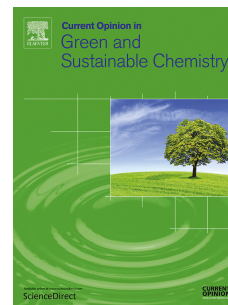


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Nitrogen-doped Nanocarbons (NNCs): Current Status and Future Opportunities

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Abstract

The current and estimated energy demand and their potential sources of supply indicate a daunting future for humanity on the planet unless sustainable solutions are developed. The scarcity, high cost and the potential environmental and health concerns related to widely used noble-metals makes the situation even worse. Thus, active participation from scientific and industrial communities is essential to replace noble-metal (or any metal) based processes with more sustainable alternatives. In that context, recent developments in heteroatom-doped (especially nitrogen) nanocarbons and their wide-ranging applications show promises towards substituting the processes, which normally utilize expensive, scarce and hazardous materials. Herein, a brief overview of nitrogen-doped nanocarbons (NNCs) is provided highlighting their significance and sustainable prospects.

Keywords

Nanocarbons, Metal-free approaches, Nitrogen-doped carbon, Supercapacitors, Electrocatalysis, Sustainable processes

Introduction

The current and anticipated future energy demands and associated environmental impacts surely pose imminent threats not only to mankind but also to every living organism and the environment on the planet.[1] The over-utilization of precious metals for various industrial processes along with their potential bio- and eco-toxicity is one of the major components of this concern. Thus, the proper utilization of natural resources and finding the sustainable alternatives to non-renewable sources undoubtedly requires the most attention.[2,3] In the quest of finding a green and sustainable alternative to the noble-metal-free (or metal-free) processes, a class of nanomaterial containing carbon nanostructures has emerged as a promising contender. The interest in this field can be attributed to the materials' high abundance, relatively low-cost (compared to metals), easy accessibility and chemical diversity and finally size- and shape-dependent properties (owing to their nanodimensions).[4]

In general, the carbon-based-nanomaterials are primarily comprised of carbon-backbones with hydrogen and other heteroatoms.[4] Based on the historical progress of this field, common organic supramolecular aggregates and polymers are excluded from this class due to their respective unique identities in the research community. The structures of these nanomaterials are composed of either sp^2 or sp^3 carbon networks where the remaining valencies of carbon are satisfied with hydrogen or heteroatoms (*vide infra*). While the connectivity and the degree of unsaturation dictate their electronic structures, geometries and other properties, the presence of heteroatoms contributes significantly to control such properties.

The carbon-based nanomaterials are normally classified based on their geometric dimensions, ranging from zero (0D) to three dimensions (3D). Though this classification seems a little skewed towards sp^2 carbon-systems like graphene, graphite etc. the newly developed synthetic techniques have also started to offer more variants of these systems (such as sp^3 carbon-systems etc.), leading to improved and innovative properties.[5] While the class of 0D mainly includes fullerene-based systems [6], the carbon nanotubes (CNTs) [7] are normally considered as 1D nanocarbons because of their unidirectional

propagation during synthesis, leading to directional properties. The most popular class of nanocarbons is probably 2D class because of the recent upsurge in graphene-based applications[8] in which the unique physico-chemical properties stem from the single layer of graphene-sheets. The 3D variants of graphene, graphite [9], encompassing multiple layers of graphene stacked together in the perpendicular direction to the graphene-plane, are classified as 3D nanocarbons. Though the properties of nanocarbons are normally governed by their dimension, the post-synthetic modifications and variability in synthetic precursors open up opportunities for further improvement. In this respect, the incorporation of the various heteroatoms (often termed as “dopants”) is garnering significant attention in recent years due to their ability to modulate the materials’ properties and consequently eventual applications.[10]

Among the dopants that are included into nanocarbons, nitrogen and oxygen are the most common ones primarily because of the ease of synthetic procedures and high abundance of the precursors. Among these heteroatoms, nitrogen dopants have been claimed to have the major impact towards improving the nanocarbon’s properties.[11] Within a short span of time, the field has witnessed a sharp growth as reported by a few sporadic reviews [11-14] documenting the specialized properties and applications of nitrogen-doped nanocarbons (NNCs), an updated coverage of NNCs appear timely. Herein, selected and important synthetic procedures, properties and the applications of *N*-doped nanocarbons are presented, highlighting the present status, challenges and future opportunities (Figure 1A).

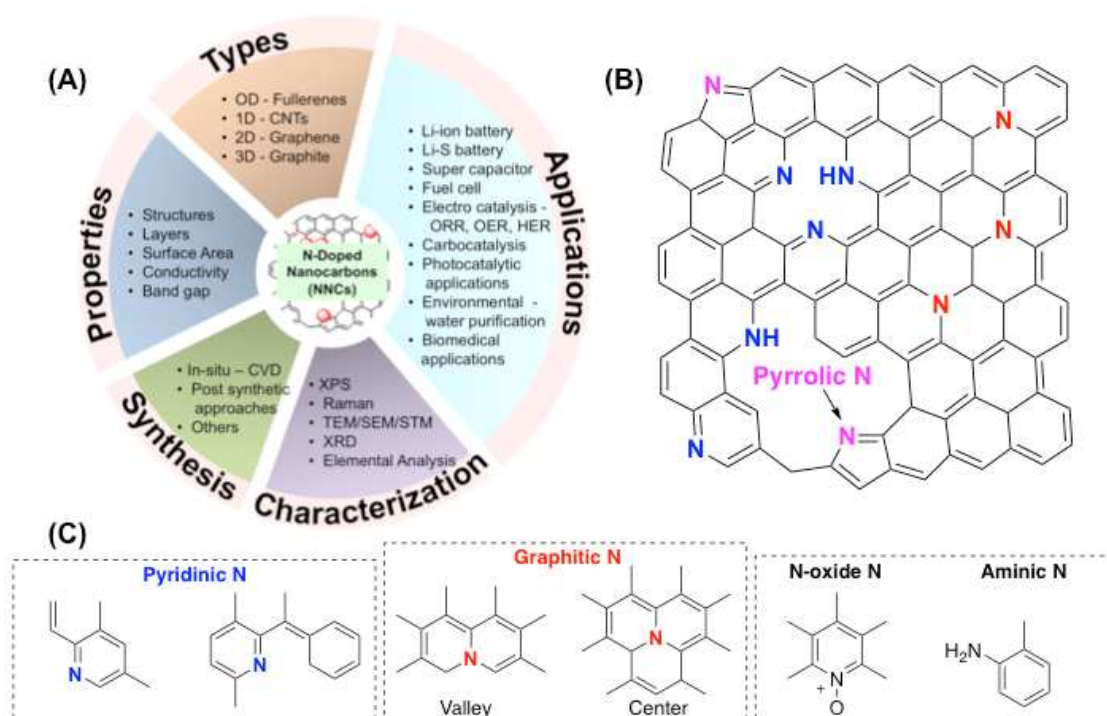


Figure 1. (A) An overview of the topics discussed in the manuscript. (B) and (C) Types of nitrogen atoms in nitrogen-doped-nanocarbons (adopted from the ref. [14]).

Present Status

Owing to the unique structural features and associated properties of sp^2 -based nanocarbons, it is more prevalent and widely studied as compared to other counterparts. Irrespective of the class, mainly three types of nitrogen atoms are found in NNCs [14] (Figure 1B, 1C): graphitic, pyridinic and pyrrolic. The major difference among these three types stems from the position of nitrogen in the carbon network/skeleton, the number of heterocyclic rings they form and the participation (or lack thereof) of their lone-pair of electrons into the carbon skeleton; these structural features directly modulate the physico-chemical properties of such nanocarbons.

The graphitic nitrogen atoms refer to those nitrogen atoms, which substitute the carbons in the graphene layer, connecting with three other carbon atoms in the skeleton. Depending on their locations (either on the edge or trapped inside the layer), they can further be classified as “valley” or “center” nitrogens. On the other hand, pyridinic and pyrrolic nitrogens represent the classes of nitrogen atoms which are parts of six and five-

membered ring, respectively. In general, for pyridine, the ring aromaticity does not involve the lone-pair of electrons from the nitrogen whereas pyrrole ring utilizes lone pair of electrons from nitrogen to gain aromaticity. Having said that, however, for the heterogeneous system, such a concept is often be overshadowed by the overall stability of the system. Additionally, depending on the synthetic procedures, there are also chances of formation of aminic as well as *N*-oxides types of nitrogen atoms, which can have a significant impact on the overall charge distribution. Though most of the synthetic procedures allow incorporation of more than one type of nitrogen atoms into the system, the lack of fundamental mechanistic understanding of nitrogen incorporation still makes the prediction process relatively difficult. The same concept can also be extrapolated to relatively less-studied sp^3 carbon-skeleton where more prevalent geometrical constraints lead to distortion in the structure, leading to noticeable changes in their electronic and chemical properties.

Synthetic Strategies

As opposed to classical “top-down” and “bottom-up” classification systems, commonly used to describe the synthetic strategies for assembly of nanomaterials, the synthetic methods deployed to prepare *N*-doped nanocarbons can be broadly divided into two routes: 1) post-synthetic method and 2) in-situ process.

As the name suggests, in “post-synthetic” method, nitrogen-free nanocarbons are mixed with nitrogen-containing precursors and the composite can be transformed into NNCs with the help of external energy sources (Figure 2). Though the high-temperature thermal treatment is normally used to carry out such transformations, recently alternating energy input system such as microwave (MAHA: Microwave-assisted Hydrothermal Treatment)[15], plasma and arc-discharge methods[16] etc. have also been reported. The pyrolysis temperature, gas-type and flow, the choice of precursors etc. are some of the variables that influence the type and the amount of overall doping. For example, Lai et al. reported that by changing the precursors and other experimental conditions, diverse types of nitrogen atoms could be obtained (Figure 2A).[17] Alternatively, nitrogen can be incorporated post-synthetically via the functionalization of nitrogenous entities onto precursor molecules, followed by pyrolysis.[18] This process allows relatively precise

grafting of the nitrogenous entity on the nanocarbon surfaces but often suffers from economic viability. Various non-nitrogenous carbons such as carbon nanotubes (CNTs) [19,20], activated carbon [21], graphene [22-24], graphene-oxide (GO) [25] and reduced graphene-oxide (RGO) [15,26] etc. and different nitrogen sources [11] such as ammonia, urea, polyaniline (PANI), polypyrrole (Ppy), dicyandiamide, ethylenediamine etc. have been used for the synthesis of NNCs. The structure of such ensuing nanocarbons tends to resemble more to the relatively stable non-nitrogenous nanocarbons whereas the incorporation (both amount and type) of nitrogen varies depending on reaction conditions.

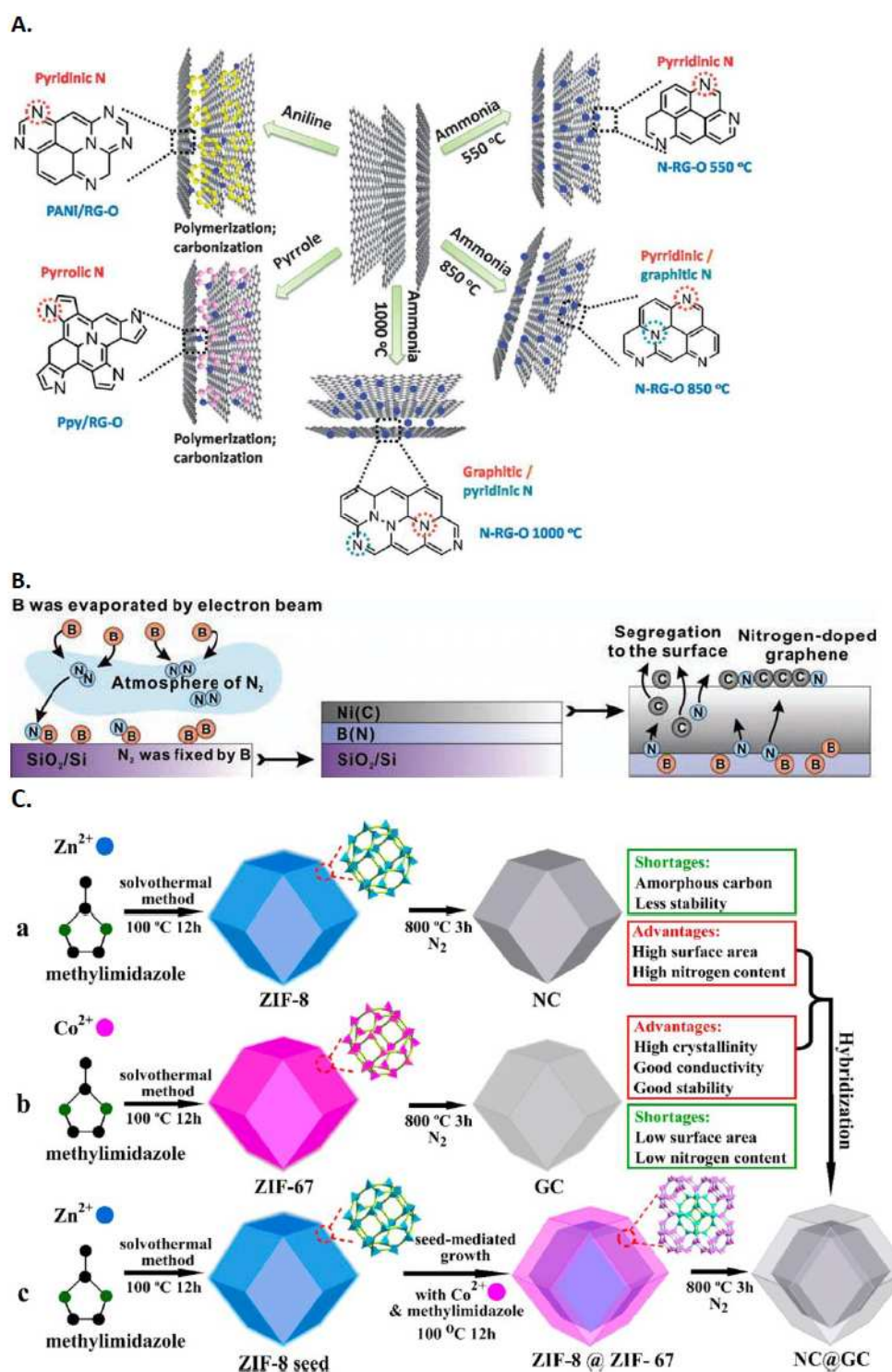


Figure 2. Representative synthetic strategies for the preparation of NNCs. (A) The synthesis of *N*-doped graphene with different nitrogenous precursors (Reprinted with permission from ref. [17]. Copyright 2012 Royal Society of Chemistry. (B) The explanation of concurrent segregation technique for the preparation of *N*-doped graphene (Reprinted with permission from ref. [27]. Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA). (C) An example

showing the synthesis of NNCs from MOF (Reprinted with permission from ref. [28]. Copyright 2015 American Chemical Society).

The “in-situ” method on the other hand, primarily involves the carbonization of a nitrogenous carbon source.[19,29,30] In this list, the most common method for the synthesis of NNCs is Chemical Vapor Deposition (CVD) technique, in which the *N*-containing precursors are injected into the chamber at vapor state at a high temperature and depending on the reaction conditions, the NNCs are deposited on a substrate (Figure 2).[31] The temperature, pressure and other conditions of the chamber, the nature of gases, the decomposition behaviors of the precursors have significant impacts on the extent of nitrogen incorporation as well as on the types of nitrogens. For an example, Zhang et al. reported a CVD technique describing a unique substrate-dependent synthesis of *N*-doped graphene (Figure 2B).^[27] In addition to pyrolysis process, a pre-synthetic or post-synthetic chemical activation strategy, as well as soft and hard-template-based synthetic tactics can be employed to improve the properties namely interaction with substrates, surface area etc. One of the major advantages of this method lies in the selection of the precursors. Since, any nitrogen-containing species, which can form a network-structure upon pyrolysis, can potentially be used for the synthesis of *N*-doped nanocarbons, the list of the precursors includes some of the unconventional materials such as Metal-Organic-Frameworks (MOFs) (Figure 2C), [28] bio-derived *N*-rich nanocomposites, [32,33] *N*-rich polymeric nanomaterials [33] and ionic liquids, [34] among others. Though the correlation between the precursors and the types of nitrogen in the nanocarbon skeleton remains elusive, the development of newer CVD and other strategies, coupled with the vast pool of available precursors is expected to bring more insight into the process for the synthesis of NNCs with improved properties.

It won't be complete if the biomass-derived synthesis of the NNCs is not included in the recent trends for the synthesis of NNCs.[35-39] Strategically, in most cases, it still requires pyrolysis of the precursors but the bio-derived unique choice of precursors have made this particular topic unique especially from the view-point of sustainable sources. In a very short period of time, this field has shown great promises, as highlighted by Luque and co-workers.[40] Now the continued research efforts are focused on

understanding the intrinsic reaction behavior of the specific biomass precursors and it is expected to achieve different NNCs as well as different composite materials with novel applications.

Characterization of Materials' Properties

The salient properties of *N*-doped nanocarbons, has provided the impetus and motivation to pursue the research in this area with varied emerging applications. The growth of sophisticated characterization techniques has helped immensely to recognize the uniqueness of the system. The structural and morphological features of nanocarbons can be visualized using different microscopic techniques and in this respect, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) have been widely utilized (Figure 3A, 3B).[41] The Selected Area Electron Diffraction (SAED) and Energy-Dispersive X-ray (EDX) Spectroscopy are also employed as useful techniques to glean information about the level of crystallinity and the concentration of dopants present in a particular nanocarbon sample, respectively. Except for a few cases, the crystallinity of the samples remains questionable and hence both Small-angle and Large-angle X-Ray Diffraction (XRD) methods are normally used to reconfirm the lattice planes. Additionally, several new developments in Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) along with elemental mapping also provide precise information about the numbers of layers and dopant's position, respectively (Figure 3C, 3D).[42] The bond-connectivity and the chemical nature of the nitrogen atoms are considered to be two important characteristics and these information can be obtained from X-ray Photoelectron Spectroscopy (XPS) to establish the structure-activity relationship. The atomic percentages of carbon and other dopants can be found from the XPS survey spectrum whereas the high-resolution deconvoluted spectra of individual elements reveal different bond-connectivity. For instance, the high-resolution deconvoluted N1s XPS spectrum shows the graphitic, pyrrolic and pyridinic nitrogen atoms at 401.5, 400.0, 398.0 eV respectively (Figure 3E).[12] In addition, the degree of unsaturation can also be found from C1s XPS spectrum after deconvolution, thus revealing the complicated network connectivity between carbon and nitrogen (Figure 3F)[43]. Raman Spectroscopy is yet another important characterization tool routinely used to calculate I_D/I_G ratio (I_D = Raman intensity related to the defect site, I_G = Raman

intensity related to the graphitic site) to assess the presence of dopants and the concomitant absence of sp^2 carbon networks (defect sites) (Figure 3G).[44] Often, the synthetic strategies for NCCs are aimed to fabricate product with the high surface area and in that case the surface area of the nanocarbons, their pore-size and pore-volumes can be calculated using N_2 adsorption-desorption experiments. The specialized knowledge about the thermal and the electrical conductivity, the optical band-gap and other properties are also routinely measured to understand a better structure-activity relationship.[45] Recently, the biomedical applications of such *N*-derived nanocarbons call for a different set of toxicological studies and several research groups are actively looking into environmental and health safety impacts of such NNCs.[46]

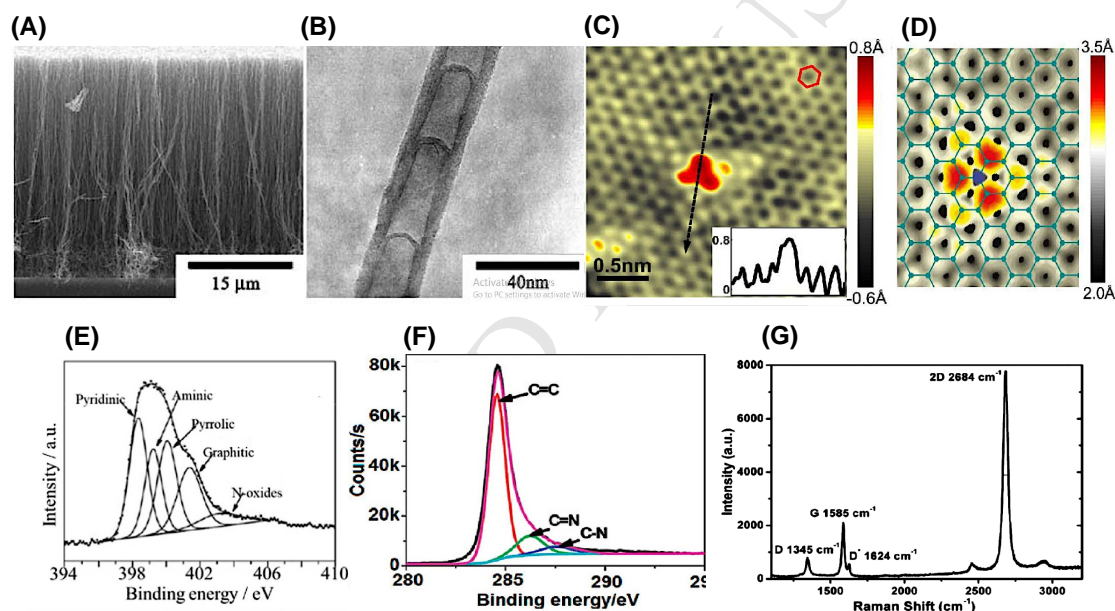


Figure 3. Various characterization techniques used to determine the structural features of NNCs. (A) SEM and (B) TEM images of N-doped CNTs (Reprinted with permission from ref. [41]. Copyright 2012 Elsevier Ltd.). (C) STM image and (D) DFT simulated image of N-doped single-layer of graphene (Reprinted with permission from ref [42]. Copyright 2018 American Association for the Advancement of Science). High-resolution and deconvoluted XPS spectra of CCNs (E) N1s (Reprinted with permission from ref. [12]. Copyright 2012 Elsevier Ltd and (F) C1s (Reprinted with permission from ref. [43]. Copyright 2011 American Chemical Society). (G) Raman spectrum of N-doped graphene (Reprinted with permission from ref.[44]. Copyright 2011 American Chemical Society).

Applications

The major reason for the emergence of *N*-doped nanocarbons is their unique properties, which allow them to be explored for diverse applications. The amount and the

nature of the nitrogen dopants can change the electronic and optical properties of these nanocarbons than their non-nitrogenous counterparts. The more electronegative nitrogen atoms (as compared to their adjacent carbons) impart significant distortions in their electronic band structures (by changing the distribution of π -electrons across the carbon networks) and influence the electrical and optical properties of the system. The difference in electronegativity between nitrogen and carbon, the intrinsic basicity of the nitrogen atoms (as exemplified by the accessibility of the lone-pair of electrons of some the nitrogen atoms) and the high surface area of NNCs contributes significantly to allow the favorable interactions between the substrates and the nanocarbons, culminating into improved activity of the later. While the high-temperature synthetic processes impart thermal stability and chemical-resistance to the nanocarbons, the dimension-specific property of *N*-doped nanocarbons also plays a significant role in designing nanomaterials for various emerging electronic and electrochemical applications.

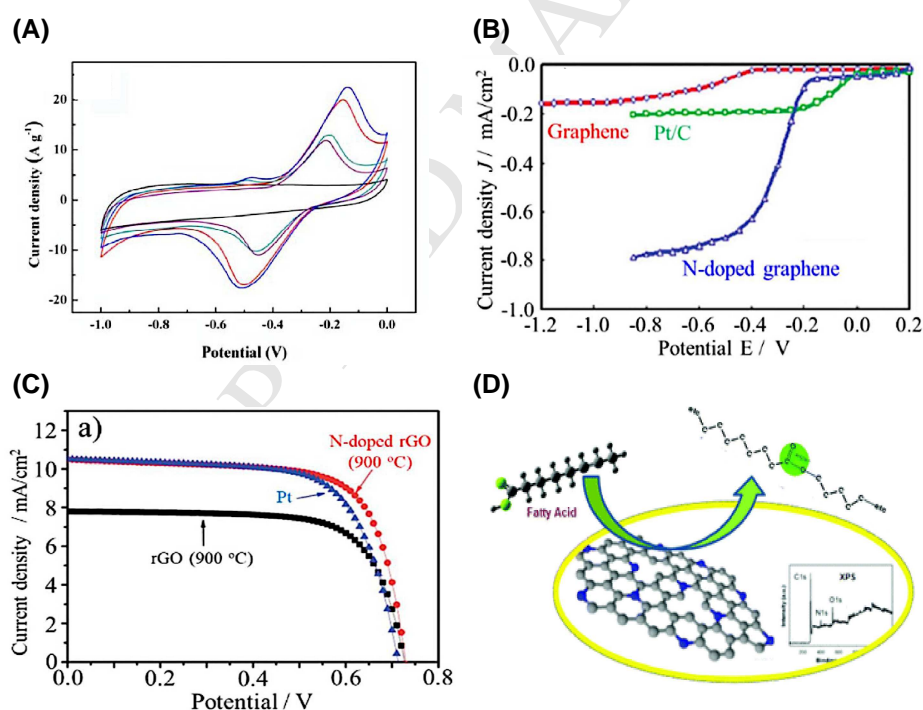


Figure 4. A glimpse of diverse applications of NNCs. (A) A cyclic voltammogram curve of nitrogen-doped carbon-coated thermally exfoliated graphene for the evaluation of supercapacitive performance in alkaline medium (Reprinted with permission from ref. [47]. Copyright 2015 Elsevier Ltd). (B) A comparison of ORR activity of graphene, N-doped graphene and Pt/C (Reprinted with permission from ref. [48]. Copyright 2010 American Chemical Society). (C) The plot of current density vs. potential to evaluate the performance of N-doped rGO in dye-sensitized solar cell (Reprinted with permission from ref.[49]. Copyright 2013 Royal Society of Chemistry). (D) N-doped rGO catalyzed esterification

of fatty acid using long chain alcohol (Reprinted with permission from ref [50]. Copyright 2016 Royal Society of Chemistry).

The development of *N*-doped nanocarbons mainly started to overcome some of the challenges related to non-nitrogenous variants of nanotubes and graphene-based nanomaterials.[10] Encouraged by the initial promises, this class of nanomaterials has been employed in almost every conceivable application where graphene and nanotubes have been used.[14] In some cases, this simple and subtle modification in an extended carbon network resulted into comparable (or sometimes better) activity than that of state-of-the-art precious-metal-based nanosystems. Because of the unique electronic properties of NNCs, their applications primarily include the electrical or electrochemical processes. Their potential as supercapacitor (Figure 4A) [16,47,51-58], anchors for Li-polysulfide in Li-S battery [59-62], electrode materials for Li-ion batteries [63-68], electrical storage devices [14,69-72], fuel cell catalysts [73] have indeed shown promises for the development of non-metal-based nanosystems. Recent studies have revealed the superior activity of NNCs (mostly supported by non-noble metal-based co-catalysts) in a variety of electrocatalytic reactions [74-89] such as Hydrogen Evolution Reaction (HER), Oxygen Evolution Reaction (OER), Oxygen Reduction Reaction (ORR) (Figure 4B) [48] etc. These nanocarbons have also been employed as sensors for the detection of several gases and other entities with high efficiency.[90,91]

Other than the electrochemical applications, several variants of *N*-doped-nanocarbons have been synthesized for environmental [92,93] and photocatalytic applications (Figure 4C).[49,94-98] For example, carbon-nitride and/or its derivatives can be effectively used as photocatalytic materials for environmental applications whereas the melamine-formaldehyde aerogel has been deployed as an absorbent for water vapor.[99] In another instance, Jain and co-workers reported a carbocatalytic esterification of fatty acid with long-chain alcohol using nitrogen-doped reduced graphene oxide as catalysts (Figure 4D) [50]. These nanomaterials have been infrequently documented for magnetic and biomedical applications [100] but significant efforts are still needed to gauge a clear outcome on their true potential.

Despite having immense potential for a range of applications, the fundamental knowledge between the activity and the different structural components remains a major hurdle to finally replace the non-sustainable choices and genuine efforts are being devoted to confront such issues.

Conclusions and Future Directions

It is undeniable that NNCs show noteworthy promises for the future development of metal-free nanocomposites. However, despite the sharp growth of the field within such a short span of time, it still requires significant efforts from the scientific community to overcome the some of the current challenges.

The synthetic strategies of this class of nanomaterials are primarily focused on the thermal carbonization of the precursor molecules. The limited knowledge about the mechanism of formation of the nanocarbons from its precursors and the concerns about the distribution of the different types of nitrogen in the carbon-skeleton confine the full potential of the synthetic processes. Additionally, the environmental and health impacts of such synthetic strategies have been overlooked till recently and from a sustainability aspect, these require special attention to ascertain of the overall greenness of high temperature synthetic procedures (preferably using more efficient alternative energy sources).

The knowledge about the origin of the activity of NNCs still is at the age of its infancy, mainly due to lack of background information. The significant advancement in instrumentation and computational methods is expected to build a better structure-property relationship, from which newer nanocarbons with novel structural features, properties (such as magnetism etc.) and their ideal applications can be predicted. Additionally, a favorable, compatible combination of other heteroatoms with nitrogen is other means to improve the present status of the applications but it demands more thorough and inter-disciplinary efforts from the research community.

The encouraging news is that both government and private sectors have identified the value of abundant and renewable carbon resources at an early stage and have

earnestly started to work in overcoming teething hurdles. Hopefully, these problems will be addressed successfully and the replacement of the industrial processes requiring precious metals by metal-free, sustainable, and greener processes comprising NNCs or other combination of hetero-atom-doped nanocarbons will be seen in near future.

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