**Nutty Carbon: Morphology Replicating Hard Carbon from Walnut Shell for Na Ion Battery Anode**

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**ABSTRACT:** Efficient Na ion intercalation/deintercalation in the semigraphitic lattice of a hard carbon derived from the walnut shell is demonstrated. High-temperature (1000 °C) pyrolysis of walnut shells under an inert atmosphere yields a hard carbon with a low surface area (59 m² g⁻¹) and a large interplanar c axis separation of 0.39–0.36 nm as compared to 0.32 nm for graphite, suitable for Na ion intercalation/deintercalation. A stable reversible capacity of 257 mAh g⁻¹ is observed at a current density of 50 mA g⁻¹ for such nutshell-derived carbon (NDC) with an impressive rate performance. No loss of electrochemical performance is observed for high current cycling (100 mA g⁻¹ → 2 A g⁻¹ → 100 mA g⁻¹). Additionally, the NDC shows remarkably stable electrochemical performance up to 300 charge–discharge cycles at 100 mA g⁻¹ with a minimal drop in capacity.

**INTRODUCTION**

Na ion batteries are emerging as a new cost-effective alternative to Li ion batteries. Similarity with Li chemistry and natural abundance make Na a promising successor to Li. Huge reservoirs of Na in the form of minerals like rock salt, sodalite, and suitable feldspars are present in the Earth’s crust. The significantly high Earth abundance of Na vis-à-vis Li (2.5% for Na vs 0.0017% for Li) makes it an economical and commercially viable alternative to Li, provided the electrochemical performance is maintained. Because Na and Li occupy the same group in the periodic table, their electrochemical performance is expected to be more or less similar. Therefore, enormous work done on Li ion batteries in the past can be the guiding force for future progress in Na ion batteries. The ongoing research in Na ion batteries involves the discovery of efficient cathode and anode materials to lead the technology toward commercialization.

Replication of the Li chemistry has already been a successful ploy for the cathode. Binary oxides, phosphates, and pyrophosphates of transition metals with Na (in analogy with Li) have come up as excellent cathode materials. So far, materials like NaFeO₂, NaCoO₂, NaNiO₂, NaNiO₂, Na₃V₂(PO₄)₃ and Na₃V₂(PO₄)₂F₃ are reported to be best-performing cathode materials for Na ion batteries. However, the design of a suitable anode material is a major challenge that is impeding the further progress in this field. A variety of anode materials including intercalation, conversion, and alloying types have been proposed for Na ion batteries. Redox alloying of Na with Si, Sn, Pb, Sb, and Bi and other sodiation/desodiation reversible redox reactions with sulfides, selenides, phosphides, and elements like phosphorus or sulfur have opened a broad choice of promising anode materials for Na ion batteries. However, huge volume expansions and lack of long-term reversibility restrict their use as commercially stable anode materials. The use of graphite also did not lead to the desirable performance because of some fundamental differences in the Na ion and Li ion intercalation/deintercalation chemistries. Although, both belong to the same group and undergo a similar one-electron redox transformation, the differences in size make graphitic intercalation of Na difficult in comparison to Li.

Carbon provides options in a variety of less ordered forms like hard carbons, carbon blacks, pet cokes, and reduced graphene oxide papers. These carbon forms have delivered highest reversible capacity close to 300 mAh g⁻¹, which is comparable to the Li ion capacity of graphite, that is, 372 mAh g⁻¹. These carbon forms, unlike graphite, possess larger interlayer separations for free intercalation and deintercalation of Na ions. Micro pores further assist in reversible Na ion storage by reversible insertion and extraction through the pores, which is different from the conventional intercalation mechanism. High-temperature pyrolysis of sugars, pro-

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teins, synthetic polymers, and biomass precursors are some of the routes to obtain hard carbons useful for Na ion batteries.\textsuperscript{36,42} Composites of these hard carbons with CNTs and graphene have delivered satisfactory Na ion performance.\textsuperscript{33−47}

However, a quest for making Na ion battery technology cheaper has shifted focus toward the use of natural precursors for hard carbons, for example, biowastes and natural products. Hard carbons derived from banana peels, lotus petiole, okra byproduct, peanut shells, natural wood fibers, or compact wood have delivered satisfactory Na ion anode performance.\textsuperscript{48−56}

In this work, we report the synthesis of hard carbons by direct pyrolysis of a densely packed cellulosic precursor, the walnut shell, and we demonstrate its use as an anode material in a Na ion battery. Earlier reports on walnut shell have asserted its role as a support for a well-known Na ion battery anode material, that is, Sn,\textsuperscript{57} and also as a support for the transition metal for catalytic applications.\textsuperscript{58,59} The nutshell-derived carbon (NDC) material showed an impressive initial reversible capacity of 257 mAh g\(^{-1}\) at 50 mA g\(^{-1}\). The material retains this capacity even after high current cycling up to 2 A g\(^{-1}\). A remarkable cycling stability with a small initial loss and stable capacity up to 300 charging−discharging cycles is observed. These performance parameters for the current material are comparable to recently reported hard carbons derived from biomass and synthetic polymer precursors.

\section*{EXPERIMENTAL SECTION}

Synthesis of Carbon Materials. Fresh nutshells were crushed and subsequently washed thoroughly, first with 2 M HCl and then with deionized (DI) water and ethanol, to remove the mineral salts and soluble organic matter. The crushed small nutshell chunks were then dried in a vacuum oven at 100 °C overnight. The dried pieces were directly subjected to pyrolysis in a tube furnace at three different temperatures, 800 °C, 1000 °C, and 1200 °C, under the flow of inert argon gas. The pyrolysis process was carried out for 6 h while increasing the temperature at the rate of 5 °C min\(^{-1}\). After pyrolysis, the carbon samples were collected and then washed with DI water and ethanol. The washed carbon samples were dried at 60 °C in a vacuum oven. The carbon materials resulting from the pyrolysis at 800 °C, 1000 °C, and 1200 °C are named NDC-800, NDC-1000, and NDC-1200, respectively. The schematic for the synthesis of the NDC carbon material from the walnut shell is depicted in Figure 1.

Characterization of NDC Samples. The different carbon samples synthesized from walnut shells were examined by X-ray powder diffraction using the Philips X’Pert PRO diffractometer with nickel-filtered Cu Kα radiation. Raman spectroscopy was performed using Lab RAMHR800 from JY Horiba. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2200FS field emission (FE)-TEM operating at 200 kV. FE-scanning electron microscopy (SEM) was performed with the help of Nova Nano SEM 450. The surface area values for all the samples were determined by the Brunauer−Emmett−Teller (BET) adsorption method (Quadrasorb automatic volumetric instrument). Cyclic voltammetry and impedance measurements were performed using a BioLogic VMP3 multichannel potentiogalvanostat. Charge−discharge measurements were performed with the help of an MTI Corp. multichannel battery testing system.

Electrode and Coin Cell Preparation for Electrochemical Measurement. The electrodes for the electrochemical analysis were prepared by coating a slurry of 5 wt % of

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{schematic.png}
\caption{Schematic illustration of the synthesis of hard carbon from a walnut shell.}
\end{figure}
poly(vinylidene difluoride) binder 15 wt % of conducting carbon (super-P), and 80 wt % of NDC materials prepared in N-methyl-2-pyrrolidone (NMP) on a carbon-coated aluminum foil. The material-coated foil after drying was cut into circular disk with the help of a punching machine fitted with cutters suitable for coin cells of CR2032. The material loadings in the range of 2.0−3.0 mg were achieved. The CR2032 cells for electrochemical testing were assembled inside an argon-filled glove box at extremely low O₂ and H₂O (0.2−1.0 ppm) concentrations. The metallic Na disk was used on the other side. The two electrodes were separated by a circular polyethylene separator soaked in the electrolyte solution. NaClO₄ (1 M) in 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) having 5 wt % of fluoroethylene carbonate already dissolved in it was used as the electrolyte.

## RESULTS AND DISCUSSION

Morphological transformation of the walnut shell upon pyrolysis into the carbon material is depicted in Figure 2. The cross-sectional morphology comparison of a fresh nutshell (Figure 2a,c) and the one pyrolyzed at 1000 °C (NDC-1000, Figure 2b,d) is shown. The continuous channels running parallel to the surface of the shell could be seen in the fresh nutshell, as depicted in Figure 2c. Upon pyrolysis, the hard shells turn into carbonaceous products, as shown in Figure 2b. The FE-SEM micrograph of the pyrolyzed walnut shell is shown in Figure 2d. The image shows that pyrolysis into the carbon product does not lead to disappearance of interlayer free spaces, rather a large number of them can be seen retained in the carbon product, although in the modified form. The presence of this type of open space can be advantageous for the better electrochemical performance because better connectivity between the carbon material and electrolyte is attainable.53,60

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The interplanar separation (averaged) of the order of ~0.38 nm is observed by the TEM fringe analysis, as can be clearly inferred from Figure 3. The particular separation, in the carbon material, makes NDC-1000 a suitable choice for reversible intercalation and deintercalation of Na ions.

The pyrolysis of the nutshell was also performed at 800 and 1200 °C in addition to 1000 °C. Figure 4a−c compares the SEM images of three carbon samples synthesized from walnut shells. It could be seen that there is no evident surface morphological distinction between NDC-800, NDC-1000, and NDC-1200 samples in the micron regime.

XRD and Raman analyses of three samples reveal that the crystal planar and atomic arrangement is not altered...
significantly with the increase in the pyrolysis temperature, the property typically associated with hard carbons. Figure 4d–e shows the XRD and Raman plots of NDC samples obtained at three pyrolysis temperatures. The XRD analysis (Figure 4d) shows that interplanar (002) separations for the three pyrolysis cases are almost similar, with the values of 0.39, 0.37, and 0.37 nm, respectively, for NDC-800, NDC-1000, and NDC-1200.

The separations correspond to the (002) peak positions of 21.78°, 22.78°, and 22.68°, respectively, as brought out by Figure 4d. An interplanar separation >0.36 nm is considered favorable for efficient Na ion intercalation and deintercalation in the carbon lattice. Thus, the NDC materials qualify for direct use as anode in the Na ion battery.36

Raman plots (Figure 4e) further establish the fact that the NDCs are the typical representative of hard carbons, as there is

Table 1. Summary of XRD and Raman Analyses

| parameter                          | NDC-800       | NDC-1000      | NDC-1200      |
|------------------------------------|---------------|---------------|---------------|
| XRD peak position (002)/(100)      | 21.78/43.89   | 22.78/44.11   | 22.35/44.16   |
| interplanar separation (002)       | 0.39 nm       | 0.37 nm       | 0.37 nm       |
| Raman G/D band position            | 1594/1331 cm⁻¹| 1586/1331 cm⁻¹| 1589/1322 cm⁻¹|
| Raman I⁰/I₀ ratio                  | 0.42          | 0.42          | 0.41          |
| in-plane crystalline size (100)    | 1.43 nm       | 2.15 nm       | 2.39          |

Figure 4. Morphological and structural characterization of NDC samples synthesized at three different temperatures. (a) NDC-800, (b) NDC-1000, and (c) NDC-1200. (d) X-ray diffraction (XRD) comparison of NDC samples synthesized at three different temperatures. (e) Raman comparison of NDC samples synthesized at three different temperatures. (f) BET adsorption isotherm of NDC-1000. (g) Pore size distribution plots of NDC-1000 obtained by the density functional theory method.
no or negligible further graphitization with the increase in the carbonization temperatures above 800 °C. The presence of Raman bands at 1320 and 1590 cm$^{-1}$ is attributed to well-known D and G bands of defective graphite. Table 1 summarizes the XRD and Raman parameters and establishes the hard carbon nature of NDC samples, as there is no improvement in $I_D/I_G$ ratios at elevated temperatures.

The low-surface area nature of NDC samples was confirmed by the BET analysis. Figure 4f–g compares the isotherm (Figure 4f) and pore size distribution plot (Figure 4g) for NDC samples. A very low surface area of 59 m$^2$ g$^{-1}$ with no pores in the micropore regime (<2 nm) was observed for NDC-1000, whereas NDC-800 and NDC-1200 displayed a surface area of 120 and 19 m$^2$ g$^{-1}$, respectively, with a similar pore distribution. Low-surface area carbons are considered ideal for Na ion batteries because the solid electrolyte interphase (SEI) layer has to form over a lesser surface area, which in turn implies a less electrolyte degradation.

The electrochemical performance of NDC samples was analyzed by cyclic voltammetry (CV), charge–discharge, and impedance analyses. The rate performance graphs, which plot capacities calculated from the charge–discharge measurement at different current densities versus the cycle number, furnish information about the current stability of the battery material. Figure 5 shows the rate stability comparisons of the NDC samples. Whereas the NDC-800 sample displays a reversible capacity of 165 mAh g$^{-1}$ at 50 mA g$^{-1}$, the reversible capacity of NDC-1000 was observed to be 257 mAh g$^{-1}$ at 50 mA g$^{-1}$. NDC-1200 displayed a reversible capacity of 254 mA h g$^{-1}$ at 50 mA g$^{-1}$. All of the samples showed good capacity recovery (98, 97, and 87%, respectively), even up to a high cycling current of 2 A g$^{-1}$. The capacities of NDC-1000 and NDC-1200 at different current densities are almost the same, further highlighting the hard nature of NDC carbons. The lower capacities of NDC-800 may be attributed to the low conductivities and resulting lower intergrain void spaces obtainable from such small in-plane crystallites (Table 1). The assignment is supported by the work of Y. Li et al. and few other reports on hard carbons for Na ion battery applications.

Table 2 compares the capacities of various recently reported interesting carbon materials with NDC-1000. It can be concluded from the table that the present carbon material is comparable to other reported carbon forms in terms of capacity and stability.

The electrochemical aspects of Na$^+$ ion storage in NDC samples were studied with NDC-1000 as a representative example. Figure 6 elucidates the electrochemical performance of the NDC-1000 as an anode material in the Na ion cell.

![Figure 6a](image1.png)

**Figure 6a** shows the CV plots (first four cycles) of NDC-1000 taken in the voltage range of 0.01–3.0 V in 1 M NaClO$_4$ in an EC–DMC (1:1, 5% FEC) solvent at a voltage scan rate of 0.1 mV s$^{-1}$. The cathodic peaks I and II observed at 1.06 and 0.49 V, respectively, are seen in the first discharge cycle only and disappear in the subsequent cycles. These two peaks are attributed to the SEI layer formation on the electrode surface through irreversible electrolyte decomposition at the mentioned potentials. The pair of cathodic/anodic peaks is observed reversibly at 0.62 and 0.02 V, respectively, and are designated as peaks III and III′ in the CV plot. The cathodic peak III (0.02 V) is attributed to the reversible reductive insertion of Na$^+$ into the nanopores formed between the semigraphitic domains of NDC-1000. Peak III′ (0.21 V) is the corresponding anodic peak of peak III and can be attributed to oxidative deinsertion of Na from the porous domains formed between the semigraphitic lattices of NDC-1000. The additional pair of reversible cathodic/anodic peaks marked peaks IV and IV′ is observed at 0.63 and 0.93 V, respectively.

![Figure 6b](image2.png)

**Figure 6b** shows the rate performance plots of three NDC samples. (a) NDC-800 in the range of 50 mA g$^{-1}$–1 A g$^{-1}$–100 mA g$^{-1}$, (b) NDC-1000 in the range of 50 mA g$^{-1}$–2 A g$^{-1}$–100 mA g$^{-1}$, (c) NDC-1200 in the range of 50 mA g$^{-1}$–2 A g$^{-1}$–100 mA g$^{-1}$.
257 mAh g⁻¹ is observed in the second discharge cycle, which remains almost constant for the next few cycles. The total capacity has contributions from the two operating mechanisms, as is evident from the CV analysis. The second (and subsequent) discharge curves are marked into two regions, with a sloping region in the voltage range of 0.93−0.08 V and a plateau region in the voltage range of 0.08−0.01 V. The sloping region (Figure 6b), which contributes 100 mAh g⁻¹ to the total discharge capacity (257 mAh g⁻¹), can be attributed to Na⁺ storage in the interlayers of NDC-1000, as discussed earlier. The plateau region (Figure 6b) remains a dominant contributor to the total capacity, that is, 257 mAh g⁻¹. The plateau capacity can be attributed to the Na⁺ insertion/deinsertion in the porous regions of NDC-1000 as confirmed by the CV analysis earlier. The charge profiles of NDC-1000 in Figure 6b also show complementary sloping and plateau regions, which agree well with the CV analysis.

Impedance analysis of NDC-1000 was performed on the fresh cell that had undergone five charge−discharge cycles, to nullify interferences from the resistances offered by the SEI layer formation. Figure 6c shows the Nyquist plot recorded on NDC-1000 in a coin cell against the Na/Na⁺ electrode. The two regions in the Nyquist plot can be clearly distinguished. The high-frequency region displays a semicircle of a smaller diameter, which implies a low charge transfer resistance \( R_{CT} \sim 180 \Omega \). In addition, an electrochemical series resistance (ESR) of 1.44Ω was observed from the first intercept on the X axis which implies low material and solution resistance. Both low \( R_{CT} \) and low ESR project NDC-1000 as a competitive Na⁺ anode material.

Cyclic stability analysis was also performed to examine the stability of the material in the working condition over a period of time that in turn reflects the durability of the device. Cyclic stability of NDC-1000 was monitored by capacity analysis over 300 continuous discharging and charging cycles carried out at 100 mA g⁻¹; the result is shown in Figure 6d. The material displays remarkable stability over 300 charge−discharge cycles after the initial reduction from 240 mAh g⁻¹ (at 100 mA g⁻¹) to 170 mAh g⁻¹. The cyclic stability so observed is quite comparable to the reported carbon materials for anode applications.

### CONCLUSIONS

In this article, we report the synthesis of a hard carbon material from the walnut shell biowaste. We show that high-temperature carbonization of compactly packed cellulose fibers in a rigid walnut shell leads to hard and dense carbon materials with a surface area of 59 m² g⁻¹, which is particularly advantageous in Na ion batteries due to lesser SEI formation than in high-surface area carbon forms. This hard carbon material possesses sufficiently separated micrographene-like sheets (>0.36 nm) in...
the semigraphitic domains to act as an ideal anode material for Na ion batteries. An excellent reversible capacity of 257 mAh g⁻¹ is observed at 50 mA g⁻¹ along with good cycling stability. A capacity retention of 71% is observed even after 300 charge–discharge cycles. Further, the carbon material (NDC-1000) shows a remarkable rate performance with 97% retention after cycling at high current densities of up to 2 A g⁻¹.

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