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# Heteroatom-Doped Carbon Allotropes in Corrosion Protection

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***Abstract:*** *Heteroatom-doped carbon allotropes, characterized by the incorporation of non-carbon elements into their structures, have emerged as promising candidates for advanced corrosion protection. This explores the significance of heteroatom-doped carbon allotropes, such as nitrogen-doped graphene in revolutionizing corrosion inhibition techniques. These materials exhibit enhanced catalytic activity, improved barrier properties, and tailored surface reactivity, making them invaluable for inhibiting corrosive processes which is a ubiquitous challenge in materials science, and demands innovative strategies for effective protection. This article focuses on the mechanisms through which heteroatom-doped carbon allotropes provide corrosion protection, including barrier protection and cathodic protection, elucidating their fundamental role in hindering the corrosion process and also highlighting their applications in diverse industries, emphasizing their pivotal role in ensuring the durability and longevity of materials exposed to corrosive environments. The challenges and future prospects associated with these materials are also discussed, underscoring their potential to redefine the landscape of corrosion protection technologies.*

**Keywords:** *Heteroatom-doped carbon allotropes, corrosion protection, Nitrogen-doped graphene.*

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## 1.0 Introduction

Heteroatom-doped carbon materials (HDCMs) have been widely studied as some of the most prominent material candidates for use in a wide range of applications, such as batteries, and supercapacitors (SCs). Over the past few years, various metal-free heteroatom-doped carbon composites have been developed by integrating different heteroatoms into carbon with different nanostructures, from single-atom doping (N, P, B, S, *etc*.) to multiple heteroatom doping (N/P/S, N/S/B, *etc*.) (Eddy *et al*., 2009, 2010). By controlling the content and types of heteroatom-containing reagents, not only the physical and chemical properties of the material can be adjusted, but also the specific surface area and pore volume can be increased *via* controlling the morphology, thereby enhancing the electrochemical performance of the material (Feng, *et al* 2021). The potential use of diverse carbon nano allotropes in corrosion protection, prevention and control is a subject of rising attention (Aslam. *et al*., 2022). Corrosion is a high-cost and potentially hazardous issue in numerous industries. It is the gradual degradation of materials due to various environmental factors, poses a significant challenge to industries worldwide. In the field of corrosion, the study of solutions to prevent metal corrosion is an important task that requires scientists to focus on research. There are many different methods to retard and prevent metal corrosion such as designing materials to avoid corrosion, selecting suitable materials in each environment, protecting surfaces with coatings, electrochemical methods, and so forth. In particular, corrosion inhibitors are used in a low-cost way with high efficiency (Mobin *et al.,* 2017). As we continue to explore advanced materials and technologies, the focus has shifted towards finding innovative solutions to prevent corrosion. One such promising avenue involves the use of heteroatom-doped carbon allotropes, a cutting-edge field in material science. Heteroatom-doped carbons have been proven to be efficient, metal-free electrocatalysts, but can be also beneficially used in the manufacturing of carbon nanomaterials for energy applications (Antonietti and Oschatz., 2018). In recent years, heteroatom-incorporated specially structured metal-free carbon nanomaterials have drawn huge attention among researchers. (Chattopadhyay *et al.,* 2022). Heteroatom-doped carbon materials represent one of the most prominent families of materials that are used in energy-related applications, such as fuel cells, batteries, hydrogen storage or supercapacitors (Paraknowitsch *et* al., 2013). Carbon materials doped with heteroatoms are a class of cost-effective and stable electrocatalysts for oxygen reduction reactions (ORR), whose activities are mainly based on the heteroatom-related active sites. (Zhang *et a;.*, 2019). The emergence of carbon materials (i.e., activated carbon, graphite, fullerenes, carbon nanotubes, diamond, graphene, etc.) provides an excellent alternative to traditional catalysts. Considerable effort has been made to develop diverse carbon-based catalysts, including carbon in itself, heteroatom-doped carbon, carbon-supported catalysts, carbon hybrids, and so on (Zhai *et* al., 2015). Carbon allotropes, such as graphene, carbon nanotubes, and fullerenes, have unique structural and electronic properties. When these carbon materials are doped with heteroatoms like nitrogen, boron, sulfur, or phosphorus, their properties are further enhanced. Heteroatom doping introduces new electronic states, alters the surface chemistry, and enhances the material's affinity for specific reactions. These modifications are crucial in tailoring the material for specific applications, including corrosion protection. This article delves into the significance of heteroatom-doped carbon allotropes and their role in revolutionizing corrosion protection techniques..

## 2.0 The Role of Heteroatom-Doped Carbon Allotropes in Corrosion Inhibition

### *2.1 Enhanced catalytic activity*

Enhanced catalytic activity refers to the improved ability of a substance to facilitate or accelerate a chemical reaction without being consumed in the process. This enhancement is often achieved through modifications at the atomic or molecular level, such as doping carbon allotropes with heteroatoms like nitrogen, boron, sulfur, or phosphorus.

In the context of heteroatom-doped carbon allotropes, enhanced catalytic activity is a pivotal property. The presence of heteroatoms introduces new electronic states within the carbon lattice, creating active sites that promote specific reactions. These modified allotropes serve as catalysts in various processes, including corrosion protection.

For instance, nitrogen-doped graphene exhibits enhanced catalytic activity in corrosion inhibition reactions. It facilitates the electrochemical reactions that neutralize corrosive species, preventing them from interacting with the underlying metal surface. This enhanced catalytic activity contributes to the effectiveness of heteroatom-doped carbon allotropes as corrosion inhibitors, making them invaluable materials for protecting metals and alloys from degradation in corrosive environments.

### *2.2 Improved barrier properties*

Improved barrier properties refer to the enhanced ability of a material to act as a protective barrier, preventing the penetration of harmful substances such as corrosive agents, moisture, or gases. In the context of heteroatom-doped carbon allotropes, the incorporation of heteroatoms like nitrogen, boron, sulfur, or phosphorus results in modifications to the carbon lattice, leading to materials with superior barrier properties.

When these heteroatom-doped carbon allotropes are applied as coatings on metal surfaces, they form robust protective layers. These layers act as barriers, shielding the underlying metal from corrosive environments. The improved barrier properties arise from several factors, including increased surface roughness, altered surface energy, and enhanced adhesion to the metal substrate. Additionally, the presence of heteroatoms introduces specific chemical interactions that hinder the diffusion of corrosive species, further enhancing the material's barrier capabilities.

Heteroatom-doped carbon allotropes with improved barrier properties serve as highly effective corrosion protection materials, ensuring the longevity and durability of metal structures in various industrial applications.

These doped carbon materials form robust protective layers on metal surfaces, acting as a barrier against corrosive agents. The presence of heteroatoms enhances the adherence of the protective layer, ensuring prolonged protection against corrosion.

### *2.4 Tailored surface reactivity:*

Tailored surface reactivity refers to the deliberate modification of a material's surface properties to achieve specific chemical interactions or reactions with surrounding substances. In the context of heteroatom-doped carbon allotropes, such as nitrogen-doped graphene or boron-doped carbon nanotubes, tailored surface reactivity involves strategically introducing heteroatoms into the carbon lattice to create specific surface sites with unique chemical properties.

The presence of heteroatoms alters the surface reactivity of carbon allotropes, making them highly selective in their interactions with different molecules or ions. This tailored surface reactivity enables these materials to selectively adsorb or react with corrosive species, hindering their ability to interact with the underlying metal surface. By controlling the type and concentration of heteroatoms, researchers can customize the surface reactivity of these materials for optimal corrosion inhibition.

In practical terms, tailored surface reactivity in heteroatom-doped carbon allotropes ensures that they can effectively adsorb corrosive ions or molecules while allowing other desired reactions to take place. This selective reactivity enhances the material's ability to inhibit specific corrosion processes, making them valuable assets in corrosion protection applications. The introduction of heteroatoms alters the surface reactivity of carbon allotropes. This modification allows for selective adsorption of specific corrosive species, hindering their interaction with the underlying metal and preventing corrosion initiation.

## 3.0 *Materials and Methods*

In the field of corrosion protection, researchers have explored various heteroatom-doped carbon allotropes, each offering unique properties for inhibiting corrosion processes. Some key materials studied in this context include:

### *3.1.1 Nitrogen-Doped Graphene (N-graphene):*

Nitrogen (N) is a neighbouring element of carbon in the periodic table, and its electronegativity is larger than that of C (Wei *et al* 2015). The incorporation of the N atom into a graphene lattice plane could modulate the local electronic properties, as it could form strong bonds with carbon atoms because of its comparable atomic size with carbon. Subsequently, it could generate a delocalized conjugated system between the graphene π-system and the lone pair of electrons from N atom. The introduction of N into carbon nanomaterials could improve both reactivity and electrocatalytic performance. As a result, the N-doped carbon materials have been intensively studied among all the available heteroatoms for doping (Wei *et al* 2015). Nitrogen-doped graphene, often referred to as N-graphene is a modified form of graphene where nitrogen atoms are introduced into the hexagonal lattice structure of carbon atoms (Gong *et al* 2009). This process, known as nitrogen doping, involves substituting carbon atoms with nitrogen atoms, leading to the formation of specific nitrogen-carbon bonds within the graphene lattice

### *3.1.2 Properties of Nitrogen-Doped Graphene*

Nitrogen-doped graphene exhibits enhanced catalytic activity due to the introduction of nitrogen atoms, which create active sites on the graphene surface (Okamoto, 2009). These active sites can facilitate various chemical reactions, making N-graphene valuable in catalysis and electrocatalysis applications (Hu *et al* 2010). While nitrogen doping introduces heteroatoms, it does not significantly disrupt the overall conjugated structure of graphene. As a result, N-graphene maintains high electrical conductivity, making it suitable for applications in electronic devices, sensors, and energy storage systems (Sun *et al* 2012).

The type and concentration of nitrogen dopants can be controlled during synthesis, allowing researchers to tailor the electronic properties of N-graphene (Kundu *et al* 2009). The tunability is crucial for specific applications, such as in electronic devices where precise control over charge carrier density is required (Wang *et al* 2011).

Like pristine graphene, N-graphene possesses a high surface area, providing ample active sites for chemical interactions (Li *et al* 2011). This property is advantageous in adsorption processes, catalysis, and as a support material for various catalysts. Nitrogen-doped graphene is used in corrosion protection applications due to its enhanced catalytic activity and ability to adsorb corrosive species. It can neutralize corrosive agents, preventing them from reaching the metal surface and inhibiting the corrosion process (Qiu, *et al* 2013). N-graphene exhibits biocompatibility, making it suitable for biomedical applications such as drug delivery, biosensing, and imaging. Its unique properties and surface reactivity enable targeted interactions with biological molecules (Wiggins and Stevenson, 2011).

### *3.1.3 Applications in Various Industries*

- **(i) Oil and Gas Industry:** Heteroatom-doped carbon allotropes find applications in pipelines and storage tanks, safeguarding them against corrosion induced by harsh chemicals and moisture.
- **(ii) Aerospace Industry:** Components of aircraft and spacecraft are susceptible to corrosion due to exposure to varying atmospheric conditions. Heteroatom-doped carbon materials provide lightweight, durable, and efficient corrosion protection solutions.
- **(iii) Automotive Sector:** Heteroatom-doped carbon coatings are used in automotive parts, offering resistance against corrosion caused by road salts, moisture, and pollutants.

**Table 1: Review of some literature on the application of carbon—doped materials as corrosion inhibitors**

| Inhibitor | Materials | Inhibition efficiency (%) | Reference |
|---|---|---|---|
| **N-dopped and N.S-codoped carbon dots** | Carbon steel | 96.40 | Ren *et al*., 2023 |
| **N-dopped carbon dots** | Steel | 90.32 | Liu *et al*., (2020) |
| **Dopamine dopped carbon dots** | Carbon steel | 92.70 | Cui *et al*. (2021) |
| **S-dopped carbon dots** | Steel | 90.00 | Lei *et al*. (2023) |
| **P-dopped carbon quantum dots** | Iron | 17.74 | Shu- *et al*.(2021) |
| **NB-dopped carbonnanodots** | Carbon steel | 35.00 | Velusamy *et al*. (2021) |
| **N,Fe-dopped carbon dots** | iron | 27.00 | Wang *et al*. (2016) |

## 4.0`Conclusion

In conclusion, Heteroatom-doped carbon allotropes represent a groundbreaking approach in the field of corrosion protection. Their unique properties, including enhanced catalytic activity, improved barrier properties, and tailored surface reactivity, make them invaluable assets in the battle against corrosion. As research continues to progress, these materials hold the key to developing advanced, efficient, and sustainable corrosion protection technologies, ensuring the longevity and reliability of various industrial applications.

The intentional introduction of elements like nitrogen, boron, sulfur, or phosphorus into carbon structures has unlocked a realm of possibilities, revolutionizing our approach to safeguarding materials from corrosive environments.

These modified carbon allotropes, with their enhanced catalytic activity, improved barrier properties, and tailored surface reactivity, offer unprecedented advantages in inhibiting corrosion processes. Their ability to neutralize corrosive species, form robust protective layers, and selectively adsorb specific molecules has paved the way for innovative and efficient corrosion protection technologies. From applications in the oil and gas industry, aerospace sector, and automotive manufacturing, to various other industrial domains, heteroatom-doped carbon allotropes have proven their mettle. They not only enhance the longevity and durability of materials but also contribute to sustainable practices through their eco-friendly nature. As research endeavors continue, focusing on optimization, scalability, and exploring novel combinations, the future of corrosion protection appears promising. With these advanced materials at our disposal, we are not just combating corrosion; we are ushering in a new era of resilient, durable, and environmentally conscious infrastructure and industrial applications. Heteroatom-doped carbon allotropes have indeed become the vanguard in our battle against the relentless forces of corrosion, shaping a future where materials stand strong against the test of time.

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**Compliance with Ethical Standards Declarations**

The authors declare that they have no conflict of interest.

**Data availability**

All data used in this study will be readily available to the public.

**Consent for publication**

Not Applicable

**Availability of data and materials**

The publisher has the right to make the data Public.

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**Authors' contributions**

Elizabeth Chinyere Nwaokorongwu (ECN) designed the work. Conceptualization and methodology. ECN and Greatman Mkpuruoma Onwunyiriuwa (GMA) were involved in the writing of the original draft, editing, proofreading and manuscript handling. ECN and Greatman Mkpuruoma Onwunyiriuwa (AEE) were involved in the supervision: Supervision initial corrections. All the authors read and approved the final manuscript.