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## Recent progress in energy conversion and storage of agricultural waste-derived (carbon/nano) materials: a review†

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Nowadays, with the mechanization of human societies, the demand for energy production and storage has also increased. Fossil fuels are running out, and thus, clean energy production using non-toxic and accessible sources is desirable. The valorization of waste materials into useful compounds is among the most important research subjects. Increasing interest in cost-effective raw materials and environmentally friendly precursors has brought agricultural residues up as promising, widespread biowaste all around the world. Rice husks (RHs), corn husks, wheat straws, sugarcane bagasse, fruit nut residues, and many other agricultural wastes have been broadly applied for designing novel materials, which can be applicable for energy conversion and storage. Agricultural waste contains useful chemical compounds, which may act as reducing, stabilizing, or capping agents, templates, precursors, etc., to produce various compounds *viz.* carbonaceous and (nano)materials. This review paper discusses the compounds that can be applicable for electrocatalytic applications for energy conversion in addition to energy storage. In fact, in this review, reports concerning agricultural waste-derived (carbon/nano)materials for energy conversion as well as energy storage devices such as different types of batteries, supercapacitors, and solar cell systems have been reviewed. The application of agricultural waste for energy conversion and storage is a very important issue due to the increase in the human population in the future, resulting in energy shortage problems. Therefore, suitable solutions must be developed for energy conversion and storage. On the other hand, the application of natural and environmentally friendly agricultural waste is very important for energy production and storage in addition to preventing the accumulation of this waste in the environment.

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### 1. Introduction

Ongoing developments in numerous industries involve constant improvements to increase their revenues. Furthermore, considering green and environmentally benign resources for different activities and the preparation of new materials could solve the rising problem of environmental pollution.<sup>1,2</sup> Many recent studies have attempted to design and establish environ-

mentally benign methods and products to control pollution discharge into the environment.<sup>3–7</sup> Extensive agricultural biowaste has always been of interest due to its safety for the environment, high availability, and extensive resources worldwide.<sup>8–15</sup> Agricultural products are nutritionally valuable, yet their by-products, often referred to as waste, are frequently discarded without being utilized. In other words, the application of waste materials for the synthesis of various catalysts makes use of inexpensive and environmentally friendly materials.<sup>16–18</sup> A huge number of agricultural residues are annually disposed of as waste.<sup>19–24</sup> The USA, China, and India are the countries with the highest number of surveys, the main focus of which has been the application and exploitation of agricultural waste, obtained from cereal crops, principally corn and wheat, as they are the main producers of this sort of crop.<sup>25</sup> Agricultural waste refers to compounds formed as a result of various agricultural processes and activities. Agricultural waste has advantages such as low price, recyclability, availability, an environmentally friendly nature, and being economical. In addition, agricultural waste is an important

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source for the production of different products, such as biofuel, biogas, antioxidants, enzymes, mushrooms, vitamins, antibiotics, and animal feed in addition to activated and porous carbons (PCs), because it is a rich source of bioactive compounds and carbon materials.<sup>20,26–32</sup>

Modern agriculture has many benefits. However, one major problem is the production of organic agricultural waste.<sup>33</sup> This waste includes the peels of fruits and vegetables, waste fruits and vegetables, and plant debris such as stems, roots, husks, pods, and leaves. The agglomeration of this unusable waste causes environmental problems. For example, in some cases, people burn organic agricultural waste in the open air, which produces CO<sub>2</sub> gas and creates environmental pollutants. Therefore, this waste must be reused for other applications such as the production of energy (biofuel and biogas), fertilizers, and animal feed. One of the most important applications of this agricultural waste is for catalytic purposes. In other words, this agricultural waste can play different roles, such as efficient supports, reducing or stabilizing agents, templates, or sources of carbon compounds, in the preparation of different types of catalysts.<sup>16,34–39</sup>

Several experimental studies over many years have made it plain that there are valuable chemicals in agricultural products and their residues, which can be used for the design and preparation of eco-friendly systems for various applications. They can be a source of carbon<sup>40,41</sup> and be used as a source of energy, which burns cleaner than fossil fuels in addition to pharmaceuticals and food additives.<sup>10,42–47</sup> The valorization of biowaste for energy production minimizes waste production as well as the emission of greenhouse gases.<sup>48–50</sup> Furthermore, the functional groups present in agricultural waste such as carbonyl, alcoholic, acetamido, phenolic, amino, and amido groups have an affinity for heavy metal ions, which are capable of forming metal complexes or chelates.<sup>51,52</sup> They are also promising for the adsorption of dyes and organic contaminants.<sup>53,54</sup> Furthermore, these resources are renewable, biodegradable, cheap, and beneficial for the manufacture

of biohydrogen<sup>55</sup> and ethanol,<sup>56</sup> and are good precursors for the production of activated carbon (AC) with a high surface area and pore volume.<sup>57,58</sup>

Lately, clean and renewable energy resources have become vital topics for researchers owing to environmental deterioration and energy shortages as a result of the overconsumption of fossil fuels.<sup>59–61</sup> Moreover, in industrial applications, the tendency toward renewable energy has been growing significantly due to demands from the world's population, which has been predicted to grow more by 2030. The energy outlook in the USA is represented in Fig. 1. For instance, biomass energy sources were used to generate 26.7 billion kilowatt hours (kWh) of electricity in 2022.<sup>62</sup> In the last few years, many attempts have been made to improve green and sustainable materials for energy conversion and storage.<sup>63,64</sup> To this end, many electrode/electrocatalytic materials have been developed.<sup>63,64</sup> Advanced energy conversion approaches include the application of fuel cells (FCs), the oxygen reduction reaction (ORR),<sup>64–66</sup> the methanol and ethanol oxidation reactions (MOR and EOR),<sup>67,68</sup> the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER)<sup>69–71</sup> and other electrochemical reactions such as the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR)<sup>72</sup> and the nitrogen reduction reaction (NRR).<sup>73</sup> In addition, a large number of green-energy storage devices such as lithium-ion batteries (LIBs)<sup>74,75</sup> and supercapacitors<sup>76,77</sup> have been widely studied and utilized. Moreover, considering the present global energy and environmental scenarios, hydrogen is assumed to be a key solution. Thus, water electrolysis is regarded as a vital source of hydrogen for the future.<sup>78,79</sup> Furthermore, microbial fuel cells (MFCs) have attracted significant attention for the direct conversion of chemical energy from fuels into electrical energy.<sup>80,81</sup> For single-chamber MFCs (SC-MFCs), O<sub>2</sub> infused through the air-cathode is considered to be an efficient electron acceptor owing to its availability.<sup>82</sup> However, the slow kinetics of the ORR, which causes poor energy conversion efficiency, low output power density, unsatisfactory stability, and difficulties in scaling up the prepara-

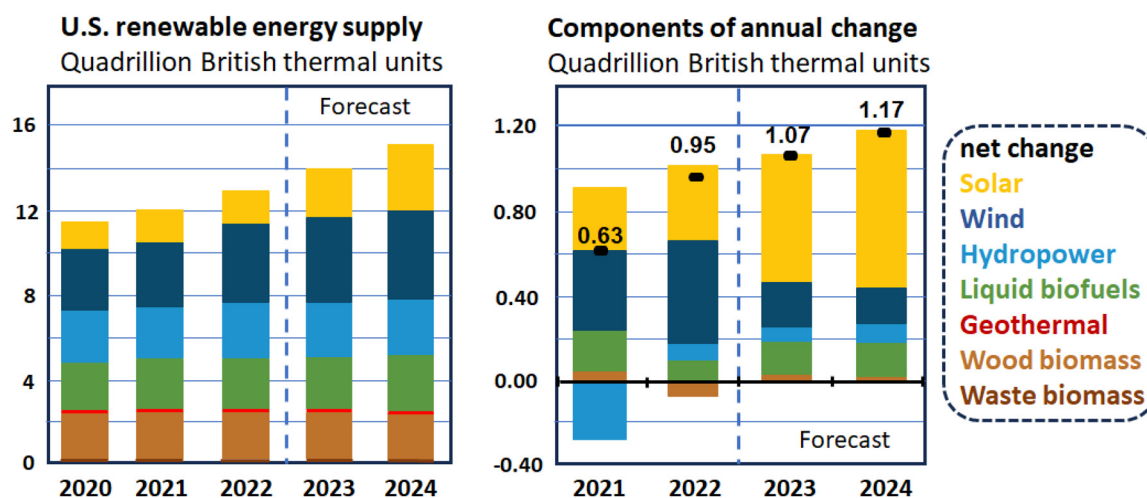


Fig. 1 The short-term energy outlook released by the U.S. Energy Information Administration.<sup>62</sup>

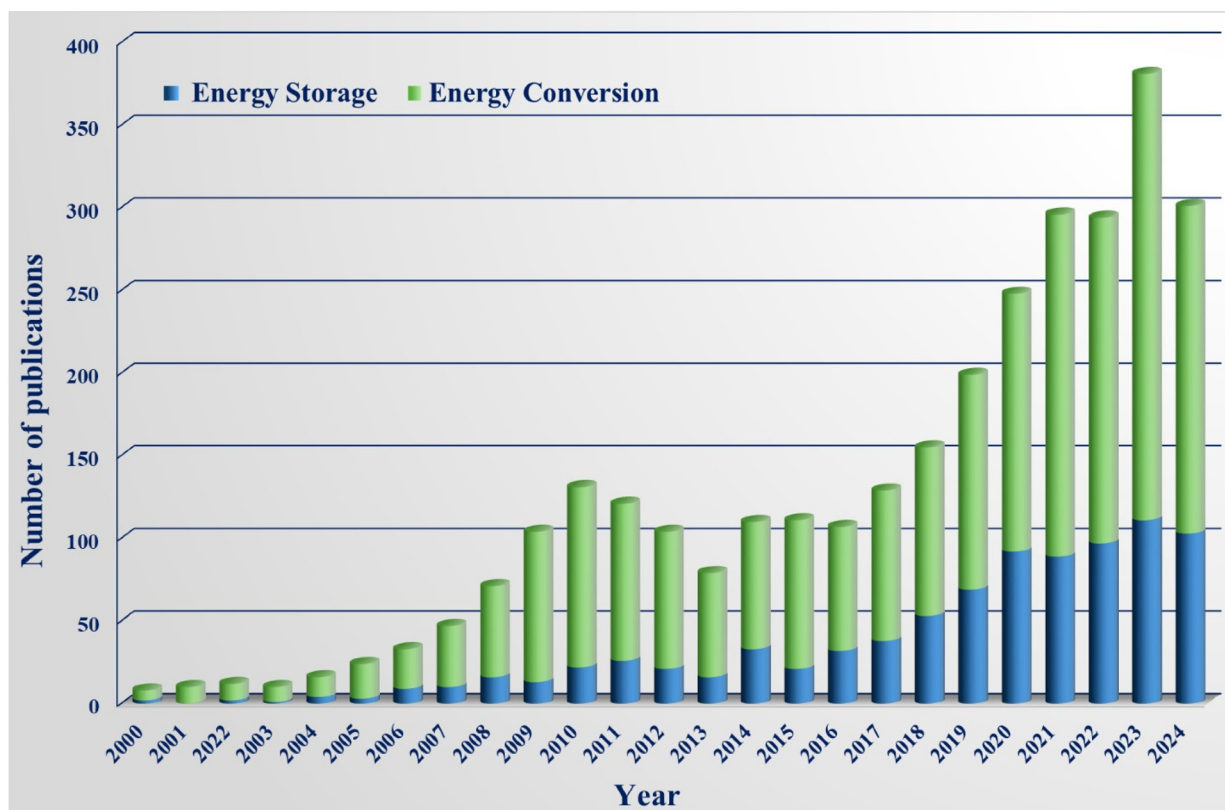


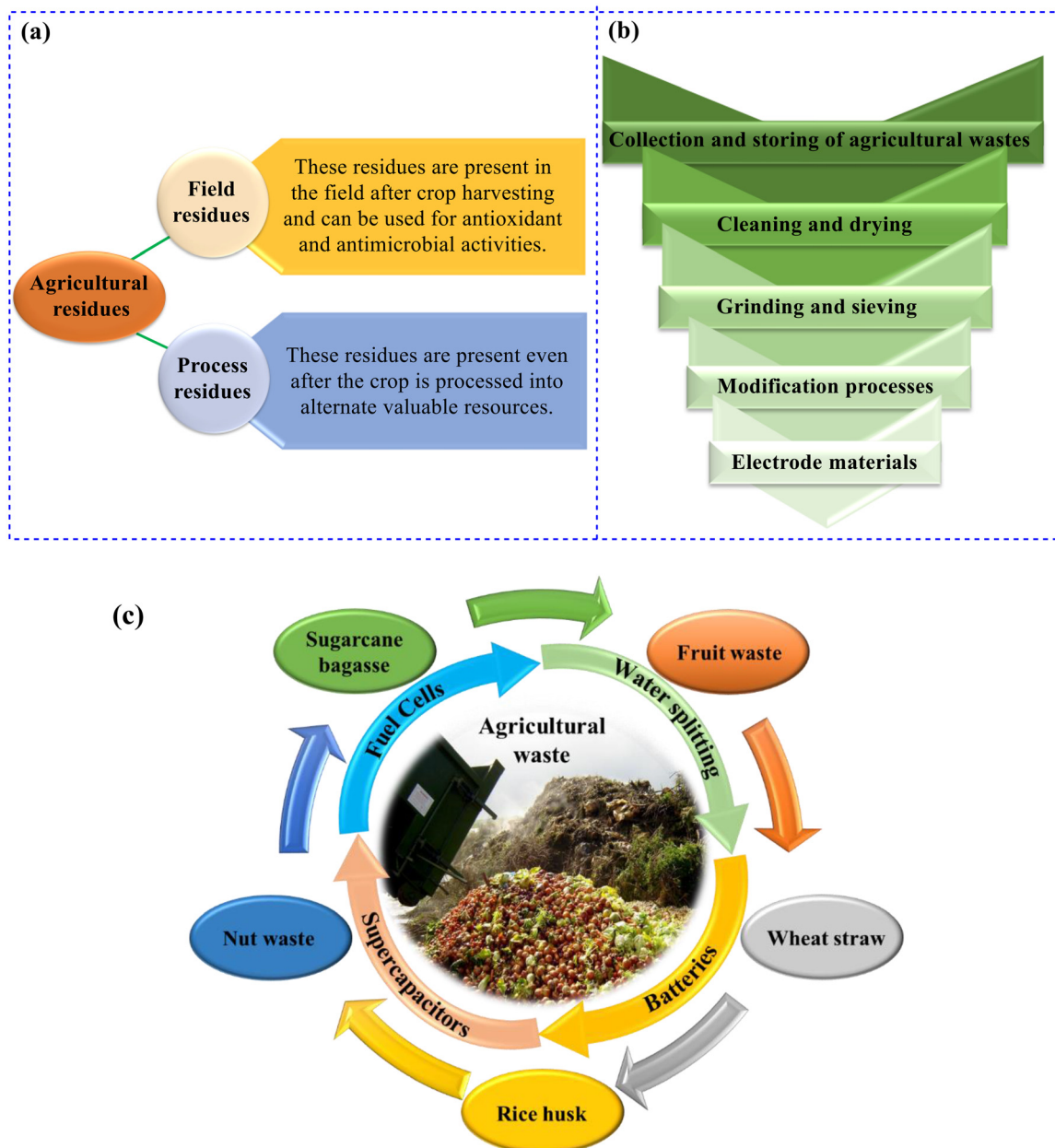
Fig. 2 Progress in interest for the application of agricultural waste in energy conversion and energy storage in the period 2000–2024 (source: Scopus; date: 24 Aug 2024).

ration of the MFC device, have inevitably restricted the widespread application of MFCs and should be improved.<sup>83,84</sup>

Today, a large number of electrodes used in various applications, such as energy production or storage, are made of carbon-based materials.<sup>63</sup> Some of these carbon materials are derived from different compounds such as biomass or organic polymers,<sup>85–88</sup> and their greatest disadvantage is their relatively low capacity in non-aqueous electrolytes. Conversely, some researchers have developed electrodes using carbon derived from polymers,<sup>89,90</sup> which can be either expensive or involve costly carbon production processes. Therefore, finding compounds that are carbon-rich and cheap is a very important issue. In this field, agricultural waste has been widely used in recent years (Fig. 2). Agricultural waste is a rich source of carbon, from which carbon can be extracted through relatively inexpensive processes and used to fabricate electrodes for various applications.<sup>91–93</sup> Another characteristic of agricultural waste is that it is a cost-effective, biodegradable, environmentally friendly, readily available, and renewable natural resource. All residues and by-products from the agriculture, forestry, farm animal, and agriculture-based industries are called agro-industrial wastes.<sup>94</sup> Duhan *et al.* and Bajić *et al.* reported that agro-industrial wastes could be categorized as agricultural residues, and this could be further divided into field residues (such as corn stalks, sunflower stalks, wheat straw, rice straw (RS), oat straw, leaves, *etc.*, remaining in the field after crop

harvesting), process residues (such as corncobs, wheat chaff, rye chaff, rice chaff, coffee husk, groundnut husk, *etc.*, obtained after crop processing) (Fig. 3a), industrial residues (such as cassava peel, potato peel, orange peel (OP), apple peel, tomato pomace, grape pomace, frying oil, *etc.*, produced by the food industry after the primary processing of raw material) and industrial by-products (whey, crude glycerol, oil cakes, bagasse, *etc.*, generated by the food industry at the end of processing).<sup>20,94</sup> These agricultural wastes can serve as efficient electrode materials for different energy conversion and storage purposes. Fig. 3b displays the general procedure for the preparation of electrode materials from agricultural wastes.<sup>14,95–102</sup> Different methods are employed for producing carbon from biowaste, each path resulting in diverse properties based on end-user requests. Porosity and surface area are the two critical aspects with significant effects on the energy storage capabilities of the carbon nanostructures generated, the high surface area of which prevents supercapacitive performance due to low porosity. Therefore, studies dealing with the tuning of the porosity in these carbons for improving the performance of energy storage devices (supercapacitors) are valuable.<sup>103</sup>

In this review, recent developments in the preparation of agricultural waste-derived (carbon/nano)materials for advanced energy conversion and storage are investigated. The applications of agricultural residues including RH, RS, wheat



**Fig. 3** (a) Categorization of agricultural waste, (b) common preparation techniques for converting agricultural waste into electrode materials, and (c) diverse types of agricultural waste for energy conversion and storage.

straw, fruit, and nut residues such as shell, pomace, stone, bagasse, *etc.* for energy conversion and storage are also reviewed (Fig. 3c).

## 2. Various types of agricultural waste

### 2.1 Rice husk

One of the primary agricultural wastes is RH, which is produced in rice-growing countries. RH is one of the side products of rice grain formed in the rice production process.<sup>104,105</sup> The results of various analyses have shown that

RH contains carbon (9.55–18.74%), oxygen (30.90–35.51%), silica (58.19–43.17%), and potassium (1.36–1.66%).<sup>106,107</sup> Internationally, approximately 545 million tons of RH are produced yearly, which is one-fifth of the gross production of rice every year.<sup>108</sup> RH is usually burned by farmers, which causes pollutants and the emission of greenhouse gases, while it can be a useful resource for various applications.<sup>109,110</sup> RH is a rich source of carbon and silica.<sup>111–115</sup> Carbon derived from RH can be converted into PC or AC.<sup>115,116</sup> RH has various uses including catalysts for chemical transformations, pollutant absorbents, and energy production and storage.<sup>116–120</sup> According to reports, RH is mostly used in the energy field to

make all kinds of lithium batteries, which could be related to the high amount of carbon in its structure.<sup>121,122</sup>

## 2.2 Fruit peels

Every year, large amounts of fruit peels are produced by the food-processing industry.<sup>123,124</sup> Fruit peels are natural compounds and are biodegradable. However, large amounts of them accumulate in nature and can cause environmental pollution. Fruit peels contain useful compounds such as carbon, flavonoids, vitamins, *etc.*, which can be converted into high-value-added materials by various methods.<sup>123,125,126</sup> One of the most important applications of fruit peels is the production of biogas and bioethanol.<sup>127,128</sup> Some fruit peel extracts have antimicrobial properties.<sup>129,130</sup> In addition, as previously pointed out, fruit peels have flavonoids in their chemical structures and can thus be applied for the synthesis of different nanoparticles (NPs).<sup>43,131</sup> Fruit peels include pomelo, pomegranate, banana, citrus, *etc.* Moreover, fruit peels are a rich source of carbon. The most important application of the carbons extracted from fruit peels is to make all kinds of electrodes. These electrodes are used for energy storage applications and are very effective because they have a natural source and are made from environmentally friendly and readily available compounds.<sup>132,133</sup>

## 2.3 Bagasse

Bagasse is produced by crushing and extraction of sugarcane juice. Bagasse is one of the most important agricultural residues in the world.<sup>134,135</sup> Different analyses indicate that sugarcane bagasse has different portions of materials including lignin, cellulose, hemicellulose, wax, and ash.<sup>136,137</sup> The materials present in the sugarcane bagasse indicate that this agricultural waste has many applications in different fields such as catalysis, fiber reinforcement in composites, adsorption of pollutants, biodegradation of crude oil polluted systems, electrodes, production of bioethanol, *etc.*<sup>138–143</sup> Bagasse is mostly applied for the production of electricity for cogeneration boilers in sugar manufacture, and the surplus electricity is exported to the grid.<sup>144</sup> As mentioned, bagasse is a rich source of cellulose and lignin. One of the ways to use this agricultural waste is to extract cellulose and lignin from it, which can then be used for various applications.<sup>145–148</sup> It is also possible to prepare carbon from bagasse and use it in different forms such as PC, AC, *etc.* to make electrodes.<sup>149–153</sup> Bagasse has mostly been used to make LIBs and supercapacitors.<sup>149,150,152,153</sup> Moreover, there are also examples of energy conversion using bagasse.<sup>134,154</sup>

## 3. Agricultural waste-derived (carbon/nano)materials for energy conversion and storage

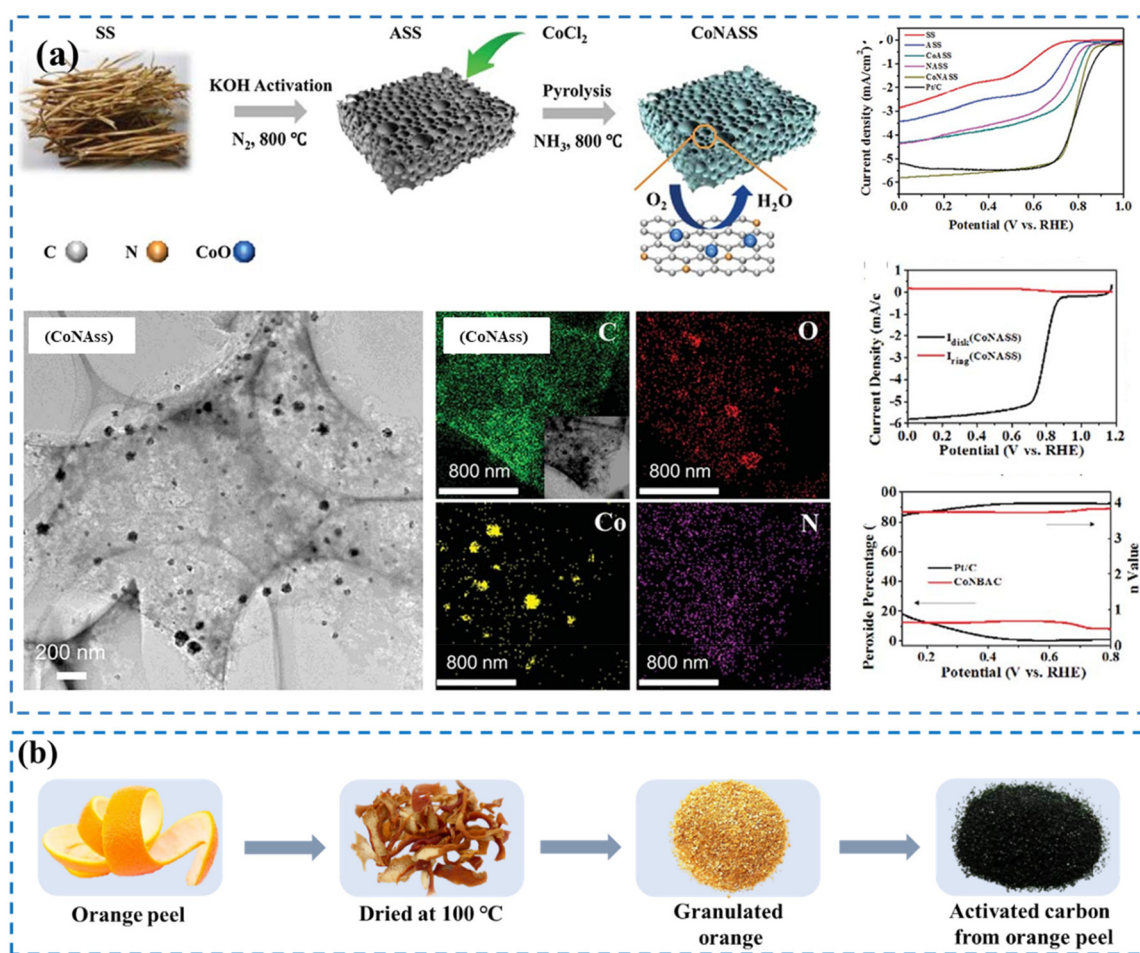
In recent years, owing to the rapid consumption of fossil fuels and as a result, the lack of energy, as well as environmental

pollution and greenhouse effects, the production of clean energy and sustainable energy conversion technologies have gradually become common and popular topics among researchers. To store and use clean energy at any time, different electrochemical energy storage devices were developed. These devices include supercapacitors, solar cells, and various types of batteries. Theoretically, the energy storage activity of the devices mentioned mostly depends on the electrode materials. Agricultural waste-derived (carbon/nano) materials are excellent choices for these purposes because these materials have many advantages such as accessibility, non-toxicity, low price, and some useful functional groups. In this section, recent studies focusing on the conversion of energy using agricultural waste-derived (carbon/nano) materials are summarized. In addition, recent progress in the application of agricultural waste-derived (carbon/nano) materials in supercapacitors, solar cells, and different types of batteries is reported.

### 3.1 Fuel cell electrode reactions

FCs are energy conversion systems, which transform chemical energy into electrical energy through fuel oxidation. These conversion systems have many advantages such as cost-effectiveness, excellent efficiency, high energy density, *etc.* An FC contains different parts, namely, electrolytes, a cathode, an anode and an external circuit called the load. The fuel and oxidant reach the anode and cathode, respectively. Fuels can be pure hydrogen (H<sub>2</sub>) and gaseous hydrogenated compounds (such as MeOH and EtOH) as well as oxidants including pure O<sub>2</sub> and oxygenated gaseous compounds (such as air and halogens). FC reactions are categorized into different groups including ORR, MOR, EOR, glycerol oxidation reaction, *etc.*<sup>155,156</sup> In this context, two types of FC reactions, namely, ORR and MOR, which use agricultural waste-derived (carbon/nano)materials, are summarized.

**3.1.1 Oxygen reduction reaction (ORR).** The ORR is a significant limiting factor to affect FCs. Therefore, various ORR electrocatalysts have been under investigation in recent years.<sup>65,156–158</sup> Furthermore, conventional compounds for the synthesis of electrode materials, such as polypyrrole, porphyrin-based materials, and metal–organic frameworks (MOFs) have some disadvantages, making their large-scale production difficult due to the relatively cumbersome and expensive preparation process.<sup>159–161</sup> Recently, there have been some studies using agriculture-based materials for ORR applications.<sup>162–164</sup> In a study in 2019, Lu and his group used soybean straw (SS) biomass as a carbon source to design cobalt and nitrogen-doped (N-D) porous biocarbon electrocatalysts (CoNASS) with a high N content (1.92%) and embedded cobalt NPs with a specific surface area of 1185 m<sup>2</sup> g<sup>-1</sup> and sponge-like structure (Fig. 4a).<sup>165</sup> The half-wave potential of commercial Pt/C (CPC) is 0.827 V (*vs.* RHE (reversible hydrogen electrode)) whereas the corresponding value for CoNASS is 0.786 V (*vs.* RHE), which shows the better efficiency of the manufactured electrode. The HRTEM and elemental mapping results for CoNASS are displayed in Fig. 4a.



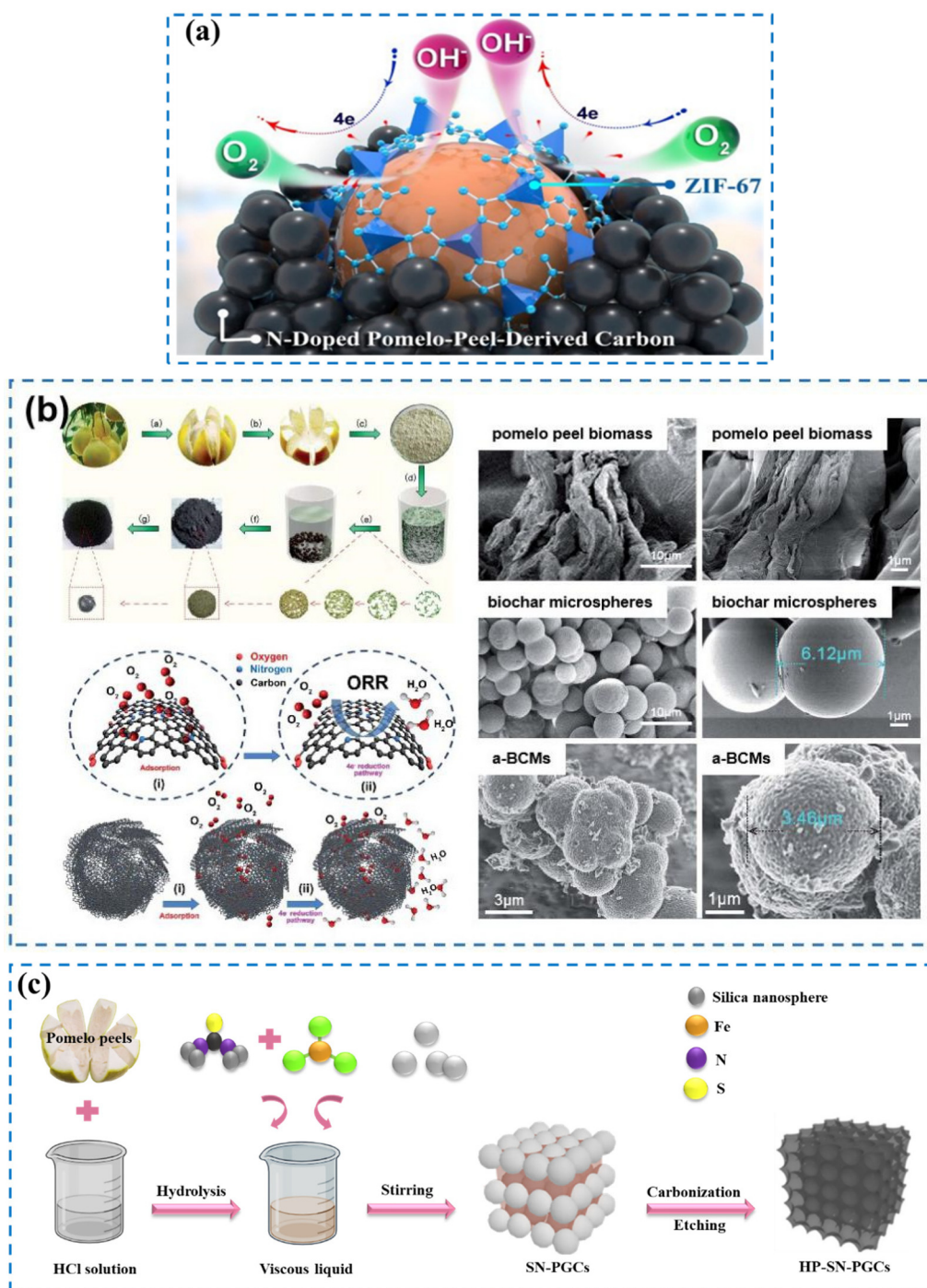
**Fig. 4** (a) Schematic representation of the formation of N and Co co-doped CoNASS, HRTEM image and elemental mapping of CoNASS, ORR performance, linear scan voltammetry (LSV) curves of SS, ASS, NASS, CoASS, CoNASS, and Pt/C in O<sub>2</sub>-saturated 0.1 M KOH solution at 1600 rpm (top), LSV curve of CoNASS in 0.1 M KOH solution at 1600 rpm obtained from rotating ring-disk electrode measurements (center), H<sub>2</sub>O<sub>2</sub> yield and *n* value of CoNASS and Pt/C (bottom). Reproduced from ref. 165 with permission from Royal Society of Chemistry, copyright 2019. (b) Steps in the preparation of AC from OP. Reproduced from ref. 166 with permission from Elsevier, copyright 2017.

The preparation of Pt-supported AC electrodes from orange peel (Pt/OP-AC) was reported by Kalpana and co-workers. The Pt/OP-AC electrode was applied for supercapacitor and ORR applications.<sup>166</sup> Their results revealed that the AC-derived OP had a high specific capacitance of 275 F g<sup>-1</sup>. This feature has made OP an excellent source for the preparation of AC. Fig. 4b shows the steps for the preparation of AC from OP.

MOFs are compounds with porous structures, which are assembled from metallic nodes and organic linkers with high specific surface areas, tunable pore structures, simplicity of functionalization, and several compositions.<sup>167,168</sup> In 2017, Yin *et al.* prepared N-D pomelo peel-derived carbon (NPC) using melamine and pomelo peel (PP) waste.<sup>169</sup> The prepared NPC showed good porosity with a high nitrogen content. It afforded a good catalytic performance toward the ORR in alkaline electrolytes. Furthermore, NPC was combined with ZIF-67 to prepare ZIF-67@NPC hybrids (Fig. 5a). The designed hybrid catalysts displayed markedly greater activities in comparison with 20 wt% CPC.

Valuable metallic ORR catalysts have been broadly applied as cathodes, owing to their high electrocatalytic potential.<sup>170</sup> However, scarcity, high cost, methanol intolerance, and a lack of stability have limited the application of ORR catalysts in MFCs.<sup>171–173</sup> In 2020, Zhou *et al.* reported the preparation of a PC cathode from RHs through hydrolysis, activation, and rolling.<sup>174</sup> This study afforded a BET surface area of 1809 m<sup>2</sup> g<sup>-1</sup> with a maximum powder density of 317.7 ± 0.4 mW m<sup>-2</sup>. In addition, Lin and co-workers prepared N-D PC from RH, which had a similar electrocatalytic performance, better stability, and MeOH toxicity resistance in comparison with the CPC catalyst.<sup>175</sup>

In another study in 2020, Deng and co-workers explored metal-free FCs based on renewable, naturally abundant PP.<sup>176</sup> They developed two kinds of N-D carbon catalysts from PP *viz.* biochar microspheres (BCMs) and their activated porous counterparts (a-BCMs) (Fig. 5b). The designed a-BCMs were employed for the cathodic ORR in MFCs. These a-BCMs showed a high porosity and great specific surface area with an



**Fig. 5** (a) Schematic representation of ZIF-67@NPC for ORR and OER.<sup>169</sup> (b) Schematic representation and images showing the preparation of BCMs and a-BCMs, SEM images, and illustration of carbocatalysis of the ORR over a-BCMs: (i) fast adsorption of O<sub>2</sub> and (ii) interfacial carbocatalysis of the ORR over the catalytically active sites via the 4e<sup>-</sup> reduction pathway, with the assistance of the conductive carbon framework. Reproduced from ref. 176 with permission from Royal Society of Chemistry, copyright 2020. (c) Synthesis route to HP-SN-PGCs. Reproduced from ref. 178 with permission from Elsevier, copyright 2019.

appropriate amount of graphitic N and pyridinic N doping in the strong conductive carbonaceous background. The utilization of a-BCMs as the cathodic catalyst resulted in a power density of 907.2 mW m<sup>-2</sup>. The SEM images of PP, BCMs, and a-BCMs are displayed in Fig. 5b.

Lignin-based mesoporous carbonaceous compounds have been the center of wide consideration in recent studies owing to their high carbon content. In 2019, Peng and co-workers reported the preparation of sulfur and nitrogen co-doped carbon nanosheets using bagasse lignin-derived carbon (LC).<sup>177</sup> The

LC-4-1000 sample afforded a large pore volume of  $1.40 \text{ cm}^3 \text{ g}^{-1}$  with a high surface area of  $1208 \text{ m}^2 \text{ g}^{-1}$ . LC-4-1000 had a higher positive half-wave potential and current density in comparison with those of CPC for the ORR in an alkaline medium.

In another study in 2019, Dai *et al.* used silica nanospheres as templates to organize highly-porous metal-free nitrogen/sulfur co-doped partially-graphitized carbon (HP-SN-PGC) in which pectin extracted from PP was a source of carbon (Fig. 5c).<sup>178</sup> HP-SN-PGC was employed as a cathode for the ORR. SC-MFC employing the HP-SN-PGC-0.5 cathode with 0.5 g silica represented the shortest start-up period (45 h) and a power density of  $1161.34 \text{ mW m}^{-2}$ , which was higher than that of Pt/C ( $1116.90 \text{ mW m}^{-2}$ ).

Biomass, including SS,<sup>165</sup> OP,<sup>166</sup> PP,<sup>169</sup> RHs,<sup>174</sup> and bagasse lignin,<sup>177</sup> is used as a carbon source to design porous biocarbon electrocatalysts for the ORR. The catalytic activities and efficiency of these electrocatalysts were compared with those of a conventional electrode such as Pt/C. In addition to economic and environmental superiority, they exhibited better performance in spite of the multi-stage and long preparation process in some cases.<sup>179–183</sup> The higher activities of electrocatalysts may be related to the porosity and active sites of carbon-based catalysts derived from biomass.

**3.1.2 Methanol oxidation reaction (MOR).** The MOR is a serious subject in studies on the direct methanol fuel cell

(DMFC) as a power source for electric/electronic vehicles and devices.<sup>184,185</sup> In the past years, there have been some studies in this field in which agriculture-based materials were used for the MOR.<sup>154,186</sup> One of the most common types of agricultural waste is sugarcane.<sup>154</sup> After extracting sugarcane juice, its residue, which is called bagasse, is widely available in nature and has produced certain environmental difficulties. Bagasse can be used for some applications. For example, in 2017, Zou and colleagues investigated the synthesis of porous  $\text{MoS}_2/\text{N-D}$  carbon ( $\text{MoS}_2/\text{CN}_x$ ), which was applied as a support for Pt (Fig. 6a).<sup>187</sup> They used bagasse waste as an efficient source of carbon materials in the MOR, due to its high surface activity and good mass performance. The prepared  $\text{Pt}/\text{MoS}_2/\text{CN}_x$  material was applied for the MOR (Fig. 6b).  $\text{CN}_x$  has rich binding sites for the growth and dispersion of  $\text{MoS}_2$  particles. According to the experimental results,  $\text{Pt}/\text{MoS}_2/\text{CN}_x$  showed a higher mass performance than CPC ( $1030.2$  vs.  $405.4 \text{ mA mg}_{\text{Pt}}^{-1}$ ). However,  $\text{CN}_x$  has plentiful attachment sites for anchoring Pt. In addition,  $\text{MoS}_2/\text{CN}_x$  has many oxygen-containing functional groups, which lead to the oxidation of intermediates (CO-species) on the active sites of Pt.

In another example in 2021, Ishak and co-workers developed an efficient technique for the manufacture of Pt NPs through a bioreduction process.<sup>188</sup> They used sugarcane (*Saccharum officinarum* L.) bagasse extract as a bio-based redu-

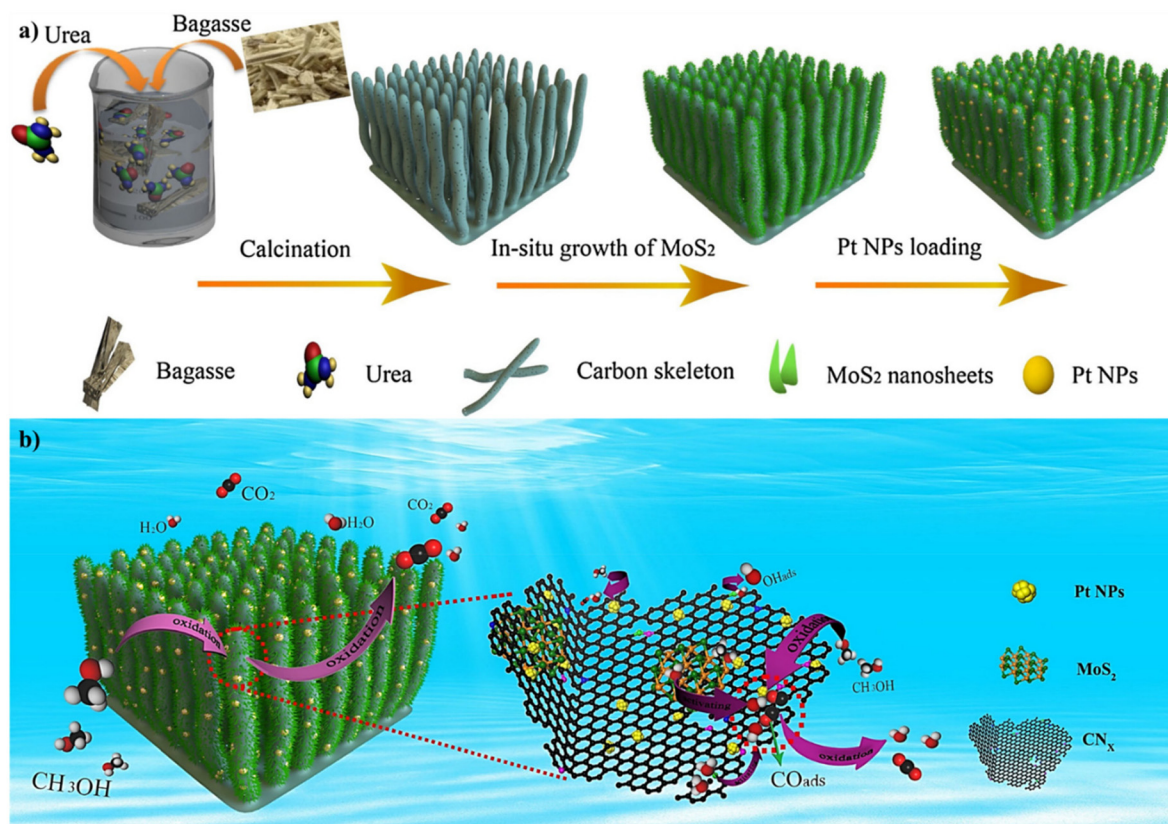
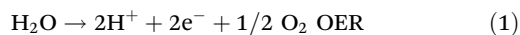


Fig. 6 Schematic representation of (a) the preparation of  $\text{Pt}/\text{MoS}_2/\text{CN}_x$  nanocomposites and (b) MOR using the  $\text{Pt}/\text{MoS}_2/\text{CN}_x$  catalyst. Reproduced from ref. 187 with permission from Elsevier, copyright 2017.

cing agent for the preparation of biogenic Pt NPs. The biogenic Pt NPs prepared have an electrochemical performance for the MOR. The biogenic Pt NPs displayed a high performance for the MOR with a high mass activity (about  $382.80 \text{ mA mg}^{-1}$ ). In addition, the green synthesis of Pt NPs based on OP extract, which is used as a green, inexpensive, and bio-based reducing agent, was developed by Karim and co-workers.<sup>189</sup> The Pt NPs prepared were then immobilized on carbon black for the MOR. Their experimental results revealed that the Pt NPs had a high performance for the MOR in a DMFC.

### 3.2 Electrochemical water splitting reactions

For many years, the application of a green source of energy has been one of the most important issues for researchers. Hydrogen, which is a green and environmentally friendly source of energy, can be produced by the electrolysis of water as well as electrochemical water splitting.<sup>190</sup> In this electrochemical reaction, water is split into its elemental components, namely,  $\text{H}_2$  and  $\text{O}_2$ . In fact, the electrochemical water splitting reaction involves two half-reactions, referred to as oxidation and reduction, which occur in the anode and cathode, respectively. The half-reactions of water oxidation and reduction are often referred to as the OER and HER, respectively. The OER and HER half reactions are displayed in eqn (1) and (2).<sup>191–193</sup> In this section, some reports on agriculture-based materials for the OER and HER are investigated.



**3.2.1 Oxygen evolution reaction (OER).** The OER is an important electrochemical reaction in electrolytic water-splitting and metal–air batteries to achieve clean energy production and efficient energy storage.<sup>194–197</sup> Today, the application of carbon derived from biowaste has attracted much consideration for the OER.<sup>198,199</sup> Among these, waste onion (*Allium cepa*) skins are important owing to their exclusive chemical

composition including S, N, and polyphenols. In a study in 2022, Kim and co-workers developed an effective technique for the synthesis of an electrocatalyst based on waste onion skins.<sup>200</sup> In fact, they developed a process for transforming waste onion skins into an efficient and very stable electrocatalyst. They prepared a core–shell material in which Fe– $\text{Fe}_3\text{C}$  particles and N-D carbon ( $\text{FO}_{800}$ ) were the core and shell, respectively. The  $\text{FO}_{800}$  material prepared displayed a high OER performance. Due to the presence of a protective carbon shell,  $\text{FO}_{800}$  showed high stability for 24 h. The  $\text{FO}_{800}$  sample displayed current densities of 10 and  $50 \text{ mA cm}^{-2}$  at low overpotentials (Ov) of 330 and 380 mV, respectively, with a Tafel slope of  $52 \text{ mV dec}^{-1}$ .

Some of the most important materials for OER catalysts are transition metal phosphates and phosphide.<sup>201–204</sup> In fact, the partially positive charge of the metals is applied as an acceptor of hydroxyl, which becomes the active center for the OER. For example, in 2022, Zhang and colleagues investigated the synthesis of an efficient bifunctional catalyst for the ORR/OER.<sup>204</sup> For this aim, they used crude wheat straw, which contained a large amount of cellulose and was a green source of carbonaceous compounds. They synthesized novel Fe/Co bimetallic phosphide NPs embedded in N, P dual-doped carbon matrix ( $\text{FeCoP}_2\text{-NPWC}$ ) (Fig. 7) for catalyzing the ORR and OER. The  $\text{FeCoP}_2\text{-NPWC}$  catalyst exhibited an excellent ORR performance with a half-wave potential of 0.85 V (*vs.* RHE) and a limiting current density of  $6 \text{ mA cm}^{-2}$ , which surpassed that of the Pt/C catalyst. It also exhibited an excellent OER performance and achieved an overpotential of 339 mV at a current density of  $10 \text{ mA cm}^{-2}$ . Subsequently, the prepared catalyst was used in a rechargeable zinc–air battery. The rechargeable liquid and solid zinc–air batteries achieved 122.5 and  $55.6 \text{ mW cm}^{-2}$  and were stable upon cycling for 110 and 35 h, respectively.

In another study, the preparation of an efficient and inexpensive bifunctional (OER and ORR applications) catalyst for Zn–air batteries was performed by Sumboja.<sup>205</sup> In fact, they used a heterostructure of carbon-containing graphitic and

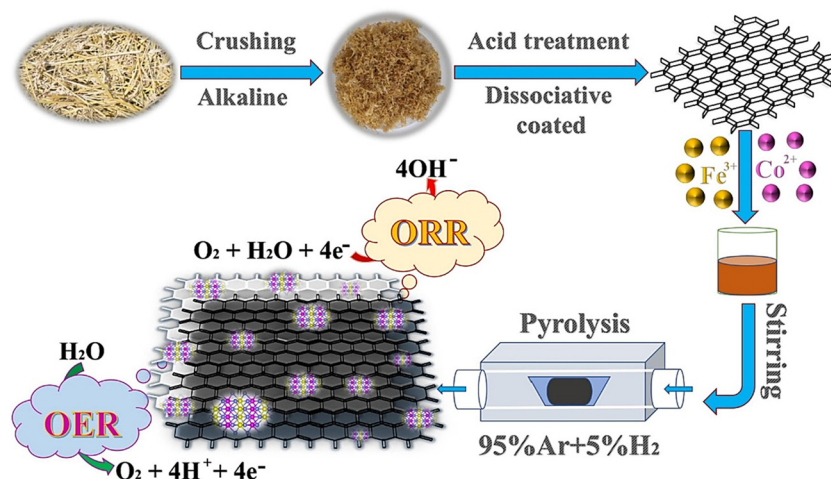


Fig. 7 Schematic representation of the synthesis of  $\text{FeCoP}_2\text{-NPWC}$ . Reproduced from ref. 204 with permission from Elsevier, copyright 2022.

amorphous carbon, which was derived from red bean pods as agricultural waste. The heterostructured carbon had a high surface area ( $625.5 \text{ m}^2 \text{ g}^{-1}$ ), showing an ORR onset potential of  $0.89 \text{ V vs. RHE}$  and an OER Ov of  $470 \text{ mV}$  at  $5 \text{ mA cm}^{-2}$ . To enhance the bifunctional performance of the catalyst, the prepared compounds were modified with nitrogen dopant and hollow FeCo NPs, to reach an ORR onset potential of  $0.93 \text{ V vs. RHE}$  and an OER Ov of  $360 \text{ mV}$ .

In the OER and ORR, waste onion,<sup>200</sup> crude wheat straw,<sup>204</sup> and red bean pods<sup>205</sup> were applied as green and low-cost precursors for the preparation of carbonous compounds to achieve heterogeneous catalysts. In some cases, more modification and functionalization are needed to reach acceptable efficiency despite the tedious preparation process.

**3.2.2 Hydrogen evolution reaction (HER).** Although non-noble metal-based carbon composites are widely utilized,<sup>206</sup> the application of biomass and agriculture waste-derived electrocatalysts is a significant consideration today.<sup>199,207</sup> Zhou and co-workers used watermelon peel to fabricate  $\text{Mo}_2\text{C}/\text{C}$  electrocatalysts through a two-step approach and pyrolysis process for HER applications.<sup>208</sup> The sample, denoted as  $\text{Mo}_2\text{C}/\text{C}-800 \text{ }^\circ\text{C}$ , showed a geometrical Ov of  $133 \text{ mV}$  to deliver a current density of  $10 \text{ mA cm}^{-2}$  in  $1 \text{ M KOH}$  solution with long-term durability for  $300 \text{ h}$ . This excellent HER performance is due to the large surface area, unique pore sizes of the  $\text{Mo}_2\text{C}/\text{C}$  electrocatalysts, and rich mass transfer of electrons.

Electrocatalyst powders based on transition metals have been broadly studied for the HER.<sup>209,210</sup> In 2020, Min and co-workers developed a self-supported  $\text{H}_2$  evolution cathode based on a PC membrane derived from PP (PPDC) with entrenched Co NPs ( $\text{Co@PPDC}$ ), which showed a high electrocatalytic performance for the HER in  $1 \text{ M KOH}$  solution with Ov values of  $154$  and  $264 \text{ mV}$  at current densities of  $10$  and  $100 \text{ mA cm}^{-2}$ , respectively.<sup>211</sup> Furthermore, the good structural integrity of  $\text{Co@PPDC}$  results in high cycling stability for  $2000$  cycles and a stable current density of  $\sim 100 \text{ mA cm}^{-2}$  at a constant Ov of  $265 \text{ mV}$  over  $12 \text{ h}$  with a faradaic efficiency and  $\text{H}_2$  production rate of almost  $100\%$  and  $1.56 \text{ mmol h}^{-1}$ , respectively.

A study by Yun *et al.* involved the successful preparation of a sequence of nano-sized bimetal (Al, Cr, and Fe) and niobium oxide NPs anchored on aloe peel (AP)-derived PC skeleton hybrids (AN/APPC, CN/APPC, and FN/APPC) through coprecipitation.<sup>212</sup> The prepared samples were used as electrocatalysts for the alkaline HER and in photovoltaic applications. The synergy between the highly conductive PC skeleton and nano-sized metal niobium oxides caused these robust poly-component hybrid electrocatalysts to display outstanding catalytic performance and accelerated triiodide reduction and the HER. A solar cell with an AN/APPC electrocatalyst afforded a high device efficiency of  $7.31\%$ , which was higher than that of Pt ( $6.84\%$ ), and the AN/APPC electrocatalyst showed an Ov of  $131.6 \text{ mV}$  with a current density and Tafel slope of  $10 \text{ mA cm}^{-2}$  and  $54 \text{ mV dec}^{-1}$ , respectively, in  $1 \text{ M KOH}$  for the HER. In addition, in 2020, Yoo and co-workers used golden shower pod biomass to synthesize PC or N-D porous carbon (N-PC). For

the HER and OER, N-PC@Ni displayed Ov values of  $179$  and  $314 \text{ mV}$  at  $10 \text{ mA cm}^{-2}$  and Tafel slopes of  $98$  and  $132 \text{ mV dec}^{-1}$ .<sup>213</sup>

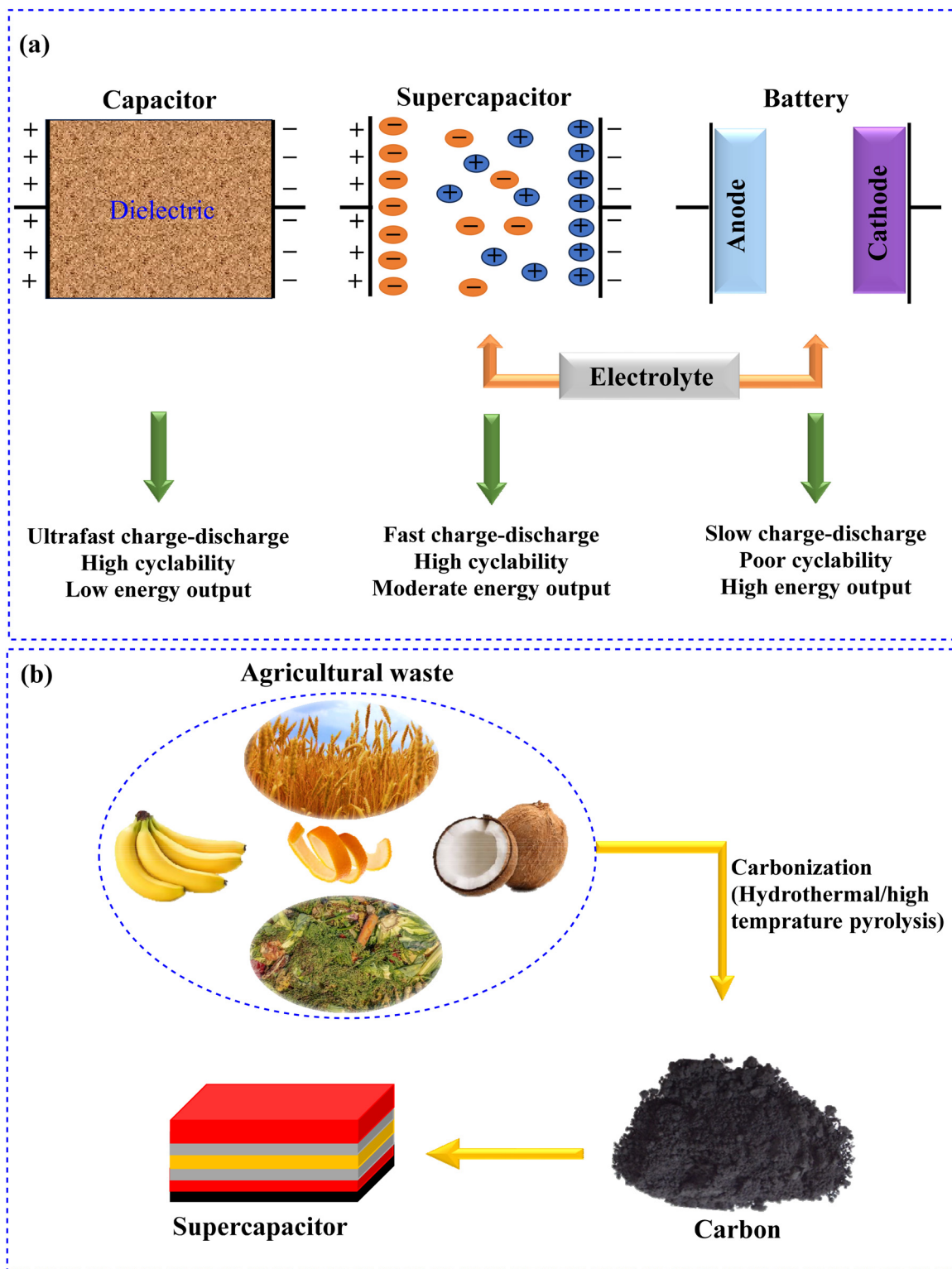
PCs derived from watermelon peel,<sup>208</sup> PP,<sup>211</sup> and AP<sup>213</sup> were used to generate heterogeneous catalysts for the HER. The catalysts prepared using waste materials exhibited good performance and stability, as indicated by essential performance data. Table S1† presents some other reports on the energy application of agricultural waste-derived materials. According to Table S1,† if PC is prepared from agricultural waste (in this table, most of the waste includes peels of various fruits such as bananas, grapefruit, pomelo, *etc.*), its specific surface area is relatively high, and as a result, it performs better. It is also possible to prepare metal-free N-D porous carbons with high specific surface areas (entry 12). In addition, this table shows that the carbon derivatives obtained from PP have higher specific surface areas than other waste and are very suitable for the ORR and OER.

### 3.3 Supercapacitors

Recently, there has been increasing interest in high power and high energy density storage systems.<sup>214</sup> Supercapacitor technology has made significant progress in recent years.<sup>215–217</sup> Supercapacitors consist of thin dielectric layers and high surface area electrodes. One noticeable advantage of supercapacitors in comparison with batteries is their higher power density. Furthermore, supercapacitors are more brilliant than traditional capacitors (Fig. 8a).<sup>218–220</sup> They have a robust thermal operating range, high power capability, many charging–discharging cycles, and a bridging function for the power/energy gap among traditional dielectric capacitors. Furthermore, agricultural waste can act as an important source for energy applications.<sup>221–224</sup> Since agricultural waste is renewable, abundant, and low-cost, its derivatives can be employed for several applications including energy storage systems.<sup>225–230</sup> It can be converted into carbon-based compounds including carbon nanotubes (CNTs), AC, porous (nano)carbon, *etc.*, which are used as electrodes (Fig. 8b).<sup>231–236</sup>

Carbon-based supercapacitors have several advantages including a fast charge–discharge rate, high power density, and long service life. Several types of biomass have been employed as precursors for carbonaceous compounds, including shaddock peel,<sup>237</sup> nuts and fruit peel,<sup>238–244</sup> RH,<sup>245,246</sup> RS,<sup>247,248</sup> wheat straw,<sup>249,250</sup> corn husk,<sup>251,252</sup> corn straw,<sup>253,254</sup> *etc.*

Table S2† presents the carbonaceous compounds from agricultural waste resources and some of their properties, which make them promising for supercapacitor applications. According to Table S2,† RH has a large specific surface area compared to other waste and its specific capacity is high, which makes it suitable for making electrodes for supercapacitor applications (entries 9, 12, 16, 17, 19, 21, 22 and 23). Carbon derivatives are prepared from them. Moreover, this table shows that most of the carbon derivatives prepared from waste are porous carbons, which are used with relatively high capacities to make supercapacitors.



**Fig. 8** (a) Comparison of batteries, conventional capacitors, and supercapacitors and (b) carbonization of agricultural waste and its applications in supercapacitors.

Biomass-derived PC materials show good conductivity, large specific surface areas and provide a framework for doping; especially N, O, P and S.<sup>255–258</sup> In addition, according to studies, the peels of citrus fruits constitute a high percen-

tage of the total fruit and are usually considered waste. Citrus fruit peels are known as good precursors of carbon since they are largely made of cellulose, hemicellulose, pectin, and lignin.<sup>259–261</sup> Mehare *et al.* developed a route to synthesize PC

materials from lemon peel for supercapacitor applications.<sup>262</sup> The synthesized compounds exhibited a high specific capacitance of  $121 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  in a system consisting of three electrodes and  $106 \text{ F g}^{-1}$  at a current density of  $0.2 \text{ A g}^{-1}$  in a symmetric device with a specific energy and power of  $11.84 \text{ W h kg}^{-1}$  and  $361.8 \text{ W kg}^{-1}$ , respectively, as well as cycling stability of 100% over 1000 cycles.

In another recent study by Li *et al.* in 2022, N, P doped PC nanosheets (NPCNs) were synthesized as high-performance supercapacitors using PP as a spongy structure to surround  $\text{NH}_4\text{H}_2\text{PO}_4$  particles as an activator and co-dopant.<sup>263</sup> Accordingly, the optimal sample obtained at a pyrolysis temperature of  $750 \text{ }^\circ\text{C}$  (denoted as NPCNs-750) showed a high specific capacitance of  $314 \pm 2.6 \text{ F g}^{-1}$  and good rate capability (retention of 82% of capacitance at  $20 \text{ A g}^{-1}$ ). Furthermore, NPCNs-750//NPCNs-750 SSC, the optimal sample, was employed as a symmetrical supercapacitor (SSC) in  $\text{Li}_2\text{SO}_4$  as an electrolyte and showed a high energy density of  $36 \pm 1.5 \text{ W h kg}^{-1}$  at a power density of  $1000 \text{ W kg}^{-1}$  with excellent cycling stability after 10 000 cycles with 99% retention.

In 2020, a research group synthesized and compared a sequence of carbon compounds from RH and bean dregs with diverse mass ratios.<sup>264</sup> The ratio of 1:1 presented a greater capacitive performance of  $319 \text{ F g}^{-1}$  at  $0.2 \text{ A g}^{-1}$  in a two-electrode system with a capacitance retention of 92.6% after 10 000 cycles. These results show that the synergistic effects of hierarchical porous structures and nitrogen content afford a promising suggestion for the production of high-performance supercapacitors. In other research, Shin *et al.* prepared AC papers as supercapacitor electrodes.<sup>265</sup> According to their results, the porosity and electrochemical efficacy of the compound depended strongly on the activation temperature. For example, the specific surface area of  $202.92 \text{ m}^2 \text{ g}^{-1}$  at  $500 \text{ }^\circ\text{C}$  increased to  $2158.48 \text{ m}^2 \text{ g}^{-1}$  at  $1100 \text{ }^\circ\text{C}$ .

Moreover, the proximate analysis of onion peels shows the presence of ~80% carbohydrates, which can be a good source of carbon.<sup>266</sup> Dhoble *et al.* effectively prepared hierarchical PC from onion peel through a double crucible system with a high specific capacitance of  $127 \text{ F g}^{-1}$  at a current density of  $0.75 \text{ A g}^{-1}$  with a capacitance retention of 109% after 2000 cycles in a three-electrode system in addition to an energy density of  $13.61 \text{ W h kg}^{-1}$  at a power density of  $200.8 \text{ W kg}^{-1}$  with noteworthy electrochemical stability and capacitance retention up to 100% over 14 000 cycles.<sup>267</sup>

In 2020, Musyoka *et al.* used hydrochar derived from waste onion peels to prepare AC.<sup>268</sup> The best sample showed a specific surface area of  $3150 \text{ m}^2 \text{ g}^{-1}$ , a pore volume of  $1.64 \text{ cm}^3 \text{ g}^{-1}$ , and hydrogen take up of above 3 wt%. It also showed a specific capacitance of  $169 \text{ F g}^{-1}$  at a specific current of  $0.5 \text{ A g}^{-1}$ . Furthermore, the compound displayed a high coulombic efficiency of 99.85% at  $5 \text{ A g}^{-1}$  after 10 000 cycles. In addition, Chaudhary *et al.* prepared ternary-doped layered graphene nanosheets from onion peel *via* a green pyrolysis synthesis method. The synthesized nanosheets were used for energy storage applications with a capacitance of  $450 \text{ A g}^{-1}$  at a current density of  $1 \text{ A g}^{-1}$  in  $2 \text{ M H}_2\text{SO}_4$  solution.<sup>269</sup>

As mentioned, biowaste is composed of carbon-rich compounds, which can be promising feedstocks for the preparation of AC as a potential electrode material in supercapacitors.<sup>270–272</sup> In 2021, Ajay and co-workers used OP as the precursor of AC (OPAC) and polyaniline to prepare polyaniline–OPAC nanocomposites as electrode materials for supercapacitors.<sup>273</sup> OPAC has a high surface area of  $904 \text{ m}^2 \text{ g}^{-1}$  and an average pore volume of  $0.5543 \text{ cm}^3 \text{ g}^{-1}$ . The polyaniline–OPAC electrode showed a specific capacitance of  $427 \text{ F g}^{-1}$  and a capacitance retention of 75% after 5000 cycles, which was better than that of pure OPAC.

In another study in 2021, Sathish *et al.* reported the preparation of S-doped graphitic carbon nitride/cobalt disulfide ( $\text{S-gC}_3\text{N}_4/\text{CoS}_2$ ) and OP-derived AC as positive and negative electrodes, respectively, to prepare a high-performance hybrid asymmetric supercapacitor with a very high current density of  $30 \text{ A g}^{-1}$  and high electrochemical stability of 89% over 100 000 cycles with a coulombic efficiency of 99.6%.<sup>274</sup>

Furthermore, bimetallic sulfides are an innovative type of electrode for supercapacitors because of their rich redox active sites, high conductivity, and wide operating potential window. In 2021, Xu and co-workers used Ni–Co sulfide hollow nanoboxes and RH AC as the anode and cathode, respectively, which afforded a remarkable energy density of  $46.7 \text{ W h kg}^{-1}$  at a power density of  $400 \text{ W kg}^{-1}$  and high cycling stability of 82.7% at  $5 \text{ A g}^{-1}$  after 10 000 cycles.<sup>275</sup>

Furthermore, Wang *et al.* prepared N-D PC from RHs in 2020.<sup>276</sup> The prepared nitrogen-containing PC (4NPC-800) showed a good volumetric capacitance of  $306 \text{ F cm}^{-3}$  at  $0.5 \text{ A g}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$  electrolyte and a superior volumetric energy density of  $15.24 \text{ W h L}^{-1}$  at  $594 \text{ W L}^{-1}$  as well as excellent cycling stability.

Moreover, wheat husk contains a high percentage of carbon, which makes it an essential precursor for AC production.<sup>277</sup> In 2021, Gul and Baig carbonized wheat husk to prepare AC (WHAC).<sup>278</sup> The  $\text{NiCo}_2\text{S}_4/\text{WHAC}/\text{Ni}$  electrode was synthesized through a hydrothermal process with a capacitance of  $1962 \text{ F g}^{-1}$  at a current density of  $1 \text{ A g}^{-1}$ .

In the same year, Niu *et al.* reported the preparation of capacitive carbons with high surface areas, uniform porous structures, and near-perfect graphitization structures employing corncob residues as the carbon source.<sup>279</sup> The material showed high specific capacities of up to  $394.9 \text{ F g}^{-1}$  at a current density of  $1 \text{ A g}^{-1}$ , a high energy density of  $8.9 \text{ W h kg}^{-1}$  at a current density of  $0.5 \text{ A g}^{-1}$ , and outstanding cycling stability (99% lifetime retention after 10 000 cycles).

Carbon dots (CDs) are well-known NPs with exceptional properties including nanometer size, various functional groups, high surface area, surface HA, and structural tunability. They can be equipped with available cheap precursors. CDs are rich in surface N and O-containing functional groups, which are known to improve electron transfer, ion adsorption, charge transport, hydrophilicity, surface wettability, and electrochemical conductivity and they can act as electron reservoirs. Moreover, they can introduce pseudo-capacitive behavior and promising contact between electrolytes and electrodes and

thus have been employed as additives in supercapacitor electrodes.<sup>280</sup> In 2019, Gomes and Hoang synthesized zucchini-derived CDs using zucchini waste with a porous nature and carbon and oxygen in the structure.<sup>281</sup> The prepared CDs were treated with graphene oxide to afford three-dimensional (3D) porous reduced graphene oxide/CD composites with a surface area and total pore volume of  $185 \text{ m}^2 \text{ g}^{-1}$  and  $0.58 \text{ cc g}^{-1}$ , respectively. The specific capacitance of the composite was  $374 \text{ F g}^{-1}$  at  $2 \text{ mV s}^{-1}$  with a high capacitance retention of 93.8% over 10 000 cycles at  $10 \text{ A g}^{-1}$ .

Moreover, biochar is known as a significant sort of carbon-based compound for preparing supercapacitor electrodes.<sup>282</sup> In 2018, Zhou *et al.* prepared PC from corn straw biochar and employed it as the electrode for electric double-layer capacitors in which the hierarchical micro-meso-macro-porosity meaningfully enhanced the activity of biochar-based carbons.<sup>283</sup> As observed, the surface area, pore volume, and maximum specific capacitance were  $2790.4 \text{ m}^2 \text{ g}^{-1}$ ,  $2.04 \text{ cm}^3 \text{ g}^{-1}$ , and  $327 \text{ F g}^{-1}$ , respectively. The prepared electric double-layer capacitors presented excellent cycling stability for 120 000 cycles at  $5 \text{ A g}^{-1}$  in alkaline electrolytes.

Furthermore, biomass-derived cellulose is a renewable, sustainable, low-cost, and biodegradable biopolymer with good thermal and electrochemical stability.<sup>284,285</sup> In 2021, Zhang *et al.* prepared an N-D PC derived from cellulose microfibrils of RS.<sup>286</sup> The organized carbon material had a moderate nitrogen doping of 1.65 at% and an ultrahigh specific surface area of  $\sim 2800 \text{ m}^2 \text{ g}^{-1}$ . In addition, the compound showed an outstanding specific capacitance of  $380.1 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  and capacitance retention of 61.8% at  $50 \text{ A g}^{-1}$ . The capacitance loss of this compound was only 4.6% after 10 000 charge-discharge cycles, indicating its good cycling stability.

Furthermore, in 2017, Song and co-workers used residual pre-cross-linked lignin from wheat straw to synthesize meso-structured carbon using Pluronic F127 and nano-sized MgO as templates with a specific surface area, total pore volume, and mesopore content of  $712 \text{ m}^2 \text{ g}^{-1}$ ,  $0.90 \text{ cm}^3 \text{ g}^{-1}$ , and 83%, respectively, which proved to be promising for supercapacitor applications.<sup>287</sup>

Different types of biomass including lemon peel,<sup>262</sup> PP,<sup>263</sup> RH and bean dregs,<sup>264</sup> onion peel,<sup>267,268</sup> OP,<sup>273,274</sup> RH,<sup>275,276</sup> banana peel,<sup>288</sup> Jackfruit,<sup>289</sup> *etc.* are employed alone or in combination with other compounds to generate PC as an active and porous component of supercapacitors. High stability, good specific capacitance, and improved specific surface area are the advantages and multi-step synthesis processes, unintelligible final structure, and the need for more modifications are the disadvantages of biowaste-based supercapacitors. However, the high demand for new sources of energy justifies research on this topic.

More studies are focusing on the preparation of supercapacitors from agricultural waste. Table S3† briefly summarizes these studies. According to Table S3,† the electrodes prepared from different agricultural wastes and metals placed on them during electrode preparation have high specific capacities. Of course, this table shows that nitrogen or sulfur-

doped carbon metal-free electrodes can also have a relatively high specific capacity (entries 2 and 4). In addition, AC and PC derived from some wastes alone are suitable options for making electrodes because they have relatively high capacitances (entries 9, 10, and 12). This shows that this waste, which includes corn husk, garlic peel, and mung bean husk, is very suitable for making electrodes.

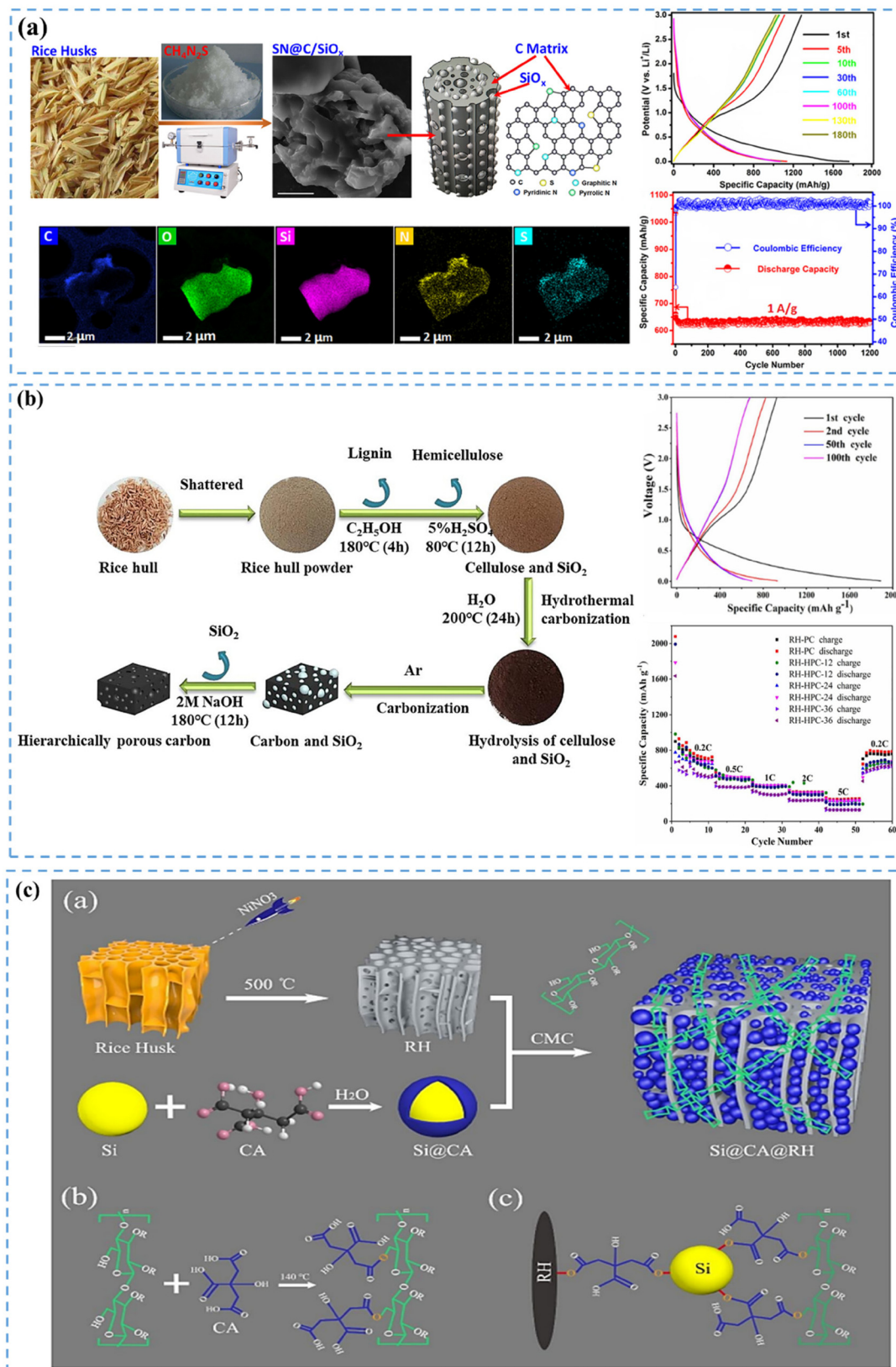
### 3.4 Batteries

Today, with the industrialization of human societies, the pursuit of sustainable development for the entire human race faces significant challenges. Burning different fuels causes global warming and air pollution. Thus, today, the production of energy from renewable sources is a very important and necessary matter. One of the most promising devices for energy storage is rechargeable batteries, which are broadly applied in electric vehicles. These batteries have many advantages, the most important of which are their simple technology and environmentally friendly nature.<sup>290-292</sup>

**3.4.1 Li-ion batteries.** Among various kinds of rechargeable batteries, LIBs are the most important owing to their great energy density, the absence of any memory results, and only a gradual loss of capability when not in use.<sup>293</sup> In other words, LIBs play an important role in today's modern world.<sup>294,295</sup> Some researchers have used natural and biowaste sources for the preparation of these LIBs.<sup>296,297</sup> In this section, the applications of different agricultural wastes for the synthesis of LIBs are reported.

One of the most commercial anodes applied for the preparation of LIBs is graphite. However, graphite cannot meet the future demands of people because of its small theoretical capacity. Thus, researchers have investigated novel promising anode materials.<sup>298,299</sup> RH is an abundantly accessible agricultural waste, which is a rich source of silica and carbon. In a study in 2021, Dawei and colleagues reported the synthesis of the RH-based  $\text{SiO}_2/\text{C}$  composite and applied it as a promising anode material for the preparation of LIBs.<sup>300</sup> On the other hand, they prepared  $\text{SiO}_2/\text{C}$  by adjusting the ash content of pyrolyzed RH with NaOH solution and studied the effect of ash amount variations on the Li storage efficiency of  $\text{SiO}_2/\text{C}$ . Their experimental results revealed that 19.2 wt% ash had a greater reversible capacity of  $886 \text{ mA h g}^{-1}$  at  $200 \text{ mA g}^{-1}$ . In another study performed by Sun and colleagues, the construction of S/N dual-doped porous  $\text{C}/\text{SiO}_x$  composites ( $\text{SN@C}/\text{SiO}_x$ ) was investigated (Fig. 9a).<sup>301</sup> For this aim, they used RH as a source of Si and C and applied thiourea as a source of N and C. The  $\text{SN@C}/\text{SiO}_x$  material synthesized, as a high-performance LIB anode, provided a remarkable particular capacity ( $1150 \text{ mA h g}^{-1}$ ). EDX mapping results for  $\text{SN@C}/\text{SiO}_x$  and the charge/discharge curves are displayed in Fig. 9a.

Today, the use of carbon materials to build new anodes is of great interest to researchers because these compounds have different advantages such as abundant pores, high specific surface areas, and stable features. Carbon-based anode materials have different pore sizes, corresponding to microporous  $< 2 \text{ nm}$ ,  $2 \text{ nm} <$  mesoporous  $< 50 \text{ nm}$  and  $50 \text{ nm} <$



**Fig. 9** (a) Schematic representation of the green route to synthesize SN@C/SiO<sub>x</sub> composite and its structure, galvanostatic discharge–charge profiles at 0.1 A g<sup>-1</sup>, and long cycling property at 1 A g<sup>-1</sup>. Reproduced from ref. 301 with permission from Elsevier, copyright 2021. (b) Schematic representation of the preparation procedure for RH cellulose-based PC material, charge and discharge characteristics and cycle curves. Reproduced from ref. 304 with permission from Elsevier, copyright 2021. (c) Graphical drawing of the self-assembly procedure for the Si@CA@RH composite, the cross-linking process between CMC and CA, and a schematic of the chemical connections of RH, CA, Si and CMC. Reproduced from ref. 308 with permission from American Chemical Society, copyright 2020.

macroporous.<sup>302,303</sup> For example, in a study in 2021, Liang and colleagues investigated the synthesis of RH-derived porous carbon materials (RH-PC and RH-HPC- $x$  ( $x = 12, 24, 36$ )) as anodes for LIBs.<sup>304</sup> For this aim, they used SiO<sub>2</sub>-derived RH as an eco-friendly source and applied it as a template for the preparation of porous hard carbon (HPC) compounds (Fig. 9b). Their results revealed that the synthesized material had an exclusive PC structure containing micropores, mesopores, and macropores. The porous carbon material hydrothermally treated for 24 h showed an excellent electrochemical performance. The discharging specific capacity of biomass hard carbon can reach 679.9 mA h g<sup>-1</sup> after 100 cycles at a current density of 0.2 C. The charge and discharge characteristics and cycle curves are displayed in Fig. 9b. In another study, the preparation of N-enriched PC/SiO<sub>2</sub> (SiO<sub>2</sub>/NC) composite derived from RH using ball milling was performed by Wang *et al.*<sup>305</sup> They used the SiO<sub>2</sub>/NC composite as an anode for LIBs. In addition, they prepared optimum SiO<sub>2</sub>/NC composites using different N precursors, such as melamine and urea, and different N-D techniques, including dry and wet ball milling. The results showed that the optimum SiO<sub>2</sub>/NC composite was prepared using urea as the N precursor and the dry ball milling technique, which delivered a stable reversible capacity of 581 mA h g<sup>-1</sup> at a high current loading of 1 A g<sup>-1</sup> in the 1000<sup>th</sup> cycle.

Recently researchers developed the application of citric acid (CA) as a coating layer for the Si surface to avoid the uncontrollable growth of the solid electrolyte interface during cycling.<sup>306,307</sup> Xu and co-workers developed a method for the preparation of a stable silicon/carbon anode composite.<sup>308</sup> They enhanced the cycling performance and stability of the composite using CA. On the other hand, Si NPs encapsulated using CA could maintain the bond with the carbon structure through ester bonds (Fig. 9c). According to Fig. 9c, CA-coated Si particles were cross-linked with sodium carboxymethyl cellulose (CMC). In addition, the RH-derived carbon network was used for the structural stability of the electrode and facilitated the electronic conduction network. The Si@CA@RH electrode showed a stable capacity and high coulombic efficiency of 2126 mA h g<sup>-1</sup> and 99.5% after 250 cycles, respectively; these values are very appropriate for high-performance LIBs.

Today, metal oxides can be applied as anode replacements for conventional carbon compounds due to some advantages such as a great theoretical capacity, cost-effectiveness, and exceptional Li storage mechanisms.<sup>309,310</sup> One of the most promising metal oxides is zinc oxide, which is very appropriate for anode materials.<sup>311,312</sup> In 2020, Liang and colleagues successfully carried out the preparation of efficient anode materials using flower-like ZnO, which was combined with hollow carbon derived from RH (RHC).<sup>313</sup> The prepared ZnO/RHC composite was used as the anode for LIBs, which displayed exceptional electrochemical activity and cycling stability. The ZnO/RHC composite had a sheet structure containing ZnO, which was coated on the biomass carbon layer to make many conductive networks. The abovementioned structure improved the electrochemical performance of the ZnO/RHC

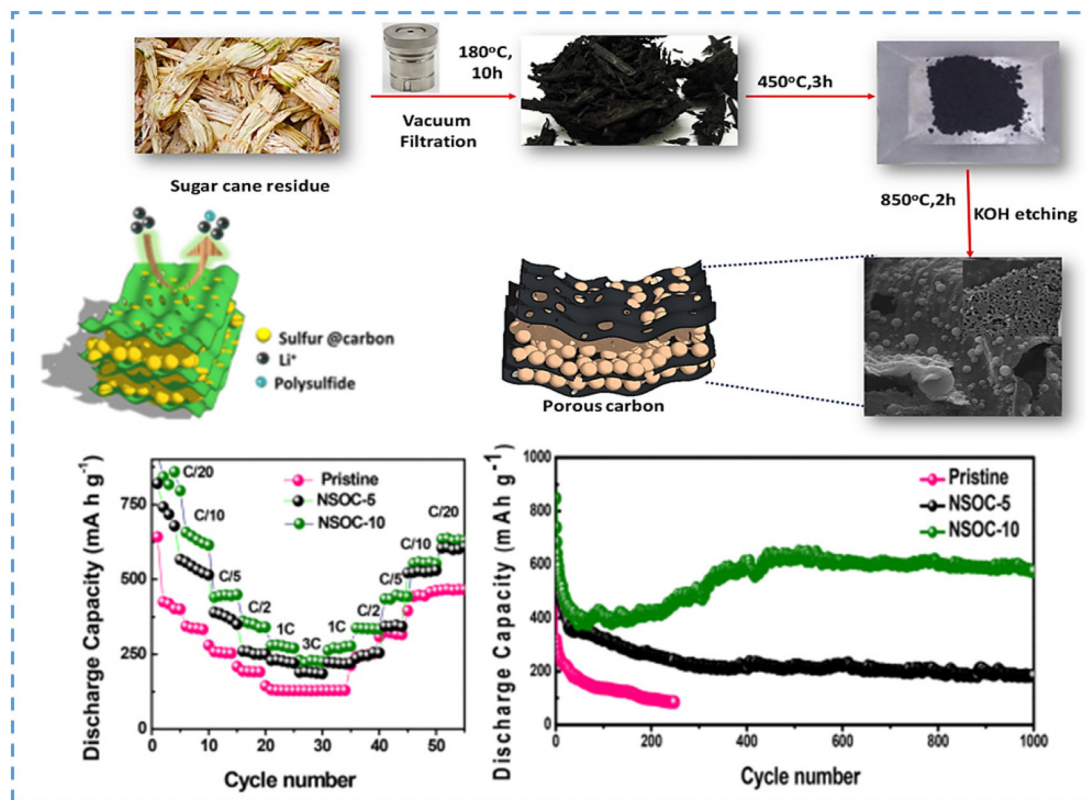
composite. The ZnO/RHC composite had the highest specific capacity of 1002.5 mA h g<sup>-1</sup> after 160 cycles at 0.2 C, which was much higher than the specific capacity of ZnO.

Graphene quantum dots (GQDs) are a member of the graphene family and their most important feature is their nanoscale dimensions.<sup>314</sup> GQDs can be applied as modified compounds to improve the properties of raw materials. In 2020, Li *et al.* reported the synthesis of AC derived from RH, which was modified by GQDs.<sup>315</sup> The prepared composite was applied as an electrode for LIBs and displayed a high electrochemical performance.

One of the most promising compounds for application in LIBs is tin oxide (SnO<sub>2</sub>). SnO<sub>2</sub> has some advantages such as abundant accessibility and environmental friendliness. However, it has some problems such as vast volume changes and little conductivity.<sup>316–318</sup> To solve these problems, Liang and colleagues investigated the preparation of an efficient SnO<sub>2</sub>@RH cellulose composite using SnO<sub>2</sub> NPs and RH cellulose through a hydrothermal technique.<sup>319</sup> For this aim, they encapsulated SnO<sub>2</sub> NPs with RH cellulose, which promoted the conductivity of the SnO<sub>2</sub> anodes. The synthesized composite was used as a promising anode for LIBs with an initial discharge capacity of 2090 mA h g<sup>-1</sup> and high capacities of 930 and 587 mA h g<sup>-1</sup> after 100 cycles at 0.2 C and 1 C, respectively.

One of the most abundant agricultural wastes is bagasse. Usually, it is burned, which is a waste of resources, and it produces air and environmental pollutants. Bagasse is a rich source of cellulose, lignin, and hemicellulose, which makes it an appropriate carbon source to prepare carbon electrodes that are applied for energy storage systems such as LIBs.<sup>320</sup> In 2021, Qin and co-workers developed an efficient and cost-effective technique for the preparation of anode materials for LIBs using carbon derived from bagasse.<sup>320</sup> They prepared N, P co-doped, bagasse-based, sheet-like mesoporous carbon (NP-BC) using NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and bagasse as raw materials. Their results revealed that the NP-BC composite had a high electrochemical performance. In another study in the same year, Ramesha and colleagues investigated the preparation of low-cost and high-performance anodes for LIBs using multi-heteroatom co-doped carbon derived from bagasse [N, S, and O co-doped carbon (NSOC-10)] (Fig. 10).<sup>321</sup> In addition, they reported the effect of HA doping on the carbon matrix and electrochemical features when applied in both Li-ion and Li-S batteries. The experimental results revealed that NSOC-10 had a capacity of 574 mA h g<sup>-1</sup> even after 1000 cycles (Fig. 10), while the undoped carbon showed only 26.6% capacitance retention within 250 cycles.

In other work in 2019, Wan and Hu investigated the synthesis of N-D biomass-derived porous carbon (N/C) as an efficient anode for LIBs.<sup>322</sup> For this aim, they used bagasse and melamine as C and N sources, respectively. The prepared N/C material had a 3D framework with a high specific surface area. The obtained N/C anode displayed a reversible special capacity of 530 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup> after 100 cycles. In the same year, Zhu and co-workers reported the synthesis of



**Fig. 10** Schematic representation of the synthesis process for N, S, and O co-doped PC, discharge capacities at different rates, and cycling performance tests of pristine material, NSOC-5, and NSOC-10. Reproduced from ref. 321 with permission from American Chemical Society, copyright 2021.

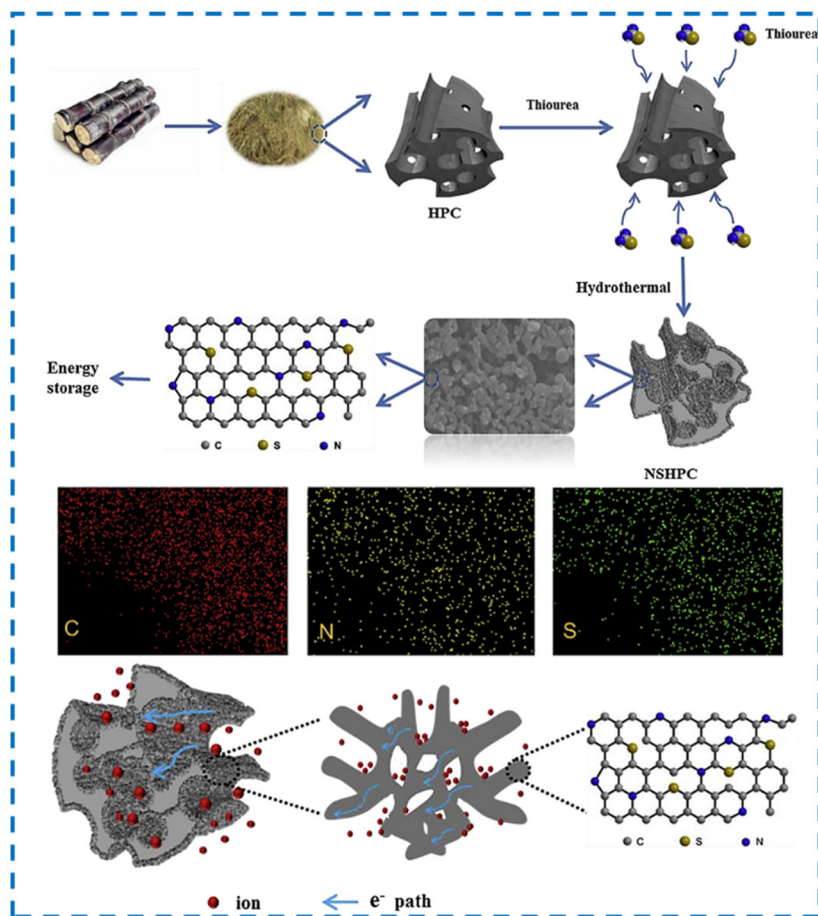
carbon materials with a hierarchical porous structure derived from bagasse by a procedure comprised of a hydrothermal treatment with thiourea (for doping N and S atoms) and carbonization (Fig. 11).<sup>323</sup> They showed that the structure of the prepared composite contained nanopores, supermicropores, and ultra-micropores and a large specific surface area ( $2419 \text{ m}^2 \text{ g}^{-1}$ ). In addition, the application of thiourea led to the production of various papillae of a few hundred nanometers in diameter on the tubular wall. The composite can be applied as an electrode and anode in supercapacitors and LIBs, respectively. As a LIB anode, it showed a capacity of  $621 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$ .

One of the agricultural wastes produced in large amounts is wheat straw, which is a cost-effective compound with many applications. One of the main constituents of wheat straw is cellulose.<sup>324</sup> In a study in 2021, Liang and colleagues developed a method for the synthesis of efficient anode materials for LIBs using cellulose derived from wheat straw and nano-sized  $\text{SnO}_2$ .<sup>324</sup> For this purpose, they separated cellulose from wheat straw by chemical treatment and used it as a coating material for nano-sized  $\text{SnO}_2$  through a hydrothermal technique. Finally, they applied thiourea for doping N and S atoms (Fig. 12a).  $\text{SnO}_2$ @wheat straw carbon ( $\text{SnO}_2$ @WSC) was applied as an anode for LIBs with a specific discharge capacity (DC) of  $1750 \text{ mA h g}^{-1}$  in the first cycle. In another study in 2019, Yan *et al.* reported the fabrication of hierarchical PC

from low-cost, novel, and abundant wheat straw (Fig. 12b).<sup>325</sup> They used KOH as an activator and the prepared biomass carbon activated using KOH (KWSC) had a microstructure and was applied as the anode material of LIBs.

One of the most useful types of biomass is PP. It is applied as an exceptional compound for the preparation of hard carbon sheets, which have been broadly used as anodes for electrochemical applications, through carbonization. In addition, PP-derived carbon can be used as a substrate for the deposition of active compounds owing to its cost-effectiveness and good conductivity.<sup>326</sup> In 2020, Zhang and colleagues reported the preparation of nanostructured  $\text{NiCo}_2\text{O}_4$  supported on carbon sheets using a hydrothermal method following thermal treatment.<sup>327</sup> Carbon materials are derived from the carbonization of PP. The prepared composite had some advantages such as a mesoporous structure and a large specific surface area. The composite could be applied as the anode of LIBs with a high reversible capacity of  $473.7 \text{ mA h g}^{-1}$  after 210 cycles at  $500 \text{ mA g}^{-1}$ .

In 2020, Wang *et al.* investigated the application of AC derived from waste buttonwoods, pineapple peels, and lettuce leaves as anodes for LIBs.<sup>328</sup> For this aim, they used KOH as an activator and then carbonized it through a high-temperature process. Their results indicated that the first discharge capacities of activated pineapple peels, buttonwoods, and lettuce leaves were 296.6, 313.9, and  $674.5 \text{ mA h g}^{-1}$  while the



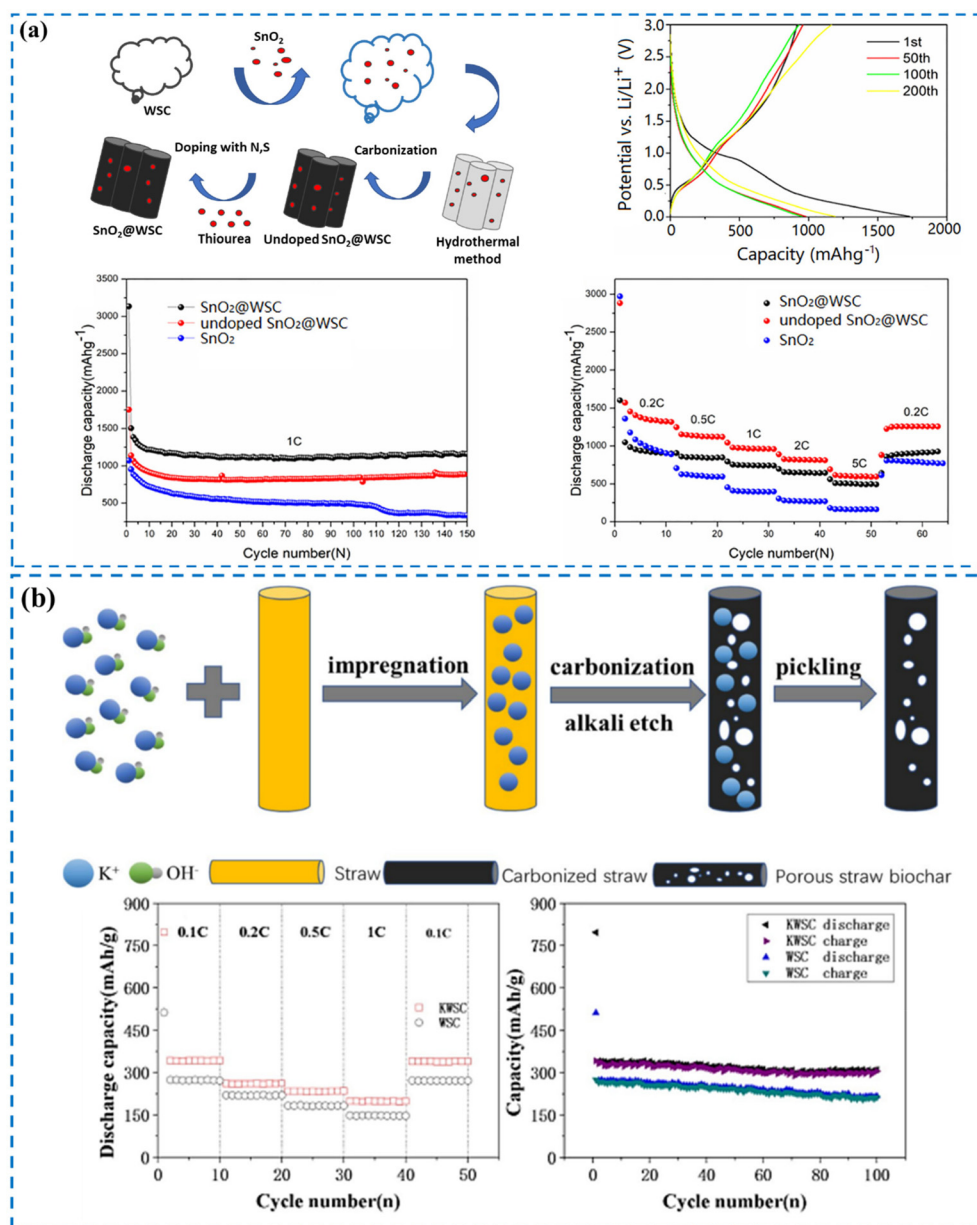
**Fig. 11** Schematic representation of the preparation process for the N–S doped hierarchical PC inherited from bagasse, EDS elemental mapping of doped hierarchical PC, and a schematic representation of transport paths for ions and electrons in the N–S doped hierarchical PC derived from bagasse. Reproduced from ref. 323 with permission from Elsevier, copyright 2019.

corresponding charging capacities were 129, 162.2, and 357.2 mA h g<sup>-1</sup>, respectively. In another example, the preparation of orange peel-derived hard carbon (OPDHC-A) was carried out by Xiang and co-workers.<sup>329</sup> For this work, they prepared a microporous structure through the pyrolyzation of OP at 800 °C and activation by KOH. The synthesized compound, which showed an initial capacity of 878 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> and 497 mA h g<sup>-1</sup> at 0.5 A g<sup>-1</sup> when applied as anodes for LIBs and Na ion batteries (NIBs), respectively. The experimental results showed that 3000 and 1000 cycling stabilities were achieved at 2 and 1 A g<sup>-1</sup> for LIBs and NIBs, respectively.

The most employed biowaste in LIB applications is RH due to the abundance of C and Si, which leads to good capacity in LIBs.<sup>300,301</sup> Some research efforts have been made regarding the influence of preparation techniques on the performance of the final composite.<sup>305</sup> Moreover, it was discovered that the modification of RH-derived carbon compounds with organic moieties,<sup>308</sup> metal oxides,<sup>313,319</sup> and GQDs<sup>315</sup> led to improved stability, better capacity, and higher electrochemical performance. From a critical perspective, it seems that reaching sufficient activity, stability, and efficiency of biowaste-based LIBs needs further investigation.

Furthermore, there are many more examples of the utilization of carbon-derived agricultural wastes for LIB applications, which are summarized in Table S4.† According to Table S4,† the most widely used agricultural waste for battery applications is RH (entries 1–61). Most compounds prepared from RH are various carbon derivatives (activated and porous carbons) and silica since it is a rich source of carbon and silica. In addition, RH has been used as a reducing agent for making nanoparticles. Other waste used in large amounts in this table is bagasse (entries 62–76), from which carbon derivatives are prepared and used for batteries. Smaller amounts of different fruit peels are also used for LIB applications. This shows that the best agricultural wastes for battery applications are RH and bagasse, which are both rich sources of carbon, and RH is additionally the source of large quantities of silica. Moreover, this table shows that the main electrolyte used for battery applications is LiPF<sub>6</sub> solution.

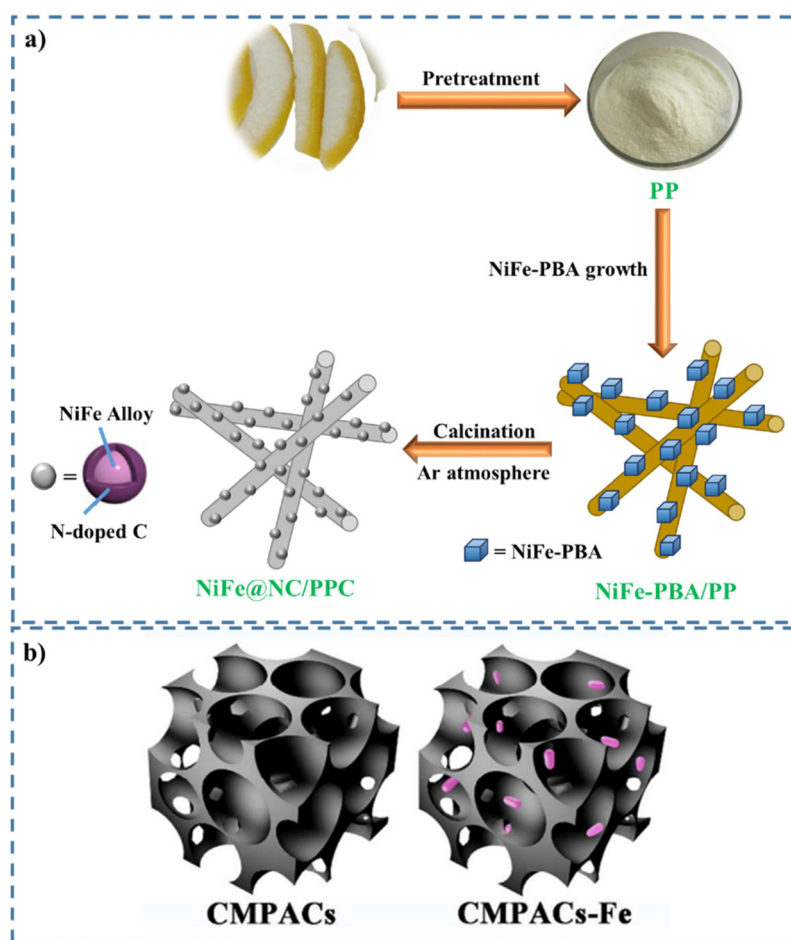
**3.4.2 Li–O<sub>2</sub> batteries.** Lithium–oxygen (Li–O<sub>2</sub>) batteries are a new generation of secondary batteries that have garnered significant attention due to their exceptionally high theoretical energy density.<sup>330,331</sup> In the cathode of these batteries, the electrochemical reaction between Li<sup>+</sup>, O<sub>2</sub><sup>2-</sup>, and electrons



**Fig. 12** (a) Schematic representation of the method for the preparation of SnO<sub>2</sub>@WSC, charge/discharge profiles of SnO<sub>2</sub>@WSC, cycling performance, and rate performance of SnO<sub>2</sub> and its composite material. Reproduced from ref. 324 with permission from Elsevier, copyright 2021. (b) Schematic representation of the method for the preparation of porous biomass carbon derived from wheat straw, charge–discharge cycling performances, and cycling capability of KWSC and WSC. Reproduced from ref. 325 with permission from Springer Nature, copyright 2019.

occurs in addition to the deposition of discharge products.<sup>332</sup> It is a very important issue to prepare an efficient cathode with an efficient electron transfer rate, Li<sup>+</sup> transfer, and oxygen transmission. In 2019, Tsiakaras and co-workers developed an efficient and cost-effective method for the fabrication of 3D self-standing electrodes for Li–O<sub>2</sub> batteries.<sup>332</sup> For this aim, they prepared a 3D composite (NiFe@NC/PPC) based on NiFe@NC core–shell NPs highly dispersed on the self-standing N-doped carbon (NC) microtubule network (NiFe@NC/PPC), which was derived from NiFe-Prussian blue analogues/PP (NiFe-PBA/PP). In other words, they used PP and modified its

surface using *in situ*-grown NiFe-PBA (Fig. 13a). The prepared NiFe@NC/PPC cathode combined the benefits of PPC (carbonized pomelo peel) and NiFe@NC (nickel-iron composite embedded in a nitrogen-doped carbon matrix) and exhibited a high specific capacitance of 13.79 mA h cm<sup>-2</sup> over 290 cycles at a current density of 0.1 mA cm<sup>-2</sup>. Zhang and colleagues reported the application of citrus maxima peel (CMP) as a precursor for the synthesis of activated carbon (CMPACs) and Fe-loaded AC (CMPACs-Fe) (Fig. 13b).<sup>333</sup> For this purpose, they used a pyrolysis method under an N<sub>2</sub> atmosphere using KOH as an activator. The prepared CMPAC-based Li–O<sub>2</sub> battery had

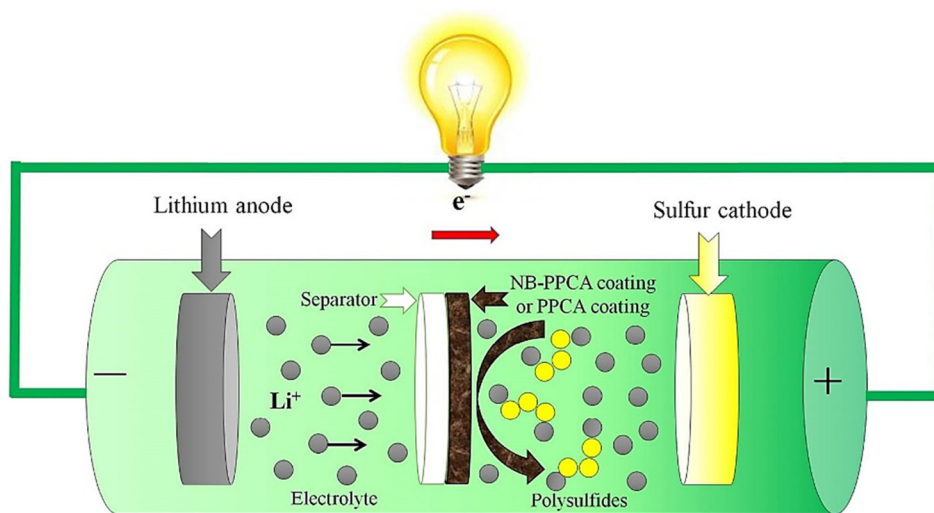


**Fig. 13** (a) Schematic representation of the preparation of NiFe@NC/PPC. Reproduced from ref. 332 with permission from Elsevier, copyright 2019. (b) Structures of the two kinds of electrodes (CMPACs and CMPACs-Fe). Reproduced from ref. 333 with permission from American Chemical Society, copyright 2018.

a high cycling performance and specific capacitance of 466 cycles and  $7800 \text{ mA h g}^{-1}$ , respectively. The two types of electrodes prepared showed high specific surface areas, porous structures, and many active sites.

**3.4.3 Li-S batteries.** Recently, rechargeable lithium-sulfur batteries (Li-SBs) have attracted much attention owing to their high theoretical specific capacity ( $1675 \text{ mA h g}^{-1}$ ) and energy density ( $2600 \text{ W h kg}^{-1}$ ).<sup>334,335</sup> Additionally, the cathode materials of these batteries (elemental sulfur) are abundant in nature, inexpensive, and eco-friendly. Diverse kinds of compounds are used for the preparation of Li-SBs.<sup>336–338</sup> Among them, agricultural wastes have been broadly reported.<sup>288,339,340</sup> AC derived from agricultural waste is a suitable choice for electrochemical applications due to its electrochemical capacitive ability and high microporous volume.<sup>223,341,342</sup> Tao and colleagues developed a type of multi-functional carbon-derived RH for optimizing the Li anode and sulfur cathode of Li-SBs.<sup>343</sup> The carbon-derived RH had a large specific surface area and  $\text{SiO}_2$  NPs were useful for confining sulfur and sulfides. The experimental results revealed that the discharge capacity of the battery was improved when the Li metal anode

was modified with a carbon/sulfur composite. In addition, the cycling stability and rate capability were improved. Yan *et al.* carried out the synthesis of banana peel-derived PC (BPPC) by pyrolysis carbonization using various amounts of KOH as an activator.<sup>344</sup> In the next step, they loaded S and the synthesized S/C composite, which was used as a cathode for Li-SBs. They showed that when the KOH activation was increased, the specific surface area, as well as the pore volume of the BPPC and the electrochemical performance of composite cathode in Li-SBs, improved. In addition, the fabrication of porous nitrogen and boron dual-doped carbon aerogels derived from PP (NB-PPCA) was reported by Zhu and co-workers,<sup>345</sup> who used a green and inexpensive approach for the preparation of a valuable and low-cost compound. The NB-PPCA material synthesized, which could reduce the interface resistance between the cathode and separator and thus improve the reaction kinetics of Li-SB, was applied as a coating on a pristine separator in Li-SBs. The cell configuration of the Li-S cell with PPCA or NB-PPCA modified separators is displayed in Fig. 14. The cell had a specific capacitance of  $586.6 \text{ mA h g}^{-1}$  after 500 cycles at 1 C and showed a good rate performance and cycling stability.



**Fig. 14** Schematic representation of the configuration of the Li-S cell for the PPCA or NB-PPCA modified separator. Reproduced from ref. 345 with permission from Elsevier, copyright 2019.

The preparation of highly porous AC compounds with micro- and mesoporosity through the carbonization of RH following treatment with  $K_2CO_3$  was performed by Le and colleagues.<sup>346</sup> In the next step, they loaded elemental S in the micropores *via* a solution infiltration technique to prepare RHAC@S composites. The prepared RHAC@S was used as the cathode for Li-SBs. With  $0.25 \text{ mg cm}^{-2}$  of S loading, the composite displayed an initial discharge capacity of  $1080 \text{ mA h g}^{-1}$  at a rate of 0.1 C. In another study, Tsiakaras and co-workers developed an efficient method for the preparation of porous biochar-coated metal NPs (CoFe@NC/PPC) through loading PBA on the PP as a carbon source, followed by calcination at a high temperature.<sup>347</sup> In the next step, the immersion melting method was applied for the injection of S to prepare S/CoFe@NC/PPC. The prepared material was applied as an efficient sulfur cathode for Li-SBs and exhibited an initial specific capacity of  $915.6 \text{ mA h g}^{-1}$  at 1 C and remained at  $447.4 \text{ mA h g}^{-1}$  after 500 cycles with a coulombic efficiency of 97.3%.

Other examples in this field are summarized in Table S5.† According to the literature, the results indicate that bagasse and RH, two types of agricultural waste, are very important for LIBs, Li-SBs, and NIBs applications.<sup>97,153,348–355</sup> Furthermore, it is important to note that in recent years, fruit peels have been used several times for LIB, Li-SB and NIB applications.<sup>356–362</sup>

### 3.5 Dye-sensitized solar cells

Dye-sensitized solar cells (DSSCs) are *p-n* junction photovoltaic devices.<sup>363–367</sup> For the first time, it was found that electricity could be produced by illuminating organic dyes in electrochemical cells. The photoanode is organized by adsorbing a dye in a porous  $TiO_2$  layer. Therefore, the dye enables the production of electricity from visible light, extending the performance of the semiconductor to collect photons at lower

energies.<sup>368–370</sup> DSSCs contain a counter electrode, a metal oxide semiconductor, an electrolyte, and a dye sensitizer. There are some photosensitizers, such as ruthenium polypyridyl complex, with various limitations such as difficult synthesis processes, the presence of heavy metals, high costs, *etc.* There are some natural and green dyes in various wastes. These pigments include betanins, anthocyanins, chlorophyll, tannins, carotenoids, *etc.*<sup>371–378</sup> For example, the extraction of natural dye from the husks, cobs, and silk of purple corn as efficient photosensitizers was performed by Swatsitang and co-workers.<sup>379</sup> These natural dye sensitizers were used for the preparation of DSSCs. The results displayed maximal efficiency (1.06%) with purple corn husk extract. In another study, Yuliarto *et al.* used *Citrus reticulata* and *Musa acuminata* fruit peels as green and efficient photosensitizers for the preparation of DSSCs.<sup>380</sup> Fig. 15 demonstrates the photosensitization process of both hesperidin and gallicocatechin dyes (which are flavonoids in *Citrus reticulata* and *Musa acuminata* pigment, respectively) under illumination. Their experimental results led to the longest diffusion length, the fastest electron transit, and the longest electron lifetime of  $32.2 \mu\text{m}$ , 0.22 ms, and 4.29 ms, respectively. In addition, some studies used agro or fruit waste peels as natural dyes for DSSCs.<sup>381–385</sup>

In 2017, Xiang and colleagues developed a method for the synthesis of N-D bagasse-derived carbon/Pt composite (NBC/Pt) through an environmentally friendly hydrothermal process.<sup>386</sup> They used bagasse as a carbon source and considered it as the counter electrode of DSSCs. The size of Pt NPs was reduced by N doping, which additionally resulted in better dispersion of Pt NPs on the carbon support. According to their results, under simulated AM 1.5 G solar illumination at  $100 \text{ mW cm}^{-2}$ , the DSSCs with the NBC/Pt composite counter electrode displayed a power conversion efficiency of 6.98%. In 2022, Kathiravan and co-workers reported DSSCs containing peels of red banana and aloe vera leaf as dye sensitizers.<sup>387</sup>

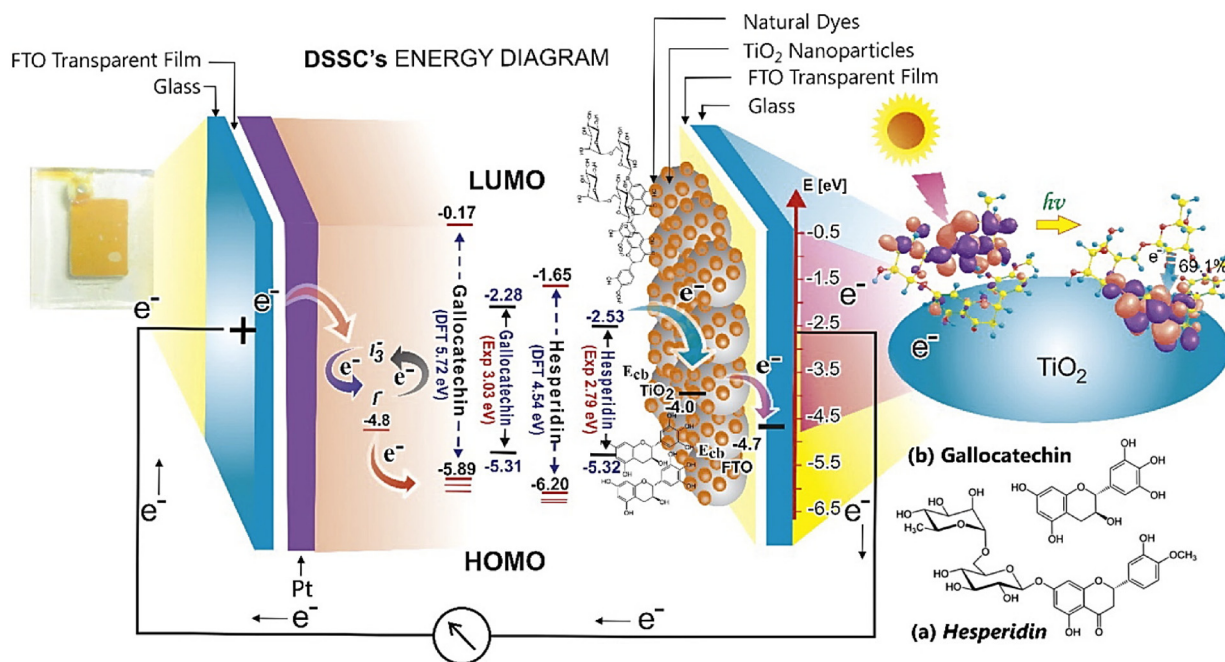


Fig. 15 The natural DSSC structure and a representation of its reaction. Reproduced from ref. 380 with permission from Elsevier, copyright 2017.

They used acetone and ethanol solvents for the extraction of dyes from these peels. Indeed, they prepared DSSCs using extracted dyes and commercial  $\text{TiO}_2$  as a sensitizer and semiconductor oxide, respectively. A high efficiency of 0.679% was obtained using aloe vera peel extract and ethanol solvent.

Generally, according to the literature, most of the agricultural wastes applied for DSSCs are fruit peels.<sup>388–390</sup> Some studies in which agricultural wastes have been used for DSSC preparation are summarized in Table S6.†

## 4. Conclusion and prospects

Recently, due to the deteriorating environment and the depletion of fossil energy, it has been promising to develop clean energy production and storage systems that utilize non-toxic and accessible sources. Numerous biowastes from agricultural resources are lost to landfill or disposal. The food industry uses fruits and discards peels and stones, or farmers consider rice the main crop and husk the side product. However, these second-class or side products can have extensive applications in various fields. The conversion of these biowastes into valuable chemicals could offer approaches for constructing sustainable energy conversion and storage systems.

Depending on outstanding properties such as low cost, accessibility, and natural abundance for agricultural waste-derived (carbon/nano)materials, these could be applied in energy conversion and storage. Therefore, this review mainly focuses on the performance of agricultural waste-derived (carbon/nano)materials for energy conversion and storage. Energy conversion involves FC electrodes and electrolytic

water-splitting reactions, namely ORR, MOR, OER, and HER, and several applications and progress in this field were reviewed. Then, the application of agricultural wastes for energy storage has also been investigated. Energy storage devices include different types of batteries like LIBs,  $\text{Li-O}_2$ , and Li-SBs, as well as supercapacitors and solar cell systems. Although graphite is used to make batteries, it does not fulfill human needs. Therefore, researchers utilized new combinations of agricultural wastes to prepare anodes for all kinds of batteries. Furthermore, the application of carbonaceous compounds to construct novel anodes is of great interest to researchers because these compounds possess different advantages such as abundant pores, high specific surface areas, and stable features. Carbons derived from agricultural waste could be applied as anodes for diverse types of batteries. Despite significant research in energy generation and storage from agricultural waste, several issues warrant further investigation:

- Using agricultural waste on an industrial scale for energy production and storage.
- Using agricultural waste in other electrocatalytic reactions such as EOR,  $\text{CO}_2\text{RR}$ , NRR, *etc.*
- More use of this agricultural waste as substrates for the preparation of heterogeneous catalysts for electrocatalytic reactions or as anodes or cathodes for energy production devices.
- Controlling the size of pores in carbon compounds derived from agricultural waste.
- In the LIB application, most of the applied agricultural wastes are RH and bagasse. As a result, an area of further research for the future is the application of other waste, such as that from the peels of fruits and nuts, for battery applications.

## Abbreviations

AC	Activated carbon
AP	Aloe peel
APPC	Aloe peel-derived porous carbon
BCMs	Biochar microspheres
BPPC	Banana peel-derived porous carbon
CA	Citric acid
CDs	Carbon dots
CMC	Carboxymethyl cellulose
CMP	Citrus maxima peel
CNTs	Carbon nanotubes
CO <sub>2</sub> RR	CO <sub>2</sub> reduction reaction
CPC	Commercial Pt/C
3D	Three-dimensional
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DMFC	Direct methanol fuel cell
DSSCs	Dye-sensitized solar cells
EC	Ethylene carbonate
EMC	Ethyl methyl carbonate
EOR	Ethanol oxidation reaction
FCs	Fuel cells
GQDs	Graphene quantum dots
HER	Hydrogen evolution reaction
HP-SN-PGC	Highly-porous metal-free nitrogen/sulfur co-doped partially-graphitized carbon
LC	Lignin-derived carbon
Li-O <sub>2</sub>	Lithium-oxygen
Li-SBs	Lithium-sulfur batteries
LIBs	Lithium-ion batteries
LSV	Linear scan voltammetry
MFCs	Microbial fuel cells
MOFs	Metal-organic frameworks
MOR	Methanol oxidation reaction
NB-PPCA	Nitrogen and boron dual-doped carbon aerogel derived from pomelo peel
NBC/Pt	N-D bagasse-derived carbon/Pt composite
N/C	N-D biomass-derived porous carbon
N-PC	N-D porous carbon
NC	N-Doped carbon
NC/PPC	N-Doped carbon/carbonized pomelo peel
NIBs	Na ion batteries
NP-BC	N, P co-doped bagasse-based sheet-like mesoporous carbon
NPC	N-D pomelo peel-derived carbon
NPCNs	N, P doped PC nanosheets
NPs	Nanoparticles
NSOC	N, S, and O co-doped carbon
NRR	Nitrogen reduction reaction
OER	Oxygen evolution reaction
OP	Orange peel
ORR	Oxygen reduction reaction
Ov	Overpotential
PBA	Prussian blue analogues
PC	Porous carbon

PP	Pomelo peel
PPC	Carbonized pomelo peel
PPCA	Carbon aerogel derived from pomelo peel
PPDC	Pomelo peel-derived porous carbon
RHC	Rice husk-derived carbon
RHE	Reversible hydrogen electrode
RHs	Rice husks
RS	Rice straw
SC-MFCs	Single-chamber microbial fuel cells
SiO <sub>2</sub> /NC	N-enriched PC/SiO <sub>2</sub>
SnO <sub>2</sub>	Tin oxide
SS	Soybean straw
SSC	Symmetrical supercapacitor
WHAC	Wheat husk-derived activated carbon
WSC	Wheat straw carbon

## Data availability

No primary research results, software, or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

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