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Efficient energy storage in mustard husk derived porous spherical carbon nanostructures

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An environment-friendly synthesis of highly porous spherical carbon nanostructures (PSCN), in situ doped with N and S, from mustard seed waste has been accomplished. The synthesised PSCN has an interconnected network, abundant active interfaces, heteroatom rich content, and notably high porosity/surface area which are favourable for fast ion transport and efficient charge storage. This active material (PSCN), when employed as lithium-ion battery (LIB) half-cell anode, shows specific charge capacity of 714 mAh g⁻¹ at a current density of 100 mA g⁻¹ even after 550 cycles with 112% capacity retention and high restoration capability. Further, PSCN/LiFePO₄ full cell LIB shows an excellent performance with highly reversible capacity of ~195 mAh g⁻¹ at 50 mA g⁻¹ current density for 400 cycles. The PSCN electrode also exhibited 257.8 F g⁻¹ specific capacitance at 0.1 A g⁻¹ current density with ~93% capacity retention after 10,000 cycles, when used as an electrochemical supercapacitor in an aqueous 3M KOH electrolyte. This work provides preparation of high valued and advanced carbon nanostructured material from renewable bio-mass wastes for high-performance electrochemical energy storage application.

Introduction

Presently, Li-ion battery and electrochemical supercapacitors are the two front-running technologies for energy storage solutions. However, the increasing energy demand and rising environmental concern have put a strong research impetus for developing eco-friendly, cost-effective, lightweight, and sustainable electrode materials.¹ Carbon, in different forms, continues to be the dominant electrode material for both of these applications.² Particularly, recent research has shown that morphology tailored hierarchically porous nanostructures can yield considerably enhanced electrochemical properties.¹,³,⁴ This is so because of the existence of abundant macropores that facilitates mass transport by improving the wettability of the electrode/electrolyte interfaces thereby shortening the diffusion pathways for the charged species and the presence of micro-and/or mesopores that provides a high surface area desired for increased reaction sites.⁵,⁶ In this vein, porous carbon derived from biomass appears to be an attractive prospect for achieving desirable molecular structures and architectures.⁷,¹⁴

Not only it will provide a green route with a low carbon footprint, but also will provide energy sustainability by the abundance, low cost, and easy processing of the naturally occurring biomass. Realizing this, a number of research work has been devoted to extract porous carbon from various biomasses and study their electrochemical properties as LIB anode e.g., wheat straw,¹⁵ rice husk,¹⁶ coconut oil,¹⁷ Avocado seeds waste,¹⁸ Starch,² Green tea leave,¹⁸ Coffee oil,¹⁹ Sweet potato,²⁰ Banana peel²⁰ etc, and also as supercapacitor electrode e.g., Apple waste,²¹ Tannin,² Natural petals,²³ Sugar cane bagasse,²⁴,²⁵ Sewage sludge,²⁶ Moringa oleifera leaves,²⁷ Sunflower Stalk,²⁸ Puffed rice,²⁹ Popcorn,³ Coconut shell,³¹ Moringa oleifera stems,³² Camellia petals,³³ etc. Some excellent recent review articles on biomass derived carbons for various energy storage applications validate the importance of this approach.³⁴,³⁷ From the morphological point of view, synthesis of spherical porous carbon has always been proved to be difficult without using hard templates or structure directing agents. Kim et al. have prepared solid spheroidal carbon by a pyrolysis technique with large average diameter of ~3 µm and a BET surface area of 5.05 m² g⁻¹.³⁹ Pol et al. have synthesized carbon microspheres (average diameter ~2 µm) through decomposition of mesitylene (C₉H₁₂).⁴⁰ Chen et al. have used polyacrylonitrile nanospheres as template to synthesis carbon nanoparticles.⁴¹ Till date, there is no report available on the synthesis of spherical porous carbon hydrothermally by template free technique, to the best of our knowledge. In the present work, we have demonstrated a facile hydrothermal synthesis and followed by activation process for the preparation of porous spherical carbon nanostructures in situ doped with N and S from black mustard seed husk and investigated its applicability as a Li-ion battery anode and also, as a supercapacitor electrode.
Experimental

Chemicals

The mustard seed husk was purchased from a local oil mill, India. Sulfuric acid, H₂SO₄ (98%, Merck, Germany); isopropanol (99%, Merck, Germany); hydrochloric acid, HCl (38%, Merck, Germany); potassium hydroxide, KOH (Merck, Germany) were used as received. For all the experiments, water purified by a 3-stage Millipore Mill-Q system (Merck, Germany) was used.

Material synthesis

Before use, the mustard seed husk was pulverized to small particles by hand grinding and washed several times with a dilute H₂SO₄ solution. Then, after further washing with water and isopropanol solution, it was dried fully. 4.0 gm of dried mustard seed husk was put into sulfuric acid and water solution (4:96 by volume) and loaded into a stainless-steel autoclave (Teflon-lined). The autoclave with the reaction mixture was heated at 180°C for 24 h in an oven. Thereafter, the reaction vessel was cooled naturally and the resulting black product was washed repeatedly with deionized water and isopropanol for removal of the soluble impurities. Finally, it was dried by keeping in a vacuum oven at 120°C for 12 h.

Preparation of activated spherical porous carbon nanostructure (PSCN)

The carbon precursor was properly mixed with KOH (1:4 weight ratio) by hand grinding method for 1 h. The resulting KOH-impregnated carbon precursor was firstly dried at 90°C for 12 h in an oven and then, annealed under argon atmosphere for 2 h at 800°C in a tubular furnace at the ramp rate of 5°C min⁻¹ for activation. After the activation process, the sample was thoroughly rinsed with 5% HCl solution to remove the unreacted KOH completely along with other inorganic impurities. Finally, water and isopropanol were used to clean the product thoroughly. After drying in an oven at 110°C for 12 h, the desired activated carbon nanostructure (PSCN) was obtained. A schematic representation of the synthesis steps is shown in Scheme 1.

Material characterisation

X-ray diffractograms were recorded by an X-ray diffractometer (Philips X’Pert, the Netherlands) in the 2θ range of 10 - 80 ° at a scan rate of 1° per min⁻¹. A Cu-Kα radiation (λ = 1.5406 Å) was used at 40 kV and 40 mA. Fourier transformed infrared (FTIR) studies were carried out in the wavenumber region of 4000-500 cm⁻¹ by a BOMEN infrared spectrophotometer in transmission mode. A Renishaw In Via Reflex micro Raman spectrometer, with excitation of an argon ion laser (514 nm), was used to obtain the Raman spectra. The morphological features were investigated by a ZEISS Supra 35 (Germany) field emission scanning electron microscope (FESEM) and a 300 kV Tecnai G² 30ST (FEI) transmission electron microscope (TEM). A Netzsch Thermal Analyzer (STA449F, Germany) was used for thermogravimetric analysis (TGA) in air at a heating rate of 10°C min⁻¹. X-ray photoelectron spectroscopic (XPS) studies were performed using a PHI 5000 VersaProbe II spectrophotometer (Physical Electronics Inc., USA) using a monochromatized Al Kα (~1486.6 eV) X-ray beam of size ~100 μm. In order to neutralize the static charges generated on the sample surface during XPS measurements, a dual-beam charge neutralization system was operated. Also, prior to acquisition of data, Ar⁺ ion sputtering was done on the sample surface (~2 mm × 2 mm) at 2 kV for removing any contaminants (estimated etching depth ~ 30±5 nm).

Electrochemical characterisation

Li-ion Battery

2032 type coin cells vs. Li/Li⁺ were assembled to evaluate the electrochemical properties of the synthesized PSCN. The PSCN working electrodes were prepared by slurry casting method. The slurry was made by homogeneously mixing the active material (PSCN), a conducting agent (Super-P carbon), and a binder (polyvinylidene fluoride) in 80:10:10 weight ratio in n-methyl pyrrolidinone solvent. The prepared slurry was coated onto a pre-cleaned copper foil and dried at 110°C for 5 h in a vacuum oven. The dried coated foils were then pressed at 40.0 tons per sq. inch, and electrodes were cut into circular disks (dia = 15 mm). The active mass loading in each electrode was ~2.0 mg. The coin cells were fabricated in Ar atmosphere inside a glove box (M’BRAUN, Germany) where, the oxygen and moisture levels were controlled at <0.5 ppm each. LIB half cells were assembled using lithium metal.
circular discs (dia = 15 mm), which act as the counter electrode and also, as the reference electrode. LIB full cells were made using PSCN electrode as the anode, LiFePO₄ (coated on aluminum foil) electrode as a cathode. In all cases, 1.0 M LiPF₆ in EC: DMC (1:2 vol%) was used as the electrolyte and Celgard 2300 as the separator. The LiFePO₄ cathode electrodes were fabricated by the same standard slurry casting procedure where, the weight ratio of KOH was used as an electrolyte. A galvanostat-potentiostat (PGSTAT 300N, Autolab, the Netherlands) was employed to conduct cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. For three-electrode cells, CVs were recorded in the potential window of -1.0-0.0 V at various scan rates of 2, 5, 10, 20, 50, and 100 mV s⁻¹. GCD measurements were performed in the same potential window at various current densities of 0.1, 0.2, 0.5, 1, 5, and 10 A g⁻¹. Electrochemical impedance spectra (EIS) were recorded by a galvanostat-potentiostat (PGSTAT302N, Autolab, The Netherlands) within the frequency range of 100 kHz to 0.1 Hz using an AC amplitude of 10 mV.

**Results and discussion**

The morphology of mustard seed husk derived carbon was examined by FESEM and TEM. FESEM image of as-prepared carbonized material shows agglomerated spherical particles with ~100-200 nm in diameter (Fig. 1a). On the other hand, the PSCN upon treatment with KOH activation and followed by annealing shows more distinct spheres with considerably lesser agglomeration (Fig. 1b). It is plausible that during the activation process KOH would etch out the ionic impurities which are likely to be accumulated in higher concentration in the agglomerated interfaces. Simultaneous reaction with the ionic and other organic impurities, and the presence of negative OH groups on the carbon nanostructures during the activation process at elevated temperature result in dissolution of the interfaces, and interparticle repulsion. After the removal of ionic and decomposed organic matters through washing the final activated material, PSCN appears to be less agglomerated with clear boundaries. The porous structure of the PSCN is not clearly visible in the FESEM micrograph (Fig. 1c). The low resolution TEM image of PSCN shows presence of interconnected spheres (Fig. 1c). The high magnification TEM image (Fig. 1d) reveals nanoporous structure and presence of thinner spherical multi-layer constituents. Such kind of nanostructure is beneficial for achieving high surface area, as well as easy electrolyte access to the inner active mass.
accessibility, and would shorten the diffusion pathway to facilitate the ion-transport. The selected area diffraction (SAD) pattern (Fig. 1d, inset) reveals the predominantly amorphous nature of the PSCN carbon nanospheres.

FTIR and TGA of the final activated sample (PSCN) were performed and the results are presented in Fig. S1 and S2 (ESI†), respectively. TGA in air shows an initial mass loss (~2.5%) due to the elimination of adsorbed water, and then the carbonaceous material was decomposed in two steps with a total loss of 90.5% up to the temperature, 800 °C. The corresponding FTIR shows (Fig. S2, ESI†) peaks corresponding to -OH, CH-, C-C, several weak peaks for other functional groups and peaks originated from residual silica. A thorough XPS analysis of the PSCN was undertaken to understand the functionality present in the SPC. The surface survey scan (Fig. S3, ESI†) shows the presence of binding energy peaks related to S2p, C1s, N1s and O1s at 164, 284.45, 401 and 532 eV, respectively. Peaks observed at the binding energy values of 103.2 and 154.3 eV are due to Si (Fig. S3, ESI†). It is noteworthy to mention that, the presence of S2p and N1s in XPS can be attributed to the in situ incorporation of S and N in the graphitic carbon skeleton of PSCN. It may be noted that the pungent odour of mustard is due to the existence of propenyl isothiocyanate (H₂C=CH₂NC),⁴⁰ which is believed to be the source of doping of S and N during its decomposition in inert atmosphere.

Fig. 2 High resolution deconvoluted XPS spectra of PSCN: (a) C1s, (b) N1s, and (c) S2p.

Fig. 3. (a) X-ray diffractogram and (b) Raman spectrum of PSCN. (c) Deconvoluted multiple peaks fit for D and G bands.

For a detailed understanding, deconvolutions of high-resolution spectra have further been undertaken and shown in Fig. 2. Deconvoluted C1s spectrum shows (Fig. 2a) sp² C=C and sp³ C-C related peaks at binding energy values 284.07 and 284.47 eV,
Nitrogen adsorption-desorption isotherms, measured at 77 K, are shown in Fig. 4. The PSCN material exhibits a type-I isotherm with a sharp adsorption knee at high relative pressure. The specific surface area is calculated to be 618 m²/g, based on the standard BET method. The BJH pore size distribution (inset Fig. 4) was obtained from the adsorption branch of the isotherm and the average pore size was calculated to be ~3 nm with a pore volume of 0.98 cc/g which implies existence of nanopores on the carbon spheres. Since, large specific surface area with nanopores is known to be favorable for high-rate electrochemical processes, we believe that the PSCN might offer high energy storage property.

**Electrochemical performance as half cell Lithium-ion battery (LIB) anode**

The electrochemical performance of PSCN has been examined firstly against Li/Li⁺ in half-cell configuration. Fig. 5a shows the CV profiles for the initial four consecutive cycles at a scan rate of 0.1 mV s⁻¹ within a potential window of 0.005-3.0V. In the 1st scan, the intense cathodic peak was observed at 0.68 V, the irreversible nature of which indicates lithium intercalation into carbon formation and carbonization of solid electrolyte interface (SEI) layer. Another peak at was observed 1.30 V, it could be due to the partial decomposition of electrolyte. Another redox couple, observed at 1.64/2.35 V, is possibly due to the presence of N and S in PSCN and can be assigned to the following electrochemical reactions: CN⁻ + yLi⁺ + ye⁻ ⇌ LiCN, and CS⁺ + yLi⁺ + ye⁻ ⇌ Li₂CS. However, from the second cycle onward, the cathodic peak at 2.35 V does not appear, and the corresponding anodic peak at 1.64 V also becomes smaller, indicating it to be an irreversible process. No further changes are apparent in the CV profiles after the 2nd cycle. The pair of peaks 1.90/1.65 V was observed in the CV is due to the in-situ doing of N and S atom in PSCN carbon material. However, the CV curves exhibit a somewhat quasi-rectangular shape, which is indicative of reversible adsorption of non-Faradaic nature. Thus, Faradic improvement of the electrical conductivity. Being a powerful tool, X-ray diffractogram, shown in Fig. 3a, shows a prominent broad peak at around 2θ = ~22.8° and a small hump at ~43.3° which could be identified with the reflections from (002) and (100) lattice planes of carbon (JCPDS file: 00-001-0646). No other peaks due to any possible second phase could be observed. The nature of the diffractogram suggests an amorphous nature of PSCN, but with a high degree of graphitization, which is beneficial for the improvement of the electrical conductivity. Being a powerful tool, XPS analyses confirm successful in situ doping of cationic species including a significant amount of silica were present. The presence of pyridinic-N, pyrrolic-N, and graphitic-N indicates doping of nitrogen in the graphitic carbon skeleton of PSCN. The S2p spectrum of PSCN has been resolved in three different binding energy peaks (Fig. 2c) corresponding to thiophene-S at 163.96 (S2p⁹/₂), and oxidized sulfur at 169 eV.43,44 Interestingly, a comparison of the fitted N1s and S2p suggests that nitrogen can accommodate itself in graphitic framework via different configurations like pyridinic, pyrrolic, graphitic-N, but sulfur can only exist in a thiophene-like structure after calcining the sample at 800 °C.44 A semiquantitative estimation from XPS shows that PSCN contains about 1.4 and 1 at% of N and S, respectively. Therefore, thorough XPS analyses confirm successful in situ doping of heteroatoms N and S as well as associated functional groups which might help in achieving enhanced electrochemical properties of PSCN. It is noteworthy that the heat-treated mustard husk usually contains a significant amount of silica and other cationic species. However, besides in situ N and S doping we observed presence of only a low amount of silica with a maximum value of ~7 wt% as confirmed by TGA (Fig. S2, ESI†). It is expected that most of the cationic species including a significant amount of silica were dissolved out during the alkalization (KOH) activation process and washing with aqueous HCl.

In order to verify the phase of the synthesized PSCN derived from mustard seed husk, powder X-ray diffraction (XRD) analyses were carried out. The X-ray diffractogram, shown in Fig. 3a, shows a prominent broad peak at around 2θ = ~22.8° and a small hump at ~43.3° which could be identified with the reflections from (002) and (100) lattice planes of carbon (JCPDS file: 00-001-0646).43 No other peaks due to any possible second phase could be observed. The nature of the diffractogram suggests an amorphous nature of PSCN, but with a high degree of graphitization, which is beneficial for the improvement of the electrical conductivity. Being a powerful tool, Raman spectroscopy was employed to further analyze the nature of mustard seed husk-derived activated spherical carbon nanostructures and the presence of structural defects. Raman spectrum of PSCN (Fig. 3b) shows two strong peaks at ~1348 and 1589 cm⁻¹ corresponding to D and G bands of graphitic carbon along with the conventional 2D (G') band at 2819 cm⁻¹, indicating the graphitic nature of PSCN.44 The intensity ratio of the D and G band (I_D/I_G), calculated from Fig.3b, shows a value of ~0.94, which, along with the broadening of D and G bands indicates the existence of structural defects within the graphitic framework.45,46 For further structural analysis, the D and G bands were deconvoluted using Lorentzian fit which resulted in five peaks (Fig. 3c). In figure 3b, two peaks centered at 1348 and 1586 cm⁻¹ can be attributed to the conventional D and G bands originating due to sp² and sp³ hybridized carbon respectively.45,47 Other peaks at 1204, 1518 and 1615 cm⁻¹ correspond to D', D'' and D‴, respectively, which have been commonly found in disordered carbon materials.46,49 The D' peak could be originated from the sp³ rich phase of disordered structure present in amorphous PSCN, and the phonon density of states in small graphitic clusters or C-H vibrations in hydrogenated carbons resulted in the generation of D' peak.46,49,50 Therefore, the Raman spectral analyses suggest the existence of structural defects which can be attributed to the in-situ incorporation of N and S in the graphitic framework as observed in XPS analysis as well as to the probable edge defects related to the morphology. The presence of such defects could have a significant influence on the electrochemical performance of PSCN.

![Fig.4 Absorption-desorption isotherms of the synthesized PSCN. The inset shows the pore size distribution.](image-url)
adsorption/desorption of Li$^+$ ions onto the disorder sites on the surface of carbon is indicated by the observed distortion of rectangular shape.

The galvanostatic charge/discharge experiments have been conducted at different current densities to measure the specific capacity of the electrodes. The first cycle charge/discharge has been done at 100 mA g$^{-1}$ current density and a high specific capacity of ~617 mAh g$^{-1}$ is obtained with ~75% of coulombic efficiency. It might be the extent of irreversible trapping of lithium inside the bulk of the carbon that would adversely affect the first cycle coulombic efficiency through formation of SEI on the surface of the electrode, which is quite common for anode materials. Occurrence of capacity fading for the initial few cycles is also quite common for carbon-based materials. The cyclability test has been carried out at a higher current density of 100 mA g$^{-1}$ for 550 cycles. The charge capacity was found to be ~714 mAh g$^{-1}$ after 550 continuous cycles with ~100% coulombic efficiency, signifying ~112% capacity retention with respect to the value at the first cycle (Fig. 5b). These results are superior to the values previously reported for other bio-material derived carbons (Table 1).

Fig. 5 Electrochemical half-cell LIB anode performance of PSCN. (a) Cyclic voltammetry of the PSCN electrode for first four cycles at 0.1 mV s$^{-1}$, (b) cycling performance at 100 mA g$^{-1}$ current density, and (c) rate performance at different current densities (100-500 mA g$^{-1}$).

The high surface area of the PSCN and the presence of sulfur and nitrogen in the PSCN could be the factors for such excellent performance as a LIB anode. However, it is observed from Fig. 5b, that initially there is a slightly decreasing nature up to 50 cycles but thereafter there is a gradual increase in capacity. The phenomenon of capacity increase during the continuous cycling process is well known and frequently reported in the literature for various anode materials, and explained to be due to the kinetically activated reversible electrolyte degradation leading to extra lithium ion insertion/extraction during the cycling processes.

The rate capability at different current density and the capacity restoration ability of PSCN electrode is shown in Fig. 5c. The cell has been tested with 100 mA g$^{-1}$ to 500 mA g$^{-1}$ of current density with ten-cycle intervals for each rate. It is noted that at 100 mA g$^{-1}$ of current density the specific charge capacity is 545 mAh g$^{-1}$, but when the current density is doubled to 200 mA g$^{-1}$, still the capacity is quite high with a value of 466 mAh g$^{-1}$ i.e., 85.5% of its initial capacity. Further, when the current density is increased to five times of its initial rate (500 mA g$^{-1}$), still 51.3% of its initial capacity is obtained (280 mAh g$^{-1}$). After that, the cell has been subjected back to its initial current rate (100 mA g$^{-1}$) and a capacity of 474 mAh g$^{-1}$ is observed indicating restoration of ~87% of its initial capacity.

Fig. 6 Full cell LIB performance of PSCN anode coupled with LiFePO$_4$ cathode. (a) Cyclic voltammetry profiles at a scan rate of 2 mV s$^{-1}$ at 1.0-3.6 V, and (b) cycling performance and the corresponding coulombic efficiencies at 50 mA g$^{-1}$ of current density.

Electrochemical performance as full cell Lithium-ion battery (LIB)
Inspirited by the half-cell LIB performance and to demonstrate the potential practical applications, we further evaluated the full-cell performance of PSCN anode by coupling it with commercial LiFePO$_4$ cathode. Figure 6a shows the cyclic voltammograms of the LiFePO$_4$/PSCN full cell for the first four consecutive scans recorded at 2 mV s$^{-1}$ in the potential window of 1.0-3.6 V. It is observed that the 2nd cycle onward, the voltammograms nearly trace each other indicating that the charge/discharge processes occurring in the LiFePO$_4$/PSCN full cell are of excellent reversibility. The average voltage profiles are at ~3 V vs. Li/Li$^+$, with high reversibility. Figure 6b shows the cycling performances of the LiFePO$_4$/PSCN full cell at 50 mA g$^{-1}$ current density for 400 cycles. The first cycle-specific charge capacity is ~195 mAh g$^{-1}$ with ~87% coulombic efficiency. The specific charge capacity has been calculated based on the PSCN electrode. From the second cycle itself and onwards, the coulombic efficiency increases to ~91%. The cell shows a capacity decay during the initial cycles but after ~100 cycles, the capacity starts increasing again. Observation of such initial decay in capacity suggests that further optimization, including mass balance for the full cell assembly, might be beneficial. It could also be due to the fact that initially the SPCN electrode was not fully activated. But, when electrode gets activated gradually during repeated cycling, the capacity increases and shows a stable extraordinary cycling performance for continuous 400 cycles with the same current rate. It shows a charge capacity of ~246 mAh g$^{-1}$ after 400 cycles, indicating excellent cycling stability.

**Table 1. Comparison of the LIB performances of carbon materials derived from bio-wastes**

| Material source and synthesis | Morphology | BET surface area (m$^2$ g$^{-1}$) | Potential region (V) | Reversible capacity (mAh g$^{-1}$/current density (mA g$^{-1}$) | Cycle number/retention % | Ref. |
|-----------------------------|------------|---------------------------------|----------------------|-------------------------------------------------------------|--------------------------|-----|
| Wheat straw                 | Fibrous structure | 24.9 | 0.0-3.0 | 344/18500 | 300/~86 | 15 |
| Rice husk                   | Porous block | 52 | 0.0-3.0 | 396/74.4 | 100/~100 | 16 |
| Carbon nanoparticles from coconut oil/ incineration, piranha treatment | Quasi-spherical morphology | 133 | 0.0-3.0 | ~250/ 100 | 90/~32 | 9 |
| Avocado seeds waste derived carbon/ Pyrolysis | Agglomerated particle | - | 0.0-2.0 | 315/100 | 100/~99.9 | 17 |
| Starch derived Carbon/ Pyrolysis | Ultradiffusion sheets | 970 | 0.001-3.0 | ~220/5C | 400/~95 | 7 |
| Green tea leave/ Pyrolysis | Agglomerated particle | 146.3 | 0.005-3.0 | 471/37.2 | 50/~89 | 18 |
| Coffee oil derived carbon/ dry autoclaving | Spherical and dumbbell-like carbon | 5.05 | 0.01-2.0 | 274/100 | 250/97 | 19 |
| Sweet potato-derived carbon/ Pyrolysis | Nanoparticle | 79.1 | 0.01-3.0 | 170/100 | 50/- | 8 |
| Banana peel derived carbon/ Pyrolysis | Agglomerated structure | 217 | 0.0-3.0 | 600/500 | 600/- | 20 |
| Hair/ Pyrolysis | Carbon Microtubes | 306.9 | 0.005-3.0 | ~658/~200 | 1000/~65 | 55 |
| Soybean/ Pyrolysis | Porous network | 1089.8 | 0.01-2.8 | 360/50 | 500/- | 56 |
| Mustard seed husk derived carbon (PSCN) | Spherical porous carbon | 618 | 0.01-3.0 | 714/100 | 550/112 | This work |

**Electrochemical supercapacitor performance at three-electrode configuration**

For evaluating the electrochemical capacitive performances of PSCN, conducting cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) for a three-electrode system in 3 M KOH aqueous solution (Fig. 7). The CV curves were measured within a potential window of 0.0 to -1.0V at various scanning rates of 2-100 mV s$^{-1}$. The CV curves of the PSCN electrode obtained at 2 mV s$^{-1}$ (Fig. 7a) unveiled a nearly perfect rectangular shape with the combination of very small pseudocapacitive nature, due to the N-doping in the sample.58 That typically observed for ideal electric double layer capacitors. However, a small hump suggests minor co-existence of the faradic reactions. Interestingly, the quasi-rectangular shape of the CV curves was maintained for all scan rates from 5 to 100 mV s$^{-1}$ without showing any appreciable distortion even at high scan rates. These results demonstrate an excellent rate capability of PSCN, and implying it to be a perfectly reversible double layer capacitor. The GCD profiles of the PSCN electrode was measured at 0.1-10 A g$^{-1}$ current densities within the potential window of 0.0 to -1.0 V (Fig. 7b). The symmetric triangular-shaped GCD curves show the reversible charge/discharge performance and excellent EDLC behaviour, concurring with the CV features.58 Further, there has been a very low voltage drop (IR drop) between charge and discharge even at high current densities implying outstanding reversibility and rate performance. The specific capacitance of electrode can be evaluated from GCD curves using the following equation:53

$$$$\text{ Capacitance of electrode can be evaluated from GCD curves using the following equation:}$$$$

$$\text{Capacitance (F/g) = \frac{\text{Charge (mAh/g)}}{\text{Current (mA/g)}}}$$
The specific capacitance of the PSCN electrode has been calculated to be 257.8 F g\(^{-1}\) at 0.1 A g\(^{-1}\) current density (Fig. 7c). As the current density is increased, the specific capacitance decreases and values of 149.3, 127.5, 112, 100, and 90 F g\(^{-1}\) at 0.2, 0.5, 1, 5, and 10 A g\(^{-1}\) respectively have been obtained (Fig. 7c). In other words, ~35% of capacitance retention is observed when current density is increased to 100 times than its initial rate, implying an extraordinary rate capability of PSCN. Long-term cycling stability is one of the important criteria for a supercapacitor electrode. The cycle stability test of the SPC electrode was done by continuous 10,000 GCD measurements at 2 A g\(^{-1}\) current density (Fig. 7d). The electrode reveals ~93% retention of its initial capacitance after 10,000 cycles exhibiting a remarkable cycling stability. A comparison of electrochemical performance of PSCN with other carbon materials derived from various bio-sources is given in Table 2.

To understand the underlying reasons for such excellent cycling stability, electrochemical impedance spectroscopy was carried out in the as-assembled state and after 10,000 cycles (Fig. S4a, b; ESI†). Fig. S4b (ESI†) reveals appearance of a semicircle in the Nyquist plot in the high frequency region for the as-assembled state indicating co-existence of faradaic process the solution resistance (R\(_s\)) and extra-coalescence resistance (R\(_c\)) with a very small value indicating high electrode kinetics.

### Table 2. Comparison of the electrochemical supercapacitor performances (three-electrode configuration) of carbon materials derived from bio-wastes

| Material source and synthesis | Morphology | BET surface area (m\(^2\) g\(^{-1}\)) | Electrolyte | Capacity (F g\(^{-1}\))/current density (A g\(^{-1}\)) | Cycle number/retention % | Ref. |
|-----------------------------|------------|----------------------------------|-------------|--------------------------------------------------|-------------------------|------|
| Apple waste/ Hydrothermal   | -          | 2000                             | 2M H\(_2\)SO\(_4\) | 365/0.1                                           | -                       | 21   |
| Biomass-derived/Pyrolysis   | Agglomerated structure | 3120 | 6M KOH | 315/0.1 | 10,000/95.8 | 59  |
| Tannin-derived carbons/Pyrolysis | -          | 2000                             | 1M H\(_2\)SO\(_4\) | 37/0.2                                           | 10,000/~55              | 22   |
| Carbon membranes derived from petals/Pyrolysis | Wrinkled flakes | 509 | KCl | 154/10 mV s\(^{-1}\) | 10,000/~90 | 23   |
| Sugar cane bagasse with urea/Pyrolysis | 3D agglomerated flakes | 623.54 | 6M KOH | 323/1 | 5000/~100 | 24   |
| Sewage sludge derived carbon (N-doped)/Hydrothermal | Agglomerated particle | 1043 | KOH | 286.68/1 | 10,000/97.55 | 26   |
| Moringa oleifera leaves/Pyrolysis | Crumpled Porous structure | 817 | 6M KOH | ~49/1 | 20,000/~100 | 27   |
| Waste bagasse/ Hydrothermal | 3D-hierarchical honeycomb-like texture | 3151 | 6M KOH | 413/1 | 10,000/93.4 | 25   |
| Sunflower Stalk derived carbon/Pyrolysis | Spherical or ellipsoidal particle agglomerates | 1505 | 6M KOH | 365/0.1 | 15,000/95 | 60   |
| Cotton stalk/ Pyrolysis | Pore structure | 1960 | 1M H\(_2\)SO\(_4\) | 254/0.2 | 10,000/~100 | 61   |
| Wood/ reflux | carbon fibers | 3220 | 1M H\(_2\)SO\(_4\) | 280/0.5 | 2000/~99.3 | 62   |
| Sunflower Stalk derived carbon/Pyrolysis | Spherical or ellipsoidal particle agglomerates | 1505 | 6M KOH | 365/0.1 | 15,000/95 | 63   |
| Carbon nanosheets derived from puffed rice/Pyrolysis | Nanosheets | 3326 | 6M KOH | 334/0.5 | 11,000/97 | 29   |
| Popcorn-derived porous carbon/Pyrolysis | Porous flakes | 3301 | 6M KOH | 348/0.2 | 10,000/95 | 30   |
| Coconut shell derived/Pyrolysis | Nanosheets | 1874 | 6M KOH | 268/1 | 5000/- | 31   |
| Moringa oleifera stems carbon/Pyrolysis | Porous nanosheets | 2250 | 6M KOH | 283/0.5 | 20,000/~100 | 32   |
| camellia petals and ammonium persulfate derived carbon/Pyrolysis | Porous nanosheets | 1122 | 6M KOH | 227/0.5 | 10,000/~100 | 33   |
| Mustard seed husk | spherical porous | 618 | 3 M KOH | 257.8/0.1 | 10,000/~93 | This |
The derived carbon material is in situ N- and S-doped and has which is cost-effective, environment-friendly and sustainable. After 10,000 cycles (Fig S4b), the semicircle disappears and the Nyquist plot inclines to become parallel to the Y-axis signifying highly capacitive behaviour. The solution resistance remains low (0.59 Ω) even after 10,000 cycles indicating excellent stability of the PSCN electrode material.

Fig. 7 Electrochemical supercapacitor performances of PSCN electrode in three-electrode configuration, (a) cyclic voltammetry at various scan rates at 0.0 to -1.0 V, (b) GCD profile at 0.1 to 10 A g⁻¹ current density, (c) variation of specific capacitance vs. current density, and (d) cycling stability test at 2 A g⁻¹ current density for 10,000 cycles.

Thus, the above experimental results demonstrate that our PSCN material has excellent electrochemical reversibility when employed as an electrode in LIB half-cell, LIB full cell, and supercapacitor applications. The ultrahigh electrochemical activity, remarkable cycling stability with high specific capacity could be attributed due to the probable reasons: (i) interconnected 3D spherical micro/mesoporous carbon nanoparticles with ordered arrangement ensures sufficient active sites accessibility, and faster ion transmission; (ii) high surface area with the large volume of macropore network can act as a ion reservoir to store electrolyte ions and advance the accessibility of the inner surfaces of PSCN material; (iii) the 3D spherical frameworks impart structural stability; (iv) presence of multidirectional porosity provides efficient pathways for fast ion transport; and (v) in-situ N and S doping in enhances the electronic conductivity facilitating charge transport.

Conclusions
In summary, we present here a simple synthesis process to prepare a carbon material (PSCN) from mustard husk waste which is cost-effective, environment-friendly and sustainable. The derived carbon material is in situ N- and S-doped and has high surface area (618 m² g⁻¹) with a spherical nanostructure, and found to be suitable for electrochemical energy storage applications. When used as LIB half-cell anode, the PSCN shows a reversible capacity of 714 mAh g⁻¹ at 100 mA g⁻¹ after 550 cycles. Further, the full cell LIB (PSCN/LiFePO₄) performance shows a very stable reversible capacity of ~195 mAh g⁻¹ at 50 mA g⁻¹ current density after 400 cycles. As an electrochemical supercapacitor electrode, the PSCN exhibits enhanced performances of 257.8 F g⁻¹ specific capacitance at 0.1 A g⁻¹ current density with retention of 93% after 10,000 cycles. Therefore, the PSCN, derived from abundant mustard husk biomass could find a range of real-world applications in sustainable energy related areas.

Author Contributions
Atin Pramanik: Conceptualization, Methodology, Writing - original draft. Shreyasi Chattopadhyay: Methodology. Goutam De: Methodology, review & editing. Sourindra Mahanty: Conceptualization, Writing - review & editing.

Conflicts of interest
The authors declare no competing financial interest.

Acknowledgements
AP thanks CSIR India for senior research fellowship (Award Nos. 31/15(136)/2017-EMR-I). SC thanks UGC, India for research fellowship (Award No. F.2-44/2011(SA-I)).

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