

Synthesis, Characterization and Applications of Nano-structured Metal Hexacyanoferrates: A Review

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Abstract

The present paper offers a review of recent work on synthesis, in situ characterization, and applications of few metal hexacyanoferrate nanoparticles with the general formula $M_4[Fe(CN)_6]_x \cdot xH_2O$ where M is transition metal. Five such metal hexacyanoferrates (MHCF's) compounds derived from Co, Zn, Fe, Cu and Ni with general introduction followed by synthesis, properties and applications of individual hexacyanoferrate nanoparticles have been featured in this article. In addition, the characterization of aforesaid nanoparticles using instrumental techniques like SEM, TEM and XRD have also been discussed.

Keywords: Transition metal hexacyanoferrates; Nanoparticles; Characterization techniques

Introduction

Nanoparticles, offer more advantages because off their high surface to volume ratio as compared to bulk materials [1]. Prussian blue analogues (PBAs) with general formula $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ and Transition metal hexacyanoferrates with the general formula $M_4[Fe(CN)_6]_x \cdot xH_2O$ are promising nanomaterials used in different applications such as biosensing, nanomagnetic, electrochromic and biomedical.

Transition metal hexacyanoferrates represent an important class of extremely stable coordination compounds [2-4]. Among the hexacyanoferrates, transition metals, hexacyanoferrate nanoparticles of zinc, cobalt, chromium, iron, nickel and copper have drawn significant attention of scientific fraternity due to their peculiar solid state chemistry and structural attributes including chemical, electrochemical, electrochromical, electrocatalytical, ion-sensing, photomagnetic and ion exchanging properties [5-9].

In addition, hexacyanoferrates exhibit both ionic conductivity as well as redox properties which makes them relevant in nanoscience [10-12].

The attention of many scientists worldwide [13] has been focused on the unique properties of hexacyanometallates (HCM) such as the possibility of forming solid films, simplicity of manipulation of structures, occurrence of multi-redox centres etc. The combination of more than one HCM, leads to important compounds which has been found to have applications in various fields like sensor fabrication [14] display technologies [15] solid state batteries [16] chemical precipitation of radioactive caesium from waste solutions [17] and hydrogen storage [18].

Most of the transition metal hexacyanoferrates have a zeolitic structure which permits the diffusion of ions inwards and outwards for maintenance of charge neutrality. Because of this virtue, hexacyanoferrate nanoparticles do not undergo dissolution upon oxidation or reduction, thereby, making these compounds very useful for diverse applications. It is possible to characterize these insoluble transition metal hexacyanoferrates with the help of voltammetry method [19] in which the compounds are mechanically immobilized on the surface of a suitable electrode. During the redox reactions, Cations which are smaller in size than the pore size of the zeolitic structure of the transition metal hexacyanoferrates, can freely diffuse in and out of the lattice structure. This has become the basis for the determination of cations using ion sensitive electrodes. Deakin *et al.*, and Thomson *et*

al., reported that electrodes coated with Prussian blue [20] and copper hexacyanoferrate [21] respectively, can be used for the detection of simple cations in solutions. Thomson *et al.*, also used nickel and copper hexacyanoferrates for the detection of nonelectroactive cations in flow systems [22]. Thallium can be determined by inserting thallium ions into the Prussian blue structure during the redox. This method was developed by Kahlert *et al.*, in 1996 [23].

Prussian blue is an inorganic polycrystalline substance which has various potential analytical applications and has been investigated extensively due to its photophysical, electrochemical, magnetic and electrochromic properties [24-26].

The reversible redox behavior of the transition metal hexacyanoferrates has also been used for developing chemically modified electrodes (CMEs) for analytical applications. These CMEs provide enhanced performance in the determination of many compounds of biological and environmental importance. These electrodes have the ability to catalyze either the oxidation or reduction of species which require a higher potential at the unmodified electrodes and the main role of the mediators incorporated into the electrode surface is to reduce the overpotential required to bring about the desired reaction of the solute species. The application of CMEs has greatly improved the capabilities of electrochemical detection particularly in liquid chromatography, because of their selectivity for the substrate and higher sensitivity [27] among the various compounds used for electrode modification, the hexacyanoferrates of transition metals are of interest. The first attempt to make use of Prussian blue for preparing a CME was made by Neff [12]. Thereafter electrodes modified with various hexacyanoferrates have been reported by other workers. Methods for the determination of sulfhydryl compounds using Prussian blue [28] and copper hexacyanoferrate [29] modified electrodes have also been carried out. The electrocatalytic oxidation of

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hydrazine is possible with the help of Prussian blue [30] and cobalt hexacyanoferrate [31] modified electrodes.

Transition metal hexacyanoferrates are capable of catalyzing the reduction of hydrogen peroxide, which is generated by redox enzymes. Due to this unique property, they are widely used in the construction of amperometric biosensors [33]. Karyakin et al. in 1994 reported for the first time selective detection of H_2O_2 by its reduction on Prussian blue (PB) modified electrodes [112]. Reduction of H_2O_2 is facilitated by the use of transition metal hexacyanoferrates because they decrease the kinetic barrier leading to lower operation potentials.

By using microemulsion method, synthesis of MHCFs with controlled size has been developed by Ding et al., 2009. They synthesized nanocubes (NCs) nanoparticles (NPs) nanorods, nanobelts and other nanocrystals by using microemulsion technique [34]. PB and other MHCF nanoparticles can be synthesized using biocompatible polymeric molecules and a bio molecular matrix, such as poly vinylpyrrolidone (PVP) [35], poly(diallyldimethyl-ammonium chloride) (PDDA) [36], Apoferritin [37], soluble starch [38] and chitosan [39]. By applying external fields to the reaction mixture like sonochemistry [40], electrochemistry [42] and photosynthesis [41], controllable synthesis of MHCF can be achieved. To achieve a controlled size of the synthesized MHCF nanoparticles is very important since all the properties of nanoparticles are size dependent. A narrow size distribution offers best properties. Methods must be developed which offers protection against aggregation as well as wide range of chemical compositions. Besides these issues, the biggest problem related to PB and its analogues is their insolubility common solvents. Due to this problem, their use in various applications was restricted and remained limited to the electrodeposited films in many cases. To overcome this problem, Sol-gel method is used which offers a simple and versatile route for the synthesis of PB and its analogues [45]. Nanodispersion can be formed which is liable for the development of new PB-based devices that can be designed with fine patterns [44].

On the contrary, only few research papers report on the direct synthesis of MHCF nanoparticles without any templating or added substances [46]. Berrettoni et al., 2010 synthesized CoHCF nanoparticles directly in solution form without any added surfactant [47].

Basic Chemistry of Metal Hexacyanoferrate Nanoparticles (MHCFs):

Keggin and Miles in 1936 discussed the structure of PB for the first time on the basis of powder diffraction patterns [48]. The authors even distinguished between the two forms of PB i.e. soluble ($KFeFe(CN)_6$) and insoluble ($Fe_4[Fe(CN)_6]_3$). The dye makers invented this term 'soluble' and it refers to the ease with which the potassium salt can be peptized. The soluble form was assumed to be formed in the presence of excess of potassium ions. Soluble form has a basic cubic structure in which iron (II) and iron (III) are located in a face centred cubic lattice. The atoms are arranged in such a way that iron (III) atoms are surrounded octahedrally by nitrogen atoms whereas iron (II) atoms are surrounded by carbon atoms. The structure of insoluble PB was also proposed to be the same except for the fact that now excess of ferric ions replaced the potassium ions in the interstitial sites.

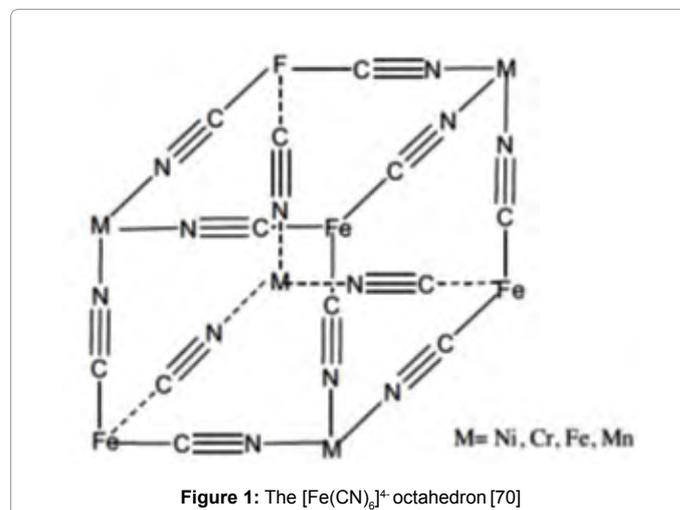
The structure of MHCF is similar to that of NaCl-type lattice in which cyano groups are cross-linked three-dimensionally and contain two different metal atoms or one metal atom in two

different oxidation states. Different transition metal atoms can be used as desirable for a particular application.

Metal hexacyanoferrates have a face-centered cubic lattice with unit cell length of 10.2 Å and with $N\equiv C$ and $C\equiv N$ ligands coordinating to the M and Fe ions respectively [49-51]. Prussian blue is a mixed valence iron (III) hexacyanoferrate (II) compound of general formula $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$, is considered to be the first synthetic coordination compound [52]. It has a face-centered cubic structure, in which Fe^{3+} is in the high-spin state and coordinated to the Nitrogen of cyano ligand whereas Fe^{2+} is in the low-spin state and coordinated to the Carbon of cyano group [53]. Although many efforts have been made on understanding the relationship between unit-cell structure [54] and various properties [55-57, 35], but a little progress have been made in controlling the growth process of Prussian blue [58, 7] and its analogues [60] with different sizes and morphologies. However, for fine-tuning the properties of the hexacyanoferrate nanoparticles, a control over both size and shape is very crucial. In recent years, cyanometallate-based coordination compounds have raised improved and emergent interest in many fields, for instance, molecular magnets [61-64], electrochemistry [65-67] and optics [68] due to their unique properties.

$[Fe(CN)_6]^{4-}$ ions are built of almost regular octahedral structure, with distorted metal ion in three dimensional coordination octahedral. Presence of little π -bonding in these hexacyanoferrate complexes is revealed by theoretical calculations [69]. The relative contributions of π - and σ -bonding can be determined qualitatively if the variation in bond lengths of complex ions of the type $[Fe(CN)_6]^{4-}$ can be expressed as a function of the central ion and its oxidation state. The structure of $[Fe(CN)_6]^{4-}$ octahedron is shown in Figure 1.

Most of the transition metal ions work as enzymes or carriers in the living system. Therefore, simple models for biologically occurring metallo enzymes might be generated that will be of wide use in developing and understanding biological systems. These ligands are also capable of furnishing an environment of controlled geometry and ligand field strength, hence even theoretically they are of great interest [71-75]. Also, synthesis of a large number of polydentate macrocyclic ligands and their metal complexes has been reported in literature [76]. Transition metals and their complexes play an important place in medicinal biochemistry. They are widely used as drugs for the treatment of numerous diseases like lymphomas, carcinomas infection control etc. This application has been well documented in literature. These complexes can even act as therapeutic and antimicrobial agents [77-83]. One of the unique properties of transition metals is their ability to exhibit variable oxidation states. Due to this unique property,



they can interact with a large number of negatively charged ligands. This property of transition metals has led to the development of metal based drugs with promising pharmacological applications. In order to provide an update on recent advances in the medicinal use of transition metals, a Medline search has been carried out to identify the recent relevant literature [84,85].

Transition metals such as zinc, copper, cobalt, manganese, iron have been reported to be essential for crops. They remain in soil in small quantity and known as micronutrient. If the deficiency of these elements is detected in soil these are recommended to be added to soil with fertilizer or in form of top dressing. It is well established fact that metal ferrocyanides act as adsorbent [86,87], ion-exchangers [88,89].

A new process for the synthesis of biocompatible mixed MHCF nanoparticles of controlled size has been reported in which variety of transition metal ions are incorporated. Prussian Blue have great catalytic efficiency to hydrogen peroxide (H_2O_2), but these polycrystalline mixed MHCF have even enhanced catalytic efficiency for H_2O_2 . The order: $FeHCF < Mn-FeHCF < Ni-FeHCF < Cu-FeHCF$ justifying as perfect peroxidase replacement with significant increase in catalytic efficiency as a function of respective hetero-transition metal ion of mixed FeHCF [90].

Few general properties extracted from various references are summarized in Table 1.

Synthesis of Metal Hexacyanoferrate Nanoparticles (MHCFs)

Among the various protocols used for preparation of MHCF, two approaches are usually followed, namely, double and single precursor methods. The former includes two ways. In one way, equimolar amounts $FeCl_2$ and $K_3[Fe(CN)_6]$ are mixed in the presence of a capping agent that provides chemical stability and helps in confining spatial arrangements. In another way, the reaction mixture is composed of a soft template and an equimolar amount of $FeCl_3$ and $K_3[Fe(CN)_6]$ [34]. The latter way employs potassium ferrocyanide as a single precursor. The slow dissociation of the $[Fe(CN)_6]^{4-}$ complex leads to the formation of the MHCF nanoparticles [91].

Synthesis, characterization and applications of Iron hexacyanoferrate Nanoparticles

Prussian blue is an inorganic polycrystalline substance possessing diverse applications and has been explored extensively because of

its photophysical, electrochemical, magnetic and electrochromic properties [92-94].

Prussian blue is known to be highly stable in acidic solutions. The high reversibility of two distinct redox reactions of PB involving the reduction of the high spin iron under formation of Prussian white (PW) and the oxidation of the low spin iron under formation of Berlin green (BG) are taken into account for the preparation of a PB battery with PB as both anode and cathode by V.D. Neff [12] for the first time. Prussian blue has been used even for the modification of various electrodes graphite electrode [93], edge plane pyrolytic graphite electrode [94] and glassy carbon electrode [95].

Different methods for the preparation of electrodes modified with PB have been described and large number of studies has also been carried out in this particular area [96]. The two forms of PB have similar structure, but possess different extents of peptization with potassium ions. Insoluble PB is produced by the replacement of potassium ions with ferric ions in a soluble PB form [97,98]. Carbon nanotubes were discovered by lijima in 1991 [99] and since their discovery CNTs have become one of the most attractive parts of nanotechnology across the globe research and research in this field have improved speedily [100,101]. These CNTs are known to possess unique physical and chemical properties such as mechanical and tensile strength, chemical stability, electrical conductivity etc. [102, 103]. Combination of PB and CNTs has drawn considerable attention of the researchers because these above mentioned unique properties can be tuned finely according to the specific purpose by chemical modifications [104]. Due to their high electric conductivity and the property of being particle carriers, CNTs are considered to be the good mediator for PB-modified electrodes [105,106].

Synthesis and characterization: Generally, Prussian blue Nanoparticles are synthesized by employing ultrasonication method.

In this technique, 0.05 M solution of $K_3[Fe(CN)_6]$ is added to 100 ml of hydrochloric acid solution of (0.1 mol/L). The resulting $K_4[Fe(CN)_6]$ aqueous solution is kept at 40 °C for 5 h under ultrasonic conditions and then allowed to cool at room temperature. The obtained blue product is filtered and washed repeatedly with distilled water and absolute ethanol and finally dried in a vacuum oven at 25 °C for 12 h [107].

Applications:

Detection of hydrogen peroxide: Hydrogen peroxide, H_2O_2 , can be detected at low potentials with the help of electrode modified

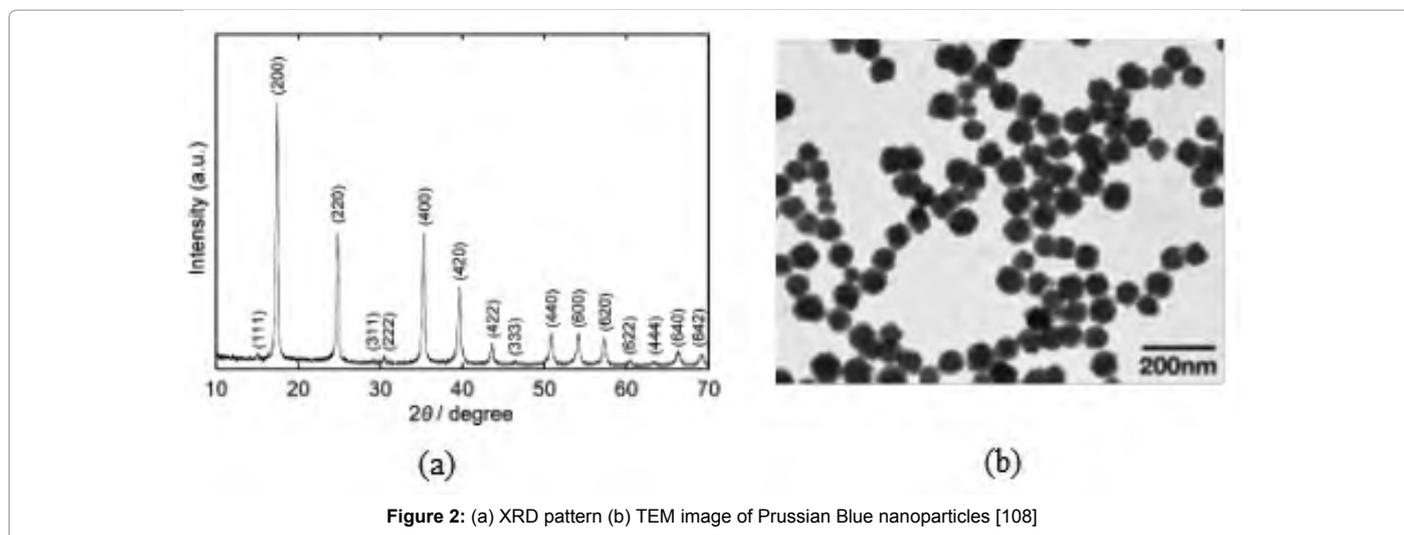


Figure 2: (a) XRD pattern (b) TEM image of Prussian Blue nanoparticles [108]

Metal Hexacyanoferrates	Properties	References
Iron hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Magnetic properties. Exhibit novel size-dependent properties which show different properties from their bulk form. Photo-induced spin transition. Redox behavior. 	<p>Sato <i>et al.</i> [143,156] Entleert <i>et al.</i> [120] Vaucheret <i>et al.</i> [58] Sato <i>et al.</i> [152], Neff [12]</p>
Copper hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Zeolitic properties. Electrocatalytic properties. Ion-exchange properties. Low toxicity and chemical stability in a large pH range. 	<p>Zil'bermanet <i>et al.</i> [131], Bennetet <i>et al.</i> [47] Guadagniniet <i>et al.</i> [133,134] Ayraultet <i>et al.</i> [95] Chen <i>et al.</i>[95]</p>
Cobalt hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Interesting chemical and electrochemical properties. Shows switching properties caused by the $\text{CoII(HS)} - \text{FeIII} \leftrightarrow \text{CoIII(LS)} - \text{FeII}$ Peculiar physicochemical properties: electrochromism, thermochromism, photochemical magnetism, and electrocatalytic and sensing properties. 	<p>Yamada <i>et al.</i> [5], Caiet <i>et al.</i>[6] Vaucheret <i>et al.</i> [7,153] Sato <i>et al.</i>[143] Sato <i>et al.</i> [143], Kulezaet <i>et al.</i> [144] Kulezaet <i>et al.</i> [145], Kuleza <i>et al.</i> [146] Yang <i>et al.</i> [148]</p>
Zinc hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Has a zeolitic structure which allows only certain ions to penetrate into and to pass out of the channels of ZnHCF ZnHCF stands out as a unique exception in that it cannot be deposited easily on surfaces like glassy carbon (GC), Pt and Au. ZnHCF is different from the other PB analogues, as it can be formed only in a certain ratio of the modification species. 	<p>Sharpe <i>et al.</i>[172] Joseph <i>et al.</i>[181] Eftekhariet <i>et al.</i>[177] Joseph <i>et al.</i>[181]</p>
Nickel hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> NiHCF films show well-defined and reproducible responses not only in supporting electrolytes containing hydrated K^+, but also other alkali metal cations such as hydrated Li^+, Na^+, Rb^+ or Cs^+. Has a cubic structure with a channel diameter of about 3.2\AA. Due to this reason, it is an effective ion-exchanger for Cs^+ ion. Water insolubility, mixed valency, high ionic conductivity, and excellent redox mediator properties. 	<p>Itayaet <i>et al.</i>[76,123] Jin <i>et al.</i> [66], Pyraschet <i>et al.</i>[66] Kulezaet <i>et al.</i>[144], Sinha <i>et al.</i>[10] Chen <i>et al.</i>[9], Balmasedaet <i>et al.</i>[162]</p>

Table 1: General properties of some nanosized metal hexacyanoferrates

with different electroactive materials. On the other hand, hydrogen peroxide, H_2O_2 , which is an important intermediary in many fields such as clinical diagnostic, food, industries, pharmaceutical, and environmental protection [109, 110]. It was discovered almost two decades ago and since then, ferric ferrocyanide has been successfully electrodeposited onto an electrode surface, and has also been reported to act as an electro-catalyst for the reduction of hydrogen peroxide [111].

Biosensors: Application of metal hexacyanoferrates for the development of biosensors was first reported by Karyakin *et al.* in 1994 [112]. The objective was to replace platinum as widely used hydrogen peroxide transducer for the Prussian Blue modified electrode. The enzyme glucose oxidase was immobilized on the top of the transducer in the polymer (Nafion) membrane. The resulting biosensor revealed advantageous characteristics of both sensitivity and selectivity in the presence of commonly tested reductants, such as ascorbate and paracetamol.

Another approach for development of Prussian Blue based biosensors was published in 1995 and involved enzyme immobilization by entrapment into Prussian Blue films during its deposition [113]. However, as mentioned, the best media for deposition of Prussian Blue is 0.1M HCl, which is intolerable for enzymes in general, and for the enzymes like glucose oxidase in particular [114]. Moreover, the entrapment of the enzyme in metal hexacyanoferrates during their deposition does not reveal adequate enzyme activity resulting in a rather low sensitivity of the resulting biosensor [115] compared to the sensitivity of the corresponding H_2O_2 transducer [116]. Except for a low-potential hydrogen peroxide transducer, Prussian Blue was integrated in biosensors as electrocatalyst for H_2O_2 oxidation [117, 118]. However, metal hexacyanoferrates are ideal electrocatalysts for oxidation of easily oxidizable compounds like ascorbate [119], which would definitely interfere in the biosensor response.

Sensitive label-free immunodetection of a cancer biomarker using Prussian Blue nanoparticles:

Espinoza-Castañeda *et al.* [120] used Prussian Blue nanoparticles as redox indicator for sensitive label free immunodetection of a cancer biomarker. For this purpose, a novel nano channel array device was presented by authors that operates with the use of PB nanoparticles. A well-defined and reproducible redox behavior was exhibited by stable and narrow-sized (around 4 nm) PB nanoparticles, protected by polyvinyl pyrrolidone. An increase in the steric hindrance is observed in case of bigger size of the PB nanoparticles compared with ionic indicators such as the $[\text{Fe}(\text{CN})_6]^{4-/3-}$ system, thereby, hindering their diffusion towards the signaling. This effective and novel PB nanoparticles-Nanochannel technology is successfully applied in a real clinical scenario such as cell culture medium. With the help of this technology, small proteins captured inside the nanochannels can be detected successfully and can also be applied for the quantification of a cancer biomarker (parathyroid hormone-related protein, PTHrP). Sensitive label-free detection of a cancer biomarker using PB nanoparticles is of great interest to study the relevant functions that this protein exerts in normal tissues and cancer.

Enhanced performance of microbial fuel cells: Performance of microbial fuel cells (MFCs) can be enhanced by electrochemical deposition of chitosan onto carbon felt followed by further modification with alginate. This has led to the formation of a biocompatible platform for the productive growth of microorganisms on the anode. The power density using Chitosin-alginate modified anode increased by 26.73%. Further, formation of Prussian blue film, on the electrochemically deposited chitosan layer, has helped in overcoming the disadvantages of using ferricyanide in the cathode compartment and also for improving the electron transfer characteristics of the film in phosphate buffer. It was found that the power density increased by 20.75% when both anode and cathode was modified as compared to the bare electrodes [121].

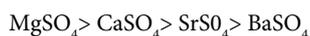
Synthesis, characterization and applications of Copper hexacyanoferrate nanoparticles

Among all PB analogues, copper hexacyanoferrate (CuHCF) possesses unique characteristics since it has the capability to present reversible redox reactions in various supporting electrolytes containing Li^+ , Na^+ , NH_4^+ , etc. [122]. This behavior is due to the zeolitic structure of CuHCF that allows the different ions to flux into its lattice. This process is necessary for the charge balance during redox reactions. In case of PB, diameters of its channels are very small, so this phenomenon is not possible and ions like Na^+ cannot move across its lattice [123]. In addition to that, CuHCF have increased stability in physiological pH solutions as compared to PB modified electrodes [124], thereby, leading to sensors with higher operational stability [125].

There is a large difference in the sorption amounts of the salts on copper hexacyanoferrates (II) and (III). In Ref. [126], it was found that these ions were retained with a decreasing affinity according to the order as:



This fact can be compared to the solubilities of the corresponding sulfates:



Water content: The study of the water content has received little attention and the reported quantity of water molecules varies over a large range: up to 20 [127]. The zeolitic properties of this class of compounds have been reported by Freise et al., [128]. Two kinds of water molecules could be present in: those linked to copper atoms, or those in the structural cavities [129].

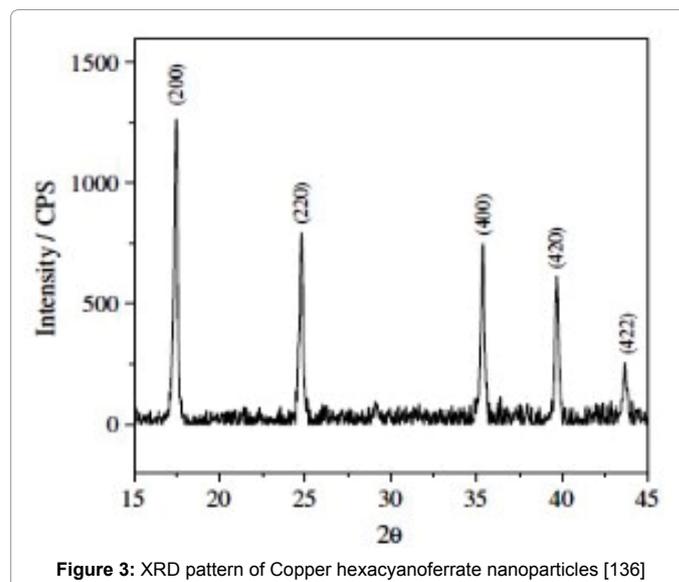
Crystalline Structure: For numerous authors of more recent studies [130,131], copper hexacyanoferrates present a cubic face-centered structure, with exchangeable cations (Cu^{2+} , K^+ , Na^+) weakly bound to the other atoms and zeolitic water molecules. However, 33% of the Fe corner sites were found vacant in a mixed sodium copper hexacyanoferrate [132].

The copper analogous CuHCF, has been successfully used for its electrocatalytic properties, demonstrating good capabilities in the determination of the hydrogen peroxide [133]. Recently, the insertion of Cu^{2+} ions into previously deposited CuHCF films on graphite substrate has been reported which leads to a Cu^{2+} loaded CuHCF displaying increased response sensitivity, with respect to the pristine electrode [134]. A structural study of several electrodeposited CuHCF based mainly on X-ray absorption technique [135] has clarified the key role of the subsequent Cu^{2+} insertion step. In particular it has been observed that it is not possible to obtain a pure electro-synthesized CuHCF by one step because the film deposition is accompanied by a second component, the Prussian Blue (PB) and that a successive second step consisting of Cu^{2+} ions intercalation enhances the amount of the pure CuHCF phase.

Synthesis and Characterization: The CuHCF NPs were synthesized as per the following equation:



CuHCF nanoparticles are synthesized by the method developed by Bioni *et al.*, 2007 [1]. The mixture of 10 mL of 20 mmol L^{-1} $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Shynth) + 0.1 mol L^{-1} KCl (Shynth) solution with 10 mL of 20 mmol L^{-1} CuCl_2 (Merck) + 0.1 mol L^{-1} KCl (Merck), in an sonication flask. The mixture is then irradiated with high intensity ultrasound radiation



for 60 min, employing a direct immersion titanium horn (20 kHz, 10Wcm^{-1}) that was dipped till a depth of 1 cm into the solution. During the mixture, the appearance of a light-brown deposit is observed. This dispersion is dialyzed over 3 days in order to obtain a very stable, light-brown colored dispersion.

Applications:

Precursors for hydroxide films:

Ganesh et al., proposed CuHCF films on ITO (Indium-Tin oxide) substrates as precursors for hydroxide films. These films can catalytically oxidize alcohols giving anodic current density of about 10 fold higher than that of any metal hydroxide modified electrodes reported [137].

Cesium removal from aqueous radioactive wastes: The use the MHCs for reducing radiocesium has drawn significant attention after the Tsunami led by earthquake in Japan on 11 March 2011. After the Fukushima nuclear accident, radiocesium was released and spread all over. MHCs have high selectivity and capacity for Cesium. This is the reason why they are preferred to be competitive ion exchangers over other materials [138]. Among the MHCs, copper hexacyanoferrates (CuHCFs) are often selected as the reagent in practical analysis for the Cs removal because of its low toxicity, low cost, easy preparation methods and chemical stability in a large pH range. Various works on the study of CuHCFs have suggested that they can be used as precipitants for cesium removal from aqueous radioactive wastes [139, 140]. However, CuHCFs being in fine powder form were difficult to separate from liquid after the treatment as well as regenerate, so columns were used which were later on discarded. Although they were proven to be harmless to humans and animals [141], the filtration was still required to remove the sludge.

Modified electrodes: Electroactive films were prepared by immobilizing CuHCF nanoparticles onto fluorine doped tin oxide (FTO) electrodes by using the electrostatic deposition layer-by-layer technique (LbL). These films exhibit electrocatalytic properties towards H_2O_2 reduction and also provide higher currents than those observed for electrodeposited bulk material, even in electrolytes containing NH_4^+ , Na^+ and K^+ . The nanoparticles assembly was used as mediator in a glucose biosensor by immobilizing glucose oxidase enzyme by both, LbL and cross-linking methods. Depending upon the immobilization method, variable sensitivities obtained. Whereas in case of electrodes,

the amount of enzyme used is much higher. Interestingly, in case of immobilization of electrodes achieved by LbL method, the linear concentration range where the biosensors can operate was 10 times higher than with the conventional crosslinking method [136].

Sensors for heavy metals: Heavy metal cations can be determined using fixed potential amperometry. For this purpose, electrochemical enzyme sensors were prepared using carbon film electrode modified using CuHCF and glucose oxidase with glutaraldehyde using crosslinking method. Different parameters were optimized like applied potential and influence of pH of the electrolyte solution. In the presence of fixed amounts of glucose, Cadmium, cobalt, copper and nickel ions were detected and also the response to glucose was tested in the absence and presence of a fixed concentration of inhibitor. Moreover, for the very first time, authors used electrochemical impedance spectroscopy in order to characterise the response of glucose biosensors in the presence of the inhibitors [142].

Synthesis, characterization and applications of Cobalt hexacyanoferrate nanoparticles

Cobalt hexacyanoferrate is one of the most promising inorganic polymers among the Prussian blue analogues. Here electron transfer is accompanied by the change of spin state of the Co ion [143]. This material is very useful because it possesses peculiar physicochemical properties such as electrochromism [147,148], thermochromism [144-146], photochemical magnetism [146] and electrocatalytic and sensing properties [147].

Two different transition metal ions (Fe and Co) are involved in the redox process of CoHCF unlike other materials of the same class; the phenomenon is driven by a metal-to-metal charge transfer. This electronic change occurs with a significant shortening of the Co-N bond length occurs from 2.08 Å (CoII(HS)) to 1.91 Å (CoIII(LS)) as a result of this electronic change [154]. This is accompanied with a significant shortening of the cell parameters from 10.30 to 9.96 Å. The occurrence of Fe (III) and Co (III) makes it possible to observe both the redox couples, FeIII/FeII and CoIII/CoII, in the same material [151]. Many authors such as Escax *et al.*, 2001 [149, 150] reported the preparation of CoHCF nanoparticles by electrochemically modifying of the electrode surface, such as carbon nanotubes [148] and nanowires [154]; by synthesis in reversed micelles [152] or water-in-oil microemulsions [153]; and on the formation of the CoHCF-silica nanocomposites [154]. Recently, CoHCFs are synthesised in a PAMAM-doped silica matrix [155, 156] where direct influence of the silica network on the physicochemical properties was observed.

Synthesis and Characterization: CoNPs are synthesized by addition of 10 mL solution of 0.01 M CoCl_2 containing 0.01 M EDTA drop wise to a 10 mL solution of 0.05 M hexacyanoferrate containing 0.05 M KCl under stirring. After complete addition, the liquid is vigorously agitated for 5 min, followed by the addition of sufficient acetone to deposit a slurry product on the bottom of the sample tube by a centrifuge. The final precipitates are dried overnight under vacuum at room temperature [157].

Applications:

Amphoteric determination of bovine insulin: A sensitive amperometric biosensor for insulin can be prepared using glassy carbon electrodes by solubilization of carbon nanotubes (CNTs) in chitosan (CHIT) together with CoHCF nanoparticles. The CoHCF-CNT-CHIT organic-inorganic system exerts a synergistic effect, resulting in the extremely enhanced insulin currents owing to the superior electron-transfer ability of CNTs and the excellent reversible redox centers of

CoNPs. [157].

Oxidation of captopril electrocatalytically: Captopril can be oxidized on the electrode surface of CoHCF/graphene nanocomposite through a surface mediated electrocatalytic reaction. This modified electrode can be efficiently used for the electrooxidation of captopril. It is observed that, in the presence of captopril, the anodic peak current for the transition of the Fe(II)/Fe(III) increases while the cathodic one decrease. However, the peak currents of the Co(II)/Co(III) transition remain almost constant [159].

Photocatalytic degradation of neutral red dye: Cobalt hexacyanoferrate (II) was used as a photocatalyst for the decolourisation of neutral red dye in presence of UV light radiation. The effect of variation of different parameters, like amount of cobalt hexacyanoferrate (II), pH of dye solution, intensity of light and concentration of dye solution were investigated and their effects on the rate of photocatalytic degradation was also determined [160].

Electrocatalytic transducer for L-Cysteine detection: Core-shell structure of CoHCF nanoparticles (iron(III) oxide core-cobalt hexacyanoferrate shell) was employed to study the electrocatalytic oxidation of L-cysteine (CySH) using cyclic voltammetry and chronoamperometry. The procedures developed for the analysis of CySH were ultrasensitive and time-saving. CySH in human urine and serum blood samples can also be analysed using the above proposed amperometric method [161].

Synthesis, characterization and applications of nickel hexacyanoferrate nanoparticles:

Metal HCFs have a zeolitic structure which allows the diffusion of ions, so, electrical neutrality is maintained. Due to this reason, they are highly insoluble materials and do not dissolve on oxidation or reduction [164]. Polymerization of ethylene oxide to commercially

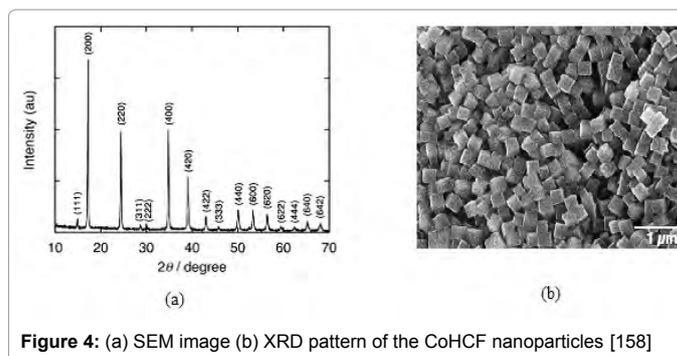


Figure 4: (a) SEM image (b) XRD pattern of the CoHCF nanoparticles [158]

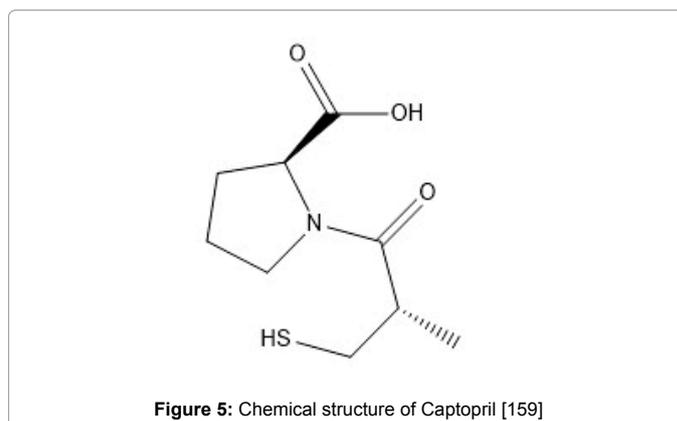
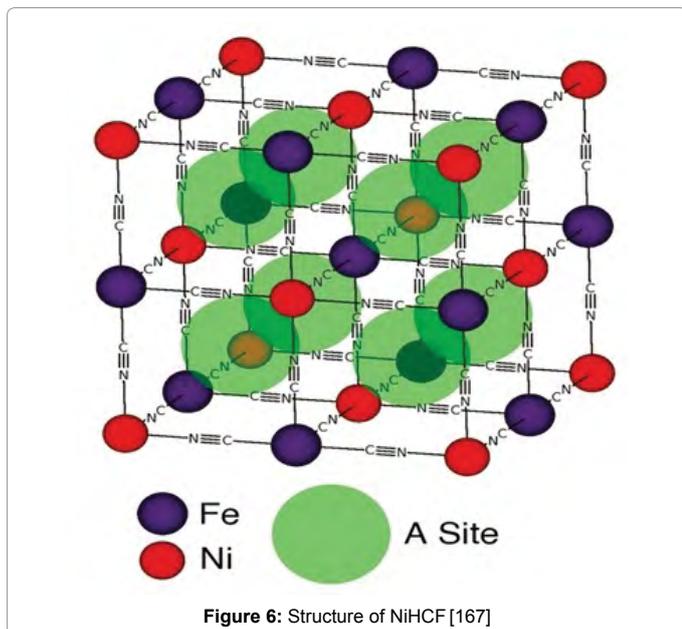


Figure 5: Chemical structure of Captopril [159]



upon oxidation or reduction excellent redox mediator properties, microporous and open channel structures, [162-164]. All these unique physicochemical properties favor the heterogeneous catalytic performance of nickel hexacyanoferrate. Structure of Nickel hexacyanoferrate nanoparticles is shown by Wessels *et al.*, 2011 [167].

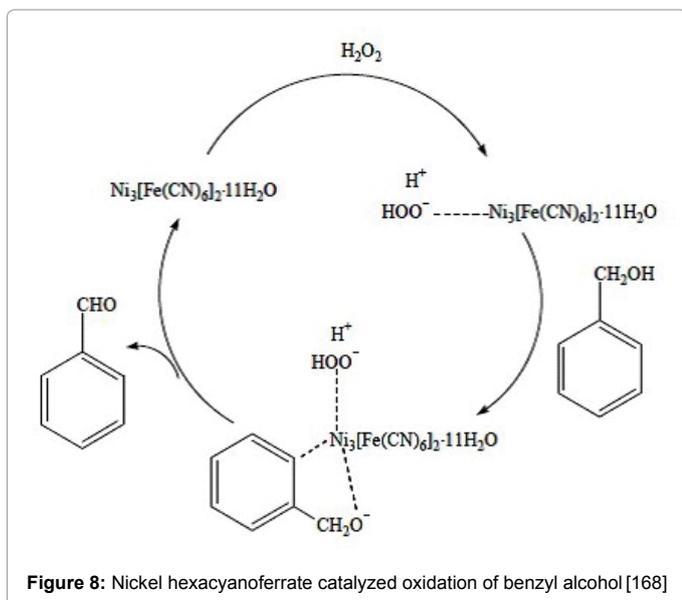
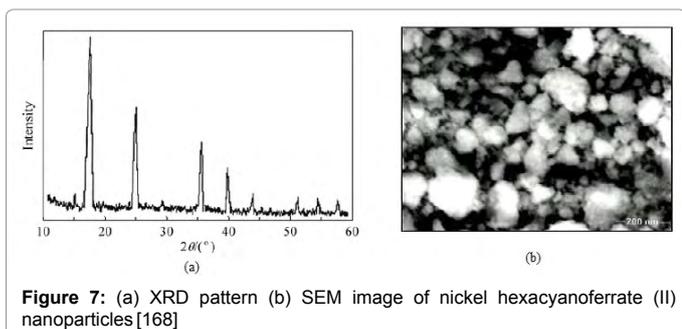
Synthesis and characterization: A 50 ml $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (0.01 mol/L) containing an equimolar amount of EDTA is added slowly to 25 ml of $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ solution (0.01 mol/L) containing an equimolar amount of KCl with constant stirring at room temperature. After complete mixing, the reaction mixture is vigorously agitated for 5 min and then kept as such for 30 min. It is filtered on a Buchner funnel, washed thoroughly, dried at 60 °C overnight, crushed and sieved with a 100 mesh sieve [168].

Application

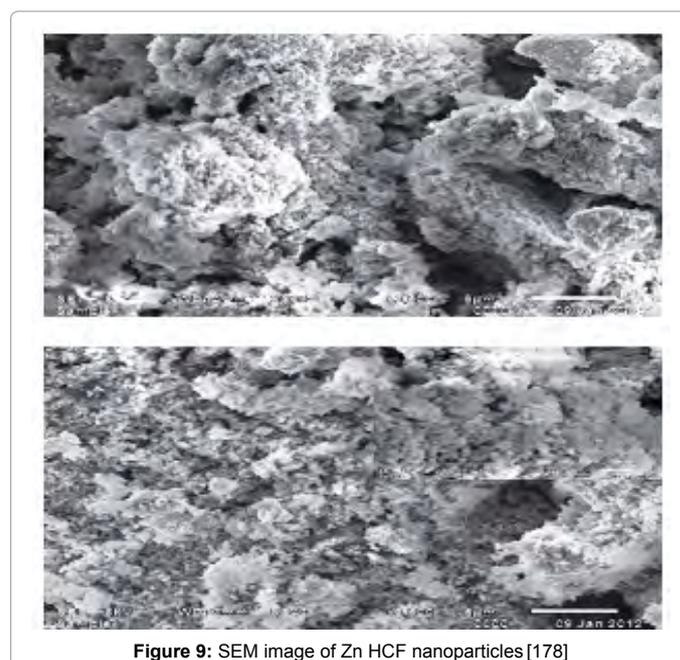
As Catalyst: Solvent-free oxidation of benzyl alcohol using H_2O_2 as an oxidant has been carried out successfully using Nickel hexacyanoferrate nanoparticles as heterogeneous catalyst. Generally, the catalytic oxidation of benzyl alcohol yields a mixture of benzaldehyde, benzyl benzoate and benzoic acid. But, NiHCF nanoparticles as a catalyst are highly selective and produce only benzaldehyde as a single product [168].

Removal of radio cesium selectively from aqueous solutions: $\text{Ni}^{\text{II}}\text{HCF}^{\text{III}}$ is incorporated with walnut shell for cesium removal. Due to its relatively high distribution coefficient and significant volume reduction, $\text{Ni}^{\text{II}}\text{HCF}^{\text{III}}$ -WS (Walnut Shell) is a promising material for very rapid Cs^+ removal from aqueous solutions [169].

Electrocatalytic oxidation of Hydrazine: Abbaspour *et al.*, [170] modified carbon ceramic electrode (CCE) with nickel hexacyanoferrate (NiHCF) nanoparticles. The proposed electrode exhibited various useful features, including fast response time, simple preparation, repeatability and good stability. Moreover, the modified electrode has a good sensitivity towards hydrazine and can be used for the electrocatalytic oxidation of hydrazine in a wide range of concentration. The authors investigated the oxidation mechanism of hydrazine on the modified electrode surface. They reported that the overall number of



important polymers has also been achieved successfully by using Nickel hexacyanoferrates as catalysts [165, 166]. Metal hexacyanoferrates have special unique properties including high surface areas, high ionic conductivities, mixed valencies, the ability to resist dissolution



electrons involved in the electrocatalytic oxidation of hydrazine was four. Also, for the determination of hydrazine in water samples, the modified electrode was successfully applied.

Ion-exchange application: Using unipolar pulse electrodeposition (UPED) method, nickel hexacyanoferrate (NiHCF) film was successfully deposited on carbon fibers. Different parameters were investigated, including the effects of pulse potential and cycle number during the film deposition on the composition, cycle stability and regeneration ability of the film. By varying the morphology, composition and electrochemical behavior of the synthesized NiHCF film with the deposition conditions, two structural analogues of NiHCFs could be generated in the finally obtained films i.e. soluble or insoluble forms. However, it was observed that a film with insoluble structural analogue showed long-term cycle stability, good regeneration ability and large ion exchange capacity [171].

Synthesis, characterization and applications of Zinc hexacyanoferrate nanoparticles

Zinc hexacyanoferrate has a zeolitic structure which allows only specific ions to penetrate into it and to pass out of the channels of ZnHCF [172]. Samantha and Basu measured the conductance of alkali metal ions through Neocerta membranes whose pores were precipitated with zinc hexacyanoferrate [173]. The results revealed that the mobility of the ions is in the order as given below:



ZnHCF films in NaCl and KCl medium can pair with K^+ and Na^+ ions. Such ion pairing behavior has also reported in the case of Prussian blue films in aqueous and acetonitrile medium [179]. But the permeability of Na^+ is less facile in ZnHCF than that of K^+ . Complete solubility of ZnHCF films in KOH is also noticed [174].

Transition metals such as Cu, Ni, Co, etc., generally form Prussian blue analogues associated with different redox potentials [175]. These analogues can be electrodeposited on a glassy carbon surface by simple electrochemical cycling in solutions of appropriate metal salts and potassium ferricyanide in an electrolyte medium in the form of thin-to-thick adherent films. ZnHCF is specifically unique amongst the rest Prussian blue analogues because it stands out as a unique exception in that it cannot be deposited easily on surfaces like glassy carbon (GC), Pt and Au, as the surface preparation procedures required for adhesion are too involved in nature [176, 177].

Synthesis and characterization: Zinc hexacyanoferrate nanoparticles may be synthesized by drop-wise addition of a solution of hexacyanoferrate salt (25mmol $K_3[Fe(CN)_6]$ in 50 ml H_2O) into a stirred solution of zinc sulphate (25 mmol $ZnSO_4 \cdot 7H_2O$ in 50 ml H_2O). The pale green precipitate is filtered off, washed with water and dried at 80 °C [178].

Applications

Photocatalytic degradation of harmful dyes: Zinc hexacyanoferrate nanoparticles can be used as a semiconductor for the photocatalytic degradation of neutral red dye. Since it is not soluble in water, thus after removal of ZnHCF nanoparticles, remaining water may be recycled in the same factory or reused in other industries or for agriculture purposes [180].

Deposition of zinc hexacyanoferrate selectively on the metal impurity sites of Single Walled Carbon Nano Tubes (SWCNT): The several metal impurities present in SWCNTs support modification of the electrode by ZnHCF and induce charge-discharge characteristics

in the resulting composite. The metal impurities in the above mentioned SWCNTs provide active sites for electrocrystallization of ZnHCF. However, the deposition of ZnHCF does not take place on the carbon surface of the nanotube. This is confirmed by the result that the deposition only take place on to the metal impurity surface sites and not to the surface of the walls of SWCNT [179].

Modification of carbon electrodes: For the first time Joseph et al. [181] reported the modification of carbon electrodes using ZnHCF thin films. When the ratio of $Zn^{2+}/Fe(CN)_6^{3-}$ is 1:1, then stable surface modification is favored, whereas any deviation from this ratio leads to electro-crystallization phenomenon. The authors observed that K^+ ions has facile entry and exit into the ZnHCF lattice as compared to other cations such as NH_4^+ , Li^+ , Na^+ etc.

Solid-State secondary cells: Jayalakshmi and Scholz [178] constructed solid state secondary cells with Prussian blue as the active material for cathodes and ZnHCF as one of the active materials for anodes. ZnHCF/PB cell can be of great importance if it is used as a primary cell. Since HCF's are non-toxic in nature, so they can be widely used in battery applications.

Few methods of synthesis and applications of nanosized metal hexacyanoferrates extracted from various references are summarized in Tables 2 and 3 respectively:

Conclusions

The unique properties of metal hexacyanoferrates (II) nanoparticles which are advantageous over existing materials concerning their analytical applications should be explored. First, Prussian blue nanoparticles. Prussian Blue is considered as the most advantageous low-potential transducer for hydrogen peroxide not only among hexacyanoferrates, but overall known systems.

Ever since the PB biosensor was invented, the Platinum has been substituted as most commonly used hydrogen peroxide transducer. The resulting biosensor showed advantageous characteristics of both sensitivity and selectivity in the presence of commonly tested reductants, such as ascorbate and paracetamol.

Copper hexacyanoferrates are used as precursors for hydroxide films which have catalytic ability towards alcohol oxidation. Moreover, CuHCFs can be used as precipitants for cesium removal from aqueous radioactive wastes because of its low cost and low toxicity, easy preparation, and chemical stability in a large pH range.

Cobalt hexacyanoferrates have advantageous application in amphoteric determination of bovine insulin using glassy carbon electrodes by solubilization of carbon nanotubes (CNTs) in chitosan (CHIT) together with CoHCF nanoparticles. Also, Captopril can be oxidized on the electrode of CoHCF/graphene nanocomposite surface through a surface mediated electron transfer (an electrocatalytic reaction).

Nickel hexacyanoferrate nanoparticles were found to be good heterogeneous catalysts for the solvent-free oxidation of benzyl alcohol using H_2O_2 as an oxidant.

Finally, Zinc hexacyanoferrate nanoparticles can be used as a semiconductor in the photocatalytic degradation of various harmful dyes such as neutral red dye.

Future Prospects

Currently, research in the field of biosensing is being carried out not only to develop faster and cheaper methods but also to increase

Metal hexacyanoferrate nanoparticles	Synthesis	Reference
Iron hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Deposition of Prussian blue on a platinum foil. Synthesis of Prussian blue nanoparticles in reverse microemulsion technique. Sonochemical synthesis of Prussian blue Nanocubes from a single-source precursor. Preparation of prussian blue nanoparticles with single precursor. Growth of nanoparticles of Prussian blue using an organic solvent, formamide. direct synthesis of PBA nanoparticles without any templating and/or added substances. 	Neff <i>et al.</i> [12] Vaucheret <i>et al.</i> [7,58] Wu <i>et al.</i> [59,60] Jiaet <i>al.</i> [91] Vo <i>et al.</i> [131] Shi <i>et al.</i> [95]
Copper hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Preparation of a film of copper hexacyanoferrate nanoparticles. Classical precipitation methods, preparation of single crystals, special preparative methods for column use, local growth method. 	Chen <i>et al.</i> [97] Ayraultet <i>al.</i> [46]
Cobalt hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Synthesis of CoHCF nanoparticles stabilized by EDTA. Preparation of MonodisperseCobalt(II) Hexacyanoferrate(III) Nanoparticles Using Cobalt Ions Released from a Citrate Complex. Electrochemical synthesis of nano-cobalt hexacyanoferrate at a sol-gel-coated electrode templated with β-cyclodextrin. preparation of CoHCF nanoparticle by electrochemical modification of the electrode surface, such as: <ul style="list-style-type: none"> Carbon nanotubes Carbon nanowires Synthesis in water-in-oil microemulsion. Formation of CoHCF-silica nanocomposites. Synthesis of CoHCF in a PAMAM-doped silica matrix. A synthetic route of CoHCF nanoparticles embedded in poly(methyl methacrylate). Synthesis of CoHCF nanoparticles directly in solution without any added surfactant. 	Qu <i>et al.</i> [157] Shibaet <i>al.</i> [158] Berrettoniet <i>al.</i> [47] Yang <i>et al.</i> [42,148,157] Qian <i>et al.</i> [151] Vaucheret <i>al.</i> [7,153] Moore <i>et al.</i> [68,154] Zamponiet <i>al.</i> [155,156], Giorgettiet <i>al.</i> [155,156] Zannottoet <i>al.</i> [58] Berrettoniet <i>al.</i> [155,156]
Zinc hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Modification of Carbon electrodes with Zinc hexacyanoferrate. Preparation of the ZnHCF film-based modified electrode. Chemical deposition of ZnHCF film onto a zinc electrode. Growth of zinc hexacyanoferratenanocubes. Synththesis of ZnHCF by dropwise addition method. Synthesis of ZnHCF nanoparticles using Zinc acetate. 	Joseph <i>et al.</i> [181] Eftekhariet <i>al.</i> [13,177] Eftekhari [177], Ali <i>et al.</i> [168] Jayalakshmiet <i>al.</i> [178] Kourimiet <i>al.</i> [152]
Nickel hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Synthesis of NiHCF nanoparticles using Nickel nitrate and EDTA surfactant. Electrochemical preparation of electrodes modified with mixed hexacyanoferrates of nickel and palladium. 	Qu <i>et al.</i> [157] Kulezaet <i>al.</i> [158]

Table 2: Methods for the synthesis of various metal hexacyanoferrate nanoparticles

Metal hexacyanoferrate nanoparticles	Applications	References
Iron hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Amphoteric detection of H_2O_2. Catalytic ability of PB is even better than that of Pt. An electrodeposited PB thin film is an excellent catalyst for both O_2 and H_2O_2 electrochemical reductions. H_2O_2 sensors based on PB modified electrodes. <ul style="list-style-type: none"> PB-modified GC electrodes. PB-modified Pt electrodes. 	Tseng <i>et al.</i> [58] Karyakinet <i>al.</i> [14] Itayaet <i>al.</i> [15] Karyakinet <i>al.</i> [14], Karyakinet <i>al.</i> [16] Mattors <i>et al.</i> [28], Karyakinet <i>al.</i> [16,17] Itayaet <i>al.</i> [15], Karyakinet <i>al.</i> [16] Garjonyteet <i>al.</i> [125], Garjonyteet <i>al.</i> [126]
Copper hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Amphoteric hydrogen peroxide sensors based on CuHCF. Electrochemical removal of Cesium from radioactive wastewater. Sensors for heavy metals at carbon film electrodes modified with copper hexacyanoferrate. The CuHCF films on ITO substrates have been recently proposed as precursors for hydroxide films 	Garjonyteet <i>al.</i> [125] Chen <i>et al.</i> [8,9] Ghicaet <i>al.</i> [142] Ganesh <i>et al.</i> [137]
Cobalt hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Amphoteric determination of bovine insulin. Application for the electrocatalytic oxidation and amperometric determination of captopril. In Photocatalytic Degradation Of Neutral Red Dye 	Qu <i>et al.</i> [157] Sattarahmadyet <i>al.</i> [159] Sharma <i>et al.</i> [78]
Zinc hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Heterogeneous catalyst for solvent-free oxidation of benzyl alcohol. Modification of Carbon electrode using ZnHCF. Use as battery electrodes in solid state secondary cells. In Photocatalytic Degradation of Neutral Red Dye. Selective deposition of zinc hexacyanoferrate on the metal impurity sites of SWCNT/glassy carbon electrode. 	Ali <i>et al.</i> [58] Joseph <i>et al.</i> [174] Jayalakshmiet <i>al.</i> [178] Sharma <i>et al.</i> [78] Boopathiet <i>al.</i> [179]
Nickel hexacyanoferrate nanoparticles	<ul style="list-style-type: none"> Selective removal of cesium from aqueous solutions. As catalyst for the Solvent-Free Oxidation of Benzyl Alcohol. For modification of electrodes. 	Ding <i>et al.</i> [34] Ali <i>et al.</i> [168] Kulezaet <i>al.</i> [144]

Table 3: Applications of various metal hexacyanoferrate nanoparticles:

integration of biological and electronic systems. With the help of MHCF nanoparticles, highly specific and selective biosensors can be developed and applied in diverse fields like bioengineering, biology and medicine, electrical engineering *etc.* Advances in any of these fields will have significant effects on the future of medical diagnosis

and treatment, where with the help of biosensing technology, the monitoring continuous diseases, prevention methods and development of more effective drugs with side effects minimized will benefited. With the current progress and exhaustive research pace of nanomaterial exploration, the sensing technology has become more and more

versatile, robust, and dynamic. No doubt, biosensor development for a task is still very cumbersome and costly due to its technical complexities, but the incorporation of nanomaterials has proved to be a big boon for this technology, chiefly due to its friendly and result oriented experimental support. Also, in the field of organic synthesis, MHCF nanoparticles are gaining attraction since they act as a source of cyanide ion. Various organic reactions can be carried out with the help of these nanoparticles. Hence, we conclude that the use MHCF nanoparticles in several fields is increasing day by day since they are non-poisonous and have unique physicochemical properties.

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