CHAPTER 1

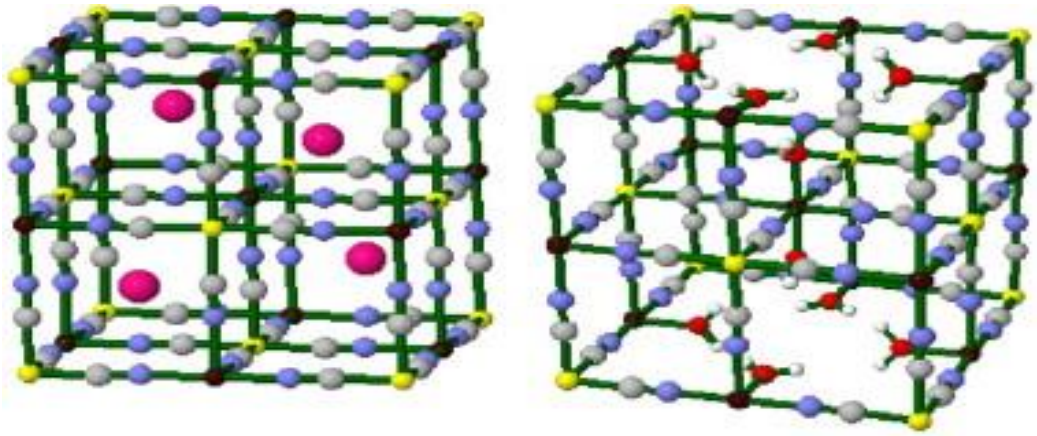
GENERAL INTRODUCTION

1.1. INTRODUCTION

According to various studies materials in their nanoscale exhibit distinct chemical and physical properties in comparison to their bulk structure. Nanoscale materials can be created by people in addition to occurring naturally (Thanh et al., 2014; Vollath and KGaA., 2008; Mauter et al., 2008; Häkkinen et al., 2003; Roco et al., 1999; Vaseashta et al., 2005; Jeevanandam et al., 2018). The scientific community has paid substantial attention to nanoparticles made of various metals. Due to their enormous surface to volume ratio, size of these nanoparticles intrigues physical, chemical, and surface electrical properties (Astruc et al., 2005). Meanwhile, because of their size-dependent optical, catalytic, and physicochemical features, the use of various metal nanoparticles (Ag, Au, Pd, Pt, and Ru) has drawn a lot of attention (Haruta et al., 1989; Hutchings and Haruta, 2005; Qu et al., 2018; Shan et al., 2012; Tang and Cheng, 2015; Wang et al., 2011b; Zhao et al., 2017). Controlling the size, shape, and chemical environment of these nanomaterials makes it simple to tailor their properties (solvent, ligand).

These materials were only utilised as colorants in several old industries. The transition metal hexacyanoferrates are an important class of useful amalgam that include the blue pigment "Prussian blue" (PB). Berlin painter Heinrich Diesbach accidentally discovered PB in 1704 while attempting to make red paint by using cochineal insects (Ware, 2008). Before the inquiry started looking into its chemical constitution and properties in the late 1930s, this synthetic coordination molecule was merely thought of as a dye. Prussian blue-type metal complexes, also known as metal hexacyanoferrates (MHCFs), have received extensive investigation and interest due to their important features, which include electrochemical (Karyakin, 2021; Karyakin et al., 2000), magnetic (Arun et al., 2013; Rogez et al., 2000; Ruiz et al., 2005), electrochromic (Ellis et al.,

1981; Varshney et al., 2003), photophysical (Pyrasch and Tieke, 2001), and electrocatalytic capabilities (Gotoh et al., 2007; Itaya et al., 1984; Kawamoto et al., U.S. Patent 20110268963 A1, November 3, 2011; Mažeikienė et al., 2011; Pandey, Indian Patent 64/DEL/2012, Jan 06, 2012; Zeng et al., 2008; Zhao et al., 2005). It is the most straightforward example of the two-metal center metal hexacyanoferrates (MHCFS). This MHCFS, an inorganic substance, has a diverse variety of qualities and capabilities and has drawn a lot of interest from scientists. As a result, various synthetic techniques have been investigated to produce MHCFs with improved properties for a variety of real-world uses. In addition, PB is highly fascinating due to its two distinctive features.



(A) **(B)**

Figure. 1.1. Soluble (left) (A) and insoluble (right) (B) structures of Prussian Blue, Fe(II)=yellow, Fe(III) = red violet, K = magenta, C = grey, N = blue, and H_2O = red (Shokouhimehr et al., 2010).

(1) its "zeolitic" effects as a result of the open crystal lattice and (ii) its strong blue color as a result of the charge transfer transition between the mixed valence iron metals (Ludi, 1981; Ludi and Güdel, 1973).

1.2 Geometry of Prussian Blue

Keggin and Miles were the first to analyze the crystal structure of PB, and they suggested, based on the powder diffraction pattern, that it consisted of a face-centered cubic (fcc) type of unit cell (Keggin and Miles, 1936). A further division into two types of PB has been made based on their structural variations. First, there is "soluble" PB; $A^{I}\ Fe^{III}[Fe^{II}(CN)_6].yH_2O$, where y=1-5 and A is a monovalent cation like K^+ or Na^+, and second, there is "insoluble" PB; $F_4{}^{III}[Fe^{II}(CN)_6]_3.xH_2O$ (Ludi and Güdel, 1973), where x=14–16. In order to keep the crystal electro-neutral, Keggin, and Miles assumed that the potassium ion accommodates the interstitial lattice location. In addition, Ludi and co-workers carefully examined the PB crystal, concluding from their electron and neutron diffraction study (Buser et al., 1972, 1977) that it includes about 14–15 molecules of water (Herren et al., 1980). The Fm3m space group is present in the crystal structure of PB, and it is designed in such a way that both iron centers are connected by the same CN ligand. Figure 1.1 shows the insoluble and soluble forms of PB, which are two separate structures (Shokouhimehr et al., 2010). Both the insoluble and soluble forms of PB have a low solvability ($Ksp=10^{-40}$) and are extremely indissoluble. While the insoluble PB has a quarter of the $[Fe^{II}(CN)^{4-}]$ unit missing from the crystal lattice to make up for the charge and neutrality, the soluble PB readily peptizes as blue colloidal sol and forms a clear solution in water. In the case of insoluble PB, this structural difference results in certain unoccupied spots. Within its imperfect crystal, water molecules of two different types are introduced: (i) co-ordinative water molecules that fill the empty space in the crystal lattice and (ii) zeolitic water molecules that are located in the coordination sphere (Boxhoorn et al., 1985; Imanishi et al., 1999). The potential of PB's distinctive open zeolitic nature

as a "chemical sponge" for adsorbing small molecules like H_2O_2 and O_2 has been extensively investigated (Boxhoorn et al., 1985).

1.3 Color of Prussian Blue

The ferrous atoms in the PB crystal are linked directly to the carbon atoms, and the ferric atoms of the same CN group are used to attach the nitrogen atoms (Ludi and Güdel, 1973). The ferrous ion (Fe^{+2}) is surrounded by a low spin (S=0) configuration of carbon in an octahedral environment, whereas ferric (Fe^{+3}) is surrounded by a high spin (S=5/2) structure of nitrogen. Although the sixth electron is assumed to prefer largely in the t_2g of the carbon hole to avoid the inter-electronic repulsion as seen in Figure 1.2, the five electrons are present in the respective orbitals of nitrogen as well as the carbon hole. The blue color of this coordination complex is explained by the charge transfer from t_2g of the carbon hole to t_2g in the nitrogen hole, which required around 14300 cm^{-1} of energy for such an electronic transition (Robin, 1962). Compared to the electronic energy (10150 cm^{-1}) assigned to the transition from the t_2g of the carbon hole to e_g in nitrogen hole, this amount of energy (14300 cm^{-1}) is more likely to resemble the coordination complexes.

1.4 Properties of Prussian Blue

1.4.1 Electrochemical

V.D. Neff was the first to report on the PB film's electrochemical nature (Neff, 1978). The electrochemistry of PB film was comprehensively studied by Itaya and co-workers (Itaya et al., 1982a), who reported that each cyclic voltammogram had two redox couples versus Ag/AgCl.

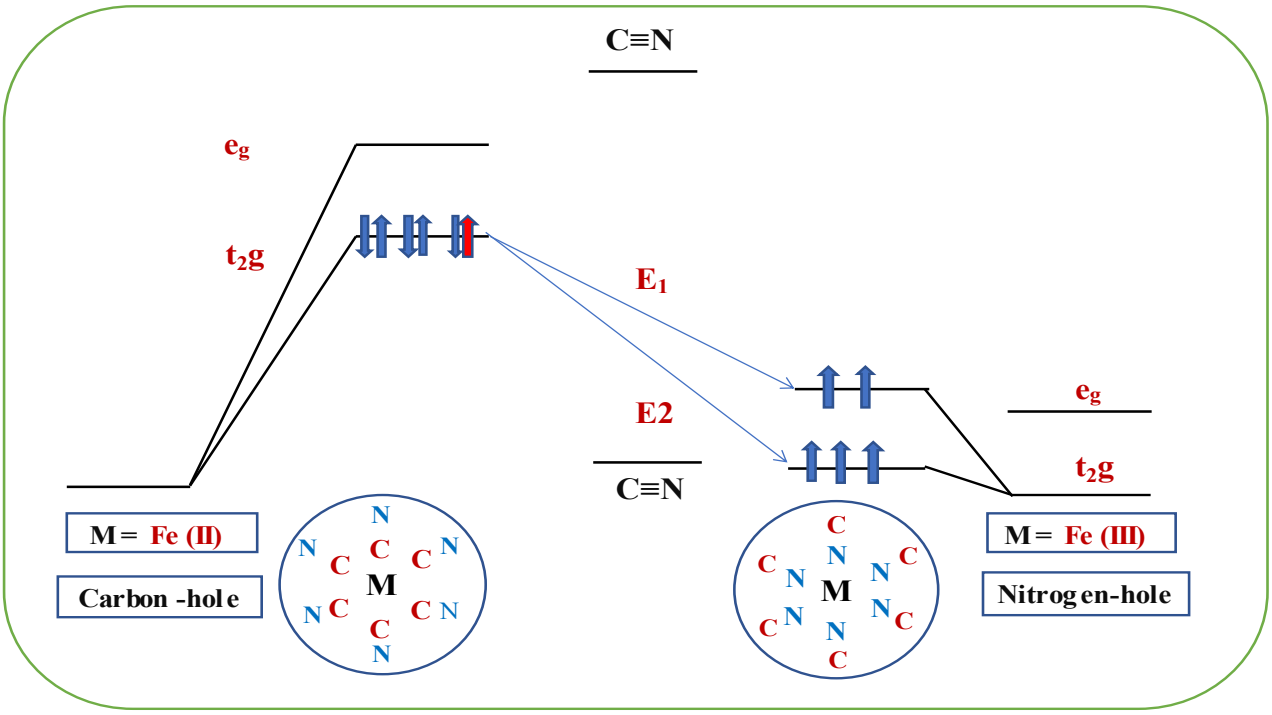


Figure 1.2. Electronic configuration of the valence electrons of Fe (II) and Fe(III) in the octahedral carbon and nitrogen hole environments, respectively.

The peak (I) associated with the redox reaction of PB to fully reduced Prussian white (PW) and vice versa was located at a lower positive potential (0.2 V). Peak (II) however, results from the reduction of PY (BG) species to PB and the oxidation of PB to fully oxidised Prussian yellow (PY) or Berlin green (BG). Due to the active involvement of the high spin system $Fe^{3+/2+}$, the response ascribed at lower positive potential (0.2 V) is plausible, however at higher positive potentials (0.9 V), low spin $[Fe(CN)_6^{3-/4-}]$ contributes and translates to the reversible redox process. The large-sized cation might easily permeate the film and aid in the PB oxidation/reduction process because it has a smaller hydrated radius, according to the Karyakin group's extensive investigation of the active contribution of supporting electrolytes (Karyakin, 2001). The reversible redox process

might be blocked by cations with greater hydrated radii after just a few cycles, which means that PB behaves best in the presence of K^+ and yet maintains its electrochemical reactivity. Similar to this, it was found that PB's electrochemical activity persisted even when additional cations including Rb^+, Cs^+, and NH_4^+ were present.

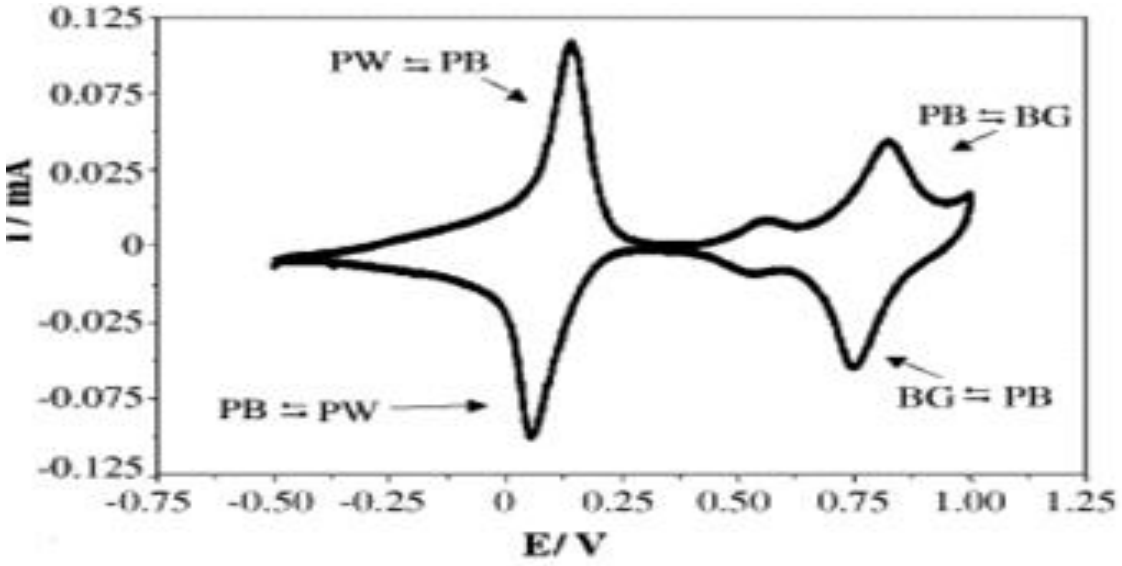


Figure 1.3. Cyclic voltammogram of a Prussian blue modified electrode showing oxidation and reduction peak (Ricci and Palleschi, 2005).

However, after just a few redox cycles, other metals like Na^+, Li^+, and H^+ frequently slow down the electrochemical activity of PB. The PB's redox property depends on the lattice channel radius and the selected cations hydrated ionic radii. Due to the PB lattice's suitable channel radius (approximately 1.6 Å), cations with lower hydrated radii like K^+ (1.25 Å), Rb^+ (1.28 Å), Cs^+ (1.19 Å), and NH^+ (1.25 Å) are easily accommodated (Ricci and Palleschi, 2005). It has also been thoroughly explored how mixed metal hexacyanoferrates of nickel, copper, manganese, chromium, gallium, indium, palladium, zinc, and silver behave electrochemically (de Tacconi et al., 2003; Düssel et al., 1996; Greene et al., 1961; Eftekhari et al., 2004).

Additionally, numerous research teams have investigated the rare-earth metals' electrochemical properties (Liu and Chen, 2002; Sheng et al., 2008; Wu and Cai. 2005). Due to a change in the charge transfer oscillation energy of the metallic center in the lattice, which causes a simultaneous change in color, PB and Prussian blue analogues (PBAs) were given the electrochromic property.

$$KFe^{III}[Fe^{II}(CN)_6] + e^- + K^+ \rightarrow K_2Fe^{II}[Fe^{II}(CN)_6]$$

Soluble "PB" Prussian White

$$KFe^{III}[Fe^{II}(CN)_6] \rightarrow Fe^{III}[Fe^{III}(CN)_6] + e^- + K^+$$

Soluble "PB" Prussian Yellow

Additionally, Ricci and Palleschi (2005) predicted that the redox process including insoluble PB would proceed as follows:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ \rightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3$$

Insoluble "PB" Prussian White

$$Fe^{III}[Fe^{II}(CN)_6]_3 + 3X^- \rightarrow Fe^{III}[Fe^{III}(CN)_6]_3X_3 + 3e^-$$

Insoluble "PB" Prussian Yellow

According to the results of the electrochemical analysis of PB; (i) both the insoluble and soluble forms of Prussian blue lose cations during the reduction process, and (ii) the soluble form loses cations during the oxidation process, while the insoluble form gains electrolyte anions. A flux of cations moves through the PB crystal's holes and channels during the oxidation/reduction process, maintaining the charge balance across the lattice.

1.4.2 Electrochromic

Any substance has the innate ability to change its color in reaction to a redox process or applied electrochemical potential. This ability is known as electrochromism. In 1978, Neff published the first report on the electrochromic behaviour of PB thin film. In order to create an electrochromic device in the latter half of 1982, Itaya first used PB as the only material (Itaya et al., 1982b). Therefore, electrochromic materials can be classified as reducing and oxidizing coloring agents, depending on how they transfer electrons. The PB can be oxidized into the pale-green PY, also known as BG, or it can be reduced into the colorless form known as PW. As a summary, it can be said that PB film displays electrochromic equilibrium between its colorless and colored states (blue), as well as quick response and high durability cycles ($5x10^6$). Due to the PB's reversible nature, these materials were identified as a prime possibility for the development of an electrochromic device (ECD), which results in a change in color in response to the usual oxidation and reduction process as follows:

$$Fe^{III}[Fe^{II}(CN)_6]^- + e^- \rightarrow Fe^{II}[Fe^{II}(CN)_6]^{2-}$$

Blue Colorless

$$Fe^{III}[Fe^{II}(CN)_6]^- \rightarrow Fe^{III}[Fe^{III}(CN)_6] + e^-$$

Blue Yellow

According to the metal composition of the PBAs, a particular structural arrangement and ease of metal substitution cause them to form, which is then used to create electrochemical devices (de

Tacconi et al., 2003; Karyakin et al., 2001). Table 1.1 summarizes the electrochromism behaviour in different MHCFs.

Table 1.1. Different MHCF's electrochromic behaviour.

MHCF'S	COLOR	
	Oxidized state	**Reduced state**
INHCF	Yellow	White
NIHCF	Yellow	Light grey
VHCF	Blue-green	Yellow
CUHCF	Yellow	Reddish brown
PDHCF	Orange	Green

1.4.3 Photo-physical

Materials based on PB and PBAs have drawn a lot of interest and have become an appealing materials for the creation of optical sensors and for the conversion of solar energy. Because the materials used in this photoelectrochemical reaction have a large molecular mass and a polynuclear mixed valent iron cyanide complex structure, these PB and PBAs modified electrodes have been used in the process (Munoz et al., 2012; Feng et al., 2021; Ghobadi et al., 2021).

As a result of the influence of irradiation in both on and off-working situations, it was discovered that photo-current created under applied preferred potential retained their stability and reversibility. According to research by Koncki, PB and related chemicals serve as hole transfer

agents during the electrochemical reaction caused by light irradiation (Koncki, 2002). Meanwhile, PB begins the photolysis of water molecules into hydrogen and oxygen in partnership with Ru(bpy) by transferring an excited electron from photo-active species (Ru(bpy)) to nanoparticles while using radiation (Zhao et al., 1998). Stepwise complex synthesis between the negatively charged (PB) and positively charged (Ru(bpy)) pendant co-polymer complexes has been used to elicit the static quenching of photoluminescent Ru(bpy) complexes by PB colloids (Zhao et al., 1998). In both the absence and presence of the I^-/l_2 redox system in the KCI solution, the photo-response of PB was studied (Upadhyay et al., 1991). The photo-current switching behaviour of PB-doped TiO2 nanocomposites was studied, and it was shown that it depended on the induced electrode potential (Szacilowski et. al., 2006).

1.4.4 Electromagnetic

Due to the following intriguing facts, PB and PBAs have been positioned as a very promising choices in the construction of molecular-based magnets: (i) They are simple to make at room temperature from $[M(CN_6)]^{n-}$ building blocks. (ii) Metal spin centers are typically organized into a 3D cubic network and covalently linked to the ligand. (iii) Formulates a wide range of structural motifs and proposes simple substitution with metallic carriers having various spin and oxidation states. Due to their extensive ferromagnetic structure, PB itself eventually maintained its magnetic properties at a low curie temperature (Tc = 5.6K). Through the bond distance of 10 Å, which results in weak exchange coupling between the metals, the PB was composed of CN-connected centers that were diamagnetic Fe (II) in low-spin d^6 F^{II} (in a strong field environment) and paramagnetic Fe (III) in high-spin configuration d^6 F^{III} (in weak field sites).

The magnetic susceptibility of PB was first reported by Davidson and Welo (Davidson and Welo, 2002). While Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} PBAs have paramagnetic metal centers with higher exchange coupling and shorter bond lengths (5Å) in the range of 3 to 50K curie temperatures (Tc) (Bozorth et al.,1956). Recently, Tokoro and Ohkoshi provided a potential summary of the magnetic functions of all PBAs (Tokoro and Ohkoshi, 2011).

1.4.5 Characteristics of Charging and Discharging

The mixed MHCFs have a zeolitic structure that makes it easier for alkali cations to intercalate and de-intercalate in the crystal during the electrochemical redox process. Additionally, a PB electrodeposited layer over ITO and SnO^2 achieved a high range of stability and reversibility in the order of 10^5–10^7 cycles and was recognized as a powerful material for battery development. In the meantime, V.D. Neff exploited PB as an anodic and cathodic substance in the genesis of secondary cells. As a result, additional MHCFs have also become an intriguing candidates for a similar development. PB and copper hexacyanoferrate (CuHCF) have been used in some methods to create secondary cells (Grabner and Kalwellis-Mohn, 1987). In order to achieve the solid-state secondary cell, significant progress has been made using the charging and discharging characteristics of solid-state PB, CuHCF-PB, and ZnHCF-PB (Jayalakshmi and Scholz, 2000 a, b). Ali Eftekhari also developed the solid-state secondary cell by combining two different transition metal hexacyanometallates as cathodic and anodic materials, as well as PB-based cathode and potassium as anodic material. In comparison to earlier findings, the disclosed secondary cell performs better in terms of elated voltage (1.5 V) and cyclability (more than 500) (Eftekhari, 2003, 2004). In order to achieve an outstanding product with an improved property, the charge transfer kinetics and cyclic stability were suggested as being crucial keys during the

optimization of PB and other MHCFs compounds. In light of this, Cui and colleagues suggested that PBAs such as copper hexacyanoferrate (CuHCF) and NiHCF nanoparticles might make strong candidates for large-scale battery appliances due to their low-cost synthesis route, long-range cyclability, stability, high-rate capability, and a higher degree of energy efficiency (Wessells et al., 2011a, b). It has been suggested to use MHCFs to successfully remove cesium and thallium from natural water (Sangvanich et al., 2010). PBNP was artificially incorporated into mesoporous silica (PBN@SiO_2), where it absorbed arsenic in the form of arsenite (As(III)) and arsenate (As(V)) (Pandey et al., 2021).

1.5 Prussian Blue and Its Analogs Modified Electrodes Application in Chemical Sensing

The electrochemical sensor is a crucial class in sensing technology since it deals with equipment that, because of its selectivity, can detect and quantify analytes at even lower concentrations. It has made major strides in this area. Electrochemical sensors are divided into three categories based on the transducer mode: conductometric, potentiometric, and amperometric. These categories deal with measuring the conductance, potential, and current of the cell, respectively. These sensors' numerous special features and functionalities have sparked a great deal of attention in the electrochemical community and have been utilized in device modification. The selective multifunctional MHCFs transform a chemically unproductive surface into a productive one to create chemically modified electrodes (CMEs) (Pournaghi-Azar and Dastangoo, 2002). These inorganic nanomaterials offer a broad range of practical applications due to their great chemical and electrochemical stability.

A variety of substrates, including glassy carbon (GC), gold (Au), platinum (Pt), and graphite paste (GP), have been widely used to prepare the chemically modified electrode of MHCFs. These MHCFs have demonstrated highly promising potential for use as electrocatalysts, energy storage materials, ion sieving materials, and sensing devices across a variety of fields. As a result, a lot of research has been done focused on how well MHCFs work for chemical sensing.

1.5.1 PB and PBA-Based Electrochemical Biosensors

A biosensor is a useful tool for keeping track of biological and living systems. The electron transport between the electrodes and the desired biomolecules is a key factor in how well these analytical devices work. Immobilizing living things on electrode surfaces is a crucial step in the creation of biosensors. Since H_2O_2 is a key and necessary byproduct of many biological activities, PB served as a redox mediator during the selective analyte detection method. As a result, much effort has been made to create PB-based biosensors, which offer alluring electrocatalysis. Karyakin was the first to show how MHCFs might be used to create biosensors by immobilizing glucose-oxidase on top of a material with the aid of a Nafion membrane (Karyakin et al., 1994, 1995). After that, numerous articles demonstrating the analytical success of PB-based biosensors towards glucose detection were published by numerous different groups (Ahmadalinezhad et al., 2009; Chen et al., 2012b; Fu et al., 2011; Jaffari and Pickup, 1996; Wang et al., 2011a; Cinti et al., 2018; Lin et al., 2015; Valiūnienė et al., 2017; Rekertaitė et al., 2019). Similar to this, MHCF-based biosensors have been created by immobilizing the appropriate enzyme to the selective layer of PB or its composites. These biosensors have been used to measure a variety of analytes, such as cholesterol (Li et al., 2003; Vidal et al., 2004), ethanol (Karyakin et al., 1996), glutamate (Wang et al., 2003), lactate (Salazar et al., 2012b), uric acid (Piermarini et al., 2013), and NADH (Gurban

et al., 2008; Radoi et al., 2007), that PB has an intriguing electrochromic feature based on its electron-transfer phenomenon, as stated earlier. As a result, an optical transducer that changes PB film absorbance (λ_{max} of 720 nm) in response to analyte (H_2O_2) concentration variation was created (Koncki and Wolfbeis, 1998a, b). The colorless PW was used to immobilize glucose-oxidase (GOx), which was then oxidized by in situ generated H_2O_2 to create the glucose biosensor (Koncki et al., 2001; Lenarczuk et al., 2001a, b). Such material was made possible to be used in pharmaceutical analysis thanks to its optical sensing capabilities.

1.5.2 An Electrochemical Sensor for Non-Electroactive Cations

The application of such nanomaterials as potentiometric and voltammetric sensors for size-dependent intercalation/deintercalation processes was further driven by the open zeolitic type of structure of PB and PBAs (Ho and Lin, 2001). Because PB has a 0.16 nm channel radius, it can pass ions with smaller hydrated radii, such as cesium, potassium, rubidium, and ammonium, which have radii of 0.119, 0.125, 0.128, and 0.125 nm, respectively. Therefore, structural analysis reveals that cations with greater hydrated radii are unable to intercalate through the crystal lattice of PB and PBAs. Scholz and colleagues have therefore created these materials as ion-selective electrodes. It was determined that the most promising MHCFs modified electrodes for K^+ (potassium ion) determination are those based on Fe (III), Ni (II), Cd (II), Cu (II), and Ag (I), while nickel (II) and cadmium (ID) based materials are well suited for radioactive species (Cs^+) determination (Düssel et al., 1996).

A lot of PB and PBAs have also been used to create sensors for K^+, Tl^+, and Cs^+ (Coon et al., 1998; Hartmann et al., 1991; Jain et al., 1982; Krishnan et al.,1990; Tani et al.,1998; Thomsen and

Baldwin, 1989; Zhiqiang et al., 1991; Estelrich et al., 2021; Mullaliu et al., 2019). The developed PB-supported ion-selective electrode was used to detect Tl^+ at concentrations as low as 2 x 10^{-8}M (Kahlert et al., 1996), which sparked attention in the pharmaceutical sector (Labianca, 1990; Ware, 2008). The Food and Drug Administration (FDA) has recognized PB as a safe and efficient medication for the treatment of metals that are contaminated, such as Tl^+ and Cs^+ and it also permits the trapping of radioactive material in the gastrointestinal system. For Na^+ ion analysis, PB sensor has been developed as nanotubes (Nguyen-Boisse et al., 2014). PB electrodes modified with CTAB (cetyltrimethylammonium bromide) were used for the transport analysis of distinctive species such as Cs^+ and K^+, Rb^+, and NH^+ ions (Vittal et al., 2008). Through selective inter-deintercalation of K^+ and comparative inhibition of Na^+, dual sensing of discriminating ions (K^+ and Na^+) was successfully attempted (Ang et al., 2011).

1.5.3 Electrochemical Sensor for Oxidizable Compounds

PB and PBAs are promising materials for the construction of electrochemical sensors. Numerous teams created electrochemical sensors based on nanocomposites and studied how they responded electro-catalytically to the cysteine molecule (Abbaspour and Ghaf-farinejad, 2008; Majidi et al., 2010; Qu et al., 2011; Sattarahmady and Heli, 2011). An electrochemical sensor has been constructed to reveal the synergistic influence of nano-dimension over the electrocatalytic performance of PB nanocomposites with gold nanoparticles (AuNP) and palladium nanoparticles (PdNP) (Pandey and Pandey, 2012c).

Similar to this, Chen et al. used PB and PBAs to measure cysteine and simultaneously developed a highly generic kinetic model for taking into account both the cysteine diffusion and the

electrocatalytic reaction (Chen et al., 2006). Reduced glutathione (GSH) electrochemical and electrocatalytic activity was investigated using a modified TiO_2 electrode made of CNFs-PDDA/PB nanocomposites (Muthirulan and Velmurugan, 2011). Additionally, a cobalt hexacyanoferrate (CoHCF) and copper hexacyanoferrate (CuHCF) modified electrode-based amperometry sensor has been created and used for glutathione (GSH) sensing (Ravi Shankaran and Sriman Narayanan, 2002). These redesigned electrodes enable the catalytic oxidation of glutathione (GSH) at extremely low overpotentials and over a wide pH range. Between the PB and the Al layer, palladium was introduced as a charge transfer bridge (Pournaghi-Azar and Ahour, 2008). Recently, the constructed NiHCF-AuNPs sensor demonstrated functionality towards GSH, and it was discovered that the size of the AuNPs had an impact on the sensor's catalytic activity (Pandey and Pandey, 2012a).

Even after successful modification over single-walled carbon nanotubes, Prussian blue nanoparticles (PBN) were found to preserve their electrocatalytic activity towards dopamine (DA) (Adekunle et al., 2012). To create electrochemical and chemical sensors for a variety of oxidizable electroactive substances, PB and PBAs have thus been extensively investigated (Karyakin, 2001; Koncki, 2002). Using CTAB (cetyltrimethylammonium bromide) functionalized SnHCF-modified graphite paste electrodes, the sensing of dopamine (DA) and ascorbic acid (AA) at the distinct oxidation peak potential has been successfully completed (Hosseinzadeh et al., 2009). A simple and regulated electrode adsorption approach was used to create the nanocomposite of PB-doped single-walled carbon nanotubes for nitrite sensing (Adekunle et al., 2011). Carbon nanospheres and graphene nanosheets were combined to create chitosan (CS) coated PBN, and Cui used the

low detection limit, quick response time, and high sensitivity of this technique to explain the high electrochemical activity of these modified nanomaterials (Cui et al., 2012).

Multiwalled carbon nanotubes that have been doped with PB exhibit excellent electrocatalytic activity for the oxidation of hydroxylamine and have a linear response that runs from 1.5 μM to 2.0 mM. (Zhang et al., 2010a). In order to fully implement hydrazine sensing, which has a high catalytic activity, many groups constructed MHCFs-based sensors (Gholivand and Azadbakht, 2011; Jiang et al., 2011; Kumar et al., 2011; Narayanan and Scholz, 1999; Yang et al., 2011). Recently, the Komkova group showed that Prussian Blue (PB)-modified boron-doped diamond (BDD) electrodes achieve the highest sensitivity to H_2O_2 (Komkova et al., 2020). Direct enzyme-free H_2O_2 sensing in a Parkinson's disease model has been accomplished using electrodeposited Prussian Blue on carbon black-modified disposable electrodes (Rojas et al., 2018). It has been established that a paper-based amperometric glucose biosensor with screen-printed electrodes modified with Prussian Blue is a sustainable, biocompatible immobilization matrix for glucose oxidase (GOx) (Sekar et al., 2014).

1.5.4 Advanced Transducer for Hydrogen Peroxide (H_2O_2)

H_2O_2 is a significant analyte that is widely employed in a variety of industries, including chemical, textile, food, and many others. It is also a by-product of numerous metabolic reactions that are catalyzed by enzymes. H_2O_2 can reduce as well as oxidize. But for such materials to break down via direct electrochemistry, a larger voltage is typically needed. To measure the electroactive materials, many electrochemical and biosensors have been developed during the past few decades (H_2O_2). Boyer made the initial attempt by using PB as an electrochemical mediator during H_2O_2

sensing (Boyer et al., 1990). While the Karyakin group was the first to introduce innovation in the selective detection of H_2O_2 at considerably lower applied voltage over the PB-modified electrode (Karyakin et al., 1994, 1995). They get to the conclusion that PB has multiples (>100) greater electrocatalytic activity towards H_2O_2 ($K = 5 \times 10^2 M^{-1}s^{-1}$) than O_2 moiety.

PB's unusual zeolitic structure allowed light-weight molecules to diffuse deeply into the material. They also assert that PB exhibits good selectivity and sensitivity (in the micromolar range) for the chosen analytes and enables H_2O_2 reduction at low potential (0.0 V vs. Ag/AgCl) (Karyakin et al., 1996). The interference from undesirable electrochemical species was minimized by the low working potential (0.0 V vs. Ag/AgCl). Additionally, under the same optimal conditions, the measured rate constant for the PB-assisted H_2O_2 catalytic reaction ($K = 3 \times 10^3 M^{-1}s^{-1}$) was higher than that for the naturally occurring peroxidase enzyme-assisted process ($K = 2 \times 10^4\ M^{-1}s^{-1}$) (Dunford and Hasinoff, 1970). Due to its strong activity and selectivity towards the water, PB refers to it as "artificial peroxidase" (Karyakin and Karyakina, 1999; Karyakin et al., 2000). As a result, numerous attempts to determine H_2O_2 using an electrode modified by PB have been made (Chi and Dong, 1995; Dostal et al., 1995; Moscone et al., 2001; Ricci and Palleschi, 2005). The electrochemistry of three electrodes configured with PB-modified screen-printed electrode shows the sensitivity towards H_2O_2, Cs, and As (Pandey et al., 2021).

The development of PB screen-printed electrodes as a transducer for H_2O_2 detection (de Mattos et al., 2003; Ricci et al., 2003). As a sensor for H_2O_2 analysis, PB and its nanocomposite have been widely used by several groups (Du et al., 2010; Gaitán et al., 2010; Haghighi et al., 2010; Komkova et al., 2013; Li et al., 2012; Mokrushina et al., 2013; Salazar et al., 2012a; Sitnikova et al., 2011). Our research team has recently completed a variety of tasks to create AuNPs-PB nanocomposites

for H_2O_2 sensing. When compared to individual PB, the electrode exhibits a noticeably increased sensitivity to the analyte (Pandey and Chauhan, 2012). Additionally, work has been expanded using changed electrodes, demonstrating the significance of palladium nano-dimension over PB's ability to electrocatalyst the oxidation of water (Pandey and Pandey, 2012b).

1.6 Contamination of Heavy Metals in Waste Water

In addition to inorganic pollutants, heavy metals are substantial water contaminants with a high degree of hazard and carcinogenicity, posing an increasing worry for ecological, evolutionary, nutritional, and environmental reasons. The term "heavy metals" refers to any metallic element with a density greater than 5 g cm-3 that is dangerous or poisonous even at low concentrations. These metallic species have negative consequences because they are non-biodegradable, resulting in their persistence, and their solubility in water, resulting in their accumulation in the food chain (Maksin et al., 2012). These metals have major health consequences, including stunted growth and development, decreased energy levels, organ damage (including the lungs, kidneys, and liver), altered blood composition, and impaired brain and central nerve functioning. Long-term metal exposure can cause a gradual deterioration of physical, muscular, and neurological degeneration, mimicking Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis, as well as many forms of malignancies and, in severe circumstances, death. Heavy metals disrupt general cell metabolism in living organisms by damaging the sulphur bonds, carboxylic acid, protein, and amino groups found inside the cell. The high concentrations of these metals in live organisms cause carcinogenic, mutagenic, and teratogenic consequences. When they accumulate in live tissues, they eventually disrupt microbial functions and have been shown to be lethal (Cimino and Caristi, 1990; Madoni et al., 1996; Carson et al., 1986; Oelme, 1979).

Heavy metals enter aquatic systems through both natural and manmade causes. Natural sources (rock outcroppings), agricultural sources (inorganic and organic fertilizers), atmospheric deposition (vehicle exhaust, tyres, gasoline/oil leakage, etc.), and industrial sources (electroplating and metallurgical activities, metal recycling, mining, etc.) are all potential sources of heavy metals in the environment. Industrial wastewater containing heavy metals is carefully controlled and must be treated before being dumped into water resources due to their high toxicity. To reduce human and environmental exposure to such dangerous compounds, stricter wastewater rules are being devised and enforced, particularly in industrialized countries.

1.7 Radioactive Materials in Waste Water

This category includes several radioactive fuel components, low-grade hazardous liquid wastes, liquid and gaseous fuel element wastes, fission products, and radionuclides such as cesium, cobalt, uranium, thorium, etc. As more nuclear power facilities are built across the globe, a significant amount of radioactive waste including wastewater is produced by a variety of activities. The use of radioisotopes in nuclear power plants and the operation of nuclear reactors produce radioactive effluent (Hailing Ma et al., 2023). In liquid nuclear waste, ^{90}Sr and ^{137}Cs are the two main radioactive elements and ^{137}Cs has a half-life of 30.17 years. Low-rate radioactive wastewaters include trace levels of ^{137}Cs together with significant concentrations of other ions that are radiologically inactive. It is highly soluble in aqueous solutions and is an alkaline element (Birol Işık et al., 2021). In addition, Cs has very high mobility due to exceptional dissolving qualities in aqueous media, leakage of Cs can have serious consequences for humans and the environment. As a result, the elimination of Cs has been considered as a major concern (Jimin Kim et al., 2020).

The nuclear industry has developed rapidly, resulting in the production of radioactive waste liquid. For instance, a sizable volume of radioactive material spilled and radioactive cesium (Cs) containing wastewater was released as a result of the Fukushima Daiichi nuclear power plant accident in Japan in 2011. Due to their radioactivity, these waste liquids have the potential to do enormous harm to both the environment and human health. The most prevalent radioactive in this type of waste liquid among them is ^{137}Cs, which produce continuous radioactivity and biological toxicity (Michael E. Kitto et al., 2015; Shanaz A. Ghandhi et al., 2015; Haixin Zhang et al., 2021).

1.8 Adsorption

Du Bois-Reymond came up with the term, although Kayser is the one who first used it in literature (Kayser, 1881). Adsorption is the aggregation of a substance at the surface or interface of any two phases, such as liquid-solid, liquid-liquid, gas-liquid, or gas-solid. The accumulating substance is known as adsorbate, while the adsorbing phase is known as adsorbent. Adsorption can be divided into two types based on the forces between the adsorbent material and the adsorbate species during the process.

1.8.1 Electrochemical Adsorption

Electrochemical adsorption takes place when an electrical potential is applied during the adsorption process. Adsorption components and electrochemistry are combined in the hybrid approach in a system that has two or more electrodes coupled to an external circuit. The formation of an interface double layer between the electrode and the solution is the fundamental idea of electrochemical adsorption. Increased rate and adsorption capacity are the goals of understanding static and dynamic electro-adsorption processes, which can be driven by a variety of interactions

between the adsorbent and the adsorbate, including dipole and electrostatic interactions (Li et al., 2016; Wang et al., 2018; da Costa et al., 2021). The electrochemical adsorption process eliminates the inferior solid phase from the waste water-based drilling fluid, allowing for recycling without the need for additional additives. It contributes to increasing the effectiveness of waste drilling fluid utilization and lowering the volume and cost of waste disposal that follows. The electrochemical adsorption to reduce and recycle waste drilling fluids avoids the possible environmental risks associated with typical solidification and landfilling techniques (Xie et al., 2018; Rana et al., 2004).

1.8.2 Physical Adsorption

Physical adsorption occurs when adsorbate species interact with adsorbents by physical forces (van der Waals forces, hydrogen bonds, etc.) (Scott et al., 1995). This is particularly typical when the adsorbed molecules do not adhere to specific places on the surface but are instead free to roam around inside the interface. At low temperatures, the adsorbate concentration increases, and the adsorption is distinguished by a low heat of adsorption on the order of 42 kJ mol^{-1} (~5-10 kcal mol^{-1}) (Edwards, 1994). Adsorbed layers with thicknesses of several adsorbate molecule diameters are generated under proper temperature and pressure conditions. When physical adsorption is involved, the material that is absorbed can be easily removed from the surface, and such adsorption is usually quick and reversible in nature.

1.8.3 Chemical Adsorption

Chemisorption occurs when adsorbate molecules form chemical bonds and are adsorbed at the active sites of the adsorbent. Adsorbate forces are usually small in comparison to adsorbate-

adsorbent binding forces in this form of adsorption, hence adsorbate placements or sites are decided by the optimum adsorbate-adsorbent bonding. The chemical reaction occurring on the surface might be exothermic or endothermic, and changes in temperature impact the amount of product generated. Higher temperatures are often preferred because chemical reactions occur more quickly at higher temperatures. Adsorption heat is typically wider than 83 kJ mol^{-1} (15-30 kcal mol^{-1}). Adsorption of this type is often irreversible and is associated with monolayer coverage. All adsorption processes, whether physical or chemical in nature, result in a decrease in free energy (Somorjai, 1994).

1.9 Challenges in Prussian Blue Synthesis and Its Analytical Chemistry

The traditional methods of PB synthesis, which include combining $[Fe(CN)_6]^{4-}$ directly with Fe^{3+}, have been extensively used by the scientific community and used in a variety of contexts.

However, such PB synthesis has the following drawbacks:

(i) The traditional process results in the formation of solid precipitate due to uncontrolled nucleation and inconsistent crystal growth.

(ii) The insolubility of the resulting PB in common solvents limits their practical applicability and limits the electro-deposition of the film in the various frames.

(iii) Functionality in PB also limits the applicability of such nanomaterials; additionally, the practicality of the same was evolved with bio-compatible ligands and demonstrating their selective binding affinity towards the biomolecules during the sensing process.

(iv) In terms of application, the stoichiometric ratio of two metals in 3D frameworks is critical for achieving materials with enhanced polycrystalline nature.

(v) Template and reversed micelles techniques are severely limited in their application.

Despite this, tried a few different synthetic approaches by using a variety of reagents in order to regulate the nanoparticle's size (Gotoh et al., 2007; Hu et al., 2012; Jia, 2011; Qian et al., 2013; Yamada et al., 2009; Zhai et al., 2008; Koshiyama et al., 2018; Zhao et al., 2019). The synthesis of Prussian blue from a single precursor $K_3[Fe(CN)_6]$ has already been shown to be dependent as a function of reducing agent for the conversion of FeIII to FeII (Jia and Sun, 2007; Yang et al, 1998) accordingly we attempted to make the PBNP using three different reducing agent (PEI, THF-H_2O_2 and EETMS) in order to understand its impact on the sensing and removal of Cs radionuclides (Prem Pandey et al., 2020; P.C. Pandey et al., 2016b; P.C. Pandey et al., 2021). One of the challenges encountered during nanoparticle production was regulating particle size, but other issues included enhancing the processability, stability, and crystallinity of materials. Hence, a new technique is required for the creation of PB-based devices, one that not only regulates particle size but also permits the stable nano-dispersion generation into different solvents. There are a number of obstacles that must be overcome in order to fully explore these materials' catalytic potential. They include: (a) determining whether or not this new approach to particle preparation can give stability while also regulating particle size. (b) Whether the size of materials in the nanoscale range can alter their catalytic performance. (c) Whether the inclusion of such nanomaterials into the heterogeneous matrix is possible using these techniques. (d) Whether or not the electrocatalytic activity of the changed materials is preserved with respect to the desired analytes. If nanoparticles have the potential for recycling that would allow for widespread use.

Taking a methodical approach to these problems is also essential. Since controlling the micro dimension of PB during synthesis is crucial for understanding their current catalytic application, it has been added to this work. These two factors have served as the primary focus of the present study.

1.10 Origin of Present Research Work

Our previous research has highlighted the importance of functionalized silanes in the development of an electrochemical sensor by showing their significance in the production of a thin film of organically modified silicate (ormosil). To modify the electrochemical behaviour of ormosil-encapsulated mediators, ion exchange and ion-recognition sites (Nafion, crown ether) have been introduced. The resulting ormosil-modified electrodes have dramatically enhanced sensitivity for the analytes while retaining the inherent feature of these organic moieties. Later, redox electrocatalysis was realized during electrochemical sensing after potassium ferricyanide was added to the ormosil film together with this organic moiety. In incorporating dibenzo-18crown-6 along with potassium ferricyanide into the ormosil film, the presence of tetrahydrofuran/cyclohexanone as a solvent in the ormosil precursors i.e; 3aminopropyltrimethoxysilane (3-APTMS) and 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane), exceptional discoveries of the single precursor conversion into Prussian blue was realized (Pandey and Upadhyay 2005; Pandey et al. 2004). These results prompted an in-depth study of the controlled synthesis of PBNPs and their mixed metal counterparts nanoparticles from a single precursor $K_3[Fe(CN)_6]$ using cyclohexanone and 3-APTMS (Pandey and Pandey 2013a, b, c). The electrochemistry of the as-prepared PBNPs was outstanding, with an electronic transfer rate constant on the order of 32.1 s^{-1} (Pandey and Pandey 2013c). A regulated synthesis of mixed metal

hexacyanoferrates was also made possible by a method similar to this one (Pandey and Pandey 2013a, b). The use of 3-APTMS, which experienced hydrolysis, condensation, and polycondensation and affected the characteristics of PBNPs for many practical applications, is the only drawback of the technique. Recent research has shown that EETMS was an essential component in the synthesis of stable PdNP and subsequently served as a model for the formation of bimetallic and multimetallic analogues (Pandey and Shukla, 2016a). This discovery prompted us to investigate the function of unexposed EETMS during the process of producing PB nanoparticles. In a stroke of good fortune, our team was able to successfully substitute 3-APTMS and cyclohexanone with tetrahydrofuran-hydroperoxide (THF-HPO), which enabled the effective conversion of potassium ferricyanide into water-soluble and stable PBNPs in the oven at a specific temperature. Tetrahydrofuran (THF) and hydrogen peroxide (H_2O_2) are two chemicals that could be used to create PBNPs, but their commercial availability is poor and they are required in order to make THF-HPO. This led us to learn more about their potential roles in this process. Also, one of the main focuses of the current research programme is the selection of various organic reducing agents like polyethylenimine (PEI), THF-H_2O_2, and EETMS which facilitates the crystalline behaviour of PB.

1.11 Objectives

The premise of this thesis is the synthesis and characterization of PBNPs and their use as a catalyst for sensing and removal of hazardous material.

Accordingly, the following are objectives for present investigation:

(i) Synthesis of PBNPs through polyethylenimine (PEI) with single precursor potassium ferricyanide to enhance biocompatibility and stability.

(ii) Synthesis of PBNPs using tetrahydrofuran and hydrogen peroxide with single precursor potassium ferricyanide that enables the functionality, solubility, and nanogeometry.

(iii) Synthesis of PBNPs using single precursor $K_3[Fe(CN)_6]$ (potassium ferricyanide) with EETMS and cyclohexanone under the ambient reaction condition to facilitate the controlled nucleation.

(iv) Optimization of functional alkoxysilane EETMS, during nanoparticle synthesis to achieve stable and uniformly dispersed nanoparticles for enhanced application.

(v) The development of PBNP as a catalyst should be tested to determine its potential for heterogeneous catalysis in a variety of forms, including homogeneous colloidal suspension, heterogeneous matrix following construction over a solid substrate such as silica (SiO_2), and modified nanosuspension graphite.

(vi) Characterization of the above synthesized nanomaterials; homogenous as well as heterogenous nanomaterials by using suitable techniques.

(vii) Application of these synthesized PBNPs; homogenous (colloidal suspension of PBNP) as well as heterogenous(insoluble Prussian blue or immobilized PBNP in a

heterogenous matrix like MSN) in the development of electrochemical sensors for the analysis of hazardous material like arsenic, cesium, and catalytic activity of hydrogen peroxide, and cesium removal through various methods, investigation of catalytic activity against cesium.

(viii) As-synthesized PBNPs utilized for fluorometric sensing and magnetic movement based sensing of cesium ions.

1.12 Work Plan

(i) Polyethylenimine and HCl mediated synthesis of nanocrystalline PBNPs by the active involvement of single precursor $K_3[Fe(CN)_6]$.

(ii) Synthesis of PBNPs using organic moiety tetrahydrofuran (THF), hydrogen peroxide (H_2O_2), and potassium ferricyanide as the only organic precursor.

(iii) To synthesize the PBNPs through EETMS and cyclohexanone from single precursor potassium ferricyanide.

(iv) Optimization of all the reactants, including the metal precursor, is required to achieve a stable nano-dispersion.

(v) To investigate how the nanoscale affects the electrochemical behaviour of PBNPs.

(vi) Synthesis of heterogenous PBNPs through THF, H_2O_2 with single precursor $K_3[Fe(CN)_6]$ over solid support like silica (SiO_2) for the analysis of hazardous material.

(vii) Application of these PBNPs in the sensing of cesium, arsenic, and H_2O_2 through the development of an electrochemical sensor for the analysis of cesium, arsenic, and H_2O_2 sensing by using cyclic voltammogram, differential pulse voltammetry,

electrochemical impedance spectroscopy, fluorometric sensing, magnetic movement based sensing and removal of cesium.

(viii) To examine the catalytic ability of PBNPs during sensing and study of its mechanistic approach.

(ix) Characterization of synthesized homogeneous and heterogeneous nanomaterials using appropriate techniques namely, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), UV-visible Spectroscopy, X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA).