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Chapter

Construction of Heteroatom-Doped Porous Carbon Architectures for Energy and Sensing Applications

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Abstract

In this chapter, we have concentrated on the main electrocatalytic oxygen processes, oxygen reduction reaction (ORR) and water splitting oxygen evolution reaction (OER), and biosensors based on porous carbon architectures, which are more important areas of research because of the rise in demand for energy management, supply, and disease diagnosis. Heteroatom-doped carbon hollow spheres are very useful because they have a large surface area, mesoporosity, spherical wall thicknesses, edge plane defect sites, catalytic active sites, and fast heterogeneous electron-transfer rates. These properties are very important for making commercial devices. This chapter provides an overview of hollow carbon nanospheres that are doped with single and double heteroatoms, as well as cobalt oxide. These carbon compounds function as dual catalysts for OER and ORR, as well as an effective electrocatalyst for the oxygen reduction process in both acidic and alkaline media. Electrocatalytically, heteroatom-doped carbon sphere-modified electrodes can simultaneously and specifically identify and determine the analytes, while also validating the target species in real samples. N-doped hollow carbon spheres coated-Co_3O_4 functioned as an efficient dual-function oxygen electrocatalyst for oxygen evolution and oxygen reduction processes and also as a biosensor for highly effective electrochemical sensing of acetaminophen. A symmetric supercapacitor using dual heteroatom-doped and SBA-15 templated porous carbon was also discussed.

Keywords: ORR, OER, heteroatoms, porous carbon spheres, biosensors

1. Introduction

Fossil fuels currently provide the majority of the world's energy needs, and as their sources continue to be depleted, a global energy deficit is becoming a major issue. Carbon-releasing fossil fuels, which are in finite supply, are the primary contributor to greenhouse gas emissions (GHGs), and other dangerous gas emissions, which are the primary causes of climate change and global warming. The constant use of fossil

fuels also pollutes the ecosystem. Environmental pollution and global warming pose a hazard to us and other living things [1, 2]. Due to the depletion of fossil fuels, devices based on renewable energy from sources, such as solar, water, wind, and tidal, will be the ideal options to meet the energy demand as a clean energy source. The scientific community is currently working to create new technologies and devices based on new renewable energy-based technologies to address the world's energy demand and reduce CO_2 emissions, which contribute to global warming [3, 4]. Electrochemistry will play an essential role in energy storage, power generation, bio- and environmental sensors, and the continuous monitoring of human life support [5, 6]. Among many technologies, electrochemical storage systems, such as batteries, fuel cells, and photo-electrolyzers, play an important role since they are effective at ambient temperatures and pressures. Extensive research efforts are being made to construct robust electrochemical systems with high energy density [7]. In electrochemical energy systems, oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), and hydrogen oxidation reaction (HOR) are the four key chemical reactions that are responsible for the crucial technological processes for the development of environmentally friendly and sustainable energy systems [8]. OER and ORR reactions, which are oxygen-based oxidation and reduction reactions, need a high applied voltage to overcome the energy barrier since they have greater overpotentials. The energy barrier of these OER and ORR reactions can be achieved at low overpotentials by electrocatalysts. Noble metal-based electrocatalysts are frequently employed to catalyze ORR and OER; however, they have a number of disadvantages, including low storage capacity and high cost. Consequently, the development of durable, selective, and highly effective low-cost electrocatalysts in difficult environments, such as acidic media, is highly desirable and preferable [9]. Theoretical simulations predict that the catalysts should effectively bind oxygen, and transition metal oxide catalysts may be used as a substitute for precious metal-based catalysts, which have free d orbitals that are easily able to bind oxygen. Transition metal oxides other than platinum group metals are cheap materials.

Because of this, transition metal oxides are thought of as a substitute for conventional precious metal oxygen electrocatalysts [10]. However, a number of challenges remain in the development of oxide catalysts for the processes of oxygen evolution and reduction, including those pertaining to catalytic activity, stability, cost, and reaction mechanism. However, OER/ORR catalysts are still less efficient for practical applications due to their sluggish reaction kinetics, and the challenging nature of multielectron transfer processes [10]. Metal-air batteries (MABs) are charged and discharged *via* OER and ORR, and the effectiveness of the catalysts plays a major role in these electrode reactions. Expensive catalysts, such as Pt (ORR), RuO_2, and IrO_2, are utilized in commercial MABs (OER). The electrode process in MABs is more costly and challenging because two distinct catalysts are used for these reactions. Thus, the development of catalysts based on non-precious transition metals that can catalyze oxygen evolution and oxygen reduction processes (OER/ORR) simultaneously is an emerging area in metal-air batteries, fuel cells, and energy storage systems [11].

Energy from fossil fuels, the environment, and health are interconnected, and burning fossil fuels, coal, and biomass causes air pollution, and other issues that have an impact on human health, including their respiratory and cardiovascular systems, are linked to a variety of health conditions. Access to clean and sustainable energy is vital to protecting human health. Biosensors can be used for continuous health condition monitoring [12–14]. The analysis of biomolecules, which are the body's main building blocks and essential for metabolism and many other biological processes

in all living things, is also important. Important biomolecules, including dopamine (DA), ascorbic acid (AA), and uric acid (UA), coexist with biological networks and are the cause of several physiological processes in the human body [15]. Dopamine (DM), one of the essential neurotransmitters, is present in the extracellular fluid surrounding the brain's nucleus, and dopamine imbalance is linked to a number of diseases [15]. Biosensors are capable of detecting the target molecules with high specificity, precision, and signal-to-noise ratio, which aids in the diagnosis, progression, and monitoring of patient therapy for diseases. Compared to conventional analytical tools, electrochemical biosensors are promising tools to provide immediate responses to challenging conditions, making them an intriguing and promising class of analytical tools [16]. Therefore, it is highly preferable to construct target-specific and robust biosensors using inexpensive materials. The electrochemical sensing of target analytes can be demonstrated to be more sensitive and selective by integrating robust, specifically built probes on electrodes. Enzymes, metal complexes, metal nanoparticles, polymers, core-shell structures, and porous carbon-based materials are just a few of the materials that have been utilized to detect target molecules thus far [17, 18].

A variety of materials based on metal and polymers have been used to perform ORR and OER and also act as active probes in biosensors [19, 20]. Currently, carbon-based materials, particularly 3D hollow mesoporous carbon sphere (HMCS) materials, are quite popular because they have distinctive properties, including hollow structures with a high graphitic degree and surface area, as well as rich active sites [21]. The forementioned characteristics are thought to enhance the mass transfer, conductivity, and chemical stability of HMCS materials. The hollow mesoporous carbon sphere (HCS) is important for ORR studies [21] because it has a great shape, a lot of mesopores, a high hierarchical surface area (2000 m^2/g), and good electrical conductivity. HMCS and heteroatom-doped HMCS have been used as catalytic active sites in electrochemical biosensors. The HMCS electrode with N doping displayed exceptional sensitivity to UA, AA, AC, and DA. In this chapter, we discuss porous carbon and heteroatom-doped porous carbon materials that are utilized for electrocatalytic ORR and OER processes, as well as the construction of biosensors for the detection of UA, AA, AC, and DA.

2. Oxygen reduction and oxygen evolution reactions (ORR/OER)

The study of the fundamentals and mechanisms of the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) at different applied electrode potentials is essential for designing the electrocatalysts.

2.1 Oxygen reduction reaction (ORR)

Numerous electrochemical energy conversion and storage techniques take advantage of the oxygen reduction process (ORR) [22, 23]. It is a multistep reaction that involves four electron transfers and is electrochemically slow. Oxygen (O_2) is first diffused toward the catalyst, and then O_2 molecules are adsorbed on the catalyst's active sites. Electrons are then transferred to the adsorbed O_2 molecules, and the reaction is then initiated. In the end, it is transformed into products and removed from the catalyst's active sites. The only catalysts that have proven to be significantly active and durable in acidic environments are those based on platinum, but these are costly. Silver-based catalysts, metal oxides, and nanostructured carbons are

examples of non-platinum catalyst alternatives that make the ORR process in alkaline as an easy process. The ORR can also undergo a two-electron reduction process and yield hydrogen peroxide. While hydrogen peroxide only requires the transfer of two electrons per oxygen molecule, whereas water requires the transfer of four electrons, this electrochemical reaction is beneficial because it has the potential to replace the energy-intensive anthraquinone process, which is currently used to synthesize hydrogen peroxide on an industrial scale [24].

2.2 Oxygen evolution reaction (OER)

The water oxidation or oxygen evolution reaction, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, is the corresponding anodic half reaction in an electrochemical water splitting system and the core electrochemical reaction in a fuel cell [25]. The oxygen evolution reaction takes place at a higher positive overpotential than ORR. It is a multistep electron transfer reaction that necessitates a significant excess potential since each step necessitates additional energy to get beyond the energy barrier, which drags total kinetics. Furthermore, each oxygen molecule needs to undergo four proton and electron exchanges during the OER, making it the more complex of the two half processes. It thereby explains most of the inefficiency of the device. In acidic environments, significant OER activity and stability have only been shown by Ir-based catalysts. Several first-row transition metal oxides show significant OER activity in alkaline media [26].

2.3 Carbon-based electrocatalyst for ORR and OER

From both an academic and an industrial perspective, the development of innovative, affordable, and effective catalytic systems is always an indispensable subject for catalysis. In this regard, low-cost, widely-available, stable, and environmentally benign carbon-based materials, such as activated carbon (ACs), graphene oxide (GO), carbon nanotubes (CNTs), ordered mesoporous carbon (OMCs), etc. have drawn considerable interest in the field of heterogeneous catalysis [27]. Because of their large surface area, high pore/volume ratio, high electrical conductivity, and porous carbons exhibit superior electrocatalytic activity compared to other carbon-based materials.

2.4 Three-dimensional hollow mesoporous carbon and heteroatom-doped carbon spheres

Porous materials are important and highly sought-after materials due to their unique characteristics and numerous applications. The three types of porous materials are: macroporous (d > 50 nm)), mesoporous (2 < d < 50 nm), and microporous (d < 2 nm). Mesoporous carbon materials are very useful and desirable for many uses because they have a large specific surface area, great electrochemical stability, excellent electrical conductivity, a huge amount of pores, and the ability to change the size and shape of the pores. In this case, hollow carbon spheres (HCSs) and functionalized hollow carbon spheres got a lot of attention because they have amazing physical and chemical properties, such as being very stable at high temperatures and chemicals, having a well-ordered porous structure, having a high surface-to-volume ratio, being able to conduct ions and electrons, and moving and diffusing mass better than other materials. Owing to these unique characteristics, well-ordered carbon spheres find a

wide range of applications such as heterogeneous catalysis, fuel cells, supercapacitors, energy storage batteries, and the detection of biological and environmentally relevant analytes [21, 28]. The synergetic and anisotropic properties can be induced by doping heteroatoms with carbon spheres, and these interesting materials exhibit enhanced responses in batteries, supercapacitors, water splitting reactions, and biosensors.

Substantial effort has been made to synthesize HCSs by different methods in order to ensure specific shell thickness from the outer and inner diameters, mesoporosity of the carbon shell, and dispersibility in the appropriate media, all of which have a significant influence on the applications of these HCSs. By adding organic or inorganic moieties to the porous structure, these HCSs' characteristics and functionality can be altered. Because of their differing electronegativity, heteroatom doping, the process of substituting some carbon atoms in the ordered graphitic carbon materials with other external elements such as boron, nitrogen, sulfur, phosphorus, and which cause electron modulation in the HCSs. These catalysts have better catalytic activity in several electrode processes, such as ORR and OER as compared to pure carbon catalysts (**Figure 1**).

Some of the common techniques followed for the synthesis of HCSs are hydrothermal carbonization, pyrolysis, chemical vapor deposition, and the Stöber method. In hydrothermal carbonization-based preparation of monodispersed carbon spheres, dehydration, condensation, polymerization, and aromatization steps are involved. In the pyrolysis, gaseous or liquid precursors are pumped through a hole and burned at a high temperature. Chemical vapour deposition (CVD) is used for the creation of solid carbon sphere thin films on flat substrates, where usually mesoporous membranes as templates are employed. The Stöber method is an efficient method to synthesize homogeneous monodisperse polymer colloidal particles and carbon spheres from silica–polymer composites [21].

Typically, templating procedures are used to prepare heteroatom-doped HCSs and HCSs. Based on the types of templates used to obtain heteroatom-doped HCSs and HCSs, two well-known templating techniques, *viz.*, hard-templating and soft-templating approaches, are followed. The hard templating approach is the common method followed for synthesizing HCSs, where rigid particles are used as hard templates and sacrificed after the formation of a mesoporous carbon framework (**Figure 2**).
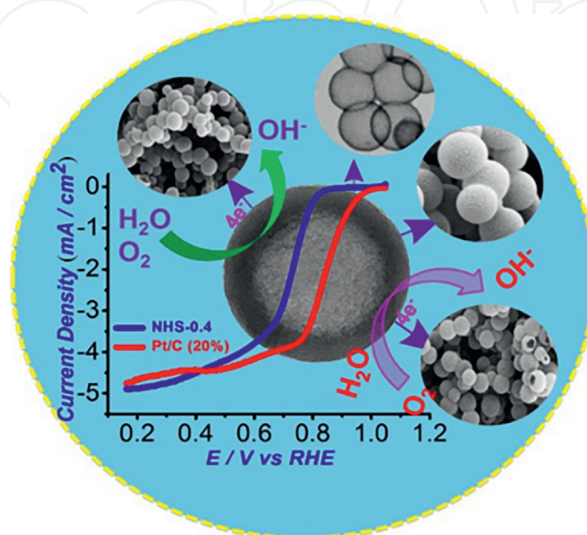

Figure 1.
Electrocatalytic reduction of oxygen by the N-doped hollow carbon spheres in an alkaline electrolyte medium.

Several steps are involved in the hard template method: (a) initial step is the synthesis of hard template materials, (b) the intermediate composite is formed by mixing the hard template materials with the carbon precursor, (c) the carbonization of the intermediate composite under an inert atmosphere, and (d) the final step is the removal of the hard template, which sacrificed by thermal treatment or etching with acid and base after the formation of the carbon shell. The generally used hard templates are silica spheres and polymer spheres such as polystyrene (PS), resin polymer (RF), Poly(methyl methacrylate) (PMMA), and zeolites. Various organic compounds are used as carbon precursors, for example, glucose, phenolic compounds, aniline, dopamine, etc. By hard templating, the product can be controlled, but it is difficult to remove the template. In the soft-templating method, HCSs are obtained by the cooperative assembly of precursor moieties and amphiphilic surfactant molecules. Here, porosity is produced once surfactants are removed by high-temperature calcination. In the soft-template approach, HCSs can be obtained by an organic-organic assembly in which surfactants, emulsion droplets, and micelles are used as soft templates (**Figure 3**) [29].

In order to successfully synthesize porous carbon compounds, there are four pre-requirements. (A) At the outset, precursors of the soft template should assemble themselves to form nanostructures. (B) combination of self-assembled soft templates with carbon precursor and formation of precursor composite. (C) Carbonization of the precursor composite, where the soft templates should be able to withstand the temperature at which carbon forms and should consequently disintegrate quickly during the carbonization period. (D) During the carbonization process, the last stage of thermosetting the carbon precursors should be finished before the temperature at which soft templates decompose. In the case of soft templating, it is hard to control the morphology of the end product but easy to remove the template materials. Two routes are followed to prepare heteroatom-doped HCSs; either posttreatment of heteroatom-containing precursors with preformed carbon nanomaterials or *in situ* doping during the preparation of nanoporous carbon materials. The *in situ* doping of heteroatoms can aid in the homogenous integration of the heteroatoms throughout the entire nanoporous carbon matrix, whereas the posttreatment process frequently results in only surface functionalization without changing their bulk properties [29].
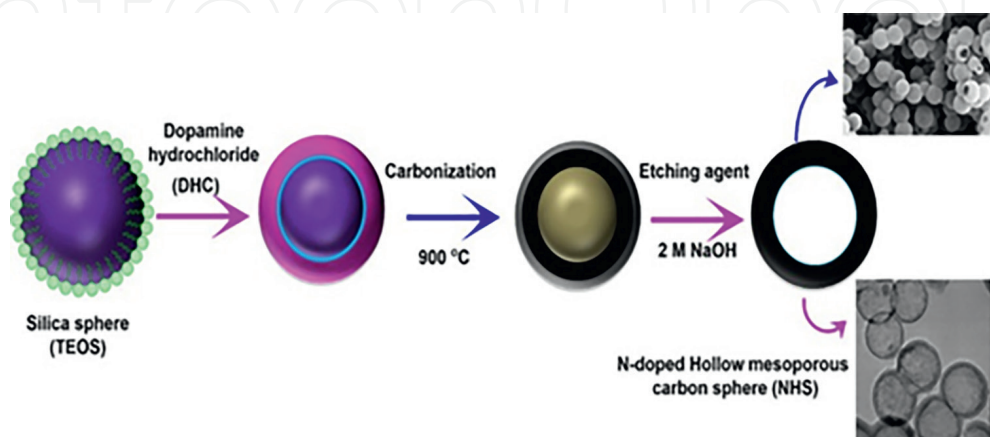

Figure 2.
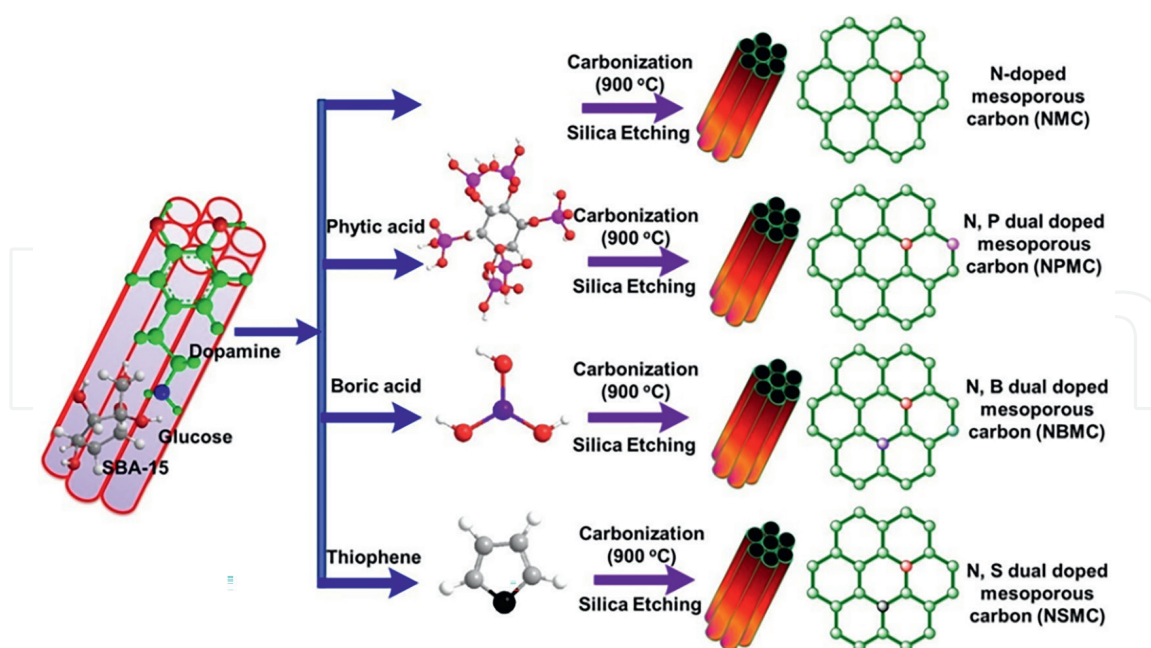*Synthesis N-doped hollow mesoporous carbon spheres.*

Figure 3.
Schematic representation of secondary heteroatoms doped nitrogen-doped carbon nanospheres NPMC, NBMC, and NSMC.

3. Biosensors

The detection of biological and environmentally relevant harmful or interesting molecules is highly desired to prevent their toxic effects, cure disease at an early stage, or protect the environment. A biosensor is an analytical tool that can detect target molecules or their interactions with a variety of sensing materials, ranging from biomolecules to nanomaterials. It has been thoroughly and intensively studied over the last few decades [30, 31]. Biomolecules, biological structures, and microorganisms are examples of biological analytes. Biosensors are devices that are used to monitor the concentration or presence of these substances. A biosensor consists of three parts: a signal transducer, which produces a signal, a reading device, and a part that uses particular binding to detect the analyte, such as chemicals or hazardous biomolecules.

Previous studies on biosensors based on biomolecules have some significant drawbacks, including unstable biomolecular reactions, low sensitivity, and low electrochemical signal intensity [32]. To facilitate the electron transfer reaction between electrodes and the biomolecules with biomolecular activity, several materials, such as conducting polymers and porous materials, were introduced. Nonenzymatic sensing has gained attention to overcome the limitations of enzymatic biosensors. Biosensors based on metal-based materials, or nanomaterials, are designed and reported to detect various analytes. Nonenzymatic sensing is more affordable and long-lasting than enzymatic electrochemical sensing, but it also has a lot of drawbacks, such as a high working potential, slow electrode kinetics, intermediate species poisoning, and poor sensing parameters. Hence, there is a high demand to design and construct target-specific and highly sensitive biosensors with low potential to achieve a commercial solution.

3.1 Porous carbon-based biosensors

To date, a wide range of materials, including porous carbon materials, core-shell structures, polymers, and metal nanoparticles, have been used to detect target analytes. Porous carbon-based materials have gained popularity recently because of their unique properties, such as hollow structures with a high graphitic degree and surface area, as well as an abundance of active sites. This is particularly the case for 3D hollow mesoporous carbon sphere (HMCS) materials [33]. The mesoporous carbons derived from hard mesoporous silica templates feature pore volumes of up to 3.0 cm^3 g^{-1}, tunable pore widths, and surface areas exceeding 2000 m^2 g^{-1}. Due to their exceptional surface area and pore volume, they facilitate the mass transfer processes and conductivity of HMCS materials. Large cavities in the HMCS materials also offer additional room for structural functionalization, which may result in enhanced catalytic activity. In recent years, heteroatom doping techniques have been applied to improve electrochemical sensing as they provide great approaches to boost the conductivity, catalytic active sites, and edge plane defect sites of HMCS materials.

When compared with the undoped and hetero-doped carbon materials, the heteroatoms induce more electrochemically active sites that can facilitate the adsorption and activation of analytes or molecules. Doped heteroatoms can provide electrochemically active sites, and they can also speed up the charge transfer between the electrode and the analyte or electrolyte by activating or adsorbing analytes or molecules. These two factors can lead to improved electrochemical sensing performance. Due to the electron donor nature of heteroatoms, which contribute a negative charge to the delocalized π bond of the sp^2 hybridized carbon skeleton and modify the electron distribution, heteroatom doping modifies the electrical characteristics and chemical reactivity of carbon [27]. Furthermore, the elements C, N, O, and P function as active sites in heteroatom-doped carbon material. These elements lead to non-covalent interactions, such as H-bonding and Van der Walls between the analyte and modified carbon surface, which increase the catalytic activity [21].

For instance, to determine L-tryptophan (Trp), Zhang et al. built a NOMC/Nafion/GCE electrode using N-doped OMC (NOMC; surface area 804 m^2 g^{-1}) containing 3.62% of N. In contrast to Nafion/GCE, CNTs/Nafion/GCE, and VX-72/Nafion/GCE, among other reference electrodes, the NOMC/Nafion/GCE sensor has
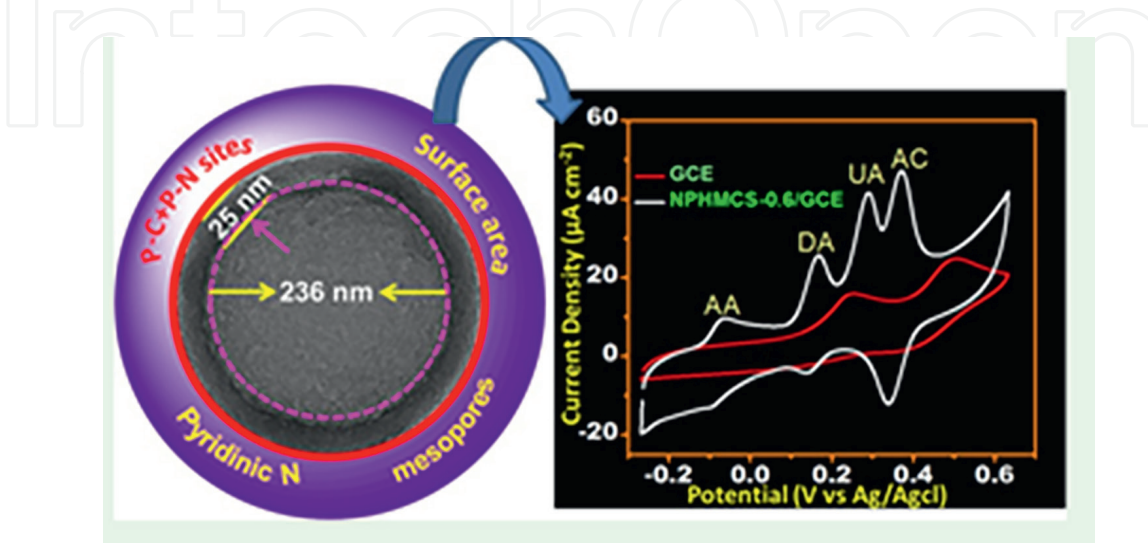

Figure 4.
Electrochemical sensing of DA, AC, and UA by N, P doped-hollow mesoporous carbon spheres.

shown comparatively better responses for Trp detection. The NOMC/Nafion/GCE biosensor offers a low detection limit of 35.0 nM, great selectivity, outstanding stability, high sensitivity, and a wide linear response range of 0.5–70 μM and 70–200 μM. NOMC has a greater specific surface area than the other reference materials, VX-72, and CNTs, with specific surface areas of 804.0, 251.5, and 132.9 $m^2 g^{-1}$, respectively (**Figure 4**) [34].

4. Oxygen reduction reaction by N-doped hollow mesoporous carbon nanospheres (NHSs)

It is highly desirable to substitute precious metal catalysts containing Pt and Pd with cheap, earth-abundant, highly concentrated pyridinic, and graphitic-N sites for the oxygen reduction reaction (ORR) [35]. In general, lower ORR activity and selectivity result from the intrinsically weak interaction between pristine carbon materials and oxygen-containing intermediates. Heteroatom doping is a promising technique to selectively customize the ORR process by regulating the binding energy through modification of carbon materials' electronic structure. When it comes to N-doped carbon catalysts, the highly electronegative N atoms can usually modify the π-conjugated system inside the carbon framework. This results in a charge redistribution that influences the energy of intermediate adsorption, selectivity, and ORR activity [36]. Usually, the doped N atoms are found as graphitic N, pyridinic N, pyrrolic N, and N oxides. Two of them have been extensively considered as the active sites of the ORR process: pyridinic and graphitic N [37]. Graphitic N is thought to play a major role in increasing catalytic activity, whereas pyridinic N is involved in changing the two-electron ORR mechanism into a four-electron one.

The selectivity toward a four-electron pathway is significantly influenced by the makeup of the graphitic N/pyridinic N site. Preferential desorption may occur before the complete reduction of oxygen by four electrons to H_2O due to insufficient adsorption of *OOH or H_2O_2 intermediates on the pure graphitic N-doped or pyridinic N-doped graphene cluster models. Because of the more stable formation of H_2O_2 than O_2 adsorption on the graphitic N site, Contreras et al. observed that an increase in graphitic N proportion in N-doped carbon nanotubes shifts the ORR onset potential toward the positive side due to the more stable formation of H_2O_2 by the dominant two-electron ORR pathway with a higher graphitic N content than O_2 adsorption on the graphitic N site [38].

In ORR investigations, hollow mesoporous carbon spheres (HCS) and heteroatoms doped with mesoporous carbon spheres (NCS) are attractive materials. It has a high number of mesopores, a hierarchical surface area (2000 m^2/g), well-shaped, and has great electrical conductivity. Edge doping of N on HCS is one of the best ways to enhance the amount of pyridinic and graphitic N, along with a large surface area [39]. The edges of the NHS structure contain pyridinic-N, which adsorbs oxygen species and enhances the reaction's kinetics, both of which would increase the ORR's positive onset potential. Simultaneously, the edges' graphitic-N improves electrical conductivity and provides a good limiting current density value.

Zhang et al. [40] reported N-doped mesoporous biomass carbon spheres with different surface areas, pore sizes, N-contents, and demonstrated catalytic ORR. They derived N-doped mesoporous biomass carbons from chitosan, which acted as a precursor for both carbon and nitrogen with different pore-forming agents, TiO_2, and iron nitrate. Three different porous carbon materials, NC-1, NC-2, and NC-3 with

surface areas of 602, 743, and 1190 m^2/g respectively, were prepared with the addition of no TiO$_2$ for NC-1, TiO$_2$ for NC-2, and iron nitrate for NC-3. Pour volumes, 2.3, 4.3, and 4.2 nm, were observed for NC-1, NC-2, and NC-3, respectively. Among the three materials, NC-3 contains the highest N atomic ratio and a high content of pyridinic-N (100%). In NC-2, only graphitic Ns are presented, and in the NC-1, more graphitic N as the main content, pyridinic N, and pyrrolic N are presented. NC-3 shows outstanding activity toward ORR in alkaline solution (4.6 mA/cm^2) compared to the other two catalysts. The enhancement of electrochemical activity of NC-3 may be due to its high surface area (1190 m^2/g) and higher pyridinic-N content (100%). Pyridinic nitrogens can be responsible for the oxygen reduction reaction (ORR) and more efficiently catalyze ORR *via* the four-electron reaction pathway.

Both soft and hard template procedures are used to prepare the majority of HCSs. As of right now, the most popular carbon and nitrogen precursors are polyaniline, acetonitrile, melamine, and phenylenediamine [21, 27]. Dopamine hydrochloride (DHC) has amine and catechol functional groups, making it one of the finest starting materials for synthesizing stable HCS. Tetraethyl orthosilicate (TEOS) easily hydrolyzes to generate Si − O − Si polymer linkages, it is an effective silica sphere structure-forming agent [41]. Hadidi et al. [42] reported a spherical nitrogen-doped hollow mesoporous carbon material that was prepared by a two-step method and had significant bifunctional ORR and OER activities. In the first step, the Stöber method was used to derive the silica templates (diameter = 170 nm ± 10%) using tetraethoxysilane (TEOS) and ammonium hydroxide sol-gel. The desired NCSs were obtained from the carbonization of a polymer composite of silica particles coated-dopamine and the triblock copolymer PEO-PPO-PEO (F127) upon heating at 400°C and at 800°C for 2 and 3 h in Ar, respectively. The NCSs have good ORR activity, which is influenced by NCSs prepared at different carbonization temperatures. Xing et al. [43] reported on N-doped hollow spheres with a large surface area, meso- and micropore volume, and N-content at different carbonization temperatures of 800–950°C. Dopamine was the precursor for nitrogen and carbon. The 950°C-activated sample has very high pyridinic and graphitic N groups with the greatest surface area (2072 m^2 g^{-1}), pore volume (1.96 cm^3 g^{-1}), hollow macropore cores (91 nm), and hierarchical micro-mesopore distributions (1.2, 2.6, and 6.2 nm) [43].

It is possible to obtain hollow carbon with a regulated morphology, a large surface area, a high pore volume, and a high pyridinic and graphitic N-ratio by varying the DHC precursor concentration and the carbonization temperature. N-doped hollow mesoporous carbon spheres (NHSs) were produced utilizing the carbon precursor dopamine hydrochloride (DHC) and tetraethyl orthosilicate (TEOS), as reported by Velu et al. [44]. This synthesis technique yielded uniformly sized, hollow, and spherical mesopores. A large surface area of 1452 m^2/g of material is formed at 900°C when a concentration ratio of 0.5 mL TEOS to 0.4 g DHC is utilized. This carbon material also possesses a significant pore volume of 0.3 cm^3/g. The significant presence of graphitic and pyridinic nitrogens and the enrichment of defect sites are the reasons for the remarkable oxygen reduction (ORR) activity in an alkaline medium. Additional electrochemical investigations revealed a four-electron mechanism at onset potential 0.84 V with a Tafel slope of 65 mV/dec and an exceptional current density of 4.9 mA/cm^2. Velu et al. [45] synthesized N-doped mesoporous carbon sheets with a large surface area and significant microporosity from DA and TEOS and investigated their oxygen reduction in basic pH medium.

In the first step, silica and polydopamine (PDA) are combined to form a composite material. This material then goes through a carbonization process, and the necessary

carbon material is extracted by silica etching the composite. N-doped mesoporous carbon sheets (NCS-1.0) were formed as a result of non-covalent interactions in the trimer of (DA)2-dihydroxyindole (DHI)-silica. This material displayed significant properties, including a large 1068 m^2/g surface area, 0.706 cm^3/g pore volume, and a layer thickness of 43 nm. The NCS-1.0 material demonstrated a remarkable oxygen reduction reaction because of its high density of graphitic and pyridinic nitrogen sites (ORR). The NCS-1.0 material exhibited a remarkable current density of 4.3 mA cm^{-2} at an onset potential of 0.88 V. The four-electron route is encouraged by the NCS-1.0's favorable combination of physical and electrochemical characteristics, which also allows for long-term stability and strong tolerance to methanol.

4.1 Oxygen reduction reaction by secondary heteroatoms doping on nitrogen-doped carbon nanospheres

The catalytic activity and electrical properties of the doped material are greatly improved by the addition of heteroatoms to carbon. N-doping is the most sophisticated procedure when compared to the other heteroatom doping techniques. When compared to Pt-based materials, single N doping still has a number of problems in attaining superior ORR activity [45]. The dual and tri-doping of heteroatoms in the mesoporous carbon (MC) structure is one tactical approach to this problem. This can result in remarkable activity since the doping increases the defect and active sites, as well as synergistic effects. Secondary heteroatom doping of N-doped MCs (NMC) with phosphorus (P), boron (B), and sulfur (S) is an ideal option to fine-tune the chemical and electrical properties [45]. Because P atoms are larger than N and C atoms, P doping in the carbon framework will project out of the plane and promote enhancement in activity. In the case of B doping, the adsorption of intermediate species of negatively charged oxygen through the B^+ active sites will increase the ORR kinetics as the electronegativity of B is lower than that of C. S doping in the C structure can increase activity due to the S and C atoms' unequal electronegativity, lack of polarization, and imbalance.

Zhang et al. [46] reported on the dual N- and P-doped mesoporous carbon (NPMC) material and its ORR activity in 0.1 M KOH. Comparing the mesoporous carbon materials (N, P-MC, and N-MC), the N. P-doped and N-doped carbon materials, showed significantly larger surface areas (305 and 300 $m^2 \, g^{-1}$, respectively), which facilitate the easy diffusion of reactants and electrolytes (68 and 31 $m^2 \, g^{-1}$, respectively). The N, P-MC material-modified electrode demonstrated excellent ORR activity at 0.84 V ($E_{1/2}$) with a diffusion-limited current density (J_d) of 5.0 mA cm^{-2}. These results were comparable to those of the conventional Pt/C electrode (E1/2 = 0.84 V and Jd = 5.0 mA cm^{-2}). They demonstrated that the active sites rendered by nitrogen of pyridinic groups and P-C bonds are responsible for better catalytic performance. The synergistic interaction between heteroatoms N and P, N and S atoms, and N and B atoms exhibits exceptional ORR activity, which is proven from N and P dual-doped graphene/carbon nanosheets and N and B-doped carbon. The results of these studies unequivocally show that tactics centered on the doping of dual-heteroatoms with carbon increase both durability and activity.

Velu et al. [47] investigated, using the same experimental conditions, the effects of doping secondary heteroatoms (P, B, and S) over N-doped mesoporous carbon. The primary N source for the synthesis of doped carbon compounds was DA, which was followed by the precursors of the secondary heteroatoms B, P, and S, boric acid, phytic acid, and thiophene, respectively. As a supporting material, Santa Barbara

amorphous (SBA-15) was utilized to determine how secondary heteroatom doping affected the ORR of the MC. The charge delocalization was altered by P doping when compared to B and S doping in the MC structure. The doped material has high pyridinic and graphitic content (28.72 and 44.42%, respectively). The remarkable ORR activity was further enabled by doping, which also raised the surface area to 971 m^2/g with 1.18 defect sites. Moreover, the Mott-Schottky analysis supports the higher flat band potential (0.548 V vs. RHE) and superior carrier concentration (5.58×10^{15} cm^3).

Mesoporous carbon (NSMC) catalysts doped with N and S dual heteroatoms are considered to be among the efficient ORR catalyst substitutes because of the dispersion of nitrogen and sulfur atoms. Rather than employing alternative individual heteroatom sources, 2D mesoporous carbon materials doped with N and S dual heteroatoms (NSMCs) were synthesized using 2-amino-3-mercaptopropanoic acid (L-cysteine), a less studied single precursor. Velu et al. [48] have employed N and S dual precursors, L-cysteine at different loadings, and silica-support 2D Santa Barbara amorphous (SBA-15). As a carbon source, glucose was carbonized at 800°C. After etching away from the silica template, MC surface NSMCs showed high quantities of defect sites (I_D/I_G 14 0.99), pyridinic (21.41 at. percent), graphitic-N (50.27 at. percent), and thiophene-S (77.16 at. percent). The resulting NSMC performed better in terms of ORR. The NSMC-0.4 demonstrated a lower R_{ct} of 10 Ω/cm^2 and a greater positive onset potential of 0.78 V vs. RHE with a current density of 2.8 mA/cm^2. ORR followed two-electron reduction process in an alkaline electrolyte solution, and an 81% peroxide was formed. The addition of the high defect sites, the heteroatoms of graphitic, pyridinic-N, and thiophene-S, mostly increases the greater ORR activity.

Mesoporous hollow carbon spheres doped with N and P dual heteroatoms acted as an effective catalyst for the oxygen reduction process in an alkaline electrolyte [49]. To synthesize mesoporous hollow carbon, precursors of phytic acid (PA) and dopamine hydrochloride (DA) are combined to create N and P dual heteroatom spheres (NPHS). Concentration and addition time intervals of PA were adjusted to yield NPHS with an exceptional sphere form and a high surface area. The addition of 0.4 g PA every 30 hours was the ideal setting for the formation of NPHS-0.4, which had a large surface area (1120 m2/g), better shell thickness (31 nm), and enriched pyridinic N, P-C, and P-N sites. This material exhibited remarkable ORR activity, following an almost four-electron ORR pathway in KOH electrolyte solution. The NPHS-0.4 modified electrode has a modest carrier concentration ((2.3×10^{15} cm^3) and a positive onset potential (0.97 V) due to its flat band potential of 0.56 V versus RHE. It shows good resistance to methanol oxidation and significant electrochemical stability when compared to the catalyst, Pt/C. A chronoamperometry experiment was conducted to determine the stability of the NPHS-0.4 electrode in a KOH solution over a period of 40,000 seconds at a constant potential of 0.2 V and 1600 rpm. Only the NPHS-0.4 catalyst showed a 14% current loss, while the commercial Pt/C catalyst showed approximately 13% loss from the initial current.

4.2 ORR and OER by transition metal oxide decorated N-doped hollow carbon sphere catalysts

Recent years have seen a significant focus on the advancement of bifunctional catalysts for oxygen reduction and evolution reactions in an attempt to address the sluggish reaction kinetics, complex electron transfer mechanisms, and high overpotential requirements that lower fuel cell stability and efficiency. Earth-abundant first-row transition metal oxides, composites of meal and carbon, and carbon materials

doped with different heteroatoms were utilized in this regard to produce efficient bifunctional OER/ORR electrocatalysis because of their remarkable bifunctional electrocatalytic activity [50]. Co_3O_4 exhibits very remarkable OER/ORR activity because it consists of two distinct cobalt sites: tetrahedral A sites containing Co^{2+} coordinated with four oxygen atoms and octahedral Co^{3+} with six oxygen atoms in B sites. However, the intrinsic poor conductivity, restricted electron hopping capacity, agglomeration, and unpredictable diffusion of Co_3O_4 limit the OER/ORR activity of these materials. OER/ORR performance was enhanced when Co_3O_4 was decorated on mesoporous hollow carbon materials because of its high stability due to the strong attachment of Co_3O_4 to N-doped carbon, a large specific surface area (SSA) and facile electron transfer [51].

Various cobalt complexes were used as a precursor to deposit active cobalt material on carbon spheres. Cobalt phthalocyanine (CoPc), one of the cobalt precursors used to deposit active cobalt material on carbon spheres, demonstrates considerable OER/ORR activity because of its extensive network structure, strong interaction between cobalt metal ion centers and aromatic rings, as well as N atoms of ligands. Using TEOS to construct SiO_2 spheres of 190 nm material with 5, 10, and 20 tetra (4-(imidazole-1-yl)phenyl)porphyrindine, Han et al. [52] developed a single metal embedded (M = Co, Cu, Fe, etc.) hollow N-doped carbon electrocatalyst. Because of the hollow substrate's improved stability and exceptional methanol tolerance, as well as its single cobalt metal sites, cobalt anchored HNCS demonstrated excellent ORR activity in acidic media. The remarkable ORR activity is mostly due to a single isolated cobalt site that greatly increases the hydrogenation of OH*.

The majority of studies followed a two-step process to synthesize metal oxide adorned N-doped hollow carbon spheres (NHCS). Fe_3O_4 nanoparticles were anchored over the carbon structure using the core-shell carbon material tetraethyl orthosilicate (TEOS) and cetyltrimethylammonium bromide in the second step of a two-step process. This resulted in a hollow N-doped carbon sphere, Fe_3O_4/N-HCSC, and it showed better ORR activity [53]. Because of the hollow core-shell porous structure, the synergistic impact of Fe_3O_4 nanoparticles and N-doped graphitic layers, and improved methanol tolerance, Fe_3O_4/N-HCSC exhibits excellent electrocatalytic ORR activity. The kinetic current density J_K (412.7 mA cm^{-2}) of Fe_3O_4/N-HCSC was significantly five times higher than that of conventional Pt/C electrocatalysts (J_K = 84.5 mA cm^{-2}). But these are template approaches, which require multiple steps, complex processes, a lot of time, and are not cost-effective to scale up. Furthermore, it is revealed that altering the metal oxide loading over a heteroatom-doped carbon sphere is an extremely difficult task for which no prior research has been conducted, particularly for bifunctional applications.

With the aid of CoPc with various loadings and a precursor dopamine hydrochloride (DA), Velu et al. [54] effectively synthesized a N-doped hollow carbon sphere embedded with highly active spinel Co_3O_4 (Co_3O_4/NHCS) with a tunable spherical wall thickness for the first time. With the use of this technique, enhanced octahedral Co^{3+} and tetrahedral Co^{2+} sites, wide wall thickness, and high SSA are achieved, allowing for efficient OER and ORR activity in basic pH media. The number of Co^{3+} and Co^{2+} sites, defect sites, doping percentage of cobalt, and spherical wall thickness are all strongly impacted by the addition of different amounts of CoPc to carbon nanospheres. A very uniform hollow carbon sphere (NHCS-0.2) with a high wall thickness (61 nm) with mild defect sites and a better surface area (445 m^2 g^{-1}) was obtained by optimally loading 0.2 g of Co_3O_4. The obtained material surprisingly outperforms the benchmark RuO_2 material in OER performance, producing a current density of

10 mA cm^{-2} at a potential of 1.80 V vs. RHE in 0.1 M KOH medium. Co$_3$O$_4$/NHCS-0.2 shows very amazing ORR electrocatalytic activity with an onset potential of 0.89 V vs. RHE, an extraordinary current density of 5.0 mA cm^{-2}, a lowered Tafel slope of 60 mV dec^{-1}, and approximately four electron transfers.

4.3 Dual N and B heteroatoms doped SBA-15 templated porous carbon for symmetric supercapacitor

Supercapacitors are electronic devices that combine the features of capacitors and batteries to store extraordinarily large amounts of electrical charge [55]. Supercapacitor devices (SCDs) can be broadly classified into three classes according to how they store charge: hybrid, electric double-layer capacitors (EDLCs), and pseudo-capacitors. In EDLCs, charges are stored physically by generating an electric double layer (EDL) at the electrode-electrolyte interface (physisorption). An important and major component of supercapacitors, the electrolyte is crucial to the balance and transfer of charges between the electrodes, and thus the performance of these devices is greatly influenced by their physical and chemical characteristics [56]. The active material's internal structure and the condition of the electrode-electrolyte interface are greatly impacted by the interactions between the electrolyte and electrode in all electrochemical reactions. Redox-active electrolytes have the ability to increase supercapacitors' capacitance in a pseudocapacitive way. The electrolytes, which function as a redox mediator in the electrolyte, can also be part of the pseudo-capacitance in addition to the pseudocapacitive electrode compounds. For instance, Lota et al. [57] employed a redox pair, iodide/iodine, in a carbon-based supercapacitor as a redox-active aqueous electrolyte.

Porous carbon doped with dual heteroatoms nitrogen and boron, PC (NBPC) material was synthesized with the help of Santa Barbara amorphous (SBA-15) silica material and then examined for the effects of their doping on the heteroatom studied for use in supercapacitors [58]. The 809 m^2/g specific surface area provided by heteroatoms N and B in NBPC makes it a highly attractive material. NBPC material exhibited the highest specific capacitance of all, at 375 F/g at 2 A/g current density, with the best rate capability and capacitance retention in 1 M H$_2$SO$_4$. Dual redox additive materials were added to the electrolyte, increasing the symmetric supercapacitor cell's specific capacity in a synergistic manner. At a current density of 3 A/g, an unheard-before high specific capacity of 929 C/g is found, and when the current density was raised to 20 A/g, 56% of the initial specific capacity remained. The energy density of the constructed symmetric cell, which used an NBPC electrode in a dual redox additive electrolyte of 1 M H$_2$SO$_4$ + 0.01 M ammonium metavanadate + ferrous (II) sulfate was 48.4 W h/kg, which is five times more than the energy density of the electrolyte alone (10.1 W h/kg). Similar to this, the NBPC electrode produced a current density in the redox additive electrolyte of 15 kW/kg, which is three times greater than the power density in the bare electrolyte of 5 kW/kg.

5. Simultaneous detection of ascorbic acid, dopamine, uric acid, and acetaminophen on hollow mesoporous carbon nanospheres

Dopamine (DA), uric acid (UA), and ascorbic acid (AA, sometimes referred to as vitamin C], are three small biomolecules that coexist in living organisms and are critical to the biochemical processes of the same [59]. The use of AA in the treatment of

mental diseases, infertility, the common cold, and cancer. DA is a naturally occurring neurotransmitter that is responsible for cardiovascular, hormonal, and neuro-organism functions, as well as Parkinson's illness. Blood and urine contain UA, and excess UA concentration can result in a number of illnesses, such as gout, Lesch-Nyhan syndrome, and hyperuricemia. Acetaminophen (AC), also known as paracetamol, is a medication used to treat pain, including backaches, headaches, arthritis, and fever. In contrast to high doses of AC, which can cause kidney and liver damage. as well as occasional fatalities, modest doses of AC have no significant adverse impact on human health. The determination of these four chemicals plays a critical role in the fields of neurochemistry, biomedical chemistry, and the study of pharmaceuticals [60]. Many analytical techniques have been created and are currently accessible for the sensing of multiple analytes, such as electrochemical methods, capillary electrophoresis, chemiluminescence, spectrometry, and high-performance liquid chromatography. With the exception of electrochemical sensors, the majority of these techniques are difficult, prolonged, and frequently call for specific equipment. By designing and integrating reliable and active candidates onto electrodes, we can electrochemically detect analytes easily with high sensitivity, selectivity, and analytes. Standard (carbon or metal) electrodes can cause low sensitivity and selectivity due to fouling by oxidation products and a significant overpotential, making it difficult to determine the analytes directly.

Carbon-based materials have gained popularity recently because of their distinctive characteristics, such as hollow structures with a high surface area and a higher graphitic degree, as well as an abundance of active sites [61]. Hollow carbon sphere (HCS) and 3D hollow mesoporous carbon sphere (HMCS) materials are potential candidates and have been used for a variety of electrochemical applications. In recent years, heteroatom doping has improved electrochemical sensing as it provides great approaches to boost the conductivity, catalytic active sites, and edge plane defect sites of HMCS materials. The initial step in this direction is mono-heteroatom doping in HMCS, notably N-doping. Because N can transport electrons, it donates its negative charge to the carbon framework, enhancing the system's electrochemical sensitivity [62].

Velu et al. [63] demonstrated an easy-to-use method for producing extremely homogenous N-doped hollow carbon spheres by using dopamine hydrochloride and TEOS. Four distinct N-doped hollow carbon materials (NHCS), NHCS-700, NHCS-800, NHCS-900, and NHCS-1000, with varying precursor concentrations, were prepared using varying carbonization temperatures (700–1000°C). The surface areas that were observed were 810 m^2g^{-1}, 480 m^2g^{-1}, 510 m^2g^{-1}, and 440 m^2g^{-1} for NHCS-700, NHCS-800, NHCS-900, and NHCS-1000, respectively. The high-temperature generated carbon material (NHCS-1000) has 44.52% graphitic sites and 32.64% pyridinic sites with defective sites (0.73) due to the interaction of the high concentration of PDA with the silica network. In contrast to the alternative materials, the modified electrode NHCS-1000/GCE showed better electrocatalytic activity and was used for the oxidative sensing of AA, DA, UA, and AC simultaneously at potentials of - 0.05, 0.16, 0.28, and 0.38 V, respectively, in 0.1 M PBS (pH 7). The sensitivity, LOD, LOQ, and linear range of the DPV approach, which was used for simultaneous detection, were found to be appealing for sensor applications. The NHCS-1000/GCE sensor was used with real samples of ascorbic acid (500 mg), paracetamol (500 mg), serum, and human urine to sense AA, DA, UA, and AC with satisfactory recoveries.

The fascinating features of dual heteroatom doping on hollow carbon have attracted significant attention in the field of electrochemical sensors, as mentioned in

earlier chapters. Doping of dual heteroatoms on hollow carbon increases the biosensor's activity and sensitivity. Particularly, adding more P sites to nitrogen-doped carbon spheres efficiently alters the sp^2 hollow carbons, and the synergism gives the hollow carbon sphere useful features. Huang et al. [64] recently derived porous carbon nanoparticles with N and P dual doping from lotus leaves by a straightforward procedure and constructed an electrochemical sensor. The glassy carbon electrode was coated with CNP (CNP/GCE) used for the determination of ascorbic acid (AA), dopamine (DA), and uric acid (UA) simultaneously in 0.1 M PBS (pH 7.0). But the material has a low BET-specific surface area (314 $m^2\,g^{-1}$), which demonstrated a modest response for the estimation of DA, AC, and UA even though it exhibited well stability and excellent analytical performance.

Hollow mesoporous carbon spheres (NPHMCS) dual-doped with nitrogen (N) and phosphorus (P) were effectively synthesized by a straightforward self-polymerization procedure by Mahanthappa et al. [65]. The effects of adding various amounts of phytic acid (PA), a P precursor, on the electrochemical sensing of target analytes were thoroughly studied. TEOS was exploited to create 3D silica spheres in an alkaline medium. Dopamine hydrochloride (DA, N source) was then combined with the spheres to create a hybrid SiO_2-PDA sphere. Using various phytic acid loadings, a 30-hour polymerization procedure was used to attain a novel SiO_2-PDA-PA hybrid sphere (P source). The products of the polymerization reaction were heated in an inert atmosphere to carbonize at 900°C after the reaction was carried out for an additional 13 hours. Ultimately, after 48 hours of NaOH etching on the SiO_2 core, NPHMCS-0.2, NPHMCS-0.4, and NPHMCS-0.6 products were produced. The carbon samples have BET-specific surface areas of 675 $m^2\,g^{-1}$, 1119 $m^2\,g^{-1,}$ and 940 $m^2\,g^{-1}$ for NPHMCS-0.2, NPHMCS-0.4, and NPHMCS-0.6, respectively. The study found that adding 0.6 g of PA (NPHMCS-0.6) increased the volume of defects by 0.99, the surface area by 940 $m^2\,g^{-1}$, the pore volume by 0.40 $cm^3\,g^{-1,}$ the pyridinic volume by 24.90%, and the mild PC + PN volume by 74.65%. Utilizing the synergistic impact of nitrogen and phosphorous doping, electrochemical sensors for the simultaneous detection of ascorbic acid (AC), dopamine (DA), uric acid (UA), and acetaminophen [AA] in 0.1 M PBS (pH 7.4) have been developed. The NPHMCS-0.6-modified GCE was the only NPHMCS-modified GCE electrode that simultaneously demonstrated a greater current response and a superior electrocatalytic response toward the four biomolecules, AA, DA, UA, and AC, in 0.1 M PBS at pH 7.4. The biosensor that was built demonstrated a wide linear sensing range across concentrations of AA, DA, UA, and AC, ranging from 5 to 6000 M, 0.5 to 2000 M, and 5 to 1200 M, respectively. Using the calibration plot, the limits of detection (LOD) for AA, DA, UA, and AC were found to be 0.032, 0.002, 0.005, and 0.020 M, respectively. The electroanalytical capabilities of the biosensor were effectively verified for the determination of target analytes in actual samples.

5.1 Electrochemical sensing of acetaminophen by heteroatom-doped hollow carbon spheres

Acetaminophen (ACAP) is a well-known antipyretic medication with a mild depressive effect that is frequently used as a COVID-19 frontline therapy to lower body temperature. Because ACAP has nonsteroidal anti-inflammatory and nonopioid analgesic properties, it is widely used to treat pain. It also lessens flu by regulating prostaglandin production in the central nervous system [66]. ACAP use in excess or for an extended period of time is the main reason for hepatic centrilobular necrosis,

which results in liver failure, damages the kidneys, and triggers idiopathic reactions. Numerous deaths have been linked to the incorrect use (overdose) of ACAP in various parts of the world up to this point. The concentration of poisonous ACAP in human blood serum is typically 10 times greater than that of general therapeutic medications $(10–25 \text{ mg mL}^{-1})$. Because of this, a practical method is needed for the rapid and accurate assessment of ACAP in noninvasive samples, as well as for determining the amount of ACAP in biofluids. These findings will significantly impact clinical diagnostics and public health [67].

Due to their distinctive qualities as electrocatalysts, ordered mesoporous carbon (OMC) materials, discussed in the previous sections, have a tremendous potential for commercialization because they are affordable, have a large potential window, and exhibit exceptional catalytic activity. Electrocatalytic activity and electron transport properties are intrinsically improved by nitrogen doping on carbon since N-doping increases the surface charge density and active sites and increases the hydrophilicity. Also, N-doing also enhances the adsorption of the reactant, and thereby improves the reaction rate. For the purpose of sensitively and selectively sensing L-tryptophan (Trp) in 0.1 M PBS (pH 3.0), Zhang et al. [34] developed N-doped OMC and showed the electrooxidation of Trp on the modified electrode, NOMC/Nafion/glass carbon electrode (GCE). This study marked the first time that NOMC was used to detect Trp. The NOMC was obtained using a mesoporous silica template made of tri-block copolymer P123 and graphene oxide (GO). The following stage involves combining ferrous chloride, o-phenanthroline, and mesoporous silica template to create a composite. After 3 hours of heating at 900°C in an argon environment, the red compound that was produced turned black. The black product first spent 24 hours in 10 M NaOH and then 48 hours in 2 M HCl to eliminate silicon and iron. The intended NOMC product was dried in the air after being repeatedly cleaned with ethanol and water. With a surface area of $804 \text{ m}^2 \text{ g}^{-1}$ and 3.62% N, the NOMC is large. When compared with other similar sensors, the modified electrode demonstrated a wider detection range with different slopes in each range, a LOD of 0.5–70.0 μM and 70.0–200.0 μM, and a limit of detection of 35.0 nM for Trp determination. For instance, GCE modified by nanoporous carbon showed a linear range of 1–103 μM and a detection limit of 0.03 μM.

Liu et al. [68] reported N and P atoms-doped carbon microspheres (NP-CMs) by the calcination of dopamine composites with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). A NP-CMs modified electrode, NP-CMs/GCE, was made and used as a biosensor for the highly sensitive electrochemical sensing of acetaminophen in 0.1 M PBS at pH 7.2. The outcomes of the experiment suggested that NP-CMs outperform N-doped carbon microspheres in terms of electrocatalytic performance. The detection limit of NP-CMs/GCE was 40 nM, and a linear relationship was observed with acetaminophen concentration from 0.07 to 30 μM. The enhanced electrocatalytic activity caused by N, P-co-doping is responsible for acetaminophen's remarkable selectivity and sensitivity in electrochemical sensing. However, this process required the addition of the highly carcinogenic flame-retardant precursor chemical DOPO, which contains P.

N- and P-doped mesoporous carbon was reported by Narmatha et al. [69] using dopamine and phytic acid as N and P precursors with the hard template SBA-15 by the nano-casting method. NP-MC has a $970 \text{ m}^2 \text{ g}^{-1}$ large surface area with a high active site content of graphitic and pyridinic moieties. Strong electron transport capabilities and exceptional electrocatalytic activity toward acetaminophen in 0.1 M PBS (pH 7) are displayed by the biosensor (NP-MC/GCE) created using this NP-MC. Under ideal

conditions, NP-MC showed the highest sensitivity and lowest LOD of 0.027 mM among the samples, with a wide linear range of 3–4000 mM. Additionally, the NP-MC-modified GCE showed excellent stability, repeatability, and reproducibility and could be used for both invasive and noninvasive ACAP detection in samples.

Various substances, such as metals and their oxides, enzymes, and polymers, were used as electrode materials for sensor application investigation to improve the poor kinetics of bare glassy carbon electrodes [70]. Transition metal oxides are a highly desirable alternative for enhancing the functionality of electrochemical sensors because of their remarkable stability, cheap cost of production, and excellent electrical conductivity. Many metal oxides, such as $NiCo_2O_4$, $CuCo_2O_4$, MnO_2, Co_3O_4, and NiO, have been employed in recent electrochemical sensor investigations [71]. In recent years p-type semiconductors constructed with Co_3O_4 materials have gained more attention due to their attractive properties, which include different oxidation states, stability, and selectivity, as well as electrical and electrocatalytic properties. A straightforward one-step polymerization technique was used to make an extremely homogenous Co_3O_4-attached N-doped hollow carbon sphere (Co_3O_4@NHCS) utilizing precursors of dopamine hydrochloride (DA) and cobalt phthalocyanine (CoPc) [72]. By varying the loading amount of CoPc, the resulting Co_3O_4@ NHCS materials' N and Co element doping, surface area, and defect sites can be effectively regulated. The optimal 200 mg loaded Co_3O_4@NHCS-2 material demonstrated exceptional electrochemical performance with a relatively large surface area, improved spherical wall thickness, richer defect sites, and high N and Co sites. The electrocatalytic activity of Co_3O_4@NHCSs on GCE was performed toward the detection of acetaminophen, a molecule that is pharmacologically significant. Excellent linear range (0.0010.2 and 1.08.0 mM), limit of detection (0.07 and 0.11 M), and selectivity were observed for the Co_3O_4@NHCSs/GCE. When applied practically, the real sample (an acetaminophen tablet) yielded an acceptable result.

5.2 Dopamine sensor by hollow mesoporous carbon nanospheres

Dopamine (3,4-dihydroxyphenyl ethylamine, or 3,4-DM), one of the most significant neurotransmitters, is present in the extracellular fluid that surrounds the brain's nucleus accumbens. The central nervous system secretes this catecholamine, which functions as a complex chemical messenger between the pre- and postsynapse of adjacent neurons. Among the numerous diverse kinds of neutrophils are serotonin, glutamate, 3,4-DM, aminobutyric acid, epinephrine, acetylcholine, and norepinephrine are few examples. Dopamine (DM) plays a vital part in many physical activities for preserving several areas of health, including hormonal, cardiovascular, mental, mobility, memory, and behavior. Stress is one of the pathological conditions that the DM monoamine is used to treat. DM concentrations in human blood normally range from 0.01 to 1.00 M. Variations in DM levels have harmful consequences on the human body and can cause a wide range of disorders. Low DM concentrations in people can cause Parkinson's disease and weak muscles, whereas high DM levels can cause drug addiction and other issues. So, for the purpose of treating and avoiding symptoms, precise DM identification is crucial [73, 74]. Several methods, including colorimetry, fluorescence, chemiluminescence, and the spectrophotometric approach, are available for DM determination. Numerous electrocatalytic nanomaterials have been created in recent studies to build DA sensors. Because of their superior electrochemical properties, such as strong electrical conductivity, chemical stability, and large surface area, metal nanoparticles, metal oxides, and carbon materials are of particular interest [75].

Developed a straightforward and efficient hard template method to anchor Co_3O_4 on N-doped hollow mesoporous carbon nanospheres using the cobalt precursor cobalt phthalocyanine (CoPc) for the sensitive detection of dopamine (DM) [76]. The best carbon material was obtained on loading 0.2 g of CoPc (Co_3O_4/NDHCS-0.2), which showed exceptional sensing capabilities for DM detection. The stability of a mesoporous hollow carbon sphere with defect sites, a large surface area, increased ornamentation of the Co center, and a greater number of octahedral Co^{3+} and pyridine N centers are primarily accountable for the exceptional sensing response. The developed Co_3O_4/NDHCS-0.2/GCE material exhibits high sensitivity (871 and 103 μA mM^{-1} cm^{-2}), low limits of detection of 11 nM and 0.516 μM, and wide linear ranges from 1.0 to 900 and 1500 to 6500 μM. The real samples were tested in a practical setting using the suggested sensor as well. Additionally, the dopamine sensor has demonstrated respectable repeatability and long-term stability.

5.3 Electrochemical sensing of antibiotic drug from poultry sustenance by N- and P-doped hollow carbon spheres

Antibiotics are substances that inhibit bacteria from growing and sometimes even kill them. Antibiotics have significantly improved both human and animal health since their discovery. Excessive antibiotic residues, on the other hand, encourage their presence in food and animals, which causes allergies, antibiotic resistance, and super-infections in people. Hence, monitoring different antibiotic medications is essential in terms of human health concerns and the environment [77]. With its antibacterial and antibiotic qualities, nitrofurantoin (NFT), a popular nitrofuran derivative, can be used to treat and prevent urinary tract infections, as well as to promote growth in animals and poultry. NFT is also frequently prescribed as a treatment for bladder cancer. However, overusing NFT can have negative consequences for people, including diarrhea, pruritus, urticaria, fever, dyspepsia, disorientation, and more. As a result, the use of the antibiotic NFT on chicken was prohibited in the majority of developed nations. In order to prevent the negative effects of NFT drugs, it is now necessary to identify and measure any chemical residues found in human biofluids and poultry feed. To ensure a safer food supply, it is imperative to analyze the NFT residues in chicken feed because these drugs have the potential to have adverse effects on human health [78].

Antibiotics can be detected using colorimetric, fluorescence, and electrochemical techniques. Electrochemical approaches, in contrast, are gaining popularity due to their high sensitivity, high accuracy, and trace detection. The high potential value needed for the electro-oxidation of these chemicals, however, is one clear disadvantage of conventional electrode materials. The utilization of carbon nanomaterials (CNMs), which have superior electrical conductivity, a wide surface area, and high electronic transport, has been a successful tactic that is garnering attention. Kokulnathan et al. utilized hierarchical $LuVO_4$ encapsulated ultrathin GRS to detect nitrofurantoin (NFT). Because of the $LuVO_4$/GRS nanocomposite's good electrical conductivity, suitable surface area, and facile redox reaction with a notable sensitivity and a low detection limit (0.001 μM), wide linear range (0.008–256.0 μM), and excellent sensitivity (1.709 μA μM^{-1} cm^{-2}) [79]. The facile synthesis of N-doped carbon quantum dots (N-CQDs) with Co3O4 using multiwalled carbon nanotubes (MWCNT) for the electrochemical detection of the antibacterial medicine nitrofurantoin (NF) and the anticancer agent flutamide (FLU) was described by Muthusankar et al. [80]. The Co_3O_4 nanocomposite loaded with N-CQDs (NCQD@

Co_3O_4) was synthesized using a microwave method. The N-CQD@Co_3O_4/MWCNTs hybrid nanocomposite sensor, which was added to the glassy carbon electrode (GCE), showed an exceptional response in the simultaneous measurement of FLU and NF, with linear ranges of 0.05–590 μM and 0.05–1220 μM and detection limits of 0.0169 μM and 0.044 μM.

N- and P-doped hollow sphere carbons were produced using a single, environmentally friendly procedure and a hard template, with varying P loadings achieved by adjusting the amount of phytic acid added for the sensing of NFT [81]. The dopamine precursor was used for both carbon and nitrogen. Three distinct samples with varying PA loadings were reported: NPSC-0.2, NPSC-0.4, and NPSC-0.6. Of them, the PA loading at 0.6 g demonstrated an enrichment of pyridinic and P-C+, P-N sites, indicating improved sensor activity. It was discovered that adding secondary dopant phosphorus to N-doped hollow carbon spheres made the carbon network work better, which had a big effect on the sensing response. The sensor based on an improved phytic acid-loaded NPSC (0.6 g) modified GCE electrode showed enhanced electrocatalytic activity with an incredibly low LOD of 0.036 M for the detection of NFT in 0.1 M PBS (pH -7.0). By controlling the redox of most of the electroactive species in physiological samples and achieving higher stability across a wide linear range (1–2500 M), NPSC-0.6 eliminated any possible interference signals. More graphitic and pyridinic sites, as well as a more durable electrocatalyst, are also made possible by the NPSC-0.6 material. Additionally, real samples were examined, including samples of human serum and poultry feed, along with high recovery rates.

6. Conclusions

It is crucial to look for effective and durable catalysts that are easy to kinetically facile, as well as abundant on earth to combat the energy problem and identify bioactive molecules and pharmaceutical ingredients. The rational synthesis of heteroatom-doped porous carbon nanostructures (HA-PCs) for the electrocatalytic ORR and OER sensing of biomolecules and drugs was covered in this chapter. N-doped porous carbon spheres decorated with transition metal oxide Co_3O_4 and their electrocatalysts' tendency for oxygen reactions, ORR and OER, as well as the capacity to detect acetaminophen, have all been reported. The method used to create the porous carbon spheres and the precursors chosen were both disclosed. By selecting the ideal precursors, carbonization temperature, and precursor concentration, it is possible to create the desired and effective heteroatom-doped mesoporous carbon nanostructures. N-doped mesoporous carbon sheets were easily and quickly obtained from DA and TEOS precursors, and the surface area and mesoporosity of the resulting N-doped carbon sheets were adjusted by changing the DA loading concentration. The ORR activity in carbon materials with heteroatom doping was enhanced by P-precursor addition time and loading. The dual redox additive electrolyte used in supercapacitors was made of porous carbon with N and B dual doping, which was produced using SBA-15 silica as the template material. The material had a large pore volume, a high surface area, and an excessive concentration of N and B functional groups. N- and P-doped MC was produced by using SBA-15 as a hard template and dopamine and phytic acid as N and P precursors by a nano-casting procedure. NP-MC-based sensors possess strong electron transport capabilities and exceptional electrocatalytic activity. TEOS and dopamine hydrochloride were used as precursors to produce N-doped hollow carbon spheres that were surprisingly consistent. To study the impact of

temperature on the electrochemical sensing capability, the carbonization temperature was changed to produce a large surface area and large amounts of pyridinic and graphitic N sites. N-doped carbon compounds containing a variety of secondary heteroatoms were prepared using a hard template method. By adding secondary heteroatom precursors, the surface area, defect sites, and pyridinic, and graphitic N edge sites can all be customized. By altering two critical factors, namely temperature and DHC loading concentration, a highly ordered nitrogen-doped hollow carbon sphere with a carbon framework was prepared using a DHC precursor. The NHS-0.4 catalyst features a high percentage of pyridinic and graphitic-N content, a thick carbon shell, a sizable volume of mesopores, defect sites, and a large surface area at the optimal temperature and TEOS/DHC loading concentration. A striking set of parameters, such as these demonstrates excellent ORR activity. This chapter urges the importance of choice of precursors, loading of heteroatoms, and carbonization temperature to reach highly efficient electroactive materials in the fields of energy storage and generating devices, as well as biosensors.

Acknowledgements

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