Materials Horizons: From Nature to Nanomaterials

Andrews Nirmala Grace
Prashant Sonar
Preetam Bhardwaj
Arghya Chakravorty *Editors*

Handbook of Porous Carbon Materials

Springer

Materials Horizons: From Nature to Nanomaterials

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Handbook of Porous Carbon Materials

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Dedicated to the memory of
Antoine Lavoisier

Foreword

The study of porous carbon materials is a comparatively adolescent discipline. It primarily gained eminence through the early eighteenth century, when the beginning of activated charcoal with well-defined structures revealed by scientists established to follow the research of this enthralling substance with a renewed vigor. In 1776, Russian Chemist Johann Lowitz revealed the preliminary discoloration properties of charcoal in liquid—a characteristic that built activated charcoal as water filters with admired preference even today. In consequence, the discovery of Graphene by Prof. Andre Geim and Prof. Kostya Novoselov in 2004 affords an enormous advance up and new measurements to materials research and nanotechnology. The multidisciplinary properties of porous carbon materials have an extensive range of applications from the medical sector to the aerospace industry. The first volume of the journal Carbon appeared in 1964, and 191 volumes of this journal had been published up to 2022 that is reflecting the massive growth of this field. This time period also observes the progress of a broad variety of experimental methods that are enabling the exploration of different characteristics of the porous carbon materials with respect to energetic, kinetic, structural, electronic, magnetic, and dynamic properties of porous carbon materials with enormous precision. The discovery of scanning probe techniques permitted atomic processes to be considered in unparalleled detail. The study of the porous carbon field in recent research ranges from phenomena correlated with nanotechnology and thin-film development to heterogeneous catalysis processes to industrial applications.

The current handbook comprises 41 chapters that are contributions written by numerous specialists in this carbon field globally and covers the main aspects of this fascinating branch of science and engineering. It should establish precious contributions to all those engrossed in this discipline. The editors and authors are to be eulogizing on the successful completion of this *Handbook of Porous Carbon Materials*. It will definitely be a work of enormous and lasting significance for the scientific community.

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Preface

Porous carbon materials such as activated carbon, carbon nanotubes, carbon nanofibers, and graphene are the novel visionary materials of this twenty-first century. These carbon materials are receiving extensive attention as novel materials to guide the prospects in the fields of electronics, biosensors, agriculture, wastewater remediation, composite materials, energy devices, hydrogen generation, secondary batteries, fuel cells, etc., not simply for nanoscaled dimensions but also due to their outstanding porosity, surface area, exceptional mechanical, chemical, physical, and electronic properties. Those who manage materials can organize technology, acknowledged by Eiji Kobayashi, Senior Scientist of Panasonic Corporation, elucidating the significance of materials science and engineering. We would interpret this quotation as researchers and scientists who control properties of materials to optimize technology and reflect on the influential growth of materials and technology on our large-scale infrastructure.

Porous carbon materials have a determinative function in the fabrication of numerous superior products around us. From the development of filter membranes to aerospace technology, none of these could be shaped devoid of these wonderful materials. The editors consider this porous materials science as the understanding of composition; characteristics of materials predicted or explained with the help of this information; experimental and theoretical tools intended and recognized for preparing, characterizing, and modifying processes. Editors also listed all-important application possibilities of these resulted materials. After defining porous carbon materials, we can simply swap this depiction for porous carbon materials discipline. Porous carbon materials are considered in all advanced applications due to their configuration, processing, characterization, and difference from the macroscopic materials. This difference is due to nanosized dimensions and porous structures.

The depiction of the porous carbon materials in this handbook pursues all fields but comprises short details of the synergy of composition, characteristics, processing, and applications. Distinctively, our aim was to point out the difference between the properties of bulk and nano-porous materials. We also discuss and explain the reasons for these differences. To accomplish these objectives, we present a reasonable description of the literature of each porous carbon materials group. The layouts pursue the

well-established configuration of the handbook with chapters as the basic units that are organized into several groups. In each chapter, authors cover materials of their proficiency; however, they centered not only on their own work, but account the remarkable and significant efforts in the society, ascertain stability between references and scientific outcomes account in tables and figures. We illustrate porous carbon materials in textbook approach for beginners in this field. We also comprise encyclopedia-like ingredients and discuss the fast space of new results. We also review and include recent research reports for the familiar readers. Ahead of scientific and ethical accuracy, we also seem for simplicity by summarizing and easy-to-follow text, well-planned and apparent figures which were all proficiently drawn by experts.

The book is divided into eight parts depicted as Parts I–VIII that cover porous carbon materials: graphene, graphene oxide, fullerenes, carbon nanotubes, activated carbon, carbon nanofibers, noble and common porous carbon-based composites, hybrid structures and solutions, and selective applications, correspondingly. This higher-level structure conforms to the porous classification of materials, and it is composed of chapters. Each chapter is self-consistent and builds up of similar parts, history, definitions, production of the given porous carbon materials, properties, and applications. All of these parts are opulently illustrated and consist of a reasonable proportion of imperative basics and recent results.

Our pleasurable commitment is to express gratitude to all authors, contributors, and colleagues who help us with the establishment of this planned and implemented handbook. Firstly, we need to recognize the conscientious work of the authors in developing the chapters which engross more attempts than a review article, and the reward is not so instantaneous and apparent. Their proficiency, energy, and time are significantly appreciated. We also would like to show gratitude for the suggestions and help of our colleagues in keeping in contact with several authors. Our book is dedicated to the memory of French Scientist Antoine Lavoisier who named the elements **carbon**, hydrogen, and oxygen and discovered oxygen's role in combustion and respiration.

The enormous workmanship of the Springer publishing team and the incessant support of the managing editors Priya Vyas and Silky Abhay Sinha are also appreciated. We also need to thank our colleagues and friends that the association with them is leaning us to understand and develop materials science aspects. Last but not least, we are thankful to our family members for their continuous support to complete this work. We wish the readers an enjoyable and advantageous time when utilizing the Handbook of Porous Carbon Materials, and we anticipate that it serves as a regularly unwrapped reference textbook.

Vellore, India
February 2022

Andrews Nirmala Grace
Prashant Sonar
Preetam Bhardwaj
Arghya Chakravorty

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Chapter 12
Core–Shell Nanostructures-Based Porous Carbon Nanomaterials for Oxygen Reduction Reaction

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1 Introduction

Core–shell nanostructures (CSNs) have attracted considerable attentions in various applications such as catalysis, electrocatalysis, energy conversion and storage (ECS), optical devices, drug delivery, biomedical, sensors, actuators, environmental remediation, heavy metal adsorption due to the presence of unique structural properties [1–5]. Zhang et al. discussed the various parameters that are needed to be addressed before synthesizing the CSNs for a particular application [1]. Here, some of the points have to be considered mainly for the synthesis of various CSNs. (1) Selecting the required CSN based on the choice of mono-, di-, multi-, or porous CSNs. (2) Fix the proper shape and size requirements for constructing the CSNs with various shapes such as core–shell, yolk–shell, and hollow–shell nanostructures with controlled particles size. (3) Constructing the CSNs with proper core and shell based on the application requirement. (4) Also selecting the core centre material with one or more materials to tune the surface and morphological properties [1]. On the other hand, Gawande et al. classified the CSNs based on the presence of inorganic/inorganic,

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inorganic/organic, organic/organic, organic/inorganic materials present in the structure [2]. The core and shell chemical compositions are also tuned based on the end-use of application. Generally, the more active materials can accumulate on the shell, and core material acts as support, so that the active material can easily react with the foreign matter and exhibit better reactivity in various applications.

Recently, CSNs were used widely in electrocatalysis applications especially in oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), etc., owing to the higher catalytic performance and the maintenance of excellent stability of the CSNs by the presence of active surfaces, defects, and higher pore volume and surface area, respectively for the electrocatalysis applications [6, 7]. Furthermore, CSNs also expressed considerable attentions in wide variety of fuel cells and battery applications [8–12]. One of the structural advantages of CSNs over other nanomaterials is the combinations of two or more materials in a single material with controlled size, shape, and morphology with abundant surface area and easy adjustable surface structure.

Recently, carbon-based nanomaterials were used widely for electrochemical reactions due to the ease of availability, possessing excellent stability under harsh environments and the presence of high surface area and low cost as compared with the platinum or other metal-based electrocatalysts [13–16]. Similarly, porous carbon (PC) also showed huge interest in various applications. Porous carbon materials can exhibit high pore volume and surface area, excellent porosity, better durability, and improved electrical conductivity. Various carbon-based materials like carbon materials derived from different biomasses, activated carbon (AC), carbon nanotubes (CNTs), graphene, or graphene oxide (GO) were used to design the CSNs with exceptional properties [17–21]. The synthesis of porous carbon-containing CSNs also gains significant attentions in the recent days [8, 10, 17].

In this chapter, we briefly describe the importance of porous carbon-based CSNs for electrocatalytic ORR activity. We also cover how the porous and non-porous carbon nanostructures on the CSNs playing a vital role on enhancing the ORR activity as well as stability. In addition, the effect of transition metals and metal oxide on the porous carbon-based CSNs was also analysed deeply for ORR. Finally, we summarize the various aspects of porous carbon-based CSNs and their future perspective for improving the catalytic activity, stability, and robustness from the recent literatures. Figure 1 clearly shows the possible directions of the CSNs-based porous carbons obtained at various methods with superior properties that can be used for ORR.

2 Oxygen Reduction Reaction (ORR)

ORR is highly important in various fuel cells and battery applications because the reaction is controlled kinetically based on the four or two-electron transfer mechanisms. In most cases, platinum (Pt)-based electrode was used in fuel cell as well as ORR activity due to the superior electrocatalytic activity of Pt-based electrode

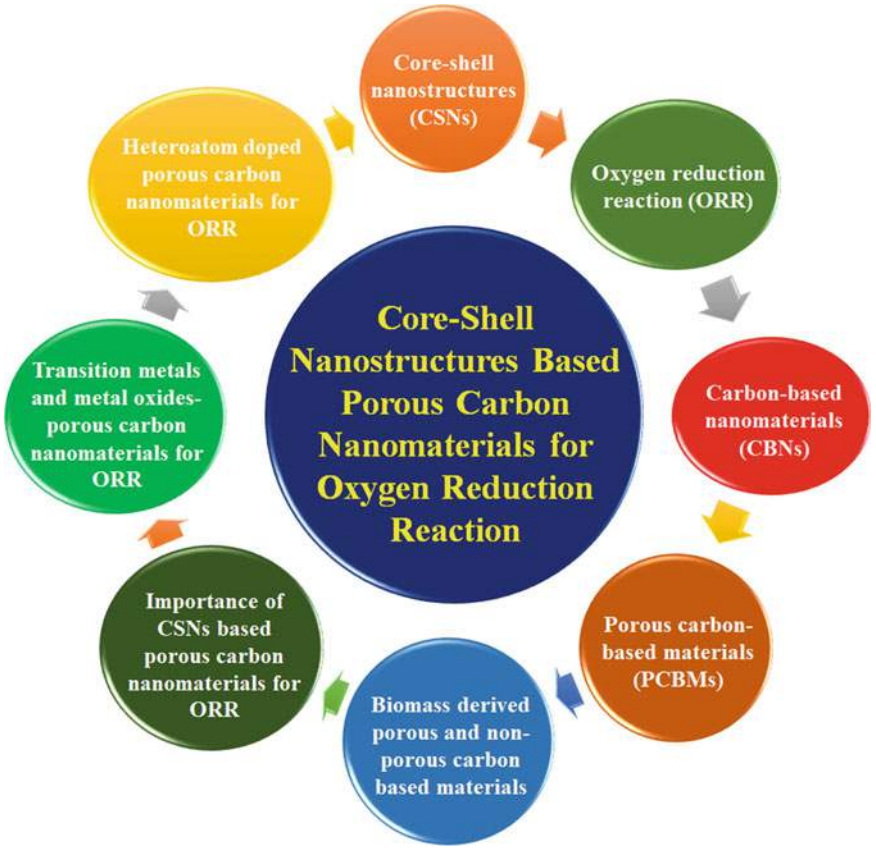

Fig. 1 Schematic illustration of various porous carbon nanomaterials with core–shell nanostructures for oxygen reduction reaction

[22, 23]. At the same time, this can show severe drawbacks such as low tolerance, expensive, and low durability. These parameters are widely lacking to use the Pt-based electrodes for such applications. Much efforts were devoted to overcome these drawbacks by reducing the Pt content, introducing heteroatoms as well as porous carbon-based materials, and use of highly abundant low-cost transition metals [24]. Recently, the CSNs with heteroatoms, Pt group free transition metals, and CSNs with PC nanostructures were expressed tremendous attentions in electrocatalytic ORR activity as well as for other applications [13, 25–29]. Porous carbon nanotubes (CNTs) and graphene-based carbon materials with CSNs can display improved electrical conductivity, alcohol tolerance, and electrocatalytic activity.

Dahal et al. obtained a PC nanofiber with core–shell nanostructures (CSNs) by first fabricating a zinc oxide-loaded polyacrylonitrile (PAN)-based nanofiber by in-situ mixing of PAN and zinc acetate in dimethyl formamide (DMF) and electrospun followed by annealing at 350 °C for 2 h to obtain a ZnO-PAN nanofiber

(Fig. 2a) [13]. The nanofiber is further modified with metal organic framework (MOF) using 2-methylimidazolate to form a zeolitic imadazolate framework (ZIF) structure on the Zno-PAN nanofiber which was further modified with boron (B) and nitrogen (N) heteroatoms using 0.1 M aqueous ammonium hydrogen borate trihydrate $(NH_4HB_4)_7.3H_2O$ and 0.1 M aqueous sodium borohydride ($NaBH_4$). The modified material pyrolyzed and washed with sulphuric acid (H_2SO_4), ethanol, and deionized water to give ZIF-8-based boron (B) and nitrogen (N)-doped PC nanofiber. The prepared nanofiber delivered an outstanding electrochemical ORR activity due to enhanced electrical conductivity as well as the presence of more active sites based on the presence of B and N heteroatoms.

Gebremariam et al. also disclosed the preparation of manganese (Mn) and cobalt (Co) loading on the carbon nanofibers followed by the surface modification with N-doped carbon obtained from by the surface treatment of the metal-loaded nanofibers with dopamine and subsequent pyrolysis (Fig. 2b) [25]. The prepared electrocatalyst can perform excellent.

ORR behaviour and also used as a cathode electrode in Zn-air battery as well as supercapacitor applications.

The oxygen evolution reaction requires higher overpotential and demonstrated a significant interest in metal-air battery and water electrolyser applications [30]. The combinations of ORR and OER electrodes were used as cathode and anode electrodes for battery application, whereas the combination of OER and HER was used in water-splitting application. OER took place by evolving a molecular oxygen via a chemical reaction with the support of four electrons and protons. Iridium (Ir)-based catalyst has displayed benchmark OER activity and stability especially under acidic condition than various transition metals or other nanomaterials [30]. Under acidic media, most of the transition metals have exhibited lower OER activity, whereas the transition metal oxides have significant OER effect only at basic condition. To overcome these drawbacks, much efforts were drawn to develop a high-performance OER electrocatalyst having significant stability at both acidic and basic conditions with almost comparable or improved activity than the Ir-based catalyst [30].

On the other hand, Pt-based electrocatalyst has displayed outstanding electrocatalytic activity for ORR as compared with various other existing materials. Both Ir and Pt are very expensive in the commercial aspects of mass production of the electrodes for practical applications. Much attentions were paid on a new these aspects and also improve the performances significantly than the commercial electrodes by creating nanomaterial that can have the ability to solve the drawbacks. The OER activity mainly studied the overpotential value of an electrode from their specific current density. A catalyst having lower overpotential can display superior OER activity [30]. The catalysts made for ORR as well as OER both have identical features based on the end-use of applications. Recently, significant attentions were paid for the high-performance bifunctional electrocatalyst containing both OER and ORR as well as OER and HER electrocatalytic activities.

The mechanisms for OER and ORR occur in acidic and alkaline environments based on the following ways [31, 32].

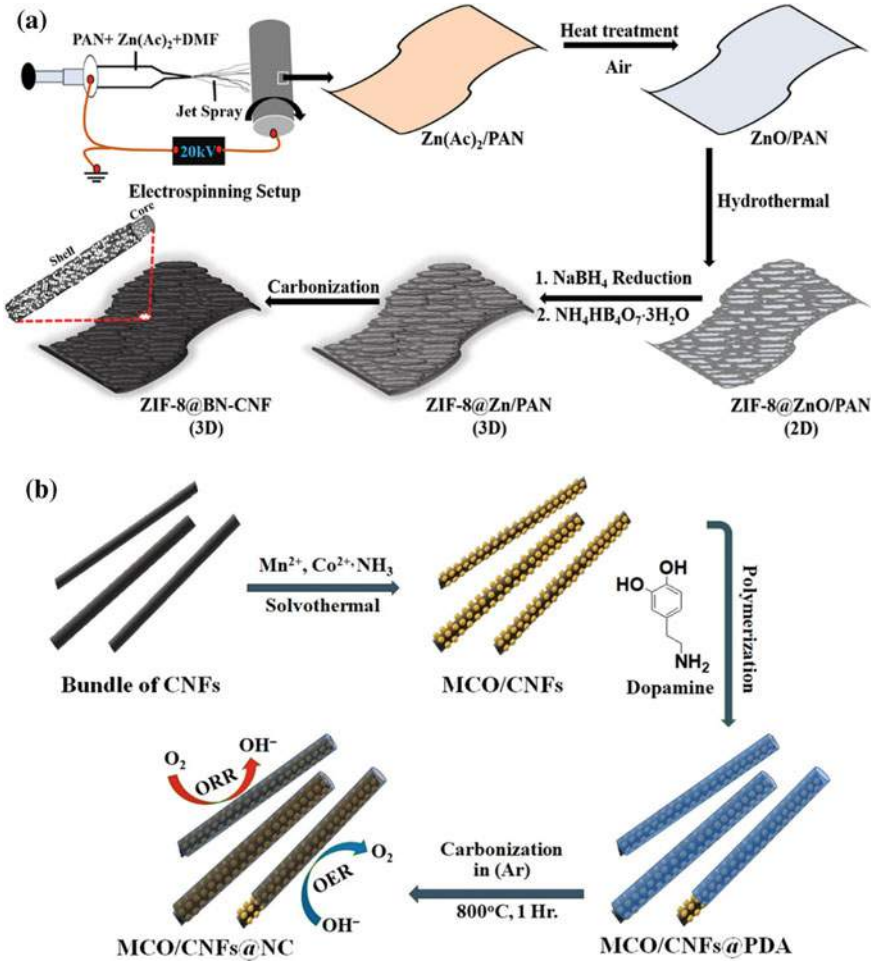

Fig. 2 **a** Schematic illustration of the synthetic process of ZIF-8-assimilated B and N co-doped core–shell 3D CNFs. Reprinted with permission from Dahal et al. [13]. Copyright 2020 Elsevier B.V. **b** Schematic illustration of synthetic route of MCO/CNFs@NC catalysts. MCO is $MnCo_2O_4$, CNFs is carbon nanofibers, and NC is nitrogen-doped carbon. Reprinted with permission from Gebremariam et al. [25]. Copyright 2018 American Chemical Society

OER	Acidic condition Alkaline condition Aprotic electrolyte	$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$ $4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^-$ $O_2^{2-} \rightarrow O_2\uparrow + 2e^-$
ORR	Acidic condition	$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O(4e^-)$ $O_2 + 2H^+ + 2H_2O \rightarrow H_2O_2\ (2 + 2e^-)$ $H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

(continued)

(continued)

	Alkaline condition	$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$ $(4e^-)$ $O_2 + 2e^- + H_2O \rightarrow HO_2^-(2 + 2e^-)$ $HO_2^- + 2e^- + H_2O \rightarrow 3OH^-$
	Aprotic electrolyte	$O_2 + e^- \rightarrow O_2^-$ $O_2^- + e^- \rightarrow O_2^{2-}$

OER is mostly dependent on pH, because under acidic or neutral conditions, two water molecules were oxidized and generate an oxygen molecule and four electrons, whereas hydroxyl groups were oxidized to oxygen and water under basic conditions [32]. On the other hand, ORR can occur at two possible routes such as two and four-electron pathways with partial or complete reduction. Both OER and ORR have some drawbacks such as slow kinetics, poor reversibility of oxygen, and high overpotential when using in metal-air battery [32].

3 Carbon-Based Nanomaterials (CBNs)

Carbon materials are mainly composed of three types of forms such as amorphous carbon, graphic, and diamond like carbon which are varied based on the arrangement of carbon atoms [33]. In early 1985, the fullerenes-based CBNs such as C_{60}, C_{70}, C_{84} were discovered and used in variety of applications due to the unique structural feature of the fullerenes [34]. Later on, CNTs with one-atom-thick tubular-shaped graphitic sheet, GO, graphene, and single-layered graphene-based CBNs were discovered via various physicochemical methods which dominate the overall research fields for the past few decades and also applied in various industrial products [34]. This is owing to the possesses of larger surface area, porosity, and superior chemical, electrical, physical, and optical properties, respectively, as compared with various other nanomaterials due to the abundant availability, flexibility, low cost, environmental-friendly, good chemical and thermal stability. CNTs have several advantages because of superior architecture obtained by the chemical vapour deposition with single or multi-layered tubular structure with uniform length and diameter, and the presence of extended SP^2 carbon would responsible for enhancing the electrical and optical properties [35]. In addition, due to an exceptional mechanical stability, flexibility, and rigidity of CNTs, which can be widely used as a filler for the development of various composites for high-yield applications.

In the recent days, noble metal-free materials such as platinum group metal (PGM) free transition metals, metal oxides, carbon-based nanomaterials (CBNs) were demonstrated with the wider applicability in various applications [36]. Among the transition metal-based material, CBNs were displayed with huge interest in catalysis, ECS, biological, and environmental applications [16, 32, 37–41]. The structural incorporation by doping of heteroatoms such as nitrogen, sulphur, phosphorous, boron, respectively, on the CBNs may also enhance the physicochemical properties [37], owing to the creation of surface defects and edges as well as the presence

of more active materials in the CBNs. Among the various CBNs, graphene, GO, CNTs, ACs illustrated a widespread usability in different application on account of unique physicochemical behaviours. So that these materials were used largely in several applications especially in electrocatalysis, ECS, biological, and environmental remediation. Baby et al. briefly reviewed the important aspects of CBNs for the treatment of heavy metals from the polluted water as well as other environmental applications [41]. The author discussed the role of various dimensional CBNs for their effective metal adsorption and remediation. Based on the structural and dimensional parameters, CBNs can show different behaviours in numerous applications.

The formation of CSNs on the graphite carbon surface by embedding with iron source has been achieved by two steps of processes such as first, mixing the graphene oxide (GO) with ellagic acid (EA) and iron (Fe^{3+}) source to form a coordination complexes between these materials which further produces a well-ordered graphitic carbon which is wrapped with iron and forms CSNs on the surface under pyrolysis in the presence of urea (Fig. 3) [42]. The prepared electrocatalyst demonstrated an outstanding electrocatalytic ORR activity because of the presence of more active sites by the metal source as well as N heteroatom comes from the carbonization of urea [42]. The surface functionalization on carbon material can show a remarkable effect in the electrocatalytic ORR activity. Various methods were used to functionalize the carbon support such as strong acidic or alkali treatments, modifying the surface functionality with heteroatoms, high-temperature pyrolysis treatment, electrochemical etching, and various other methods.

Kim et al. briefly studied the important aspects of oxygen functionalization on the carbon containing Pt catalyst (Pt/C). The oxygen surface functionalization was carried out on the carbon black (CB-O) using strong acidic solutions followed by Pt loading by incipient-wetness impregnation method and subsequent hydrogen reduction [43]. The Pt/CB-O has displayed excellent ORR activity with excellent electrochemical active surface area (EASA) than the pristine Pt/CB. These results convey

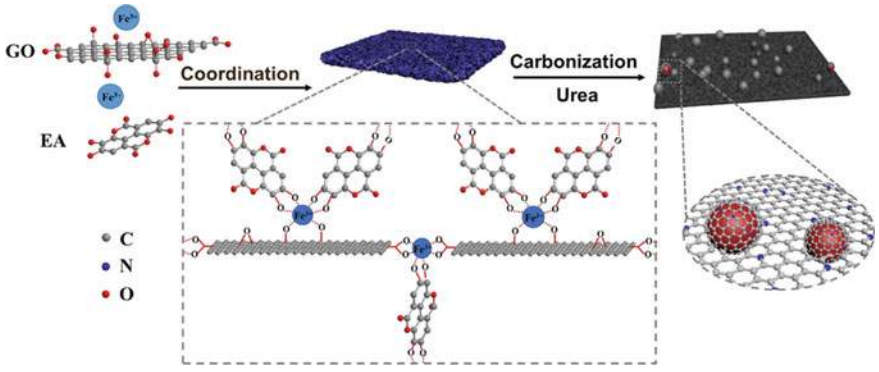

Fig. 3 Schematic illustration of the synthetic procedure for GEFs. Reprinted with permission from Zhao et al. [42]. Copyright 2018 American Chemical Society

that the oxygen functionalization on carbon could effectively improve the electrochemical ORR activity as well as stability. The main reason behind that is the partial oxidation of Pt nanoparticles in the Pt/CB-O catalyst [43]. On the other hand, doping of one or more heteroatoms such as N, B, sulphur (S), and phosphorus (P), respectively, to the carbon support can also increase the electrical conductivity and electrochemical activity for ORR due to formation of more number of active sites and defects [44–46].

4 Porous Carbon-Based Materials (PCBMs)

PCBMs also attracted huge interest for numerous applications than CBMs because of the controlled porosity and architecture. Porous carbon materials can be obtained by direct pyrolysis, chemical vapour deposition (CVD), templating method using hard (inorganic) or soft (organic) materials followed by calcination or pyrolysis, and electrospinning [47, 48]. Ma et al. briefly reviewed the synthesis of well-ordered mesoporous carbon nanostructures with higher surface areas and pore volumes using various kinds of hard and soft templates [49]. In particular, the authors suggested that the synthesis of mesoporous carbon is mainly based on the use of hard template by the following ways such as synthesis of mesoporous matrix followed by addition of necessary carbon precursor in order to modify the mesoporous structure by various approaches such as chemical vapour deposition, pyrolysis, calcination, hydro/solvothermal, and microwave-assisted methods, respectively. Further, polymerization of the organic precursor to develop an organic–inorganic hybrid material followed by carbonization and template removal using acidic or alcoholic wash to generate a highly PC [49]. The three-dimensional (3D) porous carbons and hollow carbon spheres derived from various sources have demonstrated the better hosting nature to S or various heteroatoms which can be used for battery, fuel cell, and other electrochemical applications [50, 51]. For example, S hosting on the PC can deliver outstanding electrochemical performance in lithium (Li)-S batteries on account of excellent loading of S atom on the PC [52]. Moreover, the presence copious amount pore structure and surface area in the PC can have better loading of S atom which boost the electron transport and Li-ion as well as stability.

The porous carbon synthesized by the use of metal organic frameworks (MOFs) also has huge impact in various electrochemical reactions owing to the presence of heteroatoms with significant amounts of pore structures which improve the electrocatalytic activity [53–55]. The ZIFs-based PC nanomaterial is also derived by the use of cobalt precursor with 2-methylimadazole (MeIM) which has abundant nitrogen atom in the PC and delivers an excellent electrochemical activity of ORR [56]. Luo et al. briefly discussed the important role of PC for supercapacitor applications with their effect of pore structure, surface area, surface heteroatoms and defects, and electrode design [57]. The materials with reasonable porosity, higher surface area, and superior physicochemical stability can deliver an excellent electrical conductivity.

Similarly, several research groups also discussed the use of various porous carbon-like materials for supercapacitor and other electrochemical ECS applications [58, 59]. Although various heteroatoms doping on the carbon-based materials are studied so far for ORR or other electrochemical reactions, the use of oxygen-rich carbon instead of heteroatoms is also playing a significant role in the recent days for ORR, because oxygen-rich carbon materials are directly responsible for the four-electron transfer reaction [60]. At the same time, this can show some drawbacks of reducing the electron-transport behaviour, possibility of de-bonding the conjugated structure, and difficult to incorporate larger quantity of oxygen atoms on the carbon network [60]. As like as the PCBNs obtained from activated carbon, CNTs, graphene, the mesoporous carbon nanospheres, nanoparticles, or hollow carbon nanomaterials obtained by the use of hard or soft template followed by pyrolysis also draw tremendous consideration in electrochemical ECS applications [47, 61].

Sun et al. synthesized a highly hierarchical PC by in-situ doping of N and S heteroatoms on the graphene like microstructures [47]. The porosity of the material was derived by the use of organic precursor by CVD followed by the impregnation with poly(vinylpyrrolidone) (PVP) and ammonium persulfate $(NH_4)_2S_2O_8$ in aqueous solution and pyrolysed at 800 °C in an argon/hydrogen (Ar/H_2) atmosphere followed by acid etching. The as-synthesized PC can express higher surface area and degree of graphitization, uniform porosity with well-controlled N and S doping as lead to superior electrochemical activity in Li-ion battery application due to the enhanced physicochemical properties [47]. A well-ordered mesoporous structure was fabricated by the mixing of polyaniline (PANI), dicyandiamide, and iron (III) nitrate nonahydrate $(Fe_3(NO)_3.9H_2O$ in dimethyl formamide (DMF), followed by loading of silica bead (30% ethylene glycol) and continued stirring of suspension and subsequent ultrasonication to develop a well-dispersed suspension and transferred to glass petri dishes and dried at 80 °C in an oven for overnight. The sample is further pyrolysed at 900 °C under nitrogen atmosphere to yield the N-doped mesoporous carbon (Fig. 4) [62]. The as-developed materials have excellent physicochemical properties, and also the fabricated cathode electrode demonstrated an excellent ORR activity because of the presence of well-controlled PC structure with high surface area, graphitic, and pyridinic N [62].

Roberts et al. used ice as a hard template to synthesis hierarchical porous N-rich carbon monoliths [63]. They synthesized a hierarchical PC by various approaches using melamine, graphene, or the combination of melamine and graphene as an additive to synthesize the carbon monoliths. The porous N-rich carbon monoliths was prepared by dissolving polyacrylonitrile (PAN) in dimethyl sulfoxide (DMSO) and freeze-dried under liquid nitrogen which is used as an ice template followed by lyophilization in freeze drier for 48 h to remove an excess DMSO. The obtained PAN monolith immersed further in deionized water to remove the DMSO by solvent exchange method and dried at 60 °C for 3 h. The monoliths was treated under air atmosphere at 280 °C for 1 h with the heating rate of 1 °C min^{-1}. The pyrolysis of PAN monoliths at 800 °C for 2.5 h with the heating rate of 5 °C min^{-1} in a steel pyrolysis chamber to stable and cross-linked polymer network in order to produce a hierarchical N-rich PC. An anode electrode fabricated by the use of the N-rich PC

Fig. 4 Schematic illustration of the procedure of the synthesis of porous doped carbon nanostructures. Reprinted with permission from Kwon et al. [62]. Copyright 2019 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V

delivered an excellent performance in Li-ion battery due to availability of sufficient porosity and hierarchical morphology. Moreover, the presence of more nitrogen atom in the PC is also responsible to enhance the Li-ion battery performance. Furthermore, the introduction of melamine, graphene during the preparation PC also increases the N-content as well as improves the electrical conductivity due to incorporation of conductive graphene in the PC with the reversible capacity of 300 mA h g^{-1} at 10 A g^{-1} [63].

5 Biomass-Derived Porous and Non-Porous Carbon-Based Materials

Recently, much attentions were paid on the design and development of various porous and non-porous CBMs derived from various bio-sources because of the abundant availability of the bio-sources in the earth crust [64, 65]. Biomass are mainly differentiated based on the presence of agricultural and herbaceous sources, bacteria, fungus, plants and marine algae, animal, human, and industrial waste-based biomass which accounts for the maximum ways of developing different sources of biomass [64]. Kaur et al. briefly described the important role of biomass derived-PCBNs for electrochemical ORR activity with various ways of preparation and modification of carbon networks in the porous carbons [64]. He et al. also synthesized the bifunctional PCBNs with N and S heteroatoms for ORR and supercapacitor applications [66]. The synthesized bifunctional nanomaterials showed an excellent electrical conductivity with outstanding electrochemical performance for multiple applications.

The CBNs were derived by the direct pyrolysis of bio-sources followed by some chemical treatments, also by hydrothermal or solvothermal methods, chemical vapour deposition, and some other roots [64]. These CBNs are much useful in various applications especially in electrochemical ECS applications due to an improved electrical conductivity, abundant availability of the basic resources, development of high pore diameter, surface area, and pore volume, respectively [64–70]. Sudhan et al. used a rice straw-based biomaterial to synthesize activated PC by washing chopped, dried rice straw in water followed by drying at 80 °C for 24 h in an oven and pyrolysed at 600 °C for 4 h in argon atmosphere at the heating rate of 5 °C min^{-1} (Fig. 5) [69]. The carbon material was activated further using KOH to yield activated PC which exhibits a superior activity for supercapacitor and showed also the improved electrocatalytic activity in fuel cell application [69], whereas the shell of pumpkin seeds was also used to get the PC by first activating the cleaned shell using potassium hydroxide (KOH) followed by heat treatment for certain temperature and further pyrolysis to yield highly PCBNs [71]. The carbon material played a vital role in the absorption of microwave.

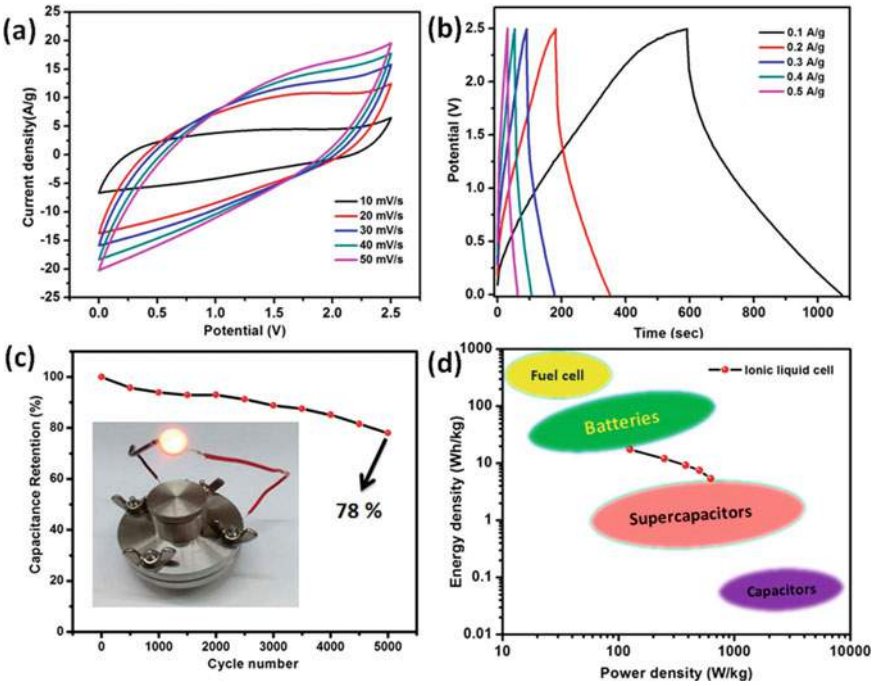

Fig. 5 **a** CV profile of the AA-RSC symmetric two-electrode cell in [EMIM] [BF_4], **b** CD profile of the AA-RSC symmetric cell at different current densities, **c** specific capacitance of the AA-RSC symmetric cell as a function of the cycle number at 0.5 A g^{-1} current density and the AA-RSC symmetric cell-powered LED (inset), and **d** ragone plot for the AA-RSC symmetric cell in an ionic liquid electrolyte. Reprinted with permission from Sudhan et al. [69]. Copyright 2016 American Chemical Society

Yang et al. briefly reviewed the important aspects of bio-derived carbon for the microbial fuel cell application [72]. Liu et al. studied the N heteroatom-doped PC for ORR activity by preparing the PC from the water hyacinth biomaterial [73]. The water hyacinth washed with deionized water and cut it in to small pieces and dried at 80 °C for 12 h followed by mixing with zinc chloride ($ZnCl_2$) at the ratios of 1:6 and pyrolysed at 600 °C as well as 800 °C for 2 h in N_2 atmosphere. The prepared carbon material was washed with 0.5 M nitric acid (HNO_3) and 1 M hydrochloric acid (HCl) and deionized water followed by dried at 80 °C [73]. Similarly, lotus root, spinach leaves, soybean straw, and raw woods were also used to prepare the high PCBMs by activating with suitable activating agents and protocols and reported the better performance in electrochemical ORR activity [74–77]. Various other biomaterials-based PC materials were also prepared in different approaches and used an electrocatalyst with superior stability and performance for ORR activity [78–80]. More recently, Sumboja et al. prepared the iron and cobalt (FeCo) loaded with N heteroatom-doped PC using the combinations of pistachio and peanut shells which displayed an excellent performed in aluminium (Al)-air battery [81]. This finding clearly tells the important role of various biomass for the preparation of PCBMs and their wider applicability in various electrochemical energy storage and conversion as well as for other applications.

6 Importance of CSNs-Based Porous Carbon Nanomaterials for ORR

CSNs are highly important in various applications because the structure is controlled preciously based on the requirements with one or more atoms either in the core or shell [82]. In most cases, core is worked as a support to the shell, so that the deposition of a thin layer of Pt could have a huge impact in the electrocatalytic application. The Pt loading is also kinetically controlled by alloying with other earth-abundant Pt free transition metals or doping with heteroatoms to make more active sites or by creating defects at the edges as well as corners in shell which could make the material much suitable for superior electrocatalytic applications [83]. Likewise, the intrinsic activity of Pt-based catalyst is also controlled by the introduction of secondary transition metals by alloying with Pt such as the formation of the chemical compositions of PtCo, PtNi, PtFe, PtCu, and PtCr which also illustrated the creation of higher mass and specific activities than commercial Pt or Pt/C catalyst [84].

CSNs have reduced the impact of higher loading Pt by the introduction of low-cost transition metal in the core which facilitates the easier display of catalytically active sites to molecular hydrogen as well as reduces the final cost of the electrocatalyst. At the same time, the introduction of only metal sources sometimes expressed poor stability against acidic and basic conditions due to decompose or precipitation behaviour at these condition. Further, the chemical, thermal, and mechanical stability and electrical conductivity of carbon or PC materials were improved using CSNs.

In addition, the introduction of heteroatoms in the PC network structure of CSNs also eases the enhancement of electrical conductivity, specific and mass activities as well as various other properties necessary to improve the performance of the electrocatalyst for ORR and other electrochemical applications [13, 25, 84].

Wang et al. developed a N-doped ZIF-67-based PC by first synthesizing ZIF-67 and pyrolysed at 600 °C for 2 h in Ar atmosphere followed by Pt loading on the shell structure by galvanic replacement mechanism (Fig. 6) [84]. The synthesized nanostructure exhibits sufficient active sites and high specific surface area as well as better tolerance with robust property and durability in the CSNs which are practically much important to the improve ORR performance. Various MOF-based PC nanostructures also demonstrated efficient electrocatalytic applications due to the constrained architecture of MOF with interesting properties based on the presence of organic–inorganic materials used to develop the materials [54, 85]. Porous material can easily control the reaction between the electrolyte and electrode due to the easier transport of electrons and protons between the pore channels which facilitate an enhanced electrocatalytic activity as compared to the non-porous carbon-based materials. In some cases, the oxygen and N-rich porous metal-free carbons also delivered outstanding ORR activity and also used for fuel cell applications due to the presence of low overpotential, large specific capacitance, long-term stability, higher surface area and controlled porosity, uniform distribution of heteroatoms on the pore channel or carbon networks, and excellent electrical conductivity [86, 87]. Similarly, the presence transition metal with heteroatom-doped porous carbons also demonstrated a significant advancement in order to improve the electrocatalytic ORR activity [88, 89]. The structural defects are also playing a vital role in upgrading the electrocatalytic activity for ORR. Jia et al. discussed in detail the various parameters such as etching, doping, ball-milling, annealing, plasma treatment, electrochemical method, photoreduction, and hydrogenation methods, respectively, which were used to create the defects in the electrocatalyst [90]. Controlling the defects and vacancies in the CSNs containing PC frameworks would improve the catalytic activity.

7 Transition Metals and Metal Oxides-Embedded Porous Carbon Nanomaterials for ORR

Earth-abundant transition metals and metal oxides are playing a pivotal role in electrochemical ECS applications due to abundant availability of the transition metals as well as their low cost as compared with the noble metals such as Pt, Ru, Ir, Au, and Ag, respectively [51, 91]. The modification of these transition metals to achieve a highly porous carbon-based transition metals also considers an effective approach in electrochemical ECS because of the generation of an excellent porosity, surface area, pore volume. Moreover, the PC would facilitate an enhanced electrical conductivity and stability. Ahn et al. modified the surface of a one-dimensional nanotubes such as porous tellurium nanotubes (Te NTs) with ZIF-8 structure and embedded further by

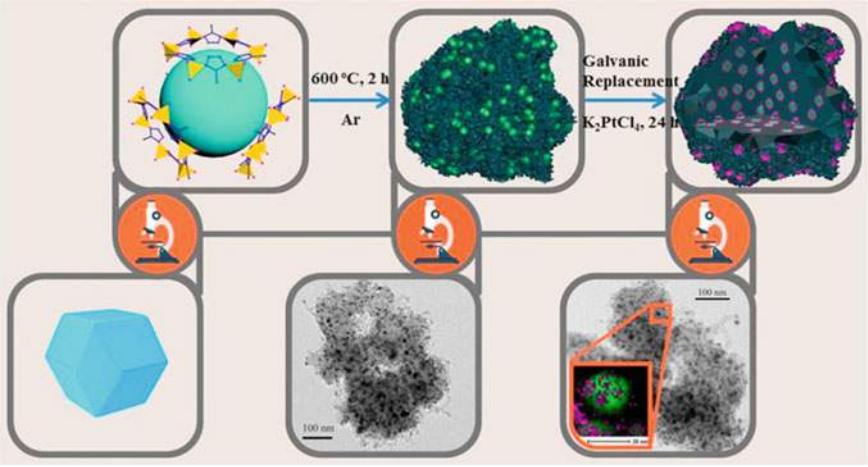

Fig. 6 Schematic of the preparation of Co@Pt-NC nanocomposites. Reprinted with permission from Wang et al. [84]. Copyright 2017 Elsevier B.V.

using dopamine hydrochloride as well as with ferric chloride and subsequent pyrolysis at 950 °C for 2 h with heating rate of 5 °C min^{-1} to yield a highly PC [92]. The electrode fabricated by using these materials delivered an outstanding ORR activity under both acidic and basic media. The well-ordered FeN_x active site present on the PC with large graphitic layers at the surface would be responsible for the efficient catalytic activity. In addition, the fabricated electrode also showed an outstanding result in zinc-air battery application [92].

Song et al. briefly reviewed the important role of non-precious transition metal-based carbon materials with N heteroatom for the ORR as well as their future use in proton exchange membrane in fuel cell application [93]. These types of hybrid electrocatalyst with M-N_xC (where M = metal source, $x = 2$ or 4 based on metal and nitrogen bonding such as MN_2 or MN_4) structures have acquired much observation in the recent days because of the low cost, earth abundant, excellent electrical conductivity, easier reproducibility, and existence of more active sites, respectively. The improvement in the electrocatalytic activity of ORR observed for the M-N_xC-based electrode would depend up on the carbon support on the transition metals because an excellent dispersibility was encountered based on the presence of carbon atom which eases better dispersibility and enhances the electrocatalytic activity for ORR [93]. In addition, the heteroatom doping on the carbon-supported transition metals also displayed better catalytic activity as compared with the absence of heteroatom [93, 94]. This is due to the creation of more numbers of active sites on the carbon-supported transition metals by the heteroatom.

The porous carbon polyhedral (PCP) synthesized with the decoration of cobalt and diselenide by simple selenization of the as-synthesized ZIF-67 with selenium by pyrolysis technique can deliver the uniform embedding of metal sources within the PCPs and also displayed an excellent properties and also manifested an outstanding

performance in the electrocatalysis of ORR (Fig. 7a) [95]. The organic ligand in the ZIF-67 structure was converted to graphitic carbon polyhedral (GCP) during the carbonization process, and at the same time, the then diselenide also loaded uniformly throughout the cobalt (Co)/GCP [95]. These can yield a stable and strong connection between the carbon surface and metal sources which ease the formation of more active sites. Moreover, the synthesized material displayed an excellent dispersibility, electrical conductivity, and also a high surface area which are responsible to show superior durability and catalytic activity in alkaline media [95]. Similarly, a recent study of synthesizing the iron-loaded ZIF-67 structure followed by pyrolysis also yields the transition metal-embedded PC which also conveys an outstanding electrocatalytic activity to ORR (Fig. 7b) [96].

8 Heteroatom-Doped CSNs with Porous Carbon Nanomaterials for ORR

Heteroatoms such as N, P, B, S, and the combination of two or more heteroatoms present in the CSNs-based PC have displayed an excellent electrocatalytic activity. These heteroatoms-doped porous carbons can be applied in various ECS applications owing to the availability of abundant active sites, surface defects as well as the presence of lone pair of electrons which boost up the electron transfer and enhance the electrical conductivity for electrocatalysis applications [97–102]. The ZIF-67-based material itself having N heteroatom from the ligand and subsequent pyrolysis may indicate the appearance of more active sites and the formation graphene like carbon in their structure which is responsible for the effective ORR electrocatalytic activity as like as the commercial platinum/carbon (Pt/C) electrode [95, 96]. The synthesis of phosphorous and iron-doped PC can be easily obtained by mixing the triphenylphosphine precursor with zinc and ferric chlorides followed by carbonization at different temperatures such as 800 °C, 900 °C, and 1000 °C, respectively, and further acid washing using hydrochloric acid followed by deionized water to get the PC (Fig. 8) [103]. Various other kinds of low-cost Pt group free transition metals and metal oxide with PC were also well executed for an effectively electrocatalytic ORR reaction, because of abundant availability, low cost, compared performance as like as commercial Pt/c electrode, possessing [29, 104–107]. More studies also performed the synthesis of much effective heteroatom-doped CSNs-based porous carbons in the recent years for ORR activities because the heteroatom doping in the CSNs as well as in porous carbons not only enhances the electrochemical activities, it also enhances various physicochemical properties which are much important in various applications.

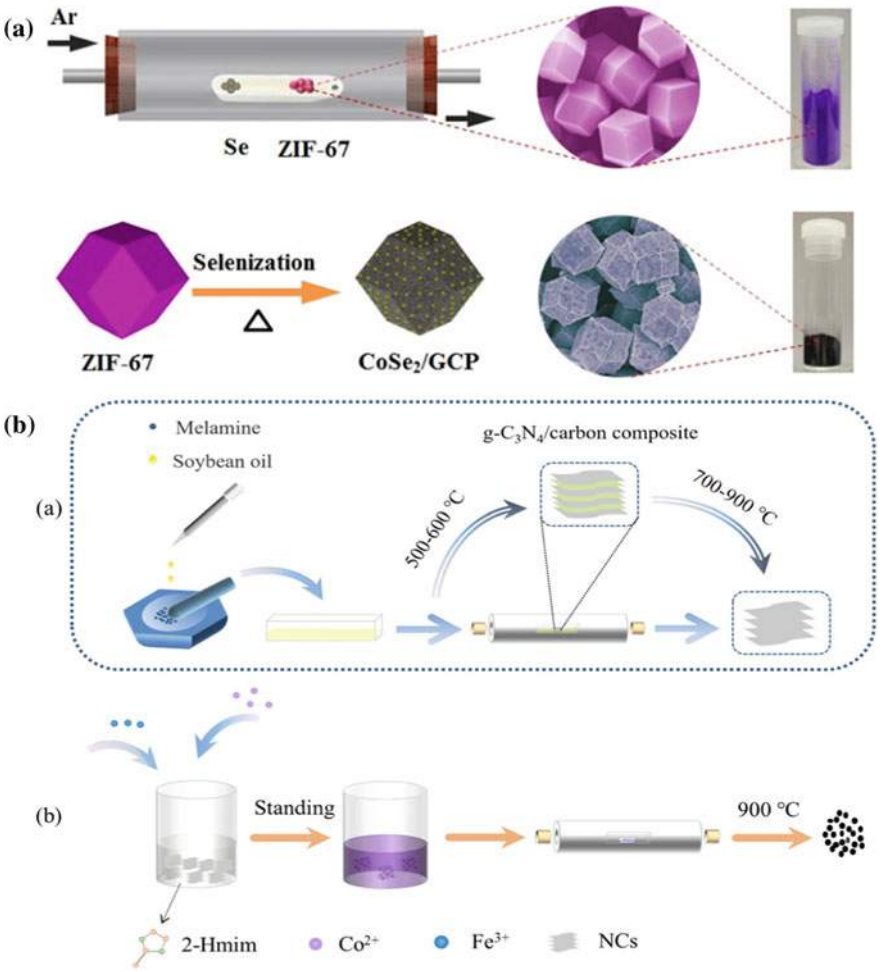

Fig. 7 **a** Schematic illustration of fabrication of ZIFs-derived CoSe2/GCP hybrid composites. Reprinted with permission from Wu et al. [95]. Copyright 2016 Elsevier B.V. **b** Schematic illustration for the fabrication of FC@NCs. Reprinted with permission from Luo et al. [96]. Copyright 2021 Elsevier Inc.

9 CSNs with Carbon Nanomaterials for ORR or OER with Supercapacitor Behaviour

Supercapacitors are playing an important role for the current demand of energy storage [108]. The materials with good cyclic performance, high specific power, flexibility, fast charge–discharge rate, high surface area, and cyclic stability can be used widely for supercapacitor application [109]. A binder-free electrode fabrication method is the most desirable approach for designing an electrocatalyst for ECS

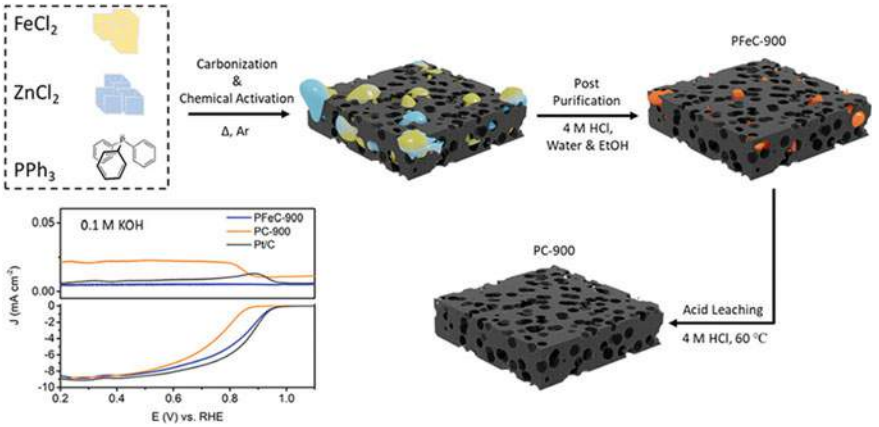

Fig. 8 Schematic illustration of the preparation of iron phosphide-doped PC for ORR. Reprinted with permission from Norouzi et al. [103]. Copyright 2020 American Chemical Society

application due to the presence of binder would increase the contact resistance of the electrode. The electrode having an electrocatalytic ORR activity with supercapacitor behaviours attracted huge interest in fuel cell and supercapacitor applications [108, 109]. Recently, numerous works were focused on ORR as well as supercapacitive behaviours using various nanomaterials [68, 108, 109]. Gao et al. prepared the nitrogen and oxygen dual-doped carbon (NODC-800); electrocatalyst obtained from catkins was used as superior ORR catalyst in alkaline fuel cell with superior capacity of 109 F g^{-1} at 0.5 A g^{-1} and maintained the stability over 1000 cycles [108]. The author also prepared N-doped PC spheres at large scale using fermented rice-based biomass as an active material. The prepared material has high porosity (1.14 cm^3 g^{-1}) with maximum surface area (2105.9 m^2g^{-1}), and outstanding electrocatalytic four-electron ORR activity [110]. In addition, the electrocatalyst also exhibits good cyclic stability and specific capacitance of 219 F g^{-1} at the discharge current density of 15 A g^{-1}. Kim et al. synthesized a nickel-mediated metal organic frameworks (MOFs)-based macroporous carbon (Ni-MOF@mC) which can deliver an outstanding electrocatalytic ORR activity and superior supercapacitive behaviour because of well-defined pore size, presence of high surface area, chemical tenability, and conductivity of the material [111]. The Ni-MOF@mC can show the specific surface area with normalized capacitance of 26.5 mF cm^{-2} as well as high capacitance performance of 109 F g^{-1}.

Likewise, a material possessing both OER and supercapacitor characteristics also displays significant interest in ECS applications [112–116]. OER took place by the oxidation of two water molecules with four electrons followed by the removal of four protons to produce a weak O–O bond [117]. The important drawbacks of OER are the need of high overpotential to reach a desirable current density as well as the use of expensive iridium- or ruthenium-based catalysts [118]. Khalid et al. have prepared highly active and low-cost electrode using natural sugar powder as a biosource by

reacting with red phosphorous to form a carbon particle [119]. The carbon-based electrode prepared from the sugar source displays the overpotential of 1.69 V versus Reversible hydrogen electrode (RHE) at 10 mA cm^{-2} current for the OER also showcases the specific capacitance of 105.8 F g^{-1} with 100% of the initial capacitance retention even after 3000 voltammogram cycles. More recently, Kale et al. fabricated a binder-free nanocrystalline cobalt sulphide (CoS) on stainless steel (SS) substrate by chemical bath deposition (CBD) that has showed a remarkable supercapacitive and OER activity [120]. The prepared electrocatalyst showcases the specific capacitance of 252.39 F g^{-1} @ 5 mV s^{-1} and maintained the initial capacitance over 1000 cycles of CV. In addition, the electrode can also present the overpotential of 300 mV@ 10 mA cm^{-2} and Tafel slope of 57 mV $decade^{-1}$. The excellent properties of the prepared electrode were due to the origination of uniform thin films of nanocrystalline hexagonal CoS on the SS substrate [120]. The surface corrosion/oxidation effects worsen the performance of most of the fabricated electrodes in both ECS [121]. This drawback can be encountered by synthesizing CSNs with conductive core and nanostructured outer shell. The core–shell FeO@$CuCo_2S_4$ was fabricated on a nickel foam (NF) substrate by two-step synthesis approaches such as hydrothermal growth of $CuCo_2S_4$ on NF substrate followed by FeO deposition on the substrate via magnetic sputtering technique. The fabricated electrode offers an excellent specific capacitance of 3213 F g^{-1} at 1 A g^{-1} and withholds over 99% of efficiency after 10,000 charge/discharge cycles. On the other hand, the electrode also displays low overpotential of ~240 mV at 10 mA cm^{-2} and Tafel slope of 51 mV dec^{-1}. Moreover, the electrode can be usable up to the current density of 100 mA cm^{-2} for over 25 h [121]. Chu et al. fabricated phosphorous-doped $NiCo_2O_4$ (P-NCO) nanowires on NF substrate by two steps such as growth of $NiCo_2O_4$ on NF substrate by hydrothermal method followed by phosphatization via pyrolysis step [122]. The P-NCO electrode can have the superior specific capacitance of 2747.8 F g^{-1} at 1 A g^{-1} as well as low overpotential of 300 mV at 10 mA cm^{-2} (1 M KOH) activity during OER.

10 Factors that Affect the Performance of Carbon Materials in ORR

There are several factors that affect the production of carbon-based materials in ORR such as surface defects and active sites, porosity, electronic configuration, types dopants, presence of inorganic impurities, acidic and basic solutions concentration, band gap. Tian et al. discussed the important role of N-content in the transition metal carbides (TMCs) as well as kind of graphitic shells that can largely affect the performance of the carbon-based electrode during ORR [123]. Carbon-based materials like carbon nanotubes, graphene, activated carbon, carbon black, mesoporous carbon, and carbon nanofibers are considered to be inactive electrocatalyst due to unavailability of catalytic active sites for the ORR [124]. At the same time, the electrocatalytic

ORR activity was increased by the introduction of heteroatoms to the carbon material via in-situ doping during the synthesis or post-treatment of the carbon material with dopants [123, 124]. In both ways, the fabricated electrocatalyst can deliver a remarkable catalytic activity for the ORR. Likewise, the introduction of some kinds of defects to the carbon material also showed much-improved ORR activity [125].

Some studies were demonstrated that the existence of less content of N in the carbon-based material after high-temperature treatment can deliver outstanding positive onset potential and also provide almost four-electron transfer number than the presence of larger contents of N in the carbon-based material [125]. Because the introduction of N atom to the C can activate the electronic structure of the neighbouring carbon atom that facilitates the active role for ORR. So, the synthesis of defective carbon with adjustable electronic configuration can play a vital role in ORR [125]. The ORR activity of the pristine carbon can also be activated by physical intermolecular charge transfer, introducing of non-metal heteroelements to the carbon matrix, and developing structural defects [126]. The introduction of boron and nitrogen dopant to the carbon would slightly alter the energy gap, whereas increasing more dopants to the carbon would significantly increase the energy gap and reduce the conductivity [127]. So, the use of average quantity of B and N on the carbon can show outstanding ORR activity. The porosity of the carbon material with various length scales as well as the presence of dopants also showed an adverse effect in the mass transfer during ORR [126]. The availability of microporosity in the carbon material can present superior ORR activity than the mesoporosity. At the same time, some studies were suggested that the mesoporosity with larger pore size and specific surface area would facilitate the easier contact of the reactant through the pore channels [128]. On the other hand, the combination of micro and mesoporosity with wider porosity as well as hydrophilic behaviour can further enhance the electrocatalytic ORR activity [129–131]. The band gap of carbon material also plays an important role to decide the ORR activity. When the dopants are attached to the same sublattice, parts of the carbon material can deliver the maximum band gap and closed, while the dopants are placed adjust to carbon sublattice [132]. The band gap of carbon material increases with increasing doping concentrations. In general, band gap is inversely proportional to the conductivity. The outstanding ORR activity was achieved with the reduced band gap of the carbon material [133]. The B and N-doped carbon material can show smaller energy gap as compared to the pristine graphene, whereas overdoping to the carbon material can lead to increase of energy gap. The lowest energy gap of the B and N-doped carbon can demonstrate the highest chemical reactivity and catalytic performance [132, 134]. We also compared various CSNs obtained with PC nanomaterials for ORR in 0.1 M KOH (Table 1).

11 Future Perspectives and Outlooks

The CSNs-based PC has attracted considerable attentions in the recent days due to the maintenance of excellent properties such as high surface area, pore diameter, pore

Table 1 Comparisons of CSNs-based porous carbon nanomaterials for ORR performance in 0.1 M KOH

Catalyst	Loading (mg cm^{-2})	Electrolyte	E_{onset} *vs* RHE	$E_{1/2}$ *vs* RHE	References
ZIF-67–900	0.7	0.1 M KOH	0.91	0.85	[135]
NC-900 (ZIF-8)	0.11	0.1 M KOH	0.83	0.68	[136]
GNPCSs-800	0.2	0.1 M KOH	0.957	0.82	[137]
NPCS-800	–	0.1 M KOH	0.95	0.83	[138]
N-doped Fe/Fe_3C@C	0.7	0.1 M KOH	0.91	0.83	[139]
CNS-800	0.28	0.1 M KOH	0.914	–	[140]
NDCN-22	0.6	0.1 M KOH	0.954	–	[141]
CoP-CMP800	0.6	0.1 M KOH	0.88	0.82	[142]
$NHPC_{1:3}$–900	0.42	0.1 M KOH	–	0.87	[143]
CNM@C	–	0.1 M KOH	0.72	0.62	[144]
$B_{1.0}$CNM@$C_{1.0}$	–	0.1 M KOH	0.78	0.68	[144]
Co@Pt-NC	–	0.1 M KOH	0.99	0.87	[84]
CoOx/Co@GC-NC	0.464	0.1 M KOH	0.957	0.858	[145]
Co@Co_3O_4@C-CM	0.1	0.1 M KOH	0.93	0.81	[146]
PCN-FeCo/C	0.2	0.1 M KOH	1.0	0.85	[147]
CoS NWs@NSC-2	–	0.1 M KOH	0.93	0.84	[148]
Co–C@NWCs	0.1	0.1 M KOH	0.94	0.83	[149]

volume, good electrical and thermal conductivity. Furthermore, the introduction of heteroatoms as well as non-precious transition metals to the CSNs-based PC also facilitates the much-improved physicochemical properties and excellent usability in electrocatalytic applications. These materials would help to replace the usability of precious metal consumption by doping of small quantity of heteroatoms as well as non-precious transition metals. This obviously reduces the product cost and delivers almost identical or better electrocatalytic behaviour and also improves the stability under acidic, basic as well as alcoholic solutions as compared with the commercial high-yield products made by the use of noble metal catalysts. So, the recent studies are largely focused under this area in order to reduce the product cost and enhancing the performance of the electrocatalyst. Especially, the nitrogen heteroatom-doped porous carbons are synthesized widely using various kinds of nitrogen-containing organic compounds because the carbonization of these materials would successfully form a negatively charged pyridinic N as well as graphitic N in their structure due to the availability of lone pair of electron by the N atom. Moreover, the presence of N heteroatom in the PC would facilitate the emergence of more active sites as well as defects in the carbon nanostructures. In the addition, the presence of carbon nearer to N atom would act like Lewis basicity which helps to absorb more oxygen molecules on the carbon sites. A noticeable change in the pyridinic N was due to conversion of pyridinic N to pyridonic N which can confirm the successful ORR activity occurred

on the N-doped PC electrocatalyst. In contrast, the presence of graphitic N also exhibits some defects and active sites in the PC which are also helpful in enhancing the electrochemical oxygen adsorption and reduction activity. Based on these reasons, the N-doped porous carbons were demonstrated as an excellent electrocatalyst for ORR activity and also illustrated an outstanding stability against alcoholic solution as well as acidic and basic conditions which are much-important properties for fuel cell and battery applications. In the addition, the hierarchical porous architecture in the PC would help the easier diffusivity oxygen molecules and electrolyte in the porous networks and improve the performance of the electrocatalyst of ORR. The heteroatom doping as well as non-precious transition metal ions or oxide doping on the porous carbons also has some drawbacks due to some sensitivity against moisture or other physicochemical changes by prolonged exposure which obviously reduces the performance of the developed products. More focused studies need to be carried out in order to enhance the electrocatalytic activity and improve the stability against various stimuli.

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