**Nitrogen Incorporation in Carbon Matrix**

**B. Viswanathan**

**National Centre for Catalysis Research**

**Indian Institute of Technology, Madras Chennai 600 036**

**Introduction**

Most of the energy conversion processes have mostly been centred around the element ‘carbon’. The element carbon has many manifestations starting from graphite, diamond, carbon nanotubes, graphene sheets and the list of these materials is ever increasing. There are various characteristics of carbon materials like the ease of production from various sources, (biomass, or fossil sources) cost of production, and ease of fabrication possibilities make these materials receiving considerable attention in recent times [1,2]. These materials have low cost, high surface area, and good mechanical and electrical properties. Moreover, these materials display high chemical and electrochemical stability [3,4]. These materials find various applications including in the development of supercapacitors [5,6] in other energy storage and conversion devices,[7] and also promote sluggish reactions like Oxygen Reduction Reaction (ORR) [8-13].

The textural modifications have been examined in various publications and their variations have been exploited in a number of applications. In conventional materials like oxides and other binary systems, doping is one of the methods to alter the electronic property of the parent substance. The choice material to be doped has to be made on the basis of various factors like ionic sizes involved in both the dopant and the doped material and also the solubility ins the solid state. Even then, there will be multiple possibilities for the doping ions to occupy in the lattice of the doped material. Two of these possibilities have been extensively exploited like substitution site and interstitial site. Depending on the position the doped species takes in the lattice, it will alter the basic usually electronic property of the base material. These aspects have been extensively considered for developing many functional semiconductors for specific applications in industry.

However, the science of doping in carbon materials is unique since the doped atoms take substitution positions in the lattice. There is another special feature doping in carbon materials is that the doped atoms can be incorporated in carbon materials by the synthesis methods adopted or the precursor materials employed. This gives unique possibilities for the location of the doped species in carbon materials. This special feature will incorporate in the doped carbon materials not only electronic property changes, but also the geometric arrangement of the doped species and they can also give rise to specific functionality. These are the unique features of doping in carbon materials. Among the various elements that can be doped in carbon materials, nitrogen occupies an important place. Even its doping in conventional binary semiconductors like TiO2 has given rise to questions (doped in lattice position or in interstitial site) and this has been debated in the literature [14].

Among the heteroatom-doped carbon-based materials, nitrogen doped carbon materials are particularly interesting from the point of materials. These systems exhibit a variety of properties like altered electrical conductivity, specific active sites for surface transformations, and other properties necessary for exploitation as solid state materials for devices in energy storage and conversion. In order to explore the full potential of these materials, it is necessary the local structure of the so-called active sites should be known and in N-doped carbon materials there are variety of such active sites**.** The interest in functionalization strategies have been promoted by the wide application potential for these materials. The state of the nitrogen atoms in the carbon materials have been identified from the values of the binding energy of 1s level of nitrogen by x-ray photoelectron spectroscopy. The pyridinic configuration is associated with the emission around binding energy values 398-399 eV. The pyrrolic species and other defect components are usually identified by emission centred around 399.5-400.5 eV. The nitrogen in graphitic configuration centred at 400-401 eV [15,16]. At higher binding energies with respect to graphitic nitrogen the observed signals are usually associated to graphitic valley N [17]. Nitrogen species at an electronegative environment like linked to oxygen gives rise to signal at higher binding energies [18]. Other nitrogen species like N-adatoms or multi-fold coordinated nitrogen species may give rise to signals near the pyrrolic nitrogen at around 400 eV. These identified species are pictorially represented in Fig.1.The binding energy values and the species associated with each of these binding energies are those that are reported in literature but however, there can be other alternate assignments.

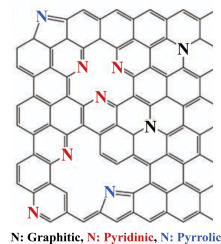


Fig.1. The possible nitrogen species in carbon materials. [Figure adopted from reference 19,22].

It is usually conceived that nitrogen doping in carbon materials can change the charge distribution in the backbone of the carbon skeleton. In addition, the specific locations in five or six membered rings can function as active centres suitably modulated by the skeleton. Because of the various possibilities of the possible active centres, the identification of specific active site for a chosen function by carbon materials like for ORR reaction is still difficult. In fact, in literature no single specific site has been identified for a chosen reaction on N-doped carbon materials due to the simultaneous presence multiple nitrogen species, the inherent surface heterogeneity, the attendant alterations in the work function of the material at the interface, the morphology of the resultant material and other resultant changes in the structural parameters. In addition, thermal treatments can change pyrrolic N into pyridinic N and also ultimately in to the quaternary N [20,21] and hence it will be difficult to exact active site as these changes can take place in situ. The synthesis and characterization of nitrogen doped carbon materials need sophisticated probing techniques which could unambiguously identify the nature of the active sites and facilitates the elucidation of the mechanism of the reactions.

It is normally conceived that nitrogen doping in carbon materials alter the electronic property of the material. This may be true and in most cases it can be so. However, the functional character of these nitrogen species in carbon skeleton and the consequent geometric factor cannot be ignored. There can be attendant strain in the carbon skeleton and this stress can also be another activated state for the resultant activity.

2. **On the synthetic approaches for the preparation of N-containing carbon materials**

Essentially, two synthetic strategies are practiced to generate nitrogen doped carbon materials. The synthetic approach employed on what type of carbon materials are required. The two strategies commonly employed is using in situ precursor materials or post treatment of the carbon material obtained. The precursors with nitrogen and carbon atoms like acetonitrile, [23] melamine [24] and polyacrylonitrile [25] were mostly employed to synthesize N-doped carbon nanomaterials. For the posttreatment strategy, carbon nanomaterials were treated in the presence of various nitrogen sources, and the nitrogen atoms replaced certain carbon atoms[26,27]. Each of these strategies have their advantages and disadvantages. The in-situ doping method offers uniform distributions of nitrogen atoms with a well-defined structure, whereas the post-treatment strategy may change the structure of the carbon precursors, such as the texture and morphology. However, the in-situ doping method often requires high temperatures and complex processes, and the chemical reagents used may be poisonous. The yield and the rates of N-doped carbon materials produced have not been well discussed in literature. In contrast to the post-treatment strategy with a surplus supply of nitrogen, in-situ doping is more effective because the synthesis of carbon nanomaterials and the N-doping takes place at the same time. Therefore, the in-situ approach shows relatively higher yield rates, which represent easy reactions which deserve more research. Though the synthetic procedures are broadly classified into two the detailed methodology [28] can be further subdivided into some subsections as follows:

1. Carbonization of a nitrogen-containing precursor (such as pyridine, melamine, and polyaniline), this can be followed by chemical of physical activation.
2. Hydrothermal carbonization of nitrogen containing compounds like glucosamine, cyanuric acid.
3. Templating methodology using nitrogen-containing precursor followed by thermal treatment
4. Post-thermal treatments of a material synthesized previously with a nitrogen containing reactant either in gas or liquid phase.

Among these methods, precursor-based method is most often employed especially using polyaniline as the starting material [29]. The materials derived by this method showed remarkable catalyst supports and also exhibited considerable activity for OR reaction [11]. The main reason for this remarkable feature is due to the functionality that can be inherently present in this procedure [30]. This aspect will be discussed subsequently.

A second methodology employed for N-doped carbon materials with high texture is based on chemical treatments through organic reactions at low temperatures [31,32]. In addition to the texture of the resultant material, the surface functionalities also are specific and hence these materials are amenable for further changes in the functionalization. This can result in the extent of doping.

The texture functionalization of pure carbon materials can be modified by suitable chemical treatments and this has been already discussed in detail [1,2]. Some general statements on the post-treatment method may be in order at this point. In addition to employing nitrogen containing precursors, which results in functionalized nitrogen in carbon matrix, other comparatively drastic physical treatment procedures like hydrothermal carbonization [33] annealing [34] plasma [35] or arc discharge [36] are also employed on a variety of carbon materials like activated carbons, carbon nanotubes (CNTs), graphene oxide (GO) and its reduced form, and other forms of carbon. In addition to the nitrogen containing precursors already mentioned other like ammonia [37], urea [38], melamine[39], cyanamide[40], dicyandiamide[41], polyaniline (PANI) and polypyrrole (PPy) [42] have also been used. It can be remarked that plasma and arc discharge methods have been less employed since the extent of the heteroatom (namely nitrogen) incorporation in carbon materials are generally less compared to the precursor methods.

3. **The state of Nitrogen atom in N-doped carbon materials**

There are various techniques that can be employed to identify the state of nitrogen in carbon frame work.Among these, photoelectron spectroscopy and temperature programmed desorption have been utilized in this connection. In X-ray Photoelectron spectroscopic technique (XPS) the value of the binding energy of 1s level of nitrogen is in the energy range 398-404 eV. The wide scan spectrum of nitrogen substituted in carbon materials treated at two temperatures are given in Fig.2.



Fig.2. Nitrogen 1s core level XPS spectra for N-CNT samples treated at (a)NCNT-L;823K(b) NCNT-H;1023 K (N1 Pyridinic N; N2pyrrolitic N; N3 graphitic N; N4 pyridine-N-oxide and N5 chemisorbed nitrogen oxide) [Figure reproduced with permission from ref.43].

The assignments of the XPS peaks to various nitrogen species appear to follow the general principles of electron density around the atom. If the electron density around the atom considered were to increase, it will result in a decrease in binding energy of the core level due to electron-electron repulsion. The assignments given (N1 to N5) are the general species that can be expected by substitution of Nin the carbon framework. However, there can be other types of nitrogen environments when nitrogen substituted carbon materials are prepared from precursor materials. This also shows that the carbon 1s spectrum of carbon species adjacent to the nitrogen substituted site needs careful examination. These aspects need attention in future research.

It is also noticed from the spectra shown in Fig 2 that as a function of heat treatment temperature, the binding energy of the 1s core level of nitrogen changes to lower binding energy value showing the net charge density increases around the heteroatom. These changes can be due to density changes or environmental changes as a result of heat treatment. This aspect has not yet received attention. If the temperature effect were to be sintering of the solid, then it should also reflect in the valence band spectrum of the solid.



Fig.3.Valence band spectra near the Fermi energy level for pure, nitrogen functionalized (as dep RT) and annealed nitrogen functionalized N-CNTs. In the inset the nitrogen 1s core level XP spectra are also shown. {reproduced with permission from Ref.44].

The observation that the Fermi level shifts towards the less negative values shows that the density of states (DOS) is altered at the Fermi level and this shift is a function of the annealing temperature. What does this mean? The reductive behavior of these materials is enhanced and possibly accounts for the special place N-doped carbon materials occupy in electrochemical energy storage and also for its remarkable activity towards ORR. This aspect will be taken up in a subsequent section.



The N1s spectra of CNx samples grown at 700,750,800, 850 and 9000 C. It is seen that a variety of nitrogen species is present in these materials and also the relative amounts of graphitic to pyridinic N in these samples vary with temperature [Reproduced from Ref 45]

It is seen that there are more than the four nitrogen species that can be present on N-substituted carbon materials. This aspect has not yet been fully explored in literature.

Nitrogen incorporated carbon materials have been frequently analyzed by XPS to identify the state of N-atom in the carbon matrix and various types of nitrogen species have been identified [1x-6x].

4. **Energy Conversion and Energy Storage Applications**

One of the prominent applications of carbon materials is their use as electrode materials. Among the various possibilities, electrode materials for supercapacitor applications assume an important place. Electrochemical capacitors (EC) are considered complementary to batteries for energy storage mainly due to their high-power density, extremely long cycle life and more reliable safety features. ECs have been widely applied in portable electronics, power back-up devices and hybrid electric vehicles (HEVs) to provide the cranking power. An Electrical double layer capacitor (EDLC) generally composed of two electrodes made of activated carbon, which are soaked in a nonaqueous or aqueous electrolyte and separated by a porous membrane separator.

Nitrogen-doped carbons (NCs) have recently demonstrated to be promising to improve the capacitance via surface faradaic reactions without sacrificing the high rate capability and long cycle life. The new NCs show good electronic conductivity, and they can be easily prepared at low

cost as stated above. To the best of our knowledge, nitrogen has been the most studied doped heteroatom (among B, P, S and N) for carbonaceous electrode materials over the past several years.

In the recent years there have been many review papers [46-55] focusing on different fields of carbon-based materials for energy storage, including supercapacitors, LIBs and H2 storage, and catalysis, such as oxygen reduction reaction for fuel cells. For example, in 2010 Inagaki and coworkers [46] reviewed the development of carbon materials used for Electrical Double Layer capacitors (EDLC). These authors suggested that carbonization, ammoxidation and steam activation could be employed to prepare Nitrogen doped carbons. They proposed two kinds of preparation methods the first group was obtained by the carbonization of melamine foam or polyaniline, while the second group was prepared by carbonizing nitrogen containing polymers and organic compounds with various templates.

Even though N-doped carbon materials (NCs) have been exploited for supercapacitor applications, still the exact role played by the doped nitrogen atoms to the exhibited properties especially the redox behavior at certain potential ranges and also the Coulombic efficiency have yet to be ascertained. The additional capacitive mechanism which accounts for the observed capacitance values observed with N-doped carbon materials has to be identified. There are a variety of synthetic strategies ranging from simple heat-treatment of carbons with nitrogen containing complexes to carbonization of nitrogen containing complexes under inert atmosphere or hydrothermal treatment have been reported in literature but the control of nitrogen content in the resulting material and also the variation of nitrogen content with different preparation conditions could not be precisely predicated. Another aspect regarding these materials is the changes in the values of surface area as a result of nitrogen incorporation in carbon matrix, though it is known that with high nitrogen content results in a low surface area. It is realized that there is still need for further investigations in the development of synthesis procedures so that the NCs can be prepared with high porosity keeping the high nitrogen content. In addition, control of the nature of nitrogen in these materials should be achieved so that electronic and chemical properties can be tuned as well as a priori predicted. For supercapacitor applications, NC-based materials are attractive because the nitrogen-enabled functionalities contribute to the pseudo-capacitance, increase the conductivity of the materials, and increase the active surface areas accessible to the electrolyte by improving the wettability of the electrodes. While nitrogen substitution in carbon materials play an important role in supercapacitor applications, however, the detailed mechanism of how nitrogen substitution affects the capacitive behavior is yet to identified. The effects of the dominant nitrogen functionalities like pyrrolic-, pyridinic-, quaternary-/graphitic-N and N-oxides with pyridine on their contribution to the capacitive values, such as pseudo-capacitance, specific capacitance as well as rate and cycle performance, in different electrolytes have yet to identified.

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