Bio-derived nanomaterials for energy storage and conversion

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Abstract
This review covers recent progress and advancements in bio-templating nanomaterials for use in energy applications. Viruses, bacteria, and fungus, as well as plant and animal biomasses such as woods, coffee grounds, and crab shells, can be used as the templates or carbon sources for metal- and carbon-based nanomaterials. Here we provide an overview of each of these materials as a template, with emphasis on the synthesis methods and qualities of nanomaterials fabricated using these templates. Research in this field is understandably diverse, as such, we aim to further its development by providing a timely summary of current research. We anticipate that this field will continue to prove highly applicable to the salient and growing topics of renewable energy.

KEYWORDS
bio-templates, energy, nanomaterials

1 | INTRODUCTION

Materials for energy storage and conversion applications are at the pinnacle of modern society due to the importance, large range of applicability, and the global desire to shift toward cleaner energy. The rising need for energy has placed a need to find suitable candidates for energy storage that are green and cost efficient.[1] As such, the ever-growing need for alternative green energy has been at the forefront of renewable energy. Further, sustainability is a hot topic for developing high-performance energy storage and conversion materials. Biomass from plants and animals are promising as alternatives to typical starting materials for the logical design and synthesis of nanomaterials to be used for energy applications. For instance, carbon black, used in lithium-ion batteries (LIBs), is a petroleum derived product and shows poor applicability to sodium-ion batteries (SIBs).[2] Therefore, finding suitable replacements for petroleum derived components in electrochemical systems is necessary to shift the paradigm toward scalable biologically derived materials.

Utilization of waste biomass allows for the conversion of waste products, such as coffee grounds, into societally beneficial materials.[2–4] Both the overwhelming abundance of biomass and the various microstructural properties of biological samples allow for a large selection of biomass to be considered, offering excellent versatility for material design. Unlike viruses or bacteria bio-template
precursors, plants do not multiply as rapidly, therefore self-assembly methods are not typical of plant derived materials. Macroscale biomass has advantages in other areas, rich in carbon and heteroatoms such as nitrogen, sulfur, and phosphorous, offering certain levels of intrinsic doping when thermally treated. Heteroatom doping, from biomass is beneficial for tuning the electrochemical properties of the resulting carbons. However, due the nature of biomass derived materials, the stoichiometry and exact levels of dopants and inorganic impurities may be variable across the large range of available options. It is of interest to further develop methods to control the levels of intrinsic dopants and minerals more precisely.

Over the past decades, scientists and engineers have approached energy related problems by looking to Mother Nature for inspiration. For instance, the natural structure of certain biomass may be particularly useful for the logical design of materials. As an example, the anisotropic nature of wood may be useful for developing materials with different properties depending on the direction of the grains when processed. Converting biomass to bioderived nanomaterials for energy storage and conversion applications is especially appealing for waste products. Developing methods to convert the already massive supply of waste to useful products is greatly beneficial to society for waste reduction, carbon sequestration, and energy related applications. By using waste materials, great promise and feasibility for commercialization may be realized. Through simply carbonizing biomass, synthesis of nanocarbons can be done in one step rather than two and they do not need any template removal after synthesis.\[5\] This is especially of interest for scalability, due to the high energy requirements of converting biomass to carbon, reducing the number of steps to process and using low cost precursors is necessary. Additionally, there is a wide variety of biological starting points, causing research into these materials to be quite broad; therefore, a review is important to advance further research development in the field. Bioderived nanomaterials have been both directly and indirectly prepared from viruses, bacteria, fungi, protists, plants, and animals.\[2–4,8,28,36,46–49,56,63–73,80–95\] The different structures, from the many different templates, offer unique features that can benefit the performance of the material synthesized.\[6\] Classification of the various applications and the structural features of the materials produced from these sources plays an important role in understanding what types of applications each precursor may lend itself to. Since there is a large range of different starting matter, there is a broad array of possible nanostructures due to the different structures associated with each biomass precursor. Even just within fungi alone there are vastly different structures possible; molds tend to form branching filamentous structures called hyphae, while yeasts may form spherical, ovular, or rod-like morphologies.\[7\] These structures may prove useful for controlling morphology and structure of the resulting biomasses. On the other hand, using plant matter such as coffee grounds allow for the synthesis of hierarchical porous carbon (HPC), and use of coconut husks allows for the preparation of mesoporous carbon.\[1,3,8\] Further, the atomic composition of biomass can be exploited in a process where the heteroatoms are intrinsically doped into the materials from sources such as proteins and DNA. These biomass precursors are typically inexpensive compared to metal that is used in oxygen reduction reactions (ORRs).\[9\]

It can be seen that various morphologies can be achieved through different biomass precursors, and a timely review of bioderived nanomaterials for energy storage/conversion applications is highly beneficial to the research community in order to further advance renewable energy technology. It is worth noting, recent contributions in the field from Lou’s group resulted in a review paper regarding the use of biomass-based materials for “green” lithium batteries.\[10\] His team’s work offers a comprehensive overview of fabrication and application of biomass and biomass derived materials, further offering mechanistic insight into the carbonization process of biomass. Recently, Yang’s group published a comprehensive review on the utilization of biomass derived carbons for energy and environmental applications.\[11\] This review offers a great section on catalytic graphitization and activation, along with providing current obstacles regarding preparation of porous graphitic carbon materials. Based on their works and our own understanding, we summarize Table 1 to present advantages and disadvantages of biomass-derived materials for energy application.

### Table 1: Advantages and disadvantages of biomass-derived materials for energy application

| **Advantages** | **Reference** |
|----------------|--------------|
| Low cost starting materials | [10,11] |
| Highly conductive 3D carbon networks | [10,11] |
| Interaction between biomass and active material facilitated | [10] |
| Various structures possible through careful selection of starting material | |

| **Disadvantages** | **Reference** |
|-------------------|--------------|
| Variable quality control | [10] |
| Low yields for high surface area materials | [10] |
| High production costs for scale up | [10] |
| Material properties vary with feedstock | [10,11] |
In this review we categorize a plethora of bioderived nanomaterials for energy related applications by several factors: origin of the biomass, structure of the resulting material, applications in various fields, and how cost effective the synthesis is when compared to the commercially available counterpart. Further, we consider the advantages of the intrinsically doped heteroatoms as well as the importance of utilizing waste materials for these applications.

## 2 Microorganism Derived Nanomaterials

Microorganisms show great promise for bio-templating nanomaterials, many microorganisms are easy to produce in large quantities, have surface properties useful to bio-templating, and have structures particularly useful to the fabrication of nanoparticles. In addition, there are available tools for modifying these qualities to further suit a given application. The bacteria *Escherichia coli*, the Tobacco Mosaic Virus (TMV) and the M13 Bacteriophage are the most common research subjects, having suitable surface properties and being commonly cultivated across many bodies of research. Other bacteria, viruses, and fungi that have been investigated as bio-templates for energy applications are summarized in Table 2 alongside the produced structure (Figure 1).

### 2.1 Viruses

Viruses are a popular bio-template for synthesizing nanomaterials used in energy applications. Many virus structures are well understood, with research dating back to the 1920s. Virus populations form precisely arranged homogenous structures, and their structures are suitably modifiable with available tools. A given viral structure can be modified in shape or functionalized using genetic tools. Virus structures as bio-templates are additionally advantaged by their lack of a membrane and their well-defined structures. These structures are often directly suitable for nanomaterial fabrication, as shown in Figure 2. Virus remains can be simply removed from bio-templated materials, and virus structures are resilient to environmental changes such as pH and temperature. Viruses can be grown in a wide variety of structures and are able to self-assemble and replicate with homogeneous populations remaining in solution.

Production of viral structures (also known as virus like particles, or VLPs) is most commonly done by growing bacteriophages in *E. coli* bacteria strains. This method is preferred due to rapid production and ease of scaling. Apart from bacteriophages, other viruses such as the plant-based TMV can be replicated through heterologous expression, where *E. coli* is genetically modified to produce virus structures.

TMV is a rod-shaped virus that has been specifically investigated as a bio-template due to the ability to mineralize its inner and outer channels, allowing for control of the width of materials created from its template. The virus consists of 2100 identical coat proteins, with a length of 300 nm, an outer diameter of 18 nm, and an inner diameter of 4 nm. These TMV VLPs can be mineralized to create semiconducting and insulating nanowires, resulting in materials that are applicable to the energy industry. TMV nanorods can be easily purified, are stable, and can be modified through a variety of methods to maximize functionality. When placed in an acidic environment, TMV nanorods will self-align head-to-tail due to hydrophobic interactions at the rod ends, allowing for nanowire templating. Niu et al. showed that this can be further stabilized through in situ polymerization of polyaniline at the rod ends. TMV nanorods have been shown to bind gold nanoparticles to their surface when modified with cysteine residue to produce TMVcys, while the wild-type virus nanorods did not.

TMV-based nanomaterials have been investigated for use in battery electrodes due to their high surface area and durability to volume expansion. TMVcys nanorods are easily bound to a metal electrode surface due to thiol-metal interactions and can then form a nano-forest structure to
increase electrode surface area.\textsuperscript{[14,21]} This is typically followed by the activation of the TMV1cys surface using a palladium catalyst and deposition of a metal oxide using an electroless deposition solution to produce metal oxide coated nanorods (see Figure 3).\textsuperscript{[14]} Liu et al. has shown that this structure can reduce mechanical and electrochemical stresses between the electrode and current collector, as well as improving reaction kinetics and cycling stability.\textsuperscript{[25]} Electroless deposition on TMV1cys has been used to fabricate nickel, cobalt, and cobalt oxide nanowire materials.\textsuperscript{[14,19,21]} TMV-templated platinum nanorods suspended in a PVA matrix exhibit conductance switching, which is applicable to digital memory systems.\textsuperscript{[26]}

Another common virus used as a bio-template is the M13 bacteriophage, a virus with a thread-like shape and a homogeneous coat of negatively charged surface protein.\textsuperscript{[27]} M13 is approximately a micrometer long with a diameter under 10 nm.\textsuperscript{[28]} M13-based cobalt oxide
nanowires can be fabricated using electrostatic interactions between the virus surface and solvated metal ions, resulting in homogeneous crystalline Co$_3$O$_4$ nanowires. Nam et al. show that modifying this process to reduce the ionic strength of the deposition solution can produce discrete nanoparticles as well as nanowires. M13 nanowires have been applied to energy storage, light harvesting, and plasmonic metamaterials.

The filamentous bacteriophage $fd$ virus has been used as a bio-template in similar situations as the M13 bacteriophage. $Fd$ virus is longer (880 nm to TMV’s 300 nm) and thinner (6.6 nm to TMV’s 18 nm) than M13 making it more suited for highly porous materials and it has a single coat protein that differs from M13 by one amino acid. $Fd$ surfaces have been shown to adsorb silica through acid-catalyzed hydrolyzation without surface modifications. $Fd$-templated silica nanostructures have been fabricated as smooth-surfed nanorods, rough-suraced nanowires, and bowtie-shape bundles.

While the bulk of virus bio-templates create rod- or wire-shaped nanomaterials, the Chilo iridescent virus (CIV) has been investigated for templating rough-surface nanospheres. CIV is a large icosahedral virus with significant internal structure and a maximum diameter of 185 nm. It has been shown that gold particles will bind to a CIV surface in solution, with increasing ionic strength of the solution lowering repulsion between metal particles and allowing more metal to bind to the virus surface. Gold-covered CIV nanoparticles fabricated this way have been shown to have a rough, irregular surface.

The various methods to use viruses as bio templates have advantages and disadvantages to each other. Biomineralization, deposition, and adsorption all use surface properties as their driving forces. These methods can all use...
pretreatment methods to control pore size. Pretreatment of deposition methods allows for control of the product shape. With proper adsorption methods, the amount of metal that binds to the surface can be controlled.

Viruses are an appealing choice for the bio-templating of nanomaterials. The methods used to produce and isolate virus structures are well established and suitable for producing VLPs in research and industrial settings. Particle populations produced this way are mono dispersed and the structures are usually resilient against chemical and mechanical damage. A wide variety of structures and surfaces are available, which can be modified without significant deviation from the normal production process. Bio-templated nanomaterials from virus structures show promising electrical and chemical properties of note to energy applications, in particular current collectors and battery electrodes.

2.2 Bacteria

Another candidate currently being investigated as a microorganism bio-template to create nanomaterial used for energy applications is bacteria. Bacteria are easy to cultivate, can be genetically modified, have uniform sizes, and well-defined morphologies. Mass production of bacteria also does not harm the environment. Furthermore bacteria can self-assemble; allowing for the preparation of monodispersed nanomaterials. This section will include different bacteria that have been utilized as bio-templates to synthesize nanomaterials. *Bacillus subtilis* (subtilis), *E. coli*, *Halobacterium salinarum*, and two strains of lactobacillus will be reviewed in the section.

Subtilis is a gram-positive bacterium that has a rod shape, a diameter of ~500 nm and average lengths from 2 to 5 μm. SEM and TEM images demonstrating the surface structure of the bacteria is shown in Figure 4. The cell wall of subtilis consists of peptidoglycan which contains the following functional groups: phosphate, teichoic acids, and carbonyl. The phosphate groups have a negative charge which allows for electrostatic interactions to occur between the surface of the cell and metal oxides. This method is visually shown in Figure 5.

Metal oxides bind to the cell via reduction on the surface, then undergo spontaneous oxidation resulting in a bacteria metal hybrid. The hybrid material is then calcined to remove organic material leaving a porous metal oxide hollow nanorod. The metal oxide product retains the bio-template’s shape. Furthermore, pore size can be controlled by the addition of modified polystyrene (PS) spheres containing amine groups. The diameter of the PS spheres can be adjusted to modify pore size. PS is used because it can be easily removed from the final product.

Additionally, subtilis can also be reacted with glutaraldehyde and then mercaptoethyamine to form thiol groups on the cell wall. These thiol groups then bind to gold nanoparticles via SH-gold interactions.

The resulting nanorods formed via this method are being investigated as potential electrodes because they have large surface areas, short ionic transfer paths, and
can accommodate Li-ion strain generated from insertion/extraction.\textsuperscript{[39]}

Furthermore, subtilis can be used as a bio-template using hydrolyzation to create titanium oxide nanosheets. The nanosheets are formed by adding T-butyl titanate to the bacterial colony suspended in ethanol. The metal binds to the surface of the cell by hydrolysis from water leaving the cell. The size of nanosheets can be controlled by varying the amount of metal in solution. The shape of the nanomaterial is controlled by phosphorus that came from functional groups that leaked through the cell wall during the hydrolyzation process. The nanosheets interlace to form a 3D matrix due to phosphorus acting as a steric barrier.\textsuperscript{[35]} To further improve the electrocatalytic capabilities of the 3D nanosheet matrix, the authors calcined the product in an inert atmosphere to form a carbon coated 3D nanosheet matrix. The carbon source was the bacteria bio-template. The carbon coated matrix is then covered in platinum via electrodeposition. Zhang proved the method can be used with multiple species of bacteria, which indicated that surface structure does not deviate the method, instead, Zhang found that the method requires bacteria that contain phosphorus molecules.\textsuperscript{[35]}

\textit{E. coli} is a gram-negative bacterium with a rod-shape, an average length of 1.4 $\mu$m and an average width of 0.6 $\mu$m.\textsuperscript{[35,40]} Nomura et al. and Zhang et al. successfully created nanomaterials from \textit{E. coli} bio-template through hydrolysis. Nomura et al. added zirconium butoxide and alcohol to the bacteria colony, forming nanorod hybrids. The hybrids are then calcined to remove the bacteria template.\textsuperscript{[40]} The main difference between the two methods is that nanomaterial synthesized using Nomura’s method retained the shape of the bio-template.

In addition to using whole \textit{E. coli} cells as bio-templates, the flagella can also be used. The size of \textit{E. coli} flagella ranges from 10 to 15 $\mu$m in length and 12 to 25 nm in diameter.\textsuperscript{[37]} Unlike using the whole cell as a bio-template, the \textit{E. flagella} must be modified to add peptide loops in order for metal-ion nanoparticles to bind to the surface, forming nanotubes.\textsuperscript{[37]} The flagellin can be genetically modified to change the order of the amino acid chains to create a more effective bio-template.\textsuperscript{[31]} that has been investigated in depth.\textsuperscript{[41,42]}

\textit{Salinarum} bacteria is an archaeabacterium that is being investigated as a potential bio-template. \textit{Salinarum} is found in extreme environments which is beneficial for bio-templating because it will allow the method to use conditions such as a very acidic or basic environment without causing damage to the structure of the template. \textit{S. flagella} has an average length of 10 $\mu$m and a diameter ranging from 10 to 15 nm. The flagella are protein based and contain no DNA. The flagella must be genetically modified with aspartate or glutamate to form carboxyl groups. These groups form the binding sites for metal ions to attach to the flagella to form nanowires.\textsuperscript{[43]} Similar to \textit{E. coli} flagella, different peptide loops can be added.

\textit{Lactobacillus} (LB) are gram positive, have cell walls consisting of peptidoglycan, teichoic acid, and teichuronic acid. The two types of LB that Zhou and his collaborators used as bio-templates are \textit{Streptococcus thermophilus} (thermophilus) and \textit{Bulgaricus}. \textit{Thermophilus} has a spherical shape with a diameter ranging from 0.5 to 0.9 $\mu$m. \textit{Bulgaricus} on the other hand, has a rod shape with lengths ranging from 1 to 5 $\mu$m and widths ranging from 0.3 to 0.8 $\mu$m.\textsuperscript{[44]} Zhou et al. used two different methods to use LB as bio-templates to create different nanostructures.

Zhou et al. proposed utilizing sonochemical conditions to synthesize nanoparticles by templating the two strains of LB. ZnS nanoparticles bond to hydroxy, phosphoryl, and carboxyl groups on the cell wall of LB are used. The hybrid
metal is then introduced to ultrasound which disrupts the organic material causing the cell to break apart and the broken pieces to disperse into the solution leaving porous, hollow ZnS spheres or rods depending on the starting template. This method using thermophilus is visualized in Figure 6.[44]

The second method Zhou proposed is a hydrothermal process. LB is added to a solution consisting of Zinc acetate and triethanolamine. The pH of the solution is set to 9 by adding ammonia to make the solution basic.[36] Triethanolamine binds to hydroxy, phosphoryl, and carboxyl groups on the cell wall of LB used. The newly metal hybrid is then calcined to remove the bacteria from the hybrid leaving porous ZnO spheres or rods depending on the starting template. The ZnO material formed has a thickness ranging from 200 to 400 nm.[44]

Bacterial bio-template synthesis methods utilize surface properties of the bacteria to bind metals. One disadvantage that all templating methods face is that the bacterial precursor needs to be removed before the product can be used. Deposition methods do not require a live bio-template, while reduction, hydrothermal, and hydrolyzation methods do. Furthermore, the live templates may mess up the product as shown in Figure 6. Bacteria must be alive during the bio-templating process, otherwise the metal will not bind to the surface of the cell.[45] Because of this, the bacteria can undergo cell division during the templating causing an uneven coating as seen in Figure 6. Another disadvantage that using bacteria as bio-template is the cell breaking before a uniform coating has been achieved. This phenomenon can also be seen in Figure 6 and Figure 7.[44]

While using bacteria templates does have these disadvantages, it also has advantages compared to other templating methods. Similar to viruses, bacteria can be modified to improve functionality. It is very easy to grow in large quantities of bacteria in a short period of time.[35–37,44] The nanoparticles are monodispersed over the bacteria bio-template, while nanomaterial synthesized from chemical means has a more uneven dispersion over the template.[37] Another advantage of using bacteria is control of the shape. A variety of shape of the original bio-template can be retained or nanosheets described by Zhang that can interlace with each other to form a 3D matrix porous microspheres can be derived.[35]

### 2.3 Fungi

Research has primarily focused on baker’s yeast as a bio-template for metal oxide nanospheres, with other fungus applications making use of particular features of a given fungus structure. Fungus-templated nanomaterials have primarily seen applications towards battery electrodes.

Baker’s yeast cells are eukaryotic, elliptical, and typically 3–4.5 μm in size, and have a surface charge.[46] Carboxyl, amide, and phosphate groups across the surface allow for surface functionalization using electrostatic interactions.[47] The surface can be further functionalized using methods like pyrolytic degradation, calcination, or fermentation.[47–49] Yeast has been used as a bio-template to form nanospheres of zirconia, zirconium phosphate, silicate, iron(III) oxide, cerium(IV) oxide, cobalt(II,III) oxide, tin(IV) oxide, and lithium iron phosphate nanospheres, microspheres, or mesoporous nanospheres (see Figure 8).[47,49–54]

Yeast templated LiFePO₄ particles were fabricated from baker’s yeast Zhang et al. in 2012. The yeast is first prepared by pyrolytic degradation, which decomposes the cell to produce active biocarbon and prevents Fe cations from oxidizing. FeCl₃ is then added, where Fe³⁺ cations coordinate to anion biomolecules in the template. Upon addition of (NH₄)₂HPO₄, phosphate groups react with iron cations to produce FePO₄ nanoparticles inside and on the yeast cell wall via biomineralization. The mineralized yeast cell is then mixed with LiOH and calcinated to produce biocarbon-coated LiFePO₄ nucleus-nanoparticles (see Figure 9). These particles are spherical, mesoporous, and are surrounded by a nuclear shell. This shell can inhibit the formation of LiFePO₄ agglomeration. The distributed nanoparticles are shown to reduce the length of the Li⁺ solid state transport paths. The surface area, pore size, and volume of these particles can be controlled; therefore, researchers were able to optimize the pore size for lithium diffusion. Coating the particle with a conductive carbon
A nanocomposite was shown to improve lithium diffusion and particle conductivity.\textsuperscript{[47]}

Biomineralization of yeast cells was also applied to create mesoporous silicate air electrode electrocatalysts, as well as mesoporous zirconium phosphate air electrodes. Pore size and shape was controlled during synthesis by modifying the reaction mixtures. Yeast’s negative surface charge was used to prevent disilicate from bonding to the yeast cell wall, allowing silica to coat on the surface. This nanoparticle was then calcinated to remove the yeast
template, leaving a mesoporous silica/carbon air electrode material.\textsuperscript{49}

Sugunan et al. formed gold microwires from the conidia of several species of fungi. \textit{A conidiun} is a fungus spore that is generated through cellular mitosis.\textsuperscript{45} Live cultures of \textit{Aspergillus niger}, \textit{Aspergillus nidulans}, and \textit{Neurospora crassa} were introduced to a solution containing gold nanoparticles and glutamate. As the fungus consumes glutamate to grow conidia, the disturbance of local charge arrangement encourages the attachment of gold nanoparticles to the growth surface. This behavior was not seen in dead fungi samples or samples without a growth medium.\textsuperscript{55}

The common forest waste fungus bran is chitin-rich, making it a good source of nitrogen. Forest bran can be carbonized to form N-doped carbon materials. Researchers have fabricated zinc-manganese oxide (ZMO) nano-cubes from fungus bran-templated carbon matrix. In this method, the fungus bran is cleaned and carbonized then activated with potassium hydroxide. The activated carbon matrix is annealed in a solution containing ZMO to form nano-cubes. This material was compared against other common materials used in supercapacitors and showed excellent cycle stability. The material is durable to ZMO volumetric expansion.\textsuperscript{56}

Fungi templating methods include biomineralization and deposition. Deposition methods utilizes the surface charge of the template, but it requires the template to be alive. Biomineralization methods prevent agglomeration but are limited by functional groups on the cell wall.

### 2.4 | Algae

Algae is also a suitable bio-template for the synthesis of nanomaterials for energy applications. Algae is easy to cultivate, a source of carbon, and found in large amounts in nature.\textsuperscript{9} The increased use of fertilizers in agriculture lead to a massive increase of algae formation. For example, in the Yellow Sea there are annual green tides, which are large amounts of Enteromorpha algae (EA).\textsuperscript{57} This large increase of algae is very harmful to the environment, therefore the benefit is utilize EA as bio-template. Similarly, in the US the agricultural run-off carried through the
Mississippi watershed results in annual dead-zones in the Gulf of Mexico. These dead-zones negatively impact the local commercial fishing industries in coastal Louisiana. Developing methods to collect and utilize these algae for energy storage and conversion offers a unique solution to combat this issue. Algal-templated nanomaterials have primarily been used in LIBs due to their ability to generate porous carbon structures that reduce ion transport paths, improve ion diffusion rates, and improve specific capacities. Algae bio-templates can be scaled at relatively low costs.

EA primarily consists of polysaccharides and proteins, providing heteroatoms needed to dope the carbon matrix. EA has channeled walls that are around 10 μm thick. The dense distribution of the cells makes EA a suitable candidate as hierarchically porous carbon. Lu et al. managed to develop a one-step method that uses pyrolysis to synthesize nitrogen-doped porous carbon (n-EA). This carbon has a honeycomb shape. This method achieves doping, carbonization, and activation in one step. Lu et al. then used n-EA to synthesize cobalt iron oxide nanowires. CoFe₂O₄ nanoparticles bind to the n-EA can be achieved by hydrothermal treatment. The carbon from the n-EA acts as a barrier to prevent agglomeration in the cobalt iron oxide nano particles. Cui et al. used a similar method to create a high surface area porous carbon aerogel (HPCA) that is shown in Figure 10.

The HPCA produced has a tube shape with diameters ranging from 5 to 10 nm. The HPCA has a surface area of 2200 m² g⁻¹. SEM images of the HPCA are shown in Figure 10. The applications of this HPCA is wide. Cui et al. tested their HPCA to be used in electrical double layer capacitors (EDLCs) and LIBs. Furthermore, they were able to attach cobalt oxide nanowires via hydrothermal treatment. Similar to Lu’s method, the nanoparticles that bind to the HPCA are at random locations. The cobalt nanowires synthesized using EA as the bio-template have lower internal resistance and increased pseudo capacitor performance compared to cobalt nanowires synthesized under the same hydrothermal method without the HPCA. The pore size can be controlled by changing the amount of KOH that is used during activation, but using more KOH reduces the yield of the HPCA.

Spirulina is another alga that has been used as a potential bio-template for energy applications. Spirulina is a blue-green alga, with a spiral coil shape that consist of many single cells. Spirulina consists primarily of protein and is a suitable carbon source. It has a length of 20 μm and a width of 200 μm. The spiral structure is very sturdy and spirulina retains its spiral structure during sonication and heat treatment.
Xia et al. synthesized lithium iron phosphate/carbon using spirulina as the bio-template and carbon source. Live spirulina is added to the solution, which consists of lithium, iron, phosphate, and glucose molecules. Ammonia is then added to make the solution basic, which is preferred to maintain the structure of the spirulina. The solution is stirred for uniform distribution, then transferred to a Teflon-lined autoclave where it undergoes hydrothermal treatment. The product is then heated at 650 °C under a mixed atmosphere to remove any remaining water. The templated LiFePO$_4$/C has an average pore diameter of 25 nm and BET surface area of 22 m$^2$ g$^{-1}$. The carbon from the spirulina connects the LiFePO$_4$ nanograins creating bridges. These carbon connections increase stability and improves the ability to store lithium ions. Further, the carbon bridges can increase grain to grain electronic contact and reduce internal resistance between the grains.[59] Figure 11 shows the synthesis methods and TEM images of the carbon bridges.
Unlike viruses and bacteria, algae cannot be easily genetically modified to improve its capabilities such as binding affinity and surface charge. Another challenge that algae faces is that it is not homogenous, therefore not all materials made from algal bio-templates are uniform. Algae also need to be cleaned, usually done by decolorization before it can be used as a bio-template. Furthermore, the algae must be alive for some of the templating methods used.

3 | PLANT DERIVED NANOMATERIALS

The abundance of plant matter on earth allows for a large range of different types of structures to be prepared for application towards energy storage and conversion materials. Over the past few years various research groups have undertaken the task of utilizing various methods to produce nanomaterials from plant matter. The large diversity of plant material allows for the preparation of large arrays of various structures due to the diversity in plant microstructures and material synthesis routes. For instance, the phytochemicals of *E. cognata* have been successfully applied as a bio-template for preparation of nanoscale particles. These works use a modified MOF preparation method to prepare two different materials from this method using the phytochemical from *E. cognata* leaves. Another popular material precursor for prospective energy storage and conversion materials is wood, due to its anisotropic nature. A common method of preparing materials from wood includes pyrolysis, resulting in a biochar with hierarchically structured pores. Further, some notable examples of biomass starting material include coffee, aloe vera, pollen, phytochemicals, wood, oatmeal, oatmeal, bean sprouts, and bamboo. To summarize, a large number of nanostructures are possible from plant matter, including fibrous materials, sheet-like structures, hierarchically porous materials, and spherical particles. In this section, various plant-based precursors are identified and evaluated based on the type of structures prepared from the plant matter (Table 3).

Commonly, to utilize plant-based biomass for energy storage/conversion material applications, thermal treatment of biomass to carbon is typical. Despite the simplicity of calcining biomass to achieve carbon, there is a large number of various modifications to this process, yielding different types of carbon matter with vastly different electrochemical properties. Regardless of how it is modified, calcining biomass to carbon has the advantages of being low-cost, facile, and non-time intensive. However, scalability is often a challenge for pyrolysis due to the hefty energy requirements for large batches. Methods such as using the pyrolysis products as fuel to help sustain the high temperatures required or using solar energy to prepare biochar may be of interest for improving the scalability of these processes.

3.1 | Wood

Wood as a precursor for energy storage/conversion materials is a hot topic due to the wide variety of various woods available to make soft or hard carbons. Wood has several advantages as a starting material such as: natural hierarchical structures, anisotropy, great mechanical properties, and the ability to tune the material for multiple functions. Further, there is an abundance of natural woods across the globe, being able to tap into this natural renewable resource offers an excellent option for carbon-based technology. More so, soft woods versus hardwoods is also a consideration when designing new materials for different applications. Softwoods are said to be homogeneous in structure with a lot of fibers; whereas, hardwoods are much denser in terms of bulk density and pore density, further offering great mechanical properties. The unidirectional channels in the wood structure allow for fast ion transport and is applicable in various devices including 3D wood, and wood paper based electrochemical energy storage devices.

In the work by Wang et al. poplar wood is converted to a hierarchically porous support for Co(OH)2 based solid-state supercapacitors. First, the wood is acid washed prior to calcination at 1000°C for 2 hours in an inert atmosphere. Next, the active material Co(OH)2 is introduced to the porous carbon through electrodeposition. Results from this study show that the wood carbon offers a hierarchically porous structure, allowing for fast ion-transport in the supercapacitor. The synthesis route of the carbonized wood and Co(OH)2 composite is shown in Figure 12A. 3D hierarchically porous electrode architecture with open channels and high specific surface areas were observed in the carbonized wood (Figure 12B-F). The wood-derived porous carbon networks not only serve as a high surface-area support to improve the load of Co(OH)2 nanoflakes (Figure 12G and 12H), but also allow fast electron conduction and ion diffusion, thus accelerating the rate performance. TEM image of the Co(OH)2@CW composite (Figure 12H) show numerous mesopores and continuous structure. The major advantage of this synthesis method is the preparation of electrode materials without the use of a binder, allowing for more active area per unit volume. Understanding the effects of thermal treatment of wood on the structure is important for developing related technology. Hierarchical porous structures are said to form when low viscosity precursor solution is infiltrated in the wood’s
| Biomass source | Processing method | Morphology | Surface area \([m^2 \cdot g^{-1}]\) | Elemental composition | Application | Reference |
|----------------|-------------------|------------|-----------------|----------------------|------------|----------|
| **Plant matter** | | | | | | |
| Coffee | Pyrolysis | Porous particles | 94.35 | – – – – | Sodium-Ion Batteries | [2] |
| | Pyrolysis | Hierarchically porous | 3549 | ~88.5% undetected | Super Capacitors | [3] |
| | Pyrolysis-Steam activation | Hierarchically porous | 541 | 82.30% 1.40% | Vanadium Flow Batteries | [4] |
| Wood | Pyrolysis | Hierarchically porous | 568.13 | – – – – | Super Capacitors | [6] |
| | | Carbon Aerogel | Porous carbon nanofiber network | 626 | ~90% (~5%) | Binder Free Electrode | [68] |
| | MgO Infiltration | | 24.7 | – – – – | Wood templated inorganics | [64] |
| Bamboo | Pyrolysis | Sheet-like particles | 2544 | 89.30% 2.10% | Super Capacitors | [72] |
| Bamboo and cassava | Pyrolysis | Porous particles | 111 | 80.70% – | Energy Storage | [79] |
| Oatmeal | Pyrolysis | Porous microspheres | 110.7 | 89.50% 4.10% | Sodium-Ion Batteries | [70] |
| Coconut | Pyrolysis | Porous particles | 1652 | – – – – | Lithium-Ion Capacitors | [8] |
| Alfalfa | Pyrolysis | Hierarchically porous | 1424.2 | 86.79% 3.34% | Ammonia Electrosynthesis | [97] |
| Pollen | Pyrolysis | Collapsed and spiky particles | 2544 | 83.18% 3.20% | Lithium-Ion Storage | [67] |
| Aloe vera | 3D Porous Network | Carbonization + inorganic infiltration | 661 | 80.50% 0.05% 13.10% | Photovoltaics | [66] |
| **Animal matter** | | | | | | |
| Crab shell | Pyrolysis | Micro-/mesoporous | 1298.2 | present present – present | Lithium-Sulfur Batteries | [84] |
| | Pyrolysis | Hierarchically porous | – | 85.64% 3.81% | Super Capacitor | [88] |
| | Pyrolysis | Nanochannel arrays | 58.26 | present – – | Lithium-Sulfur Batteries | [96] |
| | Pyrolysis-doping | Nanoflake helicities | 153 | – – – – | Lithium-Ion Batteries | [88] |
| Crab and rice husk | Pyrolysis with activation | Hierarchically porous | 3500 | 86.99% 1.67% 11.19% | | |
| Shrimp shell | Pyrolysis | Mesoporous carbon network | 447.1 | 86.93% 2.53% | Microbial Fuel Cell Catalyst | [89] |
| Fish | Calcination | Porous carbon sponge | 774 | 82.74% 2.86% | Microbial Fuel Cell Air Cathode | [90] |
| Hair | Calcination | Porous nanospheres | 379 | – – – – | Energy Storage | [94] |

(-) values are not reported.
cellular matrix, followed by subsequent calcination. It is further elaborated that heat treatment at various temperatures show the formation of nanoscale oxide pore channels, and an associated temperature dependence, affecting the connectivity and size of the nanopores.

Aside from directly carbonizing wood, it has been demonstrated that wood pulp can be used as a starting material for carbon fiber-based aerogels with noted applications toward renewable energy related materials. First, in this synthesis transparent wood nanofiber suspension in water is prepared by radically oxidizing wood cellulose pulp followed by mechanical disintegration. This step produces individual cellulose nanofibers. Next, the pulp is treated with hydrochloric acid, followed by subsequent suspension in acetone and organic acid catalyst. The suspension is then freeze dried with supercritical CO₂. Finally, the resulting cellulose aerogel is pyrolyzed between 700°C and 1000°C to prepare carbon nanofiber aerogel. Analysis of this carbon nanofiber aerogel matrix shows stacked graphite-like structures. This work is important to the field because it shows the very real possibility to prepare wood pulp derived carbon nanofiber aerogel, resulting in a cheap material preparation. Further, the excellent conductivity of the aerogels shows promise for use in commercial electrochemical energy storage and conversion devices. Other methods of preparing nanofibers from wood includes electrospinning. In a 2019 work, electrospinning is used to prepare nanofibers from a combination of wood lignin, poly(lactic acid) (PLA), and a thermoplastic polyurethane. It is found that an important factor governing the porosity of the fibers is the immiscibility of the PLA in the lignin/urethane phase, allowing for control of carbon fiber pores structure. This work is significant because it offers a unique way to utilize lignocellulosic wood waste.

Due to the structure of wood, interesting materials may be prepared by exploiting the fibrous structure and anisotropy of wood. In a recent work, balsa wood is transformed into a highly elastic, ionically conductive material. To prepare this elastic wood, the wood is first submersed in aqueous NaOH, followed by water washing, freezing, and subsequent freeze drying. During this process, it is suggested that NaOH partially removes lignin and hemicellulose, softening the wood and improving the elasticity, allowing for the wood to retain its shape post deformation. Further, the produced wood shows tunable ionic conductivity by increasing strain applied. The properties of this highly elastic wood lend itself to a variety of applications even beyond energy storage and conversion. More research should be put into applying this type of
process to a larger range of woods, allowing for optimization of the structure for particular applications. For instance, the unidirectional nature of the pores may prove to be beneficial for improving ionic conductivity and electrical properties by engineering the tortuosity of the resulting wood or prepared carbon.

Bamboo is another promising candidate for preparing uniquely structured carbons due to its microstructure. For instance, bamboo has been used to prepare sheet-like carbonaceous nanomaterials and tested for applicability in supercapacitors. Under the influence of a catalyst, nitrogen and sulfur-doped carbon is prepared and shows promise for the development of supercapacitor materials from bamboo. The detailed synthesis process is shown in Figure 13. This work develops a method to prepare highly porous bamboo derived with exceptional properties for supercapacitor material, outlining a method to achieve carbon with sheet like microstructure from biomass. Bamboo and cassava derived carbons are directly compared in a work by Singh’s group, showing high levels of graphitization. The bamboo carbon appears to have better stability, yet poorer electrochemical properties. On the other hand, the cassava showed carbon that has excellent electrochemical properties. It is suggested that, by combining the biomass, synergistic effects may be noted for future research directions.

3.2 | Coffee derived materials

Coffee is the second most consumed beverage in the world behind water, meaning that there is an excessive amount of coffee waste that needs to be managed. Similar to wood, the chemical composition of coffee is complex, naturally containing over 27 elements (most notably: Li, Na, K, P, and N). This makes waste coffee grounds an even more appealing energy related application towards storing Li, Na, and K. Over the past few years, several groups have worked on preparing and characterizing various carbon materials produced from waste coffee grounds for energy storage and conversion.

In the 2020 work by Liu et al. waste coffee grounds are converted to hierarchically porous structure from thermal treatment of coffee grounds under the influence of a catalyst and followed by KOH activation. It is suggested that the resulting carbon contains high levels of graphitization as well as a large number of pores formed from the decomposition of coffee’s phytochemicals such as caffeine. The synthesis process is schematically presented in Figure 14A. The TEM images of the obtained carbon without KOH activation (denoted MC) in Figure 14B reveals that MC possesses abundant mesopores with various diameters from several nanometers to dozens of nanometers. While HPC with KOH treatment in Figure 14F show fragmentized and thinner carbon sheets and a more amorphous structure, N₂ adsorption–desorption isotherm data in Figure 14D also shows that a significant amount of micropores is introduced by KOH activation for HPC samples. These results suggest that the FeCl₃ catalyst could create the mesopores-dominant structure and the subsequent KOH activation further introduced abundant micropores to form the hierarchical porous structure, as well as confirm that the treatment process of biomass is critical for the final carbon properties. Waste
Coffee grounds have also shown applicability in vanadium redox flow batteries as a potential replacement for bipolar graphite.\cite{4}

Aside from battery applications, zinc oxide @ carbon core-shell nanoparticles have been prepared from spent coffee as well, further applied towards direct methanol fuel cells.\cite{65} The naturally porous structure of the coffee grounds allows for infiltration of zinc precursor, upon thermal treatment and under the appropriate conditions ZnO@C is realized, showing excellent applicability towards methanol fuel cells. It has microspheres morphology shown in Figure 14E, which is drastically different from the sheet structure in the previous report mentioned above, further indicating the treatment process profoundly influences the final material properties. This work shows to be significant to the field in that the waste coffee (and many other biomass precursors) may be applied towards direct methanol fuel cells (DMFC) as well the potential to be applicable over a range of electrochemical energy systems.

Overall, a lot of work has gone into preparing functional materials from waste coffee; however, the studies that investigate coffee as a material do not entirely consider the effects of various brew types (i.e., espresso, pour-overs, cold brew) each requiring different grind settings and brew conditions. For instance, espresso extraction process uses fine grinds and hot water to prepare the coffee, extracting a large amount of the soluble compounds. Whereas cold brews extract at lower temperatures, leaving behind an excess of low solubility compounds. These extraction differences may produce vastly different carbon materials due to the size of the particles, and the additional compounds that may promote intrinsic doping. Further, the decomposition of the caffeine and other chemicals in coffee are suggested to promote the formation of voids.\cite{3} Caffeine has low water solubility at low temperatures, meaning that more may be left over, possibly increasing the amount of the voids present to make a highly porous carbon. Still more research should be put into identifying the preprocessing (brewing) conditions that affect the resulting carbonaceous materials produced from coffee. Further, during the pyrolysis of coffee, large amounts of bio-oils are released. These oils produced may also have the ability to be used to prepare active materials for energy storage and conversion applications in a similar way that \textit{E. cognata} is used in work by Shaheen et al.
4 | ANIMAL DERIVED MATERIALS

4.1 | Crab shell derived materials

A current hot topic for research is the utilization of shellfish waste biomass. The seafood industry outputs around 106 tons of waste per year, most of which is sold as low value products such as food for livestock.\(^{80,81}\) Shellfish shells have a large amount of the amine containing polysaccharide chitin, making it a great option for exploiting intrinsic nitrogen doping. Isolating chitin from shellfish shells can be achieved through either chemical treatments, or biological treatments.\(^{80,82}\) In chemical treatment routes, the shells are stripped of minerals, such as calcium, through acid washing. Next the proteins are removed using alkali treatment, followed by washing to isolate the chitin. Biological routes involve treatment with various enzymes such as papain, trypsin, alcalase, protease, and pepsin.\(^{80,82}\) Beyond this, if desired the chitin may be deacetylated with alkali treatment, or appropriate bio treatment, to produce the cationic polymer, chitosan.\(^{80}\) When carbonizing the chitin/shell waste some groups opt to just carbonize the chitin then remove minerals, the structure may be engineered by including or excluding certain steps.\(^{83,84}\)

Of the most commonly used shellfish, crab and shrimp appear to be the most researched. In 2019 Fu et al. utilized crab shells (Figure 15A) as a chitosan rich precursor for HPC materials, further testing for application in supercapacitors.\(^{85}\) To generate a porous carbon from the
crab shells, first the shells were carbonized in a furnace, followed by an acid wash, removing various carbonates and generating large pores. Next, the acid washed carbon is washed with water, dried, then activated with KOH at high temperatures. This carbon is shown in Figure 15B and 15C, where pores are clearly observed. The resulting hierarchically porous carbon is then used as a support for SrFe$_{12}$O$_{19}$ and assembled into a supercapacitor. This research is of interest because it shows a great application of shellfish waste for high performance supercapacitors, showing a 94% retention in capacity over 10,000 cycles.\[85\]

In addition to supercapacitor application, a Ca(OH)$_2$-Carbon framework has been successfully prepared out of crab shells and used as a separator material in Li-S batteries.\[86\] Because crab shells naturally contain an abundance of calcium, engineering of unique micro- and nanostructures is possible. The reported material is prepared through calcinating crab shells at various temperatures, then mixed into gelatin films to prepare the separator.\[86\] The preparation of this material is very similar to the previous preparation route, minus the acid washing. This shows great versatility and simplicity in engineering vastly different structures and chemistries from the same precursor. Interestingly, the structure of the carbon composite shows an array of nanochannels of Ca(OH)$_2$ as evidenced by the SEM images in Figure 15E and 15F. With the unique channel structure, the resulting material shows excellent performance in Li-S battery chemistry due to the ability to trap polysulfides, improving the longevity of the cells.\[86\]

Carbon nanofiber aerogels have also been prepared from crab shells, showing further application in energy storage and conversion. In a paper published in ACS Sustainable Chemical Engineering, carbon nanofiber aerogels are prepared from a multistep process where crab shell chitin is suspended in distilled water, crosslinked, freeze dried, and subsequently carbonized.\[87\] Preparing carbon as an aerogel allows for a conductive nanofibrous matrix with high surface areas, this is of interest due to the abundance of potential applications in multifarious fields. To further highlight the applicability and versatility, crab shell derived chitosan have also been prepared as a template to prepare mesoporous CoFe$_2$O$_4$/C material with helical hierarchical structures, further converting to nanoflakes under pyrolysis conditions.\[88\] The images of structural biomimicry from chiroptical chitosan membranes to hierarchically organized CoFe$_2$O$_4$/C nanomaterials are shown in Figure 16. The novel biomimetic strategy represents a great way to increase the economic value of the naturally abundant chitin sources for energy storage materials since the integrity of their structural arrangement upon replication has great potential for improved performance.

### 4.2 Shrimp shell derived materials

Shrimp shells are also a great source of porous carbon materials due to the abundance of chitin and proteins. Mesoporous carbon networks derived from shrimp shells have been reported in recent literature.\[89\] In this work, shrimp shells are acid washed, then thermally processed, producing a mesoporous carbon network high in intrinsically doped nitrogen and phosphorous heteroatoms. Further, the mesoporous carbon network is revealed to show favorable ORR properties due to the N and P dopants.\[89\] The schematic summary of the work is shown in Figure 17. This work evaluates the properties of the carbon with acid pretreatment, it may be of interest for future researchers to investigate the effects of post carbonizing acid treatments to evaluate differences in catalytic behavior, as well as material properties.

In another work published in 2020, application of shrimp shell for microbial fuel cells is evaluated for catalytic activity of the resulting carbon.\[90\] Using non-platinum group metals is of interest for catalyst development and design, as a way to reduce cost. This work is of interest because the intrinsically doped carbon shows suitable electrocatalytic activities, as a result of the nitrogen and phosphorous dopants.\[90\] The final catalyst does not rely on the use of any additional metals, precious or otherwise, showing great potential for applicability in electrocatalysts for other areas. Further, the similarities between shrimp and crab shells allow for
similar processing methods, and therefore similar materials to be prepared. Shrimp shell-based aerogels may be of interest for tuning the properties of the resulting material due to high levels of nitrogen and phosphorous doping.

4.3 Shell-less fish

Fish without shells also show great potential for applicability towards energy storage and conversion materials. Various components of fish waste (scales and bones) have shown to be good candidates for utilizing waste from the fishing industry. Fish scales and bones are interesting for biomass derived porous carbon materials due to the presence of collagen, and hydroxyapatite crystals influencing the morphology and porosity of the resulting carbons.[91]

Further, the abundance of this collagen rich biomass offers great potential for developing clean energy materials. The combination of proteins and inorganic matter allow for the preparation of porous carbon materials. Fish also contain amino acids, a useful precursor to prepare N/S co-doped hierarchically porous, these amino acids may be isolated from various biomass waste proteins.[92]

For example, fish collagen has been applied as an anode material for various battery applications, in lithium and SIB chemistries, pseudocapacitive storage mechanisms are noticed.[93] Niu et al. prepared porous carbons with tailored heteroatom doping and well-defined porosity as high-performance electrodes for robust Na-ion capacitors.[91] As demonstrated in Figure 18A, fish scale (with hydroxyapatite inside) is used as the precursor and pyrolyzed with potassium hydroxide to obtain hierarchically porous carbons at 550 °C and 800 °C, respectively (denoted HPC-550 and HPC-800). Due to the synergetic effect of potassium hydroxide and hydroxyapatite, well-define hierarchical structures with interconnected pores were obtained (Figure 18B-G). Moreover, due to the presence of heteroatoms in the collagen within fish scale, the HPCs are N,O-doped, which further improves the performance.

Another study also investigates fish-collagen derived materials for lithium, sodium, and magnesium-ion batteries chemistries, demonstrating satisfying performance.[93] This type of technology is promising for novel anode materials from animal biomass waste. Particular interest is aimed towards biomass containing proteins such as
collagen and inorganic matter such as hydroxyapatite, present in fish scales and animal bones.

4.4 Land animal derived materials

As previously mentioned, biomass sources such as animal bone, nails, and hair are promising precursors to electronically active materials for energy storage and conversion applications. For example, in the 2017 study by Liu et al. fiber based solid-state supercapacitors were prepared from human hair, using the hair as a source of fibrous carbon. This work highlights the properties of human hair and makes note that properties such as high tensile strength, elastic recovery, and slow degradation are excellent for flexible supercapacitor material. Further, the high levels of intrinsic dopants from the biomatter in the hair results in fibers with excellent properties directly from carbonizing. When nanostructure MnO₂ is deposited on the hair, the resulting solid-state super capacitors show excellent performance, attributed to the aforementioned properties of hair. This work is important to the field because most people have hair and require haircuts, having the ability to convert this waste product into something for future technology is an excellent way to advance the field. Not only that, various animals have different types of hair, it may be advantageous to study the relation between hair structure and resulting carbon properties.

In another work keratin, the protein found in hair, is converted to a “cheese like” porous carbon and applied toward zinc air batteries. The co-doping of nitrogen and sulfur are studied to determine the effects on ORR.
Animal bone is another potential waste product from the meat industry that can see use in energy storage and conversion devices. Carbon prepared from waste bones show high surface area and a unique hierarchically porous structure due to the composition of the bone. In this study, when applied as a cathode in Li-Se batteries, the resulting carbon exhibits great performance, allowing for a method to reduce the amount of animal waste that ends up in landfills.

Egg yolk has also recently been explored for applicability in energy storage and conversion materials. In 2019, Zhang et al. reported on the development of high-performance super capacitor material prepared from egg yolk. Firstly, egg yolk and iron precursor are mixed, hydrothermally reacted, and subsequently annealed, resulting in iron encapsulated nanoparticles in carbon nanotubes. The results of this study are interesting because during the process, carbon nanotubes appear to spontaneously form without any templating in a low-cost, facile method.

5 | INTRINSIC DOPING

A common point between all the carbon materials prepared from biomass of plants, animals, algae, and fungi all hold the similarity of intrinsic dopants. For instance, DNA and proteins contain an abundance of nitrogen due to the nitrogen containing building blocks. When calcinated, this nitrogen may incorporate into the carbon matrix, acting as an intrinsic dopant. This intrinsic doping ability of biomass allows for the optimization of electrochemical properties. For instance, it has been suggested that nitrogen may form three different nitrogen binding configurations, pyrrole, pyridine, and quaternary. The formation of these intrinsically bound nitrogen species in alfalfa derived carbon has been exploited to synthesize ammonia under ambient conditions, attributed to the pyridinic-N. The work by Jin et al. offers mechanistic insight into the carbonization process of biomass. First, there is the loss of water of the biomass followed by dehydration reactions and depolymerization. Next, the work describes the formation of aromatic carbon due to condensation reactions. It is likely that these two steps are responsible for any heteroatom incorporation into the carbon. Finally, the carbon forms turbostratic carbon and upon further heating high-degree crystal structures are formed. At this point, it is likely that the composition of intrinsically incorporated heteroatoms decreases.

In a later work, in developing materials for anion exchange membranes, the additional arrangements of graphitic nitrogen, oxidized nitrogen, and nitrogen bound to metal precursor are introduced. Further, in the 2019 study where alfalfa is converted to pyrolytic carbon, it is found that pyridinic nitrogen is electrocatalytically active for ammonia synthesis at ambient conditions. This work suggests that during the nitrogen reduction reaction, nitrogen vacancies are formed, acting as catalytic sites. This work is valuable in that it shows the true versatility and possibilities that come with the intrinsic doping properties of carbon derived from biomass.

In biological systems however, there is more than just nitrogen and carbon, additional heteroatoms that are formed include O, P, and S as mixed heteroatom dopants along with N, mixed heteroatom doping is conducive for applications in supercapacitors. Biomass derived carbons are regarded as a highly promising groups of materials due to many factors including the low-cost, abundance, and environmental friendliness. However, due to the nature of biomass, the exact level of dopants is incredibly difficult to control. Developing methods to control the dopant levels is important for future development of electronically active biomass derived nanomaterials. Dopant level modifications may be achieved through various methods such as acid or base treatments before or after processing. It is worth noting that in a review published in 2020, structural engineering of biomass derived carbons is discussed and includes several structural optimization strategies. Extrinsically doping the carbons may be the best option for better controlling the properties and compositions of the resulting materials. Depending on the thermal treatment atmosphere, in the case of carbonizing biomass, the processing gas may either be inert resulting in only intrinsically dopped heteroatoms, or reactive to extrinsically incorporate heteroatoms. For instance, incorporating additional nitrogen is possible through thermal treatment in an ammonia atmosphere. Additionally, porosity may also be tuned by introducing activating agents such as a mixture of carbon dioxide, water, and oxygen. Biomass structural optimization may be broken down into several strategies: hierarchical pore formation, pseudo-graphitic structure formation, heteroatom doing, and surface group functionalization. This work is important because it shows the potential for a large array of various functional carbon materials for application towards energy storage and conversion, further giving insight into engineering the material properties of biomass derived materials. Through experimentation and DFT calculations, it is determined that the reason the ORR properties are so good is due to the intrinsic dopants, resulting in more ORR active sites.

6 | CONCLUSION

Viruses and bacteria share many advantages for fabricating nanomaterials. Both template sources will self-assemble
into homogenous populations of a precise structure. This structure, and its surface functionalization, can be modified thoroughly using available genetic tools. Nanomaterials produced from viral and bacterial templates commonly have material properties that are easily applicable to battery electrodes. A significant challenge to research of viral and bacterial templating is the growth and purification of template populations. High purity viral and bacterial templates yield less product in creating the templates. Methods for doing so are well understood, cheap, and scalable; but poorly suited to producing many populations each in a relatively small size. The subsequent treatment of virus and bacteria feedstocks is often less complex, and so nanomaterials made from these stocks are likely to be scalable to industrial applications. Algal templates are very easy to gather in large quantities therefore scaling would not be an issue. Algae also provides a carbon source and can be templated using one step synthesis. Nanomaterials produced from algal templates have material properties that are beneficial to LIBs. One drawback to algal templates is that they require pretreatment before they can be used. Fungal templates can be scaled easily, have surface charges that allow for electrostatic interactions between the metals and the cell surface allowing for simple synthesis methods to be used. Like algal templates, the fungi used needs to be alive for most synthesis methods to work.

There are a great variety of plant- and animal- species. Each comes with inherently unique structure and heteroatom species and quantity. The treatment processes (e.g., acid wash, pyrolysis, and activation) also greatly influences the final carbon properties and performance. Although there are numerous research work on biomass derived carbon materials, there is no obvious trend or principle summarized to clearly guide the carbon-based material development. It would be of great importance to have a database to include carbon features (e.g., graphitization level, doping atoms, morphologies, porosity etc.) prepared from different biomass sources at different preparation conditions. With the abundant database, machine learning could be applied to discover and conclude the biomass-treatment-property-performance correlation, which will greatly guide lab work to achieve the desired carbon materials with the least time required. In conclusion, the efficient and effective utilization of millions of tons of biomass waste one earth for energy storage and conversion will tremendously lower cost and environmental effects for a sustainable future.

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CONFLICT OF INTEREST

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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