Recent advancements on metal free catalysts for oxygen evolution reaction (OER).

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Abstract: The catalytic activity of electrocatalysts for water oxidation or the oxygen evolution reaction (OER) has received significant attention in recent years due to its crucial role in various applications such as water splitting, rechargeable metal-air batteries, and fuel cells. Numerous research studies have been dedicated to the advancement of efficient, stable, and cost-effective catalysts for water oxidation, which is a primary focus of the present study in the field of renewable energies. It is the focus of this review to show the latest effort and role of metal-free electrocatalyst including P,N,S and B etc in OER process. This article will be helpful to find stable and efficient electrocatalyst. The others key performance evaluating parameters, which also influence on catalytic efficiency will be summarized. The basic procedure for Nano-particles synthesis will be recalled in detail. Challenges in this field and future predictions will also be highlighted. This review article will help to investigate in developing a finer catalyst and will offer basic understanding of OER through basic spectrum to enhance the stability

Keywords: —catalytic activity; metal free electrocatalyst; synthesis; evaluating parameters; spectrum

1. Introduction

Energy demand is continuously increasing almost 1.05% annually due to rapid growth in population.(1) The present energy sectors rely upon fossil fuels ,oil and natural gas and puts our long-term management in danger because of its limited sources.(2) Furthermore , consumption of fossil fuels has negative effect on Earth, our surroundings, climate and altogether on health.(3) The introduction of clean and sustainable energy alternatives to fossil fuels is essential to tackle the global climate change and energy crisis. As a result, recent research has focused on utilizing hydrogen as a sustainable energy carrier in the following era of fossil fuels.(4) Hydrogen is regarded as a clean fuel due to its significant calorific value, availability and positive environmental impact. Despite this favorable perspective, a clean, sustainable and reliable method for hydrogen production is still challenging.(5) Currently, the hydrogen produced through steam reforming by industrial methods, including hydrocarbons, emit greenhouse CO2 gas. An electrochemical water splitting technique is a new innovation that is able to produce green hydrogen with no emission of CO2 on a commercial scale.(6) Electrochemical water splitting comprises of two half reactions, the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER).(7) The oxygen evolution reaction (OER), occurring at the anode, presents the most challenging stage in the entire process of water splitting due to its high overpotential, Tafel slope, and sluggish kinetics. The main focus of recent study is to introduce highly efficient catalyst to overcome the kinetic barrier for OER process.(8) In OER, molecular oxygen is manufactured with the help of proton/electron-coupled reactions.(9) In general OER reactions, a total number of two water molecules (H2O) are oxidized into four protons (H+) and oxygen molecules (O2). H2O and O2 are produced as the result of oxidization of Hydrogen oxide (OH-). In alkaline solution, less power is required to generate OER reaction rather than in acidic solution. The equilibrium half-cell potential (E0 a) at a pressure of 1 atm and temperature of 250C for OER is:(10) 4OH- 2H2O (l) + O2 (g) + 4e E0 a =0.404ref V alkaline solution H2O(l) 2H+ + O2 (g) + 2e E0 a =1.23ref V acidic medium Acidic arrangement and outer current is needed to make a possible contrast of 1.23 Vref versus ordinary inert hydrogen anode (NHE) to generate OER at pHref=0.(11) Along these lines, a change in response potential, for example ~58.5 mV per unit Ph, happens hypothetically as per the Nernst equation.(12) However, to stay away from a pH impact on a given potential and to save the electromotive force around 1.24 V for OER, reversible hydrogen electrode (RHE) is normally utilized as a base cathode.(13) Creation of O2 molecule enforced to move a number of four electrons, and an actively ideal OER process happens with the help of multiple steps with a mono electron movement at each series step. In this manner, aggregation of energy at each progression makes OER energy exceptionally slow and brings about enormous over potential.(14) Hence, an electrocatalyst with high speed movement is profoundly attractive to conquer energy barriers. Moreover , the OER impetus should have small overpotential and peak steadiness just as huge globe-bounty and also accessible for a minimal price for its adaptability at a modern scale. (15) Overpotential, which is required to reduce the kinetic barrier for OER, is based on catalytic efficiency. Large overpotential requires more energy and as a result it decreases the efficiency and profitability of electrochemical process. Therefore, the OER catalyst is required to show lesser overpotential and higher stability and higher earth-abundance for its reliability at industrial scale. Iridium (Ir) and ruthenium (Ru) oxides shows remarkable performance towards OER. But these catalyst are highly expensive and not abundant in nature. Therefore, noble metal oxides limit their practical applications on commercial scale. Nobel metal catalyst such as Ir, Co, Zn etc. , as well as their alloys, furthermore compounds (boride MBx, sulfide MSx, hydroxide M(OHx), etc.) shows good activity towards alkaline electrolytes rather than in acidic medium. Similarly, transition metals such as Fe, Ni and Mn of first row shows good performance for OER because of high catalytic persuit and efficiency. Moreover, transition metals also surpass those of IrO2 and RuO2 catalyst.(16) To address these issues, non-metal catalysts are the top priority due to their stability for OER process. Therefore, metal free based electrocatalyst came to be significantly at top conceding to their availability, truncating production cost ,adequate electrical conductivitydurability as well as environment friendly nature.(17) They are also good alternatives in place of noble metal catalysts in electrochemical process. Moreover ,co-doping effect of non-metals with CNTs, CF, grhephene oxide and Ni-foam also enhance the surface area and flexibility of catalyst, as a consequence of which it shows low overpotential and high current density for the generation of O2 in OER

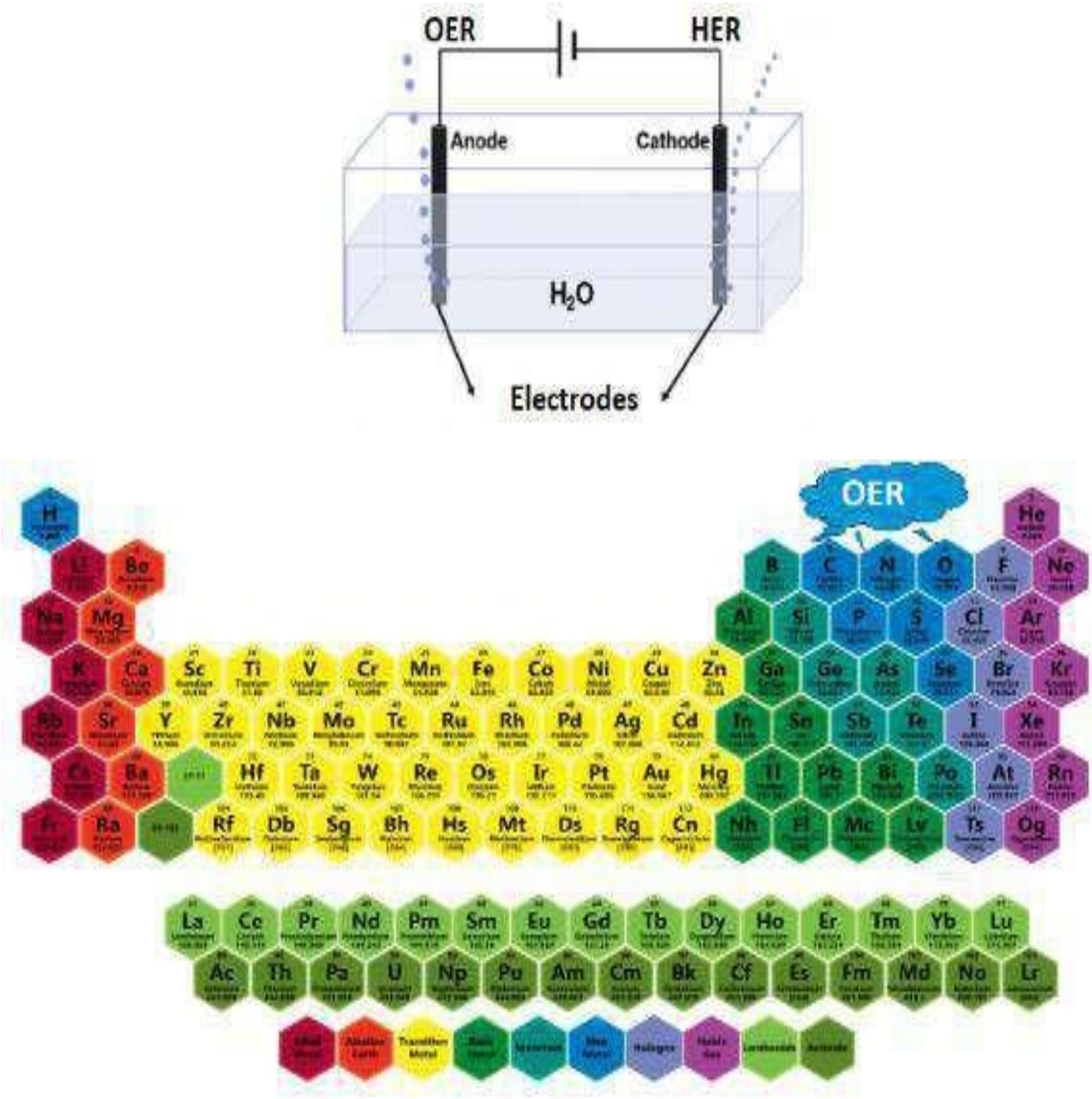

Figure 1: Schematic illustration of an electrolytic cell and the possible non- metals(B,S,P and N etc) electrocatalystscontaining elements for OER.process.(18

2. Key Performance evaluating parameters

The electrocatalyst for OER is very crucial for good rate of reaction but some other parameters also affects OER performance which are explained below.

2.1 Substrate

The working substrate/electrode plays a supreme role to find out the rate of reaction along with performance because of their different shape, range of wettability, conductivity and access of catalyst for electrolysis. Substrates are divided into two categories due to their substrate support and degree of electrolyte movement; flat surface and 3D substrate. The outer plane of electrode, such as glassy carbon (GC), Cu/Ti frustrate, as well as (ITO) indium alloy with tin oxide, which allows the electrolyte to penetrate on only one side, limits the reaction for electrocatalyst.(19) While the three dimentional electrode such as carbon cloth paper (CCP) and Nickle foam (NiF) allows the electrolyte to penetrate all sides due to their 3D structure and enhance the limit of reaction for catalyst.(20) All these electrodes have their own superiorities and drawbacks. The glassy carbon (GC) is mostly used due to their easy handling but it does not stabilize the reaction for a long time due to low catalyst loading (1mg cm-2). It weakens the bond with a catalyst, which often reduces the rate of reaction and also decreases the diffusivity of ions due to agglomeration.(21) But the CC, Ni foam-like substrate gives better results due to 3D structure which also increases the conductivity of ions and reduces the resistance barriers.

2.2 Electrolyte

The Electrolytes, such as alkaline or acidic, deeply influenced the performance of electrodes/substrate. The OER electrocatalyst is most favorable in alkaline medium but difficult in the neutral medium due to the high resistance and in acidic medium, OER performance is very poor. The main focus of the research is on OER electrocatalyst that shows better performance in an alkali media, such as group-B metals, metal-free electrocatalysts, CC, etc. The acidic medium or electrolyte cause corrosion for many electrocatalyst due to theirhigh oxidative potential. In addition, OER is highly desirable for full-range pH (0_14).

1.1 Tafel slope

The Tafel slope also helps to examine the rate of overall reaction with respect to current density for the given potential with the help of following relation.(22, 23) n =b.log(j/j0) Where, the overpotential is n, the Tafel slope is b, j denotes the current density and j0 determines the current exchange ability. So, Tafel slope and current density have an inverse relation to each other.(24, 25) The quality of OER will be good if an electrocatalyst gives low Tafel slope and high current density.

2.3 Over /Onset potential

The most prominent factor for OER is to calculate the onset potential. But it is very tough to determine absolute value. That is why, we find it at reference current density (Ejref=10) ,which is a highly accurate technique to find onset potential. Overpotential illustrates the difference between specific and thermodynamic potential.(23, 26, 27) It is calculated in mV, i-e if a catalyst shows the value Ejref=10 =1.53V, it means that it bears an overpotential of 300mV at 10mA cm-2. Commonly, if a catalyst works in between 300_400mV, then it is considered as a good quality catalyst than the other catalysts, which give an over potential below 300V. Moreover, onset potential is the point where the first molecule of water breaks into its atoms.

2.4 Activity

The efficiency of a catalyst can be easily calculated using the following formula: T.O.F = (j . A) / (4 . F . n).(26,27) Where, j represents the current density (mA cm-2) at a specific potential (mV), A represents the surface area of the electrode, F denotes the Faraday constant (96,500C mol-1), and n represents the moles of a substance. Determining the required value of T.O.F is challenging due to the varying sensitivity of catalyst elements. However, T.O.F remains a reliable parameter for comparing catalytic materials. The mass activity can be expressed as: mass activity = j / m, where m represents the mass quantity of the main electrode (mg cm-2) and j is the measured current density (mA cm-2) at a given potential.

2.4 Stability

Stability is the key feature for these requisitions. The stability of a catalyst depends upon the type of electrolyte i-e acidic or alkali and thickness of material on the electrode. Most of the catalyst shows good stability in alkaline medium but low in acidic medium. Hence, stability is the most challenging parameter for this application because easily abundant and economical conditions are required for the preparation of the catalyst. The stability of nonmetal-free-based electrocatalysts is very high due to their strong interbonding. So the exact stability for OER cannot be found easily but some technical techniques are applied to find out the stability of a catalyst via chronopotentiometry at a reference potential and current density.(27) We split up the OER catalyst into ideal or perfect (200_300mV), exceptional (300_400 mV), and gratifying (500mV) classes based on the above discussion.

2. Methods for synthesis of nanoparticle:

Different shapes of nanostructure can be synthesized by utilizing different process. The nanoparticle size in the range of 1-100 nm. Different techniques such as drying, grinding and pyrolysis are used for synthesis of nanoparticles. There are four types, which we discuss in this article are given below.

2.1 Co-precipitation method

It is a technique in which nucleation, growth, agglomeration and coarsening processes are involved simultaneously. The Reaction involved in this technique has following characteristics: The products formed under highly supersaturating condition are insoluble species. Nucleation is the main step, in which small particles will be formed.(28) Aggregation and ripening strongly effects the size, properties and morphology of the main product.(29) The following reaction is involved in co-precipitation method:

$$ZAy^{+}{}_{(aq)} + NBx^{-}{}_{(aq)} \xrightarrow{\qquad\qquad} AzBn_{(s)}$$

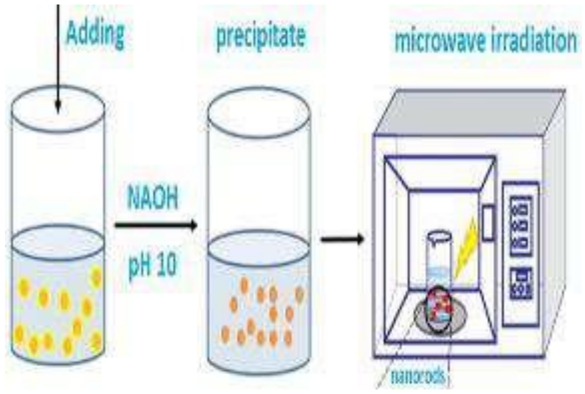

Figure 2: systematic diagram of co-precipitate method

3.1a Advantages and draw backs of co-precipitation method:

We can easily control the particle size and composition. The preparation is simple and rapid. Low temperature is required.(30) Moreover, it is highly energy efficient. But on the other side it has some disadvantages such as it is a time consuming process.(31) We cannot implement it for uncharged species. Impurities get precipitates with the product. This method is not suitable for reactants which have different precipitation rates.(32)

3.1 b Applications

Oxide produced by aqueous and non-aqueous solutions. Gaining of electrons, aqueous solutions and decomposition of metallurgical techniques are used for metals. Molecular precursors reactions used for making metal chalconides. Co–precipitate method mostly used for synthesis of ZnO2 nanoparticles for OER process.(33, 34)

3.2 Hydrothermal Method

Pure nanoparticles and good quality crystalline structures can be obtained by this method. In hydrothermal method, aqueous solution with solid is treated at elevated temperature (between 100oC to 1000oC). It is used to increase the solubility of a solution and to enhance rate of reaction between precursors.(35) The controlled morphology crystalline structure is formed by manipulating the solvent, chemical concentration and rate ofreaction. Hydrothermal technique is highly a successful approach in synthesis of nanoparticles with high crystallinity, control morphology structure due to its low process temperature, inert reaction environment, low energy consumption and positive environmental impact. In addition hydrothermal vessel is highly stable which can stand at high temperature and pressure. (36)

Figure 3: schematic diagram of Hydrothermal method(37)

3.2a Advantages and disadvantages of hydrothermal method

Required shape and size can easily be achieved.(38) Fine crystalline powder can be smoothly created. Moreover , remarkable crystallinity can be achieved.(39) But on the other hand it also has some drawbacks such as the process is not easy to control, there is restriction of reliability along with reproducibility.(38)

3.2 b Applications

The described method is very appropriate for preparation of powders of the size of nanoparticles or even for mono-crystals.(38)

3.3 Solvothermal Method

Solvothermal techniques involve the synthesis of Nano-phases using water or various organic chemicals like methanol, ethanol, and polyols as solvents, without the need for any pledges.(40) These reactions take place in a pressurized vessel, where the solvents (water and alcohol) are heated beyond their boiling points. This elevated temperature greatly accelerates the crystallization process, leading to crystal formation kinetics, that can be enhanced by up to two orders of magnitude with the aid of microwave assisted reactions, also known as microwave solvothermal..(41)

Figure 4: Schematic diagram of solvothermal method

3.3a Advantages of solvothermal method

High quality crystallized Nano crystalline structure can easily be prepared. The use of this method is strongly favored for achieving a narrow size distribution and a high degree of crystallization in Nano crystallites, as compared to the conventional oil bath heating method..(40)

3.3 b Applications

The rapid synthesis of Pt, Pd, Ag, and Au nanostructures using polyethylene glycol. Production of silver nanoparticles.(40) Furthermore, under microwave-assisted conditions, methanol serves as a reducing agent for the synthesis. Solvothermal methods are highly beneficial for creating well-crystallized and uniformly dispersed nanocrystals of nitrites, metal oxides, and novel semiconductor materials.(41)

3.4 Chemical reduction Method

In the chemical reduction method, an ionic salt is decreased in a suitable medium with the aid of different reducing agents while a surfactant is present.(42) One example of a reducing agent is sodium borohydride, which is utilized in an aqueous solution to generate metal nanoparticles.(43) These metal nanoparticles are then coated with trisodium citrate (TSC) or sodium lauryl sulfate (SLS). On occasion, stabilizers are employed in conjunction with the reducing agents. The stability of metal nanoparticles in dispersion was evaluated through

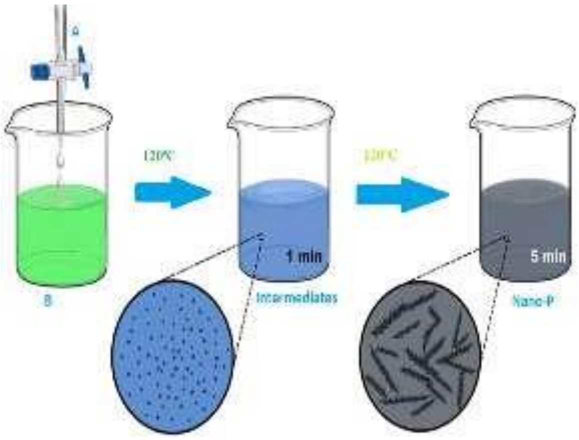

Figure 5: schematic diagram of chemical reduction method

absorbance analysis. Various reducing agents, such as sodium borohydride ($NaBH_4$), glucose, ethylene glycol, ethanol, sodium citrate, and hydrazine hydrate, are employed in the synthesis of silver nanoparticles. (40)

3.4a Advantages and disadvantages of chemical reduction method

This method is a simple technique used for synthesis of metal nanoparticles. (42) The drawbacks of Reducing agents are toxicity, they are highly expensive, have lower reducing ability, and contain impurities. (45)

3.4 b Applications

For the synthesis of copper nanoparticle using potassium borohydrate as a reducing agent. (45)

3.5 Sol Gel Method

The technique for sol-gel chemistry of transition metal oxides was initially outlined by Livege et al. in 1988. The synthesis of nanoparticles using sol-gel methods can be achieved through the following approaches: a) Mixing pre-formed metal colloids (oxides) with a sol containing matrix-forming species, followed by gelation. b) Directly mixing metals, metal oxides, or nanoparticles with pre-hydrolyzed silica sol. c) Complexation of the metal with silane, followed by reduction of the metal prior to hydrolysis.(46). This method introduces network formation using colloidal suspensions (sols) and gelatin in a continuous liquid phase (gel). Metal alkoxides and aroxysilanes are used as precursors for colloid synthesis, with tetramethylsilane (TMS) and tetraethoxysilane being the most commonly used, which form silica gel. Metal alkoxides act as organometallic precursors for various metals such as silica, aluminum, and titanium, and they are immiscible with water. Alcohol is used as a mutual solvent. The sol-gel formation involves four main steps: hydrolysis, condensation, particle growth, and particle aggregation.(47) In the direct precipitation of metals or metal oxides, metal oxide particles are typically precipitated from silica sol through low-temperature heat treatment. This technique is primarily employed for producing thin films.(46)

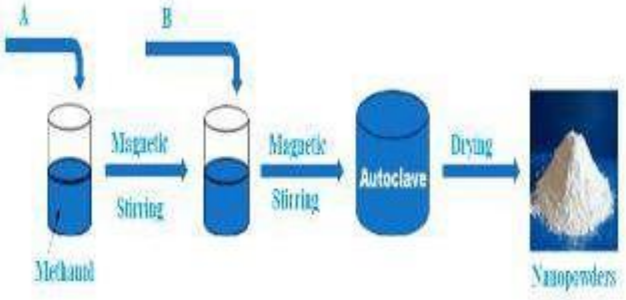

Figure 3.5: Schematic diagram of Sol gel method

3.5a Advantages

It’s very easy and simple method. Particle size and morphology can easily be controlled by continuous monitoring of reaction parameters.(48)

3.5b Applications

It is used for the preparation of zinc peroxide (ZnO2) nanostructures.(48) Preparation of NiO_2 nanoparticles and thin metal films formation.(49)

3. Metal-free based electrocatalysts

3.1 S-doped metal-free based electrocatalyst

The OER is more sluggish and challenging for overall water splitting because it required more power to generate oxygen. So to overcome this problem. we can use metal-free electrocatalyst because they have high surface area and electrical conductivity. We will discuss here some metal-free catalyst from s-doped family. Here is a catalysis-e nitrogen and sulfur based co-doped with graphite (NSGF), which exhibits good efficiency and also stability as compared to transition metals. The NSGF has a remarkable activity towards OER and fast reaction.

kinematics. It is also highly stable than OGF and GFL which are the graphene-based catalyst.(50) For preparation of NSGF we use a Hydrothermal method. In this method, OGF is treated at 180oC for 12h in low concentrated solution of thio-urea. During this process SO2, NO2, and H2O gasses were produced, and finally, we get NSGF S-doped based metal-free catalysts that are so important for OER reaction, due to large plane area and durability.

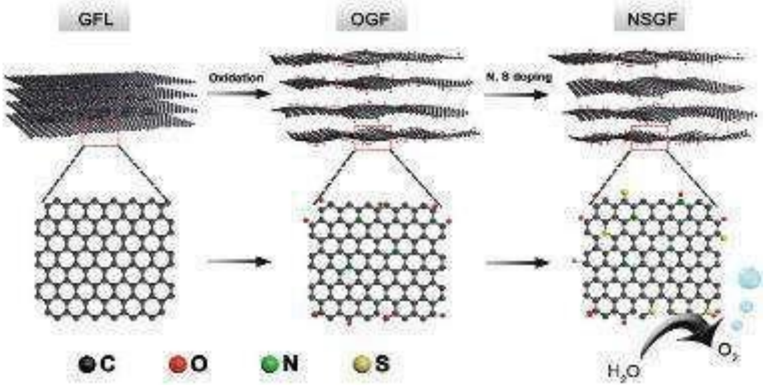

Figure 6: The procedures for fabricating an NSGF electrode 21

We have another catalyst g-C3N4, whose structure is modified by introducing sulfur S, which increased the electrocatalytic activity of the catalyst and made this catalyst durable low-cost and environmentally harmless. This is synthesized by using the Hydrothermal method. By hydrothermal method we doped sulfur with g-CNx which improves the active sites of catalyst that increases the reaction kinematics and durability of catalyst for a long time. Moreover, s-doped metal-free catalyst is a highly anti-corrosive material and also shows large current density. Synthesis and morphology structure of s-doped with g-CNx is done by natural geodes which are found easily in earth's crust at high pressure and temperature. So to prepare the catalyst, we used the Hydrothermal method which is cheap and easy to perform. If we modified the structure of an s-doped based catalyst, it may solve the major problem of OER in future, which is still challenging. (51) Zhao et al first time introduced CN-based metal-free catalyst but this was not accessible for OER due to low stability, but S-CNT based multiwall electrocatalyst boosts the activity and stability of OER due to more active sites and controlled doping. So S-based metal-free electrocatalyst may enhance the activity for OER than transition metals because S-doped CNT has a high surface area, which decreases the binding energy of atoms, due to which it is highly preferable. The activeness of mono and multilayers carbon nanotubes with respect to Ir/Cb is in the following descending order S,0.5S′-CNTs 980 °C > 20 w.t% Ir/Cb > 0.01S′-CNTs 980 °C > 0.2S-CNT 950°C > 0.1 S-CNTs 180 °C > 20 w.t% ptb/C. The hydrothermal method is a unique and low-cost method for Si-doped CNT metal-free electrocatalyst because the doping-induced nature of bonding between atoms very seriously affected the rate of reaction and durability of catalyst for OER. For future perspectives, an S-type electrocatalyst is highly preferable because of more edges and stability. (52) Superior electrocatalytic activity of sulfur coupling, doped with CNTs, demonstrates excellent performance towards OER. S-based CNTs/S-N-C metal-free bifunctional electrocatalyst is economical and highly durable for OER. The obtained MWCNTs@S-N-C nanohybrids catalyst exhibit remarkable activeness and excellent stability as compared to Pt/C for OER reaction. This catalyst is sharply more active in alkaline electrolytes for OER. Mechanism of Si-type, carbon-based is still ambitious but S-doped N, on CNTs gives a high electron-transport rate due to heteroatom doping. S-based metal-free electrocatalyst activity and stability may be enhanced by tuning its structure by using different methods.(53) The deflagration method is highly suitable for synthesis of S-doped carbon-fixed catalyst because it removes the barriers for oxygen evolution reaction and also gives superior stability. The Sitype carbon-based catalyst, synthesized by deflagration, increases the edges of catalyst and also enhances electrical conductivity. Due to their different electronegativities, the carbon atoms are positively charged and the electron transfer ability is boosted, thus the OH ions easily migrate through the membrane. By DFT calculation, we observe that the C-S-C reduces the OH adsorption power. Which also increases the OER activity and fastens reaction kinetics. The deflagration technique improved the structure of S-type metal-free catalyst and we may get better results in future.(16)

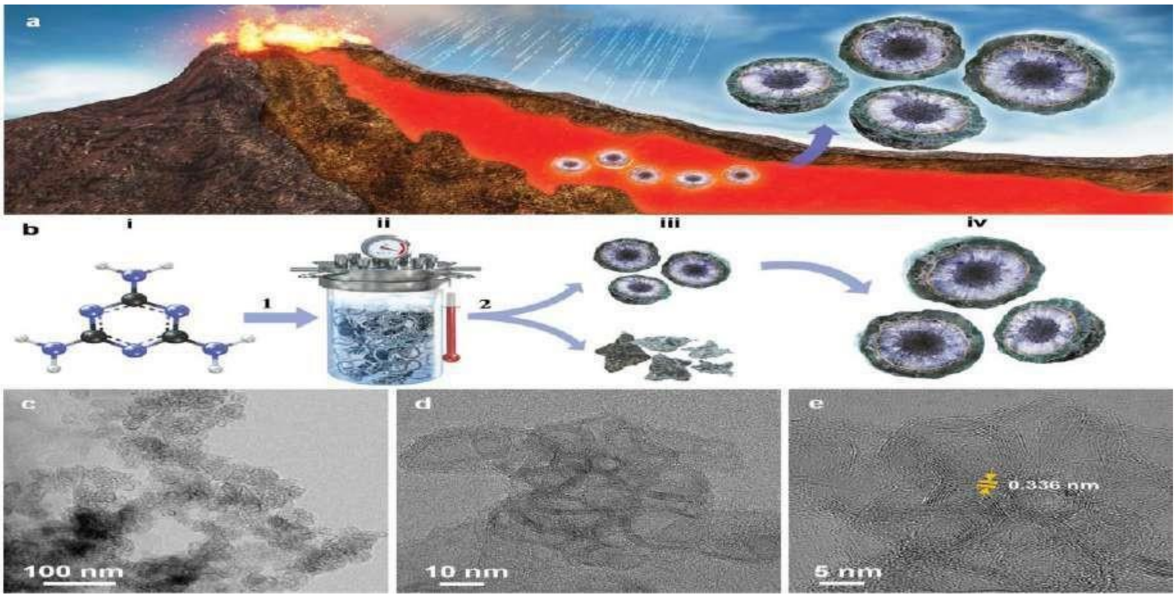

Figure 7: Synthesis of melamine nanogeodes. a) Schematic representation of the synthesis process for naturally occurring geodes in the earth's crust. b) The precursor melamine (i) in an aqueous solution is used to synthesize melamine nanogeodes (MNGs) under the hydrothermal conditions of 160 °C for 24 h in step (1) step (1). After completion of the hydrothermal reaction, the reaction mixture (ii) of MNGs mixed with a residue is centrifuged in step (2) to separate the lighter density MNGs from the higher density residue (iii). Representative images of MNGs (iv). c) TEM image of MNGs. d,e) HRTEM images of MNGs showing multiwalled closed cage structures with an interlayer distance of 0.336 nm.[22]

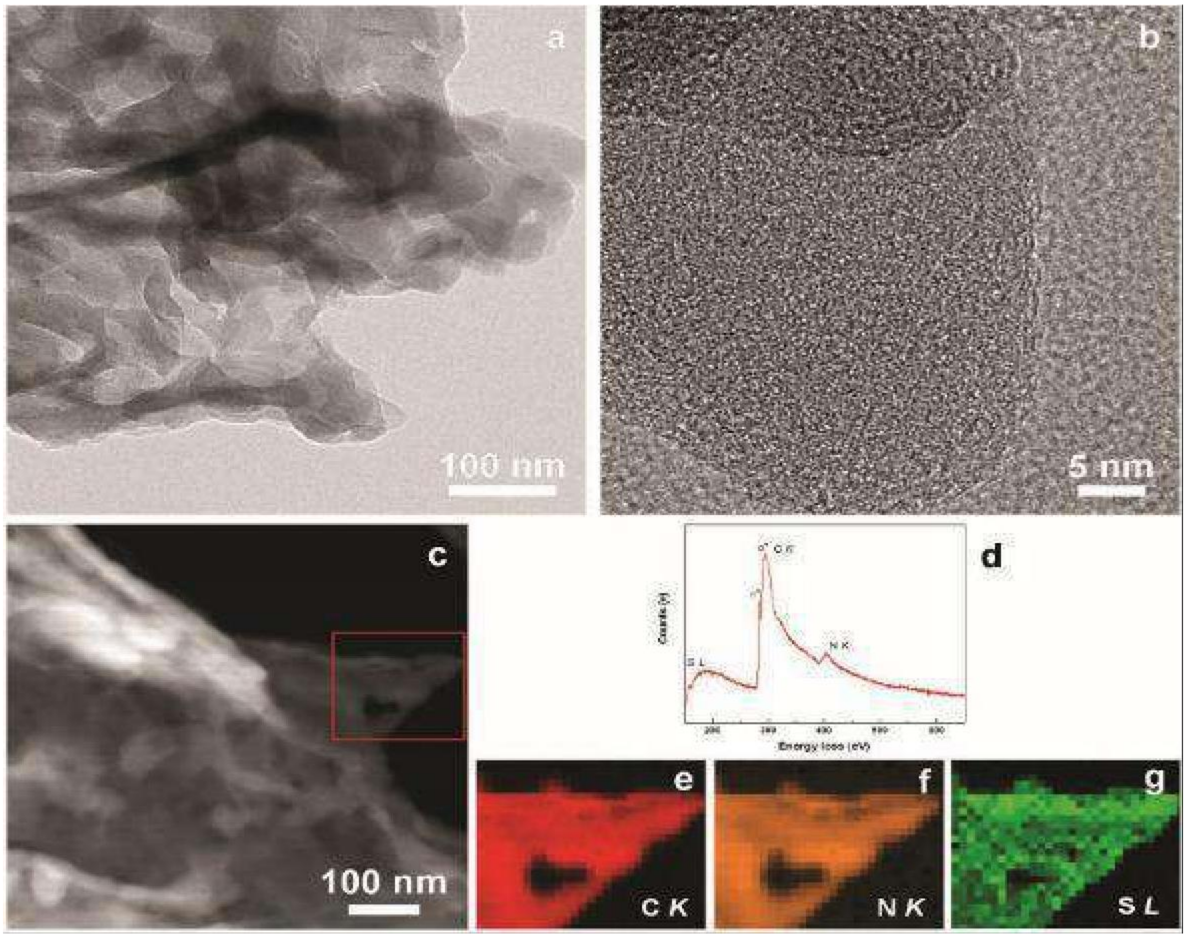

Figure 8: Demonstrates Electron microscopy characterization of improved g-CNx nanostructures as (a) TEM and (b) HRTEM image, respectively. (c) High-angle annular black field scanning TEM image. d) EELS spectra collected at the site indicated in (c). e.g) EELS elemental chart exist from the site indicated by the red box in c: e) C-K edge, f) N-K edge, and g) S-L2,3 edge

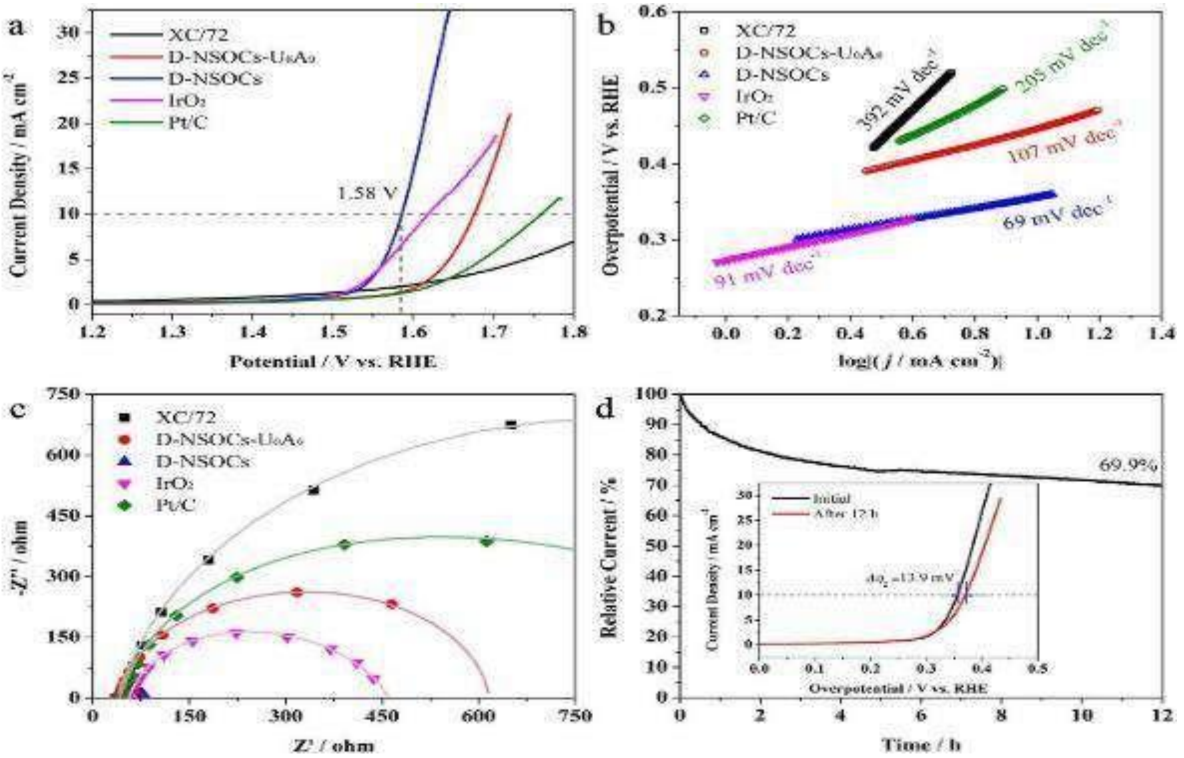

Figure 9: Illustration of Oxygen evolution reaction activity. (a) Linear sweep voltammetry (LSV) curves of the bidoped S,S′-CNT 1000 °C with respect to Ir/C in 1 M KOH at a scan rate of 5 mV s −1 , and 1600 rpm angular velocity (b) Comparison of LSV curves for various electrocatalysts at scanning rate of 5 mV s −1 . (c) Tafel plots of different S-type CNT electrocatalysts versus Ir/C. (d) Electrochemical impedance spectroscopy of various electrocatalysts at 1.68 V at a frequency zone of 0.1–10 5 Hz.[3]

Table:-1 A Comparison between current density, Over potential, and Tafel slope of Si-doped metal-free electrocatalyst For OER reported in the literature**.**

Catalyst	**electrolyte**	**Current density mA/cm^{-2}**	**Over potential mV**	**Tafel slope mV/dec**	**References**
NSGF	**0.1M KOH**	**10**	**346mV**	**96**	**21**
OGF	**0.1M KOH**	**10**	**410mV**	**133**	**21**
NG/CNT	**0.1M KOH**	**10**	**465mV**	**143**	**21**
G-C_3N_4	**0.1M KOH**	**10**	**415mV**	**128**	**21**
S-doped g-CN_x	**0.1M KOH**	**10**	**290**	**120**	**22**
S,S′-CNT 1000 °C	**1M KOH**	**10**	**400**	**95**	**23**
S′-CNT 1000 °C	**1M KOH**	**10**	**400**	**156**	**23**
MWCNTs@S-N-C	**0.1M KOH**	**10**	**440**	**–**	**24**
D-NSOCs	**1M KOH**	**10**	**158**	**69**	**25**
D-NSOCs-UoAO	**1M KOH**	**10**	**168**	**91**	**25**

1.1: B-doped metal-free based electrocatalyst

DFT calculations show that B-BCN-based metal-free electrocatalyst increases the adsorption strength of OH*/H2O respectively. Boron is an electron gainer, which provides enough adsorption power for OH and leads good OER process. As we increase the ratio of Boron in B-BCN, the reaction kinetics reach at a peak and the OER process runs smoothly due to strong adsorption for OH*. By changing the Boron ratio for a certain limit we can improve the current density, surface zone, and outer edges. Hence Lewis base concept for B-based metal-free electrocatalyst is very useful for tuning the structure of B-BCN.(54) DFT calculations showed that the BCNONF boron-based metal-free electrocatalyst overcome the barriers for OER, and it gives low overpotential, small Tafel slope, and high durability than commercial Ir/C benchmark. 3D fiber web basic highlights and allows predominent electrical conductivity. As we increase the boron up to 5%, it gives excellent mechanical strength which enhances the durability of the catalyst.(55) 3D fiber mat of boron-based metal-free electrocatalyst has a greater surface area which increases the reaction kinetics for the OER process. Boron carbon oxynitride nan fibrous (BCNONF) showed much better stability than Ir/C and pt/C counterparts and also cost-effective material than transition metals.(56) B-MWCNTs metal-free electrocatalyst does not tear down during the thermal process. The content of Boron strongly affects the catalytic performance for OER. As we increment the substance of Boron, the activity of catalyst also increases. Just like 20*B-MWCNTs exhibit good stability, activity and also low overpotential for oxygen evolution reaction than 5*B-MWCNTs and 10*B-MWCNTs. We need to modify its structure by using different preparation methods because preparation techniques also affect the atomic structure of the catalyst. If we add some quantity of nitrogen with Boron then we can enhance the stability and electron transfer ability of it. We just need to tune the structure of B-MWCNTs with doping effects.(57) Graphyne exhibits good performance for oxygen evolution reactions. But by adding Boron with Graphyne decreases the bandgap due to which it removes the barriers for oxygen evolution reaction. Boron doped with graphyne increases the active sites of catalyst which increases the activity and reaction kinematics for oxygen evolution reaction. Boron based graphyne is very beneficial for OER because of its higher charge transfer ability and low onsetpotential. The direct positive charge, thickness impact and high structural distortion absorbed by edge B- doping on GY molecule are very crucial for high OER activity. All the B-based catalysts show excellent performance than N-based and its primal counterparts. (58) The B-N dopedcatalyst presented a superior electrocatalytic performance at low overpotential towards OER. It also exhibits excellent stability than Ru/C and showed relatively high OER activity. , B-C doped build up lots of outer active sites, which increase rate of reaction and also remove barriers for reaction kinematics. This could be achieved by doping of heteroatoms with carbon atoms to exposure of active sites. The plasma synthesis process is used to make B-N based catalyst. It is injected in a tubular furnace at 900 °C with an N2 atmosphere for 2.5h to potentialy enhance electron transfer ability. Pure nitrogenbased catalyst has poor electrical conductivity and stability but when we add Boron with Nitrogen i.e BN doped, the activity and stability of a catalyst is improvedfor OER process. To control the quantity of Boron we may enhance the performance of the catalyst in the future

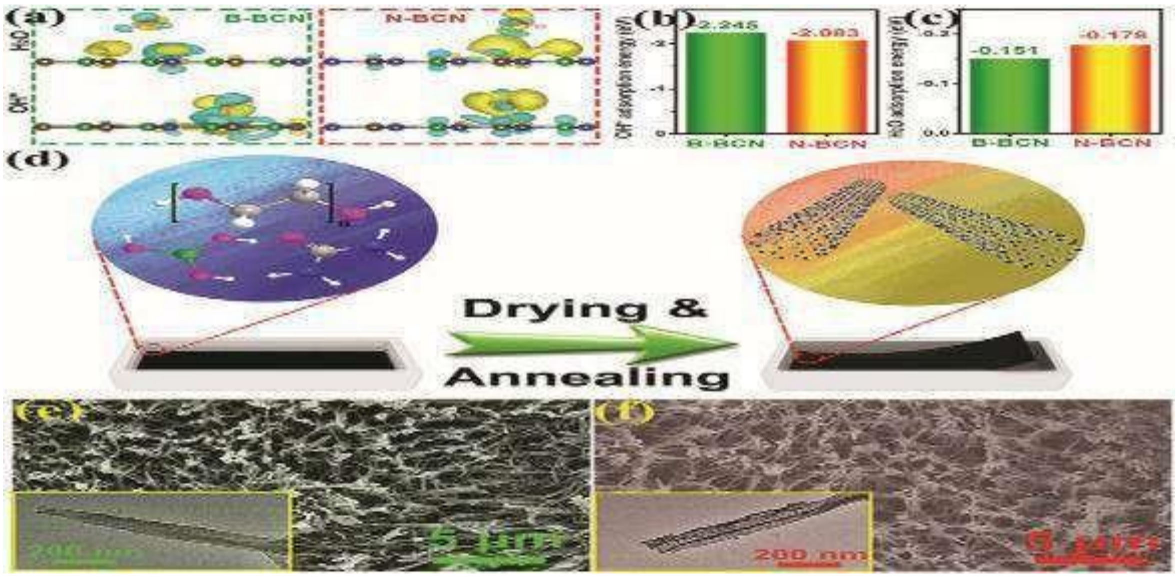

Figure 10: (a) Illutration of Charge density differences of H2O and OH* molecule adsorbed on B-BCN and N-BCN monolayer. The yellow and blue isosurfaces show electron gain and loss, respectively; (b) adsorption power of OH* molecule adsorbed B-BCN and N-BCN monolayer; (c) adsorption energies of H2O molecule adsorbed B-BCN and N-BCN single layer; (d) schematic illustration of the synthesis of BCN catalyst; (e) SEM image of B-BCN, with inset revealing the TEM image of B-BCN; (f) SEM image of N-BCN, with inset, shows the TEM image of N-BCN.[26]

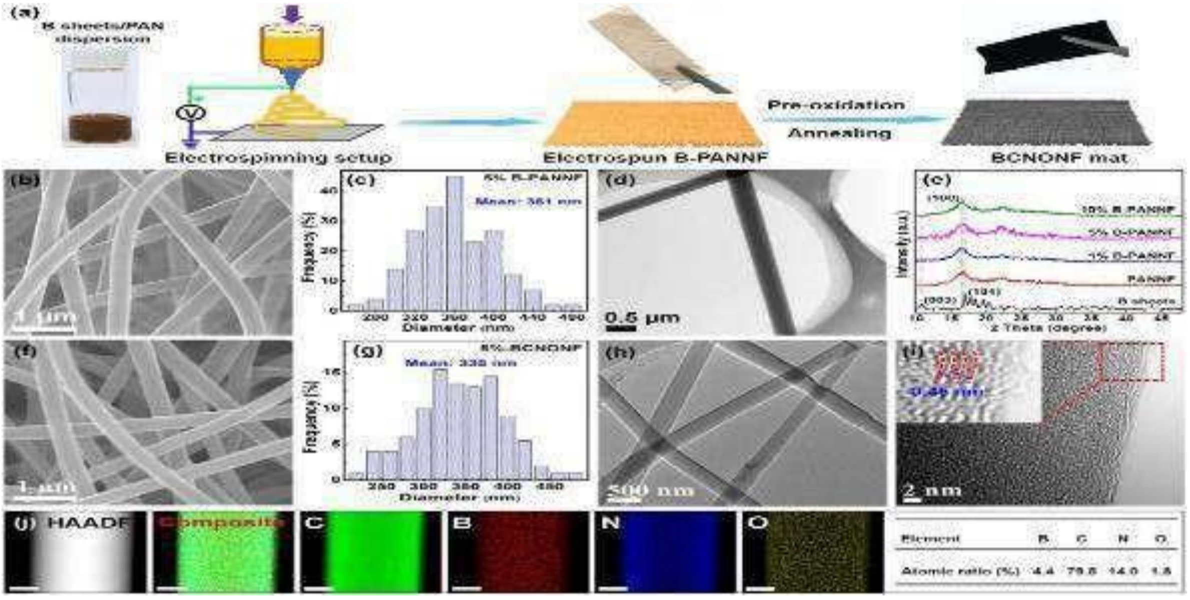

Figure 11: (a) The fabrication process for the B-PANNF and BCNONF mats. (b) Typical SEM image, (c) average diameter distribution, and (d) TEM image of the 5% B- PANNF mats. (e) XRD path of the boron sheets and the B-PANNF. (f) SEM image, (g) average diameter distribution, (h) TEM, and (i) HRTEM images of the 5%-BCNONF mats. (j) HAADFSTEM

and represent the element mappings as well as the atomic ratio of B, C, N, and O elements within a single 5%- BCNONF.[27] mats

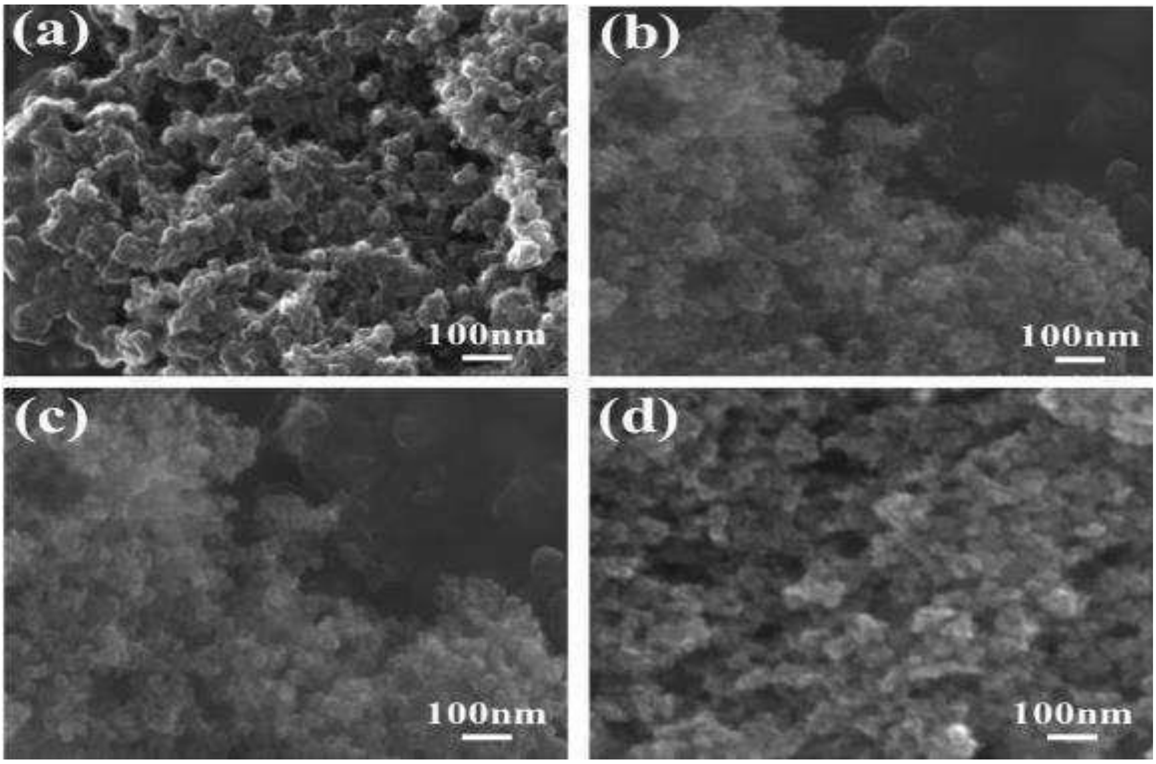

Figure 13: (a)-(d), the generated carbon atoms are round shaped and merge together, which can be explained by the diffusion-limited aggregation model. Numerous carbon particles are simultaneously produced by plasma, and they will go through a zig-zag walk, because of the Brownian motion. Thus, the particles are interconnected toward various directions through collision from other particles, generating a 3-D network with both mesopores and macropores[30]

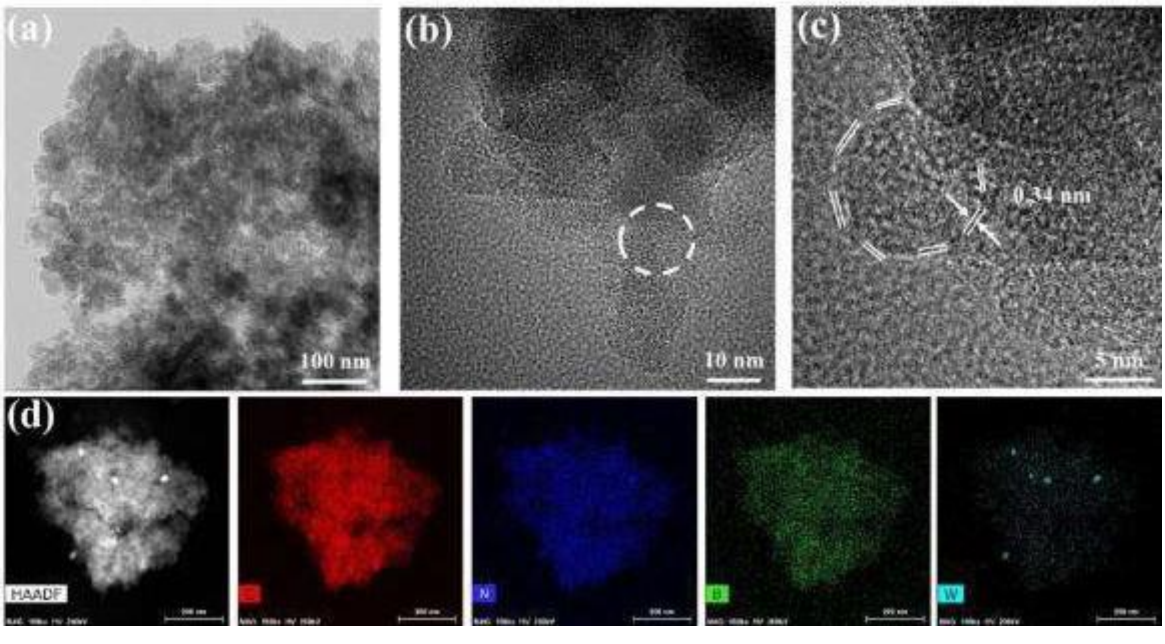

Figure 14: (a) Demonstrates the low-resolution TEM shows that carbon particles are highly spherical and agglomerated in high density, which agrees with the results from FE-SEM around 100nm. (b) provides more visualization of the carbon,

where the carbon round shap is mostly ranged around 10nm. (c) it can be observed that each carbon sphere is mainly formed by layers of crystalline [30] carbon with Boron almost 0.34nm. (d) observed structures of HAADF,C,N,B.W

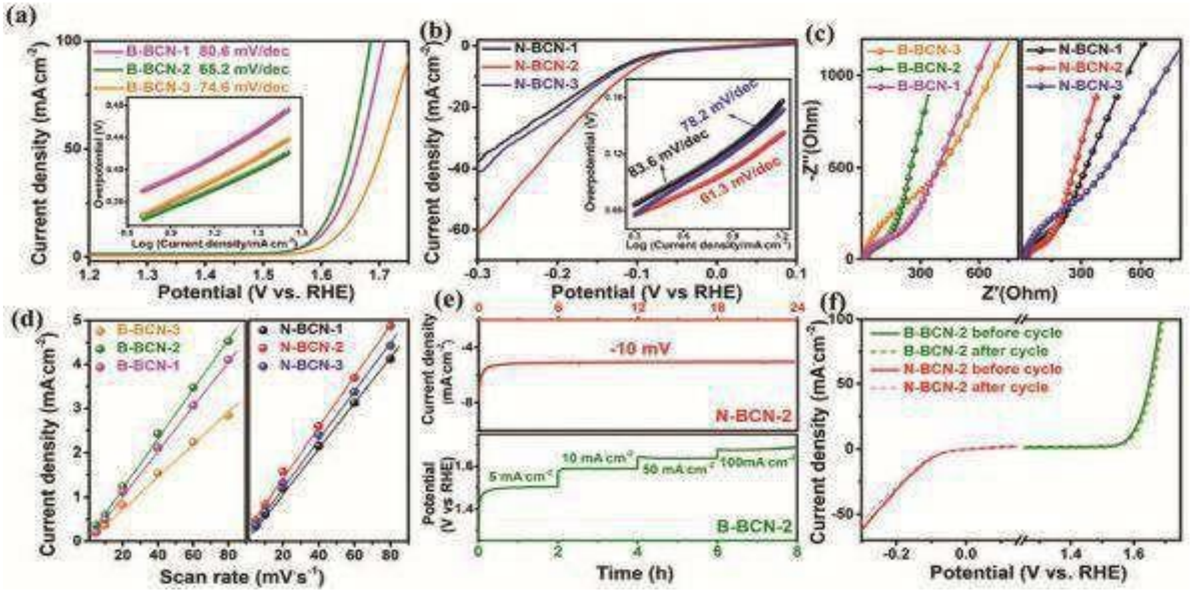

Figure 15: (a) Shows Comparison of OER polarization curve lines of B-BCN samples, with an inset of Tafel slope curves. (b) Comparison of HER polarization curves of N-BCN samples, with an inset of Tafel slope curves. (c) Nyquist plots of BBCN and N-BCN samples. (d) The fitting plots showing of B-BCN and N-BCN samples. (e) Time-dependent current density curve under static over the potential of −10 mV of N-BCN-2 sample, and the multi-step chronopotentiometry curve at different current densities from 5 mA cm−2 to 100 mA cm−2 of B-BCN-2 sample. (f) The polarization curve before and after HER and OER stability tests of B-BCN and N-BCN.[26, 59]

Table 2:- A comparison between current density, Over potential, and Tafel slope of B-doped metal-free electrocatalyst For OER reported in the literature.

Catalyst	**Electrolyte**	**substrate**	**Over potiential mV**	**Tafel slope**	**Refrences**
B-BCN	**1M KOH**	**Carbon paper**	**140**	**65.2**	**26**
5%(BCNONF)	**1M KOH**	**-**	**420**	**72.9**	**26**
20*B-MWCNTs	**N_2 Saturated 0.1M KOH**	**GC**	**155**	**-**	**27**
B1-GY	**1M KOH**	**-**	**350**	**142**	**28**

1 mM B,N-codoped	**1M O_2 saturated KOH**	**Ru/C 5wt%**	**331**	**189**	**29**
10 mM B,N-codoped	**1M O_2 saturated KOH**	**Ru/C 5wt%**	**270**	**100**	**30**

1.2: N doped metal-free catalyst for OER

Nitrogen has a different electronic configuration than carbon but nitrogen and carbon has almost same atomic structure. So we can change the electronic structure of a material by doping it with carbon nanomaterials with the lowest disturbance to carbon lattice.(59) Changed electronic structure by induced doping of Nitrogen and carbon based nanomaterials are widely used in different applications including electrolysis. Doping of carbon nanotubes with Nitrogen also shows positive effects on oxygen evolution reaction. For example: carbon nitrogen nanotubes CNNTs were prepared by Yadav et al. by chemical vapor deposition CVD.(60) The carbon nanotubes formed show excellent efficiency and high durability for OER. It has high current density and low overpotential because of high activeness of catalyst in basic solution having pH 13. This catalyst can also afford a high current for OER than another catalyst such as IrO2/C catalyst.(61) Thus the catalytic activity of a carbon -fixed catalyst is affected significantly by Nitrogen doping. The Tafel slope of C-NNTs is low as compared to pure nanotubes because doping effect intensifies the activity of catalyst. The nitrogen doped carbon nanotubes shows little overpotential than pt/C because of their high activeness towards OER at pH 13. Moreover CNNTs exhibit high electrical conductivity and also shows high rate of reaction as compared to IrO2 and pt/C.(62) Accordingly, doping with N iotas has altogether worked on the electro catalytic exercises of the carbon-based sans metal impetuses. The Carbon doped nanotubes (CNNTs) shows trancated tafel slope (383 mV dec−1) and high stability as compared to the pure nanotubes (CNTs). The tafel slope of (CNTs) is about 658 mV dec−1. So, huge distinction in Tafel slants in between the undoped CNTs and CNNTs with various nitrogen substance proposes a huge chance for tuning the synergist execution by managing the doping effect(63). Albeit specific beginning of the synergist exercises is not complete. So, ongoing examinations demonstrate the inclusion of N iotas in CNTs and actuates dynamic destinations to work with the reactive OHions of water molecules and the arrangement of O−O securities with oxygen atoms. It is shown that N-doped graphite (NGr) is introduced by (N/C, Figure 1 c) integrated from a N-rich polymer (acid aldehyde polymer) display an OER movement surpassing those of customary electrocatalysts (for example IrO2 nanoparticles) in antacid media.(64) Without any change in metal ,the enhanced N/C electrocatalyst gives very low overpotential of 1.62V at a current density of 10mV cm-2. This efficiency of N/C catalyst is due to co-doping effect of N with C. Moreover, the proceeding N-doped grapheme (NG) formed contain 2.45%N and had high quaternary-N molecule which increase the surface area of catalyst and shows good performance towards OER and this catalyst give high efficiency as compared to the same class.(36) Another Nitrogen doped grapheme catalyst with predominant action for OER was made by using an aqueous strategy with alkali and nitrogen for runner .We can change Chitin into a minimal expense N-doped carbon sheet to create an exceptionally dynamic electrocatalyst for oxygen evolution reaction (OER) through heat treatment.(37) The Chitin Ndoped carbon sheet shows very low overpotential about 1.64 V and high current density because of its large surface area and more vigorous sites of this electrocatalyst.(38) First-standards thickness utilitarian hypothesis (DFT) estimations have uncovered that self-gathered Ndoped (10 at%) fullerene would be effective for OER execution due to their improved restricting energy for response intermediates. The ability to adjust the maximum energy by manipulating the level of Ndoping has also been demonstrated, showing the influence of surface strain. The significant role played by N dopants in inducing compressive surface strain was found to be crucial in modifying catalytic activities.(65)

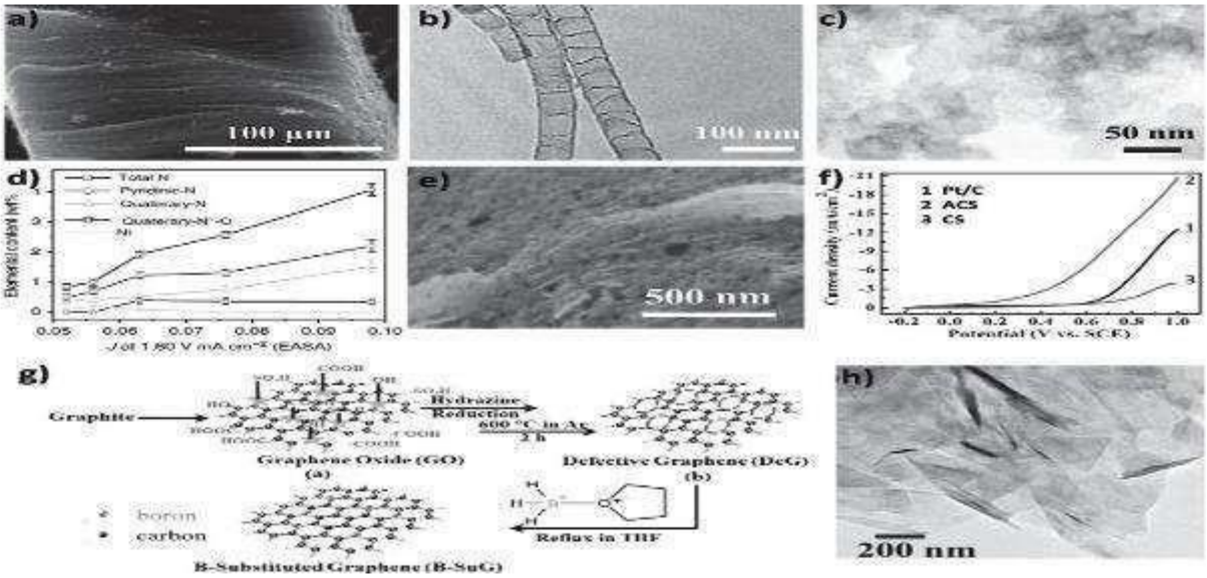

Figure 16: SEM picture of an enacted chitin-based carbon sheet (ACS). f) OER current of Pt/C, ACS, and a chitin-based carbon sheet (CS) terminal in KOH arrangement (0.1 mol L−1) at a sweep pace of 10 mV s−1 (republisheda,b) SEM and TEM pictures of CNNTs (republished from Ref. 61 with consent. Copyright 2015 American Chemical Society). c) TEM picture of N/C materials. d) Relationship between the distinctive natural substance and OER exercises of the N/C electrocatalysts (the possibilities needed to accomplish 10 mA cm−2; republished from Ref. 62 with aut from Ref. 65 with authorization. Copyright 2015 Royal Society of Chemistry). g) Schematic portrayal of the different advances utilized for the combination of B-subbed graphene (B-SuG). h) TEM picture of B-Su (republished from Ref. 69 with authorization. Copyright 2015 Royal Society of Chemistry).

G@NC metal free electrocatalyst, by control loading, is a very productive catalyst for OER. So the activity of G@NC may be enhanced by controlling the ratio of Graphene. 2D structure of N-doped metal free catalyst also give low tafel slope and overpotential which is prepared by using hydrothermal method .The active sites may be increased by graphitic N, assembled on graphene, which enhance the ability of charge transfer as well as decrease the barrier for OER.(66) Nitrogen and carbon based graphene exibit remarkable stability and activity towards OER due to codoping effect of Nitrogen with graphene. 5.0 g of N-methyl-D-glucamine (0.026

mol) and 13.6 g of sodium carbonate (0.13 mol) were mixed and combined with methanol (100 mL) at 45 °C for 30 min. The dried form of product is first dissolved in ethanol (50 mL) and then purified by using paper .The main objective of purification is to eliminate the salt by the removal of ethanol under low pressure at 40 °C for 3 h. GIL IS Synthesis by using Hydrothermal method.(67)

Table 3:- A performance overview of representative N-doped carbon materials in electro catalysis.

Catalyst	**Overpotential (V)**	**Tafel slop (mV dec^{-1}**	**Medium**	**Catalytic efficiency**	**Reference**
g-C_3N_4 tubes	**0.36**	**55**	1M KOH	**>IrO_2**	**(68)**
Porous NCNTs	**0.68**		0.1M KOH	>Pt/C	**(69)**
N-doped mesoporous carbon/CNT	**0.32**	**55**	0.1M KOH	**>IrO_2**	
N, S co-doped graphite	**0.38**	**96**	0.1M KOH		**(50)**
S-doped C_2N aerogel	**0.3**	**62**	0.1M KOH	>RuO_2	**(69)**
N, S co-doped carbon	**0.33**	**71**	0.1M KOH	≈RuO_2	**(70)**
N, P, F tridoped grapheme	≈0.58 V	**136**	0.1M KOH	≈RuO_2	**(71)**

N-advanced graphene based (N-GQDs) were explained as the model impetuses for top to bottom comprehension of the without metal OER system.(72) } It was observed that the pyridine N-oxide generates in N-GQDs could make sufficient positive charge partition through its π–π disturbance to work with the initialstep of the OH^- adsorption. Then, at the same step, the OH* assaults one more OH− to react with middle *O,trailed to generate one and more hydroxyl particle to shape the *OOH halfway.(73) the localized ions reactwith oxygen and formed O2 . in second step bonds of OH break due to delocalized of pi bond and convert intothe water molecule. Moreover Nitrogen doped grapheme reduces the adsorption energy of OH ins which generates on the catalyst surface.The arrangement of NSGF highly effected the OER performance because doping of N with SGF reduce the barriers and enhance the stability about 23% of catalyst which is almost 60 h. the nitrogen doping with SGF also shows the low over potential (0.380V) . Moreover, with the increasing of surface area and edges. it shows low tafel slope as compared to pure SGF in in alkaline solution of 0.1 m KOH.(46)

The overpotential ofo.5NS-GR/CNT is slightly low as compared to1.5N-GR/CNT because of S codoping effect. So by controlling the C-S-C composition we can increase the reaction rate during the adsorption of OH. (48,60)

1.3: p-doped metal free catalyst for OER

Phosphorus (P), as a component of Group V, shares a similar electronic configuration with nitrogen but has a larger atomic size and lower electronegativity. These properties make it attractive for creating a defect-induced active surface for the adsorption of O* (oxygen). Additionally, phosphorus can induce local charge density due to its lone pair of electrons in the 3p orbital, which can accommodate the lone pairs of electrons from O* and initiate the oxygen evolution reaction (OER) cycle.(67) Therefore, it is not surprising that edge-selectively phosphorus-doped few-layer graphene (G-P) has been reported as an efficient metal-free electrocatalyst for OER. Experimental measurements using cyclic voltammetry show that the G-P anode has a lower onset potential for OER (approximately 1.48 V versus RHE) as compared to pristine graphene (approximately 1.54 V).(74) To investigate the role of the phosphorus dopant, the limiting current from the linear sweep voltammetry (LSV) curve is normalized by the Brunauer-Emmett-Teller (BET) surface area.(75) Consequently, the specific activity of G-P (0.03207 mA cmBET−2 at 1.6 V) is significantly higher than that of G (0.00115 mA cmBET−2), indicating the significant contribution of phosphorus doping to the catalytic activity of G-P in the OER process.(76) P-doped based metal free electrocatalyst are highly favorable for OER. The doping of heteroatoms such as phosphorus and nitrogen into the carbon organization can change the synthetic and electronic properties of Nano carbons. The structure of catalyst also effects the oxygen evolution reaction. Phosphorus-doped C3N4 developed on carbon fiber paper was accounted to show high action and strength as adaptable nonmetal OER anodes in antacid media, attributable to the double elements of nitrogen and phosphorous particles.(77) The phosphorus co-doping reduce the barriers for OER and also improve the catalytic properties. We have fostered a basic and adaptable ball milling cycle to breaking the immaculate graphite straightforwardly into edge-specific P-doped graphene. G-P was shown as a proficient and strong cathode to catalyze the oxygen advancement with movement better than G in basic arrangement. The doped P assumes a significant part to catalyze OER.(76)

Table 4:- A performance overview of representative N-doped carbon materials in electrocatalysis.

Catalyst	Current density mA/cm^2	Over potential (mv)	Tafel slope mV/dec	Stability	References
G-P	10	330	62	/	(76)
(RP-BP/CNTs	263 mV	10 mA cm−2	81 mV·dec−1	/	(78)

A metal-free 2D catalyst based on BP (black phosphorus) was investigated without the use of metal bifunctional oxygen impetus. Trial studies, along with DFT estimations, confirmed the crucial role of interfacial P-N bonds in controlling the electron rearrangement between BP/g-C3N4 interfaces. Consequently, these bonds influenced the chemisorption properties of O-intermediates.(78) The resulting BP-CN-c catalyst exhibited the highest performance as an OER (oxygen evolution reaction) reactant among metal-free BP-based catalysts. Moreover, the p-doped catalyst demonstrated excellent performance and reduced resistance for the oxygen evolution reaction. Additionally, BP/g-C3N4 proved to be a cost-effective catalyst for OER. Therefore, by modifying the structure of p-based metal-free electrocatalysts, we can enhance their catalytic activity and improve the transferability of charges towards OER.(79) Black phosphorus (BP) has garnered significant attention in the field of oxygen evolution reaction (OER). However, the unstable nature and poor conductivity of BP hinder the further advancement of OER catalytic performance when used as a standalone catalyst. In this study, we present a technique that utilizes mechanical shear force to effectively combine carbon nanotubes (CNTs) and red phosphorus powder (RP) in order to create a hybrid which is a dimensionally structured (RP-BP/CNTs) electrocatalyst without the need for metallic components. This hybrid catalyst demonstrates outstanding OER performance in alkaline media. Through the ball milling process, RP undergoes in-situ phase transformation into BP due to shear pressure and high temperatures. Simultaneously, the ball milling process reduces a significant number of defects in CNTs, which combine with the lone pair of BP to form a P–C bond, resulting in a heterojunction structure. By strategically engineering the interface, the hybridization of RP-BP and CNTs enhances electro conductivity and provides remarkable durability. The results indicate that the RP-BP/CNTs hetero structure exhibits excellent OER performance, with a low overpotential of 263 mV vs. RHE at a current density of 10 mA cm−2, surpassing that of the commercial catalyst RuO2 (310 mV vs. RHE, 10 mA cm−2). The small Tafel slope indicates superior catalytic efficiency of the catalyst, while its robust structure ensures long-term stability.(78) The RP-BP/CNTs heterostructure catalyst for oxygen evolution reaction (OER) was synthesized using a simple two-step ball milling method. In the first step, RP was transformed into BP through ball milling, and then a certain amount of CNTs was added for further ball milling.(80) The introduction of CNTs led to the generation of numerous defects and exposed a large number of active sites. These defects and active sites facilitated the bonding between RP-BP and CNTs through P-C and P-O-C linkages, resulting in the formation of a stable and efficient heterostructure catalyst. Electrochemical testing of RP-BP/CNTs showed that

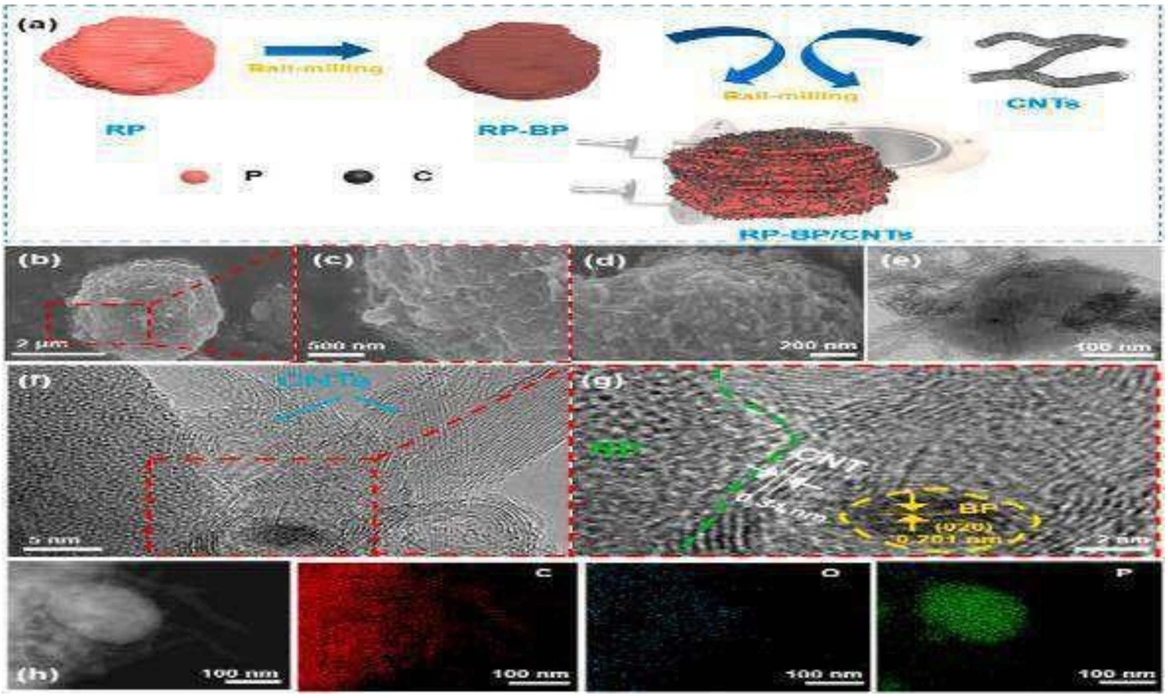

Figure 17: (a) Synthesis diagram for ball-milled RP-BP/CNTs heterostructure catalysts, (b–d) SEM images of RPBP/CNTs, (e) TEM image of RP-BP/CNTs, f-g) HRTEM images of RP-BP/CNTs, (h) HAADFS-STEM and EDS elemental mapping images of the RP-BP/CNTs heterostructure. (78)

at a current density of 10 mA cm^-2, the overpotential was measured at 263 mV vs. RHE, and the Tafel slope was 81 mV·dec^-1. Analysis of the Nyquist plots revealed that the conductivity of RP-BP was significantly enhanced after the incorporation of CNTs, demonstrating the positive impact of CNTs on the overall conductivity of the heterostructure catalyst.(81) Moreover, the RP-BP/CNTs heterojunction catalyst exhibited excellent catalytic performance for OER due to the strong covalent bonding of P-C and P-O-C. This simple two-step ball milling technique not only expands the potential industrial production of BP-based catalysts but also opens up new possibilities for their application in areas such as batteries and photocatalysis.(82)

2. Conclusion

This paper provides an overview of the recent advancements in the field of metal-free materials as electrocatalysts for oxygen evolution reaction (OER). The focus is primarily on understanding the mechanisms involved in OER electrocatalysis. Metal-free catalysts have emerged as highly efficient alternatives to precious metal catalysts for various applications such as clean energy sources, water splitting processes, and hydrogen fuel batteries. The paper examines different strategies for enhancing the performance of metal-free catalysts, including compositional doping, defect engineering, surface modifications, and the creation of catalysts doped with elements like sulfur (S), boron (B), phosphorus (P), and nitrogen (N) for multifaceted design. Tables 1, 2, and 3 present information on the materials, characteristics, preparation techniques, and behavior of reported metal-free catalysts for OER. The study concludes that metal-free electrocatalysts, specifically those doped with B, S, N, and P, demonstrate favorable performance in OER due to their ability to lower the activation energy for oxygen generation. Moreover, their strong interaction with carbon-based materials and high electrical conductivity contribute to their stability and efficiency. Doping B, N, S, etc., with carbon-based materials increases the number of active sites, thereby improving OER performance. Future research can focus on exploiting the doping effect of metal-free electrocatalysts with carbon-based materials such as carbon nanotubes (CNTs), graphene (GY), and carbon fibers (CFs). By employing annealing and electrochemical processes to dope B, S, N, etc., with graphene oxide (GO), graphene, or CNTs, enhanced stability and efficiency can be achieved. Additionally, investigating the preparation of multilayers of CNTs and graphene through annealing or hydrothermal processes, and subsequently doping them with non-metals like C, N, and S, may yield even better results in the future.

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