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Analyzing the charge contributions of metal-organic framework derived nanosized Cobalt Nitride/Carbon composites in asymmetrical supercapacitors

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Abstract

Metal-organic frameworks derived nanostructures received a recent research attention owing to their inherent porosity, stability, and structural tailorability. This work involves the conversion of zeolitic imidazolate frameworks (ZIFs) into cobalt nitride nanoparticles embedded within a porous carbon matrix (Co\(_4\)N/C). The as prepared composite shows great synergy by providing a high surface area and efficient charge transfer, that showcase an outstanding electrochemical performance by providing a specific capacitance of 313 F/g. Moreover, we meticulously conducted calculations to derive the most precise values for the surface contribution, a crucial aspect often overlooked in existing literature, thereby ensuring the reliability of our calculated measurements. The correct calculations of surface and diffusion charge contributions are itself necessary for evaluating the overall electrochemical performance of supercapacitors. For practical utility, we
successfully assembled an asymmetrical supercapacitor employing the Co₄N/carbon composite as the negative electrode that achieved an impressive energy density of 26.6 Wh/kg at a power density of 0.36 kW/kg. This study opens up new avenues for investigating the use of other metal nitride nanoparticles embedded in carbon structures for various energy storage applications.

**Keywords:** Supercapacitors; Metal Organic Frameworks; Cobalt Nitride; Porous Carbon; Surface Contribution

**Introduction**

The development of high-performance energy storage devices has become increasingly crucial in the quest for sustainable and efficient power systems. Supercapacitors have emerged as promising candidates for meeting the demands of various applications due to their superior power density, rapid charge/discharge rates, and long cycle life. To enhance the energy storage capabilities of supercapacitors, extensive research has focused on designing advanced electrode materials with high specific capacitance and excellent conductivity.

In recent years, embedding of nanoparticles in the conductive frameworks has allowed to improve the energy storage performance. The decreasing of particle size led to the evolution new physical or chemical properties. The application of this field can be estimated from the fact that the Nobel Prize of 2023 in Chemistry has given for the synthesis of quantum dots which is nothing but the emergence of materials new properties with the reduction of its size. In this regard, Zhou et al. demonstrated the increase of energy of filling the orbitals can be increased for cobalt ions by reducing the size of LaCoO₃. This enhancement led to the spin-state transition from low-spin to high-spin states for cobalt ions which ultimately provided the more active sites for the oxygen evolution reaction activity. For instance, Liu et al. demonstrated the embedding of ultrasmall Sn nanoparticles in spherical carbon structure to improve the anode performance for sodium ion
batteries. Tang et al. demonstrated SnO$_2$ nanocrystal which is grown on the porous graphene structure to improve the lithium storage. Similarly, Patra et al. showed that ultra-nanosized (4 nm) TiO$_2$ showed excellent reversibility for lithium storage due to the efficient transition of tetragonal to orthorhombic phase of ultra-nanosized TiO$_2$ which is not possible in bulk TiO$_2$. In another report, nanosized Mn has been doped in WO$_3$ with different concentration for supercapacitor applications. The nanosized Mn created the oxygen vacancies in high concentration which led to the 115 F/g of capacitance and 16 Wh/kg of energy density. Very recently, Kotok et al. reported the two step PVP assisted nanosized Ni-hydroxide with Co activation as a supercapacitor electrode. The sample delivered 1408 F/g of specific capacitance at 1 A/g. However, the discharge behavior of the electrode is more like battery type (nonlinear) than a capacitor type (linear). The formula used in the paper to calculate the discharge capacitance is for the linear discharge type behavior which give overestimate capacitance when applied to nonlinear discharge curve. However, there is no doubt the embedding of nanosized particles in conductive framework improve the energy storage performance however, embedding or growth of such nanosized particles is not an easy task and require complex reaction conditions or need multiple steps.

Very recently, metal-organic frameworks (MOFs) have gained significant attention as precursors for synthesizing functional materials. Since MOF is a highly crystalline material in which organic linker and metal part is connected with each other in a very ordered fashion. The MOF crystal is usually large and have long range order (high crystallinity) which offer a great opportunity to produce distributed metal redox product in the carbon matrix. Upon pyrolyzing these MOF, the metal part can be converted to some metal oxide/nitride/sulphide/phosphide whereas the organic linker converts to the carbon. Among them, zeolitic imidazolate frameworks
(ZIFs) have exhibited remarkable potential due to their exceptional thermal stability, large surface area, and tunable porosity. In particular, ZIF-67, composed of cobalt ions (Co\(^{2+}\)) coordinated with 2-methylimidazole ligands, has attracted interest for its unique properties and versatile applications. For instance, Pan et al. demonstrated the synthesis of ZIF-8@ZIF-67 core shell derived CoP nanoparticles/carbon structure for water splitting application which showed superior activity in term of achieving high current density at low potential and high stability\(^\text{10}\). Similarly, Ge et al. used ZIF-67 core shell as a precursor to derive CoP nanostructures in the carbon structure with reduced graphene oxide as a support\(^\text{11}\). When tested for the sodium ion battery, the sample as an anode delivered 473 mAh/g of capacity at the current density of 0.1 A/g. In another report, ZIF-67 derived CoS\(_2\)/carbon structure has been synthesized for the absorption of electromagnetic waves\(^\text{12}\). The nanosized CoS\(_2\) contributed to the enhancement in the absorption capability. The rational design of this composite aims to combine the advantages of both cobalt-based materials and carbonaceous matrices, offering enhanced electrochemical performance and long-term stability. Very recently, it has been shown that Co\(_4\)N is showing superior specific capacitance. For instance, Cao et al. confined the Co\(_4\)N nanoparticles in La\(_2\)O\(_2\)CN\(_2\) matrix on carbon cloth for supercapacitor applications\(^\text{13}\). The ultrafine Co\(_4\)N nanoparticles promoted the electron transfer dynamics which enhance the capacitance of the electrode. The electrode exhibits low potential window (0-0.5V) in 1 M KOH solution. The assembled device with activated carbon 103.8 F/g at 1 mA/cm\(^2\). In another report, Shinde et al. coupled Ni-Co\(_4\)N particles in the N-doped carbon structure for hybrid supercapacitor\(^\text{14}\). The electrode material showed battery type behavior and delivered 397.5 mAh/g of capacity. In one report, modification in Co\(_4\)N has been done with boron doping which also showed battery type behavior and delivered 817.9 C/g of specific capacity at 1 A/g of discharge rate\(^\text{15}\).
In this work, we have utilized ZIF-67 structure to deliver the nanosized Co$_4$N. Further the organic linker which is 2-methylimidazole have carbon and nitrogen source which could allow the production of porous carbon framework with N-doping as well as limiting the size of Co$_4$N. To assess the significance of the Co$_4$N/carbon composite, we compare its properties and performance with the bulk Co$_4$N and those of existing literature materials employed in supercapacitor electrodes. By highlighting the unique features of the Co$_4$N/carbon composite, this study aims to contribute to the expanding body of knowledge in the field of supercapacitor electrode materials. The exploration of this novel composite is expected to provide insights into the rational design and synthesis of advanced electrode materials, addressing the current limitations and paving the way for the development of next-generation supercapacitors with improved energy storage and power delivery capabilities. By harnessing the unique properties of ZIF-67 and the synergistic effects of Co$_4$N and carbon, this composite offers exciting possibilities for achieving high-performance energy storage devices with improved electrochemical performance and stability.

2. Synthesis and electrochemical method:

2.1. Preparation of ZIF-67: ZIF-67 was prepared by mixing a solution of cobalt nitrate (Co(NO$_3$)$_2$) and 2-methylimidazole (Hmim) in a 1:8 molar ratio in deionized (DI) water. The solution was stirred at room temperature for 24 hours. The precipitated ZIF-67 crystals were washed with water and ethanol subsequently and then collected through centrifuge and dried in an oven at 80 °C.

2.2. Synthesis of Co$_4$N/carbon composite: The as-synthesized ZIF-67 crystals were subjected to thermal conversion to obtain the desired Co$_4$N/carbon composite. This step involved a two-stage process, including carbonization and subsequent nitridation. The ZIF-67 crystals were heated in a controlled atmosphere (Ar gas), at an elevated temperature of 700, 800, and 900 °C to obtain Z-
700, Z-800, and Z-900 respectively. The carbonization process decomposed the organic ligands present in ZIF-67, resulting in the formation of carbonaceous residues while retaining the cobalt metal species. Further, all the three-metal doped carbon sample were characterized and the material with the highest specific surface area (which is, Z-800) was chosen for the nitridation process. During nitridation process, Z-800 was treated by introducing an ammonia into the reaction system at 300 °C in a tube furnace for 2 hours with a heating rate of 5 °C/min. The nitridation process facilitated the conversion of the remaining cobalt species into Co$_4$N, forming a Co$_4$N/carbon composite. The schematic of the synthesis process is shown in Figure 1.

2.3. Synthesis of bulk Co$_4$N: For the bulk synthesis of Co$_4$N, 500 mg of ZIF-67 and 20 mmol of ammonium hydroxide was dissolved in 80 ml of DI solution. The solution was transferred to the hydrothermal autoclave at 200 °C for 12 hours. The obtained product was dried in the oven and then transferred to the tube furnace at 300 °C for 2 hours with a heating rate of 5 °C/min under the flow of NH$_3$. The resultant sample was washed with ethanol and then dried in an oven at 80 °C.

Figure 1. Synthesis scheme of the Co$_4$N/carbon and Z8-800 (metal free carbon).
2.4. Electrochemical measurements

An advanced Metrohm Autolab electrochemical workstation (PGSTAT302N) has been used to evaluate the electrochemical performance of the electrode material. The characterization encompassed key electrochemical techniques, including galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). To commence the experimental procedure, the Co$_4$N/carbon composite was used as an active electrode material. This entailed the formulation of a dense slurry comprising the Co$_4$N/carbon composite active material, carbon black, and a PVDF binder. The ratio of these components was maintained at 8:1:1, respectively, within a solvent, N-methyl-2-pyrrolidone (NMP). The resultant slurry, characterized by its uniformity, was evenly drop-casted onto a Grafoil current collector, yielding an active area of $1 \times 1$ cm$^2$. The mass loading of the active material was calibrated to 1 mg/cm$^2$. Subsequently, the casted electrode was meticulously dried at a controlled temperature of 70°C for a duration of 10 hours. The electrochemical analysis of the electrode was conducted in three-electrode electrochemical cell. This configuration consisted of a Platinum wire counter electrode, an Ag/AgCl reference electrode, and the active material electrode itself, which functioned as the working electrode. In addition to the three-electrode setup, asymmetrical supercapacitor devices were meticulously assembled and evaluated. For the asymmetrical configuration Co$_4$N/carbon composite and Z8-800 electrodes were employed as negative and positive electrodes respectively. To ensure charge equilibrium in the asymmetrical device, mass balancing calculations which is discussed in result and discussion section. The polyvinyl alcohol (PVA) gel incorporated with 1M H$_2$SO$_4$ electrolyte has been used to assemble the solid-state device. To prepare PVA gel electrolyte, 1.5 g of PVA has been added in 10 ml DI water and heat to 95 °C. As the solution gets
viscous, the heating stopped and 2 ml of 1 M H₂SO₄ has been added drop wise with vigorous stirring. The cool down gel has been used as such for the device fabrication.

3. Result and Discussion

3.1. Material Characterization:

The detailed characterization method and electrochemical method is given in the supplementary information (SI) file. The confirmation of the formation of ZIF-67 is analyzed by XRD as shown in Figure S1 of SI. The XRD pattern showed the high intensity peaks of ZIF-67 which matches with the literature and shows the high crystalline nature of ZIF-67 which is one of the requirements for the uniform distribution of Co₄N through the carbon framework. Further to develop the Co₄N/carbon composite, the pyrolysis of ZIF-67 need to be done at high temperature to obtain carbon framework and metal content in it. For this, Thermogravimetric analysis (TGA) has been performed from room temperature to 1000 °C in inert atmosphere as shown in Figure S2 of SI. The sample loses very minor weight till 400 °C which is due to the removal of water and solvent molecules from the ZIF-67 pores. After 475 °C, a sudden fall in mass is observed till 640 °C contributed to 41.6% mass loss which indicates the collapse of a ZIF-67 structure. In this stage, the organic linker converted to carbon framework whereas the cobalt metal retained in the carbon structure. Therefore, after TGA, ZIF-67 derived carbon has been obtained at three different temperatures i.e. 700, 800, and 900 °C denoted as Z700, Z800, and Z900, were prepared by pyrolyzing ZIF-67 as a template under Ar atmosphere. Among the synthesized precursors, Z800 emerged as the most promising candidate due to its high specific surface area (SSA) among other samples. Z800 possessed 676 m²/g of SSA, surpassing Z700 (641 m²/g) and Z900 (151 m²/g) as shown in Figure S3 of SI. Furthermore, the nitridation steps has been performed to produce ZIF-67 derived nanosized Co₄N infused carbon composite using Z800 sample. The XRD patterns of
these samples revealed distinct variations in the crystallinity of carbon as the pyrolysis temperature increased as shown in Figure S4a of SI. In particular, the broad carbon peak at 26° in Z700 indicated a predominantly amorphous carbon phase. In contrast, Z800 displayed a relatively sharper carbon peak at 26°, suggestive of a balance between crystallinity and amorphous carbon content. Z900 exhibited the much sharper peak, signifying a higher degree of carbon crystallinity. These structural differences were further corroborated by Raman spectroscopy, which depicted similar D/G ratios, reflecting subtle variations in carbon defect structures (Figure S4b of SI). The sample Z800 exhibit the lowest I_D/I_G ratio. Further, the synthesized Co_4N/carbon composite using Z-800 were characterized. XRD of Co_4N/carbon composite (JCPDS card: no. 41-0943) showed XRD peaks at 2θ values of 44°, 51.3°, and 75.7°, correspond to the (111), (200), and (220) planes respectively matching with literature, confirms the presence of crystalline Co_4N (Figure 2a) 19. Notably, a relatively broad peak at 2θ = 26.5° is observed, indicative of carbon's presence within the composite. Intriguingly, this feature distinguishes it from bulk Co_4N, obtained via autoclave synthesis from ZIF-67, which also displays characteristic Co_4N peaks but with a significantly smaller carbon peak at 26.5° due to low content of carbon in the sample. Further analysis reveals that the average crystallite size of Co_4N within the Co_4N/carbon composite, calculated using the Scherrer equation, is notably smaller (6.38 nm) compared to bulk Co_4N (13.26 nm), suggesting that the presence of carbon hinders the formation of larger crystallites and, consequently, contributes to a lower crystallite of the Co_4N. It's worth noting that in the case of bulk Co_4N, a minor peak at 37° is observed, corresponding to Co_3O_4, signifying a minimal level of cobalt oxidation, although this peak remains relatively small in comparison to the dominant Co_4N peaks. This comprehensive XRD analysis underscores the distinct structural characteristics of the Co_4N/carbon composite compared to bulk Co_4N and provides insights into the role of carbon in
modulating crystallite size and other electrochemical properties, thus affecting the overall performance.

**Figure 2.** (a) XRD pattern of Co$_4$N bulk (blue line) and Co$_4$N/carbon (red line) and (b) Raman spectra of ZIF-67, bulk Co$_4$N, and Co$_4$N/carbon, High resolution XPS spectra of (a) C1s, (b) Co 2p, (c) O 1s, and (d) N 1s.

Raman spectroscopy was utilized to investigate the bonding characteristics and structural properties of the Co$_4$N/carbon composite (**Figure 2b**). The vibrational frequencies and peak intensities in the Raman spectra were analyzed to identify the functional groups and carbon-based structures within the composite. In the Raman spectrum of bulk Co$_4$N, a prominent peak is observed at approximately 678 cm$^{-1}$ assigned to a high-frequency vibrational mode, typically associated with the stretching vibrations of metal-nitrogen (Co-N) bonds within the crystal lattice designated as an A$_{1g}$ symmetry mode. Additionally, a lesser-intense peak at 513 cm$^{-1}$, attributed to a combination of bending and stretching vibrations of Co-N bonds, is noted, marked as an E$_{2g}$ mode. Interestingly, the Defect (D) and graphitic (G) bands of carbon are also detectable in this spectrum indicative of the presence of carbon $^{20}$. The D/G ratio for carbon in bulk Co$_4$N is approximately 0.92, reflecting the degree of disorder or defects within the carbon component. In the Raman spectrum of the Co$_4$N/carbon composite, the most prominent peak related to Co$_4$N is observed at 681 cm$^{-1}$, which can be attributed to the stretching vibrations of Co-N bonds within
the Co₄N component. Notably, the D/G ratio for carbon in the Co₄N/carbon composite is approximately 1. This suggests that the carbon within the composite possesses a lower degree of disorder. While both materials exhibit the A₁g symmetry mode associated with Co-N stretching vibrations, the distinct D/G ratios for carbon in the two samples imply variations in the nature of carbon's structural characteristics. These distinctions are likely a result of the different synthesis processes of the two materials. Further, ZIF-67 also has a peak around 684 cm⁻¹ which is present in all the samples due to Co-N vibration mode. XRD and Raman characterization confirmed the successful formation of Co₄N and the presence of carbon, XPS characterization is required to further confirm the accurate surface elemental bonding. XPS analysis was carried out to investigate the elemental composition and chemical states of the Co₄N/carbon composite. The survey scan unveiled a complex spectrum, with distinct peaks at 284 eV, 396.2 eV, 532.1 eV, and 785 eV are corresponded to carbon (C), nitrogen (N), oxygen (O), and cobalt (Co) atoms, respectively (Figure S5 of SI). For the high-resolution carbon spectra, three deconvoluted peaks were observed at 283.8 eV, 286.5 eV, and 284.9 eV in the high-resolution spectra of carbon (Figure 2c). The peak at 283.8 eV likely represents graphitic carbon (C-C bonds), the peak at 286.5 eV suggests the presence of carbon in oxygen-containing functional groups (C-O or C=O), and the peak at 284.9 eV may indicate carbon bonded to nitrogen (C-N) 21. The high-resolution spectra of cobalt (Co 2p) were resolved into Co 2p₃/2 and Co 2p₁/2 components (Figure 2d). The Co 2p₃/2 spectra exhibited two peaks at 785.5 eV and 781.36 eV, while the Co 2p₁/2 spectra displayed two peaks at 803.4 eV and 796.81 eV 22. These multiple peaks indicate different chemical states or oxidation states of cobalt within the composite. The high-resolution oxygen spectra displayed two deconvoluted peaks at 531.6 eV and 532.8 eV, indicating the presence of oxygen in various chemical states or environments (Figure 2e). The lower binding energy peak at 531.6 eV may be associated with
oxygen in C-O and C=O functional groups. The peak at 532.8 eV could correspond to other oxygen-containing species. The high-resolution nitrogen spectra were deconvoluted into two distinct peaks at 398.66 eV and 400.1 eV (Figure 2f). These peaks represent different nitrogen bonding environments. The peak at 398.66 eV may correspond to nitrogen bonded to carbon (C-N) or within the Co₄N phase, while the peak at 400.1 eV suggests other nitrogen-containing functional groups or coordination environments.

Further to examine the elemental composition, surface morphology, and the distribution of Co₄N in the carbon, we performed FESEM, EDS, and TEM analysis. The FESEM analysis provided valuable insights into the morphology and surface characteristics of the materials under investigation (Figure 3a-f). The Z800 precursor exhibited a distinctive polyhedral crystal structure reminiscent of the ZIF-67 precursor from which it was derived (Figure 3a-b). Notably, the crystal surfaces exhibited a carbon fiber-type structure, indicative of the catalytic activity of cobalt (Co) within the structure. These surface features manifested as nanotubes, a significant asset for facilitating rapid charge transfer. In contrast, the FESEM imaging of bulk Co₄N unveiled an accumulation/aggregation of crystals, reflecting a different structural arrangement (Figure 3c-d). Remarkably, the Co₄N/carbon composite displayed polyhedral morphologies akin to those observed in Z-800, albeit with surface alterations due to additional temperature treatment (Figure 3e-f). The composite's surface exhibited increased roughness (likely attributed to the integration of carbon and the extra treatment step) and featured small nanotube-like structures. The average size of the carbon structures was determined to be approximately 1.186 µm (inset of Figure 3e). Further EDS analysis has been performed to see the elemental percentage in the material (Figure 3g). The spectra revealed the presence of carbon (C), nitrogen (N), oxygen (O), and cobalt (Co). Intriguingly, the atomic percentages unveiled a nuanced distribution of these elements. While
carbon dominated the composition at 79.4 %, nitrogen was present at 4.83 %, oxygen at 8.83 %, and cobalt at 6.94 %. This elemental profile can be attributed to the unique structural characteristics of the Co₄N/carbon composite. Notably, a portion of the nitrogen was found to be directly incorporated into the Co₄N phase, constituting approximately ~1.73 % of the nitrogen atoms, forming Co₄N. The remaining nitrogen is possibly doped within the carbon framework due to the uniform distribution of nitrogen through organic linker in the ZIF-67 crystal with high degree of crystallinity. The presence of cobalt emphasized the coexistence of the Co₄N phase, while the prevalence of carbon underscored the composite's carbonaceous nature. Further the elemental mapping has also been performed which showed the distribution of carbon, oxygen, nitrogen, and cobalt in the sample (Figure 3h-l). The higher concentration of carbon can be seen in the mapping whereas the Co and N is distributed throughout the sample. Further TEM was employed to delve into the microstructural details of the Co₄N/carbon composite, providing valuable insights into the morphology and distribution of its constituent phases. At lower magnifications, the material exhibited a polyhedral structure, consistent with the observations from FESEM (Figure 3m). However, it was at higher magnifications that the true intricacies of the composite came to light. Notably, nano-sized Co₄N particles were discernible within the carbon matrix, revealing their dispersion and arrangement (Figure 3n-o). The predominant morphology of these Co₄N particles appeared spherical, contributing to the composite's overall structure. A particularly noteworthy finding was the determination of the average size of the Co₄N particles, measured at approximately 15.8 nm (inset of Figure 3o).
Figure 3. (a-b) Z-800 FESEM, (c-d) bulk Co$_4$N FESEM, (e) FESEM of Co$_4$N/carbon (inset: carbon structure size distribution), (f) single Co$_4$N/carbon structure FESEM, (g) EDS of Co$_4$N/carbon (inset: elemental composition), (h-l) elemental mapping of Co$_4$N/carbon single particle, (m-n) TEM image of Co$_4$N/carbon, (o) high resolution TEM of Co$_4$N nanoparticle in carbon structure (inset: Co$_4$N particle size distribution).

3.2. Electrochemical Characterization:

The electrochemical performance of the Co$_4$N/carbon composite derived from ZIF-67 was evaluated to assess its suitability as a supercapacitor electrode material using 1M H$_2$SO$_4$ electrolyte. Firstly, CV measurements were carried out for Co$_4$N/carbon in positive and negative
potential window. For the positive potential window, the performance of the material is not up to mark, so we had taken Z800 as a positive electrode material which showed higher performance in the positive potential (Figure S6 and Figure S7 of SI). However, for the negative potential window, Co$_4$N/carbon showed excellent performance with 0.8 V of potential window (0 to -0.8 V). CV was employed at different scan rate in the negative potential window to probe the electrochemical behavior of the Co$_4$N/carbon composite (Figure 4a). At higher scan rates (e.g., 500 mV/s), the CV curve exhibited a characteristic rectangular shape, indicative of EDLC behavior. The capacitance values calculated at various scan rates (5 mV/s to 500 mV/s) which reflect dynamic behavior. Specifically, at 5 mV/s, the calculated capacitance was 172.48 F/g, showcasing the influence of pseudocapacitive processes. As the scan rate increased to 100 mV/s, the capacitance decreased to 49 F/g, consistent with the shift toward pure EDLC-type behavior. The equations to calculate the specific capacitance and other parameters are given in the SI file.

**Figure 4.** (a) CV analysis of Co$_4$N/carbon at different scan rates, (b) GCD of Co$_4$N/carbon at different current densities, (c) Nyquist plot (inset: enlarge view of Nyquist plot), (d) Capacitance
vs scan rate (inset: capacitance vs current density), (e) CV comparison of bulk Co₄N and Co₄N/carbon, and (f) GCD comparison of Co₄N/carbon, bulk Co₄N, and activated carbon.

The GCD tests of the Co₄N/carbon composite has been done at varying current densities ranging from 1.5 A/g to 6 A/g (Figure 4b). These tests unveiled a linear charge-discharge profile, a hallmark of ideal electrochemical capacitors, highlighting the material's ability to efficiently store and release electrical energy. When calculated, at a lower current density of 1.5 A/g, the composite exhibited a specific capacitance of 312.96 F/g which decreased to 119.7 F/g as the current density increased to 6 A/g. Here the longer charging time, could be due to some irreversible faradic charge transfer probably due to the production of H₂ through the decomposition of electrolyte. Although the H₂ production is kinetically slow process which is the reason it is more prominent in slow charge-discharge, whereas when the current density increases the effect is smaller and so getting almost equal charge discharge time. Further, EIS provided valuable insights into the electrochemical behavior of the Co₄N/carbon composite, allowing us to assess its impedance characteristics. The Nyquist plot derived from EIS data revealed intriguing characteristics of the material's electrochemical response (Figure 4c). The Nyquist plot, which starts at a low impedance value of 3.2 Ohm cm², signifies the initial response of the Co₄N/carbon composite in the high-frequency region. Notably, there is no visible semicircular feature typically observed in EIS spectra. In ideal capacitive systems like supercapacitors, the charge transfer resistance is negligible, leading to a near-vertical trajectory in the Nyquist plot at high frequencies. In the low-frequency region, the Nyquist curve ascends vertically, indicating the absence of additional resistance elements or diffusion-limited processes suggesting rapid charge transfer characteristics. Further, from the phase frequency plot, the relaxation time of 318 msec has been calculated for the electrode (Figure S8a of SI). The rate performance of the electrode is given in Figure 4d. The
rate performance plot gives dynamic perspective on how the material responds to varying charge-discharge speeds. Further to access the benefit of nanosize Co$_4$N, the CV of Co$_4$N/carbon composite and bulk Co$_4$N has been compared in Figure 4e. The CV curve for bulk Co$_4$N displayed a smaller CV area, indicative of relatively lower charge storage capacity. Moreover, the CV range for the composite extended from 0.1 to -0.8 V, showcasing its broader electrochemical window. Upon capacitance calculation, bulk Co$_4$N displayed a capacitance of 132.3 F/g, whereas the composite demonstrated a higher capacitance of 151.7 F/g. This disparity underscores the superior capacitive performance of the Co$_4$N/carbon composite having lower crystallite size of Co$_4$N and more fraction of carbon content. A comprehensive comparison was also performed by including activated carbon alongside bulk Co$_4$N and the Co$_4$N/carbon composite in GCD tests (Figure 4f). The extended discharging time of Co$_4$N/carbon is indicative of its superior charge storage capacity and efficiency. It’s worth noting that the charging behavior of bulk Co$_4$N demonstrated saturation above -0.5 V, which prompted us to conduct CV within the 0.1 to -0.4 V range to capture its capacitive behavior effectively. We have performed the cyclic stability test for the electrode material as shown in Figure S8b of SI. The sample retained 59% of specific capacitance after 5000 cycles of charging/discharging. The retained capacitance is quite low in this case. Although the carbon exhibit high capacitance retention due to only EDLC mechanism. However, in this case, due to the involvement of Co$_4$N in the electrochemical process, the degradation of the active material probably the dissolution of Co$_4$N with time in the electrolyte solution led to the decrease in capacitance. In future, the exploration of other MOF based nitrides which are stable in acidic electrolyte can be explored to improve the cyclic stability. In summary, the comparative analysis highlights the Co$_4$N/carbon composite’s distinct advantages over bulk Co$_4$N in terms of capacitance, electrochemical window, and charge storage efficiency.
3.3. Enhanced Precision in Surface Contribution Analysis using Dunn’s method

Further, we delved into the intricate charge storage mechanisms of the Co₄N/carbon composite by employing a deconvolution approach to disentangle the contributions from diffusion-controlled charge storage and capacitive processes. The voltametric current response was separated into two distinct components using the equation 1 below as per Dunn’s method²⁶:

\[ I = k_1v + k_2v^{1/2}, \]  

(1)

where \( k_1 \) and \( k_2 \) represent constants, and \( v \) signifies the scan rate. In this equation, the \( k_1v \) term is associated with the capacitive current and \( k_2v^{1/2} \) is associated with the diffusion-limited current.

For the Co₄N composite, the surface-controlled contribution accounted for a substantial 76.4% of the total charge storage capacity at a scan rate of 20 mV/s (Figure 5a-b). This proportion decreased at lower scan rates, reflecting the increased diffusion contribution as ion diffusion within the material becomes more pronounced. At 10 mV/s, the contribution was 74.4%, and at 5 mV/s, it reduced to 70.6%. This observation highlights that, at lower scan rates, ions have more time to diffuse within the material, leading to a relatively higher diffusion-controlled contribution compared to surface-controlled processes. To precisely ascertain the surface and diffusion contributions, calculations were initially based on CV data ranging from 5 mV/s to 500 mV/s. Notably, as more CV curves were incorporated, the calculated surface contribution for the 20 mV/s CV curve decreased, deviating from the anticipated behavior (Figure S9 of SI). The slope and intercept, which is the indication of surface and diffusion contribution, has been calculated taking different CV data sets as given in Figure S10 of SI. The slope area increases as we converge the data sets to calculate them. In response to this challenge, an alternative approach was adopted. R-squared (R²) values, indicative of the goodness of fit in linear regression, were meticulously evaluated. The objective was to identify the data sets that exhibited a closer alignment with a linear
fit, which would in turn enhance the accuracy of the surface contribution calculations. It was observed that the R² values for the 5 mV/s to 20 mV/s data sets were notably close to 1, signifying a robust linear fit (Figure S11 of SI). In contrast, for data sets encompassing a broader range of scan rates (e.g., 5 mV/s to 500 mV/s), the R² values deviated significantly from 1 and, in some instances, approached or reached 0. This suggests that for the surface and diffusion calculation, 5-20 mV/s can be selected. To further calculate the surface contribution in 50 mV/s and above we took different scan rate ranges for R² calculation as shown in Figure S12a of SI which give us the R² value close to 1 in 50-100 mV/s scan rate ranges. The slope in the Dunn equation which directly signifies the surface contribution has been calculated for 5-20 mV/s and 50-100 mV/s scan rate in Figure S12b of SI Therefore, rather than attempting to apply a single linear fit to the broader 5-100 mV/s range, separate linear fits were applied to the more specific 5-20 mV/s and 50-100 mV/s ranges. Furthermore, the surface contributions derived from different CV data sets were plotted, allowing for a comprehensive comparison of these contributions (Figure S12c of SI). The CV depicting the surface contribution in 5-20 mV/s is shown in Figure 5a. Further we applied the Trasatti method to calculate the surface capacitance and the total capacitance of the material. Using the fact that the charge storage in the material varies inversely to the square root of the scan rate as per the following equation 2:

\[ q \propto \nu^{-1/2} \]  

(2)

where \( q \) is the charge,

The above equation can be rewritten in terms of capacitance as follows.

\[ C(\nu) = \frac{\text{const}}{\nu^{1/2}} + C_0 \]  

(3)
\[ \frac{1}{C(v)} = \text{const}' \times v^{1/2} + \frac{1}{C_T} \]  

(4)

Here, \( C(v) \) is the capacitance. \( C_O \) and \( C_T \) are the surface capacitance and maximum total capacitance, respectively. Using these equations, the plot between capacitance and scan rate has been shown in Figure 5a and Figure 5b which gave the value of surface capacitance to 135 F/g and total capacitance of 203 F/g.

Figure 5. (a) CV curve of Co₄N/carbon at 5 mV/s, 10 mV/s, and 20 mV/s, (b) Surface controlled contribution for Co₄N/carbon at 5 mV/s, 10 mV/s, and 20 mV/s calculated using slope from 5 to 20 mV/s data.

3.5. Assembling of asymmetrical device: Further we fabricated asymmetrical supercapacitor using Co₄N/carbon material as a negative electrode and Z-800 as a positive electrode We employed mass balancing formulas to ensure that both the positive and negative electrodes were appropriately charged. The formula used for mass balancing was:

\[ m_+ C_+ V_+ = m_- C_- V_- \]  

(5)

Here, 'm' represents the mass of the active material, 'C' signifies the specific capacitance, and 'V' denotes the potential window. The subscripts '+' and '-' distinguish between the positive and negative electrodes.
After careful analysis, we determined that the maximum positive to negative mass ratio should be maintained at 1:2. Co₄N was assigned a mass of 2 mg, while Z-800 had a mass of 1 mg. The assembled device was configured with a PVA-based 1 M H₂SO₄ gel electrolyte. During CV testing, we systematically explored different potential windows while maintaining a fixed scan rate of 50 mV/s (Figure 6a). As the potential window increased, we observed semi-rectangular CV curves characteristic of EDLC behavior. However, when the potential window reached 2.2 V, we noticed a small area at the edge of the CV curve. This region indicated the decomposition of the electrolyte solution, which can lead to adverse effects on the device's stability and performance.

The specific capacitance from each CV curve has also been calculated and shown in Figure S13a. The specific capacitance linearly increases with increase in potential window, however taking 2.2 V taking into account could lead to the loss of electrolyte due to its decomposition with time.

**Figure 6.** Electrochemical characterization of asymmetrical device (Co₄N/carbon//Z-800) (a) Voltage window test, (b) CV at different scan rates, (c) GCD at different current densities, (d)
Nyquist plot (inset: phase vs frequency), (e) capacitance vs scan rate (inset: capacitance vs current density), and (f) Ragone plot.

After careful consideration, we determined that the optimized potential window for the asymmetrical supercapacitor was 2 V. With the optimized potential window, we further examined the device's performance by varying the scan rates during CV testing (Figure 6b). The results revealed a notable trend in capacitance as the scan rate increased. At 5 mV/s, the device exhibited a capacitance of 169.61 F/g, demonstrating its high charge storage capacity. However, as the scan rate accelerated to 50 mV/s, the capacitance decreased to 16.39 F/g. We further assessed the performance of asymmetrical supercapacitor by conducting GCD tests across a range of current densities, specifically at 0.375 A/g, 0.5 A/g, 1 A/g, 2 A/g, and 4 A/g (Figure 6c). GCD curves exhibited a distinctive triangular shape depicting capacitive behavior. However, as the current density decreased to 0.375 A/g, a noteworthy change in the GCD curve emerged. Instead of a purely linear discharge curve, we observed non-linearity. This means, the device exhibited a more complex behavior at lower current densities, reflecting the involvement of both surface redox reactions and EDLC, coupled with the ability to access the inner regions of the bulk material. When calculated, at a low current density of 0.375 A/g, the device delivered its highest specific capacitance value, reaching 51.6 F/g. However, as the current density increased to 4 A/g, the specific capacitance decreased to 2.37 F/g. EIS was conducted on the device both before and after cycling to gain insights into its electrochemical behavior (Figure 6d). After cycling, the device exhibited an increase in resistance, which can be attributed to slight electrolyte decomposition and electrode material degradation over repeated charge-discharge cycles. The rate performance of the device with respect to the scan rate and current density is also plotted and given in Figure 6e.

Energy density ($E_D$) and power density ($P_D$) are crucial parameters for assessing the performance
of energy storage devices whose relationship can be assessed by plotting Ragone plot as shown in Figure 6f. The device exhibited an energy density of 26.6 Wh/kg at a power density of 0.36 kW/kg. The energy density and power density performance has been compared with other materials reported in the literature in the Ragone plot as well as in the Table S1 of SI file. Cyclic stability is a critical factor for the potential commercialization of energy storage devices. To assess the device's long-term performance, it underwent rigorous testing with continuous cycling specifically, 4000 charging-discharging cycles at a high current density of 10 A/g. The device retained up to 68% of its initial capacitance value as shown in Figure S13b of SI. The high capacitance and energy density confirms the benefits of nanosized Co$_4$N doping in carbon structure. Although the cyclic stability of this material is not up to the mark for the supercapacitor however in future studies other metal nitrides can be explored which has high cyclic stability in acidic aqueous electrolyte.

4. Conclusion:

In this study, we have successfully synthesized nanosized Co$_4$N doped carbon structures derived from ZIF-67 MOF, with a focus on its applicability for supercapacitor technology. The FESEM and TEM studies revealed the coexistence of carbon nanotubes like structure and nanosized Co$_4$N nanoparticles in the composite. One of the standout advantages of Co$_4$N/carbon composite is the incorporation of nanosized Co$_4$N, which showed superior electrochemical performance compared to bulk Co$_4$N. The Co$_4$N/carbon composite exhibited superior capacitance, with rate performance and capacitance retention attributes that outperformed bulk Co$_4$N. GCD testing of the assembled asymmetrical device showcased a specific capacitance of 51.6 F/g. Further we also did the in-depth calculation and steps to calculate the most accurate values for the surface contribution which is usually missing in the literature and reader can’t estimate the reliability of the calculated values.
Moreover, the device retained up to 68% of its initial capacitance after 4000 cycles at 10 A/g. The device achieved 26.6 Wh/kg of energy density when discharged with a power density of 0.36 kW/kg. The incorporation of nanosized Co₄N within our Co₄N/carbon composite demonstrates immense promise for supercapacitor applications. These findings pave the way for the development of other nitride-based electrode material using different MOF material to get the higher capacitance using the appropriate electrolyte.

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Author Contributions

V.S.: Conceptualization, Material and Electrochemical Methodology, Manuscript Writing, Data interpretation; Mansi: Manuscript Writing, Data Analysis, Electrochemical characterization; P.D.: Manuscript Writing, Structural characterization analysis and explanation; U.K.T.: Manuscript Review and Discussion; A.D.: Data Interpretation, Manuscript Review and Discussion; W.N.: Discussion, Manuscript editing; S.S.: Conceptualization, Data analysis, Discussion, Manuscript Review
Data availability

Data will be made available on request from corresponding authors.

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