

Recent research progress of paper-based supercapacitors based on cellulose

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February 26, 2023

Abstract

With the rapid development of science and technology, paper-based functional materials have become the core of the field of new materials. Recently, they have received extensive attention in the field of energy storage due to their advantages of rich and adjustable porous network structure, good flexibility. As an important energy storage device, paper-based supercapacitors have important application prospects in many fields, and have also received extensive attention from researchers in recent years. At present, researchers have modified and regulated paper-based materials by different means such as structural design and material composition to enhance their electrochemical storage capacity. The development of paper-based supercapacitors provides an important direction for the development of green and sustainable energy. Therefore, it is of great significance to summarize the relevant work of paper-based supercapacitors for their rapid development and application. In this review, the recent research progress of paper-based supercapacitors based on cellulose was summarized in terms of various cellulose-based composites, preparation skills and electrochemical performance. Finally, some opinions on the problems in the development of this field and the future development trend were proposed. It is hoped that this review can provide valuable references and ideas for the rapid development of paper-based energy storage devices.

1. Introduction

With the development of electronic devices and people's yearning for electronic devices in the intelligent era [1-6], flexible electronic devices have shown great application potential in the future portable consumer electronics and wearable devices [7-12]. Traditional flexible electronic equipment uses flexible substrates such as metal [13-15] (copper foil, aluminum foil, etc.) and plastic [16-18] (such as polyethylene terephthalate, polyethylene, polypropylene, etc.). Although these flexible substrates can endow flexible energy storage equipment with excellent mechanical properties, metal and plastic substrates have their own shortcomings. For example, metal and plastic are both hard materials with poor bending performance. Moreover, due to the weak binding force between the substrate and the active material, the active material will fall off during the use of flexible devices, resulting in poor cycle stability, which is not friendly to the life of flexible devices. Therefore, it is very important to develop new flexible materials with excellent flexibility and strong adhesion with active materials.

Cellulose is passed by glucose unit β -1,4 glycosidic bond linked natural polymer [19-21]. Its general molecular formula is $(C_6H_{10}O_5)_n$, which is the most extensive and renewable biomass resource in nature and can be extracted from trees, algae, bacteria and other substances. Its structure can be seen from atomic, molecular and macro scales (Figure1A). Its excellent aspect ratio and porous structure have important application value in the energy storage field of cellulose paper based supercapacitors [22-24]. Cellulose has attracted extensive attention in the field of flexible supercapacitors [25-27]. On the one hand, it is because cellulose

is a kind of material with rich content, excellent mechanical properties, sustainable and cheap. On the other hand, the cellulose based paper supercapacitor electrode has a controllable porous structure and pore size distribution, which is very important for the rapid transfer of electrolyte ions during energy storage. For the flexible supercapacitor, the most important thing is the design and preparation of its electrode material structure. In recent years, cellulose, including nano cellulose, bacterial cellulose, cellulose fiber pulp and cellulose paper, has been used to prepare high-performance cellulose paper based supercapacitor electrode materials [28-32]. In this field, different paper based supercapacitors show different emphasis on performance. Therefore, it is very important to choose an appropriate preparation method to prepare paper based electrodes. In this paper, the preparation methods of cellulose based paper based supercapacitors in recent years are systematically summarized and classified for the first time. As shown in Figure1B, vacuum filtration [33,34], in-situ polymerization [35,36] and printing technology [37, 38] based on the division of multi-component mixing are the main technologies for preparing cellulose paper-based electrodes at present. In addition, commercially mature papermaking process [39,40], carbonization [41,42], impregnation [43,44] and laser induced graphene technology [45,46] are also used to prepare paper based supercapacitors. In conclusion, this review is intended to provide convenient reference materials for researchers in the field of paper-based supercapacitors, so as to promote the rapid development of paper-based energy storage devices.

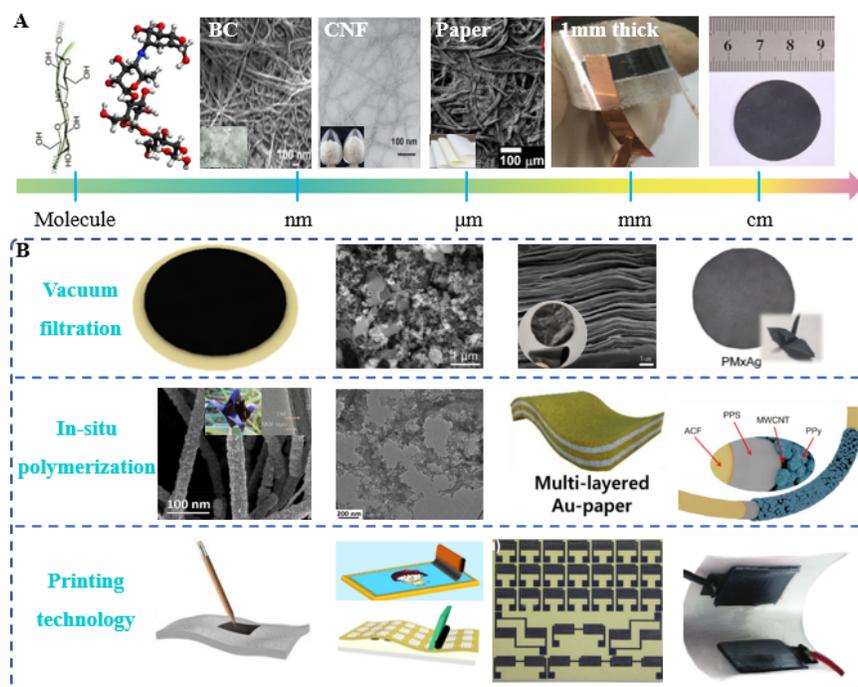


Figure1. (A) Cellulose and its composites at different levels and scales.[22,23,24,25,60] (B) Main preparation methods of cellulose based paper electrodes[59,60,65,81,85,93,98,103,106,109,110,112,118].

2 Various preparation skills

2.1 Vacuum filtration

According to the reported work on cellulose paper based electrode materials for supercapacitors, vacuum filtration is the most widely used and relatively simple method for preparing paper based electrode materials from cellulose [47]. The method is to filter the solvent (mostly water) in the homogenous electrode material slurry by pressure difference, and then form 2D cellulose paper-based electrode material through the interaction between materials. In the vacuum filtration process, the structural design between cellulose and active

materials is the key to determine the energy storage performance of cellulose based paper based supercapacitors. In the work related to this preparation process, most of the work is focused on the structural design of cellulose and carbon materials (activated carbon, graphene, carbon nanotubes and graphene quantum dots, etc.) [48-51], polyaniline [52, 53], MXene [54, 55] and other electrically active substances [56-58]. Then, the electrochemical energy storage performance is enhanced by introducing the third component active substance or electropolymerization.

In the application of traditional electrode materials, carbon based electrode materials are prepared by mixing the binder and conductive carbon black. When used as a device, the specific surface area of the active material involved in the electrochemical reaction will be reduced due to the adhesion of the adhesive on the surface of the active material, which severely limits the energy storage performance of the active material. Cellulose, as a good binder, can provide sufficient specific capacitance and good conductivity after being compounded with active materials. Cellulose provides excellent mechanical properties and porous structure. This makes the cellulose paper based supercapacitor have good mechanical and electrochemical properties.

2.1.1 Cellulose/activated carbon paper based composite electrode

In the field of supercapacitors, typical activated carbon materials with double electric layers have been widely used due to their low cost, extensive sources and mature preparation process. However, when traditional activated carbon based electrode materials are assembled into devices, it is inevitable to combine them with inactive binders (such as polytetrafluoroethylene), conductive substances (such as carbon black) and collectors (such as foam nickel). The preparation process is not only complicated, but also the prepared electrode materials lack a certain flexibility, which limits its application in flexible electronic devices. To solve this problem, Chen et al. [59] prepared porous carbon (PC)/MXene/nano cellulose (CNF) paper based composite electrode materials through simple vacuum filtration. As shown in Figure 2A, the preparation process of CNF/PC/Mxene paper-based material is shown. The paper-based electrode is first prepared by simple mixing and dispersion, and then by vacuum assisted filtration process. As shown in Fig. 2B, the author points out that the densified structure formed by vacuum filtration is the key to the excellent performance of the material. This provides a strong interface interaction between the oxygen-containing groups on the surfaces of CNF, PC and MXene, which makes paper based materials have obvious mechanical advantages. It can be seen from the microscopic image of the composite (Figure 2C) that it is inside the material. MXene provides excellent conductivity (83.1 S cm^{-1}), ensuring fast electron transfer. On the other hand, PC provides excellent double layer capacitors for the composite. And the PCs are evenly distributed between the network structures built by MXene and CNF. This also further avoids the stacking effect between two-dimensional MXene and CNF, which makes the paper based material form an intercalation structure extremely conducive to the rapid movement of electrolyte ions, and shortens the diffusion distance of ions. The test results show that the excellent structure of the paper-based material gives it excellent electrochemical performance, such as the area specific capacitance of 143 mF cm^{-2} (current density 0.1 mA cm^{-2} , thickness 0.2 mm) and $2.4 \mu \text{ Wh cm}^{-2}$ area energy density.

As mentioned above, the adhesive similar to PTFE will coat the surface of some activated carbon, resulting in insufficient activation of electrochemical performance. In the cellulose/activated carbon paper based composite electrode materials prepared by vacuum filtration similar to the above research work, cellulose molecules are only used as the adhesive and structural support of an active substance in the device. In the electrochemical reaction process, it can not provide a transfer path for electron transfer. Therefore, in paper based electrode materials, it is particularly important to build cellulose with excellent electrical conductivity and mechanical properties. Luo et al. [60] constructed BC/AB/AC paper based composite electrode materials by vacuum filtration of bacterial cellulose (BC), acetylene black (AB) and activated carbon (AC). Figure 2D shows the TEM image of the paper-based material. It can be seen that due to the existence of a large number of hydroxyl and carboxyl groups with electronegativity on the molecular face of BC, the electrically neutral AB particles can be adsorbed on its surface during the ultrasonic dispersion process, thus building conductive cellulose on the microstructure. This provides an excellent path for electron transfer in the electrochemical reaction process (Figure 2E), which greatly enhances the energy storage

performance of paper based materials. As shown in Figure 2F, the author also discussed the performance difference between PVDF as the binder and BC as the binder. It can be seen from the figure that compared with PVDF, the paper based electrode material constructed by BC has excellent porous structure and AC has more active sites for electrochemical reaction. The paper based electrode shows excellent energy storage performance (the specific capacitance is 275 F g^{-1} at current density of 1 A g^{-1}). This work provides a simple and efficient method for the construction of paper based electrode materials with excellent mechanical properties by non carbonization method, and provides an idea for the wide application of paper based electrode materials.

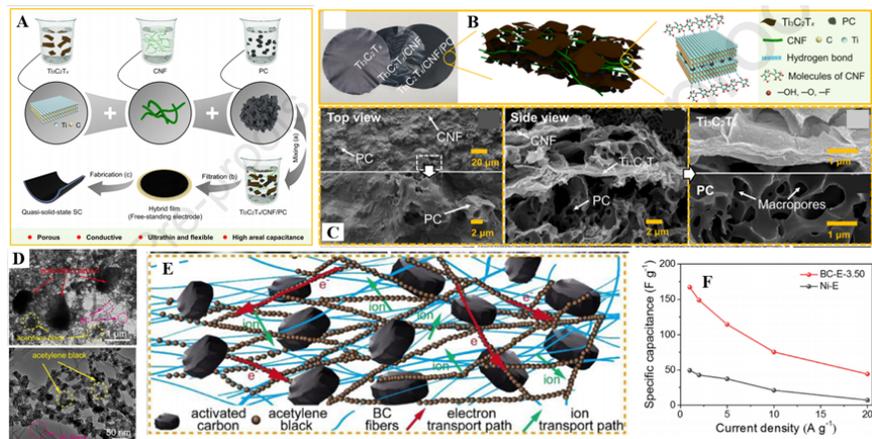


Figure 2. (A) Preparation process of CNF/PC/Mxene paper-based supercapacitor. (B) Structural diagram of CNF/PC/Mxene paper-based electrode. (C) SEM image of CNF/PC/Mxene electrode.[59] (D) TEM image of BC/AB/AC electrode. (E) Schematic diagram of electron and ion migration. (F) Comparison of electrochemical performance of BC based paper-based electrode and PVDF based binder electrode. [60]

2.1.2 Cellulose/graphene paper based composite electrode

Graphene is a two-dimensional carbon material with hexagonal honeycomb lattice structure, which is connected by carbon atoms with sp^2 hybridization[61]. Because of its excellent conductivity, ultra-high theoretical specific surface area, high mechanical strength and good thermal conductivity, it has attracted extensive attention from researchers around the world. At present, graphene has been widely used in many fields such as energy storage, sensing, electromagnetic shielding, wave absorption and environment. However, the van der Waals force and π - π bond force exist between 2D graphene sheets[62]. The electrode plates directly prepared from graphene into supercapacitors will have stacking effect, which will lead to the reduction of electrochemical reaction sites. And it is not conducive to the rapid movement of electrolyte ions, which seriously affects the performance of energy storage devices. Cellulose has a large number of hydrophilic groups, such as hydroxyl and carboxyl groups[63,64], which can interact with graphene to promote the dispersion of graphene in the solute and act as a perfect spacer between 2D graphene sheets. He et al.[65]prepared a self supporting flexible paper based electrode material with excellent mechanical properties and energy storage properties by vacuum filtration of CNF and reduced graphene oxide (RGO). Figure 3A is a schematic diagram of the preparation process of CNF/RGO paper-based electrical materials. The influence of different mass ratios of CNF to RGO on the energy storage performance of paper based electrode materials was discussed. As shown in Figure 3B, when the ratio between CNF and RGO is 1:2, the composite material shows an excellent laminated structure. This shows that at this ratio, the existence of CNF weakens the force between graphene layers to the greatest extent and limits the accumulation of RGO. And as expected, the composite also showed the best performance, with a specific capacitance of 146 mF cm^{-2} , tensile strength of 83 Mpa and excellent conductivity (202.94 S m^{-1}) at a current density of 5 mA cm^{-2} . Since RGO can only provide certain energy storage characteristics of double electric layers, the paper based energy storage materials

prepared in this study have room for improvement. For example, the introduction of the third component with excellent energy storage performance. On the basis of the former research, Qiang et al.[66]prepared CNF/RGO/polypyrrole (PPy) paper electrode materials with sandwich structure by vacuum filtration. Figure 3C shows the preparation process of the composite. First, CNF/RGO paper matrix composite was obtained by vacuum filtration. Then immerse it in $\text{Fe}(\text{ClO}_4)$ solution. Finally, the pyrrole monomer was dispersed on the CNF/RGO surface by spraying and polymerized for 30 min to obtain the CNF/RGO/PPy paper based electrode. Thanks to the porous structure of the CNF/RGO layer and the pseudocapacitance characteristics of PPy, the paper based electrode shows excellent specific capacitance (195.8F g^{-1} , 915mF cm^{-1}), excellent energy density (13.04 Wh kg^{-1}) and power density (200.6 Wkg^{-1}). Figure 3D shows the ion and electron transfer model inside CNF/RGO/PPy electrode. The author points out that thanks to the porous structure of CNF/RGO, the paper based electrode material shortens the diffusion channel of electrolyte ions in the electrochemical reaction. Moreover, the highly conductive polypyrrole layers assembled layer by layer provide sufficient pseudo capacitance. Using CNF/RGO paper-based materials obtained by vacuum filtration as the substrate, the process of introducing pseudocapacitors through in-situ polymerization similar to the above work is relatively cumbersome. The electropolymerization law is a relatively quick method. For example, Xiong et al.[67]used CNF/RGO prepared by vacuum filtration as the substrate to introduce polyaniline into composite paper based materials by means of electropolymerization (Figure 3E). Figure 3F shows the CV curve of the composite. It can be clearly seen that due to the introduction of high pseudo capacitance PANi, the paper based electrode shows greater energy storage characteristics. From the above two works, it can be seen that the cellulose/graphene paper based composite obtained by vacuum filtration can not only be directly used as the electrode material of supercapacitors, but also be used as an effective substrate material to introduce other components to prepare cellulose paper based electrode materials with better performance.

In addition to conducting polymers, metal oxides also exhibit excellent pseudo capacitive properties, which can show high energy density through reversible redox reactions. Therefore, introducing metal oxides into CNF/RGO paper based materials is also a way to improve their electrochemical performance. For example, Zou et al.[68]prepared cellulose/RGO/Ag paper matrix composites with high conductivity through vacuum filtration. Then, a paper based electrode material with high conductivity and double electroactive substances was obtained by depositing Fe_2O_3 on its surface (Figure 3G). The test results show that the symmetrical supercapacitor device assembled with this paper based electrode achieves a large area capacitance (1132mF cm^{-1}) and energy density ($226.4\mu\text{Wh cm}^{-2}$).Moreover, the device does not need additional collectors, and it also shows excellent flexibility. Therefore, the material has broad application prospects in the field of flexible supercapacitor. In a word, the addition of metal oxides has an obvious effect on improving the electrochemical performance of paper based supercapacitors.

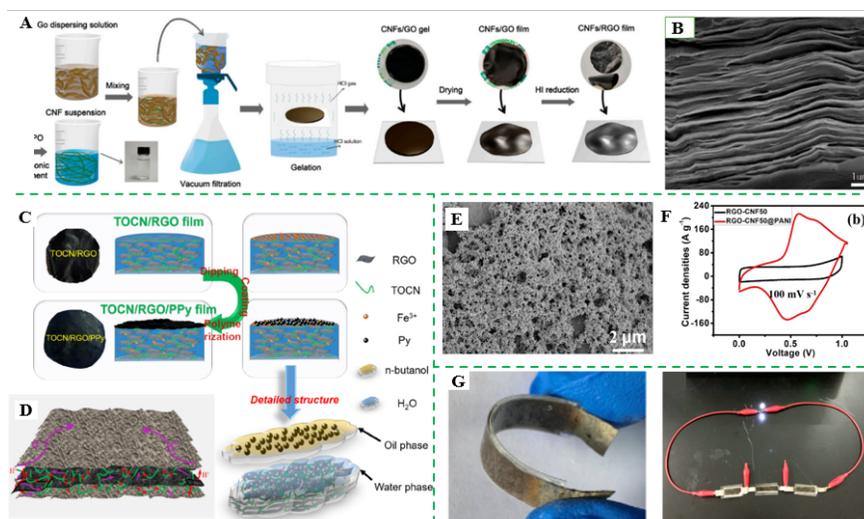


Figure 3. (A) CNF/RGO paper-based electrode preparation process. (B) SEM images of CNF/RGO electrodes. [65] (C) The CNF/RGO/PPy paper based electrode with sandwich structure was prepared. (D) CNF/RGO/PPy electrode diagram. [66] (E) SEM images of CNF/RGO/PANI electrodes. (F) Comparison of electrochemical performance before and after loading PANI. [67] (G) Cellulose/RGO/Ag paper based supercapacitor picture and light bulb. [68]

2.1.3 Cellulose/carbon nanotube paper based composite electrode

Carbon nanotubes (CNTs) have been widely concerned by researchers because their unique 1D structure endows them with excellent mechanical strength, electronic conduction efficiency, heat transfer efficiency and stable chemical properties [69]. And CNT has a large aspect ratio and easy surface modification [70], which has great advantages for its application in supercapacitors. Among them, the large aspect ratio makes it possible to form a good conductive network without using adhesives. However, CNT and graphene have the same defect, that is, due to the strong interaction between CNTs, it is a fatal defect for electrode materials [71]. Therefore, it is particularly important to find a material that can disperse CNT evenly. It is a best of both worlds method to prepare paper based composite materials by mixing with cellulose materials. For example, Fang et al. [72] prepared BC/CNT paper-based electrode materials by vacuum filtration. Figure 4A shows the preparation process of the paper-based material. It is worth mentioning that the author used juglone to chemically modify the surface of CNT, because it is difficult for unmodified CNT to show high energy density. Some studies have shown that the organic quinones rich in redox carbonyls have high theoretical capacity, so the chemically modified CNT surface has a large number of juglone molecules. The test results showed that the conductivity of the paper matrix composite prepared by juglone modified CNT was 1674 S m^{-1} (the conductivity of the unmodified composite was 1111 S m^{-1}). At the same time, the influence of the content of juglone molecules on the conductivity of paper matrix composites was also discussed. As shown in Figure 4B, when the content of juglone molecules is low, electrons can only have discrete jumps between the molecules. When the content is high, due to the crowding between molecules, electrons jump randomly in disorder during conduction. Therefore, when juglone molecules are uniformly distributed on the surface of CNT, the conductivity and energy storage performance of the composite are greatly improved thanks to the coordination between the uniformly arranged quinone molecules and CNT. The electrochemical test results of the paper based electrode showed that the modified BC/CNT paper based electrode showed a specific capacitance of 461.8 F g^{-1} at 0.5 A g^{-1} (this value was five times that of the non chemically modified electrode). The paper based electrode materials prepared in this work have better performance than most reported CNT and paper based electrode materials prepared by vacuum filtration. In conclusion, this work provides an excellent strategy for preparing high-performance paper based electrode materials by vacuum

filtration.

As shown in Figure 4C, Jyothibasud et al. [73] first treated the CNT surface with nitric acid to obtain CNT (f-CNT) loaded with a large number of hydroxyl groups. The prepared cellulose is then uniformly dispersed with the cellulose and then subjected to vacuum filtration. Finally, the cellulose/f-CNT paper based film was obtained after drying. In order to enhance its electrochemical performance, the author soaked the paper based film in the mixed solution of potassium permanganate and sulfuric acid to load manganese dioxide. The test results showed that after 120 min of loading reaction, the solid paper based device assembled by cellulose/CNT/MnO₂ paper based electrode showed an excellent specific capacitance of 1812mF cm⁻². This work shows that the cellulose/CNT paper based material obtained by vacuum filtration is also a good conductive substrate, and its electrochemical performance can be improved by introducing the third component. This provides a perfect solution for customizing high-performance flexible paper based supercapacitors.

2.1.4 Cellulose/graphene quantum dot paper based composite electrode

Graphene quantum dots refer to a quasi zero dimensional material with graphene sheet size less than 100 nm and sheet size less than 10[74]. Since its discovery in 2008[75], GQD has attracted extensive attention due to its excellent optical and electrical properties. And it has been applied to energy storage, sensing, catalysis, environment and other fields. Among them, GQD has ultra-fine size and ultra-high specific surface area because its dimensions in the three dimensions are at the nanometer level[76]. These superior properties make it a new rising star of electrode materials for supercapacitors. The composite of GQD and cellulose can overcome the shortcomings of limited specific surface area, poor conductivity and low utilization rate of cellulose. For example, Xiong et al.[77]obtained CNF/GQD paper-based composites by vacuum filtration for the first time. First, GQD was prepared by electrolysis and dialysis purification with a stone mill (Figure 4D). Then, CNF/GQD paper-based electrode is obtained by mixing GQD and CNF uniformly and vacuum filtering (Figure 4E). Figure 4F shows SEM and TEM images of CNF/GQD. It can be seen from the figure that GQD is evenly distributed on the CNF surface. Moreover, CNF crosslinked with each other to form a porous structure. This provides a fast transport path for electrolyte ions in the electrochemical energy storage process. The test results show that the paper based material can maintain an area capacitance of 118mF cm⁻² even at a high scanning rate of 1000mV s⁻¹, indicating that it has excellent magnification performance. This is mainly due to the excellent energy storage characteristics of GQD itself and the porous structure of CNF providing sufficient load sites for GQD.

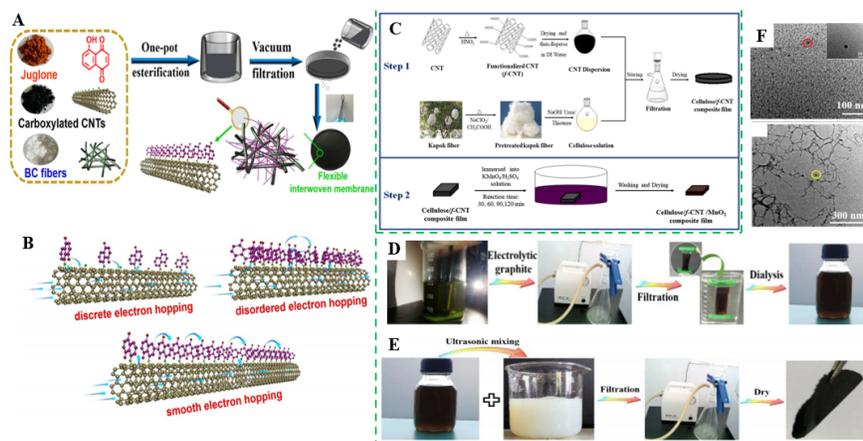


Figure4. (A)Preparation process of BC/CNT paper-based electrode modified by juglone. (B)The mechanism of electrical transfer of juglone auxiliary electrons on CNT. [72] (C)Flow chart of cellulose/f-CNT paper-based electrode and loaded MnO₂. [73] (D)GQD preparation process. (E)CNF/GQD paper based electrode preparation process. (F)TEM image of CNF/GQD. [77]

2.1.5 Cellulose/MXene paper based composite electrode

As a 2D material with high specific surface area and high conductivity, MXene has shown great prospects in the field of supercapacitor energy storage[78]. In recent years, the composite paper based electrode materials prepared by vacuum filtration of cellulose and Mxene have been fully studied. This section summarizes cellulose/MXene paper based electrode materials. When 2DMxene chips are used as supercapacitors and electrode materials of supercapacitors, stacking between layers is easy to occur. In order to solve this problem, scientists also tried to use 1D carbon nanotubes and other carbon materials as spacers to prevent their stacking. However, the preparation process of these carbon materials is complex and costly. Cellulose, as a green and sustainable renewable resource, is the first choice as a 2D active material spacer. For example, Jiao et al. [79] first prepared BC/MXene composite paper with excellent new mechanical properties and electrochemical properties through vacuum pumping power. In addition, stretchable and patterned paper based electrode materials are prepared by laser cutting process to adapt to various use environments (Figure5A). Thanks to the close stacking structure between BC fiber and Mxene lamellae (Figure5B). The prepared paper based electrode was assembled into an all solid state paper based supercapacitor, showing an area capacitance of 115mF cm^{-2} and flexible mechanical properties. This work provides a promising method for designing and manufacturing flexible electronic equipment used in different environments through the patterned scheme of laser cutting. Similarly, Tian et al. [80] prepared CNF/Mexene paper-based electrodes by vacuum filtration, which also showed excellent electrochemical performance (298F g^{-1}). The above two works show that the cellulose/MXene paper-based electrode prepared by simple vacuum filtration process has a very broad application prospect.

Although the paper based electrode obtained by direct filtration of cellulose and Mxene has good performance, it can not meet people's needs under certain conditions. Therefore, it is very necessary to improve the energy storage performance of paper-based materials through certain methods. For example, the introduction of the third component or the surface modification of MXene can improve its energy storage performance. In order to improve the electron transfer rate of MXene in paper based materials, as shown in Figure 5C, it is inspired by the structure of plant leaves. Tang et al. [81] prepared a paper based composite material with leaf like structure by vacuum filtration of cellulose, Mxene and silver nanowires (AgNWs). As shown in Figure5D, the structure diagram of natural leaf veins and prepared cellulose/Mxene/AgNWs paper based electrode (PMxAg) is similar to leaf veins. Among them, cellulose as the main pulse provides excellent mechanical properties for paper based materials and provides a transport channel for electrolyte ions. Secondly, AgNWs as the secondary pulse provides a fast channel for electron transfer. Finally, as the "mesophyll", Mxene provides sufficient energy storage capacity for composite materials. Thanks to the "blade like structure", the paper based electrode shows a specific capacitance of up to 505F g^{-1} . In addition, the author also successfully prepared large area composite paper by using paper machine. The batch preparation of this flexible supercapacitor provides a solution. In addition, surface treatment of MXene is also an effective method to improve the electrochemical performance. Previous research shows that the energy storage performance of MXene mainly comes from the=O group, while the -F and -OH groups in it have no contribution to the energy storage performance, and even more content will affect the energy storage performance. For this method, Chen et al. [82] modified the surface of MXene by KOH and high temperature treatment to reduce the -F and -OH groups on its surface. Subsequently, NFC/Mxene paper based composite electrode was prepared by combining nano fibrillar cellulose (NFC) prepared from soybean straw with modified Mxene through vacuum filtration process. The preparation process is shown in Figure 5E. The test results show that the paper electrode based supercapacitor has a specific capacitance of 303.1F g^{-1} at 1mA cm^{-2} and a capacitance retention of 92.84% after 10000 cycles. As shown in Figure 5F, Cai et al. [83] prepared SnS₂ on the surface of MXene by hydrothermal method Mxene@SnS₂ Nanosheets, then CNF was prepared by vacuum filtration/ Mxene@SnS₂ Paper based composite materials. To illustrate Mxene@SnS₂ The contribution of nano sheets to the electrochemical performance of composite materials is shown in Figure5G. The author compares CNF/MXene, CNF/MXene/SnS₂and CNF/ Mxene@SnS₂ Energy storage performance among the three. CNF/ Mxene@SnS₂ The specific capacitance of 171.6F g^{-1} is significantly higher than that of CNF/Mxene (163.3F g^{-1}) and CNF/Mxene/SnS₂ (130F g^{-1}). At the same time,

because of the light heat conversion function of SnS_2 , the assembled supercapacitor has the function of solar energy driving. As shown in Figure 5H, the discharge time of the paper-based supercapacitor increases with the increase of light intensity (under the light intensity of 1 kW m^{-2} , the energy storage performance of the device is improved by 60%).

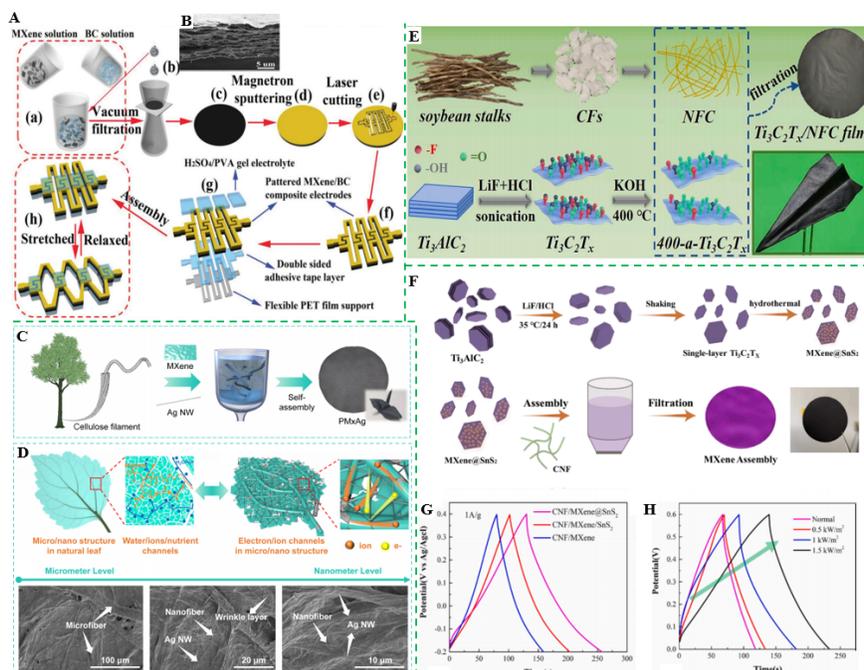


Figure 5 (A) BC-Mxene composite paper and laser cutting patterning scheme. (B) SEM image of BC/MXene composite paper section. [79] (C) PmxAg preparation process. (D) The design diagram of the micro network structure in the blade and the paper material with similar structure ion channels.[81] (E) NFC/MXene paper based electrode preparation process.[82] (F) CNF/ Mxene@SnS₂ Paper based electrode preparation process. (G) CNF/MXene, CNF/MXene/SnS₂ and CNF/ MXene@SnS₂ GCD curve at current density of 1 A g^{-1} . (H) CNF at different solar intensities/ MXene@SnS₂ GCD curve of paper-based devices. [83]

2.1.6 Cellulose/PANi paper based composite electrode

Polyaniline is a kind of conductive polymer material with excellent pseudo capacitance energy storage performance. However, when it is used as electrode material of supercapacitor, serious volume shrinkage and expansion will occur, resulting in obvious brittleness of pure polyaniline electrode material. As a 1D material with excellent mechanical properties, cellulose and polyaniline can compensate for the brittleness of polyaniline, and polyaniline provides excellent conductivity and energy storage properties. Sun et al. [84] first introduced RGO into polyaniline polymerization to obtain PANi/RGO composites. Then the cellulose/PANi/RGO paper based composite electrode material was prepared by vacuum filtration of cellulose and the composite material. Among them, the energy storage performance of the paper-based electrode was significantly improved due to the addition of RGO (the specific capacitance was 79.71 F g^{-1}). Although the specific capacitance value of the electrode is not as good as that of the paper-based electrical base. However, as an excellent pseudo capacitive electrode material, conducting polymers should be tried to construct structures conducive to improving electrochemical performance through vacuum filtration in future research. Cellulose and other conductive polymer materials are used to prepare cellulose/conductive polymer paper based electrode with more excellent performance through vacuum filtration.

Based on the above discussion on the preparation of paper based electrode materials by vacuum filtration.

Due to the simple preparation, strong controllability and similar to papermaking process, scientists have also prepared a variety of paper-based electrical materials through this process. Table 1 compares the main parameters of paper based electrodes prepared by vacuum filtration. It is obvious from the classification in the table that the process is still mainly focused on the composite between cellulose and carbon materials and MXene, and there is still a lack of research on the relationship between cellulose and conductive polymers and metal oxides. For example, cellulose and nanowire metal oxides (such as MnO_2) can also be used to prepare paper based electrode materials with excellent performance. Therefore, in future research on preparation of the paper based supercapacitor electrode materials by vacuum filtration. We can actively broaden our vision and combine more electrochemical active substances with cellulose through this simple preparation process to prepare cellulose paper based electrode materials with excellent performance. At the same time, in the era of rapid development of flexible electronics, we should also pay attention to the use of this process to achieve mass production. Among them, mature papermaking process should be the first choice. For example, Tang et al. [81] realized the batch production through the laboratory vacuum filtration results through the manufacturing process, which provides a mature guidance scheme for the production of cellulose paper based supercapacitors. In the 2.4.1 section, we will summarize the application of papermaking technology in cellulose paper based supercapacitors in detail.

Table1 Performance Parameters of Cellulose Paper Based Electrode Blended with Multi component Based on Vacuum Filtration

Electrode	Electrolyte	Capacity	Energy density at power density	Cycles	Reference
CNF/PC/Mxene	KOH/PVA	143mF cm^{-2} at 0.1mA cm^{-2}	2.4 $\mu\text{Wh cm}^{-2}$ at 17.5 $\mu\text{W cm}^{-2}$	90%, 10000	59
BC/AB/AC	6.0M KOH	276F g^{-1} at 1A g^{-1}	5.3W h kg^{-1} at 163W kg^{-1}	100%, 10000	60
CNF/RGO	0.1M H_2SO_4	146mF cm^{-2} at 5mA cm^{-2}	-	83.7%, 2000	65
CNF/RGO/PPy	1M H_2SO_4	195.8 F g^{-1} at 0.1mA cm^{-2}	13.04Wh kg^{-1} at 200.6W kg^{-1}	96.6%, 2000	66
CNF/RGO/PANi	H_3PO_4 /PVA	-	-	-	67
cellulose/RGO/silver/ Fe_2O_3	LiCl/PVA	1132mF cm^{-1} at 2 mA cm^{-2}	226.4 $\mu\text{Wh cm}^{-2}$ at 1.2mW cm^{-2}	100%, 10000	68
BC/CNT	1M H_2SO_4	461.8F g^{-1} at 0.5 A g^{-1}	41.9 Wh kg^{-1} at 1.0 kW kg^{-1}	82.4%, 10000	72
cellulose/f-CNT/ MnO_2	1M Na_2SO_4	1812 mF cm^{-2} at 1 mA cm^{-2}	251.6 μWhcm^{-2} at 0.51mW cm^{-2}	79%, 10000	73
CNF/GQD	1.5M Li_2SO_4	118mF cm^{-2} at 1000mV s^{-1}	596 $\mu\text{Wh cm}^{-2}$ and 782mW cm^{-2}	90%, 5000	77
BC/Mxene	H_2SO_4 /PVA	115mF cm^{-2} at 1 mA cm^{-2}	0.00419mWh cm^{-2}	-	79
CNF/Mxene	3M H_2SO_4	298F g^{-1} at 5mV s^{-1}	0.08 μ Wh cm^{-2} at 145 $\mu\text{W cm}^{-2}$	100%, 10000	80
cellulose/Mxene/AgNWs	1M H_2SO_4	505F g^{-1} at 5A g^{-1}	-	90.9%, 500	81
NFC/Mxene	1M H_2SO_4	303.1F g^{-1} at 1mA cm^{-2}	-	92.84, 10000	82

Electrode	Electrolyte	Capacity	Energy density at power density	Cycles	Reference
CNF/Mxene@SnS ₂	1M H ₂ SO ₄	171.6F g ⁻¹ at 10mV s ⁻¹	6.7μWh cm ⁻² at 1206μW cm ⁻²	91.5%, 40000	83
cellulose/PANi/RGOM	H ₂ SO ₄	79.71F g ⁻¹ at 0.1 A g ⁻¹	4.03Wh kg ⁻¹ at 10.40W kg ⁻¹	84.8%, 1000	84

2.2 In-situ polymerization

Cellulose, as a natural 1D flexible material with high specific surface area, is only used as a binder of electrochemical active substances, which does not make full use of its surface space. Electroactive substances such as metals, metal oxides and conductive polymers are polymerized and deposited on the cellulose surface through in-situ polymerization. Compared with the paper-based electrode where cellulose is only used as the binder, this can effectively reduce the volume of electrode material and increase the utilization rate of cellulose. In the cellulose paper based electrode prepared by this method, cellulose not only provides mechanical properties, but also provides an electron transfer path for the cellulose composite fiber deposited with active substances, which can make outstanding contributions to electrochemical energy storage.

At present, the work of depositing active materials on cellulose surface can be roughly divided into two types. The first is by mixing the cellulose dispersion with the precursor of the active substance. Then the active substance is polymerized and deposited on the surface of the cellulose fiber to form 1D cellulose composite fiber. Finally, these 1D composite fibers were filtered through vacuum to obtain paper based electrodes. It should be clearly pointed out here that cellulose in the paper-based electrode summarized in the vacuum filtration section of this paper is only used as the binder. However, the paper based electrode obtained by in-situ polymerization of active substances polymerized and deposited on the cellulose surface, and then filtered by vacuum suction, is significantly different from the previous section. Therefore, it is necessary to classify 1D cellulose composite fibers into a single category. The second type is to directly put the prepared 2D cellulose paper into the precursor solution of the active substance, and directly polymerize and deposit the active substance on the 2D cellulose paper. This section summarizes and classifies the different loading modes of active substances in the preparation process, including the paper based electrode based on 1D cellulose composite fiber and the paper based composite electrode based on 2D cellulose paper. Table 2 summarizes the performance parameters of related work.

Table2 Performance parameters of cellulose paper based electrode prepared by in-situ polymerization

Electrode	Electrolyte	Capacity
CNF@c-MOF	3M KCl	125F g ⁻¹ at 0.33A g ⁻¹
CuS-NCs/QCD /CNF	6M KOH	314.3F g ⁻¹ at 1A g ⁻¹
1D-CNF@ZnO	KOH/PVA	220F g ⁻¹ at 1A g ⁻¹
PPy@BC/Mxene	3M H ₂ SO ₄	879mF cm ⁻² at 5mV s ⁻¹
PPy@cobalt oxyhydroxide/cellulose	0.6M H ₂ SO ₄	571.3F g ⁻¹ at 0.2A g ⁻¹
PEDOT-ARS paper	ARS/H ₂ SO ₄	2191.3mF cm ⁻² at 5 mA
PPy:PSS/CNP	1M H ₂ SO ₄	3.8F cm ⁻² at 10mV s ⁻¹
PANI: PSS/CNP	1M H ₂ SO ₄	2.56F cm ⁻² at 2m A cm ⁻²
PEDOT:PSS/CNP	1M H ₂ SO ₄	854.4mF cm ⁻² at 5mV s ⁻¹
CP/Ni/Au	1M Na ₂ SO ₄	49.1F g ⁻¹ at1A g ⁻¹
Ni-paper-MnO ₂	1M Na ₂ SO ₄	1095mF cm ⁻² at 1mA c
MnO ₂ -Au-Paper	1M Na ₂ SO ₄	560.2mF cm ⁻² at 0.2mA
MnO ₂ -Au-Paper(Vertically Layered Multi-Pair Interdigital Electrodes)	1M Na ₂ SO ₄	0.974F cm ⁻² at 0.1mA c

Electrode	Electrolyte	Capacity
MnO ₂ -Au-Paper(Vertically integrated multi electrodes in a single sheet of paper)	Na ₂ SO ₄ /PVA	315.96F g ⁻¹ at 5mV s ⁻¹
PEDOT/CP	H ₂ SO ₄ /PVA	13.7F cm ⁻³ at 10mV s ⁻¹
PC-KHP	H ₂ SO ₄ /PVA	6576mF cm ⁻³ at 25 mV
PPy/Cellulose Paper	H ₂ SO ₄ /PVA	90.1mF cm ⁻² at 0.25mA
Paper/PPy/rGO	1M HCl	1685mF cm ⁻² at 2mA
ACF/PPS/MWCNT-PPy	3M HCl	3205mF cm ⁻² at 5mA

2.2.1 Paper based electrode based on 1D cellulose composite fiber

2.2.1.1 Cellulose/metal paper based composite electrode

Metals and their compounds are considered as promising electrode materials for supercapacitors because of their excellent point and storage application prospects. Due to the large number of modifiable hydroxyl groups in cellulose molecules, it provides a good platform for the construction of polymerization and deposition of metals and their metal compounds. Recent studies have shown that metals and their compounds can be well combined with cellulose fibers or polymerized and deposited on their surfaces to form 1D cellulose composite fibers with excellent energy storage properties. Finally, paper based composite electrode materials can be obtained by vacuum filtration. Zhou et al. [85] used CNF as a substrate and deposited a conductive metal-organic framework(c-MOF) with excellent electrical conductivity through interfacial polymerization on its surface, and obtained CNF@c-MOF nanofibers. Figure 6A shows the preparation process of CNF@c-MOF, first introducing carboxyl groups to the surface of CNF through TEMPO oxidation, then exchanging carboxylated CNF with Ni²⁺ ions, and finally adding organic ligands to obtain CNF@c-MOF nanofibers. CNF@c-MOF paper-based electrodes are obtained by vacuum filtration. In addition, the authors discuss the differences in the electrochemical performance of CNF@c-MOF paper-based electrodes prepared by two different organic ligands, HITP (2,3,6,7,10,11-hexamino-triphenylene) and HHTP (2,3,6,7,10,11-hexahydroxytriphenylene). Figure 6B shows a comparison of the weight ratio capacitance of two different CNF@c-MOF paper-based electrodes. It is evident that the CNF@Ni-HITP electrode prepared by HITP has a weight capacitance of 125F g⁻¹. This is mainly due to the continuous Ni-HITP nanolayers tightly wrapped around the CNFs (Figure 6C). The authors note that the continuous nucleation of c-MOF nanometers on CNF and the hierarchical porous high conductivity structure provide a fast pathway for electrolyte transport and charge transfer for CNF@c-MOF paper-based electrodes (Figure 6D). It is worth mentioning that the authors also discuss the performance of CNF@c-MOF paper-based electrodes of different thicknesses, and the results show that the increase in thickness has almost no effect on the electrochemical performance of the paper-based electrode. This opens up the possibility of customizing paper-based electrodes of different thicknesses.

Huang et al.[86]used quaternized chitosan (QCS) as the connection stabilizer between CNF and copper sulfate nanocrystals (CuS-NCs). Figure 6E shows the contribution of QCS to CuS NCs deposition on CNF fiber surface. In the absence of QCS, the deposition of CuS is mainly through the electrostatic adsorption between the electronegative CNF and [Cu(NH₃)₄]²⁺in the precursor solution of CuS-NCs. At the same time, S²⁻will lead to rapid prototyping of CuS NCs, which will lead to uneven distribution of CuS NCs on the CNF surface (Fig. 6F). When S²⁻ and QCS are added to the CNF/[Cu (NH₃)₄]²⁺precursor solution, CuS NCs are well anchored on the CNF surface (Fig. 6G) due to the electrostatic attraction formed between the positively charged QCS and CNF. In order to more intuitively check the contribution of QCS to the stable deposition of CuS NCs on the CNF surface, as shown in Figure 6H, CuS-NCs/CNF and CuS-NCs/QCD/CNF were respectively immersed in KOH electrolyte for 48h. It can be clearly observed from the figure that the paper-based electronic base shows excellent stability due to the addition of QCD. However, CuS NCs in the paper-based electrode without QCD fell off obviously. The test results showed that CuS-NCs/QCD/CNF paper based electrode exhibited 314.3F g⁻¹ high specific capacitance and high cycle stability (the capacitance retention rate was 88.8% after 5000 cycles). Rabani et al. [87] used the sol-gel method to deposit zinc oxide (ZnO) in 1D-CNF to obtain 1D-CNF@ZnO nanometer composite fibers, and

then further assembled the 1D-CNF@ZnO into an all-solid-state flexible paper-based supercapacitor. As shown in Figure 6I, ZnO nanoparticles perfectly cover the 1D-CNF surface at suitable concentrations of ZnO precursors, which is essential for their application to energy storage electrodes. In order to better illustrate the excellent electrochemical performance of this paper-based electrode. As shown in Figure 6J, the authors compared 1D-CNF, ZnO, and 1D-CNF@ZnO paper-based electrodes. It is clear from the figure that the 1D-CNF@ZnO electrode has a larger CV area and energy storage characteristics for discharge time.

Based on the above summary of the work related to metal compounds deposited on 1D cellulose, we can see that the current work is mainly focused on non-metallic oxide pseudocapacitor materials. This may be due to the non conductivity of metal oxides. As an excellent pseudo capacitor material, metal oxides can be used to prepare cellulose/metal oxide composite fibers through the above process in future research. Then, the paper based electrode material with excellent performance is prepared by compounding with the electroactive material with excellent conductivity.

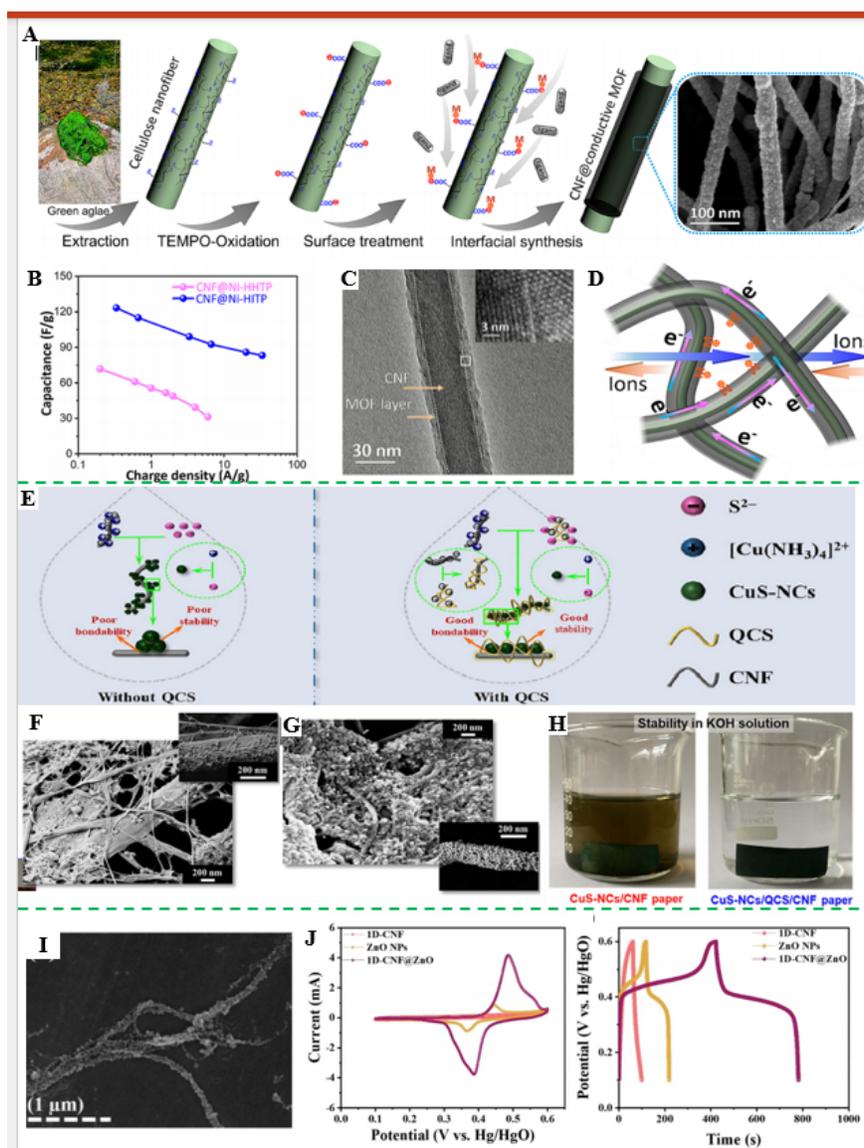


Figure 6. (A) Preparation process of CNF@c-MOF nanocomposite fibers. (B) Weight capacitance of CNF@c-MOF electrode. (C) TEM image of CNF@Ni-HITP nanocomposite fibers. (D) Schematic diagram of charge transfer and electrolyte ion transport in a CNF@c-MOF paper-based electrode.[85] (E) Schematic diagram of CuS-NCs precipitating QCS as stabilizers and binders in situ on CNF. (F) SEM image of CuS-NCs/CNF. (G) SEM image of CuS-NCs/QCD/CNF. (H) CuS-NCs/QCD/CNF paper-based electrode stability test.[86] (I) SEM image of 1D-CNF@ZnO nanocomposite fibers. (J) Electrochemical performance of CNF@ZnO electrodes. [87]

2.2.1.2 Cellulose/conductive polymer paper based composite electrode

1D composite fiber prepared by composite of conductive polymer and 1D cellulose has been reported so far. Electrodes depositing polyaniline (PANi), polypyrrole (PPy) and poly (3,4-ethylenedioxythiophene) (PEDOT) on the surface of 1D cellulose by in-situ polymerization have been prepared. However, due to the low solubility and unstable structure of conductive polymers in solvents, the energy storage performance of electrodes directly compounded with cellulose is not excellent. At present, scientists prepare paper based electrodes with excellent electrochemical performance by adding surfactants or blending 1D cellulose composite fibers based on conductive polymers with other pseudo capacitive materials. As shown in Figure 7A, Song et al. [88] used the in-situ polymerization method to uniformly deposit PPy on the surface of BC fiber to obtain 1DPPy@BC composite fiber, and then prepared PPy@BC/Mxene composite paper-based electrode by vacuum filtration of the dispersion of PPy@BC and Mxene. Firstly, 1DBC fibers as effective templates provide abundant space for the deposition of Ppy. Secondly, the hierarchical porous structure formed by the assembly of PPy@BC fibers and Mxene provides sufficient sites for electrochemical reactions. This is very important for the electrochemical performance of this paper-based electrode. Thanks to the above two points, the PPy@BC/Mxene composite paper-based electrode exhibits a mass ratio capacitance of 550F g^{-1} and an area ratio capacitance of 879mF cm^{-2} . The work is to prepare high-performance paper-based electrodes by blending 1D composite fibers with Mxene. Although satisfactory electrochemical performance can be obtained by this method, the thickness of the electrode will always be increased by blending the two components, which is detrimental to flexible microelectronic devices. It is a feasible method to introduce the second component directly into the 1D composite fiber by in-situ polymerization. Yang et al. [89] prepared 1DPPy@ cobalt hydroxyoxide/cellulose composite fiber (1DPCC fiber) by liquid phase reduction. Figure 7B shows the preparation process of this paper-based electrode. First, cobalt hydroxyoxide is reduced to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by NaBH_4 and cobalt hydroxyoxide is loaded on the surface of 1D cellulose in situ. 1DPCC fibers are then obtained by in situ oxidative polymerization of PPy. Finally, PCC paper-based composite electrode was obtained by vacuum filtration. Electrochemical test results show that PCC paper-based electrodes have a specific capacitance of up to 571.3F g^{-1} and a capacitance retention rate of more than 93% (1000 cycles). In this work, 1D cellulose composite fibers with excellent performance were prepared by two-step in-situ polymerization. The paper-based electrode also exhibited excellent energy storage characteristics, which provided a simple and fast method for preparing paper-based composite flexible energy storage electrode.

Recent studies have found that the use of redox small molecules to treat paper-based composite electrodes can also improve electrochemical energy storage performance. Small organic molecules with specific intramolecular conjugated structures, such as quinones, can be a substance that enhances the electrochemical performance of composite materials with an ideal valence. As shown in Figure 7C, Chang et al. [90] effectively improved the energy storage performance of PEDOT paper-based electrode by sodium alizarin sulfonate (sodium 1,2-dihydroxyanthraquinone-3-sulfonate) (ARS). ARS/ H_2SO_4 composite electrolyte was prepared. The results show that the supercapacitor device assembled by ARS-treated electrode and electrolyte shows excellent electrochemical performance (area ratio capacitance 2191.3mF cm^{-2} , energy density 4.87mWh cm^{-3}). This is a significant improvement over the 348mF cm^{-2} area ratio capacitance of a paper-based electrode without ARS treatment. Figure 7D shows the energy storage mechanism in the charging and discharging process of the device. Among them, the addition of ARS promotes the regeneration of PEDOT and reuses in redox reaction, which plays an important role in improving the electrochemical performance of the device. The water-soluble sulfonated polymer surfactant polystyrene sulfonate (PSS) has attracted extensive attention from researchers due to its excellent mechanical flexibility and adjustable conductivity. In this paper,

three recent works on the improvement of conductive polymer 1D cellulose composite fibers using PSS are summarized. As shown in Figure 7E, Zhang et al. [91] added PSS to a mixed solution of pyrrole monomer and CNF, and improved the loading of polypyrrole on the surface of CNF through PSS. The results show that the paper-based electrode PPy:PSS/CNF with PSS exhibits a specific capacitance of 240F g^{-1} . Similarly, Zhang et al. [92,93] also used PSS to improve the loading of PANi as well as PEDOT on the CNF surface. Figure 7F and 7G are schematic diagrams of the preparation process of PANi:PSS/CNF and PEDOT:PSS/CNF paper-based electrodes. It is worth mentioning that the addition of PSS in these three works effectively improves the cellulose loading of conductive polymers and promotes the construction of high-performance paper-based electrodes. It provides a good idea for the preparation of conductive polymer-based paper-based composite electrodes.

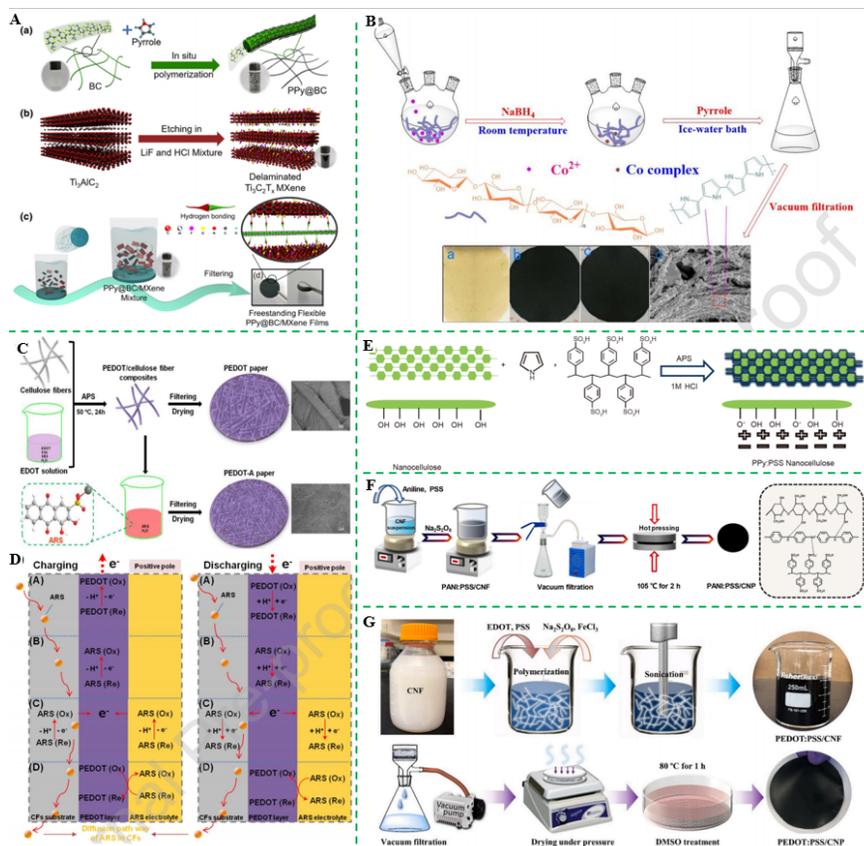


Figure 7. (A) PPy@BC/Mxene paper-based electrode preparation process. [88] (B) Preparation process of PPy@cobalt hydroxyoxide/cellulose composite flexible electrode materials. [89] (C) Preparation process of ARS modified PEDOT paper-based electrode. (D) Schematic diagram of the electrochemical energy storage mechanism of ARS modified PEDOT paper-based electrode in a three-electrode system. [90] (E) PPy:PSS/CNF paper-based electrode preparation process. [91] (F) PANi:PSS/CNF paper-based electrode preparation process. [92] (G) PEDOT:PSS/CNF paper-based electrode preparation process. [93]

2.2.2 Paper-based composite electrode based on 2D cellulose paper

2.2.2.1 Cellulose/metal paper-based composite electrodes

Due to its excellent porous structure, low cost, easy degradation and renewable, 2D cellulose paper is considered to be an ideal flexible substrate in the field of flexible supercapacitors. Zhang et al. [94] prepared cellulose paper (CP)/Ni/Au paper-based electrodes by loading nickel/gold bimetal on vitamin paper. Figure

8A shows the preparation process of this paper-based electrode. Thanks to the hydrophilic group and porous structure of CP, CP immersion in nickel salt solution can adsorb a large number of nickel ions. The metal Ni is then loaded in CP by NaBH₄ reduction. Then, CP loaded with nickel metal is entered into the electroless plating solution of Au to obtain CP/Ni/Au paper-based current collector. Finally, the carbon-based active material is deposited on its surface by electrophoretic deposition to obtain a paper-based supercapacitor electrode. The results show that thanks to the flexibility of cellulose paper, the CP/Ni/Au paper-based electrode still maintains 92.1% of the initial capacitance after 2000 bending cycles, showing excellent mechanical properties. Li et al. [95] also prepared Ni-paper by loading the filter paper with Ni metal, and then soaked it in KMnO₄/HCl solution to obtain a Ni-paper-MnO₂ paper-based electrode (Figure 8B). In order to show the excellent mechanical properties of Ni-paper as an electrode material. After 5000 consecutive bending of the Ni-paper, the resistance of the film only increased from the initial 0.8 Ω cm⁻² to 2.7 Ω cm⁻². When MnO₂ is used as the active material, this paper-based electrode exhibits an area specific capacitance of 1095mF cm⁻² at a current density of 1mA cm⁻². This is mainly due to the hierarchical porous fiber structure in the Ni-paper-MnO₂ electrode and the high conductivity of Ni, which greatly contribute to the electrochemical performance of the electrode.

General flexible energy storage devices must assemble independent electrodes, current collectors, and diaphragms. This is not only complex but also increases the size of the device. Combining all units of the device in a single substrate to build an all-in-one flexible energy storage device is a promising approach. Recently, Chang et al. [96-98] from Chung-Ang University in South Korea cleverly designed a series of integrated paper-based supercapacitors with excellent performance using paraffin heating-assisted in situ polymerization of Au. As shown in Figure 8C, the team first designed a single-layer integrated porous paper-based supercapacitor. The preparation of the device is divided into three steps, the first step is to fill the inside of cellulose paper by printing solid paraffin wax on the surface of the paper (Figure 8D(i)), then heating it to a molten state and filling it inside the cellulose paper (Figure 8D(ii)). In the second step, AgNPs are deposited on the upper and lower surfaces of the cellulose paper by drop-casting process (Figure 8D(iii)). The paraffin is then removed by methanol (Figure 8D(iv)). In the third step, the paper loaded with AgNPs gold source is soaked in Ag growth solution (HauCl₄ and hydroxylamine hydrochloride mixed solution) to obtain the Au-Paper electrode (Figure 8D(vi)). Finally, MnO₂-Au-Paper paper-based integrated electrode is obtained by electrodeposition by loading MnO₂ on the surface of Au-Paper (Figure 8E). Devices assembled by combining a paper-based electric base with a gel electrolyte exhibit a specific capacitance of 252.2F g⁻¹. To achieve a high potential window of the device, the team used the technique to fabricate five supercapacitors connected in series on a sheet of paper. The devices connected in series can exhibit a high voltage window of 4.0V, easily lighting the blue LED operating at 2.65V. As shown in Figure 8F, this technique is used to print the pattern by changing the paraffin wax as well as the heating temperature. The team prepared three vertically arranged parallel interdigital electrodes on a sheet of cellulose paper. Compared to devices assembled with single-layer interdigital electrodes. The three devices connected in parallel exhibit a larger CV curve area and a specific capacitance for discharge time. The detailed preparation process invites the reader to read the original article, which makes it easier to understand the working principle of the device. Building on the former's work, the team fabricated vertically integrated planar multielectrode devices on a single sheet of paper. The highly integrated multi-electrode, diaphragm, and current collector exist only on one sheet of paper, and once again a device that expands the electrochemical window is cleverly designed on a single sheet. Figure 8G shows a schematic diagram of multilayer device integration and its corresponding circuit diagram. Multilayer paper-based devices can exhibit greater discharge times and CV curve areas in the same voltage window than during a single layer. And it can still maintain excellent energy storage performance under a higher electrochemical window. This series of work provides an innovative idea for the ingenious design of paper-based electrodes, which is of great significance to the development of paper-based supercapacitors.

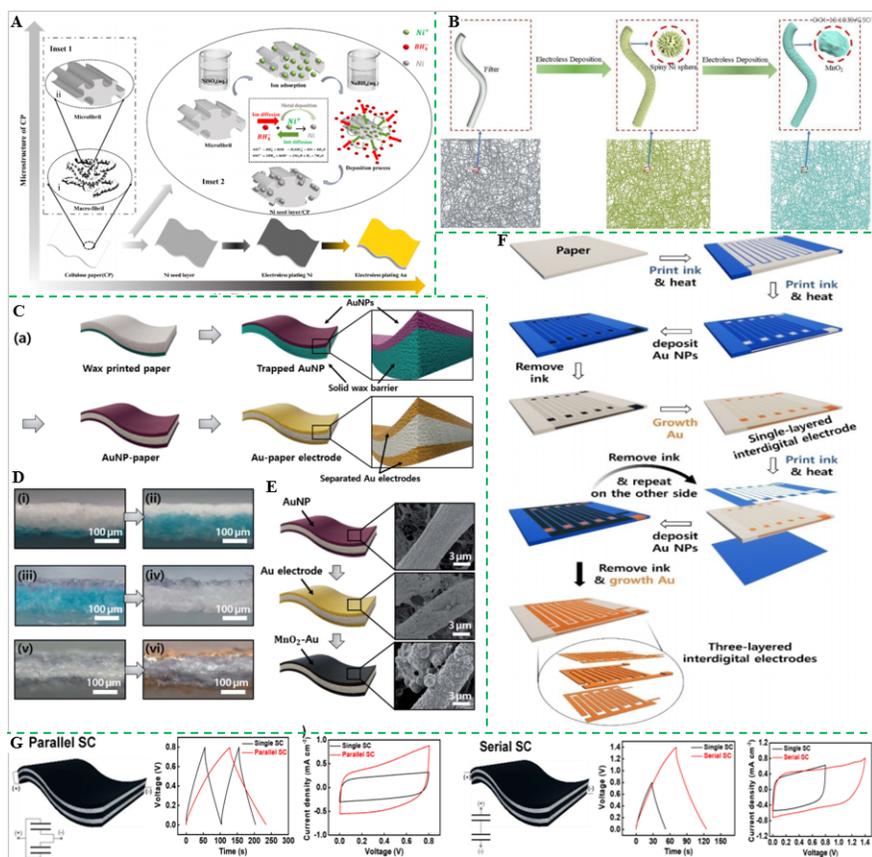


Figure 8. (A) Schematic diagram of CP/Ni/Au paper-based electrode preparation process and metal deposition.[94] (B) Schematic diagram of the preparation process of Ni-paper-MnO₂ paper-based electrode.[95] (C) Schematic diagram of the manufacturing process of vertically layered Au-Paper electrode in a single sheet of paper and its corresponding. (D) Optical photographs. (E) MnO₂-Au-Paper electrode preparation process.[96] (F) Schematic diagram of the preparation of three-layer Au-paper interdigital electrodes in a single sheet.[97] (G) Schematic diagram of series and parallel connection of vertical multilayer Au-Paper electrodes in a single sheet and their corresponding electrochemical properties.[98]

2.2.2.2 Cellulose/conductive polymer paper-based composite electrode

In view of the excellent flexibility and modifiable properties of 2D cellulose paper, two conductive polymers, PEDOT and PPy, have been widely used in 2D cellulose paper by in-situ polymerization. Li et al. [99] constructed a PEDOT/CP paper-based composite electrode by successfully loading PEDOT in cellulose paper (CP) by gas phase polymerization. Figure 9A shows a schematic diagram of the preparation of a paper-based electrode. The Fe³⁺ oxidant is first added dropwise to the CP, and then the CP adsorbed Fe³⁺ is placed in a vapor phase polymerization vessel. Finally, PEDOT/CP paper-based electrode was obtained by washing and drying. The authors prepared paper-based electrodes with different PEDOT loading amounts by controlling the number of gas-phase polymerization. The results show that the electrode (PEDOT/CP-10) after 10 polymerization shows excellent conductivity (14 Ω/square) and a volume ratio capacitance of 13.7F cm⁻³. Similarly, Heo et al. [100] obtained conductive KHO (C-KHP) by loading Korean conventional paper (KHP) with a loaded conductive ink. Then the PEDOT is loaded on C-KHP by gas phase polymerization to obtain PC-KHP paper-based composite electrode material. Finally, 1D paper-based yarn electrode was prepared by mechanical winding of PC-KHP (Figure 9B). A power supply unit formed by connecting six independent devices in series successfully charges a smart device operating at 3.6V (Figure 9C). This work

provides a conceptual reference for the practical application and large-scale production of 2D paper-based electrodes, and promotes the development of a new generation of flexible paper-based electronic devices.

In recent years, simple paper-based flexible energy storage devices have been difficult to meet people's living needs. As a device for collecting tiny energy, nanogenerators have received widespread attention. Shi et al. [101] prepared PPy/Cellulose Paper (PCC) by in-situ polymerization as the main component units of flexible supercapacitors and friction nanogenerators, respectively. As shown in Figure 9D, the TENG consists of a Cellulose Paper substrate, a negative triboelectric layer Nitrocellulose Membrane, and a PCC that acts as both a positive triboelectric layer and an electrode. Supercapacitors consist of two symmetrical PCCs, PVA/H₂SO₄ electrolytes, and a Cellulose Paper substrate. The TENG exhibits an output voltage of up to 60V and a power density of 0.83W m⁻². SC exhibits a specific capacitance of 90.1mF cm⁻². The two devices were successfully assembled into a miniaturized electronic energy storage device (Figure 9E). To obtain paper-based high-performance electrodes under high-quality loads. After the traditional in-situ polymerization process, the addition of electric double-layer graphene can improve energy storage performance (Figure 9F) [102]. The paper-based electrode exhibits a specific capacitance of 1685mF cm⁻² and a cycle stability of 92.8% (5000 cycles). In addition, the assembled solid-state paper-based device exhibits an area capacitance of 1408mF cm⁻² and a high area energy density of 147μWh cm⁻².

Aramid fiber has attracted the attention of researchers due to its excellent mechanical properties and chemical stability. In recent years, multifunctional paper-based materials prepared from aramid fibers have been widely used in various fields of social life. Yu et al. [103] formed ACF/PPS/MWCNT composites by papermaking processes with adhesive polyphenylene sulfide (PPS), MWCNTs and aramid chopped fibers. The PPS is then used as a binder for ACF and MWCNT after heating. Finally, the ACF/PPS/MWCNT-PPy paper-based electrode was obtained by in situ polymerization of PPy (Figure 9G). The synergies between PPy thanks to flexible ACF fibers, highly conductive MWCNTs and excellent pseudocapacitance properties. The paper-based electrode exhibits high specific capacitance (3205mF cm⁻² current density at 5mA cm⁻²) and excellent cycle stability (93% capacitance retention after 5000 cycles). In addition, ACF/PPS/MWCNT-PPy also exhibits excellent flame retardant properties (Figure 9H). In conclusion, bifunctional paper-based materials with excellent energy storage performance and good flame retardant performance were prepared.

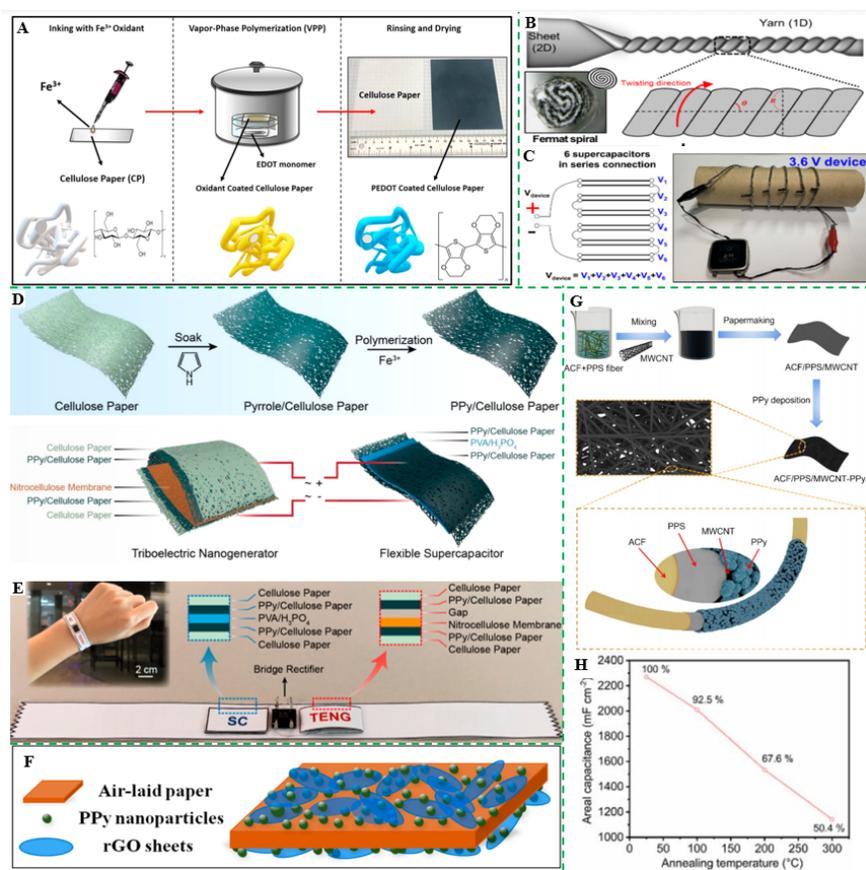


Figure 9. (A) Preparation process of PEDOT/CP paper-based composite electrode. [99] (B) PC-KHP paper-based electrode. (C) PC-KHP paper-based devices connected in series light the LEDs.[100] (D) Schematic diagram of the preparation of PCC paper-based materials and their self-charging devices. (E) PCC-based self-charging device. [101] (F) Schematic diagram of rGO/PPy/paper composite electrode material. [102] (G) Schematic diagram of the preparation process and microstructure of acf/pps/MWCNT paper-based electrode. (H) Change of specific capacitance of paper-based electrode after different temperature treatment.[103]

2.3 Printing technology

In order to realize the rapid commercial application of flexible electronic devices, mature printed electronic technology has received widespread attention. Printed electronics provides a simple, efficient and environmentally friendly manufacturing technology for the design of flexible supercapacitors. It has been widely developed in the field of flexible supercapacitors and has shown great potential. As a common printing substrate in daily life, paper is naturally favored by the majority of scientists. At present, a variety of printing technologies, including screen printing, inkjet printing, coating, writing and 3D printing, are used to prepare paper-based supercapacitors. This section summarizes the development of printing technology in paper-based supercapacitors. Table 3 summarizes the performance parameters of cellulose paper-based electrodes prepared by different printing technologies, so that readers can intuitively understand the application of this technology in the field of paper-based supercapacitors.

Table3 Performance parameters of cellulose paper-based electrodes prepared by different printing technologies

Electrode	Electrolyte	Capacity	Energy density at power density
writing			

Electrode	Electrolyte	Capacity	Energy density at power density
Cellulose paper/Graphitic/PPy	H ₂ SO ₄ /PVA	270.32mF cm ⁻² at 0.5mA cm ⁻²	24.03μWh cm ⁻² at 101.96μW cm ⁻²
Cellulose paper/Graphitic/PANI	H ₂ SO ₄ /PVA	93.64mF cm ⁻² at 0.1mA cm ⁻²	8.32μWh cm ⁻² at 39.97μW cm ⁻²
OPD@PN-V	1M H ₂ SO ₄	-	785μWh cm ⁻² and 286mW cm ⁻²
MSCs	H ₂ SO ₄ /PVA	4-8F cm ⁻³	0.36 μWh cm ⁻² and 0.21 mW cm ⁻²
paper/CNT/Ag	1M Na ₂ SO ₄	72.8F cm ⁻³ at 0.5mA cm ⁻²	9.08mWh cm ⁻³ at 0.22W cm ⁻³
Screen printing			
IP@PN-V	1.5M H ₂ SO ₄	-	39Wh kg ⁻¹ at 69kW kg ⁻¹
paper/Gr/AC	H ₂ SO ₄ /PVA	12.5 mF cm ⁻² at 0.01mA cm ⁻²	1.07μWh cm ⁻² and 0.004 mW cm ⁻²
paper/Mxene	H ₂ SO ₄ /PVA	158 mF cm ⁻² at 0.08 mA cm ⁻²	1.64μWh cm ⁻² at 778.3μW cm ⁻²
Inkjet printing			
paper/Mxene	H ₂ SO ₄ /PVA	23.4mF cm ⁻² at 0.05mA cm ⁻²	1.48mWh cm ⁻³ at 189.9mW cm ⁻³
paper/AC-Bi ₂ O ₃ /rGO-MnO ₂	KOH/PVA	455.05 mF cm ⁻² at 25 mV s ⁻¹	13.28mWh cm ⁻³ at 4.5W cm ⁻³
paper/Ox-SWCNT	H ₂ SO ₄ /PVA	33.0 mF cm ⁻² at 0.1mA cm ⁻²	0.51μWh cm ⁻² at 0.59mW cm ⁻²
PEDOT:PSS/CNF	-	5.2mF cm ⁻² at 1A g ⁻¹	0.27μWh cm ⁻² at 10.5mW cm ⁻²
PEDOT:PSS/CNF	-	2.60mF cm ⁻² at 0.05 mA cm ⁻²	0.13μWh cm ⁻² at 11mW cm ⁻²
3D printing			
CNF/AC/ graphite	CNC/ glycerol/NaCl	25.6F g ⁻¹ at 1mV s ⁻¹	0.88Wh kg ⁻¹ at 830W kg ⁻¹

2.3.1 Writing

The pencil as a very common writing instrument in life. Due to friction, the graphite particles generated by writing on the paper by the graphite rod inside it adhere to the surface of the cellulose paper. And with the pencil you can draw a variety of shapes of conductive paper, this conductive paper substrate provides an easy way to build. This pencil-based conductive paper has been used to prepare flexible supercapacitors. Zang et al. [104] used waste newspaper as a flexible substrate and bought a patterned graphite substrate through a pencil on its watch. Finally, PPy was deposited on its surface by electrochemical polymerization to obtain a paper-based composite electrode of newspaper/graphite/PPy (NGP) (Figure 10A). The electrode drawn by pencil exhibits a specific capacitance of 270.32mF cm⁻² and an energy density of 24.03 μWh cm⁻². This work shows that graphite layer paper constructed by pencil drawing can serve as a substrate for the active substance. Since then, Yeasmin et al. [105] have successfully introduced polyaniline on the surface of a paper-based material drawn by electrochemical polymerization, and the electrode exhibits an area capacitance of 93.64mF cm⁻² and a specific capacitance of 28.37F g⁻¹. With the popularity of flexible energy storage equipment, it is inevitable that there will be damage and deformation during use. This can seriously affect the performance of flexible energy storage devices. Therefore, sustainable use is particularly important for flexible devices. In response to this problem, Xiong et al. [106] introduced Vitriimer with shape memory and self-healing function into paper-based electrode, and prepared the first paper-based electrode material with shape memory and self-healing function. Figure 10B shows the preparation process of the paper-based material. A OPD@PN-V paper-based electrode material is obtained by polymerizing Vitriimer on conductive paper (OPD@PN) supported with polyaniline. The original shape can be restored by giving the initial paper-based electrode a certain shape and then processing it with a blower (Figure 10C). And after external force damage, it can also be self-repaired by blower treatment (Figure 10D). In addition, the composite exhibits excellent sensing properties. In conclusion, the introduction of Vitriimer into paper-based electrodes is a novel method for the preparation of multifunctional intelligent energy storage devices.

In order to increase the service life of the device and realize the sustainable use of flexible energy storage devices. Ma et al. [107] integrated TENG with a miniature supercapacitor (MSC) on a sheet of paper. Figure 10E shows the preparation process of the integrated device. First, interfinger-like 200 nm thick gold nanoparticles are deposited on the paper-based surface by magnetron sputtering. For the MSC unit, the gold surface is applied to functionalize its surface. The pencil-drawn paper-based electrode is then soaked in 8-Amino-2-naphthol solution for 1h. Finally, a PCA/H₂SO₄gel electrolyte is applied to the patterning

unit to obtain MCS. The TENG consists of a sliding module and a stator (the stator on a piece of paper with the MCS). When the stator moves across the stator covered by the FEP membrane, the TENG releases current to charge the MSC for continuous use of the device. As shown in Figure 10F, the TENG can charge three MSCs in series to 2.6V in 465s and successfully drive the electronics to operate. In conclusion, this work successfully prepared self-charging paper-based supercapacitors. It provides a good design idea for the integration of paper-based self-charging power supply and paper-based energy storage device in the future.

In addition to the introduction of active materials after building a conductive layer by drawing with a pencil, it is inspired by writing ink pens. Guang et al. [108] prepared an energy storage ink that can be written directly. The ink consists of CNT and Ag. As shown in Figure 10G, by assembling the ink in a ballpoint pen, the device controls its writing and provides pressure to it. Finally, the written electrode is placed at 60 °C to completely dry the ink. The results show that the prepared CNT/Ag paper-based electrode has a resistivity of $5.1 \times 10^{-4} \Omega \text{ cm}^{-1}$ and a specific capacitance of 72.8 F cm^{-3} . And after bending test, there is no effect on the electrochemical properties (Figure 10H), showing excellent mechanical stability.

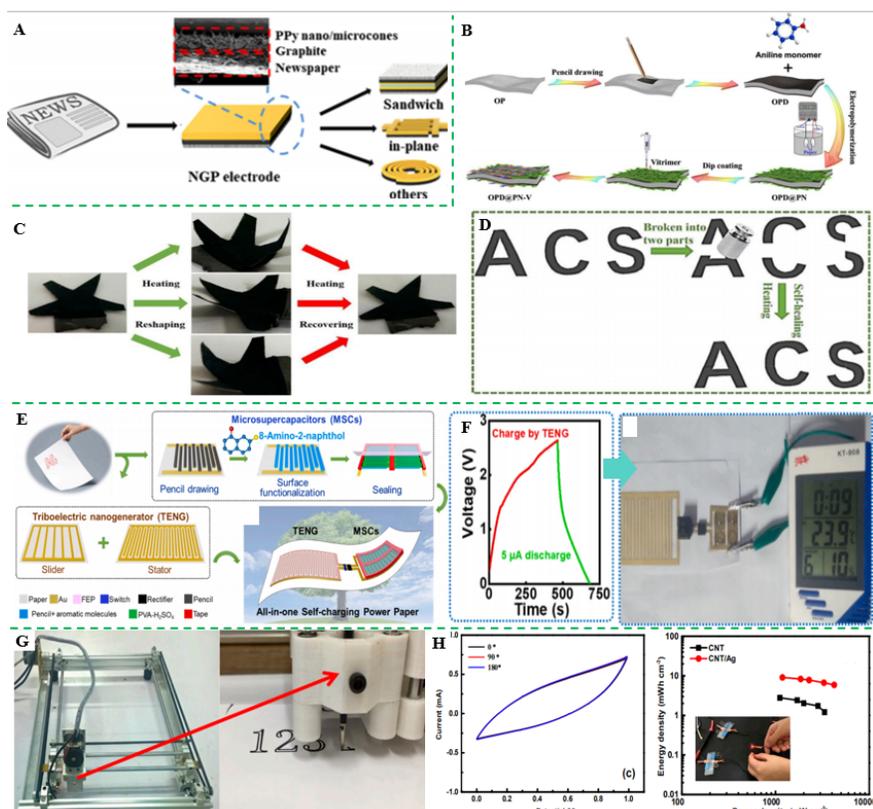


Figure 10. (A) NGP electrode preparation process.[104] (B) Schematic diagram of OPD@PN-V paper-based electrode preparation. (C) OPD@PN-V shape memory process. (D) OPD@PN-V self-healing process. [106] (E) Preparation of paper-based TENG and MSC. (F) Three series of MSC self-charging and GCD curves for power supply and applications. [107] (G) Write CNT/Ag ink directly on the surface of the paper. (H) Electrochemical performance of CNT/Ag paper-based electrodes. [108]

2.3.2 Screen printing

Screen printing is made by placing ink on a template, and then applying a certain pressure to the screen template through a scraper, after which the ink is squeezed on the surface of the substrate (such as paper) through the template during the process. Among them, the pressure exerted in the printing process and

the number of printing times will have a certain impact on the product performance. As shown in Figure 11A, Xiong et al. [109] printed conductive ink on the surface of original blank paper (OP) by screen printing technology on the basis of the former research. Then, polyaniline and Vitrimer were introduced into the paper-based electrode by electrochemical polymerization and in-situ polymerization to obtain conductive ink@polyaniline-Vitrimer(IP@PN-V) paper-based electrode. Similarly, the electrode exhibits excellent self-healing and shape memory properties. And at the same time it shows excellent photothermal conversion and electromagnetic shielding performance.

Compared with the method of introducing active materials after building a conductive layer through screen printing, it is very convenient and fast to directly prepare inks with excellent energy storage performance and directly construct paper-based supercapacitors through screen printing. Chen et al. [110] blended two-dimensional graphene with activated carbon nanofiller to prepare a composite ink (Gr/AC-ink) for screen printing. Among them, Gr/AC-ink printed on paper shows excellent energy storage performance. This is mainly due to the presence of AC to effectively prevent the stacking of two-dimensional graphene nanosheets. Figure 11B shows the synergistic effect between graphene nanosheets and AC. Compared to Gr and AC electrodes alone, this electrode exhibits excellent ion storage performance due to the distinct layered structure in the Gr/AC electrode. It can be seen from the paper-based supercapacitor built by this work. The key to the preparation of paper-based supercapacitors by screen printing lies in the design and preparation of energy storage inks. In recent years, Mxene, a two-dimensional material with excellent energy storage performance, has also been used in screen printing to prepare paper-based electrodes. In the traditional Mxene etching process, the products are generally divided into a few layers of Mxene and unetched and unstripped Mxene. The latter are generally discarded as waste, which undoubtedly increases the cost of Mxene-based supercapacitors. Abdolhosseinzadeh et al. [111] prepared paper-based supercapacitors with excellent performance by using unetched and peeled Mxene precipitate and a few layers of Mxene as screen-printed inks (Figure 11C). Among them, a few layers of Mxene nanosheets act as conductive pathways between the precipitates and act as conductive binders in the ink of paper-based electrodes, thereby ensuring the metal conductive network. Finally, the paper-based electrode prepared by screen printing of the ink exhibits a specific capacitance of 158mF cm^{-2} and an energy density of $1.64\mu\text{Wh cm}^{-2}$. And the eight paper-based devices connected in series exhibited an electrochemical window of more than 4V and successfully lit the LED lamp (Figure 11D), which is already one of the best performances of Mxene and graphene screen-printed energy storage devices. In conclusion, this work provides a low-cost idea for the preparation of this performance screen-printed paper-based supercapacitor. In particular, the "turning waste into treasure" of Mxene sediment in this work has a certain reference in the high-value utilization of energy storage.

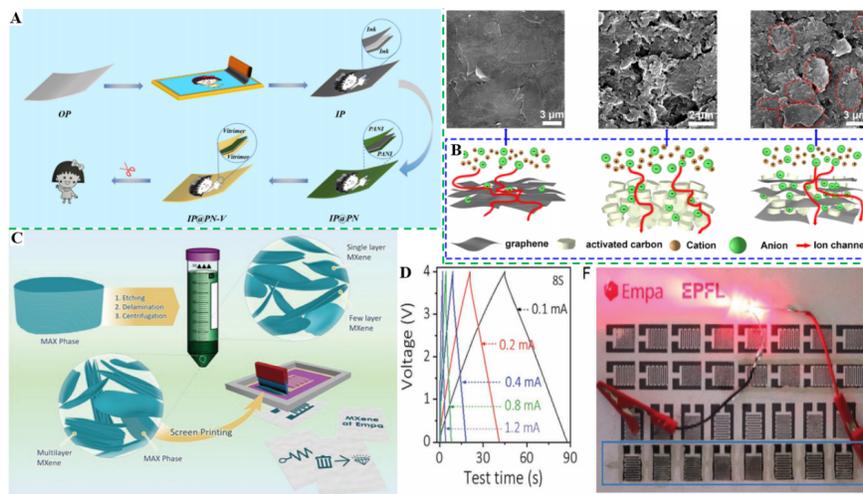


Figure 11. (A) IP@PN-V Schematic diagram of preparation of paper-based electronic base. [109] (B) Synergistic

effect of Gr and AC. [110] (C)Schematic diagram of MXene ink preparation and its application in screen printing to prepare paper based supercapacitor. (D)GCD curves of eight series connected MXene paper based supercapacitors. (E)The Mxene paper based super capacitor connected in series lights up the LED lamp. [111]

2.3.3 Ink jet printing

Ink-jet printing is a digital printing technology. The ink can be deposited on the substrate according to the designed pattern. Compared with screen printing, ink-jet printing ink is sprayed through quantitative digital control. Therefore, the distribution and thickness of the active material of the paper-based electrode prepared by the technology are more controllable. Huang et al.[112]directly sprayed a large area of MXene conductive ink on the paper surface. Then the interdigital electrode with a certain width was prepared by ultraviolet laser (Figure 12A). The geometry of interdigital electrode was optimized by UV laser. Finally, the paper based device showed 23.4mF cm^{-2} area specific capacitance and good magnification performance. In order to expand the voltage window and power supply time of the device, the author directly prepared series and parallel paper-based devices through inkjet (Figure 12B). The results show that the voltage window of the device after series connection can reach 1.2V without affecting the discharge time. At the same time, the discharge time of the two devices in parallel also increases by 100%. Compared with symmetrical supercapacitors, asymmetric electrode supercapacitors have larger voltage window and energy density. Based on this, in order to improve the voltage window of the device,Sundriyal et al.[113]prepared an asymmetric miniature paper-based supercapacitor through continuous ink-jet printing. As shown in Figure 12C, the device preparation process is shown. Firstly, rGO ink interdigital electrode is printed on paper. Then active carbon- Bi_2O_3 ink and rGO- MnO_2 ink are printed on the corresponding separate interdigital electrodes as cathode and anode respectively. Finally, PVA/KOH gel electrolyte is also printed on the electrode surface in the form of ink. Thanks to the asymmetric electrodes, the device shows a high voltage window of 1.8V. Similarly,different series and parallel devices are designed in this work, and the LED lamp with the working voltage of 3.2V is successfully lit. Similarly, after ink-jet printing, its energy storage characteristics can be improved through post-processing. For example, Jo et al. [114] prepared a water-based additive free oxidized single-walled carbon nanotube slurry for ink-jet printing. It is worth mentioning that in this work, the ink of ink-jet printing is treated with strong pulsed light to improve the electrochemical energy storage performance of the paper-based electrode. As shown in Figure 12D, under the treatment of intense pulsed light, the released gas generated by the rapid elimination of oxygen containing groups on the surface of carbon nanotubes can produce microporous structures in the ink. This is very beneficial to the diffusion of electrolyte ions and the storage of electrons. In addition, the ink is also suitable for screen printing process. In a word, this work provides a feasible method for the preparation of energy storage porous carbon based ink.

In addition to the construction of paper based supercapacitor by spraying active ink on cellulose paper, the preparation of cellulose based conductive ink has also been studied in recent years. For example, Engquist et al. [115,116] from Linköping University in Sweden reported two research efforts on inkjet printing of cellulose-based inks. As shown in Figure 12E, the team prepared a printable cellulose based ink by mixing CNF with conductive polymer PEDOT:PSS. Firstly, ink is sprayed on PET/Al/Carbon collector by ink-jet printing to form a paper-based electrode. Then the gel electrolyte is deposited on the electrode by the rod coating method. Finally, the two cured paper electrodes are combined into a supercapacitor. It is worth mentioning that in order to prevent the brittleness of the ink after forming, the author perfectly solved this problem by adding an appropriate amount of glycerin. On the basis of this work, the team improved the molding of cellulose/PEDOT:PSS ink again. As shown in Figure 12F, this work prepared a paper based supercapacitor with controllable thickness and large area through air atomization spraying of ink and screen printing of gel electrolyte. In addition, the device is combined with the flexible solar cell module to successfully prepare a self charging flexible paper based supercapacitor based on solar energy (Figure12G). As shown in Figure 3H, the integrated device irradiated by sunlight can charge the paper based supercapacitor to 0.6V in 2000s.

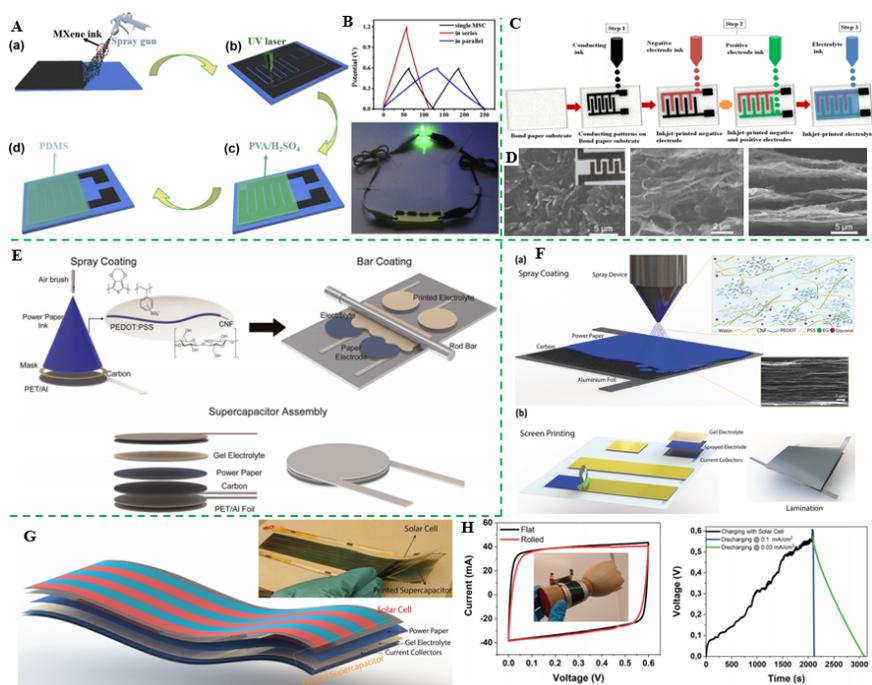


Figure 12. (A)Mxene/paper electrode preparation process based on inkjet printing. (B) Electrochemical performance of Mxene/paper electrodes. [112] (C)Preparation process of asymmetric paper-based supercapacitors.[113] (D)SEM image of CNT ink after intense pulsed light processing.[114] (E)PEDOT: PSS/CNF paper-based device preparation. [115] (F) PEDOT: PSS/CNF paper-based device preparation. (G)Based on the schematic diagram of solar self-charging equipment. (H)Electrochemical performance test of self-charging devices. [116]

2.3.4 3D printing

3D printing, also known as additive manufacturing, can continuously deposit materials to produce various structures under digital design[117]. This makes it possible to accurately fabricate flexible devices with complex structures in a short time. Aeby et al. [118] prepared a cellulose based ink for one-time 3D printing. Electrode ink is composed of CNF, water, CNC, glycerin, activated carbon and graphite particles. Electrolyte ink is composed of CNC, glycerin and NaCl. As shown in Figure 13A, the design of 3D printing paper based supercapacitor is shown. The two printed devices are folded together to form a paper based supercapacitor. In addition, the author tried to print six paper based supercapacitors in series on curved substrate (Figure 13B). And it realizes the power supply for the alarm clock with the working voltage of 3V. The paper based device also shows excellent biodegradability. After more than half of the weight can be decomposed in 9 weeks, the remaining carbon based materials can be recycled (Figure 13C). In a word, this work has made considerable reference in the field of 3D printing paper-based supercapacitors.

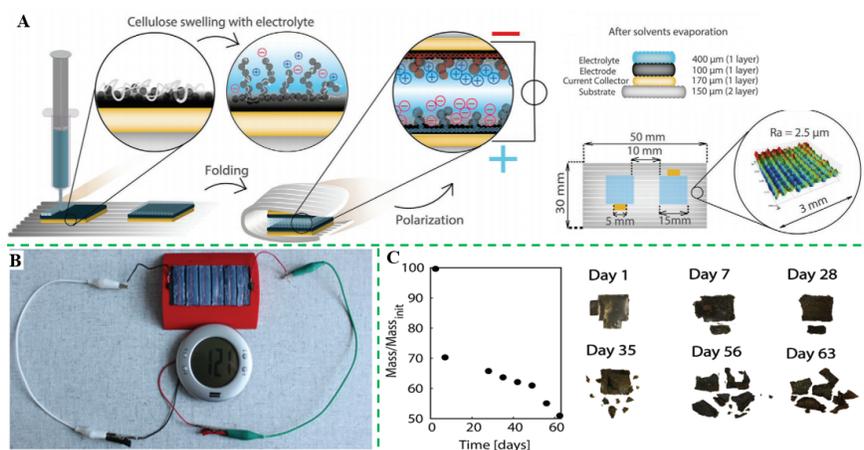


Figure 13. (A) Paper based devices for 3D printing. (B) 3D printed paper-based devices provide energy for electronic watches. (C) The degradable and recyclable process of paper-based devices. [118]

2.4 Others

In addition to the manufacturing process of paper-based supercapacitors summarized above, papermaking process, impregnation, carbonization and laser induced graphene technology are also used to prepare paper-based supercapacitors. Table 4 summarizes the performance parameters of the above preparation process related research work.

Table 4. Performance parameters of paper based supercapacitor

Electrode	Electrolyte	Capacity	Energy density at power density
papermaking process			
PANi@paper	H ₂ SO ₄ /PVA	282F g ⁻¹ at 1A g ⁻¹	2.5W h kg ⁻¹ and 0.3kW kg ⁻¹
PPy@paper	H ₂ SO ₄ /PVA	3600mF cm ⁻² at 1mA cm ⁻²	3.1mWh cm ⁻³ and 414.9mW cm ⁻²
cellulose-based ACFPs	1M Na ₂ SO ₄	24.1F cm ⁻³ at 0.5 mA cm ⁻²	-
Pouring molding			
MFC/rGO/SnO ₂	NaCl/PVA	53F g ⁻¹ at 10mV s ⁻¹	-
PEDOT:/CNF/ARS	-	435F g ⁻¹ at 0.5A g ⁻¹	8.9Wh kg ⁻¹ at 459W kg ⁻¹
carbonization			
FCP-NiCO ₂ O ₄	KOH/PVA	3115mF cm ⁻² at 2mA cm ⁻²	1.2mWh cm ⁻³ at 58.16 mW cm ⁻²
CNF/ Co ₃ O ₄	3M KOH	214F g ⁻¹ at 1A g ⁻¹	3.03Wh kg ⁻¹ at 203.1W kg ⁻¹
impregnation			
Cellulose fibre/BC/CNTs	1M H ₂ SO ₄	77.5F g ⁻¹ at 1A g ⁻¹	22.5Wh kg ⁻¹ and 873kW kg ⁻¹
laser induced graphene technology			
Paper/LIG/sodium tetraborate	H ₂ SO ₄ /PVA	4.6mF cm ⁻² at 0.015mA cm ⁻²	0.30μWh cm ⁻² at 4.5μW cm ⁻²
Paper/LIG/ NaHCO ₃	H ₂ SO ₄ /PVA	23.8 mF cm ⁻² at 0.015mA cm ⁻²	2.64μWh cm ⁻²

2.4.1 Papermaking process

Thanks to the long history of paper making technology, the paper making technology in modern society is mature enough. At present, all kinds of special paper are developed by people through papermaking process. As shown in Figure 14A, Huang et al. [119] prepared a kind of cellulose based on the disposal arrangement of polyaniline, and then prepared a paper based composite electrode through the papermaking process. The preparation of the electrode is mainly divided into three steps: first, a large number of small

branches are generated by high-speed mechanical stirring of cellulose pulp, so that more hydroxyl groups conducive to polyaniline polymerization are exposed on more cellulose surfaces. Secondly, polyaniline is polymerized on the cellulose surface to form PANi@cellulose. Finally, the PANi@paper composite electrode is obtained through an industrial paper forming machine. As shown in Figure 14B, the TEM image of PANi fiber shows that polyaniline grows vertically and tightly on the surface of cellulose. This provides a faster redox kinetics for electron/ion transfer and charge storage in the electrochemical process. And the vertically arranged PANi structure also gives the paper based electrode excellent capacitive characteristics. The PANi@paper electrode exhibits an excellent specific capacitance of 296F g^{-1} at 1A g^{-1} . More importantly, the solid paper based energy storage device assembled by the PANi @ paper electrode also has a specific capacitance of 282F g^{-1} , and still maintains excellent and stable electrochemical performance under different bending angles (Figure 14C). The large-scale preparation of paper-based electrode materials by papermaking technology is exciting. However, the prepared paper-based materials also require manual assembly of solid-state devices when applied, which undoubtedly increases production costs and time. In response to this problem, the team achieved large-scale production of integrated paper-based supercapacitors by improving the process technology [120]. As shown in Figure 14D, this technique uses cellulose from orderly stacking PPy as the raw material for paper-based electrodes. After continuous molding, pressing and drying, an integrated supercapacitor is obtained. Figure 14E shows a schematic diagram of the detailed preparation process. Firstly, the 1DPPy/cellulose pulp fiber is passed through the sheet molding machine to obtain the non-dry state PPy@paper, and then the two pieces of PPy@paper are assembled sequentially with the cellulose diaphragm obtained by pure cellulose pulp to form a sandwich structure. Finally, an all-paper-based supercapacitor device is obtained by hot pressing, drying, and impregnating the electrolyte (Figure 14F). The all-in-one paper-based device has a mass ratio capacitance of 360F g^{-1} at 0.1A g^{-1} and a capacitance retention rate of 81.7% after 1000 cycles. It is worth mentioning that by controlling the thickness of the pulp raw material in different electrodes, an integrated device with different areas of capacitance can be obtained. A series of paper-based devices in the $562\text{-}2507\text{mF cm}^{-2}$ range of area ratio capacitance were designed. This provides a fast and efficient way to industrialize mass customization of paper-based devices.

Chen et al. [121] prepared a carbon fiber (CFs)-reinforced cellulose-based activated carbon paper-based electrode (cellulose-based ACFPs) by wet papermaking, carbonization and activation. Figure 14G shows the preparation process of this electrode. Firstly, CFs were mixed with fibrillated pulp fibers evenly, and carbonized precursor paper matrix composites were prepared by papermaking process. This composite is then soaked in H_3PO_4 solution. Finally, cellulose-based ACFPs paper-based electrodes were obtained by H_3PO_4 and CO_2 double activation process. Among them, CFs in paper-based materials have a low coefficient of thermal expansion and high chemical stability, which provides excellent mechanical properties for paper-based electrodes (Figure 14H).

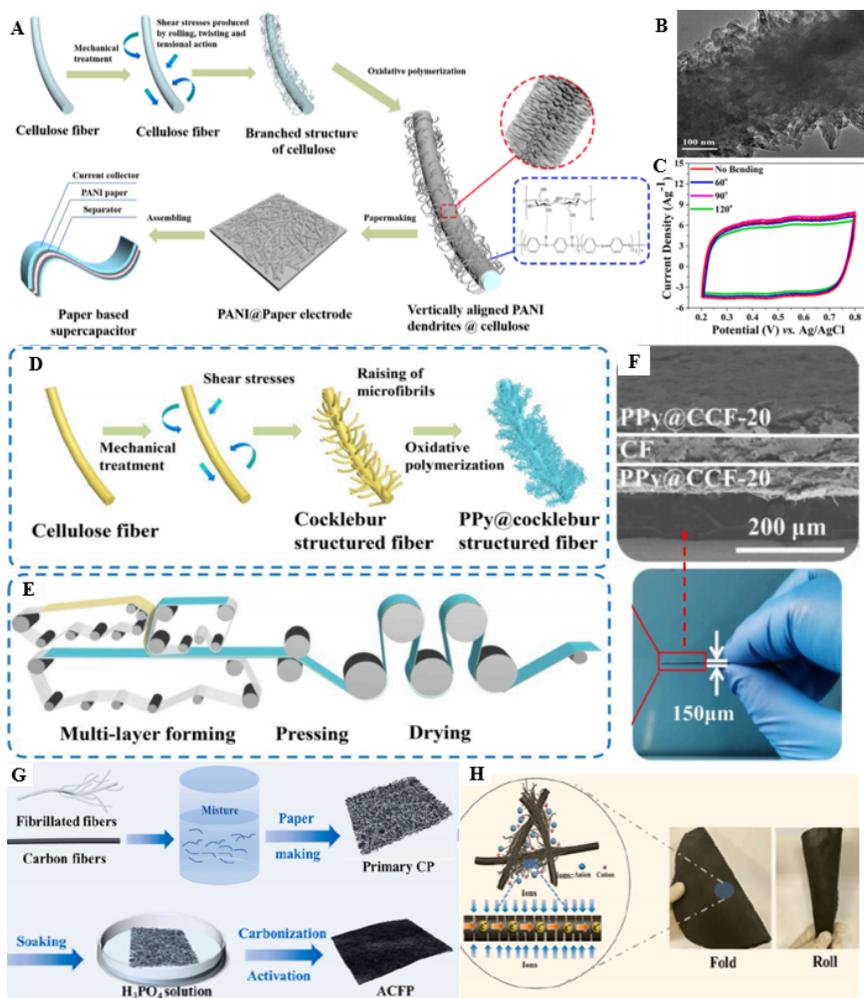


Figure 14. (A) PANi @paper preparation process. (B) TEM image of PANi @paper. (C) PANi @paper CV curves at different bending angles. [119] (D) Preparation process of PPy pulp fiber. (E) PPy@paper preparation process. (F) SEM image of a PPy@paper paper-based device.[120] (G) cellulose-based ACFPs paper-based electrode preparation process. (H) Physical photographs of cellulose-based ACFPs electrodes and electron/ion transport mechanisms. [121]

2.4.2 Pouring molding

Due to its high specific surface area, excellent hydrophilicity and excellent rigid structure, cellulose is widely used in self-assembly film forming technology. In the field of flexible paper-based supercapacitors, scientists have also tried to blend the active material with cellulose and then prepare paper-based electrodes by pouring them in a mold by using the electrostatic layer self-assembly method. For example, Garino et al. [122] poured rGO/SnO₂ synthesized by hydrothermal method with microfibrillated cellulose (MFC) blend in a PP mold. Self-assembled paper-based electrodes were then obtained after holding in air for 24 h to remove solvent moisture. Figure 15A shows an SEM image of a paper-based electrode. It is clear from the figure that MFC and rGO/SnO₂ tablets are perfectly combined. This is very important for the mechanical properties of the composite electrode. Edberg et al. [123] also prepared a cellulose-based paper-based electrode based on PEDOT by pouring molding in a mold. After testing, the paper-based electrode assembled energy storage device exhibits a specific capacitance of more than 400F g⁻¹, showing very excellent energy storage characteristics.

2.4.3 Carbonization

As a renewable biomass material rich in a large amount of carbon, cellulose is activated to prepare carbon-based fibers that also exhibit excellent electric double layer performance. However, the performance of directly using the prepared cellulose-based carbon fiber for energy storage devices is not very good. In recent years, paper-based supercapacitors prepared by compounding cellulose-based carbon fibers with substances with high energy storage activity have also shown excellent performance. Wu et al. [124] loaded carbonized cellulose-based tissue paper (FCP) with NiCO_2O_4 by hydrothermal method to obtain FCP- NiCO_2O_4 paper-based electrode (Figure 15B). On the one hand, carbonized FCP provides abundant sites for the loading of highly conductive NiCO_2O_4 . On the other hand, carbonized FCP favors the rapid movement of electrons during electrochemical reactions. Thanks to the synergistic effect of carbonized FCP and NiCO_2O_4 , the FCP- NiCO_2O_4 paper-based electrode showed excellent area specific capacitance (3115mF cm^{-2}) and excellent energy density (1.2 mWh cm^{-3}) and power density (58.16 mW cm^{-3}). As shown in Figure 15C, Rabani et al. [125] uniformly grow cobalt oxide (Co_3O_4) nanoparticles on the surface of 1DCNF. Then the resulting composite fiber is molded to obtain CNF/ Co_3O_4 paper matrix composite. Finally, CNF/ Co_3O_4 paper-based electrode was obtained by carbonization treatment at 200°C . Thanks to the excellent performance of CNF fiber and Co_3O_4 after carbonization treatment. The paper-based energy storage device assembled with this electrode can provide a high specific capacitance of 214F g^{-1} at 1A g^{-1} .

2.4.4 Impregnation

The excellent porous structure and large specific surface area of cellulose paper are considered suitable carriers for loading active materials. Among them, bacterial cellulose (BC) has an excellent length-to-diameter ratio and a network of interwoven fibers. However, after impregnation, the conductive substance and the paper-based film made of pure BC have poor mechanical properties. As shown in Figure 15D, Wu et al. [126] prepared a flexible and strong paper-based substrate by mixing cellulose fibers with BC. It is then impregnated in CNT solution. Due to the surface modification of BC by polyimide, a large number of amine groups are generated on the BC surface. The adsorption of this CNT provides excellent prerequisites. From the SEM image of the paper-based electrode, it is clear that the cellulose fibers provide the skeleton of the composite, and the CNT is uniformly loaded inside the material. The results show that the electrode has a conductivity of 0.59S cm^{-1} and a specific capacitance of 77.5F g^{-1} . It is worth mentioning that after 15,000 ultra-long cycles, its electrochemical performance is still maintained at 98.4% of the initial state, showing excellent durability and stability.

2.4.5 Laser-induced graphene

In 2014, Tour et al.[127] successfully prepared macroporous laser-induced graphene (LIG) by treating polyimide membranes with CO_2 lasers. Since then, LIGs prepared by various substrates have been widely used in various fields such as energy storage and sensing. Among them, paper-based materials have proven to be excellent precursor substrates for LIG, but because untreated cellulose paper burns easily when treated at high temperatures in air, it needs to undergo chemical treatment. Lu et al.[128] soaked the paper in 0.1 M flame retardant solution sodium tetraborate for pretreatment. This is to prevent combustion when the laser processes the paper and better produce LIG. Figure 15E shows SEM images of cellulose paper and LIG. When used as a supercapacitor, the paper-based LIG exhibits a specific capacitance of 4.6mF cm^{-2} , and the voltage and energy output of these devices can be controlled by connecting them in series and parallel. Although the LIG obtained by the paper-based material treated with flame retardant has been successfully applied to the field of supercapacitors, the capacitance performance of the device obtained by this method is still not very good. Lin et al. [129] The paper-based device prepared by combining chemical foaming and LIG exhibits a specific capacitance of 23.8mF cm^{-2} . Figure 15G shows the preparation process of this paper-based electrode. The paper is first soaked in the inorganic salt NaHCO_3 for processing. Then, the treated paper is patterned and scanned by a CO_2 laser to obtain a paper-based electrode. Finally, gel electrolyte is added to obtain a paper-based LIG device. It is worth mentioning that thanks to the foaming effect of NaHCO_3 (Figure 15F), the CO_2 laser produces a large number of porous LIG on the paper when processing it. This structure facilitates the migration of electrons and ions during electrochemical energy storage.

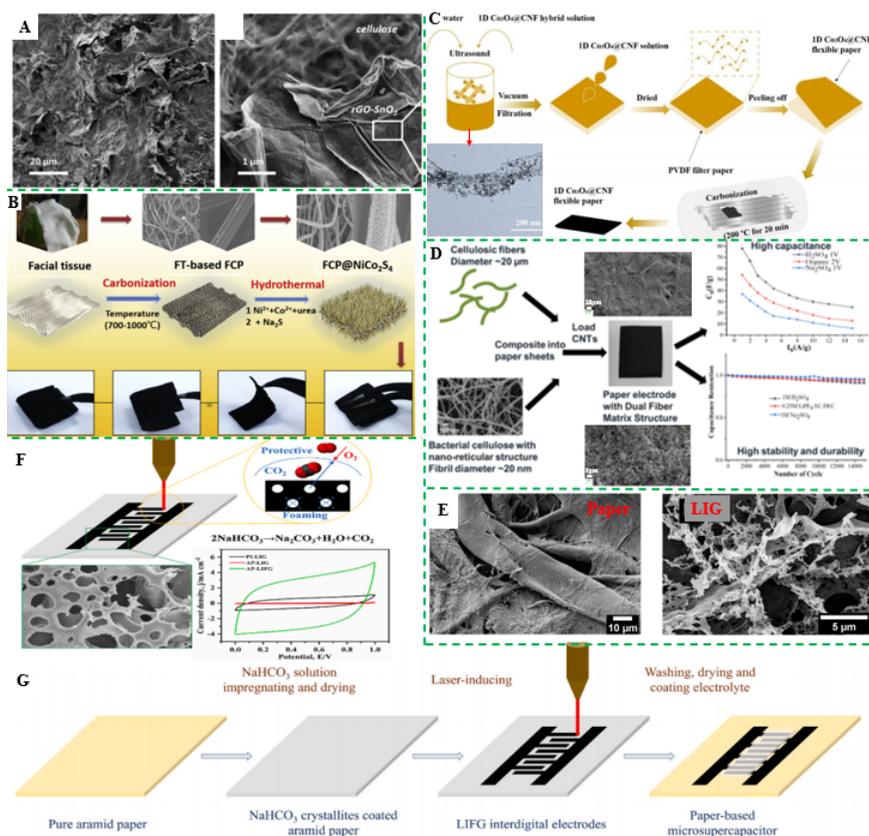


Figure 15. (A) SEM image of MFC/rGO/SnO₂ paper-based electrode.[122] (B) Preparation process and physical photo of FCP-NiCO₂O₄ paper-based electrode. [124] (C) Preparation process of CNF/Co₃O₄ paper-based electrode. [125] (D) Paper-based electrode prepared based on CNT impregnation. [126] (E) SEM images of paper and LIG. [128] (F) Preparation process of paper-based LIG devices. (G) NaHCO₃ chemical foaming mechanism and CV curves of paper-based devices. [129]

3. Summary and outlook

As a biomass resource with biorenewable, easily degradable and excellent mechanical flexibility, cellulose is considered to be the most attractive green material for the preparation of flexible supercapacitor electrodes. Especially in the context of global efforts to reduce environmental pollution, cellulose paper-based supercapacitor energy storage devices have become a current research hotspot. Among them, the porous structure of cellulose gives paper-based supercapacitors unique advantages, including high energy density, designability of thickness, design of porous structure conducive to the rapid movement of electrolyte ions, and preparation of integrated devices. In addition, the application of printing technology makes the large-scale and commercialization of paper-based energy storage devices a possibility. This paper summarizes the latest research progress of electrode related preparation methods of cellulose paper-based supercapacitors in recent years, and classifies and summarizes them to provide a rich reference for their development. Although scientists have done a lot of excellent research in the field of the preparation of cellulose paper-based electrodes. However, many problems and challenges require further research and breakthroughs (Figure 16). (1) Although cellulose paper-based electrodes prepared by different preparation methods have been used in many fields. But these methods have a common problem with energy storage. As a flexible energy storage device, the improvement of electrochemical energy storage performance (specific capacitance, energy density and power density) and designability are problems that need to be further explored and studied in these preparation processes. (2) Large-scale preparation is the most important problem restricting the develop-

ment of flexible supercapacitors. The relevant research work reported so far is limited to laboratories and has not been demonstrated on a large scale. Among them, mature papermaking technology and low-cost printing technology have become the most effective way to achieve large-scale preparation. In future research, the preparation of pulp composite active fiber by blending pulp cellulose with active materials or by in-situ polymerization is a research direction with high feasibility of large-scale preparation. In addition, the development of electroactive inks in printing technology is also a highly feasible method for large-scale preparation of high-performance paper-based supercapacitor devices. (3) In the preparation process of paper-based electrodes other than flat printing technology and LIG technology, the control of the material structure and pore size of the electrode by the long-diameter ratio of cellulose is also a very worthy of study. For example, cellulose materials with different length-diameter ratios and composite forms with active materials have an impact on the pore structure inside the electrode material. Therefore, controlling these porosities by choosing the appropriate preparation method remains a challenge. (4) The preparation of high-performance paper-based electrodes assisted by computational simulation theory has also been gradually applied. For example, COMSOL is used to carry out theoretical simulation calculations on the movement of electrolyte ions in the pores inside the electrode, and the influence of pore structure on energy storage performance is studied more intuitively. And with the help of simulation, the preparation process of paper-based electrodes can be continuously optimized and referenced. In addition, advanced finite element simulation can also be used to establish the relationship between paper-based electrode structure and mechanical properties. (5) The designability of the energy storage performance of paper-based electrodes by related preparation methods is a topic that has not been widely studied. For example, the change of thickness during vacuum filtration, the control of polymerization conditions in in-situ polymerization, and the thickness of ink in printing technology will have a certain impact on the energy storage performance of paper-based devices. Therefore, the controllable design of paper-based electrode energy storage performance by using these technologies also has an important impact on the preparation of high-performance paper-based supercapacitor energy storage devices. (6) The development trend of flexible electronics in the future when intelligent integrated equipment. The introduction of self-charging, electrochromics, self-healing and shape memory into paper-based supercapacitors, and the development of integrated multifunction devices are critical to the future development of paper-based supercapacitors. In summary, the development of cellulose paper-based electrodes in the field of energy storage of flexible supercapacitors is worthy of further exploration and breakthrough. Finally, the future of cellulose paper-based supercapacitor devices will definitely have a very promising market. We also need to continue to work hard and expect paper-based energy storage devices to enter an era of widespread application.

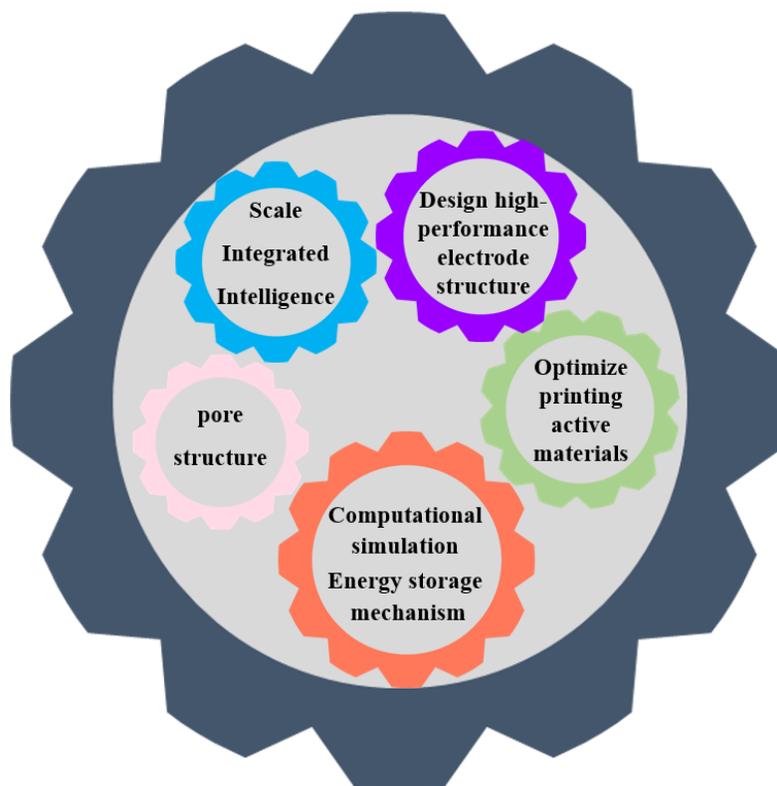


Figure 16. Future development prospects of cellulose-based paper-based supercapacitor electrode materials.

Acknowledgments

This work was supported by Supported by the fund of National Natural Science Foundation of China (22078184; 22171170). China Postdoctoral Science Foundation (2019M653853XB). Natural science advance research foundation of Shaanxi University of Science and Technology (2018QNBj-03). Major scientific and technological innovation projects in Shandong Province (2019TSLH0316).

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