Valorization of Agricultural Residues: Challenges and Opportunities in the Production of Bio-Based Materials

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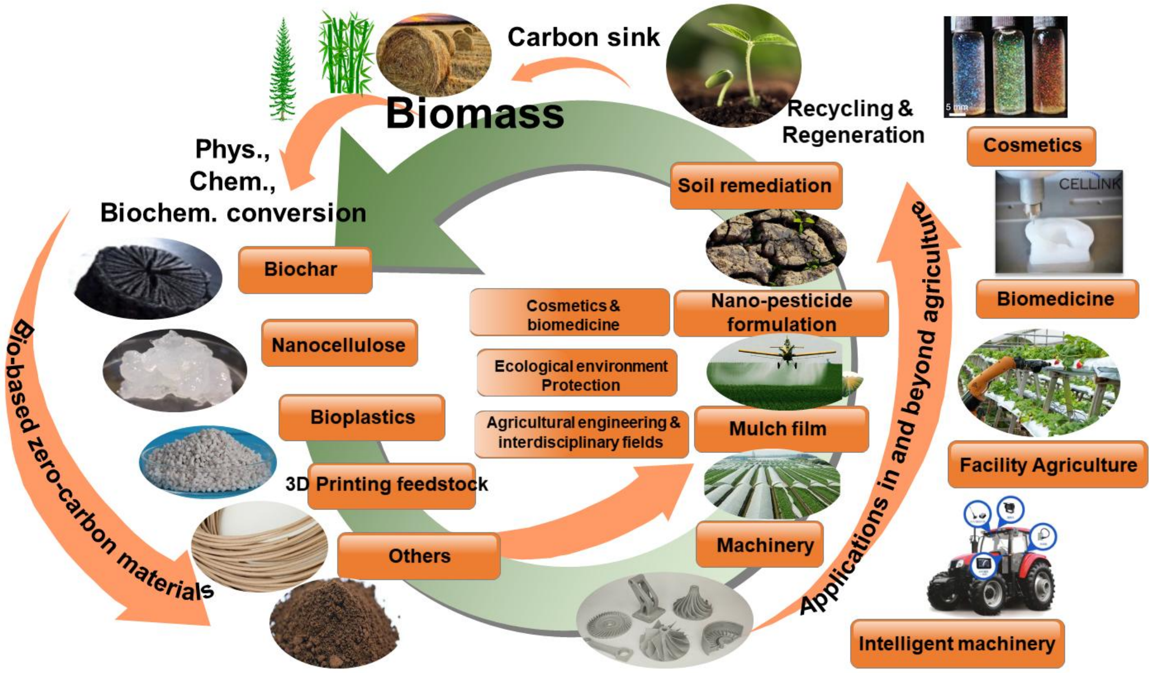
GRAPHICAL ABSTRACT



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Environmental pollution and resource waste resulting from the disposal of agricultural biomass waste have become a global issue. Consequently, the pursuit of sustainable strategies for recycling such waste biomass and achieving its efficient and high-value conversion has emerged as a critical challenge that presents for both the global academic and industrial communities. This work provides a comprehensive overview of the current advancements in recycling and conversion of agricultural biomass waste into a variety of bio-based materials, with a particular focus on the biochar, nanocellulose, and bio-based plastics. Potential applications of these bio-based materials in agriculture and beyond with high added-value, such as cosmetics and biomedicine, are discussed with representative cases study. This review also highlights the challenges and future prospects in converting agricultural residues into various bio-based materials. It is hoped that this review will contribute to the understanding and promotion of recycling and reutilization of agricultural biomass waste, offering promising solutions for sustainable development of agricultural production.

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Keywords: Biomass waste; Bio-based materials; Agricultural residue; Biochar; Nanocellulose

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INTRODUCTION

The global issue of solid waste disposal has led to environmental pollution and resource waste. In China, both urban and rural areas generate over six billion tons of organic waste annually, including agricultural and forestry residues, household garbage, domestic sludge, livestock and poultry waste, fruit and vegetable residues, and industrial organic residue waste liquid. Among these, agricultural residues accounted for around 980 million tons in 2022. If not managed properly, this solid waste has the potential to cause significant environmental pollution and resource wastage (Chen *et al*. 2020). In the last two decades, the agricultural waste biomass straw has been burned after crop harvesting. This burning produced a large amount of smoke, causing severe air pollution. The air pollution caused by straw burning is due to the large amounts of particulates (PM2.5 and PM10), NOx, CO/CO_2, and SO_2 generated (Fig. 1A) (Ravindra *et al*. 2019; He *et al*. 2020). Jiang *et al*. (2019) analyzed the total straw production in 2015 in nine typical straw-burning provinces in China, which was 460 million tons, with a total open burning amount of 93 million tons. The burning emitted 70 million tons of CO_2, 4.7 million tons of CO, 6,000 tons of SO_2, and 162,000 tons of NOx, causing serious harm to the ecological environment and human health (Jiang 2018; Jiang *et al*. 2019). Directly piling up or returning the straw by deep tillage or rotary tillage to the field might lead to severe accumulation of pests and diseases and destruction of the soil microbial ecological environment, seriously affecting the healthy growth of crops (Fig. 1B) (Li *et al*. 2018; Jiao *et al*. 2023a). Therefore, developing new technologies and processes for the efficient recycling and conversion of agricultural residues in an environmentally friendly manner is of great significance for global sustainable development.

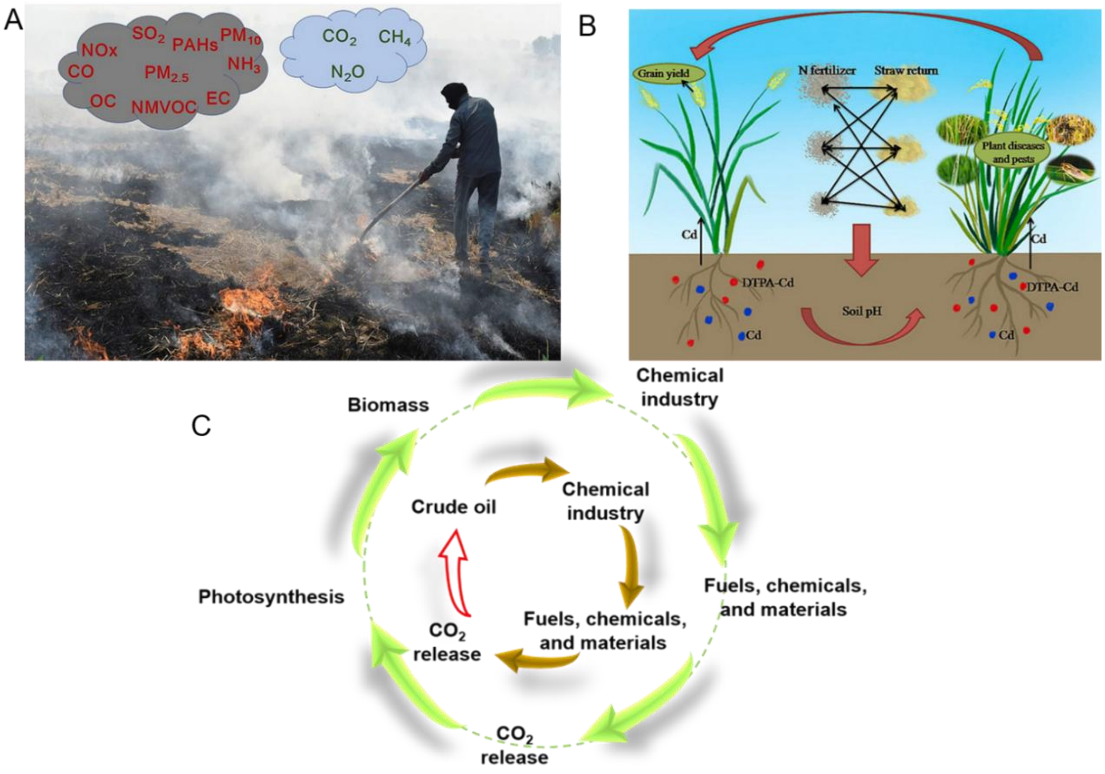


Fig. 1. Agricultural residue burning caused air pollution (A) and straw return caused potential crop diseases, pests, and heavy metal risk (B). Reprinted with permission from Elsevier, published in Ravindra *et al*. 2019; Shan *et al*. 2021. Production cycles comparison of products derived from fossil fuel and biomass (C).

Biomass waste shares similar chemical compositions with common biomass raw materials that are used for materials or chemicals production and has the advantages of high abundance, renewability, and biodegradability. This makes it a promising candidate for incorporation into the biorefinery industry, either as a supplement or a replacement for traditional fossil fuels (Fig. 1C). Agricultural waste biomass is primarily used for feed, fertilizer, and matrix, but these products have weak market competitiveness and low added value. Due to the low economic benefits of the existing agricultural residues recycling industry, farmers and enterprises lack the motivation for recycling and processing. This has led to a large amount of agricultural residual biomass resources being wasted or improperly treated, causing harm to the environment. Therefore, agricultural residual biomass processing technologies must be adopted to fabricate high value-added and functional products, while reducing or eliminating the potential secondary pollution caused by traditional processing methods. This work summarizes the current advances in recycling and reutilization of biomass waste, with a focus on the development of biomass-based materials using agricultural biomass waste or application exploration in the agricultural field and others. The benefits and risks of directly incorporating agricultural residues back into the soil, whether through plowing or composting, have been reviewed elsewhere and will therefore not be included in this review (Li *et al*. 2018; Jiao *et al*. 2023a; Fu *et al*. 2021; Urra *et al*. 2019; Ho *et al*. 2022). Preparation and application of materials based on agricultural residues, including biochar, lignocellulosic nanomaterials, biodegradable plastics, and bio-based 3D printing materials, are summarized in this paper. Challenges and future perspectives of bio-based materials from and back to agriculture, and beyond are proposed at the end of this work. This work will provide valuable insights into the recycling and reutilization of biomass waste with high-added value, serving as a promising solution to the sustainable development of agriculture.

REPRESENTATIVE BIO-BASED MATERIALS FABRICATION AND APPLICATIONS

Preparation and Application of Biochar

Biochar is a porous, carbon-rich solid substance produced by pyrolysis of biomass under oxygen-limited or anaerobic conditions. Its high carbon content, rich pore structure, and strong adsorption capacity make it a promising material for improving soil quality, increasing crop yield, and removal of environmental pollutants. The types of agricultural biomass wastes, pyrolysis temperature program (*e.g.*, the target temperature and heating rate), and pyrolysis time are key processing conditions that determine the physical and chemical properties of the resultant biochar (Fig. 2A) (Khater *et al*. 2024). Agricultural residues, such as wheat/rice/corn/cotton, sugarcane bagasse, fruit peel and core, and various crop shells/husks, are used as raw materials for biochar preparation. To enhance the physicochemical properties or functionalities of the products, modification treatments can be applied. Chemical and physical modifications, including acids oxidation, base activation, steam activation, and integration or impregnation with other functional components, are effective in tuning the specific surface area, porous structures, and surface functional groups of the biochars to endow them with special functions for applications in and beyond agriculture (Shang *et al*. 2021; Amalina *et al*. 2022).

The utilization of biochar in agriculture has been reported to bring benefits to soil, such as increasing nutrient and water retention, as well as microbial abundance, and benefits to plants, such as increasing root development, pest and disease resistance, as well as crop yield (Ismail *et al*. 2022; Jing *et al*. 2020). Additionally, adsorption and immobilization of toxic heavy metals and pesticides have also been confirmed as positive effects of the biochar application in agriculture (Fig. 2B) (Rajput *et al*. 2022). For instance, the long-term biochar application effects on soil fertility, N_2 fixation, and crop yield was evaluated by Khan *et al*. (2020, 2023). Sole application of biochar from 10-30 t biochar/ha increased the wheat grain yield by 3.2 to 13.3% and biological yield of wheat by 7.1 to 14.9%. When incorporation with organic manures (farmyard or poultry manure) or urea, the yields are much more pronounced, especially at the combination of poultry manure (150 kg/ha) and biochar dosage of 20 t/ha, which showed up to 49.7% wheat grain yield increase (Fig. 2C-D). Similarly, the utilization of 130 t/ha biochar with half of the recommended mineral fertilizers (45 kg/ha phosphorous and 30 kg/ha potassium) showed the best performance in enhancing the chickpea yield for 10.2% over the 5 years, meanwhile the organic matter in soil increased from 1.67% to 2.59%, showing significant improvement in the sustainable crop production and soil fertility (Khan *et al*. 2020). A more comprehensive review and evaluation of biochar applications in agriculture, including its effects on crop growth and yield, soil nutrient properties, and greenhouse gas emissions, can be found elsewhere (Li *et al.* 2024; Ismail *et al.* 2022; Jing *et al.* 2020).

The porous structure and high specific surface area as well as abundant interface modification strategies make biochar a promising candidate for remediation of contaminated water, soil, and air (Haider *et al*. 2022; Acosta-Luque *et al*. 2023; Nguyen *et al*. 2023; Zouari *et al*. 2024). Biomass waste including the pine sawdust and grapefruit peel were converted into thiol-modified biochars following the carbonization, microwave, and thiol modification for potential applications in mercury pollution remediation in water (Fig. 2E). The pine sawdust (BP) and grapefruit peel (BG)-based biochars were found to have porous and multilayer structure, respectively. This led to a different binding mode (hydroxyl group and π bonds for BP and π bonds for BG) and polymer morphologies of the thiolation reagent (3-MPTS) on the biochars surface (flocculent polymer for BP and spherical polymer for BG) (Fig. 2E). Mercury sorption isotherms analysis confirmed that the Hg^{2+} and CH_3Hg^+ adsorption mainly followed the Langmuir model, *i.e.*, the monolayer sorption on the biochar surface. The Langmuir maximum sorption capacities (q_m, Fig. 2E, C., (d)) of the biochars were increased after modification, especially after the thiolation, but no significant difference between the porous and multilayer biochars was observed. However, the calculated surface Hg atomic densities (ρ_{atom}, Fig. 2E (e), (f)) on the multilayer biochars were significantly lower than the porous ones (1758.0 and 1068.5 #Hg/nm^2 for BPS *vs.* 5.4 and 3.0 #Hg/nm2for BGS) owing to the difference of the biochar specific surface areas and the polymer morphologies on the surface.

Potential high value-added medical applications of biochar, especially in drug delivery, have been explored in recent years. The porous structure and tunable interface chemistry of the biochars offer benefits of high drug load and buffering capacity, enhanced drug bioavailability, and controlled, targeted, or stimulus-responsive drug delivery efficiency (Zhuo *et al*. 2023). Zinc oxide-modified biochar was incorporated into a multilayered drug delivery system for near-infrared (NIR) irradiation stimulated release of intraocular pressure-lowering drug and antibacterial drug in the treatment of glaucoma (Fig. 2F (a)) (Wang *et al*. 2021). Upon the NIR irradiation at 0.8 W cm^{-2} for 20 min, the biochar containing delivery system showed increased temperature up to 48.30 ± 4.37 °C when compared with the control group in PBS at 33.83 ± 2.25 °C, resulting a faster and sustained timolol maleate (TM) drug release to reduce the intraocular pressure (Fig. 2F (c)). Meanwhile, the prolonged release of levofloxacin (LVFX) significantly inhibited the viability of bacteria by causing the cells membrane damage and cytoplasmic leakage (Fig. 2F (b), (d), (e)). Although various applications of the biochars prepared from agricultural residues have been proposed, several factors limit their use and sustainable development at this time (Tan and Yu 2023). These include the variability of agricultural residues, the complexity of their components, potential heavy metal contamination, and uncertainties of long-term environmental and health risks. To address these limitations, standardized processing from biomass recycling, pretreatment, and thermal conversion into biochar could be a solution to ensure the consistency of the physicochemical properties of biochars. Additionally, long-term and systematic crop yield and nutrients evaluation, as well as environmental risk assessment are crucial for the safe and large-scale application of biochar in agriculture. Regarding the biochars application in medicine, rigorous biosafety evaluation should be conducted before proceeding with application tests.

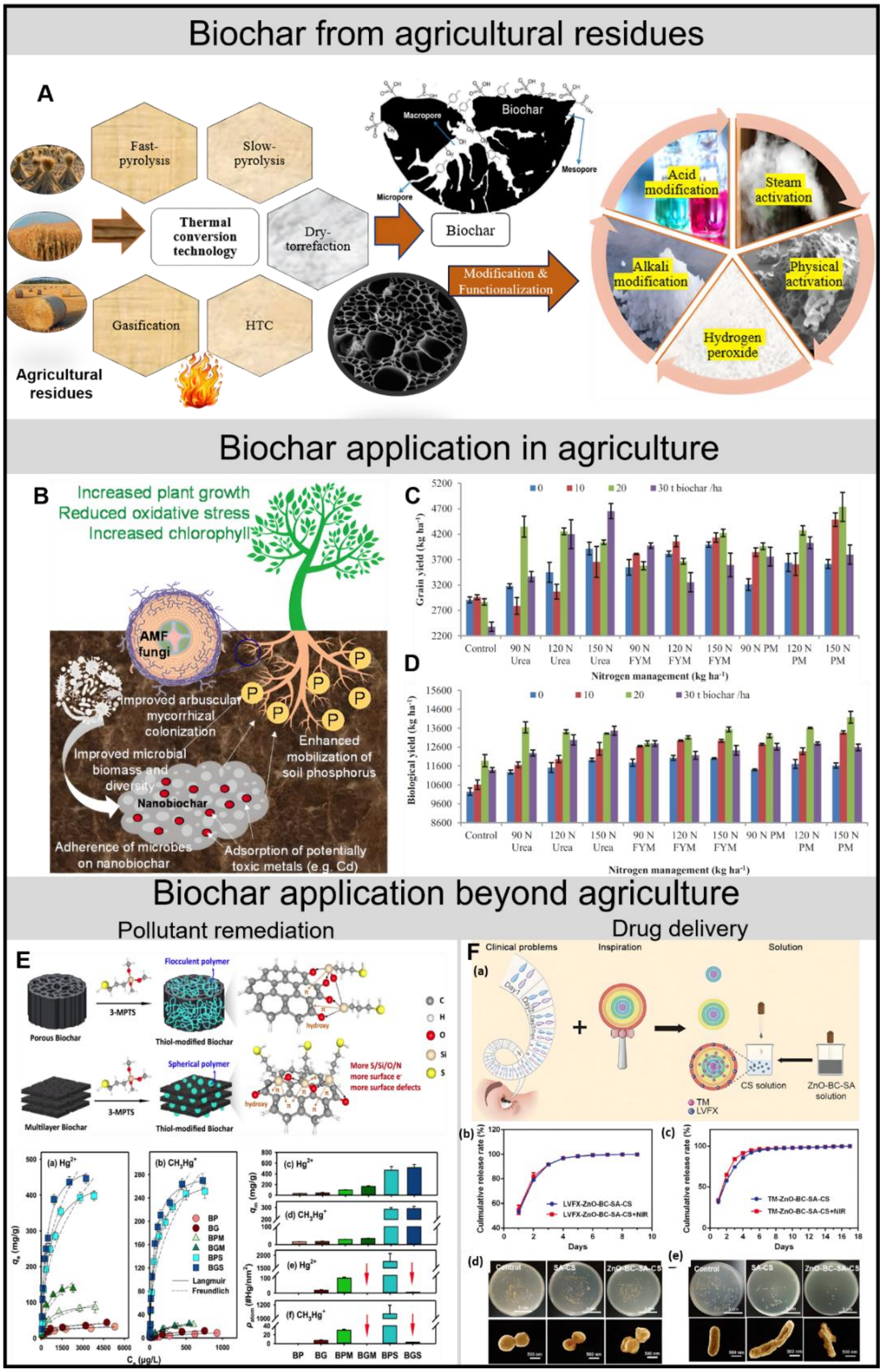


Fig. 2. Biochar prepared from agriculture residues and application in agriculture and beyond. (A) Different thermal conversion technologies and modification strategies used for biochar preparation from agriculture residues; (B) Benefits of the biochar utilization to the plant and soil; (C, D) Efficacy of the biochar utilization when combined with organic manures (farmyard or poultry manure, FYM or PM) or urea in the grain yield and crop biological yield; (E) Application of thiol-modified biochar in mercury-contaminated water remediation; (F) Incorporation of zinc oxide-modified biochar-based into a near-infrared irradiation stimulated drug delivery system for glaucoma treatment. Reprinted with permission from Elsevier (Huang *et al*. 2023, Rajput *et al*. 2022); Springer Nature (Khan *et al*. 2023); Nadarajah *et al*. 2024; Wiley (Wang *et al*. 2021)

Preparation and Application of Lignocellulosic Nanomaterials

Agricultural and forestry residues, including rice husk, sugarcane bagasse, corn cobs, wheat straw, wood sawdust, and wood shavings, are rich in biopolymers of cellulose, hemicellulose, and lignin. Since the early 21st century, with the rapid advancement of green chemistry such as ionic liquids or EDS solvent systems, and TEMPO-mediated oxidation processes, as well as mechanical nanofabrication technologies, these biopolymers have been extensively explored for production of a variety of lignocellulosic nanomaterials. When the cellulose component in various biomass waste is isolated and fabricated into materials with at least one dimension in nanoscale, the terminology "nanocellulose" is applied. This mainly includes cellulose nanocrystals (CNCs), cellulose nanofibril (CNF), and bacterial cellulose (BC), as summarized in Fig. 3A and reviewed elsewhere (Yu *et al*. 2021; Jiao *et al*. 2024). Due to their high aspect ratio, mechanical stiffness, and specific surface area, as well as their inherent biocompatibility and abundant surface functional groups for modification, nanocellulose has been explored to produce new pesticides, feed additives, slow-release fertilizers, and soil water retention agents for application in agriculture (Fig. 3B, C), packaging, and other value-added application in cosmetics and tissue engineering (Fig. 3D, E) (Klemm *et al*. 2011; Kashan *et al*. 2022; Ji *et al*. 2023; Liu *et al*. 2019).

A CNFs-based composite hydrogel (MC) system that consist of porous metal organic frameworks (MIL-100(Fe)), CNFs, and N-vinyl caprolactam (NVCL) was prepared by free-radical polymerization for achieving temperature and pH dual-responsive release of fertilizers (Fig. 3B, (a)). The resultant composite hydrogels not only achieved the controlled release of urea at suitable pH 7.0 and temperature around 30 °C to ensure a high fertilizer utilization efficiency, but they also showed significant increase in the water-retaining ratio due to the high affinity of water to CNFs and porous structure of the MIL-100(Fe) (Fig. 3B, (c)). A 30 days lasting slow-release of fertilizer has also been confirmed with the assessment of nitrogen contents in soil (Fig. 3B, (b)). These fertilizer and water management benefits contribute to the healthier growth of the model crop wheat, as shown in Fig. 3B, (d) (Lin *et al*. 2021). Another nanocellulose-based pesticide delivery system (TA/Cu-XCM@βCNC) was developed for crop protection by β-cyclodextrin (β-CD) adsorption onto CNCs surface and model pesticide (XCM) loading, followed by chelation of tannic acid (TA) with copper ions (Fig. 3C, (a)). The incorporation of TA sharply lowered the contact angle of the loaded pesticide suspension on the *O. fragrans* leaves from 82° to 47°, enhancing the deposition and retention of the suspension. Meanwhile, the TA-Cu^{2+} coordination can be degraded in acidic medium (*e.g.*, oxalic acid and citric acid) due to the acidification produced by fungus and the fungi-infected plants, enabling the pH-responsive release of the loaded XCM. Antifungal activity of the formulated XCM delivery system against the pathogenic fungi *R. solani* and *C. capsici* was confirmed to have high inhibition efficiency by both the fungal growth colony measurement (Fig. 3C, (b)) and crisscross assessment (Fig. 3C, (c)). The delivery system also exhibited high insecticidal activity against *O. nubilalis* larvae with 97% mortality, highlighting the efficacy of the CNCs-based pesticide delivery system in crop protection for sustainable agriculture (Ning *et al*. 2023).

Nanocellulose has been demonstrated to exhibit potential high value-added applications in cosmetics as a rheological modifier, moisturizer, antioxidant, and sunscreen, as well as in biomedicine for use as a drug carrier, tissue engineering scaffolds, and wound dressings. A bacterial nanocellulose-based microneedles (MNs) patch delivery system demonstrated the potential for enhancing the cosmetic ingredients penetration applications by inserting into the skin and delivering the bioactive rutin (Fig. 3D, (a), (b)). Cytocompatibility of the microneedles system was confirmed with a cell viability of 105.9 ± 7.9% after in vitro culturing the human keratinocytes cells with the MNs extract for 24 h (Fig. 3D, (d)).

Histological examination upon the skin insertion capability of the MNs into porcine skin revealed that the MNs insertion can create cavities with depths up to 99.3 μm, enabling the effective delivery of cosmetic ingredients into the dermis (Fig. 3D, (d)). A 24 h *in vivo* skin tolerance assessment of the MNs on volunteers' volar forearms indicated that MNs application caused no significant impact on the stratum corneum hydration (Corneometer), skin redness (Chromameter (a^*)), and skin barrier function (TEWL) (Fig. 3D, (c)), suggesting the safety and practicality of the MNs system (Fonseca *et al*. 2021). Considering the feasibility of producing BC and other types of nanocellulose from agro-industrial and forest residues as cultivation alternatives or as lignocellulosic raw materials, one can anticipate high value-added applications of nanocellulose derived from biomass wastes in cosmetics and biomedicine (Rodrigues *et al*. 2024; Yu *et al*. 2021).

A recent work demonstrated the feasibility of extracting ultra-pure nanocellulose from forestry residue sawdust using a combination of soda pulping, elemental chlorine-free bleaching, and TEMPO-mediated oxidation followed by homogenization in a clean room (Fig. 3E, (a)). The resulting nanocellulose exhibited high zero-stress viscosity and typical shear-thinning behavior, as well as instant self-recovery properties, enabling smooth 3D printability and stable structure fidelity. The extremely low endotoxin level (< 1.6 EU/g) and (1,3)-β-D glucan content (3.13 μg/g) in the extracts of both the nanocellulose and its freeze-dried aerogel ensure the biosafety of the nanocellulose in biomedical applications, as validated by the proliferation of fibroblast cells in the bioprinted scaffolds (Fig. 3E, (a)) (Jiao *et al*. 2024).

To further extend the functionalities of the nanocellulose-based biomaterials, surface engineering strategies, such as physical adsorption, chemical crosslinking, and bioconjugation have been adopted to meet specific requirements of the nanocellulose-based biomaterials in the designed applications (Shi *et al*. 2022; Jiao *et al*. 2023b). For instance, a nanocellulose-based multi-functional wound dressing was prepared *via* bioconjugation of CNFs with ε-poly-L-lysine (EPL) followed by bioprinting, chitosan crosslinking, and freeze-drying (Fig. 3E, (b)). The hemostasis activity of the 3D composite scaffold was confirmed with a low hemolysis ratio of 1.73% and high blood absorption 872%; meanwhile the bioconjugated EPL offering the scaffold with decent antimicrobial activity against *E. coli*, *P. aeruginosa*, and *S. aureus*.

Efficient conversion and sustainable development of agricultural residues-based nanocellulose materials are expected to control the agricultural biomass-waste pollution from the source and improve the quality and efficiency of agricultural product production. However, the complex raw material components, variable impurities, and difficult purification present challenges in the preparation of nanocellulose from agricultural residues and application beyond agriculture, especially in biomedicine (Liu *et al*. 2017a,b). Additionally, high production costs remain a challenge to the industrial application of nanocellulose in agricultural products. Therefore, the development of agricultural waste biomass-based nanocellulose with high quality for application in high value-added fields, such as biomedicine or pharmacy, could be one solution to make up for the high production cost (Liu *et al*. 2016; Yu *et al*. 2021; Biranje *et al*. 2022, 2023). Using low-cost agricultural waste biomass as raw materials to prepare full-component nanofibers that meet agricultural production applications is expected to be another solution to this challenge.

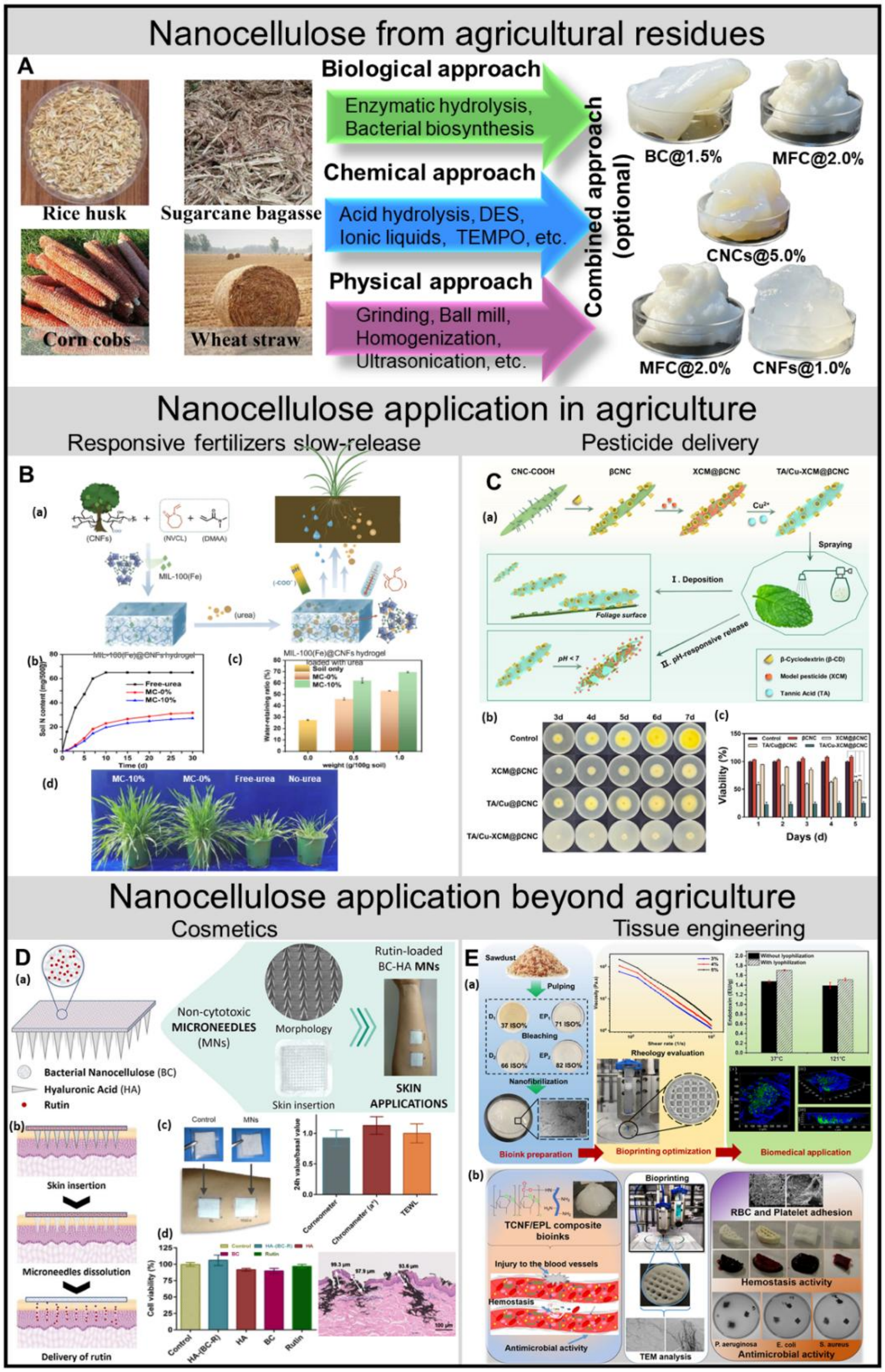


Fig. 3. Nanocellulose prepared from agriculture residues and application in agriculture and beyond. (A) Sources and pathways for conversion of agriculture residues into different types of nanocellulose; (B) Construction of CNFs-based responsive composite hydrogel for fertilizers release; (C) Preparation of CNCs-based pesticide carrier system with pH responsiveness, efficient antifungal, and insecticidal efficacy; (D) Skin application of nanocellulose-based microneedle patches for enhancing the cosmetic ingredients penetration; (E, a) Extraction of ultra-pure nanocellulose from sawdust for bioprinting application; (E, b) Functionalization of TCNF with ε-poly-L-lysine (EPL); and bioprinting of wound dressing with hemostasis activity and antimicrobial activity. Reprinted with permission from Elsevier (Fonseca *et al*. 2021; Lin *et al*. 2021; Jiao *et al*. 2024); Springer-Nature (Biranje *et al*. 2023) RSC (Ning *et al*. 2023).

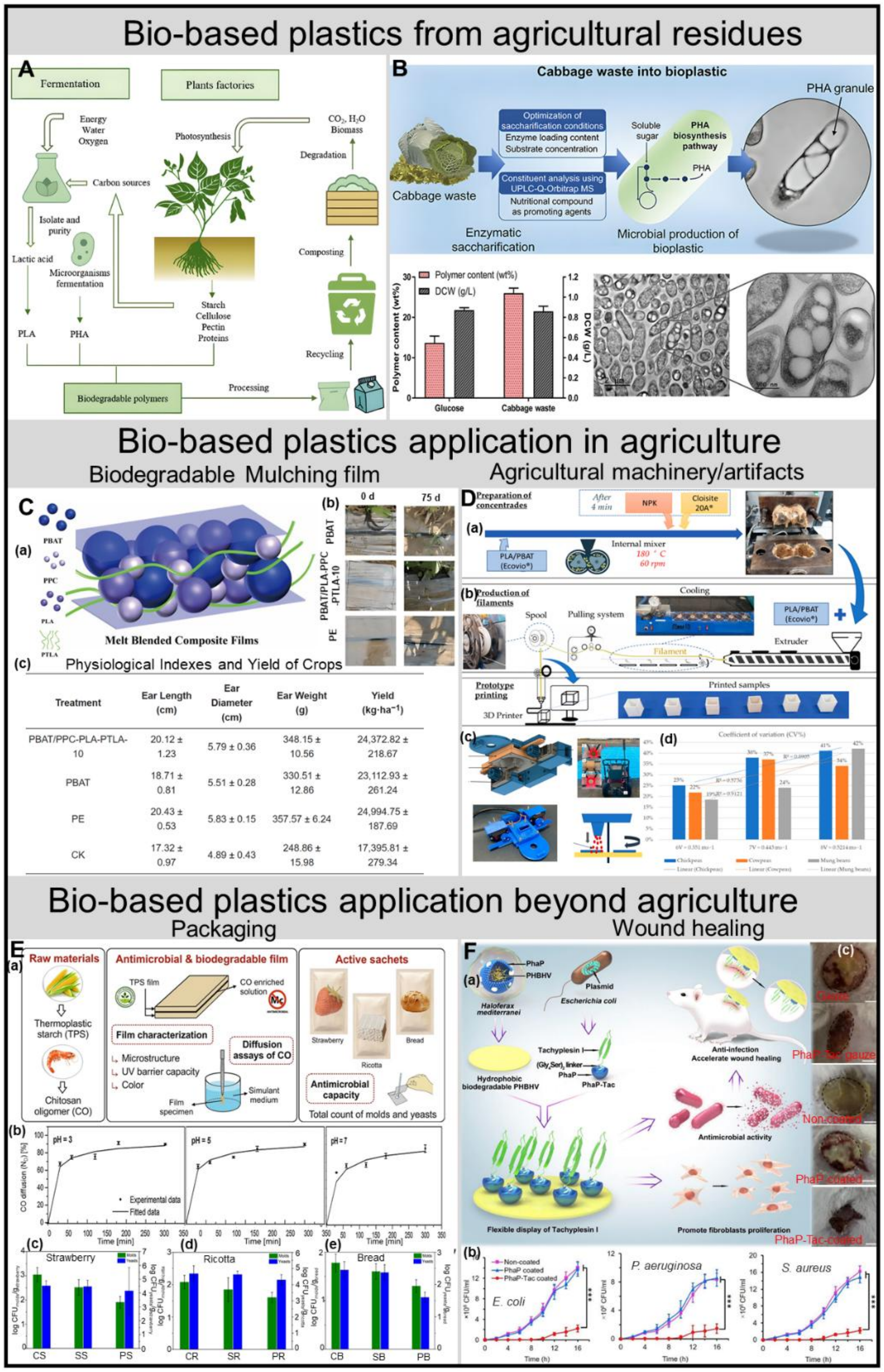
Preparation and Application of Bio-Based Plastics

Petrochemical-based plastics have experienced significant growth and have made great contributions to the global economic development since the invention of Bakelite in 1907, owing to their excellent properties. However, the depletion of non-renewable energy sources and the severe environmental pollution caused by non-biodegradable plastics necessitate the development of recyclable and biodegradable alternatives, thereby facilitating the rapid advancement of bio-based plastics or biodegradable polymers (Thiruchelvi *et al*. 2021; Babar, *et al*. 2023). Biomass, including various agricultural and forestry residues, is abundant in a variety of biopolymers such as cellulose, hemicellulose, starch, protein, and pectin, which can serve as carbon feedstock of microbial fermentation in the production of bioplastics, such as PLA and PHA/PHB (Fig. 4A) (Zhong *et al*. 2020; Vigneswari *et al*. 2024). Currently, valorization pathways for various agricultural and forestry residues into bioplastics mainly include: (1) mechanical, chemical, or biological pre-treatment of biomass waste, followed by a blending route. For instance, vegetable wastes, including spinach stems, tomato pomace, and cocoa shells, were blended with PLA with a content of up to 30%wt, followed by extrusion and hot-pressing to prepare biobased films for potential agricultural mulching application (Merino *et al*. 2022). (2) The next pathway is microbial fermentation of the biomass hydrolysate, which mainly consist of reducing sugars, into platform chemicals such as lactic acid and succinic acid, followed by chemical polymerization into the corresponding bioplastics, such as PLA and BioPBS (Kato *et al*. 2024). (3) The third pathway is microbial fermentation of the biomass hydrolysate with synchronized biosynthesis of bioplastics in engineered microorganisms (Vigneswari *et al*. 2024). For instance, Yang *et al*. (2024) demonstrated the feasibility of bioconverting the cabbage waste (CW) into PHA through enzymatic saccharification and microbial fermentation processes. The sugar conversion yield of CW can reach up to 90.4% under optimal hydrolysis conditions using cellulase and pectinase at 45 °C for 24 h. The engineered *Escherichia coli*, which incorporates the phaABC operon, can utilize the CW hydrolysate as a carbon source to produce the poly(3-hydroxybutyrate), achieving a polymer content of 26.0% or a dry cell weight of 0.86 g/L (Fig. 4B), showing promising prospects for the sustainable production of biodegradable plastic. Getachew and Woldesenbet (2016) used the sugar cane bagasse, corn cob, teff straw, and banana peel as raw material to produce PHB, and Paswan *et al*. (2023) used cotton stalk as raw material to produce PLA.

These abovementioned biobased plastics, especially PLA, have the greatest application potential in agricultural production for the use of agricultural mulch. This option has gained global attention from governments, enterprises, and research institutions due to the significant contribution of film mulching technology to crop yield (increasing yield by 20 to 30%) and enriching the fertility of the soil microenvironment after biodegradation (Menossi *et al*. 2021; Serrano-Ruiz *et al*. 2021; Mahmoud *et al*. 2022). However, the low ductility or high fragility, slow biodegradability, and high cost of pure PLA-based agricultural mulch have limited its broad application and thus necessitate the modification or blending with other components, such as PBAT, starch, and PHA, to meet the requirements of agricultural mulch. For instance, the composite agricultural mulch can be fabricated by melt-blending of PLA, PBAT, and compatibilizer PTLA or chain extender, followed by pelletization and single-screw extrusion film blowing (Fig. 4C, (a)) (Guo *et al*. 2024) or heat pressing (Lyu and Han 2023). The prepared composite mulch exhibited significant increase in the mechanical strength (58.6% increase) and water vapor barrier properties (70.3% increase), as well as a 30-days degradation extension (Fig. 4C, (b)), thus leading to an increase in maize yield of 5.4% compared with the PBAT film (Fig. 4C, (c)). Application of such composite mulch not only brings benefit to the crop yield, but also enriched the soils microbial community, especially the degrading bacteria *Sphingomonas*, *Bacillus,* and *Streptomyces* (Zhang *et al*. 2019). Additionally, a two-year lasting field experiment confirmed that the residues of such biodegradable mulch in soil had no significant effect on the succeeding crop yield, while the mulch residue could improve the soli health in terms of the soil structure indicators, including the bulk density, porosity, and organic matter content (Gao *et al*. 2021).

Another representative application of bio-plastics in agriculture is the 3D printing of intelligent agricultural machinery or artifacts used in facility agriculture. For instance, using 3D printing technology to customize the production of special facilities, agricultural machinery spare parts, or functional materials for innovative agricultural production. The agricultural machinery accessories, such as drip irrigation core valves, water pump paddles, and hydroponic substrate trays, have been 3D printed using bio-based PLA, PBAT, PHA, *etc*. (Wang *et al*. 2020; Zhu *et al*. 2020). Based on the tunable biodegradability of the PLA/PBAT, de Silva *et al*. (2022) fabricated a PLA/PBAT-based 3D printing mineral fertilizer slow or controlled release system for agriculture applications. The mixed mineral fertilizer was incorporated into the PBAT/PLA blend (Ecovio®) in an internal mixer and then subjected to filament production in a single-screw extruder for prototype printing of biodegradable planting artifacts with nutrients release (Fig. 4C, A, (b)). A PLA-based seeder was 3D printed and integrated with an autonomous vehicle for seeds broadcasting application (Fig. 4C, (c)) (Minn *et al*. 2023). The fabricated seed broadcasting system was capable of spread multi-crop seeds with variable seed distribution uniformity by adjusting the 3D printed seeder speeds (Fig. 4C, (d)). With the incorporation of deep learning-based intelligence, such intelligent agricultural machinery can also be used in precise fertilizers and pesticide applications for higher crop productivity.

Utilization of various eco-friendly bio-based plastics in packaging applications is increasingly being developed to replace all fossil-based plastics and achieve carbon neutrality. The global production capacity of bioplastics in 2023 was around 2.18 million tonnes, with the bio-based and biodegradable ones (PLA, PHA/PHB, PBS, and starch blends) accounting for 46.6%, and the values are projected to expand to a total production capacity of 7.43 million tonnes and 60.4% in 2028 (Ghasemlou *et al*. 2024). Except the aforementioned bioplastics such as PLA, PHA/PHB, and PBS, starch and other natural polymers as well as their derivatives are currently contributing to a vast share of global bioplastics. A comprehensive overview of starch-based bioplastics, including those derived from agriculture residues, in food packaging applications has been reviewed elsewhere (Gonçalves *et al*. 2024). However, further enhancement in performance and functionality, along with stimuli-responsive modification of bioplastics-based packaging materials are in a development trend, which broadens their application scope and added value. For instance, a thermoplastic starch (TPS)-based antimicrobial film was fabricated in a sandwiched structure *via* thermo-compressing of a chitosan oligomer coating layer between two TPS films for packaging perishable food to extend their shelf-life (Castillo *et al*. 2017) (Fig. 4D, a). The incorporated chitosan oligomer was able to migrate from the film in a wide media pH range (Fig. 4D, (b)) to significantly inhibit the growth of molds and yeasts in the packed strawberries, ricotta, and breads (Fig. 4E, (c), (d), (e)).



(c) Physiological Indexes and Yield of Crops

Treatment	Ear Length (cm)	Ear Diameter (cm)	Ear Weight (g)	Yield (kg·ha⁻¹)
PBAT/PPC-PLA-PTLA-10	20.12 ± 1.23	5.79 ± 0.36	348.15 ± 10.56	24,372.82 ± 218.67
PBAT	18.71 ± 0.81	5.51 ± 0.28	330.51 ± 12.86	23,112.93 ± 261.24
PE	20.43 ± 0.53	5.83 ± 0.15	357.57 ± 6.24	24,994.75 ± 187.69
CK	17.32 ± 0.97	4.89 ± 0.43	248.86 ± 15.98	17,395.81 ± 279.34

Fig. 4. Bio-based plastics prepared from agriculture residues and application in agriculture and beyond. (A) Schematic illustration the pathways of bio-based plastics production and their life cycle; (B) Valorization of cabbage waste into the bioplastic PHA *via* enzymatic saccharification and microbial biosynthesis; (C) Fabrication of a PLA-based biodegradable composite mulching film for corn crop planting; (D, a-b) Incorporation of fertilizer into the PLA-based filaments for 3D printing of agricultural artifacts with fertilizer release; (D, c-d) 3D printing of PLA-based seed broadcasting system integrated with autonomous agricultural machinery; (E) A thermoplastic starch-based biodegradable film with antimicrobial capacity to package perishable foods; (F) Immobilization of antimicrobial peptides-modified PHAs onto the PHBHV to fabricate an anti-infective wound dressing. Reprinted with permission from ASC (Yang *et al*. 2024); Elsevier (Castillo *et al*. 2017; Xue *et al*. 2018); da Silva *et al*. 2022; Guo *et al*. 2024; Minn *et al*. 2023; Zhong *et al*. 2020

In the field of healthcare, particularly in biomedical and pharmaceutical research and development, as well as clinical applications, bioplastics demonstrate significant potential for value-added applications. Currently, bioplastics such as PLA, PHA, BioPBS, and starch and its derivatives are being utilized in the development of wound dressings, drug carriers, tissue engineering scaffolds, biodegradable implants, and various medical devices (Nanda *et al*. 2022; Tareq *et al*. 2023; de Souza and Gupta 2024). Among these, PHA has attracted increasing attention from researchers due to its intrinsic biological activity, superior biocompatibility, broad functionalization potential, and versatile processability by various biofabrication process, such as electrospinning, solution casting, and various additive manufacturing methods (Bonartsev *et al*. 2019; Mehrpouya *et al*. 2021; Żur-Pińska *et al*. 2023). Although certain biological activities of PHAs have been reported, modification or functionalization of the PHAs-based biomaterials still is needed to achieve desired functionalities or therapeutic effectiveness. For instance, biofunctional poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBHV) film with antimicrobial activity and fibroblast-proliferative property was prepared for enhancing the healing of infected wounds (Fig. 4E, a) (Xue *et al*. 2018). A fusion protein consisting of PHAs-granule-associated protein (PhaP) and an antimicrobial peptides, tachyplesin I (Tac), was first biosynthesized in an engineered *E. coli*, followed by surface immobilization onto a *H. mediterranei*-produced PHBHV *via* hydrophobic interaction (Fig. 4E, a). Both *in vitro* and *in vivo* antimicrobial activity evaluation confirmed the significant reduction in the growth and colonization of both Gram-negative and Gram-positive bacteria in the presence of functionalized film (PhaP-Tac coated) (Fig. 4E, b). Upon the dressing with the modified film (PhaP-Tac coated) for 15 days, the size of the *P. aeruginosa* and *S. aureus* infected deep-wound showed significant reduction with a healing ratio of 76.2% compared to gauze (healing ratio 10.8%) and other groups (Fig. 4E, b). In another work, the PHBHV membrane was functionalized by incorporation of nanoceria into the electrospinning solution to enhance the cell proliferation and angiogenesis in the diabetic wound healing (Augustine *et al*. 2020). Similarly, PHAs that consist of 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HHx) monomers were modified by blending with silk fibroin and then subjected for electrospinning of bone tissue engineering scaffolds (Ang *et al*. 2020).

CHALLENGES AND OUTLOOK

Despite the increasing innovation and development of bio-based materials that have been derived from agricultural residues in recent decades, large-scale industrial production of related products is still in its infancy. This has further resulted in relatively high production and application costs for these bio-based materials, leading to weak commercial competitiveness relative to their less eco-friendly non-biobased counterparts. Although agricultural biomass and residues are abundant in nature, the diverse types, seasonal availability, scattered distribution, and low energy density of agricultural residues lead to challenges in their collection, storage, and transportation, resulting in high application costs and undermining the advantage of low costs associated with agricultural waste (Divyabharathi *et al*. 2024). Additionally, the technologies for the efficient and high-value conversion and utilization of agricultural residues are still immature for industrialization. Most existing reports have remained at the laboratory research stage or have focused only on the conversion and application of some high-quality biomass or partial composition, making it difficult to achieve comprehensive utilization of all components. At last, some of the current technologies struggle to meet the requirements of clean production and ecological safety during the conversion of these biomass waste, which can easily lead to secondary pollution or pose long-term environmental hazards (Purnama *et al*. 2022; Kumar *et al*. 2023; Simanke *et al*. 2024).

Under the core guiding principle of "Reduction, Reuse, Recovering, and Recycling," achieving a closed-loop economic cycle of "resources—products—recycled resources—recycled products" through clean production and comprehensive waste utilization is an inevitable choice for global sustainable development (Fig. 5) (Antar *et al*. 2021; Francioso 2024). To address the aforementioned challenges and "green and low-carbon" goals, it is important to break through the bottleneck of core process technology for low-cost production and realize the large-scale production and integration of bio-based material series products. Based on the distribution and categories of agricultural residues, adopting a strategy of localized and material-specific approaches to classify and separate different types of biomass resources and their components, while developing the most cost-effective products with high application potential, is an inevitable pathway for the practical implementation of agricultural residues conversion technologies. Additionally, merging with existing industry chains, *e.g.*, pulping and papermaking, food processing, and agricultural engineering, or upgrading the traditional production process for the new bio-based material processing technology could be an effective strategy for achieving large-scale production at a low cost and facilitating application in currently available market (Stasiškienė *et al*. 2022; Tardy *et al*. 2022).

The life cycle assessment and economic feasibility of converting agricultural waste into biochar, along with its functional modification and application in agriculture and environmental pollutant management, is still incomplete and not comprehensive. Additionally, the safety of biochar production and application in relation to the ecological environment, including the mitigation of greenhouse gas emissions and the safety of water bodies and soil, remains unclear (Kamali *et al*. 2022; Tan and Yu 2023; Shen *et al*. 2024). Moreover, the application technologies of biochar in high-value areas such as energy storage and conversion, as well as biomedicine, are still immature, primarily constrained by the low structural stability and high impurity content of biochar (Pierson *et al*. 2024). Despite all these, consideration of biochar applications in agriculture for fertilizer delivery, water retention, and soil quality enhancement is still active in seeking the most promising solutions for the comprehensive utilization of agricultural residues at this stage (Fig. 5).

Currently, the development of nanocellulose or lignocellulosic nanomaterials from agricultural residues faces a dilemma. Existing nanocellulose conversion technologies for high value-added applications, such as in food, cosmetics, and biomedicine often use raw materials with high purity, while agricultural residues typically have complex composition and high impurity content. Conventional purification processes, such as cooking (chemical pulping) and bleaching, often cause secondary pollution and resource waste, making the production costs and applications in traditional agricultural processes uncompetitive. On the other hand, although nanocellulose has great application potential in high-value fields such as cosmetics and biomedicine (Fig. 5), these applications impose strict requirements for the biosafety and purity of nanocellulose (Mateo *et al*. 2021; Liu *et al*. 2023; Jiao *et al*. 2024; Li *et al*. 2024). Therefore, it is essential to continue exploring new green, efficient, and low-cost nanomaterial processing technologies for agricultural residues, which could enable the return of impurities-containing lignocellulosic nanomaterials (*e.g.*, the lignin-containing CNFs) to agricultural applications (Shi *et al*. 2024; Chen *et al*. 2023). At the same time, for application scenarios demanding rigorous quality control, advanced purification techniques and functionalization methods should be implemented to meet biosafety standards.

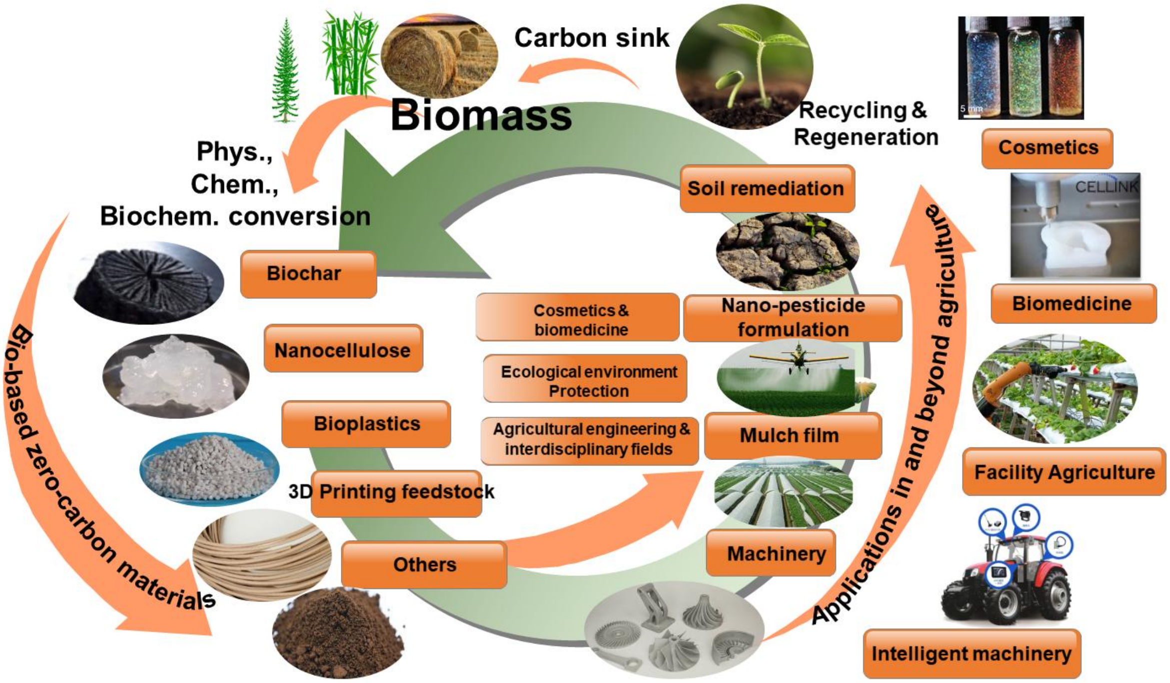


Fig. 5. Roadmap for development of bio-based materials from and back to agriculture, and beyond

Insufficient breakthroughs in key core technologies, persistently high production costs, and the relatively small scale of application markets are the main challenges facing the current development of the bio-based plastics industry. The production and conversion of bio-based plastics using agricultural residues as raw materials are particularly affected by seasonal fluctuations in raw material supply and the complexity and variation of different raw material components. Overall, while starch-based bioplastics and PLA have initially achieved large-scale production and application, conversion and production of these bio-based plastics directly from biomass waste still face significant challenges. Their comprehensive costs remain relatively high, and their performance, *e.g.*, product quality stability, mechanical properties, processing performance, and long-term impact on environment, is still not high enough to reliably replace the corresponding petroleum-based competitors (Moshood *et al*. 2022). Furthermore, the microbial biosynthesis of PHA is affected by the high content of impurities in biomass waste. The biosynthetic efficiency of most current strains still struggles to meet the requirements for large-scale production and widespread application in low value-added fields, such as the agricultural mulching (Fig. 5). Additionally, it is important to note that in the context of agricultural applications of PLA-based materials, special attention should be paid to their biodegradation requirements. Effective decomposition of these materials demands specific processing conditions, including controlled composting environments with temperatures above 55 °C, sufficient moisture levels, and active microbial populations. Improper disposal and accumulation in soil at ambient temperatures could potentially compromise soil quality and adversely affect crop growth as traditional plastics do (Satti *et al*. 2018; Slezak *et al*. 2023). Therefore, there are several key technical and process challenges need to be addressed in the future process of converting agricultural waste biomass to produce bio-based plastics (Thomas *et al*. 2023; Zhao *et al*. 2023; de Souza and Gupta 2024), including (1) How to achieve breakthroughs in the graded separation and pretreatment of agricultural waste biomass into fermentable hydrolysate with low impurities; (2) How to construct engineered bacterial strains with high tolerance to inhibitors and impurities, capable of conversion and synthesis of bioplastics at high-efficiency; (3) How to simplify and efficiently separate and purify bio-based plastics from the fermented liquid.

CONCLUSIONS

Agricultural residual biomass represents the world's largest "green carbon" resource. The efficient conversion and utilization of their residues not only can address potential environmental pollution but also can offer a solution to the dilemma of resource shortages. Without doubt, the deeper research and development, large-scale production, and widespread application of environmentally friendly bio-based materials in various areas will continue to drive the supplementation and eventual replacement of traditional petrochemical-based plastics, serving as a significant driving force for global sustainable development. However, the transformation of agricultural residues into representative bio-based materials and their reapplication in agriculture or other potentially high value-added fields still face challenges from many aspects. These include immature technologies in raw materials pretreatment, processing technologies, application promotion, and recycling. Recent years have seen the emergence of innovative biomass extraction and processing technologies, *e.g.*, biomass green solvents, nanolization processing, and AI-assisted synthetic biology. Coupled with an increasingly mature market for bio-based materials applications, these advancements have opened new avenues for addressing the aforementioned technical challenges. Meanwhile, as countries worldwide strictly implement "plastic restriction" policies, many petrochemical companies have begun upgrading their traditional industries and actively investing in biochemical engineering for bio-based materials production. This shift has laid the foundation for the low-cost, large-scale production and widespread application of bio-based plastics. Therefore, it can be foreseen that a closed-loop bioeconomic based on the conversion and utilization of various biomass waste will be an indispensable part of global sustainable development.

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