

# ***The Progress in Synthesis of Efficient Carbon-Based Anode Materials for Sodium Ion Batteries***

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**Abstract:** With the increasing demand for clean energy, Sodium-ion batteries (SIBs) have become a potential substitute for lithium-ion batteries because of their low cost, high safety and abundant sodium resources. However, the energy density of sodium ion batteries is low, and the development of electrode materials, especially negative electrode materials, is facing challenges. Due to their low cost, simple preparation process, and high electrochemical stability, carbon-based materials have emerged as the most promising anode materials for commercialization. In this paper, the applications of hard carbon, soft carbon and graphite in sodium ion batteries are reviewed, and their sodium storage mechanism, preparation methods and modification strategies are discussed.

**Keywords:** Sodium ion battery, Carbon-based cathode, Modified

## **1. Introduction**

With society's development and environmental needs, the demand for clean energy is surging. But clean energy has issues like low energy density, high costs, large - scale collection equipment requirements, weather - sensitivity, and uneven distribution. So, stricter battery requirements emerge, and developing high - intensity - density, long - lasting - cycle - life electrode materials is a hot research topic. Lithium - ion cells are extensively applied in numerous sectors. However, as industrial energy demands grow, scientists seek alternatives. Sodium, similar to lithium, has cost and safety advantages.

As a substitute, The Earth's crust contains sodium, which is one of its most abundant elements. with low extraction costs and abundant reserves, giving it a clear advantage in raw material costs. Additionally, the electrolyte concentration of sodium-ion batteries is lower, further reducing costs. Moreover, sodium-ion batteries have higher safety and are less prone to overheating or explosions. However, Owing to the reduced energy density of sodium - ion batteries, they are currently mainly used in low-energy-density scenarios, such as static energy storage. Nevertheless, sodium-ion batteries perform well in low-temperature environments and fast-charging applications, making them suitable for high-cold and high-power-demand scenarios. Sodium - ion batteries are capable of supplementing or even substituting for conventional lithium - ion batteries, and significant progress has been made in current research and development, such as layered materials, polyanionic compounds, and Prussian blue analogs. However, since sodium has a larger radius and molar mass compared to lithium, which is not conducive to the stability of electrode chemical reactions, and most lithium battery electrode materials are not suitable for sodium, Developing cost - effective, high - efficiency anode materials is essential for promoting the commercialization of sodium - ion battery

(SIB) technology. A wide variety of precursor sources are available for carbon - based materials, which are the most commercially attractive anode materials. It is in the area of seeking low - cost and high - efficiency energy - storage solutions to substitute for lithium - ion batteries that research and development in this field is an important direction in the energy - storage domain. For example, Zhou et al. [1] determined that augmenting the disorder in the microstructure was an effective way to enhance the sodium - storage performance of carbon anodes made from phenolic resin. Oxygen functional groups can be incorporated into the carbon material via pre - oxidation treatment. Additionally, Zhang et al. synthesized a novel hard carbon by carbonizing a mixture of sucrose and phenolic resin. Furthermore, carbon - based alloy - type composite materials (CAC) developed by Seeram et al. have been prevalently employed in the efficient formation of anodes, thereby improving electrochemical behavior and providing key support for SIBs (the biggest difficulty for the monetization of sodium-ion batteries is limited energy density), as the carbon component can mitigate volume changes and improve conductivity. To further advance the commercialization of SIBs, especially considering manufacturability and functionality.

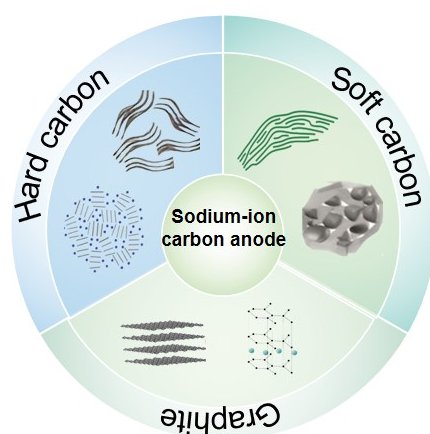


Figure 1: The different anode materials of SIBs

This article presents the research regarding carbon anode materials for SIBs. It encompasses functional alterations of traditional hard carbon materials as well as the evolution of new composite materials. Second, by optimizing the microstructure and chemical composition of materials, the electrochemical properties of sodium - ion batteries can be enhanced. This enhancement encompasses improving the first - cycle Coulombic efficiency, cycle stability, and rate capability. Finally, The future trends and difficulties of sodium - ion batteries are collated and forecasted.

## 2. Carbon anode materials for sodium-ion batteries

The anode material of sodium-ion batteries plays a crucial role in battery performance. Among different kinds, carbon - based materials possess the benefits of being inexpensive, simple to prepare, having a relatively high capacity, and demonstrating good electrochemical stability. They also come in various forms, such as single-walled/multi-walled nanotubes and graphite. The diverse morphological structures can be tailored to different needs to improve battery conductivity. Therefore, the research and development of carbon anode materials are of great importance. This paper mainly discusses three types of anode materials: hard carbon, soft carbon, and graphite.

Graphite, soft carbon, and hard carbon can be converted into each other under certain conditions. Due to the weak cross-linking between graphene layers, soft carbon can be graphitized after heat treatment at temperatures between 1500°C and 3000°C [2].

## 2.1. Sodium storage mechanism

Based on prior reports, researchers have categorized the sodium - storage process into three components: capacitive adsorption, nanopore filling, and intercalation within carbon layers. Two regions of the HC sodium storage discharge curve, namely the high - potential sloping region (2~0.1 V) and the low - potential plateau region (0.1~0 V), are related to each sodium storage mechanism. The diffusion coefficient of sodium ions can be partitioned into three segments: 1. When the discharge voltage is higher than 0.1V, the diffusion speed is approximately square centimeters per second. This corresponds to adsorption on the surface, defects in the inter - layer areas, and amorphous zones, all of which are advantageous for high - rate performance and cycle stability [3]. 2. As the voltage ranges from 0.1 to 0.05V, the diffusion coefficient diminishes gradually. This is because the accumulation of sodium ions causes enhanced repulsion, which is related to adsorption - interlayer intercalation. 3. When the voltage drops to the cutoff voltage of 0.01V, it corresponds to interlayer intercalation / pore filling, where some sodium ions are reduced by the carbon material, repulsion decreases, and the diffusion coefficient increases. The calculation formula is as follows:

$$\frac{R^2T^2}{2n^4A^2F^4C^2\partial^2}$$

### (1) Insertion and Filling

Hard carbon materials are capable of having numerous nanoscale pores. These pores can be represented as a series of graphene sheets arranged in a card - house - like pattern. In 2000, Stevens and Dahn were the first to put forward the “insertion - adsorption” mechanism along with the “House of Cards” model in order to account for the electrochemical data of glucose - derived hard carbon anode materials. The model is composed of randomly stacked aromatic fragments, similar to a house of cards, creating parallel graphite - like nanodomains and nanoscale pore regions. They suggested that the charge storage mechanisms of Na and Li in hard carbon are alike. Specifically, the high - potential sloping region and the low - potential plateau region respectively correspond to the intercalation of alkali metals between carbon layers and the adsorption of alkali metals in nanopores. Moreover, XED tests were utilized.

### (2) Adsorption and Intercalation

Techniques like in - situ XRD mapping have demonstrated that the sodium storage process adheres to an “adsorption - intercalation” mechanism. In the discharge - charge process, Na ions initially adsorb onto the active sites on the surface of hard carbon, which leads to the sloping of the voltage curve. Subsequently, they intercalate into the graphene layers to generate NaC<sub>x</sub>, resulting in a flat voltage plateau. This finding offers novel concepts for the design of carbon materials. For instance, by adjusting the interlayer spacing to the range of 0.37 - 0.38nm, the sodium storage capacity can be enhanced. Additionally, designing non - porous carbon can boost the Coulombic efficiency, thereby satisfying practical application requirements.

### (3) Adsorption, Intercalation, and Filling

In 2015, Bommier et al. [4] put forward an “adsorption - intercalation - filling” model for hard carbon. They assessed kinetic properties via galvanostatic intermittent titration (GITT) measurements, probed into the sodiation mechanism of hard carbon, and uncovered distinctions from the cardhouse structure model in the sodium storage mechanism of hard carbon. They held the view that the storage mechanism of the sloping part of the potential curve stems from defect site storage, whereas the storage mechanism of the low - voltage horizontal region is the result of the joint

influence of the intercalation among graphene sheets and sodium ion being adsorbed on the pore surface. In line with this principle, Zhang et al. [5] suggested that, taking EPNHC as an instance, if the interlayer distance of hard carbon materials can be properly regulated and their degree of order enhanced, not only can the plateau capacity (capacity associated with sodium intercalation into long - range ordered carbon structures) be augmented, but also the total storage capacity can be elevated.

## 2.2. Preparation and application

Currently, the carbon precursors for synthesizing hard carbon mainly come from three sources: biomass waste, sugars, and polymers. Stevens and Dahn first reported that glucose-derived hard carbon exhibits a reversible capacity close to  $300 \text{ mAh g}^{-1}$ . Plants are rich in cellulose, providing abundant carbon sources, and biomass hard carbon is a renewable material with a simple preparation process and no environmental pollution, making it an environmentally friendly material. Its raw materials are widely sourced and low-cost, such as coconut shells, fruit shells, pomelo peels, as well as plant and seafood waste. Under traditional treatment methods, these agricultural wastes are mostly incinerated, which is detrimental to environmental protection. Since biomass hard carbon is rich in cellulose, it is a suitable carbon source for preparing carbon materials to replace resin precursors. Biomass - based carbon materials exhibit a wide variety of forms. Notably, porous carbon and materials derived from carbon possess a large specific surface area, helping to improve electronic conductivity. Wang et al. [6] designed an N, P co-doped hard carbon (Tea - 1100 - NP) derived from tea, which possesses a wide interlayer spacing and an appropriate specific surface area. The electrode has a high reversible capacity of  $326.1 \text{ mAh g}^{-1}$  at a current density of  $28 \text{ mA g}^{-1}$  and a high initial Coulombic efficiency (ICE) of 90%. Zhu et al. also showed that biomass carbon materials have diverse shapes, especially porous carbon and carbon-derived materials, which have a large specific surface area, helping to change electronic conductivity, proving the broad prospects of biomass carbon materials.

As a polymer, its chemical and physical parameters can be adjusted to meet different usage scenarios. Adrian Beda et al. [7] produced that after high - temperature pyrolysis at a temperature exceeding  $1000^\circ\text{C}$ , they created sustainable hard carbon. This hard carbon has a small surface area, a chaotic structure, and a high carbon output. The solvent significantly affects the preparation, determining the formation time of the polymer resin and affecting cross-linking. Using water as a solvent results in higher cross-linking. Various experimental parameters can enable the adjustment of the carbon texture. Under water solvent and room-temperature thermal polymerization, the BET specific surface area is the highest (about  $80 \text{ m}^2/\text{g}$ , under other conditions  $< 10 \text{ m}^2/\text{g}$ ). A green, simple, and scalable method for preparing phenolic resin. Wang et al. [8] prepared low-surface-area hard carbon spheres (PF - HCS) from phenolic resin through a simple and sustainable hydrothermal method and found that PF - HCS treated at  $1250^\circ\text{C}$  has the outstanding electrochemical performance, with a reversible capacity of  $311 \text{ mAh/g}$  and demonstrates good cycle stability. By regulating the morphology, size, and pore structure, it is anticipated that PF - HCS can be employed in low - cost sodium - ion battery systems. The commercialization of sodium - ion batteries in large - scale power storage and other fields is being promoted.

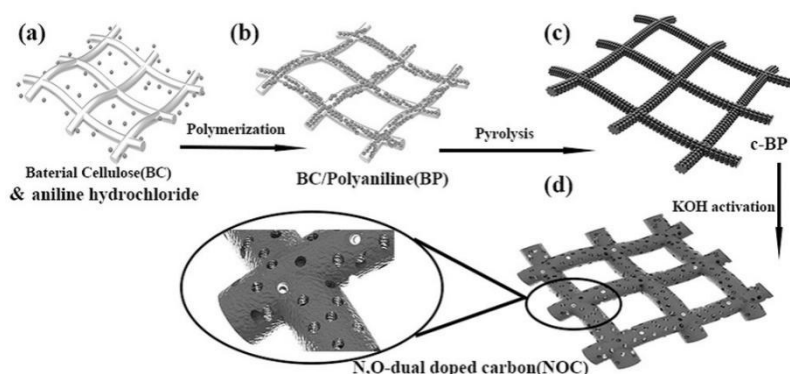


Figure 2: Schematic illustration of the nitrogen and oxygen dual-doped carbon (NOC) network composite

### 3. Graphite

Graphite holds crucial significance in the battery domain, especially serving as an anode material within lithium - ion batteries. It serves as a frequently - used anode material in lithium - ion batteries, having a capacity of  $372 \text{ mAh g}^{-1}$ . However, graphite is not suitable for sodium-ion batteries (SIBs) because the intercalation of sodium in graphite is very poor and unstable, which results in an electrochemical capacity amounting to just  $35 \text{ mAh g}^{-1}$  [9]. Although graphite has some potential characteristics as a negative electrode material for sodium-ion batteries, it has not been widely used and faces numerous challenges. Graphite's layered structure suits lithium-ion batteries but faces challenges in sodium-ion batteries due to sodium ions' larger radius ( $0.102 \text{ nm}$ ) and graphite's small interlayer spacing ( $0.335 \text{ nm}$ ), causing slow diffusion and instability. Sodium-graphite compounds (Na-GIC) are unstable, leading to low capacity and poor cycling. Researchers, like Zhao et al., propose graphite blending to reduce electrode expansion and enhance conductivity, bridging industrial and academic needs for next-gen anodes.

#### 3.1. Sodium storage mechanism

**Positive Electrode Reaction:**  $\text{NaMnO}_2 \rightarrow \text{Na}_{1-x}\text{MnO}_2 + x\text{Na}^+ + xe^-$

**Negative Electrode Reaction:**  $\text{C} + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{C}$

**Overall Reaction:**  $\text{C} + \text{NaMnO}_2 \rightarrow \text{Na}_{1-x}\text{MnO}_2 + \text{Na}_x\text{C} \quad (0 \leq x \leq 1)$

Sodium storage mechanisms can be categorized based on the electrochemical processes involved: intercalation (carbon-based and other materials), conversion reactions (transition metal compounds), alloying (Bi, Sb, Sn, Ge, Pb, P), conversion-alloying dual reactions, and organic materials. Intercalation - type substances generally show relatively low theoretical specific capacities, and these capacities might not satisfy the demands of high - energy - density sodium - ion batteries (SIBs). In spite of such difficulties, substantial endeavors and experimental advancements have been achieved over time because of their outstanding cycling performance.

#### 3.2. Preparation and applications

The operating mechanisms of sodium-ion batteries (SIBs) are highly analogous to those of lithium-ion batteries (LIBs). However, the sodium storage capacity of graphite is much lower than its lithium storage capacity. Nevertheless, various methods have been discovered to enhance its capacity, primarily by doping graphite with other elements such as N and P to form composite materials. For example, Tao et al. [10] synthesized N, P dual-doped hollow carbon fiber/g- $\text{C}_3\text{N}_4$  membranes employing filter paper as an initial material. When used as an anode, the flexible membrane exhibited

ultra-high capacity, excellent cycling stability, and rate performance in both lithium and sodium-ion batteries. Weng et al. [11] prepared 2D graphite - phase carbon nitride (g -  $C_3N_4$ ), which serves as a prospective negative electrode material for sodium - ion batteries due to its low cost and excellent stability. However, it suffers from poor electrical conductivity and a low sodium - storage capacity. C/g- $C_3N_4$  composites were prepared by one-pot pyrolysis of urea and asphalt. DFT showed that carbon doping reduced the diffusion barrier of  $Na^+$ , increased the sodium storage capacity to 254 mAh  $g^{-1}$  (twice as much as pure g- $C_3N_4$ ), and significantly improved the rate performance and cycle stability. The assembled sodium ion battery (with sodium roseate as the positive electrode) showed a Coulomb efficiency of 99.8%, and the capacity of 14000 cycles at 1 A  $g^{-1}$  did not decay. Recently, Wang et al. [12] synthesized N,O-dual doped carbon (NOC) materials are developed as anodes for Na-ion batteries (NIBs) to enhance sodium storage. The NOC composite exhibits high capacity (545 mAh  $g^{-1}$  at 100 mA  $g^{-1}$  after 100 cycles) and excellent cycling stability (240 mAh  $g^{-1}$  at 2 A  $g^{-1}$  after 2000 cycles). With 3D porosity and N,O doping, it provides active sites that improve performance. The NOC is synthesized via a simple solution process, allowing for easy adaptation to other N,O-doped carbon materials for applications in catalysis, energy storage, and solar cells. (as shown in Fig.2)

#### 4. Soft carbon

Soft carbon, or non-graphitizable carbon, differs from graphitizable carbon in performance. Graphitizable carbon has a stable layered structure, offering flat charge-discharge platforms and good cycling stability in sodium-ion batteries, but its sodium-ion diffusion is slow, leading to poor rate performance. Non-graphitizable carbon, with its disordered structure and defects, provides more sodium-ion storage sites and excels in high-rate charge-discharge, enabling fast charging. However, its complex structure results in less flat platforms, faster capacity decay, and reduced initial Coulombic efficiency resulting from side reactions. Refined preparation procedures are capable of enhancing its performance.

##### 4.1. Sodium storage mechanism

In HC, the morphology control before carbonization is relatively easy. However, for soft carbon (SC), the carbonization process usually occurs through the formation of pitch in a molten state, making it infeasible to control and maintain its morphology before carbonization. Nevertheless, the ideal rate capability of SC makes it an excellent electrode choice for all-carbon metal-ion capacitors. Jing et al. [13] successfully prepared the ZnS/NSC composite was successfully put together. It was made by calcining zinc pyrithione and activated with  $Na_2CO_3$ . This composite shows the feature of ZnS nanoparticles embedded in N,S - co - doped carbon. This composite (A-ZnS/NSC) exhibits a mixed-crystal structure, higher surface area, and enhanced bridges (C-S-Zn and S-O-Zn bonds). As an anode for sodium-ion batteries, it demonstrates improved electrochemical performance with a reversible capacity of 516.6 mAh  $g^{-1}$  at 100 mA  $g^{-1}$ , 96.9% capacity retention after 100 cycles, and excellent rate performance (364.9 mAh  $g^{-1}$  at 800 mA  $g^{-1}$ ). Zinc borates are promising anodes for  $Na^+$  storage but be afflicted with low rate performance and inferior cycling durability. Zhang et al. [14] investigated a new way of synthesis with the guidance of an intercalator is proposed to enhance rate performance and cycling stability in N, B co-doped carbon/zinc borates (CBZG). This procedure assures consistent precursor spread and merges combustion activation and solid - state reactions for scalable fabrication. Thereby, it betters both rate ability and cycling endurance.

## 4.2. Preparation and application

There are numerous reports on the precursors of soft carbon, including PVC, pitch, petroleum coke, and hydrogen-rich precursors are often key factors in generating soft carbon. When hydrocarbons are used as raw materials, mesitylene is a typical example. With its abundant hydrogen content, it effectively promotes the formation of soft carbon under specific synthesis conditions. Thermoplastic polymers are also significant, such as poly(styrene), which, with its unique molecular structure, precisely guides the reaction path towards the formation of soft carbon when participating in reactions; poly (ethylene oxide) and poly (propylene oxide) are no exception. During the synthesis process, through interactions with other substances in the reaction system, they ultimately result in the derived carbon exhibiting the characteristic electrochemical behavior of soft carbon. To better compare the performance and differences between hard carbon and soft carbon.

## 4.3. Modification mechanism

### 4.3.1. Doping

Regarding sodium - ion batteries, researchers have performed wide - ranging and intensive studies on carbon - based materials, aiming to heighten their rate performance and cycle longevity. It is well known that the functionality of SIBs mainly depends on the functionality of electrode materials, which is influenced by their diverse compositions as well as different microstructures and morphological characteristics. Currently, a common and effective strategy is to dope carbon-based materials with elements such as nitrogen (N), sulfur (S), boron (B), and phosphorus (P) to enhance the sodium storage capacity of anode materials and thereby promote the overall optimization of sodium-ion battery performance.

Doping with nitrogen represents an efficient approach for enhancing the efficiency of biomass - derived carbon. The addition of nitrogen atoms can improve the solid - liquid mass transfer of carbon obtained from biomass. In electrochemical energy storage arrangements, this promotes more complete contact between the electrolytic solution and the electrode component, quickening the ion transport process at the solid - liquid boundary. Additionally, nitrogen doping significantly improves the transmission efficiency of electrons and ions, optimizing the electrical properties of carbon materials, making the conduction of electrons within the material more smooth and reducing the migration resistance of ions. These features endow nitrogen - doped biomass - derived carbon with wide - ranging application prospects in energy - storage domains like batteries and supercapacitors.

Sulfur doping of biomass carbon can expand the carbon layer spacing and generate an uneven spin density. This structural change reduces the resistance and distance of ion migration and enhances the surface electronic performance. The uneven spin density may affect the electron cloud distribution of the material, thereby influencing its electrical and electrochemical properties. At the same time, co-doping often endows materials with superior performance through a synergistic effect. Jing et al. [15] used a novel hybrid material, Composing of extremely tiny Sb nanoparticles enclosed within an N - doped carbon nanonecklace (Sb/N - CNN), it has been fabricated for the initial time via electrospinning and in - situ substitution. As an anode for sodium-ion batteries, the Sb/N-CNN demonstrates excellent rate performance (314 mAh g<sup>-1</sup> at 20 A g<sup>-1</sup>) and remarkable cycling stability (401 mAh g<sup>-1</sup> after 6,000 cycles at 1 A g<sup>-1</sup>), surpassing other Sb-based materials. The superior performance stems from the unique necklace-like structure, which facilitates rapid electrolyte diffusion provides more active sites for Na<sup>+</sup> insertion/extraction, mitigates stress from volume changes during cycling, and lowers electrode resistance. This work offers an effective strategy for designing advanced energy-storage materials. (Sb/N-CNN as shown in Fig. 3)



Figure 3: Diagrammatic representation of the preparation process of Sb/N-CNN

### 4.3.2. Activation

During material pyrolysis, hydrogen bonds break, causing the decomposition of lignin, cellulose, and hemicellulose. This decomposition may give the synthesized materials a more porous structure. These pores can hold more sodium ions during sodium - ion insertion. Defects and porosity are vital for enhancing hard carbon's capacity and electrochemical performance. Biomass carbon activation, a key to improving its performance and application potential, includes physical, chemical, and template activation. Currently, custom - made carbon materials can address the kinetic deficiencies of carbon negative electrode materials in sodium - ion batteries.

The physical activation process relies on clearing the blocked adsorption medium, promoting the expansion of the pores formed in the precursor materials, and generating new pores through the selective oxidation of carbon precursors. The key influencing factors of this process include air, carbon dioxide, and temperature. Within a certain temperature range, as the temperature increases, the reaction rate between carbon and the activating gas accelerates, and the number of new pores and the pore size increase. For example, Zhang et al. [16] synthesized N, O, and S doped porous carbon CMFO (as shown in Fig. 4) employing a biomimetic mineralization simultaneous combustion strategy. This strategy makes the precursor components uniformly mixed, forming a honeycomb-like structure and rich pores, etc. The CMFO structure and ether-based electrolytes facilitate sodium storage and have excellent performance in sodium-ion batteries.

Chemical activation happens at high temperatures. The activating agent reacts with raw materials, causing pore expansion in precursor materials, as well as raw material dehydration or dissolution to form pores. For potassium - based activating agents, during high - temperature reactions, the generated active substances react with carbon, and gaseous potassium metal inserts into the carbon lattice interlayer, widening the carbon layer spacing and creating numerous micropores. The concentration of the activating agent is vital. A low concentration causes insufficient activation and pore - forming difficulty, while a high one over - corrodes the carbon material and damages its structure. Different activating agents have distinct chemical properties and reactivities, leading to variations in the porosity and surface chemical features of carbon materials from biomass, which impacts their application performance in adsorption, catalysis, energy storage, and other fields.

Template activation is about assembling organic carbon precursors and coating them on a template's surface to create a 2D structure. Templated carbon's high capacity might result from two aspects. One is its unique interconnected pore structure, which shortens the diffusion length between the electrode **and the carbon base**. The other is that using intermediate phase asphalt as the carbon precursor can form a carbon microstructure with a distinct structure and high conductivity, unlike other precursors. For instance, Wenzel et al. [17] first showed that a layered pore structure from nano - casting can yield a high - sodium - capacity carbon anode with good rate performance at room temp.

Template selection and dosage affect the carbon's pore structure; smaller templates make smaller - pored microporous carbon, and more template boosts porosity.

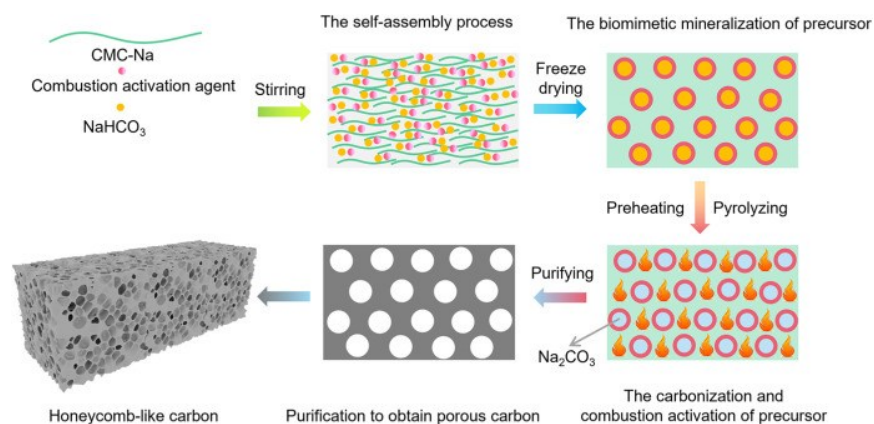


Figure 4: Illustration of the synthesis process for CMFO

## 5. Summary and outlook

This paper comprehensively reviews the research on sodium - ion battery carbon anode materials. It deeply analyzes hard carbon, soft carbon, and graphite, covering their features, preparation, **sodium retention mechanisms**, and modification strategies. Hard carbon has good sodium storage but its complex structure and high resistance limit rate performance. Soft carbon has good rate performance yet low first - cycle Coulomb efficiency. Graphite has sodium - insertion issues and its theoretical capacity can't meet high - energy - density needs, though modification helps. Doping and activation improve material performance, yet challenges like structural stability, interface compatibility, and cost - effectiveness remain. Upcoming research should be directed towards optimizing material microstructure and interfaces, developing high - performance composites, and exploring greener preparation methods to advance the commercialization of sodium - ion battery carbon anodes and meet requirements of high energy density and high power for storage systems.

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