

Chapter 1

Introduction & literature survey

This chapter deals with the basic introduction of carbon materials, porphyrin, conducting polymers and their hybrids with various synthesis methodologies for electrochemical applications mainly in supercapacitors. This chapter also includes the importance of modification of materials and their effect on electrochemistry along with literature survey, research gap and motivation.

1.1. Background

The multifunctional hybrid materials are getting more attention among scientists and researchers, because of their large surface area and unique electrical redox properties. Such materials are also preferred for the fabrication of the electrodes giving an efficient performance in the electrochemical energy storage, sensors, catalysis, electronics and optoelectronics applications [Gomez-Romero et al. (2004), Romeroa et al. (2005), Sun et al. (2016)]. In this regard, various kinds of nanomaterials including metal nanoparticles (NPs), carbon-based nanomaterials, graphene (GR), quantum dots (QDs), carbon nanotubes (CNTs), nitride-based composites and polymeric nanoparticles have been widely accepted [Sun et al. (2016), Kotal et al. (2013), Song et al. (2013), Dong et al. (2012), Zhu et al. (2014), Freeman et al. (2013), Kumar et al. (2012)]. Energy is a very crucial need for our societal existence. As the population increase, the consumption of energy also increases, which forced scientists to find an alternative efficient energy sources and storage systems. Regarding energy storage, supercapacitor showing to their exceptional and excellent properties is getting more interesting and considerable attention in consumer electronics, industrial power and memory back-up system [Zhang et al. (2009)]. Enormous research efforts have been dedicated to the development (synthesis and assembling) of electrode materials for excellent electrochemical properties [Zhu et al. (2011), Xiao et al. (2013), Sawangphruk et al. (2013)]. But at present, the electrochemical performance is not only one parameter. More to the point performance, environmental friendliness, stability, low cost, processability and durability have also become research challenges and motivated to the synthesis of sustainable electrode materials [Wu et al. (2019), Lu et al. (2014)]. Carbonaceous nano-allotropes such as CNTs, activated carbon,

charcoal, CQs, graphene, are playing a considerable role as sustainable energy materials due to the unique combination of chemical and physical properties, easy availability and eco-friendly nature [Staaf et al. (2014), Frackowiak et al. (2001)]. Bio wastes are now considered as a good source of porous carbon and become a hotspot for researchers in electrochemical supercapacitor [Divyashree et al. (2016), Huang et al. (2019)]. Though, carbon-based material has a lack of redox center and limited interface area towards electrolytes which provides unsatisfactory energy density. The coupling of redox-active component (metal oxides as well as conducting polymers) in the carbon matrix is performed to achieve better performance [Wu et al. (2019), Zhao et al. (2018), Chen et al. (2017), Dubal et al. (2018)]. Conducting polymers (CPs) a different class of polymeric materials that can conduct the electricity or charge through polymer chain and have an excellent ability for further functionalization [Nizakati et al. (2018), Zidi et al. (2016), Zhang et al. (2018)]. Easy laboratory synthesis, lightweight, good conductivity is the striking feature of the CPs and provides alternative redox components to replace the metallic parts with increasing eco-friendliness [Snook et al. (2011)]. Over the metal oxides, the conducting polymers (CPs) gained much attention and used frequently in present nanotechnology replacing the metallic counterparts [Snook et al. (2011)]. In addition, the presence of hetero atoms in the carbon matrix can also facilitate electrochemical performance. With increasing the demand for environmentally and economically electrodes materials, organic supramolecules and macrocyclic compounds are regarded as promising candidates for these purposes. Porphyrin an organic macrocyclic has some special kind of electronic structure, redox and bonding capability (by the transition, non-

transition and chemical functional groups). Therefore, porphyrins become popular research hotspots for artificial electrochemical and photoelectrochemical systems [Mayer et al. (2006), Engelmann et al. (2002), Kumar et al. (2017), Zhao-Karger et al. (2019)]. Recently, the porphyrin-based electrode has reported for catalysis [Carballo et al. (2016), Coros et al. (2018)], supercapacitors [Cheng et al. (2019), Gao et al. (2017)], rechargeable batteries [Zhang et al. (2015), Xu et al. (2015), Shin et al. (2014)], and redox-flow batteries [Ma et al. (2018)]. Chemically, a porphyrin system having conjugated C and N with an 18 π -conjugated electron also called the “pigments of life”. Due to strong π - π interactions and functionality sites in porphyrin, people start to incorporate or functionalize with other components and results in a composite (porphyrin associated with carbon nanotubes, carbon nanospheres, carbon nanosheets) which shows synergistic improvement in their performance [Gervaldo et al. (2010), Supriya et al. (2018), Wang et al. (2017)]. As an early phase, studies of CPs functionalized carbon materials like CNTs, graphene were carried out to improve the performance, which can take advantage of the state of the art of CPs integration with porphyrin. There are few researches also published on porphyrin and CPs based composites for sensor, optical, solar cells etc. [Peshoria et al. (2018), Wang et al. (2019), Mahmood et al. (2018)], therefore this field needs to expand in energy storage areas also. In the subsequent paragraphs, our thesis is going to discuss historical knowledge about carbon, porphyrin-based nano-materials and its hybrid with CPs. The present thesis gives a contribution toward developing the electrode materials by the functionalization of carbon nanosheets and porphyrin with CPs via *in-situ*

chemical polymerization process and their potential electrochemical application, especially for supercapacitors.

1.2 History of carbon and carbon-based nanomaterials

Carbon makes up a large number of materials having diverse texture, structure, and applied in different technological devices [Kotal et al. (2013), Yan et al. (2016), An et al. (2001), Cazorla-Amoros et al. (2014)]. Antoine Lavoisier (in 1772) was first who get acknowledge for the discovery of carbon and suggested that the diamonds are analogs of carbon. Carl Wilhelm Scheele (in 1779) showed that graphite was like charcoal and is another allotrope of carbon. The physical, as well as chemical properties, vary widely as their allotropic forms like graphite, fullerene, quantum dots, diamond, and amorphous carbon [Yan et al. (2016), Cazorla-Amoros et al. (2014)]. Carbon has good catenation power which makes them very interesting and results in a diverse compound and complexes. They produced many kinds of nanomaterials as (CQDs) which are having zero-dimensional, (CNTs) 1 D, graphene 2D structure, graphite and diamond 3D structure [Cazorla-Amoros et al. (2014)]. The graphite allotropic forms are opaque, black and have high conductivity with anisotropic nature, while the allotropic forms of a diamond are highly transparent and have a very low electrical conductivity. The thermal conductivity of the diamond is highest among the known materials. Diamond is one of the hardest materials which exist on earth. On the other hand, graphite is very soft. The 2D sheets like graphene extracted by the chemical oxidation and exfoliation of the bulk graphite. The popularity of carbon-based materials is due to a unique set of properties such as good conductivity, thermal stability, enormous surface area, corrosion resistance, high

chemical stability and mechanical properties [Yan et al. (2016), An et al. (2001), Cazoria-Amoros et al. (2014)]. Therefore, several research publications were published since 1900 [Cazoria-Amoros et al. (2014)]. Recently, some 3D hierarchical nano-materials are also reported with some special kinds of surface area and very high electrochemical performance. Walker (1990) stated, carbon is old but new material exhibits in various forms having extraordinary properties in terms of thermal, chemical, electrical, and mechanical, and own a unique position in nano-science and technology [Cazoria-Amoros et al. (2014)].

1.2.1. Types of carbon-based nanomaterials

Carbons are vital and fundamental elements for sustaining all lives on earth, in forms of organic compounds include cellulose, proteins, nucleic acids and so on. Many forms of carbon-based nano-materials or nano-allotropes have been developed in the past few decades. Some of them like fullerenes, nanotubes, nanodiamonds, quantum dots, graphene, graphite, and they all are used very frequently in present technology and research [Yan et al. (2016), An et al. (2001), Cazoria-Amoros et al. (2014)]. When their size scales in nano-level, these carbon nano-materials exhibit exciting structural and functional properties. The major contribution behind this paragon is their hybridization state and high surface area to volume ratios. Carbon orbital's can undergo sp , sp^2 or sp^3 hybridization based on bonding suitability and produced different kinds of materials with different shapes and structures [Cazoria-Amoros et al. (2014), Shehzad et al. (2016)]. Based on the dimensions scale the nano-carbon allotropes are classified under the following classes as shown in Figure 1.1.

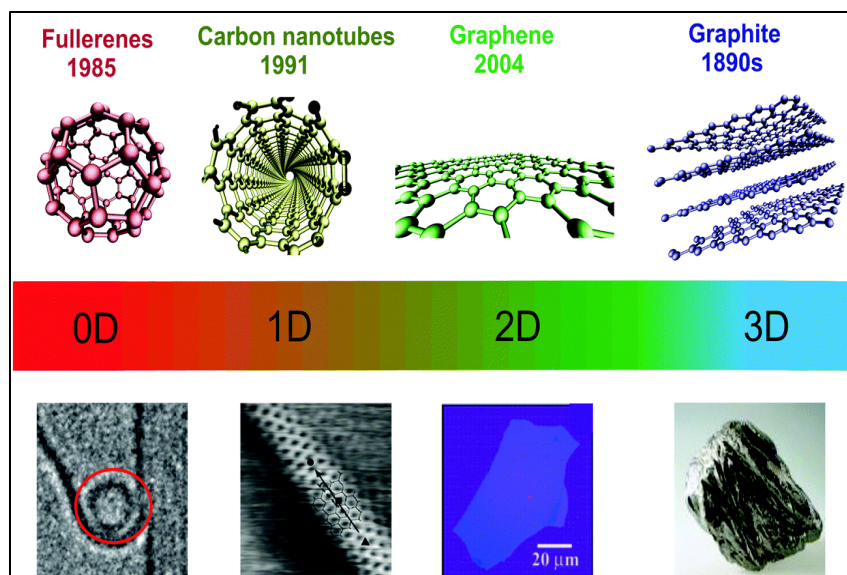


Figure 1.1 classifications of nano-carbon allotropes based on dimensions scale, Ref.

[Shehzad et al. (2016)]

1.2.1.1 Zero-dimensional (0D) carbon nanomaterials

Those nanomaterials having all three dimensions in the nanoscale are categorized as 0D nanomaterials. CDs are quasi-spherical shaped nanostructures of 0D carbon nanoallotropes with diameters range between 2 and 10 nm as shown in figure 1.2. It shows amorphous in nature and imparts photoluminescence properties. However in the case of fullerene [Cazorla-Amoros et al. (2014)], it also has 0D shaped structures with a closed hollow cage, but chemistry is totally deferent. Fullerenes also called buckminsterfullerenes or buckyballs, are ball-like structures made up of a mixture of sp^2 and sp^3 hybridized carbon atoms of 5-membered or 6-membered rings (shown in figure1.2). The C_{60} is the most abundant and simplest member of fullerene where 12 pentagonal and 20 hexagonal rings haven been investigated and reported [Eklund et al. (1995)].

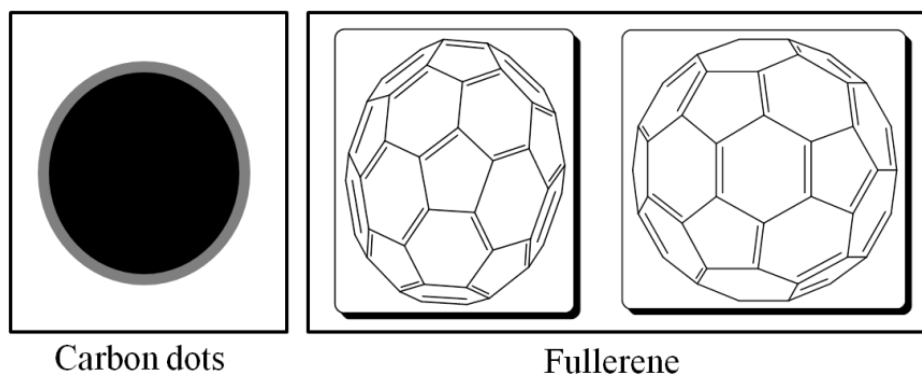


Figure 1.2 pictorial representations of carbon dots and fullerene

1.2.1.2 One dimensional (1D) carbon nanomaterials

In this class of nanomaterials, two dimensions are in the nanoscale range of 1–100 nm and the remaining other one dimension in macroscale. Nanofibers, nanorods, nanowires, and nanotubes are some examples of 1D nanomaterials [Tiwari et al. (2012)]. CNT is 1D carbon nanoallotropes [Cazorla-Amoros et al. (2014), Shehzad et al. (2016)] and Iijima et al. (1991), Iijima et al. (1993) was the first scientist who discovered this molecule. CNTs are broadly classified as multi-walled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT). Two models are used to describe the structures of MWCNT namely the Russian Doll model and Swiss roll model (as illustrated in figure 1.3). In most cases, the SWCNT has a diameter ~ 1 nanometer, with a tube length that can be many millions of times longer. CNTs have a very large aspect ratio i.e. length-to-diameter ratio which is significantly larger than for any other material. The interlayer distance in MWCNT is about 3.4 \AA as close to the distance between graphene layers. The Russian Doll structure is more common over the other form.

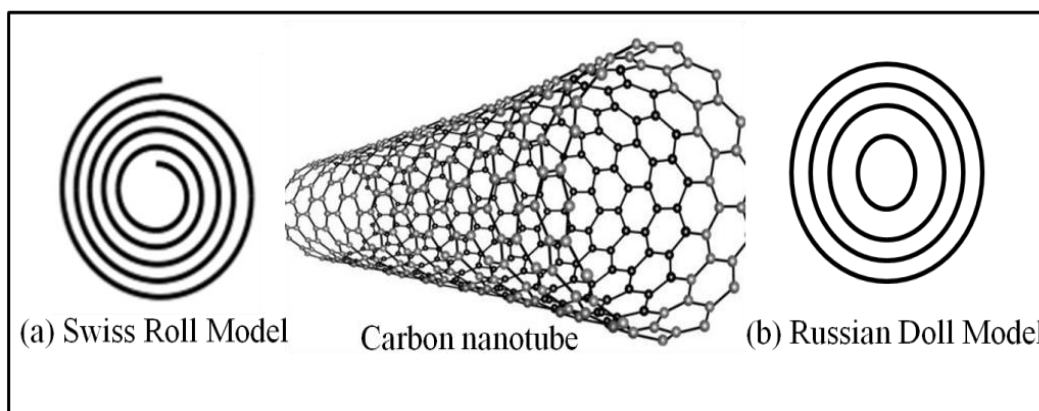


Figure 1.3 pictorial representations of the MWCNT structures

1.2.1.3 Two-dimensional (2D) carbon nanomaterials

In this class of nanomaterials, nano thin-films, nanosheets and nanowalls where two dimensions are outside of nanoscale and one dimension is in nanoscale [Tiwari et al. (2012), Shehzad et al. (2016)]. 2D materials sometimes called single-layer materials, consisting of atomic dimensions thickness single layer. Graphene is a one-atom-thickness planar sheet of sp^2 -hybridized carbons that was isolated in 2004 by the Geim et al. (novel prize 2010) and is considered as the world's first 2D material [Notarianni et al. (2016)]. The graphene term was recognized by Hanns-Peter Boehm in (1962) for describing single-layer carbon foils. Though, the theoretical study was reported by Wallace et al. (1947). Due to remarkable properties, graphene has considerable attention in the development of multidisciplinary technological applications [Yan et al. (2016), Cazoria-Amoros et al (2014), Shehzad et al. (2016)]. The pictorial representation of the graphene 2D sheet has been shown in Figure 1.4.

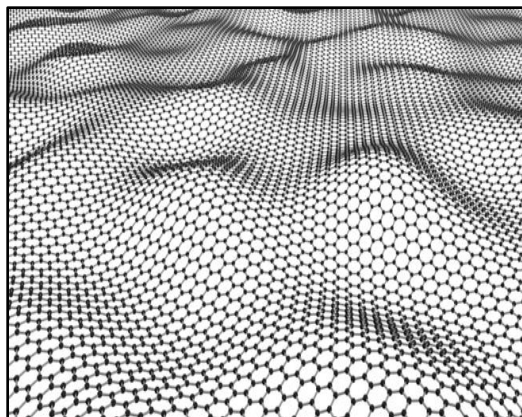


Figure 1.4 pictorial representation of graphene sheet [Ref- matter. univie.ac. at]

1.2.1.4 Three-dimensional (3D) carbon nanomaterials

In this class of nanomaterials, all dimensions are in macroscale and that is composed of the interconnection between nano-scaled individual blocks. Diamond and graphite are a good example of 3D nonmaterial having sp^3 and sp^2 hybridization and produced different shape and structure. The diamond has a tetrahedral structure however the graphite has a sheet-like structure. Importantly, various kinds of 3D porous networks can be assembled from 2D a nanosheet and are expected for considerably rich in their performance [Shehzad et al. (2016)]. In the past few years, various kinds of carbon-based 3D nano-materials are studied very frequently with advanced performance for the majority of the technological applications [Yan et al. (2016), Cazorla-Amoros et al. (2014), Cao et al. (2011)]. Due to their extraordinary surface area and unique electronic properties of such materials is very hopeful for supercapacitors and batteries [An et al. (2001) , Shehzad et al. (2016), Notarianni et al. (2016), Cao et al. (2011), An et al. (2018)]. Heteroatom enclosed carbon materials have unique electronic arrangements and wettability which is a crucial factor to facilitate charge

movement between electrode and electrolytes [Tahir et al. (2014), Tahir et al. (2015)]. Therefore, different types of 3D hierarchical and expanded carbon materials doped with heteroatom e.g. N, P, S, O have been reported for good electrochemical applications [An et al. (2018), Tahir et al. (2015), Zhang et al. (2013), Yang et al. (2018), Yu et al. (2012)]. A wide range of composites having 3D hierarchical and porous structure are also reported where some foreign materials such as organic molecules inorganic/metal nanoparticles, and polymers, are implied to incorporate into the matrix of nano-carbons[Xiao et al. (2013), Sawangphruk et al. (2013), Wu et al. (2019), Choudhury et al. (2020)]. Bio-waste (both plant and animals) is comprised of organic matter and also it consists mostly of elements like carbon, oxygen, hydrogen and nitrogen which could generate special hierarchical porous carbon and also fulfill the requirements like cost, sustainability etc [Bi et al. (2019), Chen et al. (2016), Chen et al. (2013), Chang et al. (2015), Hao et al. (2014), An et al. (2017)]. Recently, research has focused on the generation of activated carbons from biomass owing to their versatile properties such as self-doped heteroatoms, high specific surface area, and a wide range of porosity. Several kinds of microstructures of 3D biomass-based carbon were highlighted in figure 1.5, having enormous potential for supercapacitor applications [Bi et al. (2019)].

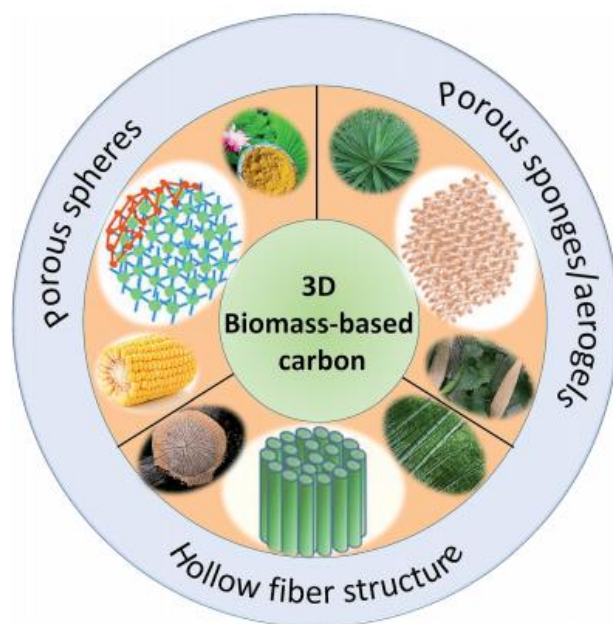
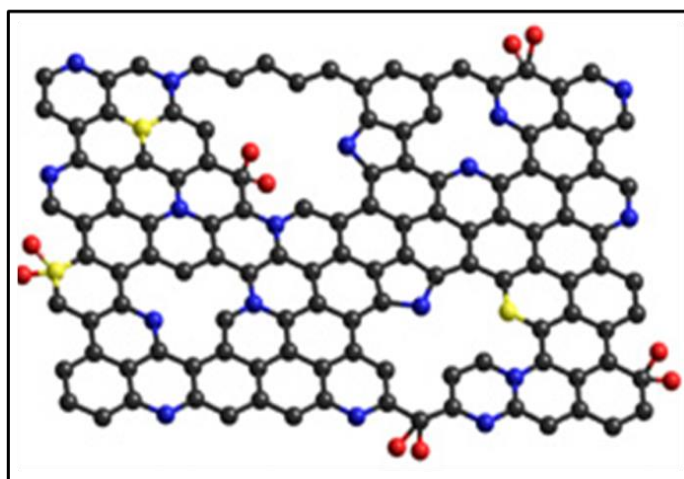


Figure 1.5 Different forms of 3D nano-structured carbon derived from biomass [Bi et al. (2019)]

1.2.1.5 Heteroatom doped carbon nanomaterials (C_aY_b type)

Figure 1.6 shows the pictorial representation of the heteroatom atom doped 2D graphene sheet. Such heteroatom wears differences in the electronegativity, bond length and atomic radius. Therefore, the adjacent carbons from heteroatom feel some positive charge and new defects that can be a foundation for a special type of electronic structure, arrangements and beneficial for electrochemistry and charge transfer and promoting the reaction [Chan et al. (2012), Zhou et al. (2013)]. Heteroatom (Y is N,P,S and O) doped nanocarbon materials are considered to be an advanced and promising candidate for the electrochemical research and have been explored much more [Zhang et al. (2013), Yu et al. (2012), Subota et al. (2011)]. Among these heteroatom, N is more electronegative, and due to the higher electronegativity, nitrogen-doping brings much interest that reason

for a positive charge on the vicinity carbon atoms and improved in their electrochemical properties by breaking the density of state (DOS) [Tahir et al. (2015)]. In this connections, a variety of nitrogen-doped carbon materials like CNTs and carbon nano-fiber, rGO have been prepared via in-situ or post-treatment process by using some nitrogen sources [Xu et al. (2019), Liu et al. (2010)]. Some literature is presented here as the nitrogen-doped carbon materials from melamine (Terrones et al. (1999), acetonitrile (Xia et al. (2005), polyaniline (Vinu et al. (2007), Lei et al. (2009), polypyrrole (Chang et al. (2007), Shrestha et al. (2010), dicyandiamide (Liu R. et al. (2010), Liu et al. (2010), benzylamine, (Munoz-Sandoval et al. (2017), [Meng et al. (2019)] and so on...



Heteroatom doped carbon sheets

Figure 1.6 pictorial representation of heteroatom atom doped 2D graphene sheet [Ref-matter. univie.ac. at]

1.2.2 Synthesis methods and sources for nano-carbons

A variety of nanostructure of carbon material, such as nanotube, fibers, hollow fibers, thin films, and hierarchical, activated carbon blocks are reported in literatures [Wallace et al. (1947), Awasthi et al. (2011), Zahid et al. (2018), Pandolfo et al.

(2006), Noked et al. (2011), Frackowiak et al. (2007), Pollak et al. (2008), Noked et al. (2009), Zhang et al. (2009)]. To synthesis nanocarbons, various kinds of methodology like chemical methods, electrochemical, hydrothermal, and pyrolysis have been used. Laser ablation [Amans et al. (2017)], chemical vapor deposition [Harutyunyan et al. (2002)], arc-discharge [Arora et al. (2014)], fame synthesis [Li et al. (2009)], and high-pressure carbon monoxide (HiPCO) [Remy et al. (2015)] are very sophisticated techniques for the synthesis of super quality graphene and CNTs. These methods are showing some advantages and disadvantages like harsh conditions and the complexity of the process. The pyrolysis is one of the most promising and simple method for the synthesis of different nano-structured 3D porous carbons from hydrocarbon-rich organic waste. Bio-waste derived porous carbons have received an increasing amount of awareness in electrochemical supercapacitors, because of their noteworthy advantages in terms of low cost, large and adjustable pores, active surface area, low toxicity, chemical inertness, flexibility, and physicochemical properties [Bi et al. (2019), Chen et al. (2016), Chen et al. (2013), Chang et al. (2015), Hao et al. (2014), An et al. (2017)]. For the more understand about the activated carbons from biomass waste, some important and effective electro-active carbon nanomaterials are tabulated here (see table1.1).

Table 1.1 various kinds of nano-carbons and their source materials.

Sources	Synthesis methods	resulted materials	Surface area (m²g⁻¹)	Ref.
Human urine	Pyrolysis followed by acid-treatment	N doped PC	1330.6	[Razmjooei et al. (2017)]
Human hair	Pyrolysis	Carbon flakes	1306.0	[Qian et al. (2014)]
animal bone	Pyrolysis	Hierarchical porous carbon	-	[Huang et al. (2011)]
Fish scale	Hydrothermal	Hierarchical lamellar porous carbon	-	[Chen et al. (2010)]
Cow dung	Pyrolysis	N doped AC	128.5	[Zhang et al. (2015)]
Sugarcane bagasse	Pyrolysis	AC	1939.9	[Wang et al. (2018)]
coffee shells	Pyrolysis	AC	842.0	[Jisha et al. (2009)]
potato starch	Pyrolysis	activated carbon spheres	2342.0	[Zhao et al. (2009)]
Wood	Pyrolysis	AC	2793.0	[Phiri et al. (2019)]
Sunflower seed shells	Pyrolysis	AC	2509.0	[Li et al. (2011)]
Corn straw	Pyrolysis	Hierarchical biochar carbon	2690.0	[Qiu et al. (2018)]
Rice husk	microwave oven	AC	-	[Ahamad et al. (2018)]
Cotton gloves	Pyrolysis	Hierarchical nano carbon	1435.0	[Wei et al. (2017)]

Since the bio-waste from natural resources or industrial waste is rich in carbon content. Therefore, it is now to be considered an important source for porous and electro-active carbon and fulfill the requirements for low-cost, green three-

dimensional porous and supercapacitor electrode materials [Jisha et al. (2009), Chen et al. (2010), Zhihong et al. (2019), Chen et al. (2016), Chen et al. (2013), Chang et al. (2015), Hao et al. (2014), An et al. (2017), Wei et al. (2017), Zhang et al. (2015), Wang et al. (2018), Qiu et al. (2018)]. In our thesis research work, two different types of nano-carbon are used. The first one is g-C₃N₄ prepared from Urea and the second is bio-waste (water hyacinth plant) derived highly porous carbon and used as electrode materials. Thereafter, to practice for high-performance, I have applied a thin layer conducting polymer coating over the surface of carbon material via the *in-situ* chemical polymerization process.

1.2.3 Functionalization of carbon material with conducting polymers

Since the carbon-based materials have good porosity, high surface area, which is a basic need for electrode materials in numerous electrochemical applications and engineering areas. The energy storage in the pure carbon nanomaterial occurred via the EDLC process, which shows long cycling stability. Lots of publications have been reported based on such nanomaterials in various journals of scientific domains [Cazorla-Amoros et al. (2014), Jisha et al. (2009), Chen et al. (2010), Zhihong et al. (2019), Chen et al. (2016), Chen et al. (2013), Chang et al. (2015), Hao et al. (2014), An et al. (2017), Wei et al. (2017), Zhang et al. (2015), Wang et al. (2018), Qiu et al. (2018)]. Although, due to lack of redox activity, EDLC materials suffer some disadvantages like low energy density, and restricts their use in the fields of high energy density based applications [Uppugalla et al. (2014)]. To enrich the capacitive performance of carbon materials, different kinds of methodologies have been developed. They combine some redox-active components (pseudocapacitors) to

carbon materials (EDLC), which is a very effective and logical way to improve its electrochemical performance [Uppugalla et al. (2014), Lee et al. (2016), Kavil et al. (2018), Wang et al. (2019), Veerakumar et al. (2020), Zhou et al. (2014)] (Figure 1.7). In this consequence, a series of composites include carbon materials, transition-metal oxides (MO_x like-vanadium oxide V_2O_5 , molybdenum oxide MoS_2 , ruthenium oxide RuO_2 , manganese oxide, cobalt oxide, nickel oxide, oxide/cuprous oxide etc.) and conducting polymers has been reported as electrode materials.

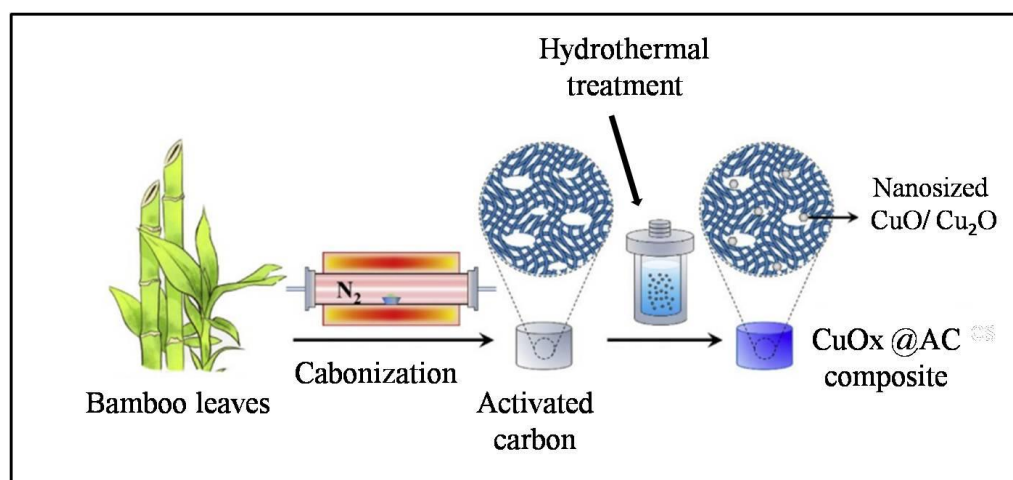


Figure 1.7 Graphical illustration of the preparation of CuO_x/AC composite. [Wang et al. (2019)]

No doubt, the composites of metal compounds assisted in carbonaceous material have a higher specific capacity as compared to conventional carbonaceous materials, but due to high cost, toxicity and brittleness, the metallic counterparts will suffer some limitation which can overcome using the CPs [Shah et al. (2020)]. Therefore, CPs are now getting more attention for electrode material research as they have an essay in processing, high charge density, low cost. In this way number of reports has been

available showing advancement in their electrochemical performance. Snook et al. (2011) report some composites of conducting PPy with CNTs, Rakhi et al. (2012) reported conducting polymer/carbon nanocoil composite electrodes for efficient supercapacitors, Uppugalle et al. (2014) synthesis a hybrid material of heteroatoms doped carbon/polyaniline, Zhou et al. (2014) demonstrated the electrospun carbon nanofibers surface grown with carbon nanotubes and Polyaniline, Lyu et al. (2018) worked Yeast-derived N-doped carbon microsphere/polyaniline composites, Wang et al. (2019) reviewed on carbon/polyaniline hybrids for supercapacitor. Chen et al (2015) prepared PEDOT/g-C₃N₄ binary hybrid, Shayeh et al (2018) reported polyaniline coated reduced graphene oxide/g-C₃N₄/Ag₂O composite. In this, the conductive layers of CPs over the external surface of carbon in the composite not only minimize the active material loss or defects but also open a new charge transport path with shorter path length. In this way, the composites materials (CPs associated carbonaceous) shows a synergic improvement in electron conductivity and leading to better electrochemical performance as well as their kinetics for charge storage. Based on this hypothesis, we planted the work on surface functionalization of g-C₃N₄ with conducting polymer PIn (see chapter 3) and surface functionalization of bio-mass waste-derived AC with conducting polymer PANi (see chapter 5).

1.3 Porphyrin

Porphyryns are indispensable, a highly conjugated macrocyclic bio-organic molecule in which four pyrrole rings are interconnected with each other via methylene group (-CH₂-) as building block units (see Figure 1.8). They possess 18 π -electrons delocalized around the macrocycle that eases the transportation of charge and self-

assembly through π - π stacking. In nature, various essential process (including photoreactions, O_2 transportations) is governed under the porphyrin [Supriya et al. (2018), Mahmood et al. (2018)]. Porphyrins are thermally and chemically very stable and hence motivate the researchers to design an artificial system for widely technological practical in catalysis, light-harvesting and energy storage. [Zhang et al. (2015), Coros et al. (2018), Gao et al. (2017), Song et al. (2019), Chidembo et al. (2010), Cheng et al. (2019)].

1.3.1 Structure and derivatives of porphyrin

In porphyrin, there are three sites e.g. meso-carbon, beta carbon and a central cavity, which able to functionalize further to get desired properties. At the central region, four N are present which can bind with metals and results MN_4 type complex. The introduction of metals in their cavity, porphyrin can significantly change the electrochemical properties. In this sense, various alkyl/aryl group and transition and non-transition metals are used to derivatize the porphyrin Figure. 1.8. Because of strong π - π interaction that gets restacking and hence, the efforts have been prepared towards achieving improved activity by functionalization/combining them with conducting materials.

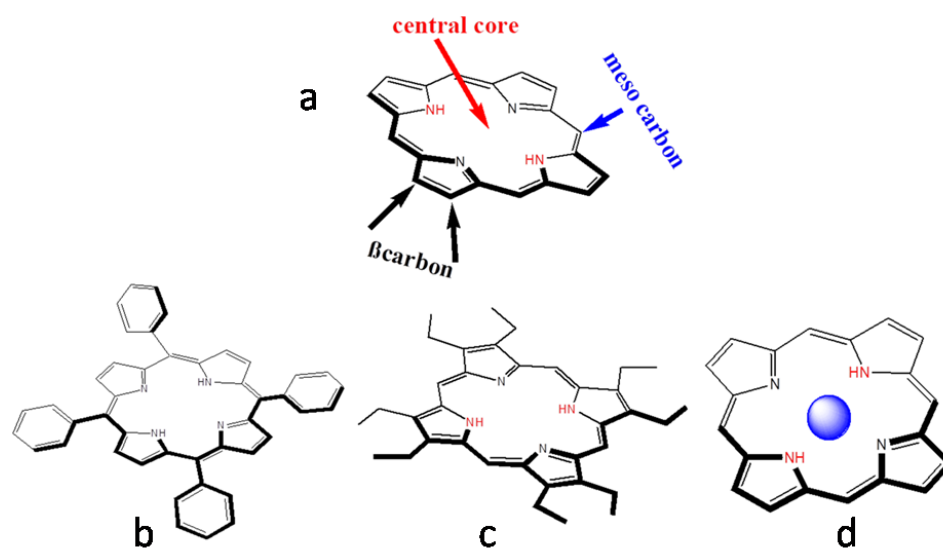


Figure 1.8 Structure of porphyrin (a) and their derivatives, TPP (b) OEP (c) metal bonded porphyrin (d)

1.3.2 Functionalization of the porphyrin with Conducting polymer

Due to their extraordinary binding chemistry and a wide range of tunability, the porphyrin has attracted and a great deal of research interest [Supriya et al. (2018)]. Lots of methodologies (where porphyrins interact with nano carbons via covalent as well as non-covalent bindings (see figure 1.9)) has adopted worldwide to attention their catalytic, energy storage, electrochemical oxygen reduction reaction, sensors, photovoltaic etc. Such heterogeneous electro-catalysts acquire high electrochemically accessible surface area, fast electrons transfer, and stability. Cheng et al. (2019) have reported Mn(II)-porphyrins polycondensation polymer (THPP-PA-Mn) as potential electrode materials for supercapacitors. Zhang et al. (2015) synthesis Zn (II) 5,10,15,20-tetrakis[(carbazol-9-yl)phenyl]porphyrin (Zn-mTCPP) based conjugated microporous polymers (CMPs) for supercapacitor.

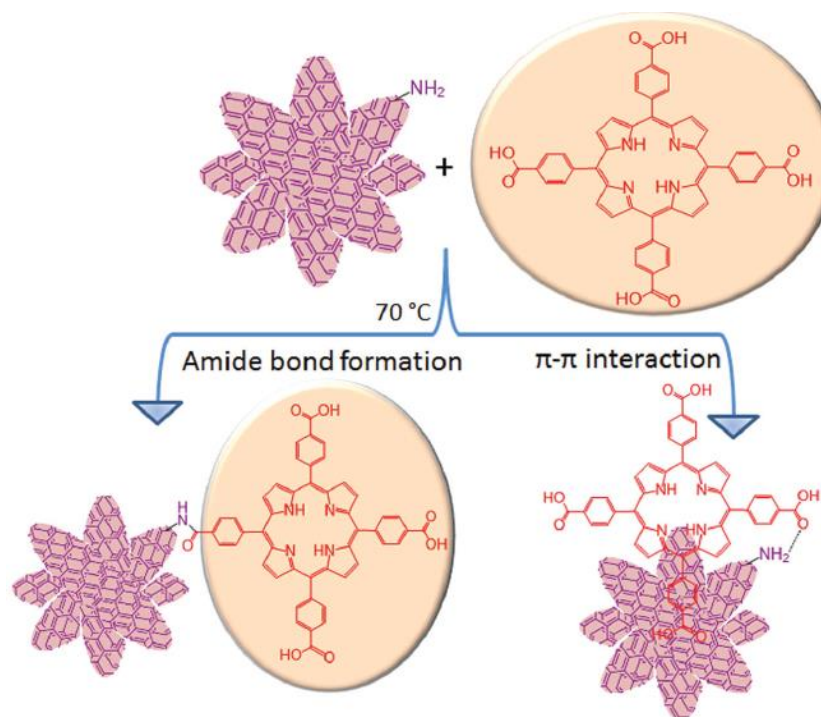


Figure 1.9 Nanohybrid formations between porphyrin and a carbon nanohorn via covalent and non-covalent bonding [Supriya et al. (2018)]

To address the electrochemical advancement in the wide range of applications, several extensive porous nanohybrids based on porphyrin/metalloporphyrin with CNTs/GO/rGO, π -conjugated organic small molecules/polymers derivatives have rationally designed. Song et al. (2019) synthesis cobalt-porphyrin modified 3-dimensional graphene hydrogel, Chidembo et al. (2010) are prepared nickel(II) tetraaminophthalocyanine (NiTAPc)/multi-walled carbonnanotube (MWCNT) nanocomposite for supercapacitors, Yang et al. (2014) published Al-TCPP-Co/carbon cloth (Al-TCPP-Co/CC) as the working electrode in the electrochemical detection of hydrogen peroxide. They all find after incorporation or combination of porphyrin with graphene and other carbon matrices, the surface structure of resultant nanohybrids becomes highly porous and allows more charge accessibility from electrolytes to the

electrode. As a literature survey, numbers of work have done so far where the hybrid of nanocarbons either with porphyrin or with CPs and published their outstanding technological and electrochemical performance, but there are only a few reports have published for functionalization of porphyrin with CPs. In this way, the combination of the porphyrin with the CPs may also give a potential option to improved electrochemical properties and stability. Paul et al. (2009) published polypyrrole functionalized with Fe-porphyrin for CO sensor and their schematics representation of the possible interaction of conducting PPy with porphyrin as figure 1.10. They investigated the Fe center plays a crucial role in the interaction of CO gas and make it facile, and change in resistance was excellent in polypyrrole functionalized Fe-porphyrin as compared to pure PPy. Over the past few decades, hybrids of porphyrin with CPs are receiving hot fields for electrochemical applications. Peshoria et al. (2019) worked on porphyrin@polypyrrole hybrid and its electrochemical sensor and respective schematics representation of the porphyrin@polypyrrole hybrid is shown in figure 1.11. Wang et al. (2019) reported PPy functionalization SnTPP for improved optical limiting performance. In this, the PPy nitrogen linked with Sn (metal in porphyrin center) via axially coordinated mode which affects their charge transfer process (Schematic diagram shown in figure 1.12). Based on this option, people work on a combination of porphyrin with CPs and utilizing for energy applications. Recently Deyab et al. (2019) prepared a hybrid of PANI@Co-Porphyrins for supercapacitor, and PANI/Zn-porphyrin composites for PEMFC applications are reported [Deyab et al. (2020)]. The obtained CPs/ porphyrins composites have a

multi-step reaction in which primarily they insert metal into the porphyrin cavity in specific conditions and subsequently associate with CPs.

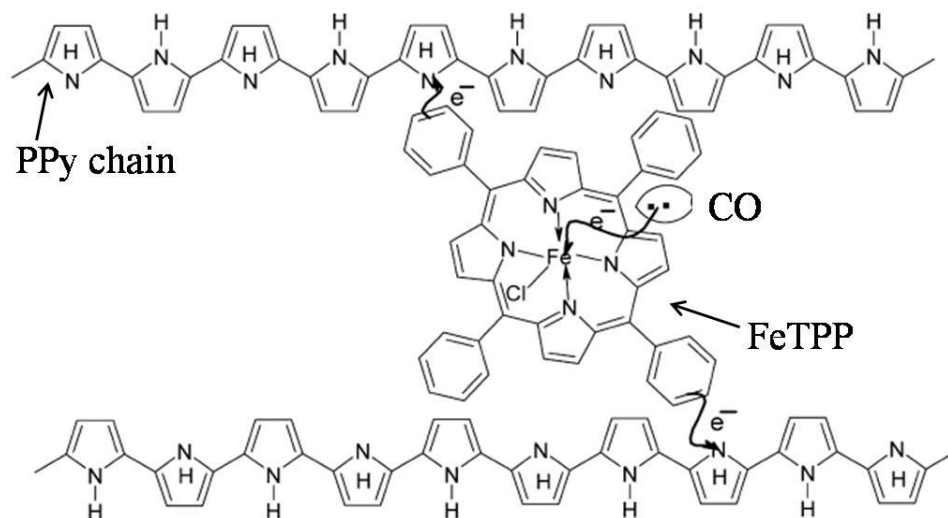


Figure 1.10 Schematics representation of the possible interaction of conducting PPy with porphyrin. [Paul et al. (2009)]

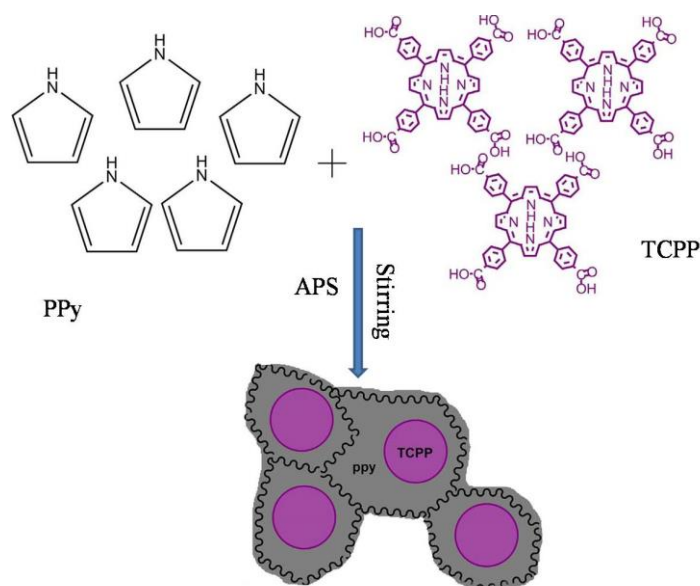


Figure 1.11 Schematics representation of the porphyrin@polypyrrole hybrid [Peshoria et al. (2019)].

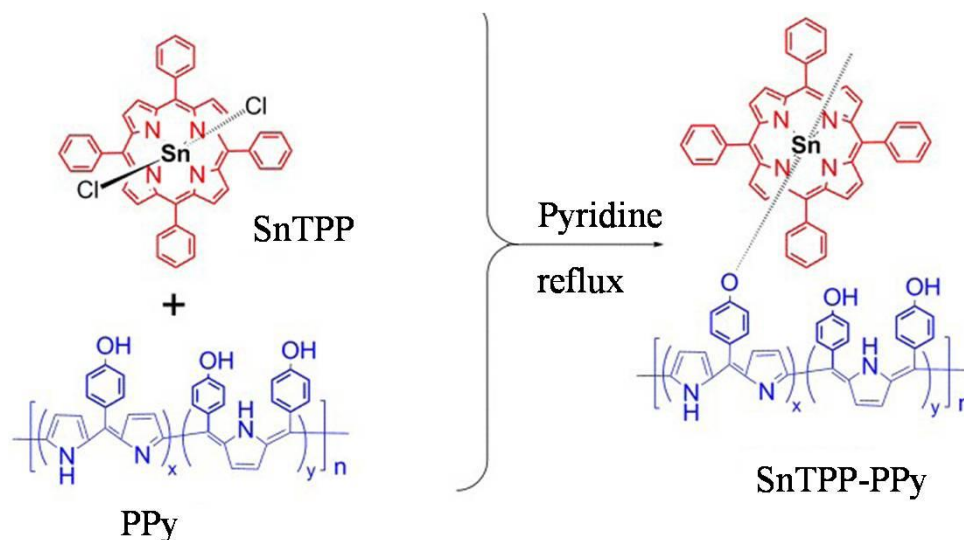


Figure 1.12 Presentation of bonding between SnTPP and PPy and synthesis of PPy-SnTPP Ref. [Wang et al. (2019)]

Since the reduction in the synthesis steps which are a motivating factor for further research. This issue has been overcome by stabilizing a facile one-step *in-situ* process for the synthesis of Fe-octaethylporphyrin/polyindole (Fe-OEP/PIn). Our choice of OEP has been motivated by many factors such as (i) high solubility in chloroform (CHCl_3), (ii) ease of preparation of M-complexes and (iii) minimum π electronic interference. To the best of our knowledge, there is no example of the functionalization of PIn with OEP based materials for electrochemical applications (discussed in chapter 6).

1.4 Conducting polymer

CPs are now considered as organic semiconductors because they can pass the electricity similar to those of inorganic counterparts. A polymer having a long range of π -conjugated polymeric chains and possessing with metal-like electronic properties

are categorized as CPs [Zhang et al. (2018), Seifalian et al. (2018)]. Over the discovery of highly conducting polyacetylene (PA) in 1976, the CPs field has become a hot position for research. PA exists in two isomeric forms as cis and trans where trans-polyacetylene is the conducting polymer. Cis- polyacetylene is not a conductor. The oxidation of PA backbone (iodine doping) was first performed by these three scientists Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid (awarded Nobel prize in Chemistry 2000) and observed a significant improvement in the conductivity of PA with 10 fold [MacDiarmid et al. (2001), Ghosh et al. (2016)]. Thereafter, various types of CPs have been developed including polyaniline (PAni), polypyrrole (PPy), polyparaphenylene (PPP) polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), Polyindole (PIn) and others [Ghosh et al. (2016)]. Some CPs and their respective monomer units are illustrated in Figure 1.13.

Due to their unique electrical properties, lightweight, flexibility and favorable synthesis approach the CPs are denoted as leading materials in academic, industrial, science, and technologies [Snook et al. (2011)]. This opens new doors for researchers to the exploration of CPs. Zhang et al. (2018) reviewed the recent progress and future aspects of CPs with various applications (as represented in Figure 1.14).

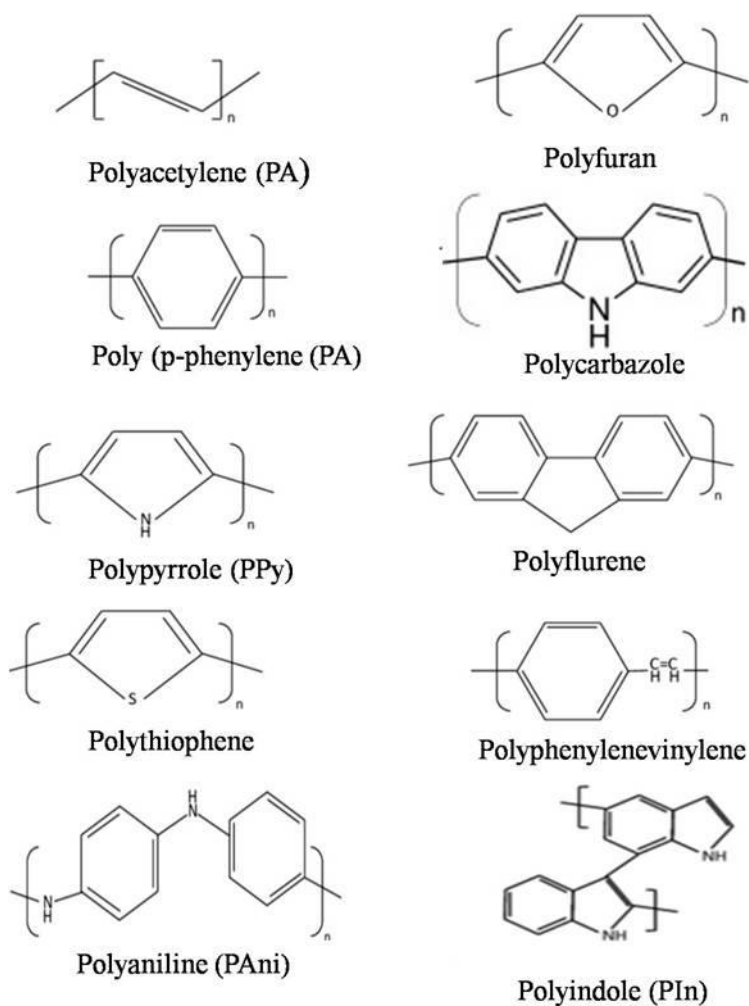


Figure 1.13 Monomer units of different CPs

1.4.1 Polyindole (PIn) and polyaniline (PAni)

Polyindole (PIn) and polyaniline (PAni) has been considered as one of the versatile conducting polymers due to its low cost, high capacitance, and easy synthesis. All CPs have some merits and demerits. PIn containing benzene and pyrrole both components in the same matrix and giving unique properties. It possesses high thermal stability but due to hindrance, the long chain of polymers not formed. However, in the case of PAni, aniline is constructing units in which benzene rings having an amine

group. This has a good position to (less hindered para position) link and gives a long chain of the polymer. PANi gives various forms depending on its oxidation levels, known as pernigraniline base, emeraldine base, leucoemeraldine base which make some unpredictable results. Among them, the emeraldine base form has a solubility problem and makes it difficult to process PANi. However, PIn is not presenting such structures.

1.4.2 Synthesis methods of CPs

There are three major steps (as oxidation, coupling, and propagation) that occur during the polymerization and serve as key components for determining the properties of CPs (physical as well as chemical). There are various methods applied, such as chemical oxidation, electrochemical potential, inclusion, and microwave to trigger the oxidation step [Ghosh et al. (2016), Kumar et al. (1998), Marcasuzaa et al. (2011)]. Among them, the chemical polymerization is a very important, effective and simple way to surface modification. Therefore, our main focus is around chemical methodology as discussed in detail under the next headings.

1.4.2.1 Chemical methods

In chemical methods, the nature of oxidizing agents, solvents and the concentration of reagent is key points for the polymerization. This method can produce a bulk amount of polymers. PIn and PANi can be synthesized via chemical oxidative polymerization of their respective monomers. Various kinds of oxidizing agents like ammonium persulfate (APS), FeCl₃, H₂O₂, KMnO₄, HAuCl₄ and KIO₃ etc. have been reported in suitable solvents [Gupta et al. (2011), Joshi et al. (2011), Kumar et al. (2013), Tiwari

et al. (2015), Verma et al. (2020)]. Based on the solubility of oxidizing agents and monomer units into aqueous and non-aqueous solvents, two different routes of polymerization have been stabilized as *In-situ* interfacial and interfacial synthesis. Pictorial representation of *In-situ* interfacial and interfacial synthesis is shown in Figure 1.15.

1.4.2.1.1 In-situ interfacial synthesis

When the oxidizing agent dissolved in one solvent and the monomer units not soluble in the same and goes to another solvent, these methods are required. These solvents are completely immiscible to form an interface between two solvent [Kumar et al. (2013)]. Based on this, many reports are available in which the polymer obtained at the biphasic interface. The fibrous PIn has been synthesized under the same methods where an aqueous solution of FeCl₃ used as oxidant to polymerize indole monomer at interface of water/dichloromethane (DCM). Similarly, ammoniumpersulphate (APS) which are soluble in water was performed that resulted in nanoparticles of PIn.

1.4.2.1.2 In-situ interfacial synthesis

This method is applicable when both the oxidizing agents as well as monomer units are dissolved in the same solvent. If two or more solvent used, they should be mixed to get one phase (monophasic system). Microsphere structured PIn have prepared by digesting of monomer units in aqueous media under ethanol and then APS as well as H₂AuCl₄. This method is very effective and frequently used for surface modification, composites formation with other nanomaterials. Based on these various

nanocomposites of GO, rGO, CNT, MoS₂, WSe₂, ZnO, Co₃O₄, V₂O₅ are reported [Dubey et al. (2015), Choudhary et al. (2019), Verma et al. (2020)].

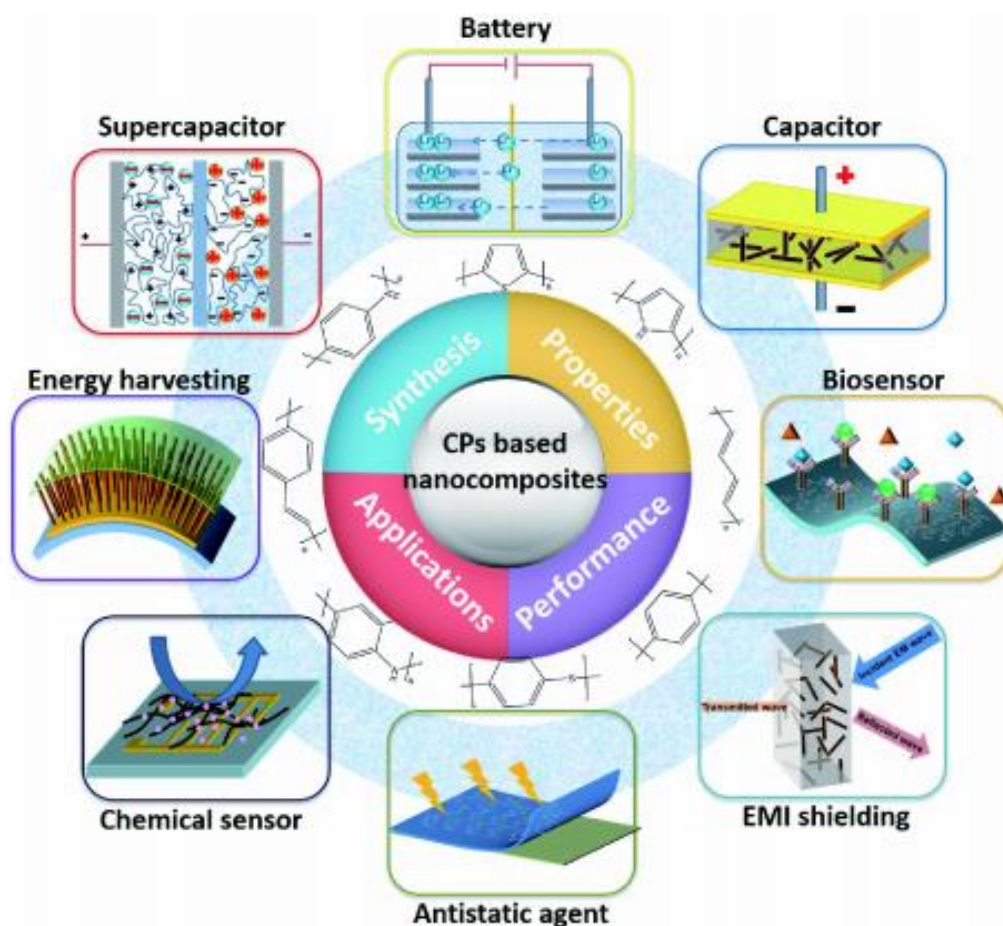


Figure 1.14 Applications of CPs [Zhang et al. (2018)]

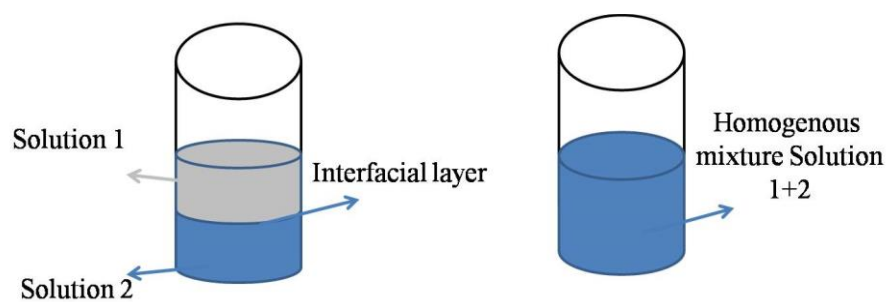


Figure 1.15 Pictorial representation of *In-situ* interfacial and interfacial process of CPs synthesis.

1.5 Applications

Since the carbon exists in various structures from macro to nano levels and showing lots of advanced features like high porous, eco-friendly, cost-effective and unique surface area as well as electro-activity. In this connection, the number of technological applications (mechanical, electrical and electrochemical) has reported based on nano-carbon either alone or in composites with MO_x, porphyrin, CPs as shown in figure 1.16. Energy is a very basic need for all human beings throughout the globe. For this, lots of state of arts like coal, fuel cell and batteries have used since long back. However, due to limited sources, poor performance and pollution, the finding of other alternatives efficient and clean energy storage systems are the prime concern. Supercapacitor is alternative mean, devoted to energy storage are the state of arts that can tender sufficient power densities and energy densities to inflated power entailing purposes.

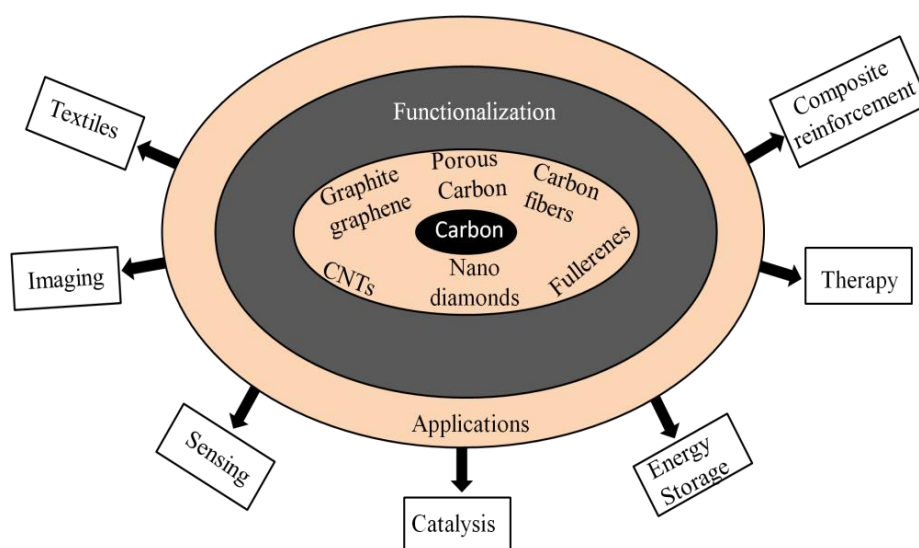


Figure 1.16 Pictorial representations of applications of carbon-based nanomaterials

1.5.1. Supercapacitors

For the sake of environmental protection and replacement of fossil fuels, in present days supercapacitors are considered more essential and convenient means for energy-related solutions. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, have significant attention because of their high energy and power density, elongated cycle life (>100000 cycles), and speedy charging-discharging rates [Muzaffar et al. (2019), Bi et al. (2019)]. With rapid growth in the renewable system, the development of portable electronic vehicles or hybrid electric vehicles (with low CO₂ emissions), foldable phones and wearable electronics, the supercapacitors and batteries are getting popular. Based on the fundamentals of their charge storage, supercapacitors have been classified into two class (1) electrochemical double-layer capacitors (EDLCs), and (2) pseudocapacitors (figure 11). In the case of EDLC, the charges are accumulated on the surfaces of electrode materials under electrostatic forces however in the latter case the charges stored on electrodes via the Faradaic redox mechanism (schematic diagram of charge storage mechanism Figure 1.17) [Bi et al. (2019)]. However, based on the charge accumulation or redox reactions at electrodes, supercapacitors are categorized further into three main classes viz. (1) EDLC (2) pseudocapacitor and (3) hybrid supercapacitor (HCs). For a more reliable understanding of supercapacitors types, working mechanism, a chart represented here as in figure 1.18. When combining these two, hybrid supercapacitors formed and possess higher energy densities as well as power densities than the normal EDLC and

pseudocapacitor. This favors hybrid supercapacitors, towards their use compared to other energy storing systems.

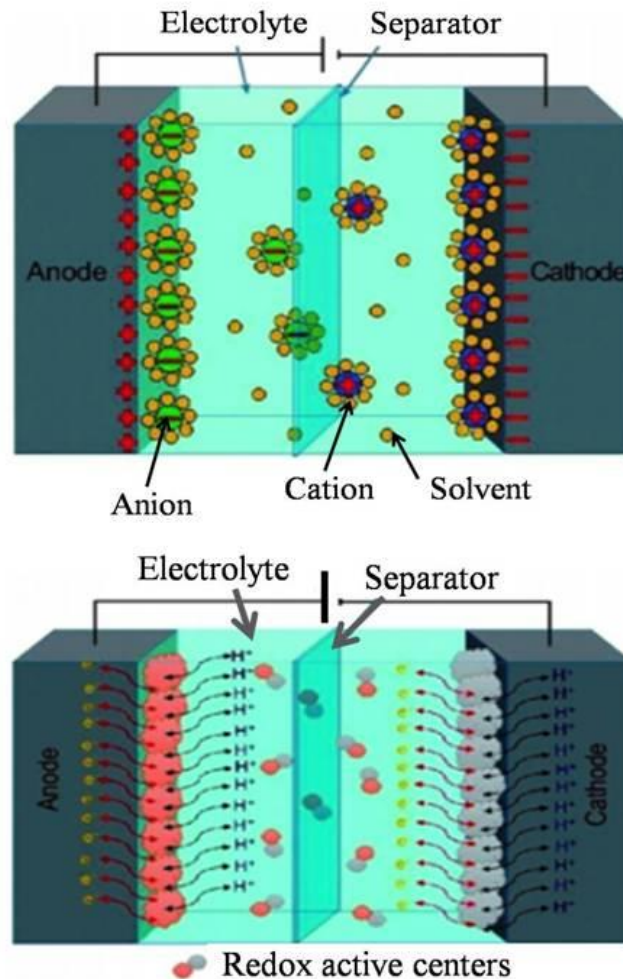


Figure 1.17 Schematic diagram of charge storage mechanism in an EDLC (at top) and pseudocapacitor (down) [Muzaffar et al. (2019)].

Further HCs are classified into three types: (1) Composite, (2) Asymmetric and (3) Battery-type. Among these, composite HCs became the main research hub of the scientific community nowadays to discover novel electrode material with enhanced

electrochemical properties (i.e. high gravimetric and volumetric capacitance) [Thakur et al. (2016), Moussa et al. (2016), Poonam et al. (2019), Nijib et al. (2019)].

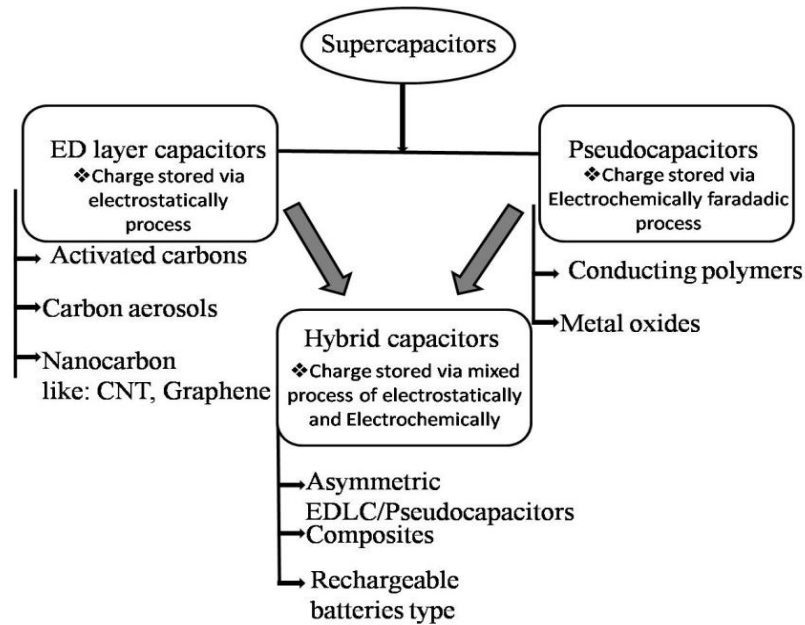


Figure 1.18 Categorical representation of types of supercapacitor

The importance of a supercapacitor can illustrate under the Ragone plot as shown in figure 1.19. Comparatively, supercapacitors possess reliable and tunable energy densities as well as power densities than the normal fuel cells, batteries and capacitor [Wang et al. (2019), Bi et al. (2019)].

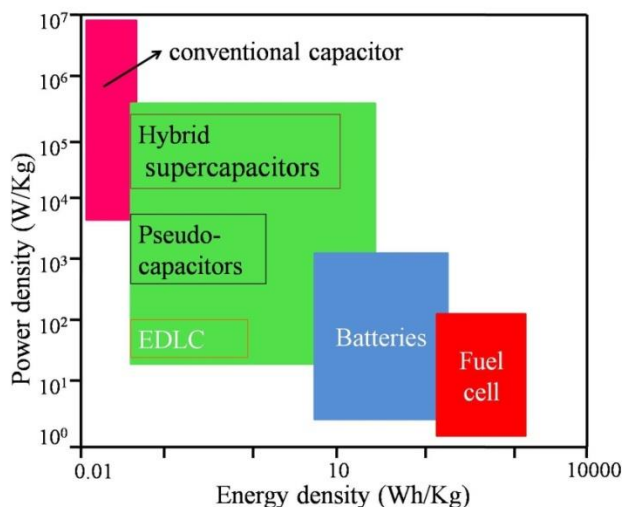


Figure 1.19 Ragone plot for various energy devices.

In this, the position of supercapacitors is very clear and important having balanced performance as compared to the batteries and fuel cells in terms of specific energy as well as the specific power in the Ragone plot [Muzaffar et al.(2019),Wang et al. (2019)].The efficiency of supercapacitors is influenced by the conductivity, surface area and overall resistance of the electrode material. Thus, it is important to improve the performance of g-C₃N₄, porous carbon-based materials for supercapacitors, which are still remaining.

1.6 Scope of the work objective of the thesis

There are various reports available on designing of electrode materials for supercapacitors including carbon-based nanomaterials, MO_x as well as CPs via various processes. After literature survey and above investigation, we find that carbon-based materials suffer some drawbacks when used in its pure form like poor conductivity, poor electroactivity, re-stacking as well as processability. There is still a need to find some new source of highly porous carbon, and their hybrids having better electrochemical properties. Porphyrin and its metallated counterparts are also reported

as electro-active materials. However, for its CPs functionalization, a few reports are available among which most of them are multistep reactions. First, metal is inserted in the porphyrin central cavity and then post functionalization has been applied. Therefore, there is a need to explore more functionalizations with different CPs and facile methods of metal insertion in the porphyrin center core for various technological applications. In this consequence of resolving such issues of carbon-based nanomaterials (as poor conductivity, re-stacking as well as processability) and functionalization of porphyrin under the facile in-situ step, following major objectives are proposed for polymers functionalized porphyrin and carbon materials for electrochemical applications:

1. Synthesis of carbon materials and metal-porphyrin
2. Carbon materials and metal-porphyrin functionalized with polymer
3. Characterization of above-synthesized materials for their electrochemical applications
4. Development of supercapacitors

1.7 Organization of the dissertation

The thesis dissertation is divided into seven chapters as follows based on the research which has been done during Ph.D. work that has either been published or are presently under review/revision.

Each chapter is organized as.

Chapter 1 gives an introduction about carbon materials, porphyrin conducting polymers and their hybrids with electrochemical applications including the importance of modification and their effect on electrochemistry, literature survey, research gap and motivation.

Chapter 2 deals with brief information about instrumentation which is used during research work.

Chapter 3 deals polyindole functionalized g-C₃N₄ surface which includes the synthesis of g-C₃N₄ and Polyindole also and as-synthesized materials are characterized using XRD, UV-vis, FTIR, Raman, SEM, and TEM. This hybrid used as electrode material for supercapacitor.

Chapter 4 describe the preparation of an electro-active, high porous carbon from bio-waste (*Eichhorniacrassipes*) and as-synthesized materials are characterized using XRD, FTIR, TGA, BET, and SEM. This hybrid used as electrode material for supercapacitor.

Chapter 5 deals with polyaniline applies to functionalized carbon surface as obtained from bio-waste surface which includes the synthesis of Polyaniline and as-synthesized materials are characterized using XRD, FTIR, XPS, BET, TGA, SEM, and TEM. This hybrid used as electrode material for supercapacitor.

Chapter 6 deals Polyindole functionalization with Fe inserted-octaethylporphyrin which gives a new and facile strategy to Fe insert in OEP central core surface which includes the synthesis of Polyindole, and as-synthesized materials are characterized using UV-vis, FTIR, NMR, XRD, XPS, SEM and AFM. This hybrid used as electrode material for supercapacitor.

Chapter 7 includes the conclusion of the thesis work and some future plane.