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Carbon Aerogels Derived from Industrial Wastes and Biomass Sources: Charasteristics, Characterization, and Applications

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Abstrac. Biomass derived carbon aerogels (BDCAs) have become a major area of interest because of their high potential for functionality and novel structure, which makes them potential candidates for environmentally friendly next generation carbonaceous materials. This review discusses the synthesis route for developing porous carbon structures from renewable biomass such as cellulose, lignin, hemicellulose and chitosan through sol-gel processes, freeze-drying, supercritical drying, carbonization and activation. Moreover, reorganizes BDCAs according to their precursors by describing common features and possible applications of cellulose-based, lignin-based, hemicellulose-based, and chitosan-based aerogels. In addition, characterization methods such as SEM, BET analysis, FTIR and XRD are explained the surface morphology, pore structure and chemical constitution of the aerogels. Due to high surface area, lower thermal conductivity and high electrical conductivity, the BDCAs are suitable for energy storage applications, catalysis and environmental application. This review also supports the role of BDCAs for the development of new sustainable technologies and the reduction of negative environmental effects of conventional materials.

Keywords: Biomass, carbon aerogels, water treatment, energy storage, porous aerogels.

Introduction

In recent years BDCAs have attracted much more attention of scientists due to their unique properties and potential applications. These materials have synthesized from industrial wastes [1], biomass sources such as agricultural waste, forestry waste and other renewable organic sources, which make them an environmentally friendly alternative to conventional carbon-based materials [2, 3]. Their functional advantages combined with their renewable origin emphasize their potential to play a significant role in sustainable technological advancement. Sol-gel, lyophilization, supercritical drying, carbonization and activation techniques are used to synthesize BDCA by converting natural renewable precursors such as cellulose, lignin or chitosan into a carbon-based porous structure. The process of obtaining BDCAs involves, carbonization of biomass precursors, followed by the removal of non-carbon elements, which results a highly porous [4], lightweight, and conductive material production. High specific surface area (SSA), which can exceed 2500 m^2/g is one of the key advantages of BDCAs. These characteristics combined with low density and excellent electrical conductivity of BDCAs, make them appropriate solution across energy, environmental and industrial applications, including super capacitors [5], catalysis [2], environmental remediation [6]. For instance, BDCAs have shown great ability to facilitate rapid ion transport and electron transfer, make them important as electrode materials in supercapacitors and batteries. The porosity and functionality of the BDCA surface allow the synthesis of materials with specific properties tailored for specific applications [4]. These materials can also exhibit tunable physical and physical properties, representing a stable and versatile class of materials with a wide range of potential applications. These versatile characteristics are particularly important in areas such as water treatment, where BDCAs can be used as adsorbents to remove pollutants from wastewater [6]. Keirabadi et al, 2019 investigated carbon aerogel derived from alginate modified with protonated cross-linked chitosan to remove nitrate from water. In addition, their biocompatibility and degradability make them suitable for drug delivery systems and tissue engineering in biomedical applications [7]. Manipulation of the structure and properties by changing the precursor and synthesis method allows the synthesis of materials with a given functionality [8]. with combination of large surface area, low density and superior conductivity as well as the ability to tailor their properties, make them crucial for future technological advancements, as shown in (Figure 1) many studies describing the versatile usage of BDCAs. As research in this area continues to tailor, their biocompatibility and degradability will make them suitable for biomedical applications such as drug delivery systems and tissue engineering scaffolds [9].

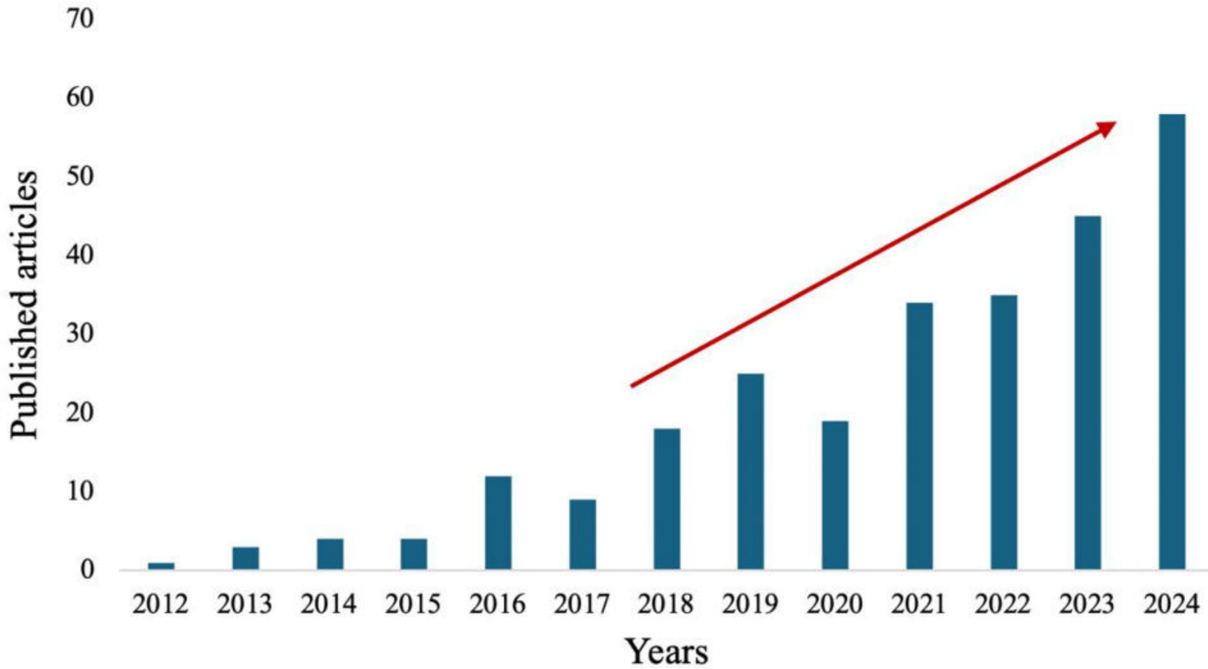


Fig. 1. - A scheme of published articles about BDCAs. Taken from Scopus

This review underscores synthesis of carbon aerogels (CAs) from agriculture sources, examining their properties, synthesis processes, their significance and potential impact across various fields, highlighting the need for further research and exploration of their multifaceted applications, represents a comprehensive overview of the synthesis, characteristics, and applications, focusing on the green synthesis methods as versatile and efficient approaches for their production. As shown in (Fig. 2) many studies have been done on synthesis of these materials from biomass agriculture wastes, such as oil palm, rice husk, and coconuts which explore the versatility and promise of these particles in protentional applications. However, most of the studies have centered around their catalytic, energy storage, and supercapacitors applications thus, the need for research on biomedical, diagnostic/therapeutic and water treatment applications of these materials necessary to be given more attention.

1. BDCAs

BDCAs are novel class of materials derived from renewable resources and eco-friendly alternatives for traditional aerogels. These materials recycle from natural precursors, which are both economical and sustainable. BDCAs in contrast to traditional aerogels that could use synthetic or non-renewable components is an example of green chemistry, suitable for a variety of high-performance applications due to their lightweight, large surface area, and superior porosity [2, 10, 11]. which aims to reduce environmental impact and improve functional efficiency [2, 12].

1.1. Types of CAs

BDCAs categorized based on the primary natural polymers from which they are derived, each of them offers distinct properties. Cellulose-based aerogels are the most widely studied one, celebrated for their lightweight structure and high mechanical strength, particularly well-suited for thermal insulation applications due to their low thermal conductivity and stability. Lignin derive carbon aerogels are known with high carbon yields and efficient for using in energy storage systems to utilize the intrinsic carbon richness of lignin. In addition, hemicellulose and chitosan-based aerogels are known for their improved thermal stability and high electrical conductivity, making them valuable in electrochemical systems and energy storage devices [6, 13].

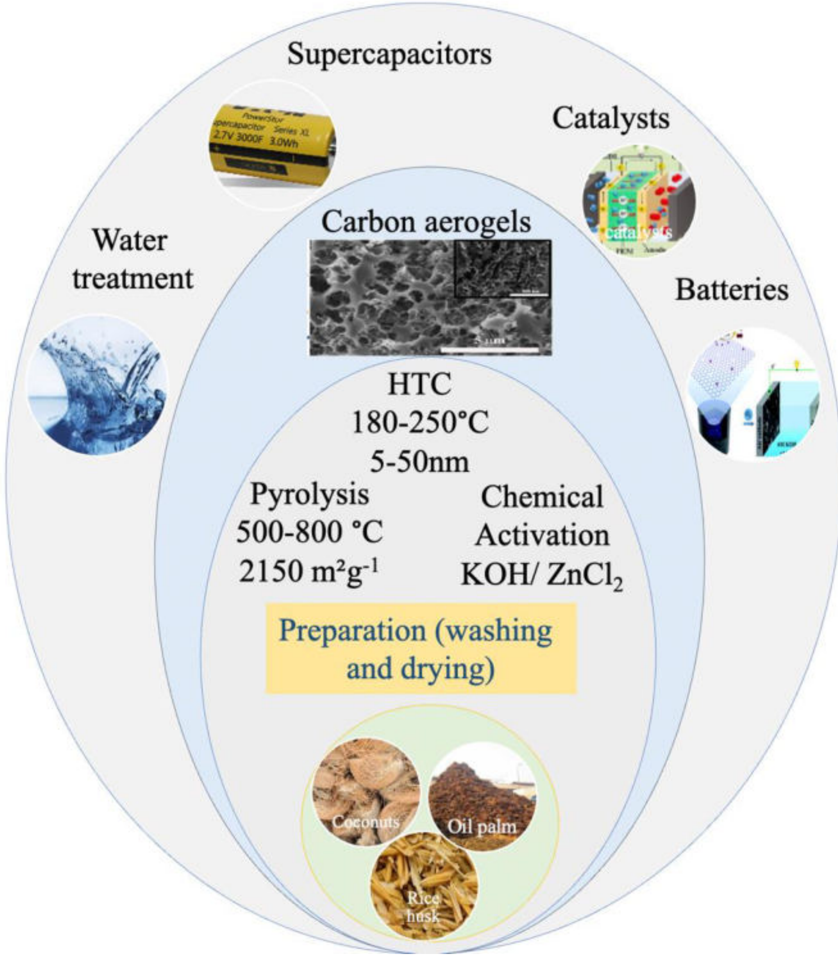


Fig. 2. - Graphical abstract of CAs taken from biomass agriculture wastes and their protentional applications

1.2. Characterization

Characterization of BDCAs plays a crucial role in understanding and optimizing their properties for target applications. These aerogels are usually evaluated based on their surface morphology, pore structure, chemical composition and crystalline structure. Microscopies such as SEM and TEM techniques play an important role in visualizing the complex nanostructures and pore size distribution of BDCAs, required for applications requiring high surface interaction such as adsorption and catalysis. The surface morphology and porous structure of CAs prepared with different lignin to cross-linker ratios were examined by Karaaslan et al., 2022 (Fig. 3) [14]. It depends on the composition of aerogels, the structure of pores and the shape of carbon particles changed significantly. Samples with lower lignin to cross-linker ratios (CA-L87 and CA-L81) showed a three-dimensional porous network structure composed of interconnected particles (Fig. 3A-D), which is typical for CAs with mesopores (2-50 nm). On the other hand, the samples CA-L68 and CA-L56 had no visible mesoporous network structure but composed of either spherical carbon particle with sizes ranging from (1-3 μm) or micron-size pores (Fig. 3E-G). Interestingly, higher magnification SEM images revealed that CA-L68 and CA-L56 samples had secondary carbon particles with less than 50 nm and additional surface features suggesting the presence of micropores (Fig. 3F-H).

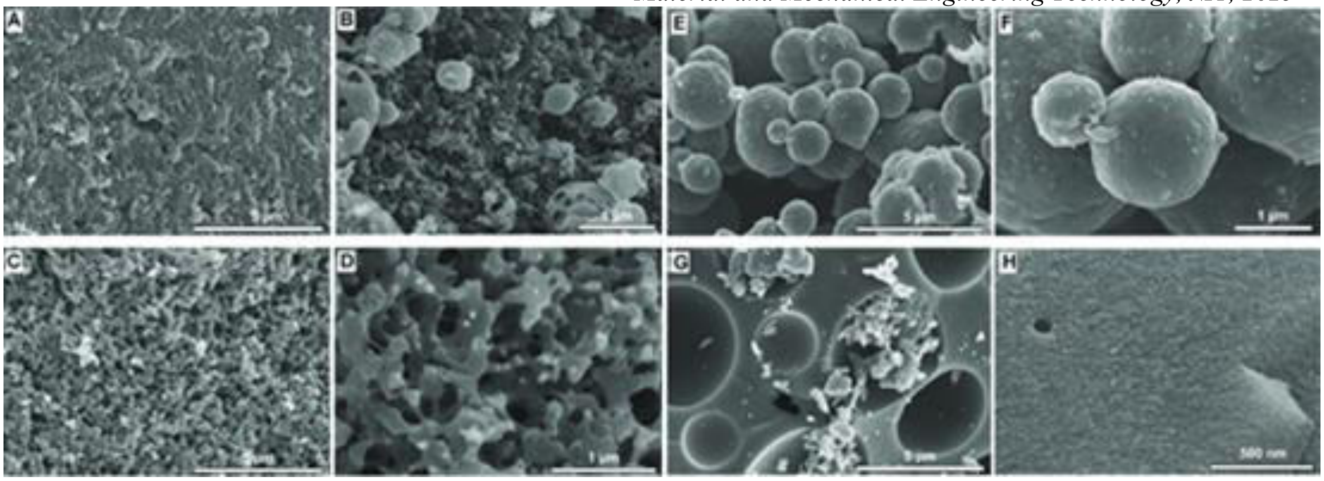


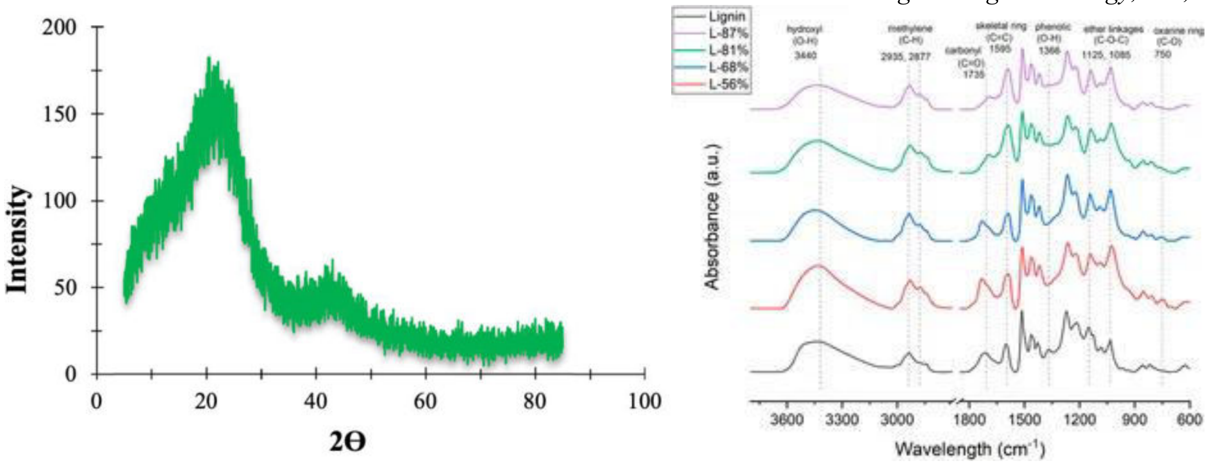
Fig. 3 - SEM images of lignin CAs; (A, B) CA-L87, (C, D) CA-L81, (E, F) CA-L68, and (G, H) CA-L56, showing the effect of lignin content on surface morphology microstructure and porosity taken from [14]

Brunauer-Emmett-Teller (BET) analysis is frequently employed or assessing of SSA, the total pore volume (Vt) was obtained from the nitrogen adsorption isotherm at ($p/p0 \sim 0.99$) and the specific surface area was determined using the BET method [14]. Increased surface area and pore size which shown in (Table 1), provides insights into the aerogel's capacity for adsorption make them crucial for environmental remediation, gas adsorption and industrial application [11].

The crystalline structure and degree of graphitization of these aerogels are often examined using X-ray Diffraction. The X-ray diffraction pattern of the CAs before surface modification is shown in (Fig. 4a). As expected, the carbon phase peaks can be seen at $2\theta=23°$ which corresponds to the (002) plane and the broad peaks at 2θ of about 43° corresponds to the (100) plane refection [15]. As the level of graphitization directly impacts these properties. this characterization is valuable for applications where electrical conductivity and thermal stability is required. Spectroscopies such as FTIR and Raman Spectroscopy are used Complementing these techniques to analyze the functional groups present in the carbon aerogels materials, lead a deeper understanding of chemical composition. For instance, FTIR spectra of lignin aerogels and CAs were recorded from (600 to 4,000 cm^{-1}) at a resolution of (4 cm^{-1}) using a Bruker Invenio-spectrometer. FTIR spectra of lignin and aerogels with different lignin contents confirmed the structural changes of lignin after crosslinking reaction (Fig. 4b). The peaks characteristic to lignin's hydroxyl (O-H) stretching at (3,400 cm^{-1}) and aromatic skeletal vibrations at (1,595 cm^{-1}) and (1,510 cm^{-1}) shifted in the spectra of all aerogels after the reaction. For the region corresponding to C-H stretching of methyl and methylene groups, the intensity of (2,935 cm^{-1}) peak increased, and a new peak appeared at (2,877 cm^{-1}) [14]. This information is crucial for tailoring the aerogels to exhibit specific surface chemistry conducive to enhanced catalytic activity or selective adsorption [9].

Table 1. Comparison of surface area and pore size of CAs based on their precursor materials

Type of BDCA	SSA (m^2g^{-1})	Pore Size (nm)	Reference
Cellulose-based Cas	200 – 900	2-50	[10]
Lignin-based Cas	300 – 700	1-30	[6, 16]
Hemicellulose-based Cas	150 – 600	5-20	[13]
Chitosan-based Cas	200 – 800	2-40	[16]
Mixed Biomass (e.g., Cellulose-Lignin)	400 - 1,000	1-60	[2]
Activated Biomass Cas	1,000 - 2,500 (after activation)	0.5-10	[9, 11]
Alginate-based Cas	470	2-50	[7]



a) b)

Fig. 4 - a. XRD pattern of the CAs before surface modification [7] and b. FTIR spectra of lignin aerogels with different crosslinker to lignin ratios corresponding to 44, 68, 81, and 87 wt % of lignin (all spectra normalized with skeletal vibration band of lignin at 1,510 cm $^{-1}$) taken from [14].

1.3. Applications

As shown in (Fig. 5), their combination of unique properties and synthesis methods allows them to function effectively in a variety of applications. Their stability increases their attractiveness for use in energy storage [12, 14], catalysis [17, 18], thermal insulation [10], and environmental remediation [7, 17, 19], meeting both performance and environmental requirements (Table 2). CAs act as electrode materials which can rapidly store large amounts of charge in supercapacitors, enhancing efficiency in energy consumption [14]. Improvement in conductivity and large surface area can lead to increase energy storage capacity and cycling stability which is highly useful in supercapacitors and batteries. These materials provide stable and durable anodes or cathodes for batteries, increasing battery life and reliability [12].

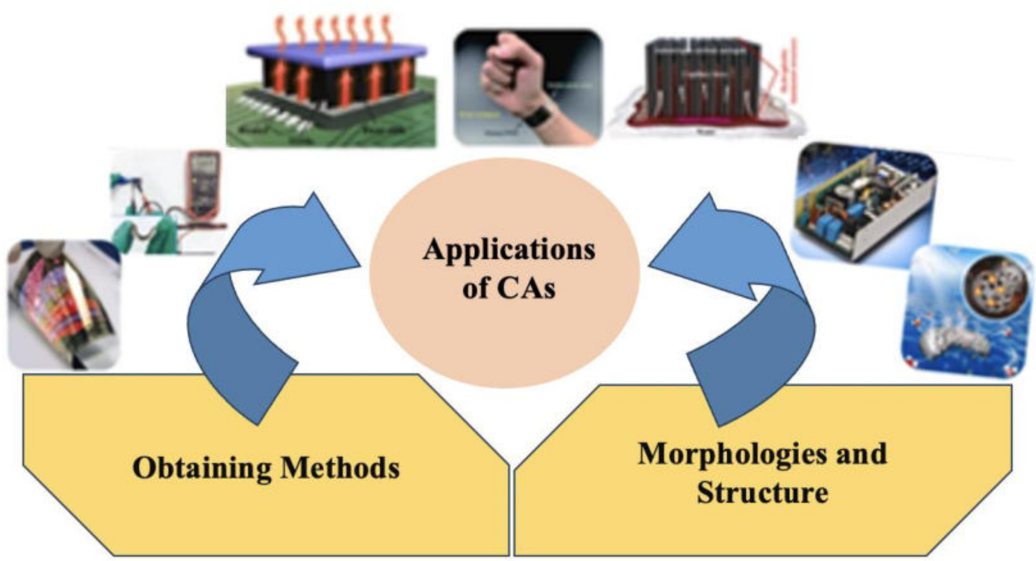


Fig. 5 - Versatile applications of CAs.

In electro-catalysis, BDCAs are highly valued for their performance in oxygen reduction reactions (ORR) and oxygen evolution reactions (OER), which are crucial in fuel cells and metal-air batteries. Due to the open structure and surface activity of CAs, energy transformations through the catalytic reactions can be carried out with high rates. This efficiency arises from their capacity to facilitate quick and frequent movement of large quantities of mass, together with a large number of active sites that enhance the performance of fuel cells and batteries [2]. Cellulose-derived CAs have low thermal conductivity and high thermal stability, making them suitable for use in energy-efficient construction materials. in addition, thermal insulation characteristics make these materials appropriate for applications in temperature-sensitive electronic devices, assisting heat dissipation management. CAs has high insulating properties without adding significant weight, especially valuable in current construction where lightweight is considered as priority [10].

Table 2. BET analysis for BDCAs with comparison of synthesis methods and applications

№	Synthesis method	Type of aerogels	SSA (m^2g^{-1})	Porosity	Application	Ref.
1	Hydrothermal carbonization and activation	BDCAs	700-1200	Hierarchical microporous	ORR/OER bifunctional oxygen electrodes	[2]
2	Freeze-drying and carbonization	Renewable biomass-based aerogels	300-800	Mesoporous to macroporous	Structural design and functional regulation	[6]
3	Sol-gel method with mannitol addition	Carbonaceous aerogel/mannitol composites	500-900	Stable, interconnected	High thermal-energy-release and shape stabilization	[9]
4	Template-assisted carbonization	Sustainable CAs	400-1000	Mesoporous/ macroporous	Energy storage applications	[12]
5	Gelation and freeze-drying	Biomass-based aerogels for insulation	600-1100	Ultra-low density	Building insulation materials	[13]
6	Alkaline activation of softwood kraft lignin	Lignin-derived CAs	700-1200	Mesoporous	Supercapacitor electrodes	[14]
7	Pyrolysis of biomass precursors	CAs for gas adsorption	300-1200	Microporous to mesoporous	Gas adsorption and separation	[11]
8	Hydrogel synthesis and freeze-drying	Cellulose aerogels	400-800	Nanoporous structure	Thermal insulation	[10]
9	Hydrothermal treatment and modification	Alginate-derived CAs	500-1000	Modified mesoporosity	Nitrate removal in water	[7]
10	Pyrolysis and chemical activation	Activated cellulose aerogels	600-1000	Interconnected microporous	Dye treatment in wastewater	[17]
11	Carbonization and activation	Rice husk ash-derived aerogels	200-500	Microporous	Primary cells and energy storage	[20]
12	Thermochemical treatment of biomass	Softwood-derived CAs	800-1200	High porosity	Hydrophobic/oleophilic sorbents	[19]

BDCAs have been used as a removal for pollutants through their adsorption abilities, suitable for environmental remediation application. These materials may promptly engage with a pollutant and remove it due to their high porosity; therefore, may be used in water and air purification for instance as absorbents of oil/ water mixtures [19]. as they have been effective in the water purification by discharging oil, heavy metals, organic dyes and gaseous toxins from the water. Here, CAs play a positive role of protecting the environment the mitigation of pollution by enhancing fast adsorption of the pollutants, which makes them sustainable approach for pollution management [11, 19].

Conclusion

BDCAs offer a novel category of materials that can be derived from renewable biomass raw materials and offer a sustainable replacement for carbon-based materials. The review emphasized synthesis methods and properties such as high specific surface area, low density and good electrical conductivity of BDCAs in relation to their use in energy storage, catalysis, and environmental remediation applications. Analytical techniques have been employed for understanding important features regarding the structural and chemical nature of BDCAs to ensure that they are nearly perfectly tailored for the required performance. Thus, increasing the role and relevance of BDCAs in the development of innovative technologies is the further development of research and the overall flexibility and eco-friendliness of BDCAs. Future studies should aim to improve their performance and explore new areas of application in order for BDCAs to contribute significantly to global challenges such as energy efficiency and environmental sustainability. After all, BDCAs hold major promise for advancing innovation in materials science and promoting a more sustainable future.

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