

Unique One-Step Strategy for Nonmetallic and Metallic Heteroatom Doped Carbonaceous Materials

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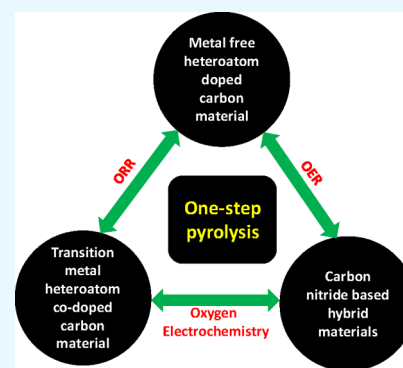
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ABSTRACT: Nonmetallic and metallic heteroatom doped carbonaceous materials have garnered tremendous research attention due to a potential replacement to the precious Pt-group and (Ru, Ir)-oxide based catalysts and are essential part of the next-generation electrode catalysts for fuel cells, electrolyzers, and metal–air batteries. In this regard, we focus on three important categories of carbonaceous material, namely, metal-free heteroatom doped, transition metal heteroatom codoped, and carbon nitride (C₃N₄) based hybrid materials. Implications of various strategies, using one-step pyrolysis technique have been discussed for the effective design of heteroatom modified carbonaceous electrocatalysts. In this minireview, we outline the richness of one-step strategy for designing electrochemically active heteroatom doped carbon, transition metal–heteroatom codoped carbon, and C₃N₄ derived hybrid materials in the perspective of electrochemical energy conversion and storage devices. We also outline the future research direction in the development of highly efficient and sustainable electrocatalysts for oxygen electrochemistry. Finally, we wind up the article with the challenges and outlook on heteroatoms and transition metal–heteroatom codoped carbon material as an efficient and low-cost electrocatalysts, thereby promoting the development of this important area.



INTRODUCTION

With the ever-growing demand of clean and sustainable energy resources, the development of low cost and efficient energy technology has received tremendous attention in recent times. Various electrochemical energy devices such as fuel cells, metal–air batteries, and water electrolyzers are the front-runners in this pursuit.¹ Commercial adoption of these devices lies in the electrocatalysts used to promote the otherwise complex and sluggish oxygen electrochemistry. The oxygen electrochemistry includes the oxygen reduction and evolution reaction (ORR/OER).¹ Most of the electrocatalysts face the issue of unwanted overpotential, owing to the involvement of multielectron transfer and a variety of reaction intermediates. The increased overpotential directly influences the energy efficiency and lifetime of electrochemical devices. Efforts have been made to trim down the overpotential along with improved exchange current density by rational design of electrocatalysts. It is widely acknowledged that the noble metal-based catalysts such as Pt, and Ru/Ir-based systems are known to possess high activity toward ORR/OER.^{1,2} In addition to the high cost, as electrocatalysts in fuel cells alone contribute 50% of the total cost, and scarcity of these noble metals, their monofunctionality and pH selectivity has further delayed their wide-scale commercial adoption.

The seminal contribution by Yeager in 1964 opens new insights in carbon–transition metal based electrocatalysts.³ Inspired by this, various groups including ours have devised

various pyrolysis strategies to improve the potency of carbon based systems for efficiently catalyzing the ORR/OER processes.^{1,2,4} In general, the carbon based materials owing to its interesting properties such as the variety of possible structures (0, 1, 2, and 3 D), excellent electrical conductivity, microporous structure, chemical inertness, and the ability to host various hetero atoms have made them preferable materials of choice in catalysis. The inert character of pure pristine carbon owing to strong delocalized π -electrons can be easily modified/disturbed by the hetero atom doping.

The nonmetallic heteroatom doping in the carbon nano-structure offers an efficient way to institute the electrochemically active sites and widely studied heteroatoms comprising N, B, P, S, F, etc.⁵ The difference in electronegativity between carbon and heteroatoms leads to the redistribution of charge and spin density of the carbon atoms in the lattice, thus effectively regulating the overall work function and modulating the adsorption energy of the reactants at the active sites which lead to the enhanced activity.⁵ The introduction of transition

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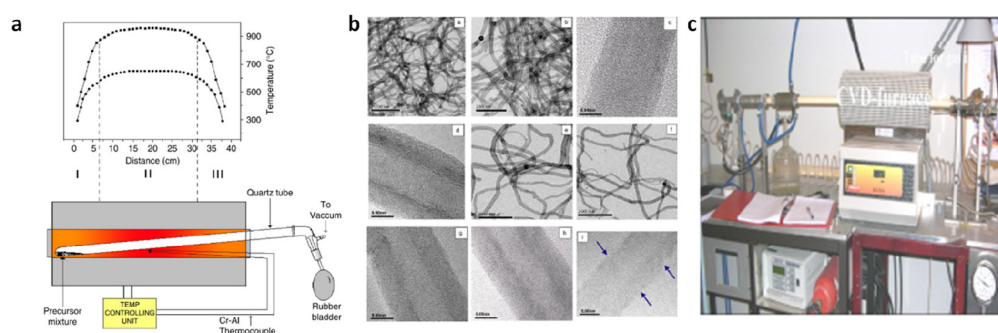


Figure 1. (a) Schematic diagram of the one-stage pyrolysis setup and calibrated temperature profile across the furnace. (b) TEM images of as-synthesized carbon nanotubes at (a) 650 °C and (b) 950 °C and respective HRTEM images (c) and (d). TEM images of purified CNTs synthesized at (e) 650 °C and (f) 950 °C and the respective HRTEM images (g) and (h). Defects on the side wall of a purified MWCNT (i). (figure adapted with permission from ref 7. Copyright 2007, Elsevier Ltd. (c) Photograph of the chemical vapor deposition (CVD) experimental setup (figure adapted with permission from ref 9.

metal with nonmetal heteroatoms like N further regulates the catalytic activity toward ORR/OER. Moreover, in the context of gas consuming and evolving reactions like ORR/OER, porosity plays a central role in the utilization of large specific surface area, suitable mass transport by allowing the accessibility of reactant species, and electrochemical active centers rendered by heteroatom incorporation. Various strategies have been employed to achieve the pertinent porosity, where the templates such as silica, porous alumina, polystyrene, and cellulose have been utilized and resulted in the targeted porous carbon materials which indeed exhibit impressive performances.⁶ In this regard, the direct one-step synthesis approach offers an excellent versatility to assimilate all the required features needed for ideal electrocatalysts, with ease. Importantly, the final electrocatalysts designed by one-step pyrolysis do not require any cumbersome or complex post-synthesis processes which otherwise not only adds cost but can be time-consuming and environmentally offensive too.

In this review, we summarize the rationally designed heteroatom enriched electrocatalysts, mainly carbon based systems, by one-step pyrolysis strategy for oxygen electrochemistry (ORR/OER). We have also discussed the metal-free/ C_3N_4 -based hybrid materials and a new class of transition metal/ C_3N_4 based hybrid electrocatalysts reported for ORR/OER.

■ SYNTHESIS OF CARBON NANOSTRUCTURES

This article mainly discuss the electrocatalysts designed by employing one-step pyrolysis; there are various other techniques too, which have been explored by researchers around the globe and documented in previous reviews. In line with the one-step synthesis, Mahanandia et al. developed a very facile and effective one-step pyrolysis strategy to design a variety of pristine carbon nanotubes (CNT, Figure 1a,b) which does not require any sophisticated machinery and carrier gas like that in the chemical vapor deposition system (Figure 1c).⁷

This user-friendly one-step pyrolysis gives us a unique opportunity for in situ modification of CNT and other targeted carbon nanostructures by simply controlling the pyrolysis temperature, ramping rate, appropriate precursor selection, and their position in the electrical furnace. By simply using a precursor mixture of two carbon sources of different boiling temperatures, benzene (C_6H_6 , bp ~ 80.1 °C) and hexamethylenetetramine (HMT, $(C_6H_{12})_6$, N_4 , bp ~ 280 °C) with ferrocene, it has been possible to design branched CNTs with nitrogen doped/undoped intratubular junctions (Figure 2a–f).

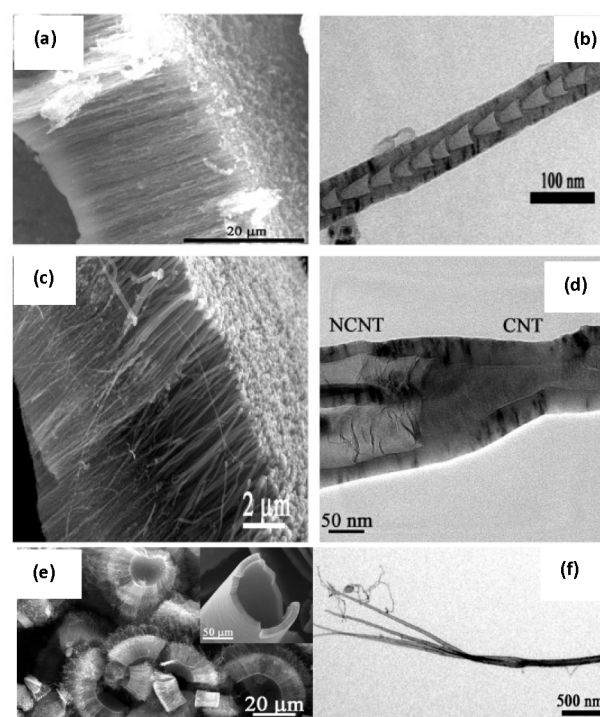


Figure 2. (a,b) SEM and TEM images of aligned NCNT prepared from single step synthesis of pyridine. (c–f) SEM (c,e) and TEM (d,f) images prepared from benzene and HMT mixture by single-step process. Adapted with permission from ref 8. Copyright 2013 Elsevier Ltd.

Interestingly, the intratubular junction behaves as a Schottky diode.⁸ The following sections discuss the effectiveness of one-step synthesis for designing electrochemically active carbon nanostructures.

■ METAL-FREE HETEROATOM-DOPED CARBON MATERIALS

The substitution of certain carbon lattice with heteroatoms such as N, B, S, P, F, etc., has been widely exploited to develop the efficient electrocatalysts for ORR/OER.⁵ The different electronegativity of the heteroatoms (N, B, S, P, F, etc.) and the carbon atoms disrupts the lattice arrangement of carbon. In addition, the atomic size difference leads to a change in the geometry of the local proximity of the heteroatom, resulting in the structural

defects. The heteroatom may help alter the electronic cloud around neighboring sp^2 carbon atoms by breaking their electroneutrality to create the charged sites favorable for reactant and reaction intermediate adsorption irrespective of dopants nature, i.e., electron-rich (as N) or electron-deficient (as B).¹⁰ One-step pyrolysis has been successfully employed to design and develop heteroatom doped/codoped carbon based systems. Among various choices, N-doped systems have been studied widely owing to the fact that one N atom can possibly stimulate 4 surrounding carbon atoms electrochemically due to the electronegativity difference. Besides, the availability of a lone pair of electrons can conjugate π -electrons with ease.

■ N-DOPED CARBON MATERIALS

N-doped carbon materials are considered as ideal and widely studied for ORR among other heteroatoms, owing to their low cost, high availability, and good and stable catalytic performances.⁵ Density functional theory (DFT) calculations revealed that strongly electron withdrawing N dopant could facilitate the charge redistribution and enhance the ORR activity.⁵ The common bonding configuration of N dopant in a given carbon matrix are pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N. Pyridinic-N atoms located at the edges or in vacancies of the graphitic carbon layer; pyrrolic-N are incorporated into the pentagonal ring and graphitic-N where N atoms replace the carbon atoms in the carbon plane. It is well accepted that pyridinic-N contributes to the high ORR activity catalyzing at low overpotential via 4-electron transfer pathway.¹ The recent study observed the decisive role of graphitic-N, too, as the remarkable active sites for facilitating the excellent ORR compare to the precious Pt-based catalysts.¹¹ It has been found that the graphitic nitrogen incorporation modulates the C–N bond length closely to the O–O bond length resulting in increased oxygen adsorption, an important requirement to design efficient oxygen electrocatalysts. In this line, Haque et al. have developed an attractive methodology of simple pyrolysis of amino MOF at the various temperatures for selective incorporation of graphitic N.¹¹ Despite this, the debate is still on to elucidate the role of pyridinic-N and graphitic-N in the facilitation of ORR. To shed some more light, Yu et al. have studied the synergistic effect of the pyridinic-N (N_p) and graphitic-N (N_G) very recently by modulating the overall electronic structure of N-doped carbon for ORR, and activity descriptive factors have been set as a ratio of N_p and N_G .¹² This group synthesized various nitrogen-doped carbon nanostructures which are named N@CNTs, NCNTs, N@RGO, and NG. The intensity of electron transfer (I_{ET}) and ratio of $N_p:N_G$ exhibits the reverse volcano plot followed by the relation of ORR activity with the ratio $N_p:N_G$, as shown in Figure 3a,b.

It may be noted that I_{ET} initially decreases and then increases with $N_p:N_G$ ratio. I_{ET} decreases from 0.5 to 0.02 mg^{-1} as $N_p:N_G$ increases from 0 to 0.55 and then increases from 0.02 to 0.6 mg^{-1} as the ratio is increased from 0.55 to 1.33. It is interesting to note from Figure 3b that a direct correlation of I_{ET} with ORR activity (the kinetic current density, J_k), which infers the identical reverse volcano plot relation for J_k vs $N_p:N_G$ ratio. It has been concluded that the synergistic effect of N_p and N_G plays an important role in improving the ORR kinetic current density.

It is important to note that, though these heteroatom-doped carbon based systems have been recommended for ORR which is a gas consuming reaction, they are equally capable to promote the OER which is a gas evolving process and happen to be the reverse of ORR. In this line, N-doped carbon materials have

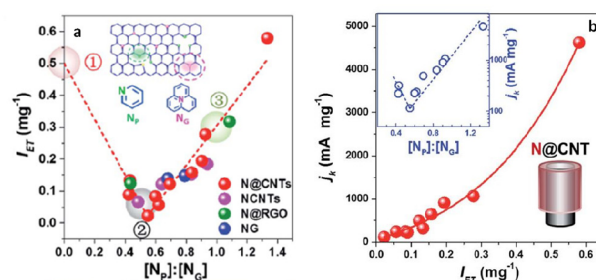


Figure 3. (a) Dependence of I_{ET} on the content ratio of pyridinic to graphitic nitrogen ($[N_p]:[N_G]$) measured by XPS. Three representative graphene structures, with $[N_p]:[N_G]$ ratios of 0, 0.5, and 1, represented by (①, ②, ③), corresponding to the points highlighted by pink, gray, and green balloons, respectively; (b) dependences of kinetic current densities (j_k) of the ORR at -0.7 V vs Ag/AgCl on the intensity of electron transfer and $[N_p]:[N_G]$ ratio (inset) of N@CNTs with a coaxial cable structure as shown in the lower right panel. J_k has been obtained according to the Koutecký–Levich (K–L) equation, and normalized by the mass of NCs. Reaction conditions: the LSV tests have been performed in O_2 -saturated 0.1 M KOH from -1 to 0.2 V at a scan rate of 5 mV/s under different rotation rates. Adapted with permission from ref 12. Copyright 2018, Royal Society of Chemistry.

been prepared by pyrolyzing melamine and nickel nitrate hexahydrate mixture at different temperature (600, 700, 800, 900, 1000 °C) and explored the OER activity.¹³

■ METAL-FREE HETEROATOMS BEYOND NITROGEN (F, S, P, OR B-DOPED CARBON MATERIALS)

Similar to the N atoms, more electronegative F and S atoms and less electronegative B and P atoms relative to the carbon would also be able to modify the charge distribution of the adjacent carbon atoms, and, hence, to the enhancement of catalytic activity can be anticipated.¹⁰ For example, F-doped carbon electrocatalyst with porous structure has been synthesized through a facile one-pot simple pyrolysis approach, benefiting from the abundant defect and large surface area due to the F dopant exhibit the comparable ORR activity to that on Pt/C.¹⁴ Different from the N atom, less electronegative B dopant incorporated in the carbon matrix gets a fractional positive charge and served as the active sites for adsorbing O_2 molecules. B–C bond plays a vital role in enhancing the ORR activity; in particular, the graphitic-like BC_3 structure is believed to be the important site by improving the electric conductivity and improving the ORR performance.¹⁵ In this regard, the one-step pyrolysis gives additional degrees of freedom and better control of instrumentation. Recently, by simply using a quartz tube of larger diameter, we have successfully grown the boron-doped CNT (BCNT) directly on the fuel-cell gas diffusion layer (GDL), the carbon paper, Figure 4) with varying B atomic content.¹⁶ Direct growth of BCNT on GDL using one step offers the 3-fold effectiveness. First, it avoids the use of binders (e.g., Nafion, thus associated cost). Second, it ensures the seamless integration of electrocatalysts on GDL which provides a facile way for electron transfer during the reaction and, third, the uniform electrocatalysts thickness across the GDL.

It has been further observed that the codoping of more than one hetero atom in a carbon nanostructure further boosts the oxygen electrochemistry owing to the synergistic effect resulting in the decrease in the activation energy of associated reaction ORR/OER. For instance, Zhi et al. have synthesized the S, N enriched hierarchical porous carbon material by paying special

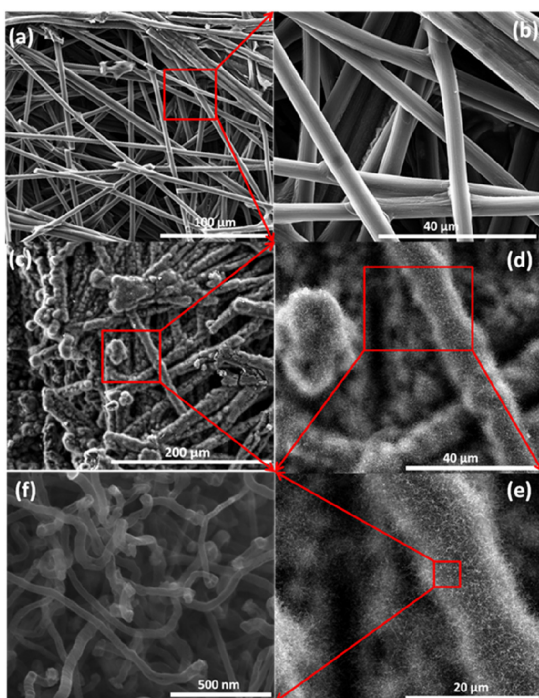


Figure 4. (a,b) SEM micrographs of bare-carbon paper at various magnifications. (c–f) SEM micrographs of directly grown BCNT on carbon paper at different magnifications. The red boxes show the magnified portions of the sample. Adapted with permission from ref 16. Copyright 2017, Elsevier Ltd.

attention to different local environments and reported to exhibit reversible oxygen electrochemistry which outperforms the Pt/C catalysts.¹⁷ Furthermore, Zhang et al. synthesized the mesoporous carbon codoped with N and P having a large surface area of 1663 m²/g through one-step pyrolysis of a polyaniline aerogel in the presence of phytic acid to develop a bifunctional air electrode for primary and rechargeable Zn-air batteries.¹⁸ Recently, combined theoretical and experimental study demonstrated that N-/B-doped graphene based electrocatalysts having moderate binding energies for ORR intermediates and, therefore, offer better ORR activity over S-/P-/O-doped carbon nanostructures, which is confirmed by the volcano-shaped relationship between ORR activity and binding energies of ORR intermediates on various heteroatom-doped graphene based electrocatalysts.⁵ Furthermore, in the B- and N-codoped carbon nanostructure (CNS), the fundamental issues arise from the bonding, i.e., B and N are bonded together or located separately. Because of the neutralization effect of the p-type and n-type dopant, these two dopants can form B–N moieties with completely different electronic structure, which eventually leads to distinct ORR activity. It is observed that B–N bond formation in the codoped CNS are electrochemically inactive owing to the neutralization effect as the carbon π -electrons are transparent to B–N domains. The bonded B–N moieties contribute little to the activation/conjugation of the π -electron resulting in weak interaction between O₂ and codoped CNS with little charge transfer, and O₂ cannot be reduced. However, in the case of the B–C–N, i.e., separated case, electronic distribution around the active sites disturbs the π -electronic delocalization, and makes it effective for ORR activity. Therefore, the effort has been made by Zhao et al. to boost the ORR activity through rational engineering of the electrocatalyst with the least/negligible B–N bond.¹⁰ Recently, Zheng and his group have demonstrated very

unique and simple one-step pyrolysis to synthesize the N,P,S-tridoped porous carbon nanosheets and studied toward the ORR.¹⁹ It is observed that the tridoped nanostructures exhibit better catalytic activity over monodoped and bidoped carbon nanostructure.

■ TRANSITION METAL–HETEROATOM-CODOPED CARBON MATERIALS

Even though doping with heteroatoms improves the catalytic performance of carbon, further introduction of transition metals into heteroatom-doped carbon could boost catalytic efficacy toward ORR/OER. To this date, significant efforts have been devoted to developing low-cost efficient transition metal (TM) based catalysts for OER and ORR. For example, TM oxide, hydroxide, phosphide, carbide, nitride, sulfide, and selenide possess high activity for OER and/or ORR.⁴ However, the large-scale and sustainable production of TM-based electrocatalysts is, in general, greatly obstructed by their poor conductivity and low stability. It is widely noted that carbon nanomaterials possess excellent conductivity and stability. Therefore, by coupling the carbon material with TMs may emerge as the hybrid electrocatalyst. The hybrid electrocatalysts not only assimilate the feature of individual component (carbon and TMs) but also exhibit features such as new chemical and physical properties derived from the synergy of the carbon nanomaterials and TMs (Figure 5), thereby realizing the higher activities of OER and/or ORR.

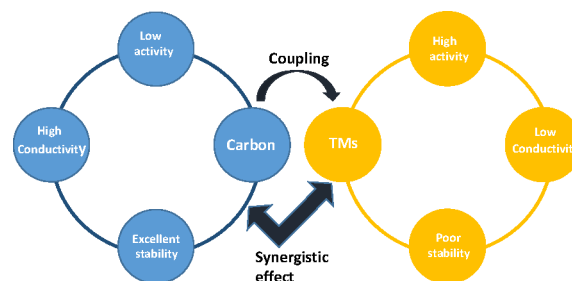


Figure 5. Illustration of the synergistic effect of TMs and carbon nanomaterials in TM heteroatom-codoped carbon material.

■ TRANSITION METAL–N-CODOPED CARBON MATERIALS

M–N–C (M = Fe, Ni, Co, Mn, Cr, Ru, Mo, etc.) based carbon materials have emerged as efficient electrocatalysts where TM coordinated with the nitrogen atom (M–N_x) act as the active sites to facilitate the adsorption of O₂ followed by the O··O bond stretching and breaking in alkaline medium. For example, (Fe/Co)–N–C single atom catalysts have been widely studied for ORR due to their high abundance and high performance in alkaline/acidic medium. Furthermore, interaction of TM with N atoms could increase the rate of charge transfer and reduce the local work function of carbon which triggers the high catalytic activity.

Very recently, Nandan et al. studied the promotion of inner sphere electron transfer (ISET) on homogeneously dispersed Fe–N_x centers for energy efficient ORR (Figure 6).²⁰ The catalysts have been prepared through one-step pyrolysis of ferrocene and dicyandiamide at 950 °C for 3 h. Incorporation of pyridinic nitrogen for effective Fe–N_x centers has been achieved by simply controlling the temperature and ramping rate. The

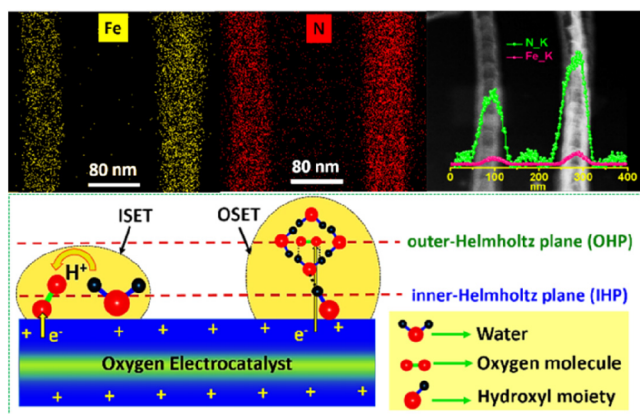


Figure 6. Uniformly distributed Fe–N_x moieties across NCNT for energy efficient promotion of ISET during ORR. Adapted with permission from ref 20. Copyright 2020, American Chemical Society.

study indicates the preferred electron transfer mechanism involved for ORR, i.e., ISET, which ensures the direct interaction Fe–N_x with O₂. Similarly, the versatility of one-step pyrolysis to design single-atom enriched electrocatalysts beyond Fe/Co/Ni has been explored, thereby developing the tungsten–nitrogen coordinated carbon (W–N₂–C₂) systems, less well studied electrocatalysts for ORR (Figure 7).²¹ For this, a physical mixture of dicyandiamide and tungsten salt when

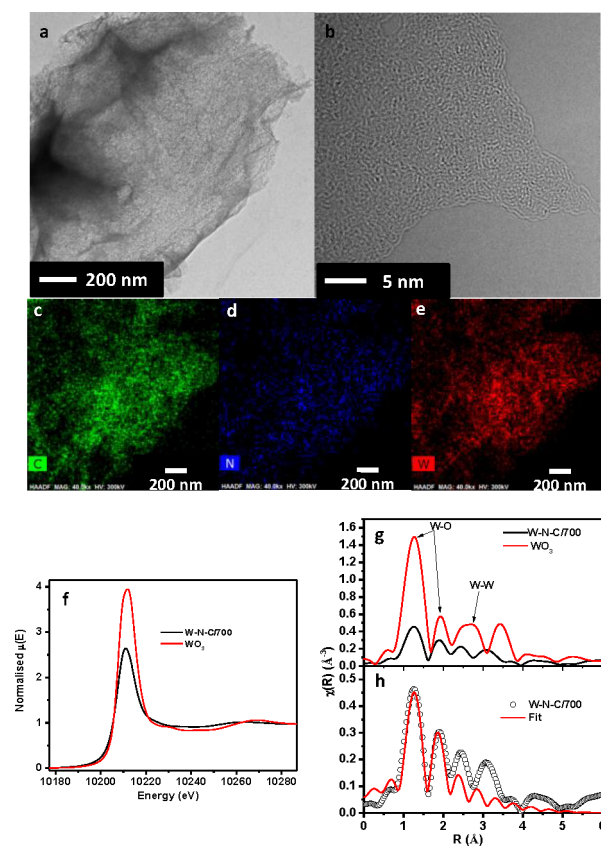


Figure 7. (a) Bright field TEM image, (b) HRTEM image, (c–e) corresponding EDS mapping of C, N, W elements, respectively, for W–N–C/700, (f) Normalized XANES spectra at W L3-edge along with standards, (g) Fourier transformed EXAFS spectra of W–N–C/700 at W L3 edge, and (h) fitted spectrum. Adapted with permission from ref 21. Copyright 2020, American Chemical Society.

subjected to a controlled pyrolysis at optimized temperature of 700 °C yields atomically dispersed W–N₂–C₂ rich electrocatalyst with appreciable oxygen reduction activity and excellent cyclic stability.

One-step pyrolysis has also been used by Nandan et al. to develop biomass derived Ni based hybrid electrocatalyst in an N-doped carbon matrix using apple seeds (containing the cyanogenic glycosides which acts as the nitrogen source). First, the apple seeds are soaked overnight in aqueous solution of Ni salt. These soaked seeds after drying, subjected to one-step pyrolysis at 850 °C (Figure 8a) which results in an efficient

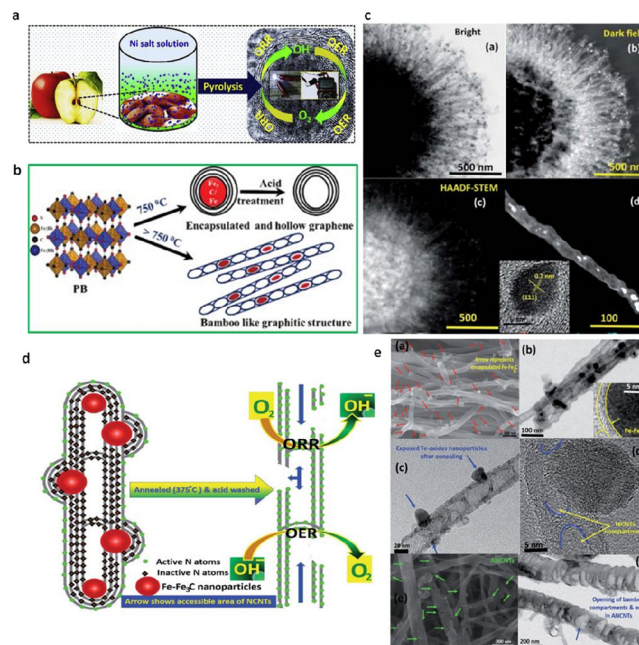


Figure 8. (a) Methodology used for developing nanocomposites for efficient bifunctional electrocatalyst where apple seeds are used as nitrogen and carbon precursors. Adapted with permission from ref 22. Copyright 2019, Elsevier Ltd. (b) Schematic representation of facile syntheses of Fe/Fe₃C nanoparticle encapsulated in N-doped graphitic layer and bamboo-like graphitic nanotubes. Adapted with permission from ref 23. Copyright 2015, Royal Society of Chemistry. (c) Bright-field, dark-field, and HAADF-STEM images of FN25R; HAADF-STEM image of one of the NCNTs from FN25R with HRTEM indexing of one of the encapsulated FeNi nanoparticle in NCNTs. Adapted with permission from ref 1. Copyright 2018, Royal Society of Chemistry. (d,e) Schematic for the maximum exposure of active sites by opening the bamboo compartments via annealing and acid washing of Fe–Fe₃C entrapped in NCNTs for ORR and OER and respective TEM images. Adapted with permission from ref 6. Copyright 2017, Royal Society of Chemistry.

bifunctional oxygen electrocatalyst.²² Barman et al. have reported a single source precursor Prussian blue (iron(III) ferrocyanide) for the synthesis of Fe/Fe₃C nanoparticles encapsulated in N-doped graphitic layer and bamboo-like graphitic nanotubes through a simple one-step pyrolysis which shows appreciable oxygen bifunctionality in alkaline medium shown in Figure 8b.²³ A slight controlled one-step pyrolysis methodology can also be used to design three-dimensional (3D) carbon nanostructures. To realize the 3D structure, Nandan et al. have optimized the pyrolysis conditions of melamine, ferrocene, and nickelocene. The anthocephalus cadamba shaped carbon nanostructures comprising FeNi encapsulated radially

grown nitrogen-doped carbon nanotubes (Figure 8c) assimilate the ORR potency of M–N_x (M = Fe/Ni)/C–N_x centers and OER capacity of FeNi bimetallic nanoparticles.¹

It is important to note that the M–N_x active sites within the carbonaceous material are either suppressed due to the nanoparticles in close vicinity or reside on the inner wall of the nanotube-like structure, which is inaccessible by the reactant species. To achieve the optimum activity in heterogeneous catalysis, the maximum density of active sites must be available and exposed for accessibility by the reactant species. One of the unique strategies to expose the large density of M–N_x active sites anchored within the carbon nanostructure has been discussed by Nandan et al. In order to maximize the utilization of the active centers, Fe–Fe₃C nanoparticles entrapped in graphitic layer and hollow structure of NCNT have been obtained by pyrolyzing the melamine with a comparatively large amount of ferrocene followed by the controlled annealing at 375 °C in an oxygen environment. The controlled annealing removes a few protective graphitic layers wrapped around Fe–Fe₃C; subsequently, the acid treatment provides an opening to the bamboo compartments of NCNTs. This catalyst is referred as ANCNTs as shown in Figure 8d,e.⁶ This innovative strategy offers maximum accessibility of the active sites rendered by the nitrogen moieties in the inner walls of NCNT and are greatly beneficial to boost the bifunctional oxygen electrochemistry.

■ TRANSITION METAL–OTHER HETEROATOM-CODOPED CARBON MATERIALS

In addition to N, other heteroatoms such as B, P, S, etc., have also been introduced with TM to uplift the electrochemical efficacy of carbon based systems. Theoretical studies have demonstrated that due to the strong electronegativity of the neighboring N atoms, TMs show high reaction free energy for the adsorption of intermediate product, resulting in the increase in the reaction potential barrier. Through the introduction of a foreign atom such as S, B, P, etc., the electron donating character of TMs can be modified mildly, which will reduce the potential barrier and improve the intrinsic activity of TM–N_x-doped carbon materials. For instance, a phase-pure Co₂P nanoparticle encapsulated N,P-codoped carbon nanotubes (denoted as Co₂P/CNT) has been realized through a facile one-step strategy as shown in Figure 9a. This method is free of toxic, pyrophoric alkylphosphine as the phosphorus source and does not require any sophisticated instrumentation or expensive precursors. This methodology may be extended to other transition metal phosphides.⁴ Figure 9b reveals the in situ synthesis mechanism with the temperature. The structure–property correlation indicates that the intrinsic catalytic activity of the Co₂P nanoparticles is preserved by encapsulating N,P-codoped carbon layers, which delays the leaching as well as being beneficial for electronic conductivity.

In addition, N,S-codoped Fe containing highly porous carbon has been obtained through the efficient and cost-effective in situ one-step pyrolysis treatment of thiourea and iron acetate at 700 °C in Ar atmosphere with high electrochemical accessible surface area. The dual N,S-doped Fe catalysts show high catalytic activity toward ORR in both alkaline and acidic medium, greater than that of the Fe–N–C. It has been concluded that the electron donation from thiophene-S to the surrounding Fe–N_x sites would modify the electronic structure of the latter.²⁴ It is observed that the electron distribution of Fe in S,N-doped Fe catalyst (i.e., S₂FeN₄) is closest to the Fermi level, indicating that S₂FeN₄ would be more active to promote

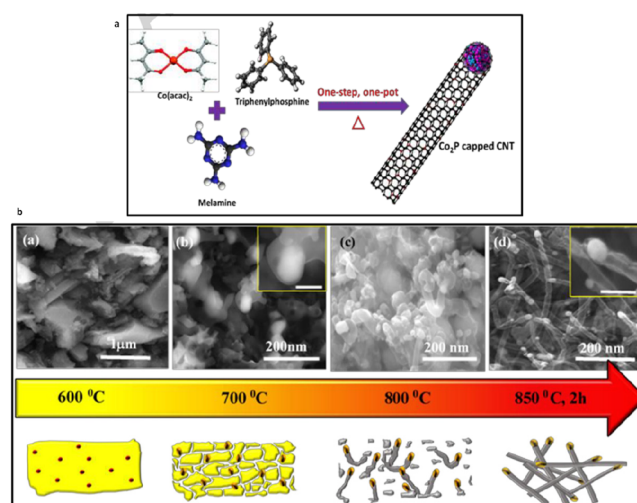


Figure 9. (a) Schematic illustration of the one-pot, one-step synthesis procedure of Co₂P/CNTs, (b) FESEM images of the samples isolated at various stages during the reaction process. (a) Co₂P-gC₃N₄-600, (b) Co₂P/NC-700, (c) Co₂P/NC-800, and (d) Co₂P/CNT-850 maintained for 2 h. Adapted with permission from ref 4. Copyright 2016 Elsevier Ltd.

electron transfer in due course of the reaction as compared to FeN₄, which enhances the catalytic activity. The d-band center is adjusted to optimize the adsorption of the intermediate on S₂FeN₄ (i.e., neither too strong nor too weak) and according to the Sabatier principle. Furthermore, the calculated free energy of each elementary reaction indicates a change in the rate-determining step following the doping of sulfur in the Fe–N–C system. This concluded that S doping in Fe–N–C boosts the ORR efficacy over pristine Fe–N–C catalyst. B,N-codoped carbon nanostructures with the negligible/least B–N bond facilitate excellent ORR activity. These heteroatoms in the carbon nanostructures in the presence of iron moieties further enhance the ORR activity and are able to exhibit the OER too, owing to the synergy between Fe moieties and B,N-codoped carbon nanostructure. Along this line, NCNT and Fe/Fe₃C nanostructures co-embedded in B-doped mesoporous carbon nanostructures have been designed through the very simple and efficient rational methodology which prevents/suppresses the formation of B–N bonds. The introduction of plenty of defects, local heterogeneity, and high specific surface area in conjunction with very negligible B–N bond formation lead to the remarkable bifunctional oxygen electrochemistry.²

■ METAL-FREE/C₃N₄ BASED HYBRID MATERIAL

In addition to the transition metal/carbon and transition metal compound/carbon electrocatalysts as discussed above, the other nitrogen-rich carbon system like g-C₃N₄ has also been used to design a variety of hybrid material for photocatalytic as well as electrocatalytic studies. The inevitable poor conductivity, inadequate surface area, and low charge mobility limit the direct adoption of pristine g-C₃N₄ as a catalyst support or cocatalyst. To circumvent these limitations, various g-C₃N₄ based materials have been designed by controlled introduction of the conductive materials to enhance electrical conductivity, good structural integrity, large surface area, and improved electrochemical stability, giving rise to unique chemical and electronic coupling effects between them. Zheng et al. have developed the g-C₃N₄@carbon metal-free catalyst for ORR through facile, simple, and

cost-effective methodology by the uniform incorporation of $g\text{-C}_3\text{N}_4$ into the mesoporous carbon in order to enhance the electron transfer efficiency of pristine $g\text{-C}_3\text{N}_4$.²⁵ In an attempt to explore the full potential of $g\text{-C}_3\text{N}_4$ for complete oxygen electrochemistry (ORR + OER), Wu et al. have designed a mesoporous interconnected network of N-doped carbon/ $g\text{-C}_3\text{N}_4$ nanocomposites from chitin. The authors concluded that the mesoporous interconnected network ensures better charge and mass transfer resulting in the reduced overpotential for complete oxygen electrochemistry. Inspired by the synergistic effect of codoping in carbon nanostructures like CNTs and graphene, efforts have also been made to institute heteroatoms like B/P/S in $g\text{-C}_3\text{N}_4$ -based electrocatalysts. The synergistic effect, high porosity, and better exposure of active centers of boron-doped $g\text{-C}_3\text{N}_4$ results in superior ORR and OER activity as compared to that of pristine $g\text{-C}_3\text{N}_4$.²⁶ Similarly, the electronic as well as geometric synergistic effect with increased $sp^3\text{-C}$ in P,S-codoped C_3N_4 results in the optimized electrocatalytic centers for better ORR/OER activities.²⁷

■ TRANSITION METAL/ C_3N_4 BASED HYBRID MATERIALS

Metal–nitrogen–carbon (M–N–C) coordination is the most plausible alternative to the precious metal based catalyst for sustainable ORR and OER activity. This section focuses on the molecule-level $g\text{-C}_3\text{N}_4$ coordinated transition metal ($\text{M}-\text{C}_3\text{N}_4$) as a new class of electrocatalysts for oxygen electrochemistry. The presence of metal moieties tunes the local electronic structure in the vicinity of transition metal and emerges as an electrochemically active $\text{M}-\text{N}_x$ site. Zheng et al. have conducted theoretical evaluation and experimental study of the $\text{Co}-\text{C}_3\text{N}_4$ complex with the single atom coordinate Co atom, as an efficient electrocatalyst for ORR and OER in alkaline medium.²⁸ The combined theoretical and experimental study suggests that high activity originates from the precise $\text{Co}-\text{N}_2$ coordination moieties in the C_3N_4 matrix. Furthermore, DFT study indicates that the d-band positioning of the catalyst influences the catalytic performances of the new class of molecule-level $\text{M}-\text{C}_3\text{N}_4$. Herein, the multiwalled CNTs have been used as support to enhance the conductivity and to expose the electrocatalytically active sites $\text{M}-\text{C}_3\text{N}_4$ as shown in Figure 10a,b. Similar studies have also been carried out for rest of the transition metals (Fe, Ni, Cr, Mn, Cu, Zn) and C_3N_4 based electrocatalysts for catalyzing ORR and OER. The concomitant theoretical analysis with the experimental results is presented in Figure 10c–f. Wang et al. synthesized the composite of carbon supported Fe-doped graphitic carbon nitride ($\text{Fe}-g\text{-C}_3\text{N}_4@\text{C}$) via facile and simple one-step pyrolysis using Fe salt/dicyandiamide at 750 °C.²⁹ Zhao et al. have developed Ni- $g\text{-C}_3\text{N}_4$ synthesized through one-pot pyrolysis methodology by using Ni acetylacetonate ($\text{Ni}(\text{acac})_2$) and dicyandiamide (DCDA) as precursors at 650 °C and utilized it as an excellent electrocatalyst for bifunctional oxygen electrode.³⁰

■ SUMMARY AND OUTLOOK

In summary, this review provides an overview of the recent development in rational design of wide range of carbonaceous electrode material using simple and effective one-step pyrolysis for efficient oxygen electrochemistry. Emerging carbon nanostructures comprising the metal-free heteroatom-doped carbon and transition metal–heteroatom-codoped carbon, C_3N_4 based hybrid materials greatly influence the selectivity, activity, and

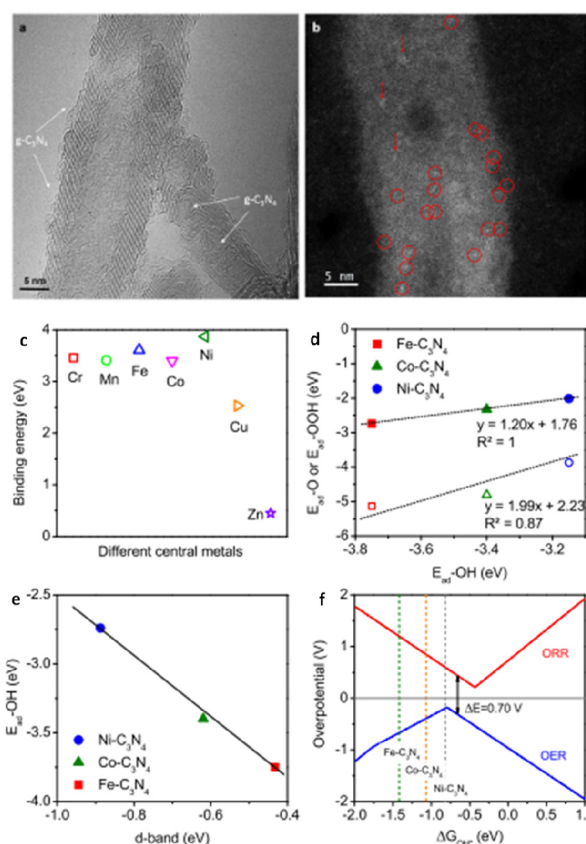


Figure 10. (a) High-resolution TEM and (b) HAADF-STEM images of $\text{Co}-\text{C}_3\text{N}_4/\text{CNT}$. Circles and arrows in panel b indicate single Co atoms and Co clusters, respectively. (c) Binding energy of various 3d transition metals in a $g\text{-C}_3\text{N}_4$ framework. (d) Scaling relationship of $E_{\text{ad}}-\text{OH}^*$ vs $E_{\text{ad}}-\text{OOH}^*$ (filled symbols) or $E_{\text{ad}}-\text{OH}^*$ vs $E_{\text{ad}}-\text{O}^*$ (open symbols) on $\text{M}-\text{C}_3\text{N}_4$ models. (e) Dependence of $E_{\text{ad}}-\text{OH}^*$ with the d-band position on $\text{M}-\text{C}_3\text{N}_4$ models. (f) Dual volcano plot for ORR and OER on $\text{M}-\text{C}_3\text{N}_4$ models. Adapted with permission from ref 28. Copyright 2017, American Chemical Society.

stability toward ORR and/or OER. This review points out on the versatility of one-step pyrolysis, a world in itself, and its potential for the rational design of carbon based electrocatalysts for the service of electrochemical energy conversion and storage devices. It gives countless degrees of freedom for rational design of electrocatalysts without any sophisticated machinery requirement. Overall, the user-friendly one-step pyrolysis gives a unique opportunity for in situ modification of carbon nanostructures by simply controlling the pyrolysis temperature, ramping rate, appropriate precursor selection, and their position in the furnace.

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Notes

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