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Subburaj, Surender, Thomas, Shalini, Kavipriyah, M.N. and Subramanian, Balakumar 2024. Phosphorus-doped carbon nitride for enhanced supercapacitor performance and energy storage applications. *Inorganic Chemistry Communications* 170 (Part1) , 113266. 10.1016/j.inoche.2024.113266

Publishers page: <http://dx.doi.org/10.1016/j.inoche.2024.113266>

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# Phosphorus-Doped Carbon Nitride for Enhanced Supercapacitor Performance and Energy Storage Applications

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## Abstract

Exploiting the advantages of graphitic carbon nitride doped with phosphorus (xP-CN) electrodes were designed for high-performance hybrid asymmetric supercapacitor via facile hydrothermal and thermal decomposition techniques. The structural, surface chemistry, functional and morphological characterizations evidence depict successful phosphorus incorporation in Carbon Nitride (CN). X-ray photoelectron spectroscopy analysis shows that phosphorus (P) atoms have replaced corner carbon atoms in the CN structure. These findings clearly demonstrate that the presence of phosphorus doping improves the electrochemical activity of the electrodes. The designed three-electrode system has a specific capacitance of 189.36 F/g with a current density of 1 A/g. Phosphorus doping has been discovered to play a significant role in improving both specific capacitance and cycling stability. The capacitance retention of the two-electrode solid-state device has 97.2% after 5000 cycles. These electrochemical evaluations reveal that the xP-CN electrode

exhibits superior electrochemical performances than pristine CN. This doping strategy for CN presents a novel and efficient approach for crafting high-performance supercapacitors.

## **Keywords**

Carbon Nitride, Phosphorus doping, Electrochemical measurements, Specific capacitance, Energy storage.

## **1. Introduction**

Solar energy, chemical energy, tidal energy, and wind energy have recently emerged as the trendiest new energies that can be transformed into electricity [1-3]. The use of supercapacitors (SC) in energy storage applications can supplement the requirement for sustainable energy sources to fulfil population growth and environmental pollution needs[4]. Across the globe, various research groups and industries are developing electrochemical energy storage systems that includes supercapacitors for a variety of applications that include portable gadgets in addition to electric vehicles[5-8]. Supercapacitors (SCs) have attracted considerable attention as promising energy storage devices, thanks to their outstanding power density, safe operation, rapid charging and discharging capabilities, environmentally friendly characteristics, and long-lasting cycling performance[5, 9-12]. Supercapacitors fall into three distinct types owing to their storage mechanisms: electric double-layer capacitors (EDLCs), pseudo capacitors, and hybrid capacitors. Furthermore, supercapacitor devices can be commercialized in three ways: symmetric, asymmetric, and hybrid[13]. These devices are sustainable energy storage solutions with a wide range of uses, including portable and flexible electronic gadgets, the automotive industry, hybrid electric cars, and defense-related technologies[14]. EDLCs operate on the electrochemical double layer energy storage principle. EDLCs can store charge either electrostatically or by a non-faradaic process that does not transfer

charge between the electrode and electrolyte. When voltage is applied, ions in the electrolyte diffuse over the separator and onto the pores of the oppositely charged electrode as a result of opposite charges being attracted to one another by the potential difference[15]. In contrast to EDLCs, which store charge electrostatically, pseudo capacitors store charge in a faradic manner. This process involves the transfer of charge between the electrode and the electrolyte[16]. When a voltage is given to a pseudo capacitor, reduction and oxidation reaction occur on the electrode material, allowing charge to travel through the double layer[17]. The third type hybrid supercapacitor follows the storage mechanism of both pseudo-capacitors and EDLCs. Nonetheless, managing the energy requirement presents various problems for researchers studying improved materials for supercapacitors. These materials should function as electrodes, increasing the surface area that encounters the electrolyte, enhancing the electrochemical activity, and crucially, sustaining the structure of the electrode materials throughout prolonged discharge and charge cycles[18-20].

Carbon-based materials, transition metal hydroxide, transition metal oxide, and electro-conductive polymeric materials are prominent electrode materials for supercapacitors[20-23]. However, though all of them have huge potential, each of them has a distinct drawback such as a low energy density, erratic electrochemical performance, excessive cost, or lack of efficiency. In the supercapacitor electrode materials field, two-dimensional graphitic carbon nitride has received considerable interest, due to its physicochemical characteristics and rhythmic carbon-to-nitrogen network[24-26]. It also offers facile synthesis, more active reaction sites for electron acceptors/donors and large additional pseudo-capacitance behavior[27-29]. On the other hand, the electrochemical functionality of raw g-C<sub>3</sub>N<sub>4</sub> (CN) is constrained by its moderate conductivity and surface area, which results in low specific capacitance[30-32]. The electrochemical functionality of g-C<sub>3</sub>N<sub>4</sub> can be strengthened through different strategies, including doping. Dopants in

appropriate sites certainly enhance the electrochemically active sites available and make it easier for ions to accumulate charge at the electrolyte-electrode interface, which enhances capacitance performance. Generally metallic dopants (Cu, Zr, W, Fe, K, Mo, Ag) and non-metallic dopants (B, S, N, C, O, P) are used to enhance the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>[33-35]. In particular, many reports are available on non-metallic P doped g-C<sub>3</sub>N<sub>4</sub> to enhance the visible light photocatalytic activities[36]. Previously, it was demonstrated that phosphorus as a dopant that improved the CN structure's physicochemical characteristics and photocatalytic activity[37]. In general inorganic (hydrochloric acid, sulfuric acid, and phosphoric acid) or organic acid doping (sulfosalicylic acid, phytic acid and p-toluene sulfonic acid) has been used for the synthesis of P doped C<sub>3</sub>N<sub>4</sub>[38, 39]. Among them, phytic acid is a weak organic acid due to its inositol hexaphosphate structure, and it has various advantages such as being biocompatible, environmentally benign, and affordable. There are numerous sites for phosphorus incorporation in the CN structure. Two types of carbon (bay and corner) as well as two types of nitrogen (edge and bridge) can be replaced by phosphorus. The substitution of carbon is preferred among these potential forms of incorporation, though the substitution of nitrogen is still possible. As a phosphor amidic or phosphorimidic moiety, phosphorus can occupy the positions at the edges and defects of the CN structure. It can also be interstitially bound to nitrogen in the cavity of CN sheets. With respect to the previous report on P doped g-C<sub>3</sub>N<sub>4</sub> for supercapacitor applications, the novelty of this work lies in the fabrication of asymmetric supercapacitor (ASC) device with P doped g-C<sub>3</sub>N<sub>4</sub> as the active material.

In this work, CN was doped by P atoms with phytic acid as a source, which was investigated by simple hydrothermal and thermal decomposition technique. This strategy is to probe the effect of phosphorus doping in graphitic carbon nitride for electrochemical application.

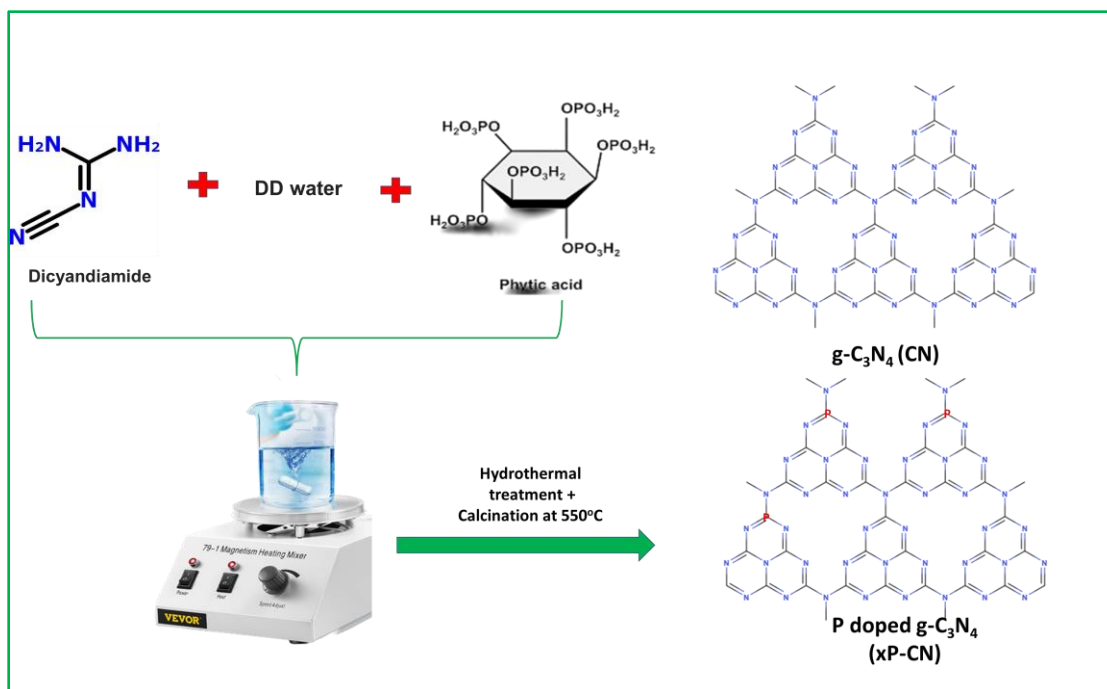
## **2. Experimental Section**

### **2.1 Materials**

Dicyandiamide and Phytic acid were purchased from Sigma–Aldrich. Activated Carbon, N-methyl pyrrolidone (NMP), Potassium hydroxide (KOH) and Polyvinylidene difluoride (PVDF) were obtained from Merck Chemicals. Deionized water was acquired from the Millipore water purification plant for synthesis and washing purposes.

### **2.2 Preparation of phosphorus doped CN**

Initially, 3 grams of dicyandiamide was dissolved in 50 ml of deionized water by constant stirring to get a clear solution and three different volumes of phytic acid (0.5 ml, 1.0 ml, and 1.5 ml) were added dropwise to the above solution. The homogenous solution was transferred to the autoclave and placed in the oven for 12 hours at 180 ° C. The product was then washed with ethanol as well as DI water followed by drying in vacuum oven for overnight at 60 ° C. The final material was annealed at 550° C for 3 hours to achieve phosphorus doped carbon nitride. The pure CN was prepared by the same procedure without adding the phytic acid (represented in Fig.1).



**Fig.1 Schematic illustration of the synthesis procedure for xP-CN electrode material**

## 2.3 Materials Characterization

The phase identification was investigated by powder X-ray diffraction (XRD) (PANalytical, Aries, The Netherlands with Cu K $\alpha$  radiation,  $\lambda = 0.15405$  nm). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was implemented for examining the chemical structures and surface properties of materials. The functional groups of materials were evaluated by Fourier transforms infrared (FT-IR) spectroscopy (MODEL FTIR-6300). The surface morphology and composition of the materials was observed by Field emission scanning electron microscope (FESEM) (Carl Zeiss MA15/EVO). The HRTEM images were recorded on a JEOL JEM 2100F microscope working at 200 kV. The specific surface area and pore size distribution was obtained from the N<sub>2</sub> adsorption-desorption isotherms and calculated by the Brunauer-Emmett-Teller (BET)s method using QUADRASORP SI analyzer.

## 2.4 Electrochemical measurements

The electrochemical capabilities of prepared electrodes were examined in a three-electrode arrangement attached with the CHI- CV electrochemical workstation. The as-prepared materials (1 cm × 1 cm), platinum wire and Ag/AgCl electrode were employed as working electrode, counter electrode, and reference electrode, respectively. The working electrode was made by combining the as- synthesized p doped CN, activated carbon (AC), and polyvinylidene fluoride (PVDF) in an 80:10:10 weight ratio. Then, a 1 cm x 1 cm processed Ni foam substrate was coated with the produced slurry, which was then dried in a vacuum oven at 80 °C overnight. On the nickel foam, the active mass of the active electrode material was measured to be 2 mg. Using electrochemical techniques, cyclic voltammetry (CV), galvanostatic charge/discharges (GCD) the potential window of 0 V to 0.48 V (3 M KOH electrolyte solution) and cyclic stability were carried out. The specific capacitance and areal capacitance were calculated from CV and GCD data according to the following equation[40].

Specific capacitance

$$C_{sp} = \frac{\Delta t * I}{m * \Delta V} \quad (1)$$

Where,  $I$  is the applied current (A),  $V$  represents potential window (V),  $m$  is the mass of active material (g), and  $t$  is the discharge time of one cycle (s).  $C_{sp}$  is the specific capacitance (F/g) of the electrode materials.

## 2.5 Fabrication of the all-solid-state asymmetric supercapacitor device (ASC)

The all-solid state asymmetric supercapacitor device was fabricated to commercialize the electrode materials as they were prepared. In the whole cell arrangement, activated carbon and the

produced nanocomposite were used as anodes and cathodes, respectively. Both electrodes were prepared using the afore-mentioned technique. All the three solid-state supercapacitor devices were assembled by using anode and cathode, in between the electrodes 3 M KOH PVA gel electrolyte was used as a separator and it was sealed carefully. An investigation was conducted on the electrochemical behaviors of the asymmetric solid-state supercapacitor device. Furthermore, the energy and power density of the device was calculated from the following equations.

$$E = \frac{C_{sp} \times \Delta V^2}{2} \quad (2)$$

$$P = \frac{\Delta V \times I}{2m} \quad (3)$$

where  $C_{sp}$  is the specific capacitance (F/g),  $E$  is the energy density (Wh kg<sup>-1</sup>),  $\Delta t$  is discharge time (s) and  $\Delta V$  is the cell operation potential (V),  $P$  is the power density (W kg<sup>-1</sup>),  $I$  is the discharge current (A), and  $m$  is the average mass of two electrodes (g)[41].

The columbic efficiency ( $\eta$ ) of the fabricated device can calculated from the below equation.

$$\eta = \frac{T_d}{T_c} * 100 \quad (4)$$

Where  $T_d$  and  $T_c$  are discharge and charge time respectively.

### 3. Result and Discussion

#### 3.1 Structural analysis

Figure.2a depicts the XRD patterns of CN and xP-CN materials. As can be observed, the CN has an intense peak at 27.7°, which is a distinctive (002) plane peak resulting from the interlayer stacking of aromatic planes in the CN structure (JCPDS No 87-1526)[42]. Another small

diffraction peak at  $13.1^\circ$  represents the (100) plane, which is assigned to aromatic systems of in-plane structural packing motif [43]. The (100) plane peak disappeared in the P-CN and revealed its in-plane structural packing has P atoms. The highlighted peaks are still present in phosphorus doped g-C<sub>3</sub>N<sub>4</sub>, demonstrating that the textural structure of CN is not altered throughout the phosphorus doping technique. It is worth noting that when phosphorus concentrations increase, the diffraction peaks expand and lose intensity, signaling that more flaws in the structure arise along with phosphorus doping. Furthermore, the peak location of the (002) plane gradually shifts from  $27.7^\circ$  to  $27.4^\circ$ , which is most likely due to phosphorus heteroatoms being infused into the lattices of g-C<sub>3</sub>N<sub>4</sub>, resulting in greater lattice distortions and an increase in inter-planar distance with increasing phosphorus amount. These findings are consistent with prior reports on g-C<sub>3</sub>N<sub>4</sub> [44]. The Debye-Scherrer formula was used to calculate the average crystallite size of the developed electrode materials [45].

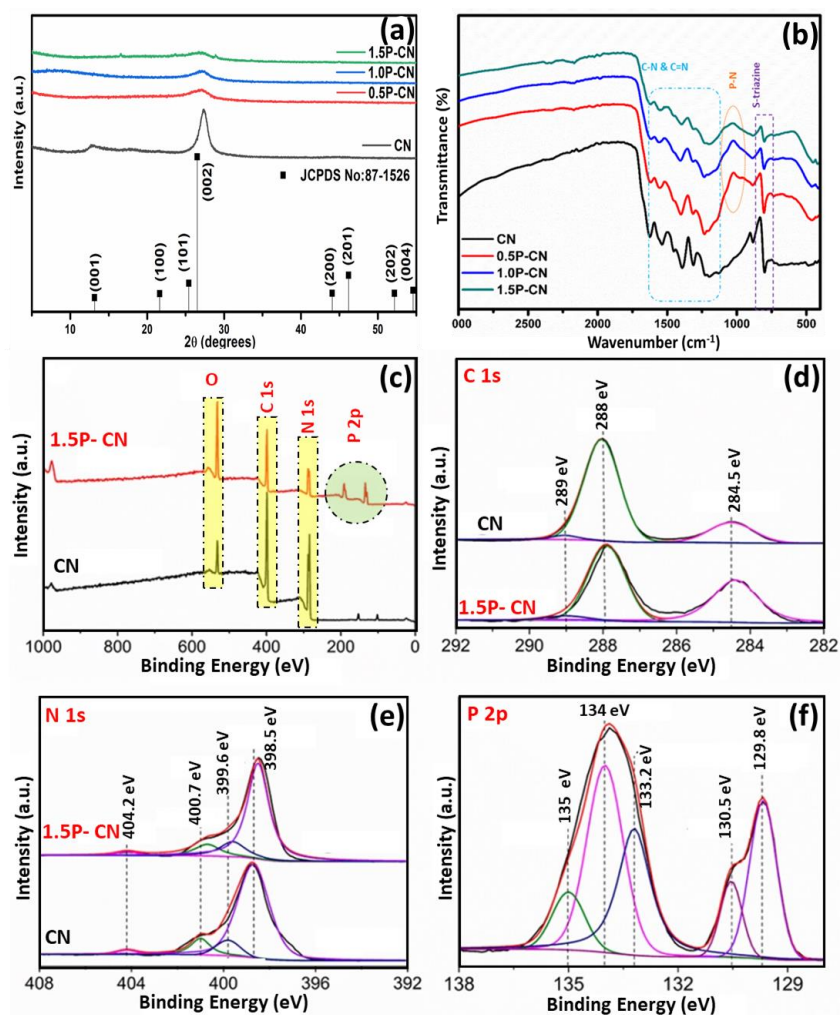
$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (5)$$

Where, D is the average crystalline size of the materials,  $\lambda$  is the wavelength of the X-ray beam, K is the slope factor (0.9),  $\theta$  is the Bragg diffraction angle, and  $\beta$  is the full width at half maximum (FWHM). The average crystallite size of xP-CN material was found to be in the range of 30.5 - 35.9 nm.

### 3.2 Functional groups analysis

FTIR measurements were performed to determine the surface chemical bonding properties of the developed electrode material. As shown in fig. 2b, the FTIR properties of xP-CN are comparable to those of CN, indicating that the fundamental network structure of CN remains unchanged upon P doping. C=N and C-N heterocycles exhibit typical stretching vibration modes

in many bands ranging from 1200 -1700  $\text{cm}^{-1}$ . The sharp band at 810  $\text{cm}^{-1}$  represents the tri-s-triazine unit's usual out-of-plane bending vibration. There are phosphorus-related groups present, as seen by the extra peaks in the xP-CN FTIR spectra. The P-N stretching mode produces the band at 1064  $\text{cm}^{-1}$ . Overall, the present study shows that the P element is successfully integrated into CN without altering the fundamental architecture of CN[46].



**Fig.2. (a) XRD patterns, (b) FTIR spectra, (c) XPS survey spectra, (d) high resolution C 1s spectra, (e) high resolution N 1s spectra and (f) high resolution P 2p spectra of CN and xP-CN electrode materials**

### 3.3 Elemental composition and binding state analysis

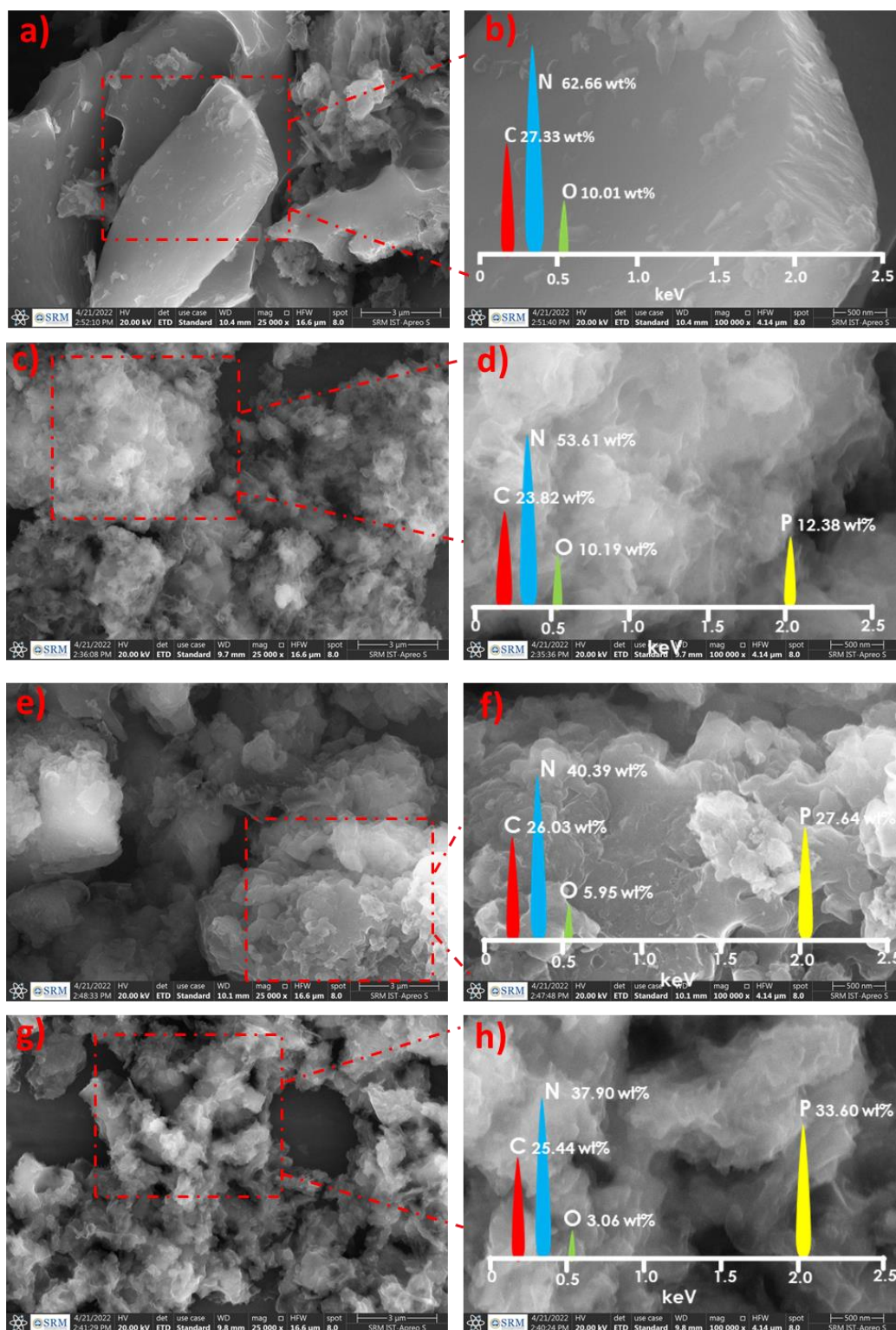
XPS analysis was used to determine the surface chemical compositions and oxidation states of the produced xP-CN electrode material, which is depicted in fig.2 (c-f). The XPS survey spectra of CN and 1.5P-CN are shown in fig. 2c. They primarily consist of the elements C, N and O. Additionally, the 1.5P-CN spectrum contains P elements, indicating that phosphorus element has been evidently present in the matrix of CN. Oxygen comes from the contamination for exposure in air. All the XPS spectra's peak locations are calibrated with C 1s at 284.5 eV. As seen in fig. 2d, the C 1s XPS spectrum of CN and 1.5P-CN could be deconvoluted into three peaks, each of which corresponded to a different type of carbon impurity, sp<sup>2</sup>-hybridized carbon in an aromatic ring (N-C=N), and C-C, with binding energies of 289 eV, 288 eV, and 284.5 eV, respectively[47, 48]. Figure. 2e exhibits the N 1s peak, which includes four contributions[49]. The peaks for 1.5P-CN shift to lower binding energies, showing that the N in CN has enriched electrons. The peak of 1.5P-CN at 398.5 eV is an aromatic N atom that has undergone sp<sup>2</sup> hybridization and is bound to carbon atoms (C=N-C)[50]. Furthermore, the N1s peaks at 399.6 and 400.7 eV correspond to tertiary N linked to carbon atoms via N-(C)<sub>3</sub> and N-H side groups, respectively.

The 1.5P-CN sample exhibits the P 2p XPS peak at approximately 133.2 eV (Fig. 2f). P 2p's binding energy in P-C and P-N bonds is around 133.2 and 134 eV, respectively. [51]. The peak at 135.0 eV can be attributed to oxidized P at the surface, whilst the peaks at 129.8 and 130.4 eV are the typical peaks of P on the CN. As a result, it is reasonable to assume that the P 2p peak at 133.3 eV originates from P-N bonds that emerged in the CN textural structure by swapping out the lattice C atoms by P atoms, which indicates that P atoms replace C atoms in the C-N framework[52, 53]. It has been found that the binding energy of P-C coordination is 1-2 eV lower than that of P-N species. Therefore, it is confirmed that P atoms are located at the corner-carbon site of carbon

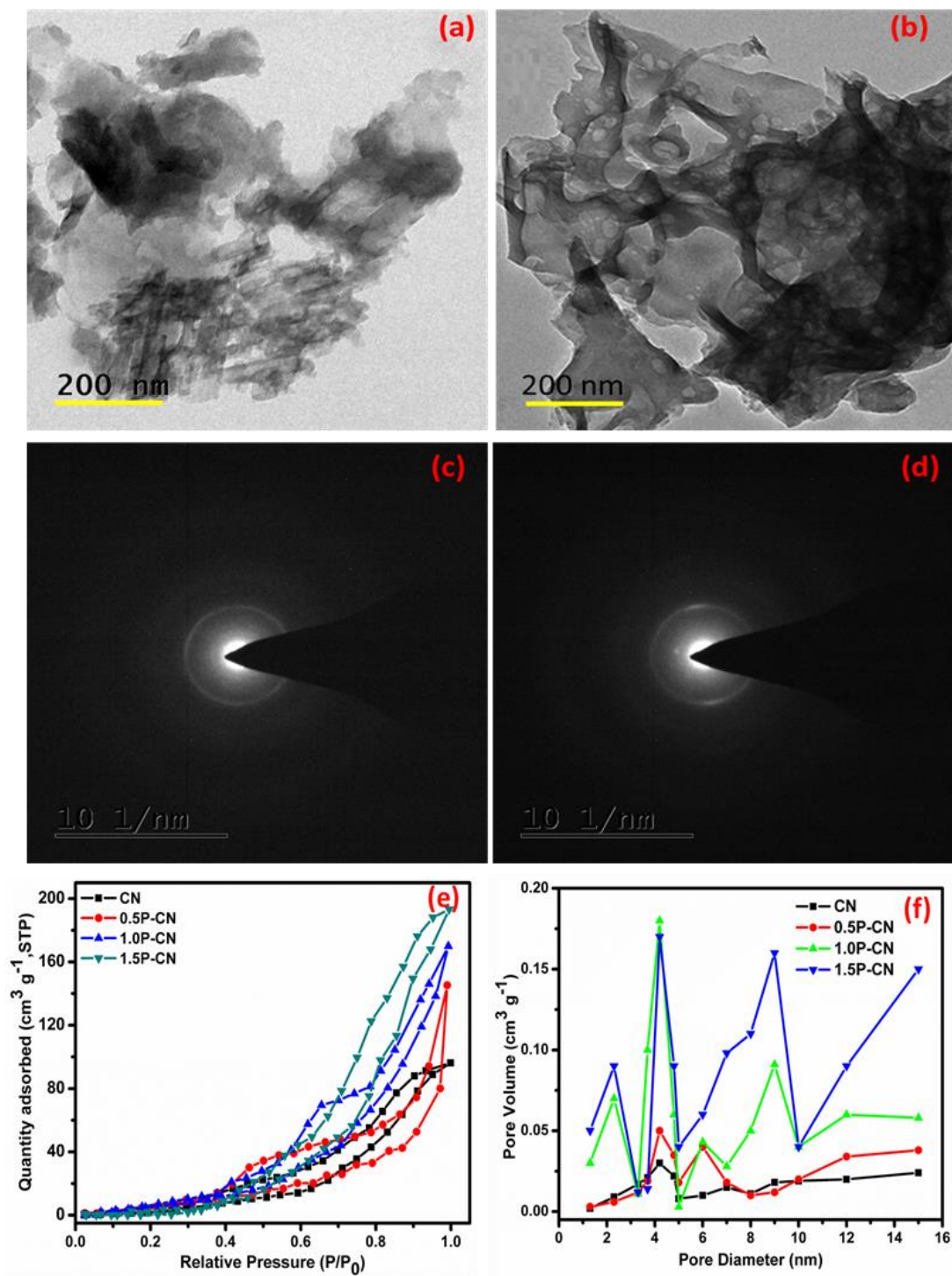
nitride matrix[53]. It is widely accepted that P has five valence electrons while C has only four. When the P atom is introduced into the CN structure, four of these five electrons constitute covalent bonds with the N neighbors, allowing the P atom to take on the planar structure. The P atom's remaining lone electron will delocalize into the p-conjugated triazine ring[46]. Overall, the results from XPS additionally confirm the incorporation of phosphorus atoms into the triazine heterocyclic ring configuration of the CN matrix.

### **3.4 Morphological, elemental, and surface area analysis**

The morphological behavior of the fabricated electrode material was examined by the FESEM technique. The CN and xP-CN are evident aggregations made up of a large number of two-dimensional (2D) thin sheets. These sheets are lamellar and massive stacking sheets, with an uneven form and a thickness of ~20 nm. Further, after the P doping the sheet size obviously shrunk compared with CN. This morphology has more active sites and larger surface area compared with pure CN, which improves the capacitance performance by allowing ions to accumulate at the electrode-electrolyte interface. The presence of the component elements was investigated with the help of EDS elemental spectra. As seen from Fig. 3 (b, d, f, h), the spectra confirm the presence of three major elements (C, N, and P) that are uniformly distributed in the electrode material.



**Fig. 3 FE-SEM images of electrode materials (a, b) Pure CN, (c, d) 0.5P-CN, (e, f) 1.0P-CN and (g, h) 1.5P-CN, (insert images EDS spectrum of corresponding electrode materials)**



**Fig. 4 HRTEM images of (a) CN (b) 1.5P-CN and SAED patterns of (c) CN (d) 1.5P-CN, (e) BET surface area and (f) pore-size distribution of CN and xP-CN electrode materials**

TEM images show that both CN and 1.5P-CN are composed of stacked sheet-like architecture as shown in fig. 4 (a, b). Surface of CN (fig. 4a) is smooth and flat with transparent agglomeration structure, whereas the surface 1.5P-CN (fig. 4b) is formed with plenty of curving sheets. As a result, the latter has a larger surface area than that of the CN because of phosphorus doping on the CN structure. HR TEM results consistent with the FESEM observation. Furthermore, the selected area electron diffraction (SAED) pattern of CN and 1.5P-CN reflected polycrystalline nature with a few bright spots (fig.4 c, d), which are well matched with the XRD results.

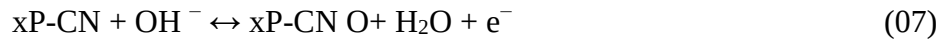
The high-surface area and porosity of the materials have a substantial impact on their electrochemical performance. The specific surface area and pore size distribution of as-prepared material has been calculated using Brunauer-Emmett-Teller (BET) method. Figure. 4(e, f) shows the nitrogen adsorption-desorption isotherms and pore size distributions of the xP-CN materials. As shown in fig. 4(e), the nitrogen adsorption-desorption isotherms of all prepared materials showed typical IV isotherms with evident H3-type hysteresis loops, indicating a mesoporous structure (2–50 nm). The calculated surface area for the electrode materials were CN (55.34 m<sup>2</sup>/g), 0.5P-CN (78.21 m<sup>2</sup>/g), 1.0P-CN (99.23 m<sup>2</sup>/g) and 1.5P-CN (138.21 m<sup>2</sup>/g). The increasing of P doping enhances the surface area of the electrode material, the results well corroborated with FESEM analysis. In addition, the BJH pore size distribution of the developed materials is shown in fig. 4(f). The average pore diameter obtained from the BJH pore size distribution is 1.21, 2.37, 3.15 and 4.47 nm for CN, 0.5P-CN, 1.0P-CN and 1.5P-CN respectively. According to these findings, increasing the phosphorus doping resulted in an increased pore volume with a higher surface area when compared to the pure CN electrode material. The enhanced specific surface area and extremely porous properties of the xP-CN material may be favorable for more active redox

reaction sites during electrochemical performances, which enhances the specific capacitance values in the supercapacitor performance.

### 3.5 Electrochemical measurements

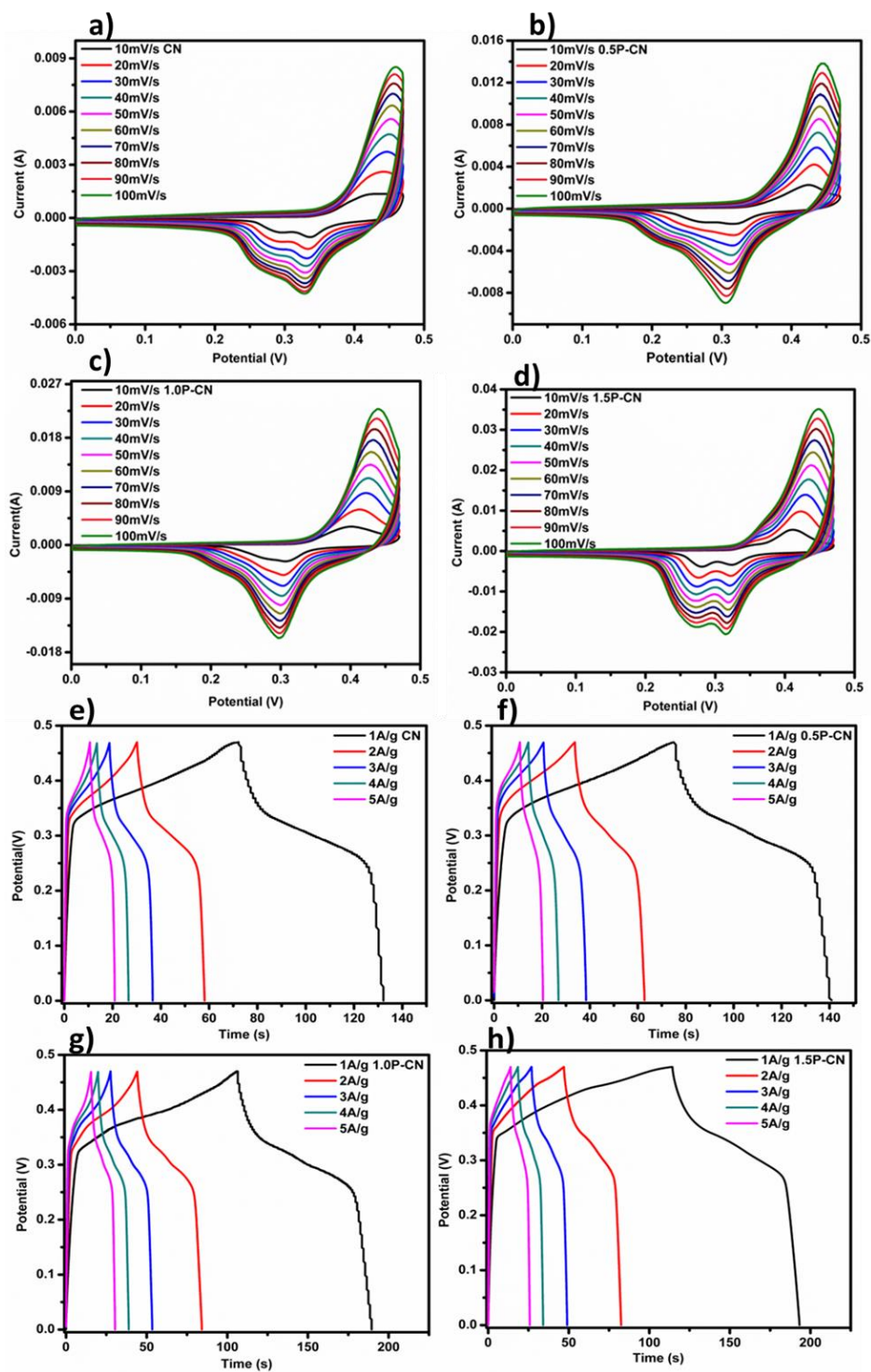
In a half-cell approach with an aqueous (3 M KOH) electrolyte solution, the electrochemical performances of the produced electrodes were investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques. The CV curves of developed electrodes (xP-CN) have been examined at different scan rates ranging from 0 to 100  $\text{mV.s}^{-1}$  with a potential window of 0 - 0.48 V, as shown in fig. 5(a-d). In the alkaline electrolyte medium, all four electrode materials showed oxidation and reduction peaks, showing their pseudocapacitive nature. The possible faradic and non-faradic reaction may be explained by the below equation (5-7). When the scan rates increase, the shape of the CV curves changes, and the corresponding oxidation and reduction peaks shift evenly to the right and left sides due to electrochemical polarization, confirming the materials' high-rate capabilities. The reversible redox reaction causes redox peaks in all sweep rates of all electrode materials. Phosphorus-doped CN had a larger capacitive area and superior electrochemical super capacitive performance than bare CN. This could be due to the presence of phosphorus in the  $\text{g-C}_3\text{N}_4$  structure, which can result in increased surface area and capacitance. In addition, two different reduction peaks were found in the sample, which could be attributed to the action of phosphorus in the CN matrix. Ansari et al. reported a similar pattern in their investigation[54]. Furthermore, the exceptional performance of the xP-CN electrode material might be attributed to the incorporation of P atoms into the CN matrix.

Faradic Reaction:



Non-Faradaic Reaction:

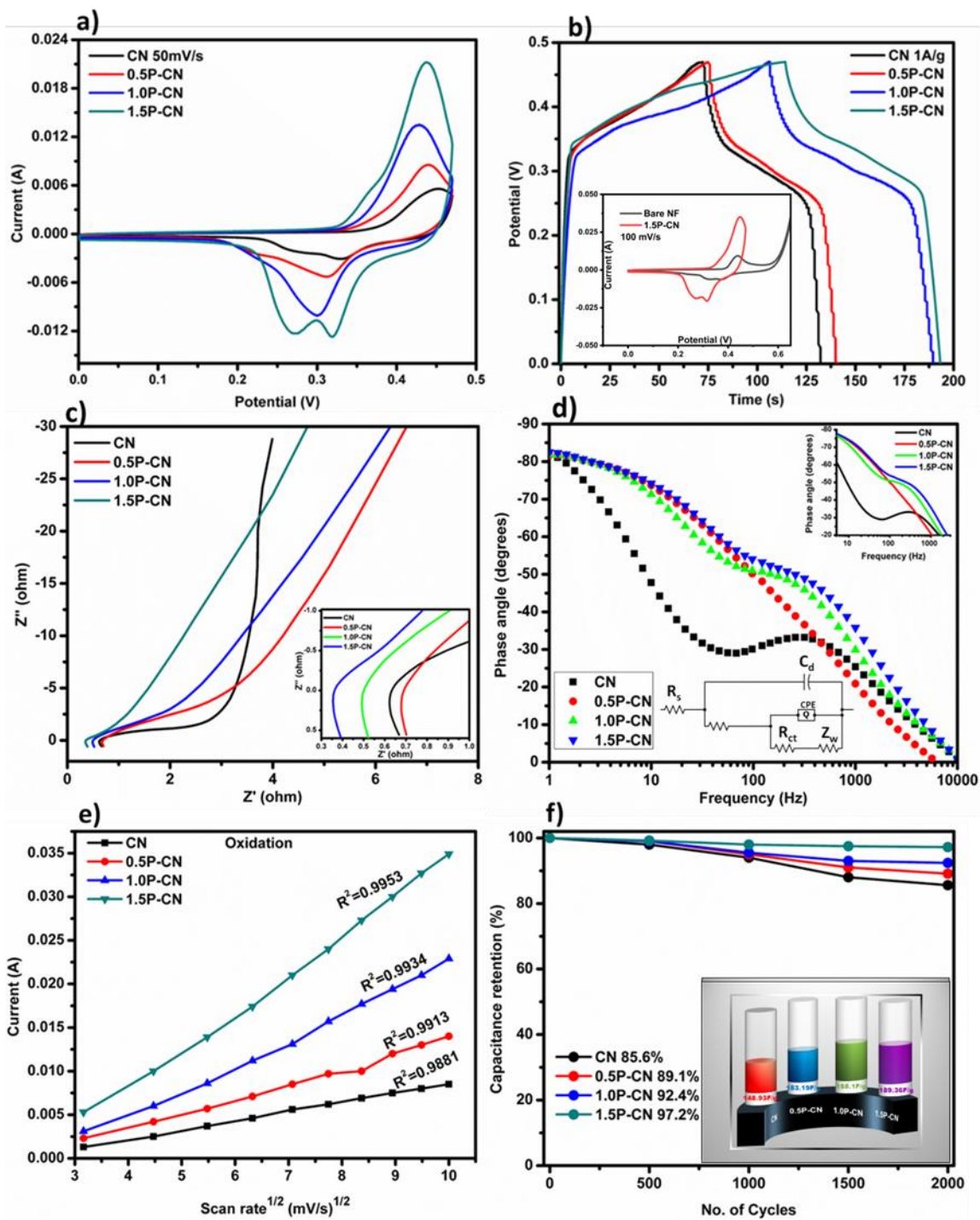




**Fig.5** Cyclic voltammetry response of (a) bare CN (b) 0.5P-CN, (c) 1.0P-CN, and (d) 1.5P-CN over various scan rates and GCD plot of (e) bare CN (f) 0.5P-CN, (g) 1.0P-CN, and (h) 1.5P-CN over different current densities

One of the most common approaches for testing the capacitance behaviors of electrode materials is galvanostatic charge-discharge (GCD) techniques. The GCD curves of xP-CN electrode materials were obtained at various current densities (1 - 5 A/g), as shown in fig. 5(e-h). With a potential window of 0 - 0.48 V. The P doped CN electrode was anticipated, has a longer discharge time than the bare CN materials. During the charge/discharge processes, the GCD curves of all three electrodes exhibit a non-linear shape, indicating that an oxidation-reduction mechanism is involved between the electrolyte solution and the electrode. 1.5P-CN electrodes exhibit a longer discharge time, which indicates a very low solid/liquid interface resistance, minimal energy loss, and higher  $C_{sp}$  values. These results show the enhancement in GCD curve attributed to the p doping in CN network. These obtained results were well matched with the CV analysis.

Figure.6 (a, b) shows the comparison of CV and GCD curves of all three electrodes at a current density of 1 A/g. The specific capacitance ( $C_{sp}$ ) of the electrode materials was computed from the discharge curve using eq (1), and the values obtained are displayed in fig.6 (f-inset). According to these findings, specific capacitance values subsequently fell when current densities increased for all the four materials, revealing a reverse correlation between current densities and specific capacitance. In general, materials with the lowest capacitance are those with high current density during the charge/discharge process since  $\text{OH}^-$  ions will not permeate within surface of the electrode in the fixed time frame. In comparison to the other electrode materials, the 1.5P-CN attained a maximum capacitance of 189.36 F/g at a current density of 1A/g. Due to their large surface area and increased conductivity attributed to incorporating P atoms to the CN network, 1.5P-CN electrode materials exhibit high specific capacitance.



**Fig.6** Cyclic voltammetry response of (a) xP-CN at a scan rate of 50 mV/s, (b) comparison of the GCD curves of the xP-CN at current density of 1 A/g and Frequency–response analysis by EIS for xP-CN working electrodes (inset: CV response of Bare Nickel foam and

**1.5P-CN) (c) Nyquist plots, (d) Bode plots, (e) Linear fit of anodic peak current ( $I_{pa}$ ) vs square root of the scan rate and (f) Capacitance retention % , Specific Capacitance value (inset) of xP-CN electrode materials**

To explain the reaction kinetics and electrical connectivity of the fabricated electrode, electrochemical impedance spectroscopy (EIS) was emphasized. Figure. 6(c) shows Nyquist plot of the xP-CN electrode material, with the frequency range from 100 kHz to 0.01 Hz. Nyquist plot has three significant regions, which are the high, middle, and low frequency. Figure. 6(c) shows that the 1.5P-CN material has the arc radius of  $0.398 \Omega$ , which was lower than pure CN ( $0.661 \Omega$ ), indicating enhanced charge carrier transport at the interface. This plot also demonstrates an imperfect semicircle in the higher frequency region which oversaw the redox process's electron migration kinetics at the electrolyte-electrode interface. The good capacitance behaviors was confirmed by the straight line in the lower frequency region [55].

Figure. 6(d) displays the response-time data obtained from the Bode plot of various electrodes (frequency vs. phase). In these data, the internal resistance values of the Nyquist plot showed an identical pattern. Using the expression, Response time ( $\tau$ ) =  $1/2\pi f$ , the material's response time has been estimated from the knee frequency values ( $f$ ) at phase angle  $-45^\circ$  [56]. The response time of the 1.5P-CN (1.8 ms) material is 10 times less than that of pure CN (18.6 ms). A shorter response time is mainly attributed by the 1.5P-CN electrode material's shorter ionic diffusion pathway through the p doped CN matrix. Additionally, the longer ionic diffusion way in the material with higher internal resistance results in shorter reaction times. The bode angles of the fabricated electrode materials ranged from  $(81-82^\circ)$ , which further proves their supercapacitor nature.

The linear correlation trace of the xP-CN electrode material is shown in fig.6 (e). The  $R^2$  values are highlighted in fig.6 (e), and for 1.5P-CN material, the  $R^2$  value is 0.9953, equal to the correlation coefficient of anodic peaks which was higher than the undoped CN electrode material. The reported values showing the oxidation process were followed the diffusion-controlled mechanism[57].

As we know the cycle stability of the electrode material is the most important property in the commercial supercapacitor. Charging discharging experiments evident that the fabricated electrode with 1.5P-CN has prolonged cyclic stability at a current density of 0.5 A/g, which is shown in fig.6 (f). After 2000 cycles the capacitance retention of the same sample has been calculated as 97.2%, but bare CN electrodes can only retain 85.6%. These results conclude that the higher rate of capacitance retention may be due to the presence of P atoms, which improve the internal architecture, mechanical and cyclic stability of the electrode material. The obtained results were compared with the previously published results in table 1.

**Table:1 Comparative electrochemical behavior of the g-C<sub>3</sub>N<sub>4</sub> based electrodes with the existing literature**

| <b>Electrode</b>                                       | <b>Electrolyte</b>                    | <b>Current density (A/g)</b> | <b>C<sub>sp</sub> (F/g)</b> | <b>Stability</b> | <b>Retention %</b> | <b>Ref</b>       |
|--------------------------------------------------------|---------------------------------------|------------------------------|-----------------------------|------------------|--------------------|------------------|
| NiO/g-C <sub>3</sub> N <sub>4</sub> -NS                | 1.0 M Na <sub>2</sub> SO <sub>4</sub> | 1.0                          | 161.3                       | 5000             | 85.3               | [58]             |
| MnO <sub>2</sub> / g-C <sub>3</sub> N <sub>4</sub> -NC | 0.5M Na <sub>2</sub> SO <sub>4</sub>  | 1.0                          | 211.1                       | 1000             | -                  | [59]             |
| TiO <sub>2</sub> / g-C <sub>3</sub> N <sub>4</sub>     | 2.0 M KOH                             | 1.0                          | 125.1                       | 1000             | 100                | [60]             |
| CuO-GCN                                                | 6.0 M KOH                             | 0.5                          | 154.5                       | 2000             | 94                 | [61]             |
| CN                                                     | 3.0 M KOH                             | 0.5                          | 148.93                      | 2000             | 85.6               | <b>This work</b> |

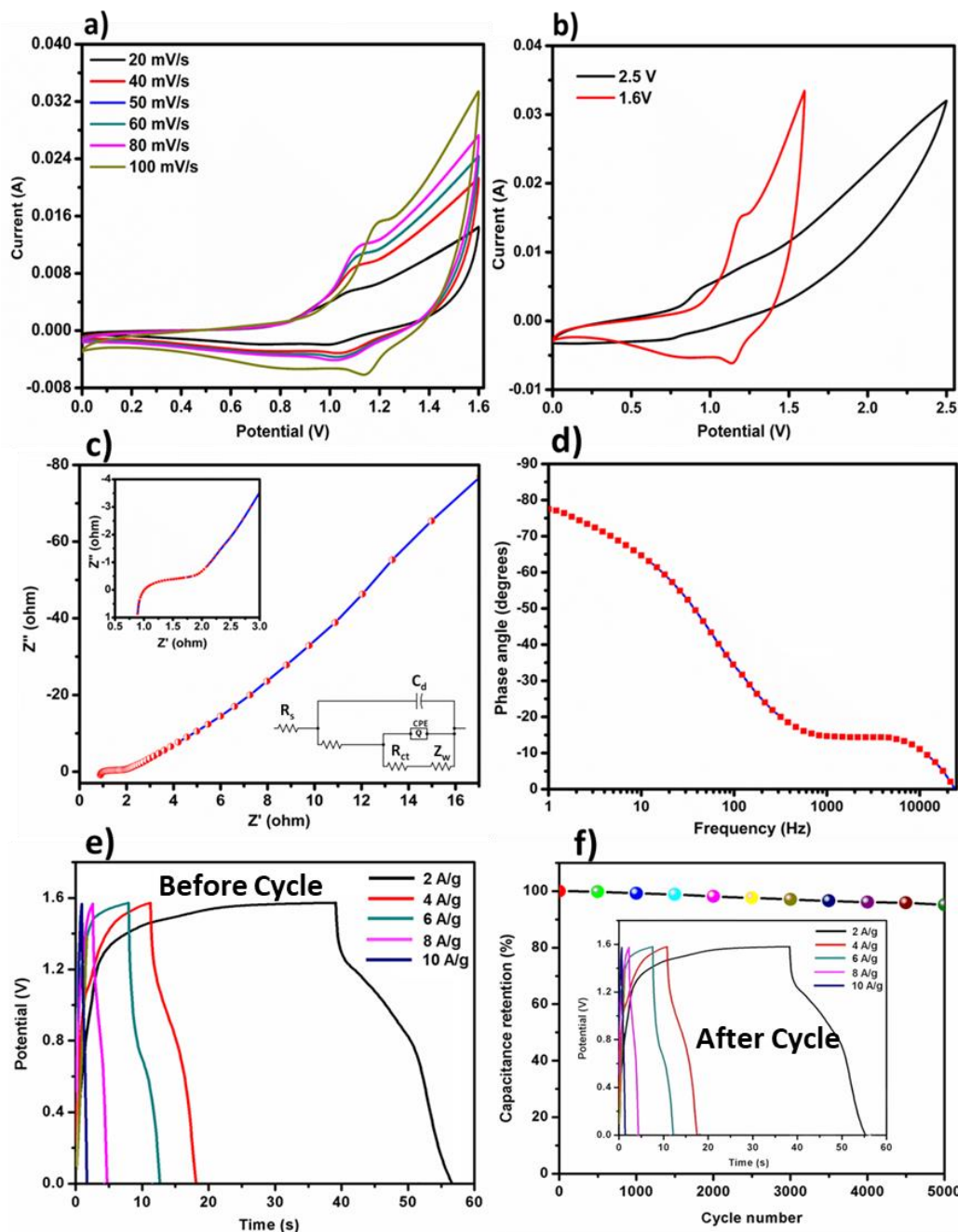
|         |           |     |        |      |      |                  |
|---------|-----------|-----|--------|------|------|------------------|
| 1.0P-CN | 3.0 M KOH | 0.5 | 185.1  | 2000 | 92.4 | <b>This work</b> |
| 1.5P-CN | 3.0 M KOH | 0.5 | 189.36 | 2000 | 97.2 | <b>This work</b> |

### 3.6 Electrochemical behavior of fabricated asymmetric supercapacitor

A standard solid-state asymmetric supercapacitor device has been constructed with fabricated xP-CN electrode to analyze the real time performance. The asymmetric supercapacitor device has been constructed with AC/NF||PVA-KOH||xP-CN/NF, in which the xP-CN /NF the cathode material, activated carbon AC/NF as an anode material and gel electrolyte (PVA-KOH) perform as a separator. According to charge balance theory the mass ratio was maintained as 1:3. Interestingly, the working potential window range up to 1.6 V was expected to be applied for the device due to the capacitive behaviors of the anode and cathode materials. The CV curves of the fabricated ASC devices were produced at various potential ranges from 0.1 to 1.6 V at a scan rate of 50 mV.s<sup>-1</sup> and the results are shown in fig. 7(a) which support the claim. The device's potential window was optimized in the outcomes at 1.6 V, which is closely in line with the value that would be predicted theoretically.

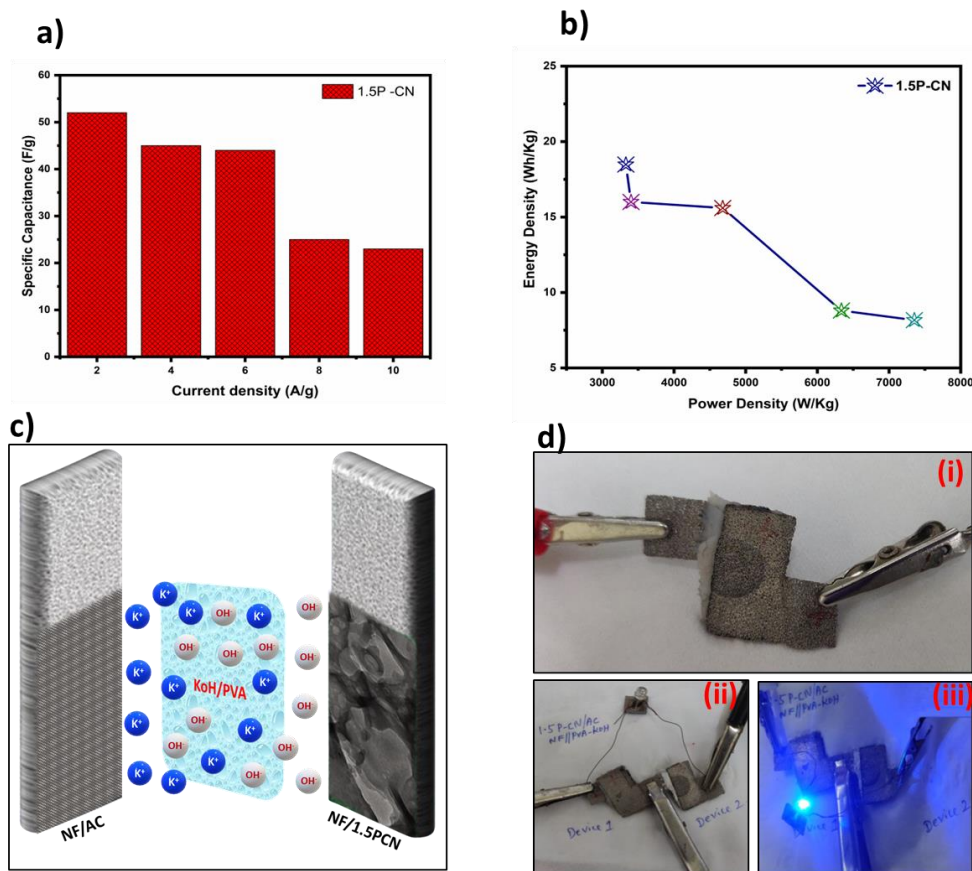
The CV studies had been carried out with multiple scan rates between 20 and 100 mV.s<sup>-1</sup> in the potential range of 0.0 to 1.6 V for the fabricated ASC device. The obtained CV curves confirm that the fabricated electrode material has capacitive behavior with great reversibility for all the scan rates. Additionally, charge-discharge characteristics of the device have been examined at varied current densities, as illustrated in fig. 7(e). The output curve has an asymmetrical shape that results from Fabry-Perot charge transfer processes.

The specific capacitance of the fabricated ASC device has been calculated from the GCD curve and equation (1). This improved electronic structure, coupled with the expanded specific surface area resulting from phosphorus doping, enhances the overall performance. The beneficial number of active sites and expanded pores contribute to its enriched characteristics. This strategy of doping offers a new and efficient route for the fabrication of high-performance supercapacitor. Additionally, using equations (2) and (3), the energy and power densities at different current densities were calculated.



**Fig. 7 Supercapacitor device (asymmetric) a) CV profiles at various scan rates b) various operating potential window of AC/NF||PVA-KOH||1.5P-CN/NF two ASC device (c) Nyquist plots, (d) Bode plots, (e) GCD profiles at various current densities before cycle test, and (f) Capacitance retention % after 5000 cycles (insert image: GCD after cycle test)**

Figures. 6 and 7 display the impedance spectra of CN and xP-CNs, as well as the equivalent circuit of xP-CN (inset in Fig. 6(c) & 7 (c)). The circuit includes ohmic resistance ( $R_s$ ), double layer capacitance ( $C_d$ ), constant phase element (CPE), diffusion resistance ( $Z_w$ ), and charge transfer resistance ( $R_{ct}$ ). Figure. 7(c) depicts the Nyquist plot used to investigate charge transfer kinetics between the electrode and electrolyte. The acquired data suggests lower resistance ( $0.772\Omega$ ), indicating high electronic conductivity and rapid transfer mechanism between the electrode and electrolyte. This enhanced performance is attributed to the phosphorus doping of CN. The bode angle of the ASC device shown in fig. 7(d) has the value of  $78.2^\circ$  with capacitance behavior. The GCD (before the cycle test) for the ASC two electrode were measured with different current densities (2 - 10 A/g) which was shown in fig. 7(e). This GCD confirms that the ASC device has good discharge time. Additionally, the specific capacitance of the ASC device is computed and plotted as bar diagram in fig. 8(a). The fabricated device has an utmost specific capacitance of 52 F/g at 2 A/g. The cyclic stability test of the ASC device also carried out for 5000 cycles, which, shows the reliable stability with 97.2 % capacitance retention (fig. 7(f)). The insert image in fig. 7(f) shows the material experiences minimal degradation and remains effective over time, which is especially important for real-world applications where consistent performance is required over thousands of cycles. The coulombic efficiency of the fabricated device is also calculated over 2000 cycles (99.5%) using equation (4). This demonstrates that the amount of charge acquired during charging is equal to the quantity lost during discharging. Additionally, the proportion remains constant as the number of cycles increases. Further the 1.5P-CN electrode delivered a superior energy density of 18.48 Wh/Kg and power density of 3328 W/Kg at 2 A/g which were presented in Ragone plot in fig. 8(b).



**Fig. 8. Fabricated asymmetric supercapacitor (a) Specific capacitance, (b) Ragone plot, (c) Schematic representation, and (d) Photograph of two electrode ASC device (i) two electrode device (ii) two ASC devices connected in series before charging and (iii) ASC device during discharge energizing blue LED.**

The working mechanism and schematic representation of fabricated ASC device shown in fig. 8(c), which explains the ion exchange process of electrolyte- electrode interface. The fabricated ASC device was checked with blue LEDs for commercial applications, which is shown in fig. 8(d (i-iii)). Initially, the fabricated two ASC devices were series connected and charged for 40 s and then during the discharging process, the red LED was connected and glowed for over 180 s. The fabricated ASC device demonstrates outstanding overall electrochemical performance, which

confirmed the practical applicability in advanced electronic applications. Further increasing the doping level of P, modification of surface morphology and optimization of ASC device will enhance electrochemical performance.

#### **4. Conclusion**

In summary, Phosphorus atoms were successfully amalgamated in CN via facile hydrothermal with subsequent thermal annealing techniques. FESEM and HRTEM obviously reveal that the xP-CN material has noteworthy morphological changes with more active sites. P doping facilitating the surface area augmentation. Subsequent electrochemical analysis indicated that the phosphorus doped CN electrode exhibits higher electrochemical activity than undoped CN owing to changes in electronic structure as well as surface site proliferation. From the three electrode experimental studies, it is found that the specific capacitance of 1.5P-CN is 189.66 F/g. Further development of a two-electrode-based device revealed an outstanding stability of 97.2% after 5000 cycles. Further to that, supercapacitor with 1.5P-CN produced a superior energy density of 18.48 Wh/Kg and 3328 W/Kg power density at 2 A/g. Further, it is demonstrated that the fabricated devices were energized by a blue LED over 180 s, providing the suitability of XP-CN as a new type of electrode candidate for high performance electrochemical application. These findings promisingly concluded that doping in CN approaches lead to a novel and efficient strategy to fabricate high-performance supercapacitors.

#### **Credit authorship contribution statement**

**S. Surender:** Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review and editing. **T. Shalini:** Conceptualization, Methodology, and Investigation. **Kavipriyah M N:** Conceptualization. **S. Balakumar:** Conceptualization, Validation and Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## Acknowledgement

The author Dr.S.Surender, gratefully acknowledges the UGC, New Delhi for awarding Dr D. S. Kothari Postdoctoral fellowship (PH/20-21/0011) to support this research work. The author also acknowledge DST-FIST Funded X-Ray Diffractometer Facility and TANSCHERGP funded CV Electrochemical work station, National Centre for Nanoscience and Nanotechnology, University of Madras.

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