low-cost, high-performance flexible electronics applications. Thick electrode design with high mass loading is a promising direction to further improve the energy density on a device level for practical applications. Moreover, pore engineering to promote ion conductivity and maximize the ion storage capacity is desirable for near future applications. In addition, given the relatively high cost of nanocellulose produced by state-of-the-art manufacturing techniques, new manufacturing techniques with both large scalability and low cost are in urgent need for practical application. Last but not least, advanced integration techniques, especially enabled by stable and highly conductive solid-state electrolyte, are desirable for nanocellulose-based integrated, flexible, and high-safety electronics applications.

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ACKNOWLEDGMENTS

L. Hu acknowledges support from Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DESC0001160.

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