

## **Plant Derived Nanoporous Carbon Materials: A Brief Review On Sustainable Alternative With Advance Applications**

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### **Abstract**

Increase in agricultural production has resulted in the accumulation of plant-based materials which can be used as starting materials for various sophisticated applications. Low cost, easy availability and low toxicity makes these carbonaceous materials much needed for various applications. These plant-based biomass is a good natural source to produce nanoporous carbon materials. This review gives an overview about various plant derivatives used for the synthesis of nanoporous carbon materials. Most of these biomass materials are plant wastes which otherwise add to pollution. These bio materials are carbonized and activated using various activation agents to form nanoporous carbon materials with excellent surface properties. Out of its myriad applications, this review focuses mainly on the adsorption of polluting chemicals as well as their effectiveness in energy storage systems.

**Keywords** Nanoporous carbon materials, carbonization, hierarchically porous structure, adsorption, supercapacitors

### **1. Introduction**

Carbon based nanomaterials have created immense designation in the field of material science owing to their lucrative properties and multifaceted applications. The emergence of nanotechnology has paved the way for the development of various types of carbon nanomaterials taking the benefit of its atomic structure and bonding characteristics[1-3]. Carbon network with different pore size along with the presence of various hetero atoms make them available for various sophisticated applications. The applications of nanoporous carbon materials (NPCM) for adsorption, separation and as catalyst in the multidisciplinary fields are well established[4-7]. Attractive properties like exceptionally high surface area, high pore volume, good stability, non-toxicity, low cost etc. enable them for various applications[8-12]. In a broader term, NPCM can be defined as carbon structures with enclosed porosity, but its properties and applications are

strictly in accordance with its surface morphology, chemical composition, electrical conductivity etc.[13-16]. Depending on the pore diameter and the porosity, the NPCM are classified as i) micro porous (pore size < 2 nm) ii) meso porous (pore size 2-50 nm) and iii) macro porous (pore size > 50 nm).

Earlier, thermal pyrolysis was the only method used for the conversion of plant derivatives into NPCM. In this method, plant derivatives were converted into biochar with low surface area. However, activation during pyrolysis of plant materials or activation of the obtained biochar resulted in NPCM with high surface area. Now researchers are finding new methodologies for the synthesis of NPCM with improved properties. The most important steps in the production of NPCM involve the selection of raw materials, carbonization and activation process. They can be obtained from any carbon containing materials of origin, however, the earlier synthetic approaches relied entirely on coal, petroleum, coke, charcoal etc. as precursors. The obtained porous carbon materials from petroleum sources were used as a decolourizer in the sugar industry and as effective adsorbent in gas masks during world war I [17-20]. High demand for these adsorbing materials for the industrial purpose slowly shifted their synthesis from polluting and non-renewable sources to environmental friendly, renewable resources with economic advantages and sustainability. The synthesis of novel NPCM with tuneable surface and functionalities from various plant-based precursors is comparatively a new area but is rapidly gaining momentum due to its versatile properties and applications. A host of studies and literature reports have been published which firmly establishes the role of plant based precursors for the synthesis of NPCM. So in short, the synthesis of nanoporous carbon and its applications can be considered as an old story with exciting new chapters [21].

Several reviews are available describing the synthesis and applications of NPCM in different fields including separation and adsorption [22-25]. But till date, review based on the synthesis of these valuable materials explicitly from plant derived sources and applications has not been published. An attempt to fill that gap, this review mainly focus on the synthesis of NPCM from different plant based materials and the application of these novel materials in various fields like electrode material for super capacitors, adsorption, separation etc.

## **2. NPCM from plant derived sources**

Various plant based materials have been used for the synthesis of NPCM with different pore features and surface functionalities. In the following sections, we will briefly explain the different plant sources, methodologies and activation agents used for the synthesis of NPCM and its applications.

### **2.1 From fruit shells and fruit peels**

Factors such as economic viability, easy availability, renewability, sustainability etc. can be considered as the reasons for the exploration and designing of NPCM from fruit waste based materials [26-28]. Normally, the conversion of biomass into NPCM can take place either through chemical or by physical means. In chemical method, the raw materials are subjected to high temperature in presence of acid or base and physical method on the other hand is done in presence of CO<sub>2</sub> or steam. In a typical chemical method, moderate temperature is applied for the conversion

of biomass into biochar in the first step. Second step involves the chemical activation which normally takes place in the inert condition at elevated temperature. In another type of chemical carbonization, chemical agents are added along with the raw materials during carbonization. Similarly, physical transformation involves the formation of biochar followed by activation by physical agents like CO<sub>2</sub> or steam [29].

Fruit consumption is always associated with the generation of fruit shells and fruit peels as waste. Efficient and sustainable utilization of these waste materials are a major concern. Earlier works in this research area using fruit peels, mainly focused on the removal of environmentally polluting dyes from the effluents. Hameed et al., used NPCM from durian peels for the removal of acid green 25 (acid dye) [30]. Durian, an edible fruit, is widely used in Southeast Asia and the peels are usually discarded. The above research group used these peels and carbonized them at 80 °C for 24 h. after acid treatment with 3 % HCl for 4 h. without any type of activation. There was a significant influence of pH on the adsorption process. The adsorption was maximum in the acidic pH owing to the availability of positive centres on activated carbon which helped in the electrostatic attraction with the dye anions. From the correlation coefficient value, it was found that the adsorption values were suited for monolayer adsorption as shown in the Langmuir isotherm model with maximum capacity of 63.29 mg/g at 30 °C. The fruit of *Catalpa bignonioides* were taken by researchers as the precursor for the synthesis of NPCM as a low cost and abundant alternative [31]. The surface area of NPCM increased from 756.68 m<sup>2</sup> /g to 896.02 m<sup>2</sup> /g with an increase in the amount of ZnCl<sub>2</sub> from 15 to 30% (w/w) but a concentration of ZnCl<sub>2</sub> above 30 % again reduced the surface area. When used for the adsorption of positively charged methylene blue dye, the adsorption was maximum at the basic pH and maximum adsorption capacity was found to be 299.4 mg/g. It was found that the adsorption mainly depends on textural properties, surface morphology and surface functionalities of NPCM and activation process is the key factor determining all these characteristics. Patawat et al., used *dipterocarpus alatus* fruit for the synthesis of NPCM by trying activation with various activating agents like ZnCl<sub>2</sub>, KOH and H<sub>3</sub>PO<sub>4</sub>, which was then effectively used for the removal of methylene blue [32]. In recent time, lot of modification has been proposed in the synthesis of NPCM owing to their unique surface features which can be utilized for various applications. High surface area and high surface to volume ratio are the basic requirements of any energy storing materials. NPCM with these attributes along with nanoelectronic properties are best suited for such applications [33-38]. Another important fruit peel which is normally discarded is citrus peels. Citrus peels are mainly composed of cellulose and lignin which can serve as good carbon precursors [39]. Kim et al., fabricated NPCM containing potassium (K) from citrus peels by simple pyrolysis in which citrus peels were soaked in KOH solution and dried at 80 °C. The dried materials were then pyrolyzed at 800 °C for 2 h. under inert atmosphere in tubular furnace. They observed that these materials were in the form of nanosheets with thickness around 12 nm along with supreme physicochemical properties compared to the carbonized citrus peels without KOH activation (Fig. 1). At lower temperature, KOH helped in the formation of carbon nano sheets and at elevated temperature, metallic potassium got penetrated these graphitic layers. As the temperature increases, rapid removal of intercalated potassium leads to the formation of nanopores solely depending on heating rate and ratio of KOH to citrus peels. XPS analysis confirmed the presence of hetero atoms like nitrogen and oxygen as part of various functional groups and they act as redox host for sodium ion storage. Nitrogen adsorption and desorption isotherm tests were performed to understand the pore characteristics. The pore size was found to be between 1-5 nm as shown by the pore size distribution plot. Superior electrochemical

properties of these materials made them acceptable to be used as cathode material for sodium ion storage.

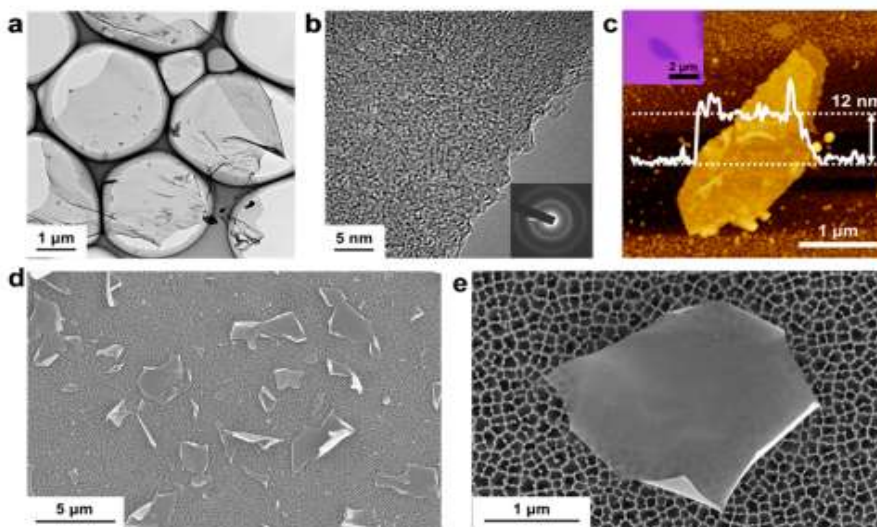


Fig. 1.(a & b) FE-TEM images of NPCM at different magnifications (c)AFM image, the inset shows an optical image (d & e)FE-SEM images at different magnifications(Reproduced from Kim et al. 2016, with permission from American Chemical Society)

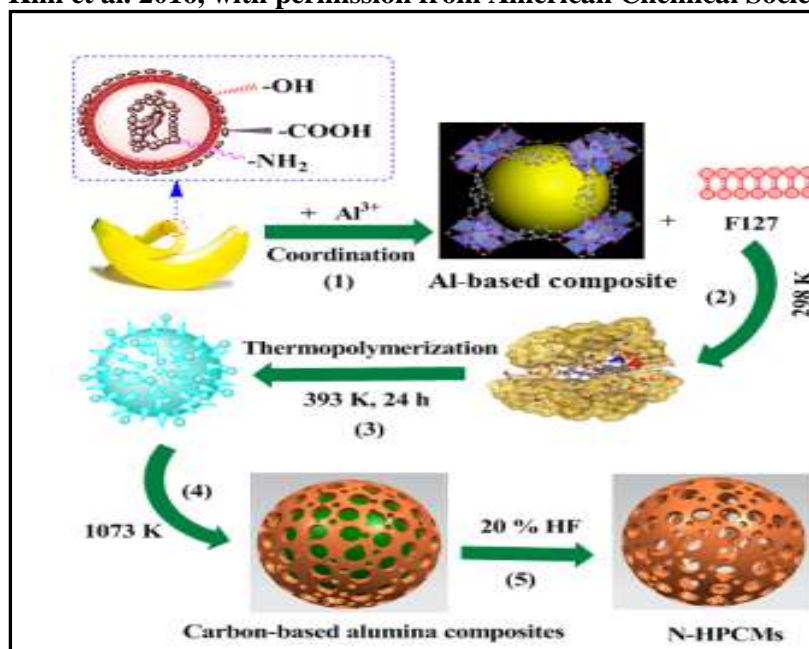


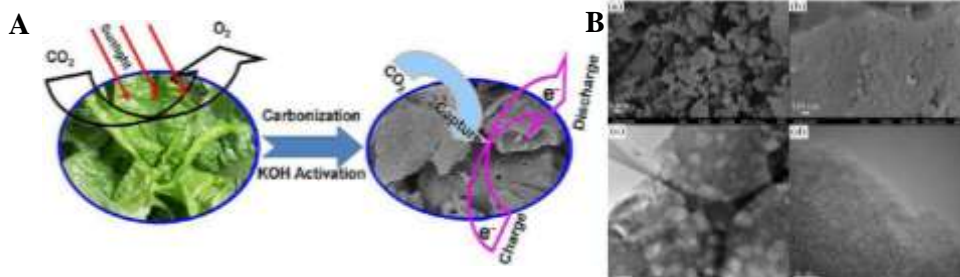
Fig.2. Schematic representation of the formation of NPCM through a hybrid dual template way (Reproduced from Liu et al. 2014, with permission from Elsevier)

Another research work carried out by Wang et al., using pomelo peels as bio precursor were able to produce NPCM with pore size of 0.69 nm under KOH activation [40]. They experimented with different weight ratio of KOH and pomelo peel powder as 1:1, 2:1, 3:1 and found that the surface area, pore volume and pore size of NPCM with 2:1 ratio is far superior than the other two samples. Unlike the common applications of NPCM, a completely new application was targeted in this work where NPCM were used as solid phase microextraction (SPME) fibre by coating it on a stainless steel wire. This was used for the extraction of benzene homologous in water and soil samples. Using banana peels as precursors, Al-based composite and amphiphilic triblock copolymer F127 as dual template, Liu et al., developed doped NPCM with tunable surface area, pore volume and mesopores with average size of 2.72-4.03 nm [41]. They showed excellent results for CO<sub>2</sub> adsorption and bilirubin removal (Fig. 2).

## **2.2 From plant leaves**

Leaves are an important class of green sources which can be utilised for NPCM synthesis. Mostly, the leaves which are not edible and discarded as waste has been used for the synthesis. Leaves mainly contains protein, starch, cellulose, hemicellulose and pectic substances which are in fact good sources of carbon, oxygen and nitrogen<sup>42-44</sup>. Even though fruit peels and shells has been used earlier, initial work of NPCM synthesis using leaves were started with spent tea leaves by Hammed in 2008<sup>45</sup>. Tea being the most popular beverage worldwide, the spent tea leaves are normally discarded after its extraction using hot water. The procedure for the synthesis of NPCM from spent tea leaves involved the boiling of tea leaves with water until it was free from tannin. These spent tea leaves were then oven dried at 60 °C for 48 h., powdered and used as adsorbent for the removal of methylene blue dye. An important limitation of this study is the lack of any type of activation steps which is important for the nanoporous generation. SEM images of the adsorbent do not clearly provide information about the pore size. But they were able to remove 95.5 % of dye with an optimum dose of 3.5 g per liter of dye solution. The adsorption process followed pseudo second order kinetics indicating the adsorption as chemisorption. To increase the porosity in NPCM prepared from leaves, Wang et al., used celtuce leaves as precursors and KOH for the chemical activation<sup>46</sup>. Pyrolysis and chemical activation were performed in two steps where the leaves were pyrolysed at 600 °C in argon atmosphere and then chemical activation was done using KOH at 800 °C for 1 h. in the same inert condition. Experimental techniques like Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Brunnauer-Emmett-Teller (BET) were performed to understand the surface morphology, pore volume, pore size and specific surface area. The increase in surface area and nanopore generation with KOH activation was well explained. At higher temperature, carbon react with KOH to form K<sub>2</sub>CO<sub>3</sub> and metallic potassium. K<sub>2</sub>CO<sub>3</sub> on further decomposition resulted in the conversion of carbon as CO<sub>2</sub> and the generation of nanopores. They were also able to explain different stages of pore formation and carbonization at different pyrolysis temperatures by Thermo Gravimetric Analysis (TGA) and XPS analysis. Desorption of water and decomposition of carbohydrates take place below 450 °C. High temperature and KOH activation resulted in the removal of heteroatoms resulting in the microporous structure with highly appreciable surface area. This specific surface area (SSA) was found to be upto 3400 m<sup>2</sup>/g with nanopore size ranging from 0.5 to 5nm. These two lucrative properties enable NPCM obtained

from celtuce leaves as a good candidate for CO<sub>2</sub> adsorption with an adsorption capacity of 6.04 mmol/g at 0 °C and 4.36 mmol/g at 25 °C under ambient pressure (Fig.3).



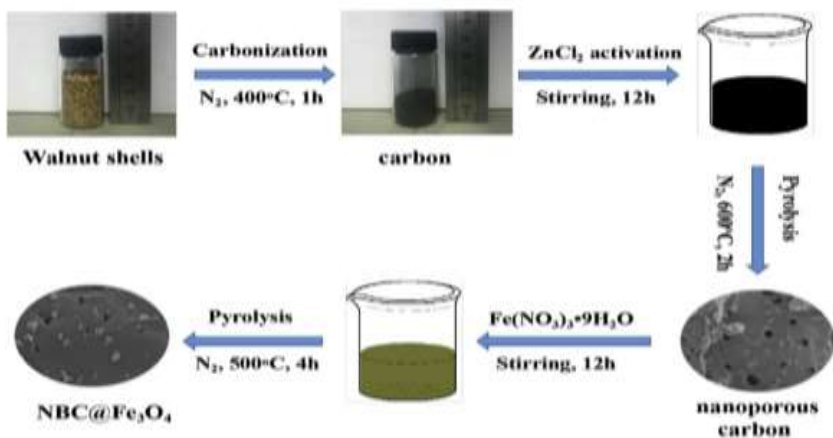
**Fig. 3. (A) Process of formation of NPCM from waste celtuce leaves. (B) (a&b) shows the SEM images of NPCM at different magnification and (c&d) TEM images of NPCM at different magnification (Reproduced from Wang et al. 2012, with permission from American Chemical Society)**

Ameen et al., used palm leaves and other palm tree residues for the synthesis of hydrochar using hydrothermal carbonization with acid as catalyst [47]. Mild acids like citric acid and ascorbic acid were used, which helped in dehydration and carbonization. But the pore size of the hydrochar obtained was significantly higher, as at high temperature the walls of the nearer pores were affected resulting in higher pore size. Chanpee et al., used oil palm leaves to prepare NPCM and used KOH activation to obtain micropore structure using hydrothermal method [48]. This was another work where researchers used hydrothermal methodology instead of traditional pyrolysis to prepare NPCM. Hydrothermal treatment was carried out at 200 °C for 12 h. and the hydrochar obtained was dried and further carbonization was carried out at 800 °C for 1 h. under N<sub>2</sub> flow. For activation, the hydrochar was then mixed with KOH and heated for 1 h. at 800 °C. The resultant NPCM had an average pore size of 2.5 nm and specific surface area of 1685 m<sup>2</sup>/g. It was then used as an adsorbent to remove organic pesticide paraquat and other pollutants from water.

### 2.3 From nutshells

Another green material used for the NPCM synthesis was nut shells owing to its abundant availability, easy preservation, relatively high carbon content, natural pore features and low cost. Coconut shells forms a major part among them and many value added products are being made out of them. The general chemical composition of nut shells consists of lignin, polysaccharides, cellulose and hemicellulose. Several research groups have reported the synthesis of NPCM from coconut shell and its applications. Some of the advantages of these renewable materials includes low cost, availability in abundance and the obtained NPCM are of high purity and optimum porosity. Vargas et al., reported the synthesis of activated carbon monoliths from coconut shells and was effectively used for the CO<sub>2</sub> adsorption [49]. An important observation made by the authors was that the role of activating agents varies with the type and nature of precursors used for the synthesis of NPCM. They found H<sub>3</sub>PO<sub>4</sub> as an activating agent has no effect in the generation of micro and mesoporosity when coconut shells were used as precursors while they greatly influenced the porosity when the precursor was African palm stones. Physical activation of coconut shells using CO<sub>2</sub> was performed by another group to obtain microporous carbon with pore

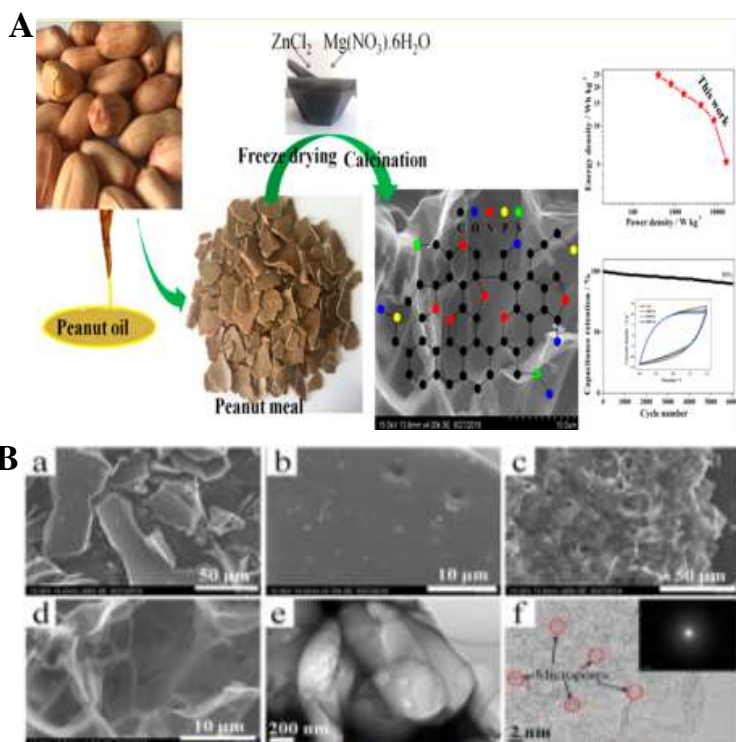
volume from 0.31 to 0.65 cm<sup>3</sup>/g and SSA from 686 to 1327 m<sup>2</sup>/g by varying the time of activation. 5.6 mmol/g of CO<sub>2</sub> was adsorbed by these NPCM at 0°C whereas it was less than 4mmol/g in the former case [50].Tangsathitkulchaie et al., used coconut shells as the raw material for the synthesis of NPCM in which they carbonized the coconut shells to obtain coconut shell char by pyrolysis at a temperature range of 250-500 °C in the nitrogen inert atmosphere [51]. It was found that the porous properties of the NPCM, such as pore volume, surface area and average pore size increases with increase in carbonization temperature. The average pore size observed was in between 0.8 to 2.2 nm. In the application part, diffusional transport model was used to predict the diffusion of CO<sub>2</sub> with adsorption and the results indicated a linear model [52]. Another noteworthy work in this regard was done by Yang et al., where they used KOH as an activation agent. With minimum amount of activation agent and low reaction temperature, they were able to synthesize NPCM with pore size <1 nm. Carbonization of the coconut shells were carried out at 500 °C for 2h. under nitrogen flow. The KOH activation was carried out at 600 °C. for 1 h. under N<sub>2</sub> flow of 400 mL/min with a heating rate of 5 °C/min. The obtained product was then characterized by different instrumental techniques like XRD, SEM and TEM. BET was used to find the specific surface area (S<sub>BET</sub>), Harvath–Kawazoe (H–K) method was used to find the pore size distribution and t-plot method was used to find the micropore volume. It was observed that the SEM images of carbonized coconut shell before activation consists of a smooth surface with no pores whereas the activation resulted in the microporous carbon structure with 0.6 nm pore size. The CO<sub>2</sub> adsorption capacities were measured at different temperature and pressure conditions and was around 3.56 to 4.23 mmol/g at 25 °C under 1 bar and 4.63 to 6.04 mmol/g at 0 °C under 1 bar. A noticeable work using walnut shells for the synthesis of NPCM was reported by Qiu et al., where they used walnut shells as precursors and KOH as activation agent [53]. Synthesis involved the calcination of walnut shells at 400 °C for 1 h. under N<sub>2</sub> atmosphere and further KOH activation at different temperatures from 500 °C to 900 °C for 2 h. It was found that after carbonization, other than inherent pores present in the nutshell, NPCM exhibited more micropores due to KOH activation. In this work, researchers observed the collapsing of pore structures at higher temperatures such as 900 °C. With 600 °C activation, a specific surface area of 736.2 m<sup>2</sup> g<sup>-1</sup> was obtained which showed highest efficiency for microwave absorption as application. Eventhough they got 1101.4 m<sup>2</sup> g<sup>-1</sup> specific surface area at 800 °C activation, the microwave absorption ability decreased due to poor impedance matching, in which a large amount of microwave radiation got reflected at the surface of the sample than absorbed due to lesser nanopores.



**Fig. 4. Schematic diagram of formation of NPCM from walnut and its composite with Fe<sub>3</sub>O<sub>4</sub>(Reproduced from Zhou et al. 2019, with permission from Elsevier)**

Same research group modified the work by changing the activation agent and by synthesising a composite of NPCM with magnetic Fe<sub>3</sub>O<sub>4</sub> using walnut as precursor [54]. They experimented with ZnCl<sub>2</sub> as an activating agent as it reacts with lignin to form 3D micropore structure (Fig.4). Another modification done in this work included the generation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the surface of NPCM for a better microwave absorption. The synthesis was a two-step process where NPCM was generated in the first step by ZnCl<sub>2</sub> activation and NPCM-Fe<sub>3</sub>O<sub>4</sub> composite was prepared in the second step. The composite formation helped in improving the impedance matching and it was found that the materials with magnetic properties has good impedance matching. Due to properties like chemical stability, anti-oxidation etc. Fe<sub>3</sub>O<sub>4</sub> was used in the composite material. For the composite preparation, Fe<sub>3</sub>O<sub>4</sub> was blended with NPCM for 6 h. at 60 °C and then annealed at 500 °C for 4 h. under nitrogen atmosphere. The obtained composite was showing a good microwave absorption ability than carbonized sample. The adsorption abilities of NPCM from nuts were experimented by Joshi et al., where they used Areca catechu nut powder as precursor and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as activating agent [55]. Less polluting and easy elimination possibility by leaching with water makes H<sub>3</sub>PO<sub>4</sub> better activation agent than ZnCl<sub>2</sub>. Nanomaterial surface morphology was studied by varying the carbonization conditions like ratio of precursor to activation agent, carbonization temperature, time of carbonization etc. The experimental results showed that 400 °C and 3 h. of carbonization resulted in NPCM with specific surface area of 2132.1 m<sup>2</sup> g<sup>-1</sup> and a large pore volume of 3.426 cm<sup>3</sup> g<sup>-1</sup>. These NPCM with hierarchical porous structure was used for the adsorption of methylene blue dye. The adsorption of cationic dye methylene blue was maximum when the pH of the medium was highly alkaline. A good correlation coefficient for Langmuir adsorption isotherm indicated homogeneous monolayer adsorption with a maximum adsorption of 333.3 mg/g. Similarly, a lot of nutshells have been used to prepare NPCM for methylene blue dye adsorption and they included cashew nut shells [56], apricot kernel shells [57], coconut shells [58], walnut shells [59], waste apricot [60], hazelnut husks [61], buriti shells [62] etc. Another research work of synthesizing NPCM from nutshells using H<sub>3</sub>PO<sub>4</sub> as activation agent involved the carbonization of argan shells [63]. Medicinally important argan oil is obtained from argan nuts which is the native plant of Northern Africa. In a recent study, apart from the traditional uses like cooking and heating, these nutshells have been used effectively for the synthesis of NPCM as reported by Mokhati et al., Different characterization techniques and experimental data indicated the presence of C, O and trace amount of N in the carbonized sample with a specific surface area of 1542 m<sup>2</sup> g<sup>-1</sup> and pore volume of 1.04 cm<sup>3</sup> g<sup>-1</sup>. They consists of mainly mesopores with comparatively large pore diameter. Sodium diclofenac and Paroxetine are anti-inflammatory and antidepressant drugs respectively, which are widely used nowadays. Due to their toxic properties, they are heavily contaminating soil and water. NPCM obtained from the argan nut shells has been successfully used for the adsorption of these drugs. The removal capacity of NPCM towards these two drugs were 214 mg g<sup>-1</sup> and 260 mg g<sup>-1</sup> respectively which is mainly due to π-π interaction and H-bonding interactions. Throughout the work, the performance of NPCM was compared with commercial activated carbon and the results indicated lesser micropore generation and low adsorption capacity for NPCM than commercial sample. Hence, modification in the synthetic methodology is required to have more micropores which will be beneficial in the adsorption process.

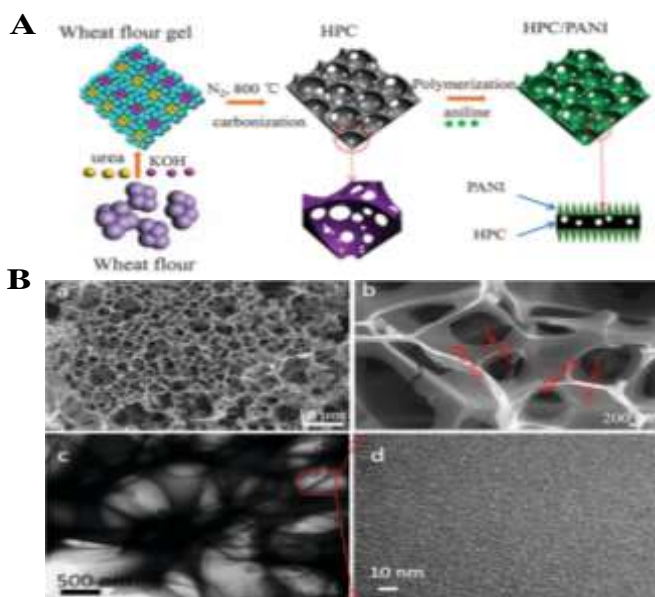
Bioprecursors containing hierarchically porous carbon has been used for the synthesis of NPCM as they have large surface area with heteroatom doping. Peanut meal obtained after the removal of peanut oil is a rich source of elements like N, P and S. Zhao et al., used peanut meal as the precursor and a combination of magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and  $\text{ZnCl}_2$  in the mass ratio of 1:1 as activation agents for the synthesis of NPCM (Fig.5). Synergistic effect of two activation agents can improve the specific surface area and total pore volume of NPCM. They claimed that N-P-S co-doped NPCM has excellent specific capacitance to be used as promising candidate for energy storage applications [64]. SEM and HRTEM images shows the hierarchical porous network with plenty of micropore structures. BET model gave the specific surface area as  $2090 \text{ m}^2 \text{ g}^{-1}$  and pore volume as  $1.42 \text{ cm}^3 \text{ g}^{-1}$ . The authors also claimed that N, P and S forms active sites, which helps in improving the capacitive performance by contributing to additional pseudocapacitance [65-70].



**Fig. 5. (A) Schematic illustration of the formation of NPCM from peanut meal. (B) (a & b) shows the SEM images of carbonized peanut meal without activation at different magnification, (c & d) SEM images of NPCM at different magnification and (e & f) TEM and HRTEM images of NPCM along with SAED pattern at the inset (Reproduced from Zhao et al. 2019, with permission from American Chemical Society)**

## 2.4 From grains and grain husk

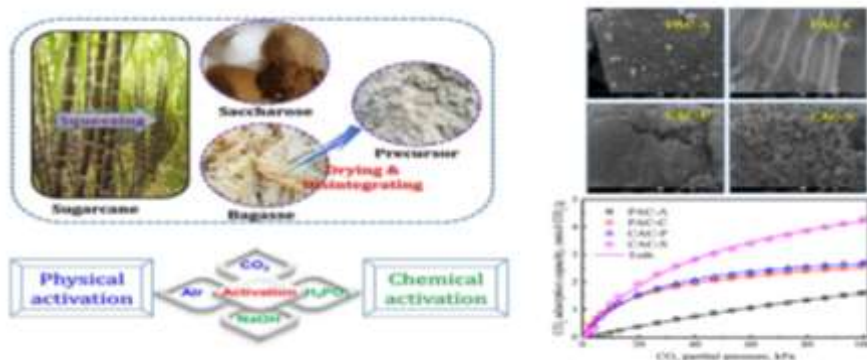
Another important type of plant derived biomaterials used for the synthesis of NPCM are grains and grain husk. Among them, rice husk is considered as major agriculture waste in rice producing countries. The major composition of rice husk is cellulose, hemicellulose, lignins and some pectins. Many researchers have tried to utilize these rice husk to produce some value added products out of them and thereby reducing the environmental impact. Fang et al., have used them to fabricate a composite of NPCM with magnetic particles and utilized them effectively for the electromagnetic wave attenuation [71]. According to them, the porous characteristics of material obtained after carbonization of rice husk is mainly due to volume shrinkage and the removal of compounds of silicon at higher temperature. These NPCM has supreme properties like low density and high specific area. The composite of NPCM with magnetic particles of Fe and Co enhances the permittivity and permeability which is essential for electromagnetic absorption. Post modification synthetic procedure was adopted for the synthesis of NPCM-Fe composite and pre modification treatment was performed for NPCM-Co composite to prevent the rapid sublimation of Co compound. Dielectric loss and magnetic loss happened due to the presence of Fe and Co magnetic particles along with the porous nature of NPCM helped in the dissipation of electromagnetic waves. In another work, Yu et al., modified NPCM, obtained from wheat flour, with polyaniline(PANI) to improve the electrochemical performance as supercapacitors [72]. The synergistic effect of these two materials, where PANI enhanced the electrical conductivity of NPCM and porous structure gave stability for PANI, has been worked out effectively. KOH was used as both template and activation agent and urea as nitrogen doping agent. Synthetic procedure involved the carbonization of a mixture of wheat flour, KOH and urea at 800 °C under inert atmosphere. The SEM image of the obtained N-doped NPCM revealed hierarchical porosity with micro pores of 1-4 nm. It has a specific surface area of 1294 m<sup>2</sup> g<sup>-1</sup> with good electrical conductivity. In situ polymerization was used to grow PANI nanowires on the surface of NPCM and the resultant PANI- NPCM has a high specific capacitance of 1080 F g<sup>-1</sup> with high energy density and power density. These excellent electrochemical performance were effectively used in energy storage systems (Fig.6).



**Fig. 6. (A) Schematic illustration of the formation of PANI/NPCM composites. (B) (a & b) shows SEM images of NPCM at different magnification and (c & d) TEM images of NPCM at different magnification (Reproduced from Yu et al. 2016, with permission from WILEY-VCH Verlag GmbH & Co.)**

## 2.5 From Corn straw and sugar bagasse

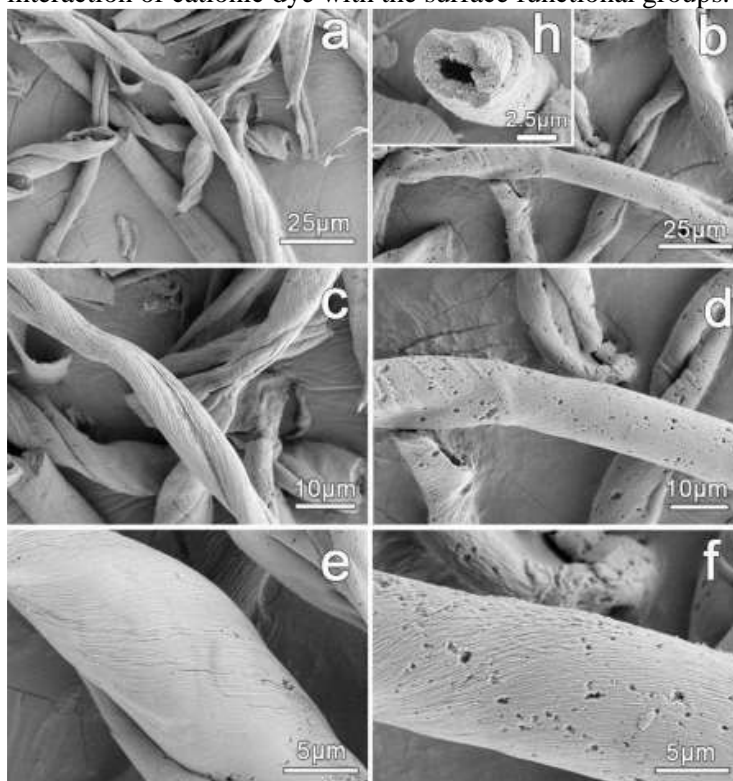
Exceptionally high SSA was obtained for NPCM when the precursor was corn straw along with very high Effective SSA (E-SSA) which is essential when used as electrode material in supercapacitors. Corn straw, an agricultural waste, mainly composed of lignocellulose materials and can be considered as cheap, easily available and nontoxic carbon source. Researchers adopted hydrothermal methodology for the NPCM synthesis and chemical activation using KOH [73]. Corn straw with distilled water was taken in the autoclave and heated for 12 h. at 180 °C and then activated with KOH in the tube furnace at 900 °C for 1 h. under inert atmosphere. Characterization of NPCM were done using XRD, XPS, Raman spectra, SEM and HR-TEM. N<sub>2</sub> adsorption/desorption study revealed porous morphology with plenty of mesopores along with micropores. The obtained porous structure was predominantly mesoporous with SSA of 3237 m<sup>2</sup> g<sup>-1</sup> and E-SSA of 1771 m<sup>2</sup> g<sup>-1</sup>. These two synergistic effects of high SSA and abundant mesopores enabled them to show good capacitance. Another noteworthy work was reported by Guo et al., where they used biowaste sugarcane bagasse for preparing NPCM and activated it using different activation agents to be used as accomplished adsorbent for CO<sub>2</sub> [74]. Mitigation of pollutant is a major problem and in this work they were keen on addressing the pollution problem due to sugarcane bagasse and CO<sub>2</sub>. Researchers have already succeeded in developing NPCM from bagasse for CO<sub>2</sub> adsorption, but, for the first time the effect of various activation agents on adsorption was done in this work [75-76]. To study the effect of various activation agents, they treated the sugar bagasse with air, CO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and NaOH. The synthetic methodology involved physical activation, where bagasse was treated with air and CO<sub>2</sub> separately in a two-step process and chemical activation by direct pyrolysis using H<sub>3</sub>PO<sub>4</sub> and NaOH (Fig. 7). From various instrumental analysis, it was observed that the chemical activation endowed NPCM with superior pore characteristics than physical activation. SSA using NaOH activation was 1149 m<sup>2</sup> g<sup>-1</sup> which was much higher than other activation agents. In the application part, NaOH activated NPCM showed static CO<sub>2</sub> uptake (4.28 mmol CO<sub>2</sub>/g at 25 °C and 1 bar) and great dynamic CO<sub>2</sub> adsorption capacity (1.31 mmol CO<sub>2</sub>/g in 60 °C and 10% CO<sub>2</sub>) which was well ahead of other activation agents.



**Fig. 7. Schematic illustration of the formation of NPCM from sugarcane bagasse (Reproduced from Guo et al. 2019, with permission from Elsevier)**

## 2.6 From wood chips and fibers

Bamboo chip is another lignocellulose material which is a solid waste without any economic value and causes environmental problems if not disposed properly. Jawad et al., used these easily available and cheap carbon resource for the synthesis of NPCM as a renewable precursor by activating KOH [77]. Synthesis involved the carbonization of mixture of bamboo chip and KOH in a tubular reactor at 700 °C for 1 h. under N<sub>2</sub> atmosphere to obtain uniform pore structure. These NPCM were used for the removal of methylene blue dye. Four parameters have been monitored such as the effect of bamboo chip dose, solution pH, temperature and time on methylene blue removal. It is very interesting to note that the dye adsorption was maximum when the bamboo chip amount was 0.1 g, solution pH was 10 and the temperature was 40 °C. According to the authors, the interaction between adsorbent and adsorbate could be both electrostatic and chemical interaction of cationic dye with the surface functional groups.



**Fig.8. SEM images of cotton fiber at different magnifications. (a, c & e) NPCM obtained after calcination. (b, d & f) NPCM after swelling and calcination process. Inset in h shows the cross-section of cotton fiber after swelling and calcination (Reproduced from Liu et al. 2016, with permission from American Chemical Society)**

Hierarchical porous carbon nanofibers were synthesized from natural cotton fibre as they are biodegradable and nontoxic. NPCM with hierarchical porous structures are important when used as electrode material as the macro pores facilitate ion transportation at high rate, interconnected meso pores helps in ionic diffusion and high SSA of micropores endow the structure with efficient adsorption. No template synthetic method was adopted by Liu et al., for the hierarchical porous structure where they pre-treated cotton fiber with NaOH/urea [78]. Two step synthetic procedure was adopted where they treated cotton fibre with activation agents in the first step and then the carbonization of the pretreated material at 800 °C for 2 h. The obtained NPCM showed good electric double layer capacitance and cycling stability which was highly favorable when used as electrode material for super capacitors (Fig 8).

The detailed study of research on NPCM from plant based materials point out the fact that most of the literature work have concentrated mainly on the adsorption of pollutants using the pore features of NPCM. The mechanism of formation of NPCM by carbonization in presence of activation agents involves steps like bond breakage, decomposition, cross linking etc. A clear understanding of these mechanism is essential for enhancing their performance for specific applications. Surface functionalities and tuning of these functional groups for various applications can be added as another future scope of this research area. Introduction of target specific functional group on the surface makes NPCM more efficient and effective in the adsorption process. The nanocomposites of NPCM with other carbon nanomaterials will improve its physical and chemical properties and can be used as future material for energy applications. We have collected data related to NPCM from decade old research to till date and found that adsorption and energy storage applications are the main areas focused and still there are plenty of opportunities for NPCM to be used in catalysis, sensing, separation of various chemical components etc. which shall be explored on priority basis. A list of plant sources, activation agents used for their activation, reaction conditions and applications are summarised in Table 1.

**Table 1: Summary of the plant precursors, synthetic conditions and applications of NPCM.**

Plant based Precursors	Activation agents	Synthesis Temperature (°C)	Time (h.)	SSA (m <sup>2</sup> g <sup>-1</sup> )	Applications	Reference
Durian		80	24		Acid dye	30
Catalpa bignonioides	ZnCl <sub>2</sub>	600	1	896.02	Methylene blue	31
Dipterocarpusalatus	ZnCl <sub>2</sub> , FeCl <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , KOH CO <sub>2</sub> and steam	500	1	843	Methylene blue	32
Citrus	KOH	800	2	1167	Electrode material for sodium ion storage	39

Pomelo	KOH	800	2.5	1770	Solid phase micro extraction	40
Banana	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	800	3	700-2100	$\text{CO}_2$	41
Spent tea		60	48		Methylene blue	45
Celtuce	KOH	800	1	3400	$\text{CO}_2$	46
Oil palm	KOH	800	1	1685	Paraquat	48
Coconut	$\text{H}_3\text{PO}_4$	450	2	1150-1330	$\text{CO}_2$	49
Coconut	$\text{CO}_2$	800	1	686-1327	$\text{CO}_2$	50
Coconut		250-550	2		$\text{CO}_2$	51
Coconut	KOH	500	2	1817	$\text{CO}_2$	52
Walnut	$\text{ZnCl}_2$	400	1	1101.4	Microwave absorption	53
Areca catechu	$\text{H}_3\text{PO}_4$	400	3	2132.1	Methylene blue	55
Cashew nut		500-900	1	518-678	Methylene blue	56
Apricot kernel	Levulinic acid	65	8		Methylene blue	57
Coconut		600	3		Methylene blue	58
Walnut		90	24		Methylene blue	59
Apricot	$\text{ZnCl}_2$	500	1	1060	Methylene blue	60
Hazelnut husks	$\text{H}_3\text{PO}_4$	500	3	770	Methylene blue	61
Buriti	$\text{ZnCl}_2$			843	Methylene blue	62
Argan	$\text{H}_3\text{PO}_4$	400	2	1542	Diclofenac, Paroxetine	63

Peanut meal	ZnCl <sub>2</sub> and Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	800	2	2090	Electrode material for supercapacitor	64
Rice husk		1000	2	533	Electromagnetic wave attenuation	71
Wheat flour	KOH	800		1294	Electrode material for supercapacitor	72
Corn straw	KOH	180	12	3237	Electrode material for supercapacitor	73
Sugarcane bagasse	air, CO <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub> and NaOH	750	1	1149	CO <sub>2</sub>	74
Bamboo chip	KOH	700	1	720.69	methylene blue	77
cotton fiber	NaOH/urea	800	2	584.49	Electrode material for supercapacitor	78

### 3. Conclusion

Applications of NPCM obtained from plant based waste materials are gaining momentum as they are capable of replacing costly and environmentally hazardous chemicals in multidisciplinary research areas. This review mainly focused on plant sources which are converted into NPCM by various carbonization processes. These precursors includes plant leaves, fruit shells and peels, nuts and nut shells, grains and grain husk, wood chips and fibers etc. It is found that the nanoporous structure developed by carbonisation and activation are effectively used for separation and adsorption applications. It is observed that many of them have hierarchically porous carbon framework with magnificently large surface area which enabled them to be involved in myriad applications. Considering the renewability, abundance, low cost, ease of synthesis from plant based precursors and the tunable surface characteristics of the obtained NPCM, they can be considered as potential resources for future sustainable applications.

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