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Opinion

Sustainable Materials via the Assembly of Biopolymeric Nanobuilding Blocks Valorized from Agri-Food Waste

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Abstract: This paper presents an overview of current state-of-the-art agri-food waste valorization for developing advanced materials via the nanoscale assembly of biopolymeric building blocks. Emphasizing the imperative shift from a linear to a circular economy, the environmental impacts of agri-food waste, including its substantial contribution to global carbon dioxide (CO_2) emissions and resource depletion, are underscored. This study explores the potential of harnessing proteins and polysaccharides extracted from agri-food waste to synthesize advanced materials, such as films, hydrogels, and aerogels. The two categories of fibrillar nanobuilding blocks, including exfoliated fibrils from structural biopolymers like cellulose, chitin, silk, and collagen, as well as self-assembled protein nanofibrils from different proteins valorized from food industries' waste, are showcased. These biopolymeric nanofibrils can be further assembled to develop hierarchical advanced materials, with many applications in energy, environmental fields, and beyond. However, in this context, there are critical considerations, including the sustainability of the valorization methods, challenges associated with the heterogeneity of food waste, and the imperative need for a life cycle assessment to ensure complete sustainability. The delicate balance between integrating waste into the food chain and exploring alternative scenarios is discussed, along with challenges related to the short lifespan of agri-food waste, its heterogeneity, and the economic viability of valorization processes. Finally, the ongoing pursuit of developing high-performance, sustainable materials and the importance of societal cultivation to foster a circular economy mindset are discussed.

Keywords: agri-food waste; biopolymers; circular economy; nanobuilding blocks assembly; valorization

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1. Introduction

In this opinion article, I aim to share my insights on the current state of the art in agri-food waste valorization to develop advanced materials via the self-assembly of biopolymeric building blocks.

Our planet Earth finds itself pushed beyond its stable environmental boundaries due to the rapid surge in industrialization, a growing reliance on fossil fuels, and detrimental human activities [1]. The outcome of this profound shift manifests in far-reaching consequences, including global warming, climate change, freshwater scarcity, and chemical pollution [1,2]. These challenges represent a significant threat, emphasizing the pressing need for collective action to safeguard the future of our planet.

According to estimates, 800 million people worldwide are currently experiencing hunger, while 2 billion are facing deficiencies in micronutrients [3,4]. The paradox becomes apparent as one third of all food produced for human consumption is wasted or lost [5]. Addressing the global issue of agri-food waste is vital, knowing that 25% of global CO_2 emissions come from the agriculture and food sectors [6], 70% of freshwater resources [7], and 30% of the world's energy are utilized to produce food from farm to fork [8]. Recognizing the significance of this problem, one target of Sustainable Development Goal (SDG) 12 (responsible consumption and production) is explicatively dedicated to addressing food waste. Target 3 of SDG12 is to, "By 2030, halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses" [9].

Plastics, on the other hand, have emerged as a major global environmental concern due to their non-biodegradable nature, as they persist as environmental pollutants. Furthermore, their production from fossil fuels amounts to a 4.5% share of global CO_2 emissions [10].

At present, it is increasingly evident that we must shift from a linear economy characterized by the take–make–waste model to a circular economy [11], where waste is viewed as a valuable resource for materials development [12]. Additionally, due to their devastating impacts on our environment, there is a pressing need to transition from petroleum-based materials to those derived from nature, such as biopolymers.

A promising solution to reduce food waste, particularly that of the inevitably produced byproducts of the food industry, is to incorporate it into a new production line for developing new and innovative products [5,13]. Various compounds found in food waste, including proteins, polysaccharides, lipids, and polyphenols, can be successfully valorized to produce advanced products [5,14].

By taking this approach, we can transform the global issue of food waste into a solution that addresses other pressing global concerns. This not only shifts the carbon footprint of food waste from positive to negative [5], but also allows for the utilization of developed products and materials in tackling issues like water purification [12,15] and the production of bioplastics [16,17]. Furthermore, adding value to waste and elevating it to a high-commodity product will bring economic and industrial benefits [18,19].

2. Advanced Materials via the Nanoscale Assembly of Biopolymeric Nanobuilding Blocks

Two key biopolymers, i.e., proteins and polysaccharides, can be upcycled to produce advanced materials such as films, hydrogels, and aerogels by reassembling their building blocks.

Polysaccharides are complex biopolymers composed of long chains of sugar units linked by glycosidic bonds. They are crucial in various biological and industrial applications, particularly in developing sustainable materials derived from agri-food waste [20].

Proteins, essential components of the human diet, also play a pivotal role in developing sustainable materials, particularly when sourced from agricultural by-products or sidestreams [5]. Using the proteins extracted from these sources can significantly impact their potential for various technological applications, aligning with the overarching goal of creating environmentally friendly materials. Proteins, as linear polyamides composed of 20 amino acids, exhibit diverse chemical compositions and complex tertiary and quaternary structures. Their interactions can be precisely controlled, leading to constructs with high mechanical strength and toughness [21]. Proteins, being amphiphilic, interact specifically with other proteins or secondary macro-molecules, displaying varying affinities to different biopolymeric interfaces [22].

To begin, it is crucial to distinguish between the two approaches to preparing nanobuilding blocks: exfoliation and self-assembly. The building blocks of structural biopolymers can be hierarchically exfoliated. Additionally, there is the potential to prepare nanobuilding blocks based on proteins through their self-assembly into well-ordered structures. In subsequent sections, I will delve into each of these methods of nanobuilding block preparation.

2.1. Nanobuilding Blocks via the Exfoliation of Structural Polysaccharides and Proteins

In a top-down processing strategy, structural biopolymers such as cellulose, chitin, silk, and collagen can be broken down into nanobuilding blocks, which are then reassembled to construct advanced materials via a bottom-up approach [23].

Structural biopolymers are predominantly extracted from biomass through two main approaches: (1) extraction through the solubilization of the respective biopolymer and its subsequent precipitation, or (2) the purification of biomass fibers to isolate a solid, generally fibrous biopolymer by solubilizing its surrounding matrix polymers. In addition to their isolation methods, exfoliating nanofibrils from these biopolymers is critical to unlocking their full potential for nanomaterial development [20].

The exfoliation of nanofibrils from biopolymers is commonly achieved through mechanical methods such as high-pressure homogenization, ultrasonication, or shear forces, which effectively disassemble the hierarchical structures, creating nanoscale building blocks for diverse applications [24].

Next, I will explore common structural biopolymers, providing insights into their purification processes and the subsequent exfoliation of their nanobuilding blocks.

Cellulose

Cellulose is a primary structural polysaccharide abundantly synthesized in nature, with approximately 0.1–1 Gton produced annually [20]. The primary commercial sources of cellulose include wood and agricultural residues. Although traditionally extracted from these sources, cellulose often coexists with hemicelluloses and lignans, affecting its purity. Various cellulose derivatives, such as those produced from dissolving-grade pulps, further expand the material's applicability [20].

The most common method for isolating cellulose fibers is through pulping, where the matrix around cellulose is removed, and polysaccharide–lignin associations are cleaved. Kraft pulping, a chemical process using sodium hydroxide and sodium sulfide, is widely employed. Mechanical pulping is an alternative, though less frequently used. The solubilization of matrix polymers during these processes is based on the dissociation of matrix bonds and increased polymer solubility upon degradation or chemical modification. Notably, these processes alter the chemical structure of amorphous matrix polymers, such as lignin, impacting the resulting biopolymers. Mechanical treatments like homogenization or sonication can be applied to exfoliate nanofibrils from cellulose. These processes break down the cellulose fibers into nanoscale dimensions, producing cellulose nanofibrils with enhanced properties for various applications [20,24].

Chitin

Chitin is another structural polysaccharide synthesized in insects, mushrooms, and crustaceans. Upon deacetylation, chitosan, a soluble form of chitin, is formed. Chitin exhibits distinct properties due to its acetyl groups, participating in hydrogen-bonded networks. Chitin is the only positively charged polysaccharide, which enables it to have electrostatic interactions with negatively charged surfaces and molecules [25]. Chitin is extracted through sequential acidic and alkaline treatments to remove proteins, polysaccharides, and inorganic components. The strong interactions between chitin and proteins pose challenges in extracting pure chitin, leading to residual protein content bound to chitin. Mechanical methods like high-pressure homogenization or enzymatic treatments can exfoliate chitin nanofibrils. These approaches break down the hierarchical structure of chitin, leading to the isolation of chitin nanofibrils with improved purity and unique properties [25].

Silk

Silks and silk fibroin, structural proteins renowned for their mechanical strength and β-sheet-rich architectures, represent a unique class of proteins with the potential for outstanding mechanical properties. Silk fibroin, as the main proteinaceous building block, holds promise as a sustainable material, and insights gained from its study may unlock the optimal implementations of other proteins in material science [26].

Silk fibroin, extracted from silk cocoons, undergoes processes like degumming to remove sericin. Silk nanofibrils can be exfoliated through mechanical methods, such as high-shear mixing or ultrasonication. These techniques disrupt the hierarchical organization of silk fibroin, isolating silk nanofibrils suitable for various nanomaterial applications [26].

Collagen

Collagen, a foundational protein in the extracellular matrix of connective tissues, presents itself as a remarkable structural biomolecule with distinct properties. Collagen protein fibers from animal tissues, particularly in leather-making processes, showcase hierarchical structures contributing to their mechanical strength. Rich in triple helix motifs, collagen fibers form an intricate network, imparting resilience and stability to various tissues in the human body. The collagen fiber's hierarchical organization, akin to silk fibroin, is an inspiring template for developing materials with exceptional mechanical properties [27].

Collagen, derived from animal tissues through processes like leather-making, can be exfoliated into nanofibrils through enzymatic treatments or by mechanical means. Enzymatic digestion breaks down collagen fibrils into their nanoscale components, while mechanical methods such as shear forces or homogenization can be employed to achieve exfoliation. These processes yield collagen nanofibrils with unique structural and functional characteristics for diverse applications in nanomaterials [27].

2.2. Nanobuilding Blocks via the Self-Assembly of Proteins

Proteins from sources like whey, soy, and rapeseed can be converted into protein nanofibrils through self-assembly, with dimensions around a couple of nanometers in diameter and lengths up to a couple of micrometers [5]. Amyloid fibrils, a novel category of nanofibrillar materials, exhibit distinctive surface functionality and an exceptionally high surface-to-volume ratio. Comprising repetitive core sequences, including hydrophilic and hydrophobic amino acid segments, folded within fibrillar and often twisted structures, these nanofibrils typically have diameters ranging from 5 to 10 nm and lengths, extending up to several micrometers. Characterized by supramolecular polymers rich in β-sheet secondary structures, amyloid protein nanofibrils adopt a cross-β structure with β-strands perpendicular to the fibril axis [28,29]. Fabricating these nanofibrils involves denaturing and self-assembling various proteins under acidic conditions and elevated temperatures [29].

Various proteins can be isolated from agri-food waste for amyloid fibril production [5,17,30]. To harness this potential, diverse extraction and recovery processes for proteins from animal- and plant-based food waste have been explored. In the dairy industry, whey proteins are recovered through ultrafiltration and diafiltration, yielding nutritious whey protein concentrate (WPC) and isolate (WPI). Plant proteins, categorized as albumins, globulins, prolamins, and glutelins, are extracted from oilseeds and cereal grains using acids, alkaline solutions, salt, enzymes, and alcohol–water solvents. Techniques like isoelectric precipitation, ultrafiltration, and diafiltration are employed to purify these proteins, while considering temperature, pH, and additives. The upcycling and purifying of proteins from diverse food waste streams contribute to sustainability by transforming waste into valuable resources [5].

2.3. The Re-Assembly of Nanobuilding Blocks into Advanced Materials for Energy and the Environment

The biopolymeric nanobuilding blocks obtained by both the methods of exfoliation and self-assembly can then be applied as building blocks to construct new biopolymer-based materials. While I will not delve extensively into the intricacies involved due to the abundance of existing literature on the subject [20,23,31–34], it is worth noting that the primary method for processing biopolymers (colloidal matter) involves using solvents [5,20,23,27]. This approach encompasses the assembly of macromolecules, coacervation [35], and various other techniques to produce capsules [35,36], membranes [37,38], hydrogels [39,40], aerogels [30], and fibers [41,42], offering a broad spectrum of potential applications in the energy and environmental fields, including water purification [28,37,38], bioplastics [13,17], and green bioelectronic and energy-related materials [18,43].

The most successful initiatives in agri-waste valorization for material production are related to the development of bioplastics. Numerous cases highlight the effective utilization of cellulose, chitin, and protein sidestreams in bioplastic production. For example, startups such as InventWood and Cellugy actively demonstrate their production of cellulose biomaterials. In terms of water purification applications, BluAct is a startup specializing in developing high-tech membranes based on protein nanofibrils. These membranes can be produced on a large scale and exhibit superior efficacy in purifying water of a broader range of pollutants, including heavy metals, organic pollutants, viruses, and bacteria. In the field of bioelectronics, although there is promising scientific research, especially on silk and nanocellulose, there remains a need to transition these scientific advancements into viable and widely available products (scaling up and commercializing). These examples showcase some diverse initiatives and successes within agri-waste valorization, particularly in the self-assembly of biopolymeric building blocks for advanced functional materials.

Based on their applications, bio-based materials offer the potential of their reuse or recycling. For instance, aerogels made from protein nanofibrils can undergo regeneration through a straightforward acid-washing process [44]. These regenerated aerogels can then be effectively reused for removing pesticides, pharmaceuticals, and phenolic compounds over three consecutive cycles with no significant changes in their removal performance [44]. Yet, when it comes to managing the end-of-life phase of these materials, various recycling methods, including mechanical, chemical, and organic, can be employed [45]. Mechanical recycling involves reusing waste as a valuable raw material for further processing. Chemical recycling, on the other hand, focuses on feedstock recycling. Additionally, organic recycling uses methods such as anaerobic digestion or composting. Compared to chemical and mechanical recycling, which can be more expensive and less favorable due to the need for enhanced systems to separate bio-based materials, organic recycling emerges as a sustainable alternative [45].

3. Critical Considerations

While valorization conveys a sense of sustainability, ensuring that the methods and chemicals employed in the process are also sustainable is crucial. Furthermore, it is essential to consider the specific limitations associated with valorization. Despite numerous reports highlighting the enormous potential of biopolymeric self-assembly for sustainable materials, it is necessary to address and discuss the limitations that warrant consideration explicitly. Drawing upon a detailed examination of the literature [46,47] and personal experience in the field, I have identified seven pivotal considerations requiring comprehensive attention in the context of agri-food waste valorization (Figure 1). These parameters intricately cover various aspects of the process, spanning from ecological sustainability, technical feasibility, and practicality to economic viability and societal acceptance.

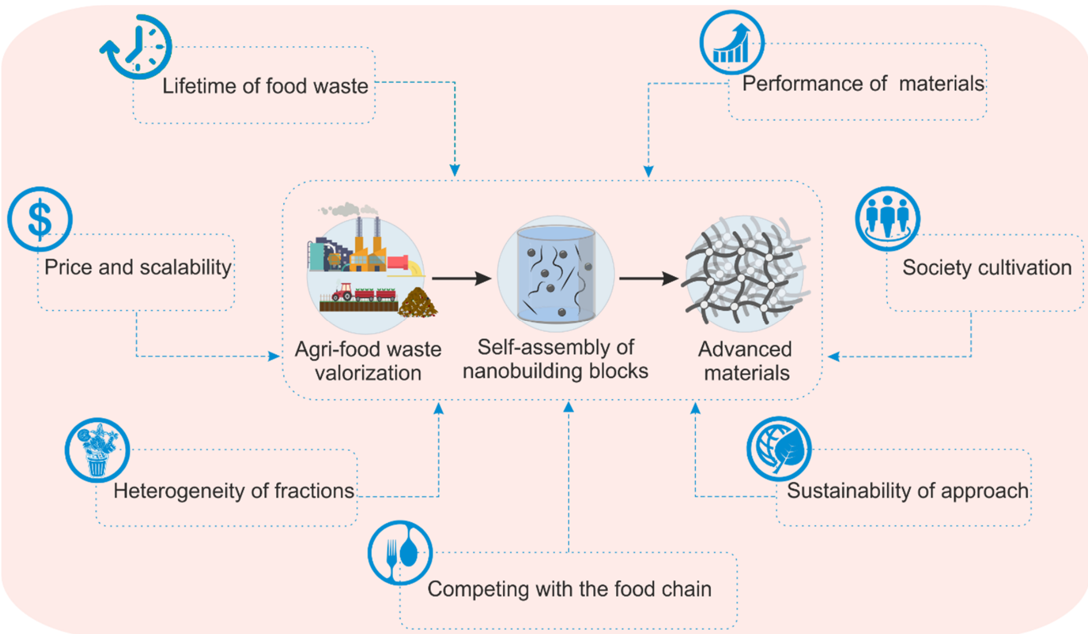

Figure 1. Critical considerations in agri-food waste valorization for developing advanced materials.

3.1. Competing with the Food Chain

There is a delicate balance between utilizing waste within the food chain and exploring alternative scenarios. In the hierarchy of food waste valorization, the primary focus is on valorizing waste and byproducts within the food chain before considering other scenarios [48]. While waste from the food sector holds immense promise, certain byproducts harbor antinutritional compounds, rendering them unsuitable for direct human consumption. A case in point is the rapeseed cake, rich in protein yet tainted with phytic acid, hindering mineral absorption in the human body [49]. Similarly, keratin, constituting around 90% of chicken feathers, is unsuitable for human consumption due to its difficulty in digestion [50,51]. Moreover, various food industry sidestreams pose unique challenges that make their direct integration into the food chain impractical or undesirable. One example is the lignocellulosic biomass derived from agricultural residues or certain fruit and vegetable peels. While these materials are abundant and rich in cellulose, they are often challenging to incorporate into traditional food products due to their fibrous and indigestible nature [52]. Additionally, certain agri-food waste streams exhibit complex compositions that require specialized processing to make them suitable for human consumption. For instance, the outer shells and husks of certain grains and nuts contain valuable compounds but may also contain undesirable compounds, such as tannins or phytates, which can affect taste and nutritional quality, hindering their direct integration into the food chain [53].

3.2. Lifetime of Food Waste

The period for converting food waste is typically short, primarily due to its perishable nature [54,55]. The short lifespan of agri-food waste and byproducts poses a challenge in promptly executing valorization processes. Given the high water content in most agri-food waste and sidestreams [46], the risk of biological growth is elevated [54,55], adding complexity to the valorization process that demands rapid execution. While drying may be considered, this requires energy input [56]. Moreover, in valorization, procedures like exfoliation or self-assembly to obtain building blocks, as well as the production of biocolloidal solutions, are typically carried out in aqueous environments [20]. Consequently, drying and a subsequent re-dispersion become counterproductive in these cases. In recognizing the intricate balance between preservation and valorization, exploring alternative avenues to address the specific requirements of diverse valorization techniques is imperative. The development of innovative preservation techniques or the integration of energy-efficient drying methods tailored to the unique characteristics of agri-food waste could represent promising directions for enhancing the efficiency and sustainability of valorization processes [56]. Moreover, exploring novel approaches that mitigate the risks associated with biological growth during the interim stages of waste handling could offer valuable insights into optimizing the entire valorization chain.

3.3. Heterogeneity of Fractions

The heterogeneous nature of food waste introduces a layer of complexity to valorization [57]. Understanding the heterogeneity within food waste fractions is pivotal for developing effective valorization strategies. Mainly, household food waste displays notable variability, impeding biopolymers' straightforward extraction and assembly for material production. Consequently, valorization methods face challenges in achieving a standardized approach due to the ever-changing nature of these organic residues. This variance favors valorization methods such as anaerobic digestion. By harnessing microorganisms to break down organic matter, anaerobic digestion is an effective method of extracting energy and valuable byproducts from the diverse organic compounds in household food waste [58]. In contrast, food waste and sidestreams obtained directly from industry tend to have a more homogeneous composition and condition [47], thereby facilitating the production of high-value materials through biopolymeric assembly.

3.4. Sustainability of Approach

The concept of waste valorization aligns with sustainability, but the methodologies and processes involved in this valorization must also be sustainable. The use of hazardous chemicals, energy-intensive processes, and the risk of secondary pollution are significant risk factors to overall sustainability, requiring careful consideration. A crucial and practical tool for assessing the sustainability footprint of valorization scenarios is a life cycle assessment (LCA). An LCA provides a quantitative and qualitative analysis of environmental impacts, allowing for the optimization and enhancement of the sustainability of entire valorization scenarios. It involves four key steps: goal and scope definition, inventory analysis, impact assessment, and interpretation [59]. Collecting life cycle inventory data is the most time-consuming and data-intensive aspect of LCA studies [60]. This challenge is particularly pronounced in agri-food waste valorization, where the agri-food industries often withhold access to process data. This limited access hampers our comprehensive understanding of the environmental impacts associated with agri-food waste valorization processes. By studying each phase of the life cycle, from material extraction and production to use and disposal [5], one can identify areas for improvement, implement eco-friendly practices, and ensure that the benefits of valorization endure without compromising broader sustainability goals.

3.5. Price and Scalability

For sustainable materials to gain industry acceptance, they must not only be environmentally friendly but also economically viable [61]. Despite the cost-effectiveness of raw materials from food waste, intricate processes can inflate end-product prices. In waste valorization, the economic viability of transportation becomes a critical factor, mainly when dealing with high volumes of waste [62]. Efficient waste collection logistics are essential to ensure that increased operational costs do not compromise the environmental advantages of valorization. To address this challenge, strategically locating valorization facilities near the food industry emerges as a critical strategy. This not only minimizes transportation distances and their associated costs but also fosters a more integrated and circular system [63]. Furthermore, scalability is a crucial consideration in the production of biopolymeric materials. Specific lab-based processes may not be feasible for continuous implementation in industry or in a cost-effective manner. For instance, in bioplastic packaging, most biopolymers lack the thermoplastic properties required for processes such as injection molding, which poses challenges in leveraging existing plastic technology for their production [64]. Nonetheless, there is the potential to employ other established industrial processes, such as solvent casting methods [17] or 3D printing [65], for these purposes, albeit with necessary modifications.

3.6. Performance of Developed Materials

The quest for sustainable materials necessitates not just an equivalence but a surpassing of the properties of their traditional petroleum-based counterparts. Bridging the gap between biopolymers and conventional materials is an ongoing challenge, yet the trajectory of technological advancements and dedicated research suggests a narrowing divide [64]. The intersection of material science, engineering, and environmental studies is propelling the development of high-performance, sustainable materials [66] that not only meet but exceed the expectations set by their traditional counterparts. For example, there is still a gap between the properties of bioplastics and their conventional petroleum-based counterparts. Emerging innovative techniques and advanced processing methods are needed to enhance the mechanical, thermal, and barrier properties of biopolymers [67,68]. Moreover, integrating nanotechnology and innovative materials holds promise in creating materials with superior performance characteristics [69].

3.7. Society Cultivation

Yet, despite the growing awareness of the need for a circular economy, a segment of the population persists for whom the concept of obtaining materials from waste may not be inherently appealing. Overcoming this resistance requires a concerted effort to foster a culture that not only understands the principles of a circular economy but also embraces the idea of waste as a valuable resource [70]. One way to achieve this perspective shift is by highlighting successful case studies and innovative solutions. Singapore's NewWater facility is a compelling example of the effectiveness of wastewater reuse [71]. This facility has not only revolutionized water management in the region but also exemplifies the potential of transforming waste into a valuable resource. Drawing inspiration from such success stories is crucial in instilling confidence in the public regarding the efficiency and safety of recycled materials. Educational initiatives play a crucial role in fostering a societal mindset that values circular economy practices and engages proactively in them [72]. Beyond theoretical discussions, practical experiences are invaluable in shaping perceptions. For instance, organizing guided tours for schoolchildren and the general public to visit advanced waste treatment facilities can provide them with firsthand experiences. These visits can showcase the advanced technologies employed, assuring the public of the stringent quality controls in place to ensure the safety and reliability of materials derived from waste. Furthermore, integrating circular economy principles into the educational curricula at various levels can contribute to long-term societal change [73]. Future generations can develop a natural inclination toward circular practices by incorporating lessons about resource conservation, sustainable production, and waste reduction into their learning. This educational approach aligns with global efforts to enhance environmental literacy and foster a sense of responsibility toward sustainable living. It is also essential to address the economic aspects of circularity, emphasizing the potential for job creation and economic growth associated with a transition to circular business models [74]. The circular economy has the potential to generate new industries, job opportunities, and innovative business models, thereby making the concept more appealing to a broader spectrum of the population.

4. Conclusions

The journey towards agri-food waste valorization for advanced material development is both promising and challenging. Its promising potential lies in its ability to upcycle biopolymers, i.e., proteins and polysaccharides from agri-food waste, and use the obtained nanobuilding blocks, through reassembly, to create advanced materials, providing sustainable solutions across various applications. Despite the extensive potential benefits, addressing challenges such as competing with the food chain, the perishable nature of the waste, and the heterogeneous composition of its fractions is essential. Sustainable approaches, from extraction to processing, are crucial, requiring careful consideration of the methodologies, energy consumption, and chemicals utilized. The economic viability and scalability of waste valorization processes are critical for industry acceptance. Despite the challenges, ongoing technological advancements offer avenues to bridge the performance gap between biopolymers and traditional materials. The societal mindset must evolve, with educational initiatives pivotal to cultivating an understanding and appreciation of circular economy principles. As we navigate this transformative journey, the harmonious integration of technology, sustainability, and societal engagement is crucial for realizing the full potential of agri-food waste in shaping a more circular and sustainable future.

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