Prussian Blue: History, Miscellaneous Uses and Analytical Applications-A Review

Rimsha Rey Khan* and Jamil Anwar
Department of Chemistry, University of Management and Technology, Lahore, Pakistan.
f2020140011@post.umt.edu.pk*

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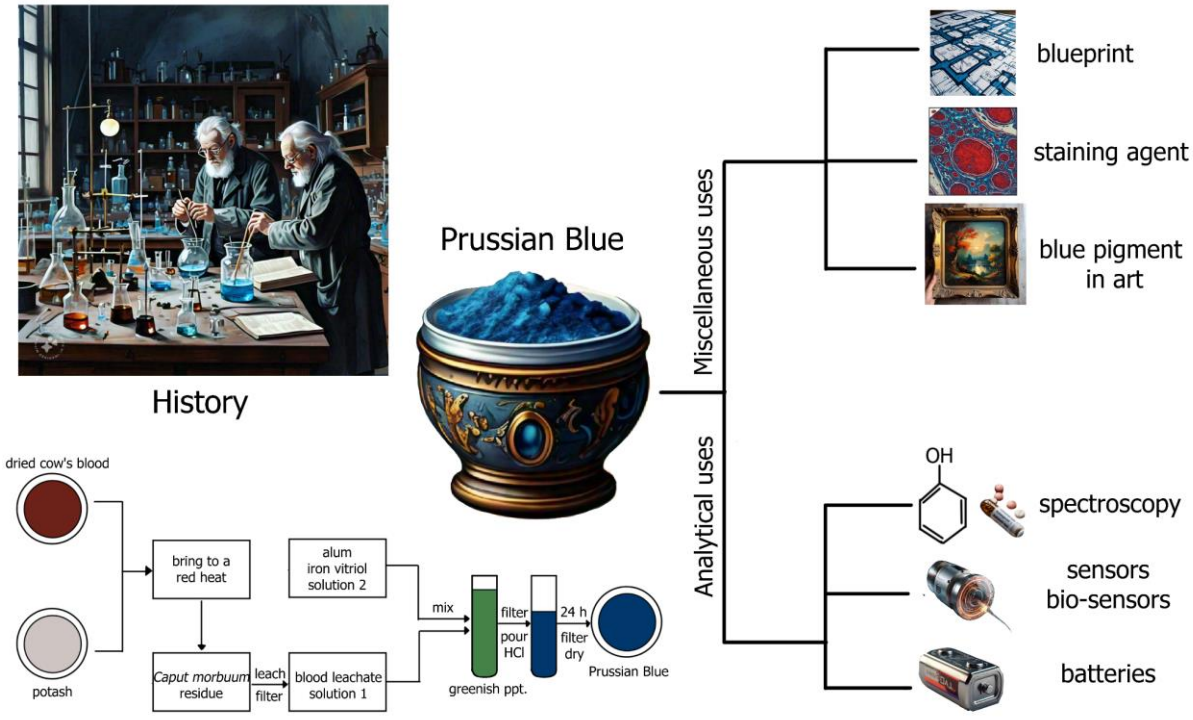
Summary: Since the accidental discovery of Prussian Blue in 1706, the blue chemical has been extensively employed in a number of commercial applications. It has been used as a color for paintings, dye for textile, antidote for heavy metal toxicity, staining agent in histopathology, and by machinists and toolmakers for spotting metal surfaces. In addition, due to its unique electrochemical properties, Prussian Blue has been vastly studied as storage of electric energy and used as a battery material. The electroanalytical applications of Prussian Blue and its different analogs have also been thoroughly investigated and used as sensors and biosensor for last few decades. Very recently the investigations have been made on the use of nanoparticles of Prussian Blue in biomedicine.

The deep blue color and easy formation of Prussian Blue as a result of redox properties of iron ions, made it an excellent coloring reagent, which shows absorption around 700nm, for the spectrophotometric determination of a large variety of materials like phenols, sugars, drugs, ascorbic acid, antibiotics, adrenaline, hydroxy urea, dopamine, and penems in a vast range of substances such as soil, fruit, vegetables, pharmaceutical preparations and tobacco. Similarly, on the basis of Prussian Blue, a number of sensors and biosensor schemes have been developed for the detection and determination of a number of substances. Prussian Blue has a fascinating and interesting history along with its miscellaneous uses since the start of 18th century. In this review an attempt has been made to cover the history, miscellaneous uses and analytical applications of Prussian Blue employed as spectrophotometric reagent and a biosensor.

Graphical Abstract:



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***To whom all correspondence should be addressed.**

Introduction

History

Original Inventors

To trace the origins of Prussian Blue, we must first step back into the world of alchemy. Around 1700, Berlin was a vibrant hub attracting intellectuals and alchemists, with alchemy still focused on transforming base metals into gold. Although chemistry began separating from alchemy in the 17th century, this distinction was not fully established until the 19th century. In 1706, scientific understanding was still far from concepts like atomic theory or the periodic table.

Two key Figs emerge in this history. Johann Konrad Dippel (1673–1734), a renowned alchemist, was invited to Berlin by Count August of Sayn-Wittgenstein. Although famed for his gold-making claims, Dippel gained notoriety for producing a foul-smelling animal oil — a traditional remedy distilled from dried beef blood. Through repeated distillations involving potash (K_2CO_3) and burnt lime (CaO), he refined the oil into a pale-yellow form, though it remained intensely odorous, a process he described as "messy and arduous," the oil retained a strong odor. Skeptical contemporaries derisively called it "stink medicine." Nevertheless, Dippel's bold claim that it was an Elixir of Life, promising restored vitality, cure for all ailments, and eternal life, led to its major commercial success [1].

The second key Fig, Johann Jacob von Diesbach, came from a prominent Bernese family and moved to Berlin in 1701. He specialized in trading and producing pigments, notably Florentine Lake, made from Mexican cochineal insects. [2]. The fertilized females of the cochineal insect (Dactylopius coccus) were dried, ground into a powder, and then the pigment carminic acid was extracted using hot water [3, 4].

Accidental Error

In 1706, Johann Jacob von Diesbach accidentally created a deep blue pigment while attempting to make Florentine Lake using dye, iron sulfate, and potash. Consulting with Johann Konrad Dippel, they traced the unexpected result to potash contaminated with animal blood or oil. This fortunate mistake led to the creation of a new pigment initially called Prussian Ultramarine, later renamed Prussian Blue or Berlin Blue.

At the time, blue pigments like ultramarine were rare and costly, so Prussian Blue quickly gained popularity among Berlin's artists. The Friedrich Stadt Chronicle of 1706 records its invention, noting its economic and artistic significance. Given its value, Diesbach and Dippel kept the production method secret to protect their monopoly.

However, in early 1707, Dippel fled Berlin after being arrested for insulting the Swedish king, leaving Diesbach to continue the pigment's production [5].

Frisch Enters the Game

After Dippel's departure, Johann Jacob von Diesbach, though skilled in experimentation, lacked marketing expertise. He partnered with Johann Leonhard Frisch (1666–1743), an experienced chemist and natural salesman, to promote the pigment. While Diesbach focused on production, Frisch successfully marketed Prussian Blue across Europe, highlighting its affordability compared to ultramarine. A scholar and member of the Royal Prussian Academy of Sciences, Frisch later introduced the term "Berlin Blue" in a 1710 publication, marking its first scientific recognition [6, 7]. In this article, which essentially served as an advertisement, Frisch refrained from revealing any details about the production process of Prussian blue.

It was only a matter of time before the highly profitable production process of Prussian blue was exposed. Early private recipes for the pigment had already begun to circulate [8]. The mystery was resolved abruptly in 1724, when J. Woodward fully disclosed the production process in the Philosophical Transactions of the Royal Society [9]. Georg Ernst Stahl (1660–1734) provided a detailed account of this well-known story in his book, published nearly 25 years after the discovery of Prussian blue, in 1934 [10].

The Correspondence of Frisch and Leibniz

A key piece missing from the history of Prussian Blue is the correspondence between Johann Leonhard Frisch and Gottfried Wilhelm Leibniz in Hannover, first published in a book in 1896 [11]. This book features 37 letters exchanged between 1706 and 1716. Frisch, as noted by Kraft, kept the process of making Prussian Blue secret, even from Leibniz. In his letters, Frisch claimed to have invented or improved the pigment and simplified its production. Meanwhile,

Prussian Blue gained popularity in Europe over the more expensive Ultramarine. Frisch's correspondence with Leibniz seemed aimed at using his influence to boost sales. Unlike Diesbach, an alchemist involved in experimentation, Frisch was more of a salesman. He also never mentioned Dippel, the second inventor, to Leibniz. In 1712, Frisch informed Leibniz that Italians were interested in buying the pigment's secret but offered too little, so he chose to keep it exclusive.

Frisch kept the production of Prussian Blue secret primarily for profit. In his letters to Leibniz, he emphasized his commercial success without revealing production details. While Diesbach made the pigment, Frisch sold it, especially outside Berlin. By 1712, demand outstripped supply. In 1715, Frisch told Leibniz that profits from Prussian Blue had enabled him to buy land near the city for botanical experiments with mulberry trees and other plants [12]. Additionally, a letter from Hasperg a friend of Leibniz, revealed that someone in the Netherlands was also producing Prussian Blue, but the quality was inferior to the Berlin version. This individual was likely Dippel, who had moved to the Netherlands and continued the production and sale of the blue pigment there [13].

How the Secret was Out

Diesbach and Frisch managed to keep the secret of Prussian Blue's production for no more than 20 years, until John Woodward, a member of the Royal Chemical Society in London, revealed the entire manufacturing process in 1724. In the same issue of the Transactions of the Royal Society, London, another Royal Society member, John Brown, also published a detailed account of his experimental work [14].

John Brown's account relied on a letter from John Woodward, who, not being a chemist, asked Brown to verify his findings. Brown repeated the experiments with metals like silver, copper, mercury, and bismuth but only achieved the bright blue color with iron. The origins of how Woodward learned the secret remain intriguing; Kraft initially overlooked this but later addressed it in a follow-up paper [15], that Woodward received the production method from Leipzig, Germany. According to records from the Royal Society in London, Caspar Neumann was the individual who sent two letters to Woodward in England [16]. Kraft describes Neumann as a typical 18th-century German apothecary-chemist. Specializing in pharmaceutical and food chemistry, Neumann published 24 papers, mainly in Latin. Though not originally from Germany, he moved to Berlin in the early 18th century to work at the Royal Court Apothecary. He later moved to London, where he worked for the wealthy surgeon and amateur chemist, Abraham Cyprianus [17].

Caspar Neumann lived in London until 1719, during which time he forged friendships with members of the Royal Society, including Newton [18]. While in London, Neumann likely met John Woodward and later sent him letters about Prussian Blue from Germany. After returning to Berlin in 1719, Neumann resumed his role as Royal Court Apothecary and wrote to Woodward in 1723. In his first letter, he revealed that Frisch was producing a blue pigment used as a substitute for Ultramarine. Neumann never asked Frisch for the process but deduced some ingredients through experiments, requesting his findings not be published under his name. He believed Frisch was the sole inventor, unaware of Diesbach and Dippel's roles, and there is no record of Diesbach working with Frisch after 1716 [13]. In his second letter, Neumann detailed the manufacturing procedure of Prussian Blue, which Woodward published in the Transactions of the Royal Society in 1724. Woodward followed Neumann's instructions and published the information under his own name. According to Neumann's first letter to Woodward, Neumann developed the procedure for producing Prussian Blue through his own experiments after learning about the main reagents, and it may not necessarily be the same method used by Dippel and Diesbach in Berlin.

In 1725, a year after Woodward's [11] and Brown's [16], publications, the French chemist Étienne François Geoffroy reported that Prussian Blue was being produced in large quantities in London and that this pigment was of superior quality compared to that made in Berlin [19]. Geoffroy also published the details of Woodward's and Brown's findings in French, along with some of his own experimental results [19, 20]. By 1725, the manufacturing process for Prussian Blue was publicly accessible across Europe, and the secret was no longer concealed. Since its discovery, Prussian Blue and its variants have been used widely beyond their initial analytical applications.

Etymology and Military Symbol

The pigment was named "Prussian Blue" after its origin in Prussia, a major European power at the time, which helped popularize it. It was also called Berlin Blue, Brandenburg Blue, Parisian Blue, and Paris Blue in different regions, but "Prussian Blue" became the enduring name. From the early 18th century, it became the primary color for the uniforms

of Prussian Army infantry and artillery regiments [21]. Prussian Blue, made from blood and iron, was first used to dye the army's uniforms, giving it its name. As the army grew under Frederick the Great, the pigment symbolized Teutonic strength and aggression. It remained a ceremonial and off-duty color for German soldiers until World War I, when it was replaced by field grey [22].

Hydrogen Cyanide from Prussian Blue

In 1752, French chemist Pierre J. Macquer conducted additional experiments on Prussian Blue, revealing that the pigment could be broken down into an iron salt and a volatile component (HCN gas), which could then be used to regenerate the pigment [23]. Thirty times latterly, Swedish druggist Carl Wilhelm Scheele insulated hydrogen cyanide from Prussian Blue in its pure form for the first time. This new acid was named Blausäure, meaning "blue acid" in German, due to its origin from Prussian Blue. In English, it became known as Prussic acid. The term "cyanide" in hydrogen cyanide is derived from "cyan," which is not only an English term for a shade of blue but also the Greek word for blue (Ancient Greek: κύανος), again reflecting its connection to Prussian Blue. Hydrogen cyanide, even in small amounts, is one of the most lethal poisons. It occurs naturally in relatively high concentrations in cyanogenic plants like almonds and cassava [24-26]. Historically, leaves or flowers from such toxic plants have been used for poisoning or executions. For instance, the ancient Romans used cherry laurel leaves for execution (known as "cherry death"), and Emperor Nero used them to poison members of his family [27]. Certain species of laurel plants can contain 1 to 2.5% cyanogenic glycosides [28].

While the historical use of cyanide derivatives like hydrogen cyanide and its connection to Prussian Blue provides important chemical insights, it is crucial to note that modern applications of PB-based sensors and electrodes do not face the same selectivity issues or interferences as the toxic properties of cyanide compounds. The development of Prussian Blue in electrochemical applications, especially for sensors, ensures high specificity for target analytes, such as hydrogen peroxide, potassium ions, and other ions, without the interference from cyanide derivatives.

Moreover, the environmental concerns regarding the use of cyanide derivatives are minimized in these newer applications. Current research has focused on designing PB-based sensors and electrodes that are stable, environmentally friendly, and non-toxic, significantly reducing the risk associated with cyanide byproducts. The proper handling and disposal of any cyanide-containing compounds are, of course, essential to prevent environmental contamination, but such issues are generally not relevant to the PB-based sensors used in modern electrochemical analysis.

This shift has moved away from the toxic legacy of cyanide, and the current focus is on making PB-based technologies safer and more sustainable for various scientific and industrial uses.

Prussian Blue and Blue Print

Before the blueprint process, technical drawings were copied by hand, which was slow and prone to errors. In 1842, British scientist Sir John Herschel developed the cyanotype process, using light-sensitive chemicals to create images. By the 1870s, it became popular for reproducing architectural and engineering plans. The original drawing was placed on translucent paper over a sheet coated with ammonium iron citrate and potassium ferrocyanide. When exposed to light, the chemicals formed a blue emulsion (Prussian Blue) where light was not blocked, creating a white outline of the drawing. The resulting blue sheet became known as a "blueprint." Over time, the term expanded to refer to any detailed plan, though blueprints are still used for large-scale drawings. Today, despite modern printing methods, "blueprint" remains in use [29].

Prussian Blue as Heavy Metals Antidote

Prussian blue's ability to bind with monovalent metal ions makes it effective as a sequestering agent for detoxifying certain toxic heavy metals, particularly cesium and thallium [30]. It works by interacting with these metals in the intestines, where the complex formed is then excreted through the stools. This process helps to reduce damage to other organs and tissues by removing the harmful metals from the body.

Cesium-137 is commonly used in small quantities for calibrating radiation detection equipment, such as Geiger-Mueller counters, and in larger amounts for medical radiation therapy to treat cancer. Therefore, there is a possibility of human exposure to this radioactive isotope. Historical cases of Cs-137 poisoning have been documented [31]. Pharmaceutical-grade Prussian blue is specifically used to treat individuals who have ingested thallium (Tl^+) or radioactive cesium ($^{134}Cs^+$ or $^{137}Cs^+$). The International Atomic Energy Agency (IAEA) reports that an adult male can safely consume up to 10 grams

of Prussian blue daily without significant harm. The U.S. Food and Drug Administration (FDA) has approved 500-mg Prussian blue capsules as a safe and effective treatment for certain cases of poisoning, when produced under the conditions of an approved New Drug Application [32, 33].

Prussian Blue as Staining Reagent

Iron is crucial for life, but it can also be toxic because it generates free radicals that can damage cells. To protect itself, the body employs iron-storage proteins. Hemosiderin is one such iron-storage complex found within cells, predominantly in phagocytic macrophages, and becomes particularly evident when haemoglobin breaks down due to haemorrhage.

Prussian blue is a extensively used histopathology stain employed by pathologists to descry iron in vivisection samples, similar as from bone gist or spleen [34]. This stain serves both diagnostic and research purposes. During the staining process, tissue sections are first treated with hydrochloric acid to denature the binding proteins of hemosiderin and release iron (III) ions. Potassium ferrocyanide is then added. The ferric ions react with the potassium ferrocyanide, forming Prussian blue. Although hydrochloric acid and potassium ferrocyanide can be used separately, most modern formulations combine them. The original staining method, developed by German pathologist Max Perls (1843–1881), used separate solutions of potassium ferrocyanide and acid, a technique historically known as "Perls Prussian blue" [35]. Iron deposits in the tissue react to form a blue or purple dye, which can be visualized as blue or purple deposits as shown in Fig 1 [36].

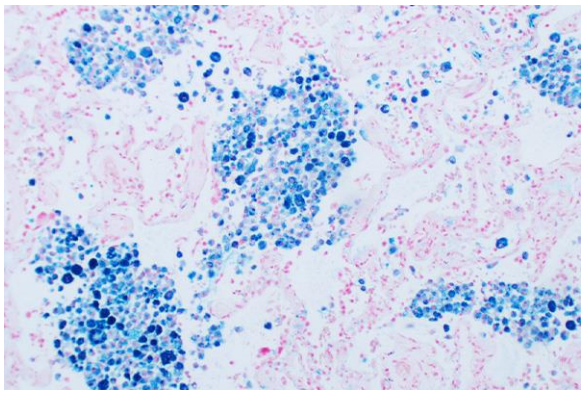

Fig 1: Prussian Blue Stain [36].

Color That Changed the World of Arts

The 1704 Berlin laboratory accident had a major impact on art, introducing an affordable, colorfast blue pigment that quickly spread across Europe. Factories soon refined its production, and the first synthetic pigment was used in painting, flags, postage stamps, clothing, and even dyeing tea leaves [37, 38]. For the art community, this scientific breakthrough was revolutionary. The influence of Prussian blue extended beyond Europe, attracting artists from around the globe. Before Prussian blue's discovery, artists relied on expensive and often imported blue pigments like indigo, smalt, azurite, and ultramarine derived from lapis lazuli [3]. Artists had traditionally struggled to find an affordable, stable, brilliant blue color for their artworks. A blue pigment that was less expensive, non-toxic, color-fast and readily available would be a godsend [39]. Finding an affordable, stable, and brilliant blue pigment had long been a challenge for artists. Prussian blue, with its cost-effectiveness, non-toxicity, and colour-fastness, was a major breakthrough.

The demand for this new color was immense, leading to its wide relinquishment in both oil painting and watercolour oil. The earliest known use of Prussian blue was in Pieter van der Werff's 1709 painting "Entombment of Christ" in the Netherlands [14]. Subsequently, artists across France, Italy, the Netherlands, and other European countries incorporated the pigment into their works as shown in Fig 2 [40].

Fig 2: Pieter van der Werff, “Entombment of Christ”, 1709 [40]

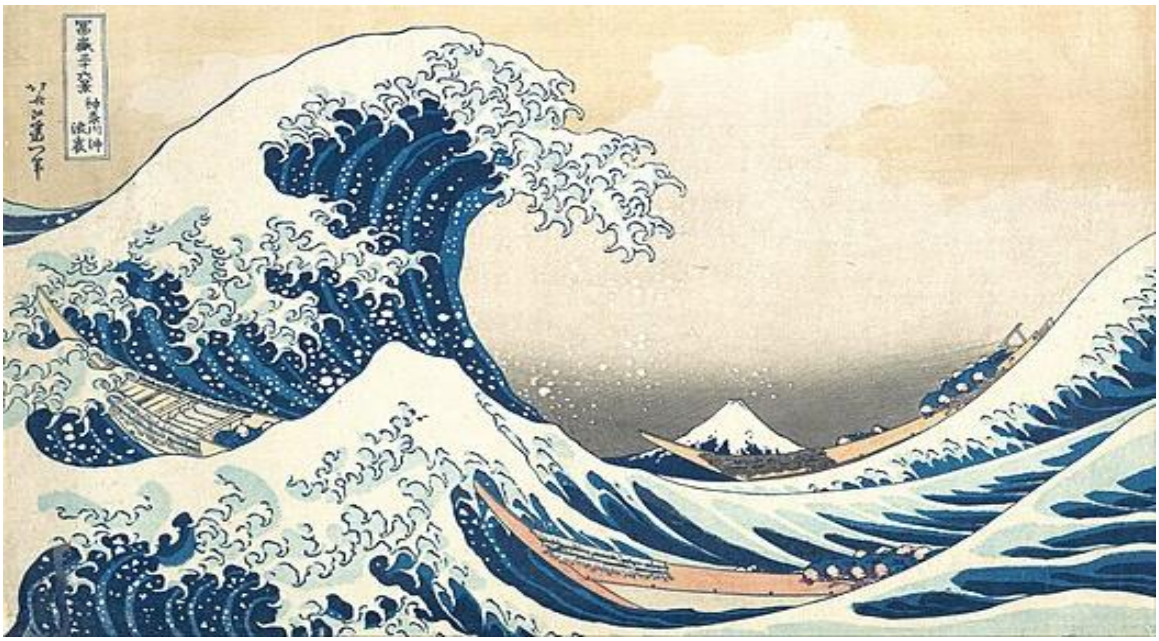

Fig 3: Katsushike Hokusai, Great Wave off Kanagawa, (1830) [45].

In the following decades, pure Prussian Blue produced a rich hue but was versatile for mixing. Combined with yellow, it created greens—van Gogh famously used it with chrome yellow for garden scenes. Watteau mixed it with ultramarine, while Lancret used ultramarine for skies and Prussian Blue, sometimes blended with green, for Figs [41]. During the 18th century, Prussian blue was constantly combined with white lead to achieve lighter tones, although this practice appears to have lowered its resistance to fading [42].

Blue Revolution in Japanese Art:

Prussian blue's impact extended beyond Europe and reached Japan, where it was described by commentator Henry D. Smith as a "blue revolution" [43]. The use of Prussian blue in Japan peaked in the early 19th century. Previously, Japanese woodblock artists had used blue dyes made from dayflower petals or natural indigo. These dyes were prone to fading with light exposure, causing the blues in many 18th-century prints to gradually shift to tan or beige [44]. Prussian Blue allowed artists and printmakers to create more vibrant, durable blue tones. Hokusai's famous 1830 work, The Great Wave off Kanagawa, used Prussian Blue alongside traditional indigo for its striking effect as shown in Fig 3 [44, 45].

Prussian blue's value extended beyond artwork and was quickly adopted for use in inks, including those for postage stamps. A notable example is the Mauritius 1847 two-pence stamp, which is now considered one of the rarest and most valuable stamps in the world [41].

Modern Uses of Prussian Blue and its Analogues:

Prussian blue and its analogues hold significant promise as materials for batteries. Extensive global research is underway to evaluate their potential for use in sodium-ion batteries. Recent advancements in sodium- ion battery technology suggest they could be feasible druthers to lithium- ion batteries for large- scale stationary storehouse. Prussian blue analogues offer benefits such as excellent electrochemical stability, low cost, and high-rate capability [46]. Researchers are exploring ways to synthesize derivatives of Prussian blue by incorporating various transition metal ions, aiming to leverage their open framework structure and other electrochemical properties to develop affordable and durable sodium-ion batteries [47, 48].

Prussian blue nanoparticles are currently being explored for cancer diagnosis and treatment. Researchers are investigating various methods to deliver therapeutic and imaging ligands specifically to tumour sites and are developing techniques to enhance the tumour-targeting and ablation capabilities of these nanoparticles [49]. Beyond cancer treatment, Prussian blue nanoparticles are garnering increasing interest for use in immunosensors, bioimaging, drug delivery, and

as therapeutic agents. Their large internal pore volume, adjustable size, ease of synthesis and surface modification, good thermal stability, and favourable biocompatibility make them highly appealing for these applications [50]. Prussian blue nanocubes have also been utilized as imaging tools in stem cell therapy. Researchers have used them as contrast agents to guide stem cell injections during surgery and to monitor stem cell treatments in the spinal cord afterward [51]. Recently, Prussian blue has been employed to safely remove nanoplastics from water, with researchers reporting the successful elimination of 99% of microplastics using this method [52]. Currently, research is increasingly focusing on Prussian blue analogues and their nanoparticles, with new applications, particularly in medical science, being continually discovered.

Analytical Applications

Spectrophotometry

Pharmaceutical analysis

Some common antibiotics videlicet ampicillin, amoxicillin trihydrate and cefazolin sodium have been anatomized using the Prussian blue response. attention of HCl used was optimized at different absorbance values. Linear range was set up to be 2- 12 µg mL^{-1} for ampicillin, 5- 13.5 µg mL^{-1} for amoxycillin and 3- 12 µg mL^{-1} for cefazolin with absorbance peak at 700 nm [53]. Othman and Saffar also carried out spectrophotometric analysis of amoxicillin maximum absorbance of Prussian Blue product was set up to be at 663 nm. Linearity was observed in the range of 5- 50 µg 10 mL^{-1} and the system was successfully applied for the determination of medicine in pharmaceutical medications [54].

Prussian Blue method has also been employed to determine cephalosporin antibiotics. The blue complex is formed when the antibiotics are added to a solution of iron (II) and hexacyanoferrate (III) in acidic media. HCl was selected for hydrolysis due to producing intense color and fast reaction. It was found that optimum concentration for development of the colored product was 1ml of 0.03 M $FeCl_3$ and 0.25 M of 0.008 M hexacyanoferrate (III) [55]. Gouda and Hassan determined etodolac in pharmaceutical preparations using the Prussian Blue method. Linearity was found to be in the range of 2-18 µg mL^{-1} with the limit of quantification (LOQ) of 0.76 µg mL^{-1}. Maximum absorbance of the colored complex was measured at 725 nm. Relative standard deviations were found to be less than 0.76 % with percent recoveries of 99.87-100.21 % [56].

Adrenaline was also estimated in pharmaceutical products by employing the Prussian Blue reaction. It was found that Beer's law obeyed up to 2.0 ppm. Detection limit was found to be 0.017 µg mL^{-1} [57]. Guo *et al*. determined dopamine hydrochloride in pharmaceutical, banana, urine and serum samples by employing the Prussian Blue reaction. The absorption spectra showed maximum absorbance of soluble Prussian Blue product at 735 nm. Influence of ferric chloride and potassium ferricyanide were tested at different concentrations and it was found that absorbance was maximum when using 1 mL ferric chloride. Potassium ferricyanide showed maximum absorbance at using a volume of 0.8 mL. It was also noted that absorbance reaches maximum at room temperature. Furthermore, effect of organic solvent and different acids were also studied and it was observed that increasing amount of acid concentration resulted in decreased absorbance. Linearity was found to be in the range of 0.05-6.00 µg mL^{-1}. The detection limit was found to be at 0.045µgmL^{-1} [58].

Other than that, spectrophotometric determination of penems, Radiogardase-Cs, mefenamic acid and loratadine drug has also been carried out using the Prussian Blue reaction. For penems, three pharmaceutical forms were selected for analysis namely Imipenem, Meropenem and Biapenem. Maximum absorbance was recorded at 725 nm for first two drugs and 745 nm for the later. Linear range observed for Imipenem was 0.02-0.12 mg mL^{-1}, for Meropenem was 0.02-0.1 mg mL^{-1} and for Biapenem was 0.02-0.1 mg mL^{-1} [59]. The structures of Imipenem, Meropenem and Biapenem are shown in Fig 11.

For Radiogardase-Cs determination, Prussian Blue was first made to react with a base to form iron (III) hydroxide which reformed iron hexacyanoferrate on reacting with acid. The formed nanosuspension of Prussian Blue showed maximum absorption at 710 nm. Linearity was found in the range of 0.1-100 µg mL^{-1} [60]. Mefenamic acid and loratadine (Fig 5) were estimated by their reaction with Prussian Blue. The former method showed maximum absorbance at 715 nm while the later showed highest absorption at 460 nm. Additionally, for mefenamic acid, linearity was carried out in the range of 3.0-14.0 mg L^{-1} while for loratadine, it was 2-18 µg mL^{-1}. Both methods resulted in good linearity with correlation coefficient of 0.99 [61, 62].

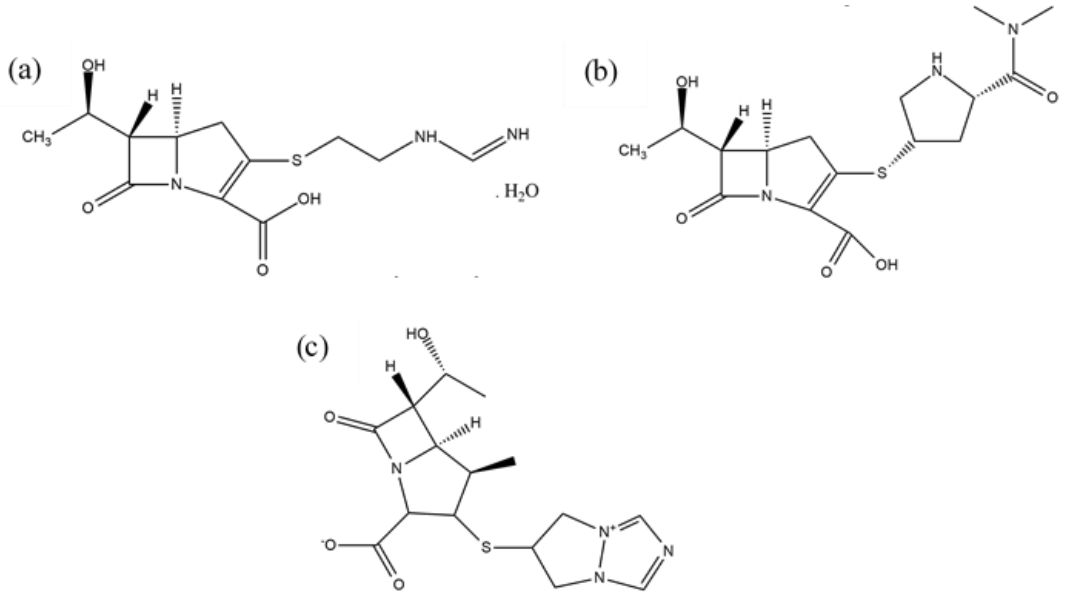

Fig 4. Structures of :(a) Imipenem, (b) Meropenem and (c) Biapenem.

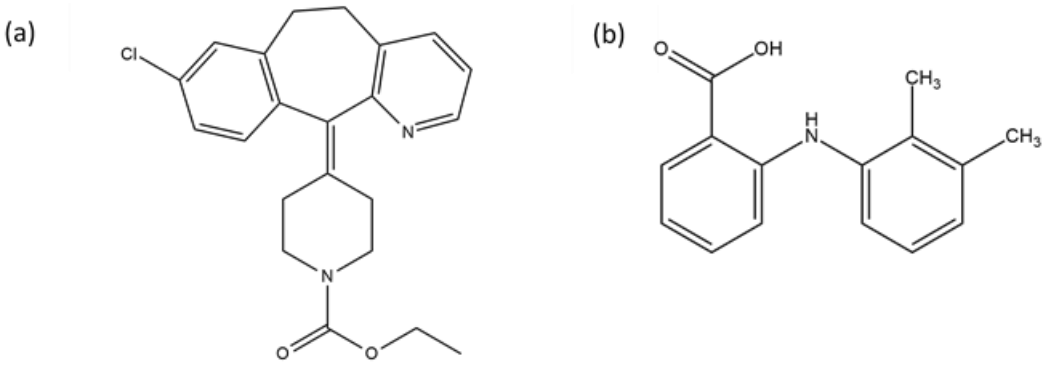

Fig 5: Chemical structures of: (a) Loratadine and (b) Mefenamic acid.

Tetracycline and Vancomycin have been determined based on hexacyanoferrate and iron (III) reaction to form Prussian Blue product. Maximum absorbance of the product was recorded at 700 nm and the linear range was found to be 1.5-25 ppm for Tetracycline and 1.8-24 ppm for vancomycin. It was also found that hydrochloric acid results in maximum absorbance and faster reaction among other acids. 0.35 M HCl was selected as optimum concentration for acid and the effect of heating time and temperature was studied. It was also found that the presence of other excipients like talc, glucose, starch, magnesium and sucrose didn't interfere with the concentration of both drugs [63]. Abbasi and Mahmood determined hydroxyurea in capsules using ferric reduction to ferrous ions and reacting it with potassium ferricyanide to form Prussian Blue. Linear range was found to be 0.05-5 ppm of hydroxyurea with a corresponding molar absorptivity of 2.4×104 mol^{-1} cm^{-1} [64].

In a recent work reported by James and Honeychurch, digital image colorimetry was employed for the assay of acetaminophen. The reaction involved reduction of ferricyanide to ferrocyanide which then reacts with iron (III) to form Prussian Blue (eq. 1 and 2) that could be detected by spectrophotometry or digital colorimetry. The method involved using the RGB color space to construct calibration curve where red component was used for regression analysis. Maximum absorbance of the Prussian Blue complex was found to be at 700 nm. Linearity was found to be in the range of 10-50 µM acetaminophen resulting in excellent correlation of 0.9959. Comparison of the RGB method with the UV-visible spectrophotometry resulted in limit of

detection (LOD) of 3.3 µM for RGB and LOD of 2.7 µM for spectrophotometry [65].

$$C_8H_9NO_2 + [Fe(CN)_6]^{-3} \rightarrow [Fe(CN)_6]^{-4} + Oxidation\ Products \quad (1)$$

$$3[Fe(CN)_6]^{-4} + 4Fe^{+3} \rightarrow Fe_4[Fe(CN)_6]_3 \quad (2)$$

Estimation of reducing sugars

Prussian Blue method has been successfully used for the spectrophotometric analysis of sugars, phenols and pharmaceutical products. The estimation of sugars is based on ferricyanide reduction method where Prussian Blue is formed when excess ferric iron is added to the mixture. Gum ghatti, gum Arabic, Duponol or oxalic acid are added for stability of the sol. Mateles devised a novel method to determine reducing sugars using oxalic acid as stabiliser for the Prussian blue mixture and omitting the gum ghatti solution. The spectrophotometer analysis of glucose was carried out at 520 mµ and the plot remained linear upto 300 µg of glucose [66].

For the determination of reducing sugars in soils, the Prussian Blue method involved reduction of ferricyanide ions in alkaline medium the absorbance of which was measured at 690 nm. The authors carried out a comparison analysis of different colorimetric methods including the Prussian Blue method for the determination of sugars in soils. It was found that the Prussian Blue method was most sensitive and can detect 1 µg of glucose. The calibration analysis showed that D-glucose concentration remained linear up to 20 µg and not more than that. However, it is crucial to note that the Prussian Blue method for the determination of soils lacks specificity and other reducing agents present in soil can affect the absorbance resulting in positive error. These agents can be removed by treating the soil extract with K-saturated cation exchange resin [67].

Another flow-injection spectrophotometric method was carried out by Liu and Jiang in which Prussian Blue method was employed to determine total reducing sugars in tobacco. The procedure involved three reaction steps, the first step being hydrolysis of sucrose. The second step was the oxidation of sucrose and the third step was formation of ferric ferrocyanide, called Prussian Blue, the absorbance of which was measured at 690 nm. It was observed that concentration of hydrochloric acid affects hydrolysis rate of sucrose. Calibrations of glucose and fructose were also carried out and it was found that both sugars could be used as a standard for the determination of total reducing sugars. Linear range of glucose was found to be from 0.5 to 15 mgL^{-1} while that of Fructose was 0.5-20 mgL^{-1}. Analysis of the total reducing sugars in tobacco samples showed the percent recovery values in the range of 90.4-97.5 % [68].

Huang *et al*. determined reducing sugars in vegetables using the potassium ferricyanide-iron (III) reaction. Sugar is used to reduce potassium ferricyanide which in turn reacts with iron (III) to form Prussian Blue. Linear relationship was found to be in the range of 0.8-4 µg mL^{-1} and the recovery ratio for samples was found to be between 99.61-100.34 % [69].

Analysis of total phenols

A method was devised for the analysis of total phenols in fruits and vegetables using the Prussian Blue reaction by Budini *et al*. The strawberry extract was made to react with 0.008 M $K_3Fe(CN)_6$ and 0.1 M $FeCl_3$. Absorbance of the complex was measured at 700 nm and at a constant temperature of 23 ± 0.05 ºC. Quantitative determination of ascorbic acid and anthocyanin was also carried out using the same procedure that resulted in increase in concentration during fruit ripening. However, total amount of phenols was found to decrease during the same ripening stage and ascorbic acid played an important role in optical density of the Prussian Blue complex. Therefore, Ascorbic acid concentration was subtracted from the total phenol content and the method remained linear up to 10^{-4} M of epicatechin. Tannin phenols were estimated by vanillin hydrochloride method, the calibration of which showed the same trend as that of Prussian Blue method. The devised Prussian Blue method was found to be 20 times as sensitive as the vanillin method and 3 times as sensitive as the titanium method [70].

Faujan *et al*. also carried out analysis of phenolic content along with antioxidant activity of Malaysian traditional vegetables. Prussian Blue assay was carried out by the reduction of ferrous (Fe^{+3}) to ferric (Fe^{+2}) by the phenolic compounds. The formation of blue color indicated quantity of phenols that could be measured by a spectrophotometer. The method remained accurate for concentration a s low as 1.10^{-6} mg mL^{-1}. Results indicated that total phenolic content of water extracts ranged from 3.50 to 7.82 mg GAE while that of ethanolic extract ranged from 1.84 to 11.54 mg GAE. Highest antioxidant activity was found in water extracts of Etlingera elatior (75.6 %) and ethanolic extracts of Sauropus androgynus (78.1%) [71].

Estimation of ascorbic acid:

Nobrega and Lopes carried out flow-injection spectrophotometry of ascorbic acid (vitamin C) in pharmaceutical products using the Prussian Blue reaction. The reaction involved the classical quantitative test to detect Fe^{+} using hexacyanoferrate (III). The first step is the oxidation of iron (II) to iron (III) as shown in equation (3):

$$Fe^{+2} + [Fe(CN)_6]^{-3} \rightarrow Fe^{+3} + [Fe(CN)_6]^{-4} \quad (3)$$

In the second step, iron (III) reacts with hexacyanoferrate ion to form hexacyanoferrate (II) ferric complex known as Prussian Blue (eq. 4).

$$4Fe^{+3} + 3[Fe(CN)_6]^{-4} \rightarrow Fe_4[Fe(CN)_6]_3 \quad (4)$$

In the third step, ascorbic acid reduces iron (III) to again iron (II) (eq. 5), the absorbance of which can be measured at exactly 700 nm as shown in Fig 13 [72].

$$2Fe^{+3} + C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^{+} \quad (5)$$

Ascorbic acid solutions were prepared from 5.0×10^{-6} to 1.0×10^{-4}. It is important to note that ascorbic acid solutions were prepared in 0.014 M nitric acid to avoid oxidation of the compound. Ascorbic acid solution was injected through a carrier stream along with the injection of 0.014 M nitric acid solution. The lowest concentration of ascorbic acid that could be determined spectrophotometrically was found to be around 3×10^{-7} M. It was observed that the sensitivity depended on the location of the confluence point. Best sensitivity was achieved at confluence point of 10 cm. Studies on effect of iron (III) showed that the iron concentration should be higher than that of ascorbic acid. However, using very high concentration of iron (III) resulted in loss of linearity.

Matei *et al*. also used Prussian Blue method for the estimation of ascorbic acid along with its kinetic study. Fresh samples before storage and after one-to-nine-month storage were investigated. The half time values were found to be between 2.9×10^{-3} hours^{-1} and 4.3×10^{-3} hours^{-1}. Spectrophotometric determination of ascorbic acid has also been carried out in honey, propolis, fruit juices, grapes and pharmaceutical samples using the Iron (II) and hexacyanoferrate reaction for the formation of Prussian Blue [73-78].

Colorimetric determination of ascorbic acid was also carried out based on the inhibition of the peroxidase (POx)-like activity of Prussian Blue nanocubes (PB NCs) capped with citric acid. It was observed that absorbance at 652 nm decreases with an increase in ascorbic acid concentration from 0.4 µM to 4.5 µM with a linear range of 0.4-405 4 µM. Observed detection limit was found to be as low as 35 nM and increase in ascorbic acid concentration resulted in blue to colorless solutions [79].

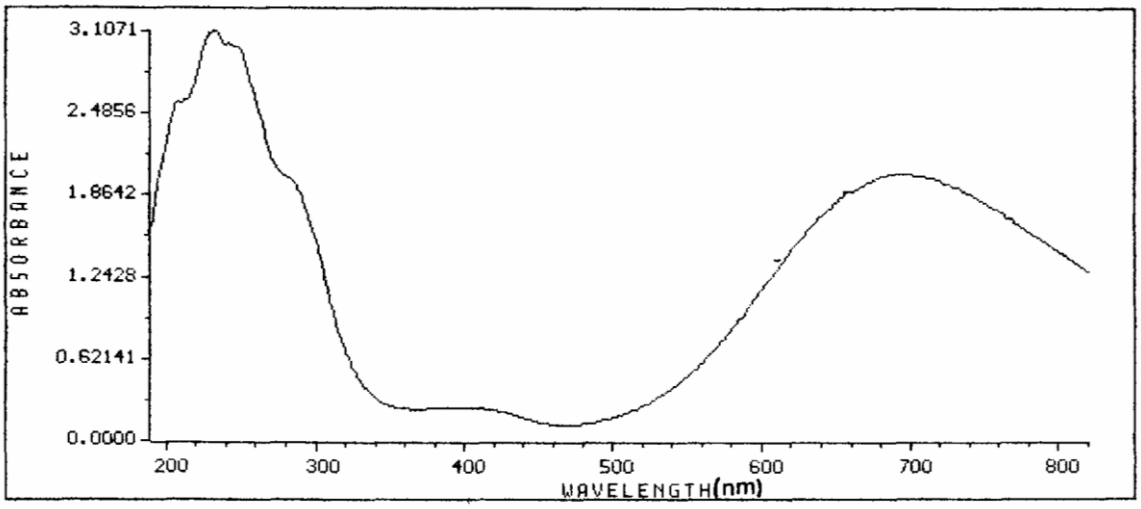

Fig 6: Absorbance curve of Ascorbic acid with maximum wavelength at 700 nm [72].

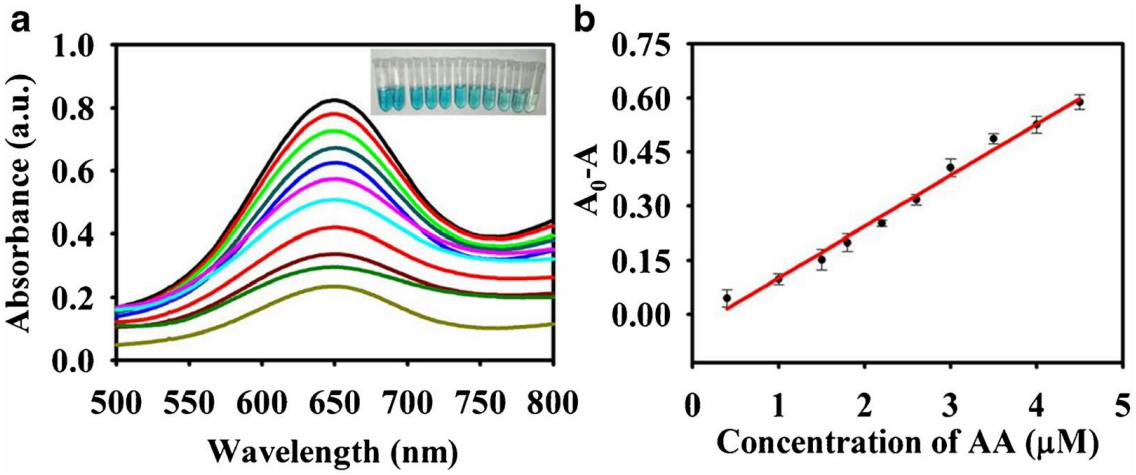

Fig 7: UV-Vis spectra of H2O2-TMB incubated with PB NCs at various concentrations of AA, with the inset displaying the photos of the corresponding solutions. (a) The analytical wavelength is set at 652 nm. UV-Vis absorbance spectra of H2O2-TMB with PB NCs in the presence of ALP at different activities, and incubated with AAP, (b) Calibration plot [79].

A strip test based on Prussian Blue immobilised onto polyvinyl alcohol (PVA) was reported by Kuswandi *et al*. The method involved non-electrochemical process by absorption of hexacyanoferrate (III) in the modified PVA membrane. The absorbance calculations of the film were carried out on 716 nm. The sensing mechanism was determined by the conversion of Prussian Blue to a colorless product after addition of ascorbic acid. The strip test was applied to the determination of ascorbic acid in fruit juices and compared with that of iodometric titration [80].

Chlorine determination

Excessive chlorine in disinfectant products can be hazardous to health and requires monitoring of the product's quality. One of the most commonly used methods to determine chlorine is spectrophotometry. Wasito *et al.* carried out spectrophotometric determination of chlorine in disinfectants employing the Prussian Blue reaction. In this method, determination of chlorine in the samples was performed based on Prussian Blue degradation. The sample containing chlorine was stirred until homogeneous and the absorbance was measured at 750 nm. Percentage of degradation of Prussian Blue was calculated using the following equation (6):

$$\%\, Degradation = 100 - \frac{(Abs_{sample} - Abs_{blank}) \times 100}{Abs_{control}} \quad (6)$$

Formation of Prussian Blue was optimized at different conditions before making calculations and actual degradation of the product. Chlorine was added in six concentrations (Fig 15) to record the linearity in the range 1.5-11.0 mmolL^{-1}. Accuracy was determined by using the standard addition technique with three different concentrations taken in replicates [81].

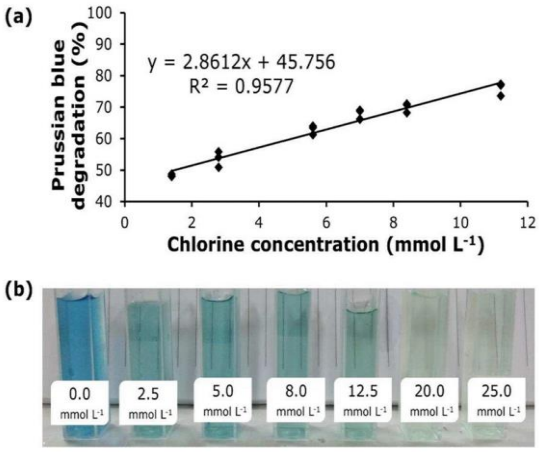

Fig 8: Degradation profile of Prussian blue after incubation with chlorine. (a) Linear regression based on the calibration curve, and (b) color changes of Prussian Blue degradation at different chlorine concentrations. The conditions included 2.0 mmol L^{-1} ferro sulfate, 3.0 mmol L^{-1} potassium ferricyanide, and 0.5 mol L^{-1} hydrochloric acid, with an incubation time of 15 minutes [81].

Determination of Prussian Blue nanoparticles in rat tissue:

Ding *et al*. determined Prussian Blue nanoparticles in rat tissues including whole blood, liver, kidney, heart, lung and spleen in the presence of endogenous iron interferences. Inductively coupled plasma-optical emission spectroscopy was used for assay with yttrium as internal standard. Accuracy and precision were measured using standard addition technique at concentrations 0.4-3.2 µg mL^{-1} on three different days for kidney, heart, lung, spleen and blood. The size of synthesized Prussian Blue nanoparticles was found to be 75.95 ± 1.09 nm (Fig 16) and a zeta potential of -36.88 ± 2.48 mV. Iron content in whole blood and tissues was estimated by using the equations 7 and 8:

$$Iron\ concentration\ in\ whole\ blood = \frac{iron\ concentration\ (\mu g\ mL^{-1}) \times sample\ stock\ solution\ volume\ (50\ mL)}{blood\ volume\ (0.2\ mL)} \quad (7)$$

$$Iron\ concentration\ in\ tissues = \frac{iron\ concentration\ (\mu g\ mL^{-1}) \times sample\ stock\ solution\ volume\ (50\ mL)}{tissue\ sample\ mass\ (0.2-0.3\ g)} \quad (8)$$

For the liver tissue the precision was 7.84 % and accuracy between 99.88 % to 102.37 %. The accuracy and precision for kidney, lung, heart, spleen and blood was found to be between 98.74 % to 102.09 % for intra-day and 6.17 % for inter-day [82].

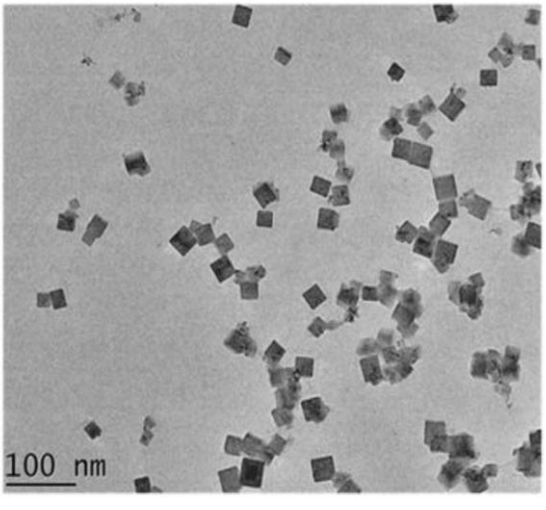

Fig 9: Transmission electron microscope image of Prussian blue nanoparticles showing their cubic shape [82]

Electrochemistry

Sensors and biosensors:

A vast variety of Prussian Blue (PB) electrodes and thin films have been reported in the literature with their applications in electrochemistry. However, it is essential to note that while PB-based sensors have demonstrated significant electrochemical properties, they are not without limitations. These limitations, particularly when compared to newer sensor technologies, need to be considered for better understanding and further advancements in the field. Akahoshi and Toshima reported a novel method for the preparation of Prussian Blue electrodes such as platinum, glassy carbon and SnO_2. The electrode was prepared in a solution of ferric-ferricyanide, the reduction of which took place on SnO_2, glassy carbon and Platinum electrode. Blue color is formed on the electrodes due to formation of Prussian Blue (PB) at the beginning of electrolysis. The cyclic voltammograms of the reduction of PB on platinum electrodes showed that the electrode potential was obtained up to 100 mV sec-1 and the waves obtained for platinum electrodes were much higher than that of SnO2 which is probably due to ohmic resistance in SnO2 electrodes. The behavior observed on glassy carbon was similar to that of the platinum electrode. The stability of Prussian blue on the electrodes was set up to be excellent and no declination of the peak height was observed under repeated scanning. The PB absorption spectrum showed peak at 690 nm while another band at 430 nm showed the formation of Prussian Green complex. Cyclic voltammetry showed stable PB layers and platinum had better performance due to lower ohmic resistance. [83].

Another method was devised for the preparation of PB film on electrodes by reacting with aqueous ferric ferricyanide solution in the presence of HCl. A large platinum foil was used as a counter electrode and a saturated calomel electrode was used as a reference electrode. The electrode potential for SnO_2 disk electrodes was measured from 0.6 to 0.2 V at 50 mV s^{-1}. Rate of deposition for glassy carbon and platinum electrodes was found to be the same while that of Au electrode was faster as compared to other substrates. For SnO_2 electrode the deposition rate was very small (0.08 mC cm-2). Considering the cyclic voltammograms the platinum electrode showed 5-10 % decrease in charge after stepping the electrode potential between 0.6 and -0.2 V vs. saturated calomel electrode. The deposition was faster on Au compared to Pt and glassy carbon while SnO_2 showed minimal deposition [84].

Table-1*:* Materials determined by spectrophotometry using Prussian Blue.

Materials	Ref.	Materials	Ref.
Ampicillin	**[51]**	**Tetracycline**	**[61]**
amoxicillin trihydrate	**[51]**	**Vancomycin**	**[61]**
cefazolin sodium	**[51]**	**hydroxyurea**	**[62]**
amoxicillin	**[52]**	**acetaminophen**	**[63]**
Cephalosporin	**[53]**	**glucose**	**[64]**
etodolac	**[54]**	**Sugars in soils**	**[65]**
Adrenaline	**[55]**	**Sugars in tobacco**	**[66]**
dopamine HCl	**[56]**	**Sugars in vege**tables	**[67]**
penems	**[57]**	**Phenols in fruits etc.**	**[68, 69]**
Radiogardase-Cs	**[58]**	**Ascorbic acid**	**[70-74]**
Mefenamic acid	**[59]**	**Ascorbic acid**	**[75-78]**
loratadine	**[60]**	**chlorine**	**[79]**

Redox-active Prussian Blue on metalated plasma polymer surface modified electrodes have been prepared and detected using photothermal detection with comparison to diffuse reflectance. The metal containing plasma polymer was prepared by depositing volatile metal carbonyl the coating of which was done on the carbon rod electrodes. These iron containing plasma polymer electrodes were surface modified by Prussian Blue by exposing electrodes to cyclic voltammetry in 0.1 M KNO_3 and 0.005 M $K_3Fe(CN)_6$ cycling from -0.2 V to +1.2 V. Average potential values for the PB were found to be 0.89 V and 0.21 V and it was found that the electrode could undergo several thousand reduction-oxidation cycles in solution containing water. One thing to note in this case is that the Prussian Blue electrodes deposition was in soluble form as compared to previous works in literature where PB electrodes were insoluble form. PB formed in soluble form (unlike traditional insoluble PB films) are highly durable redox cycling [85].

Prussian Blue modified electrodes have also been used for the H_2O_2 reduction in the presence of O_2. The electrodeposition was done by applying a constant potential of 0.4 V within 60 s. The fabricated Prussian Blue electrodes were quite stable in acidic and neutral conditions. Cyclic voltammetry results showed that Prussian Blue electrodes dried over night at room temperature were more stable than that of freshly prepared. Dried overnight films were more stable than fresh ones while considering stability under neutral and acidic conditions [86]. Prussian Blue cathode has been used to fabricate potassium secondary cell employing a potassium anode. A platinum electrode was employed for the electrodeposition of cathode and a thin film of Prussian Blue was applied on the cathode. The potassium battery designed was similar to that of the lithium batteries. The cyclic voltammogram showed oxidation of PB at a eventuality of 0.86 V, while reduction to Prussian White passed at 0.18 V. The electrolyte solution for the non-aqueous battery was 1 M KBF4 in 3:7 EC/EMC and it was found that the cell had an excellent cyclability for more than 500 reversible cycles [87].

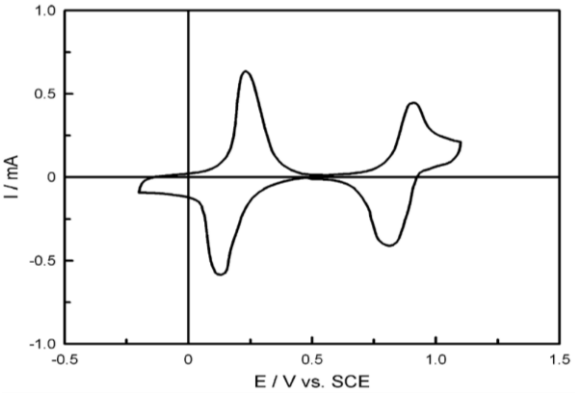

Fig 10: Cyclic voltametric behavior of the PB film electrode in a nonaqueous electrolyte solution of KBF_4. Scan rate 10m Vs^{-1} [87].

Prussian Blue nanoparticle modified graphite electrode has also been fabricated and applied to the reduction of H_2O_2. The working electrodes were prepared using rods of solid spectrographic graphite with an outer diameter of 3.05 mm. The prepared Prussian Blue nanoparticles had size of 35 ± 8 nm. Cyclic voltammetry results showed one reversible pair of redox peaks for Prussian Blue nanoparticle modified graphite electrode in the potential range +0.35 and –015. No redox peaks were observed for the simple electrode. No H_2O_2 reduction was observed using bare electrode while Prussian Blue nanoparticle modified graphite electrode Nafion exhibited a good electrocatalytic activity towards H2O2 reduction. The estimation wind for H_2O_2 determination was direct over 2.1×10^{-6} to 1.4×10^{-4} M mol L^{-1} with limit of discovery(LOD) of 1.0×10^{-6} mol L^{-1} [88].

Prussian Blue and its analogues have their vast applications in sensors due to their energy storage, electrochromic, electroanalytic and membrane properties. For fabrication of an alkali ion detector, thin flicks of Prussian Blue were electrochemically deposited on interdigitated array (IDA). The IDA consisted of two fingered electrodes deposited on Si/SiO2 substrate. PB films were then deposited on the electrodes each with thickness of 300 nm thick (Fig 8). The fabricated chemiresistors can show detection limit up to 10^{-4} [89].

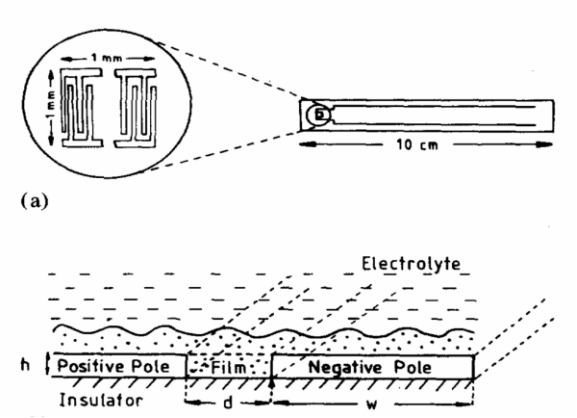

Fig 11: Geometric configuration (a) and cross-sectional view (b) of an interdigitated array electrode: finger width w = 7 µm; gap between fingers d = 3 µm; finger height h = 0.3 µm [89].

Mattos *et al*. reported a novel fabrication method for the preparation of sensors and biosensors based on Prussian Blue modified gold and platinum electrodes. Prussian Blue was deposited on the screen-printed electrodes galvanostatically. For Pt electrode, an improvement of surface coverage (from 2 to 16 mmol cm^{-2}) was obtained when the time was increased from 100 to 240 s. Both Pt and Au electrodes showed goof electrochemistry with an electrode potential of 30 mV at a deposition time of 100 s. This can be attributed to the fact that reversible redox interconversion takes place between Prussian blue and Prussian White. The electroactive electrodes were then tested for catalytic reduction of H_2O_2 which showed that the cathodic peak increased by 10 % and anodic peak was decreased by 30 %, indicating a catalytic reaction. The Prussian Blue modified gold sensor accounted for better reduction for H_2O_2 than the platinum sensor. The current response was set up to be 7000 nA which was doubly as advanced than the platinum detector. Hence Prussian Blue gold sensor yielded better sensitivity for glucose rather than platinum sensor [90].

Another Prussian Blue nanotube sensor based on potassium and sodium ions was fabricated by Ang *et al*. Electrodeposition of Prussian Blue (PB) nanotubes was carried out using 30 potential cycles in a solution of potassium ferricyanide, ferric chloride, potassium chloride and hydrochloric acid with a potential sweep of -500 mV and 600 mV at a scan rate of 50 mV s^{-1}. The voltammetry results showed that the cathodic peak shifts in the anodic direction with increasing potassium ion concentration with a slope of ca. 119 mV. In contrast, the same cathodic peak shifts in the opposite direction with the increasing sodium ion concentration in the presence of constant amount of potassium ions with a slope of ca. -59mV against the logarithm of sodium ion concentration. Hence, a dual sensor is possible due to Prussian Blue influence by both potassium and sodium ions. By keeping one ion concentration constant, other can be determined in samples like human saliva or artificial saliva. The linear ranges for potassium ion sensor were 0.80-63, 4.0-160, 8.0-310 mM while for that of sodium sensor were 0.8-23.7, 4.2-114, 34-770 mM [91]. Ma *et al*. also reported a hydrogen peroxide sensor based on DNA modified and Prussian Blue electrode. Polyvinylpyrrolidone (PVA) based Prussian Blue (PVP-PB) nanoparticles were prepared for sensor fabrication. A gold electrode was polished by sandpaper and ultrasonicated in distilled water and ethanol respectively. After that, the electrode was placed in H_2SO_4 (5 mM) until voltametric curves were stable. The treated Au electrode was then immersed in DNA suspension at room temperature and then immersed in the PVP-PB nanoparticle suspension (Fig 19). The response of the sensor for the reduction of H_2O_2 showed that a pair of redox peaks were observed at 0.15 V and 0.23 V [92].

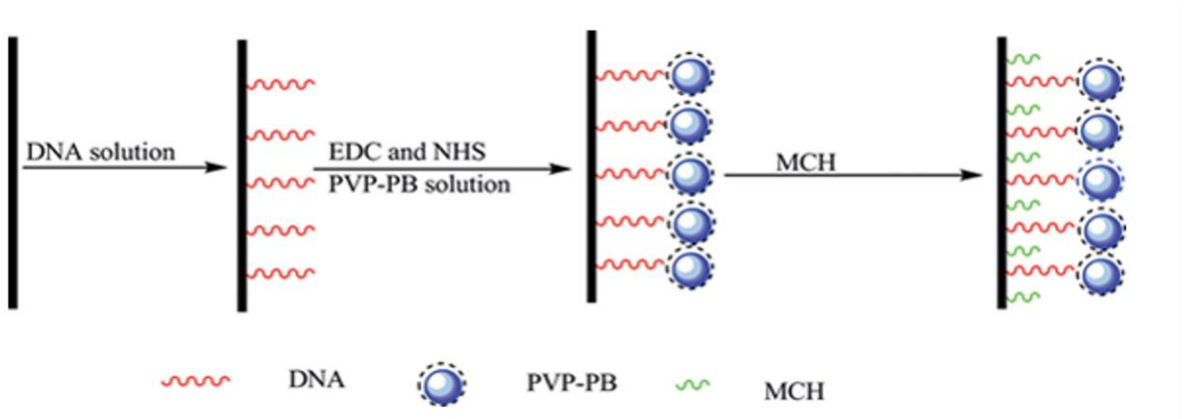

Fig. 12: Schematic of the preparation process for the Au=DNAPVP-PB electrode [92].

Prussian Blue electrode has also been used as a sensor for electroactive cations in aqueous solutions. The cyclic voltammetry results showed that the potassium ions are transported into the film while the waves for the sodium ions are non-existent [93]. Prussian blue nanoparticle-based sensors have also been used for the detection of hydralazine in pharmaceutical samples. Colorimetric detection of hydralazine is carried out in acetic acid buffer where it reacts with potassium ferricyanide and iron (III) solution to form Prussian Blue as shown in Fig 20 [94].

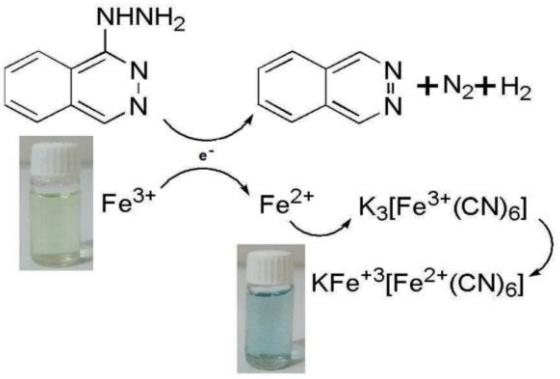

Fig 13: Schematic representation of the colorimetric detection mechanism for Hydralazine [94].

Sheng *et al*. developed a novel sensing technique for hydrogen peroxide based on Prussian Blue nanoparticles on polyaniline coated halloysite nanotubes. Electrochemical deposition is applied to get Prussian Blue polyaniline coated halloysite nanotubes (PB-PANI-HNTs) under the protection of PVP. The prepared modified glassy carbon electrode was subjected to cyclic voltammetry between -0.2 V to 1.2 V with a scan rate of 50 mV s^{-1} for 10 cycles in an oxygen free solution. The cyclic voltammetry (CV) results showed no response for bare glassy carbon electrode. However, the CV curve of modified electrode showed a pair of redox peaks near 0.2 V. Two pair of well-defined peaks can be observed from the voltammogram located at +0.2 V and +0.9 V which shows Prussian Blue reduction to Prussian White. It was also found that the peak current of PB-PANI-HNTs was higher than that of Prussian Blue electrode. When hydrogen peroxide was gradually added, the reduction peak decreased which indicates the electrocatalytic activity of modified electrode towards H_2O_2. Amperometry study showed the fabricated sensor possessed good electrocatalytic activity in the linearity range 4 to 1064 µM with a limit of detection (LOD) 0.226 µM [95].

Koren *et al*. reported a new type of H_2O_2 fiber optic sensor based on Prussian Blue to Prussian White redox cycle for the analysis of biological samples. The rechargeable sensor was prepared by dispersing an optical fiber in a solution of Prussian Blue and Cr-YAB in ethanol/water. Calibration of the sensor was carried out between 10 to 100 µM of H_2O_2 concentration with a limit of detection at 0.4 µM. The sensor was successfully applied to the determination of biological samples like enzymatic reactions, determining H_2O_2 concentration in complex natural biofilms and hydrogen peroxide concentration in activated neutrophils [96]. Another H_2O_2 sensor was reported by Jerez-Masaquiza *et al*. that was based on Prussian Blue deposited at ZrO_2 doped carbon nanotubes glassy carbon modified electrode. Chronoamperometry and cyclic voltammetry was used to detect electrocatalytic activity of the sensor. Constant potential of 1.0 V vs Ag/AgCl was applied and aliquots of hydrogen peroxide were added successively every 20 s. Potential range for cyclic voltammetry was from -0.2 V to 1.2 V at a scan rate of 40 mV s^{-1}. The linear range for H_2O_2 detection was found to be 3×10^{-5} to 6×10^{-4} mol L^{-1} with a detection limit of 3.5913 µmol L^{-1} [97]. Prussian Blue biosensing devices have also been fabricated for distance-based measurements. These devices are based on µPADs, the support material for which, is a paper. The paper-based sensing device is prepared by wax printing technique and applied to ascorbic acid determination. The biosensor was also applied to glucose determination, vitamin samples and drugs containing ascorbic acid. For Glucose the linear response was between 18-180 mg dL^{-1} while for that of ascorbic acid was 0.25 mmol L^{-1} to 4.0 mmol L^{-1} [98].

Chaudhary *et al*. reported a new type of Prussian Blue sensor for glucose determination using electrodeposition technique. For observing electrochemical properties of the sensor, an electrode potential was applied between 2.5 V and -1.5 V with time interval of 3 s. The absorbance was kept at 450 nm. The sensor exhibited good performance within the range of glucose from 0.5 to 3.5 mM which can be seen from the cyclic voltammogram in Fig 14 [99]. H_2O_2 detection has also been carried out using a TiO_2-ZrO_2 doped carbon nanotube glassy carbon modified sensor based on Prussian Blue deposition. The developed electrode presented linearity in the range 100 to 1000 µmol L^{-1} for hydrogen peroxide detection in milk samples [100].

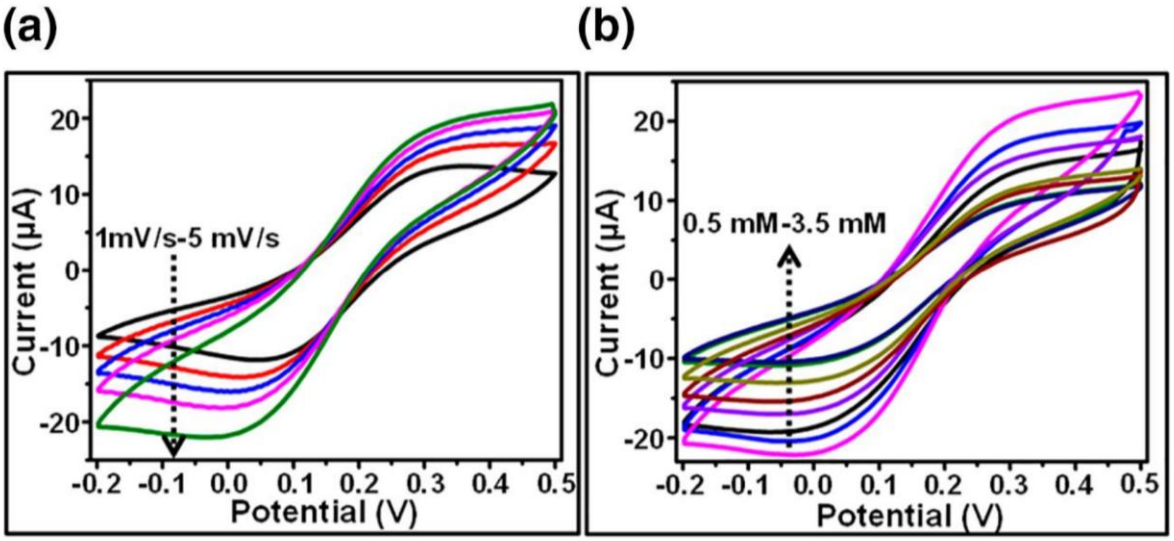

Fig 14: (a) Cyclic voltammograms (CV) of the flexible PB electrode at varying scan rates, and (b) the CV of the active electrode with the sequential addition of glucose concentrations at a constant scan rate [99].

Antimony tin oxide (ATO) Prussian Blue (PB) based sensors have also been fabricated for the electrochemical sensing of K^+ ions. A screen-printed paste is combined with ATO and Prussian Blue which is a cost-effective method to develop novel electrochemical sensors. Cyclic voltammetry results showed good redox behavior of PB based electrode for potassium ions detection with a linear range from 0.1 to 10 mM [101]. Other than that, Prussian Blue multi-walled carbon nanotubes functionalized polypyrrole nanowire arrays (PPY-MW-CNTs-PB) have also been reported in literature for electrochemical sensing of H_2O_2 and microRNA detection. The nanowire arrays were prepared on a glassy carbon electrode by copolymerization technique. The modified electrodes were then incubated in 0.1 µM amino-functionalized DNA. The modified nanoelectrode showed excellent electrocatalytic activity towards hydrogen peroxide reduction in the range 5 µM to 0.403 mM [102].

Electrochemical and optical sensing of chlorine has also been carried out using Prussian Blue (PB) sensor. The electrodes were prepared by reduction of Glass |FTO | PB electrode to Prussian white by cyclic voltammetry. The electrode potential was swept from -0.50 to +0.40 V at a scan rate of 40.0 mV s^{-1}. Optical absorption spectroscopy showed maximum absorbance at 710 nm with a linear detection range from 1.7 to 99.2 µmol L^{-1} for estimation of free chlorine [103]. Furthermore, Prussian Blue sensors have been used for enzymatic and non-enzymatic multi-analyte detection where a low cost and easy to use disposable device was made composed of ink modified with Prussian Blue. Estimation of H_2O_2, glucose and uric acid have been carried out using the sensor [104]. Recently, Liete *et al*. developed a Prussian Blue sensor for bacteria detection in protection clothing. The sensor was fabricated by stamping the Prussian blue solution dissolved in Edolan SN on polyester. Escherichia coli and Staphylococcus aureus were selected as Gram-negative and Gram-positive bacteria and the color shift from Prussian Blue to Prussian White was used as a detection mechanism for bacteria on textiles [105].

Other applications:

Sodium ion batteries are considered low-cost competitor for Lithium-ion batteries. Prussian Blue (PB) and its analogues have been used to fabricate sodium ion batteries. Lu *et al*. described a novel electrode based on PB and its analogues (Fe, Mn, Ni, Cu, Co and Zn) for the preparation of a sodium battery [47]. Nickel based Prussian Blue analogues were also fabricated for sodium storage by Zhang *et al*. The composite was synthesized by coprecipitation method. the effect of doping with cobalt and iron on the electrochemical performance of Ni-PB was systematically investigated through theoretical calculations and electrochemical tests [106]. Other than that Prussian Blue has been used for hydrogen storage and coordination of hydrogen and copper atoms. Hydrogen is absorbed by porous Prussian Blue analogues, that means there is some direct interaction between hydrogen and copper atom [107].

Table-2: Comparison of Fabrication Methods, Electrochemical Behavior, and Applications of Prussian Blue (PB)-Based Sensors.

Reference	Fabrication Method	Electrode Materials	Target	Key Findings	Electrochemical Behavior	Applications
[83]	Electrolysis in ferric-ferricyanide solution	Platinum, Glassy Carbon, SnO_2	Prussian Blue (PB) formation	PB formed on electrodes, stable under repeated scanning	Cyclic voltammograms (CV) showed higher current on platinum	Electrochemical analysis, PB sensor stability
[84]	Electrochemical deposition with ferric ferricyanide and HCl	Platinum, Gold, Glassy Carbon, SnO_2	PB deposition rate	Au electrode faster deposition, SnO_2 slower	CV showed 5-10% decrease in platinum electrode charge	Electrochemical sensors, PB deposition study
[85]	Metal carbonyl deposition, followed by cyclic voltammetry	Iron containing plasma polymer electrodes	PB for redox cycling	High durability of soluble PB electrodes	Cyclic voltammetry showed stable redox cycles	Long-term redox cycling, durable PB electrodes
[86]	Electrodeposition at 0.4 V	Glassy Carbon	H_2O_2 reduction	Stable in neutral and acidic conditions	CV showed stability of PB films	H_2O_2 detection, stability under varied conditions
[87]	PB electrode on platinum cathode	Platinum	Potassium secondary cell	Excellent cyclability for over 500 cycles	Oxidation at 0.86 V, reduction at 0.18 V	Potassium battery, energy storage
[88]	Electrode modification with PB nanoparticles	Graphite	H_2O_2 reduction	Good electrocatalytic activity, reversible redox peaks	CV showed one redox pair for PB nanoparticles	H_2O_2 detection, electrocatalysis
[89]	Electrochemical deposition on interdigitated array (IDA)	Si/SiO_2 (IDA)	Potassium and Sodium ions	Dual sensor for K^+ and Na^+ ions	Shifting redox peaks with ion concentration	Alkali ion detection in biofluids
[90]	Galvanostatic deposition of PB on gold and platinum	Gold, Platinum	H_2O_2 reduction	Better sensitivity for H_2O_2 with gold	Cathodic peak increased by 10%, anodic peak decreased by 30%	H_2O_2 detection, electrochemical sensors
[91]	Electrodeposition of PB nanotubes	Not specified	Potassium and Sodium ions	Dual sensing for K^+ and Na^+	Cathodic peak shift with ion concentration	Dual ion detection, biofluid analysis
[92]	DNA immobilization on gold electrode, PB nanoparticle coating	Gold	H_2O_2 reduction	Redox peaks observed at 0.15 V and 0.23 V	Stable redox cycles for H_2O_2 reduction	DNA-based biosensing for H_2O_2
[93]	PB on electrode	Not specified	Potassium and Sodium ions	Only K^+ detected, no response for Na^+	Specific for potassium ion detection	Electroactive cation detection
[94]	Colorimetric PB formation	Pharmaceutical samples	Hydralazine	Color shift indicating PB formation	Colorimetric detection for hydralazine	Pharmaceutical detection
[95]	PB-PANI-HNTs on glassy carbon electrode	Glassy Carbon	H_2O_2 reduction	Enhanced electrocatalytic activity for H_2O_2	CV showed higher peak current for PB-PANI-HNTs	H_2O_2 detection, sensor development
[96]	PB and Cr-YAB on optical fiber	Fiber optic sensor	H_2O_2 in biological samples	Rechargeable sensor for biofilm analysis	Linear range: 10-100 µM	H_2O_2 analysis in biological systems
[97]	PB on ZrO_2-doped CNTs glassy carbon	Glassy Carbon	H_2O_2 detection	High sensitivity in the electrochemical detection of H_2O_2	Linear range: 3×10^{-5} to 6×10^{-4} M	H_2O_2 detection in various samples
[98]	Wax printing on paper	Paper-based µPAD	Glucose, Ascorbic acid	Disposable, low-cost sensors	Glucose: 18-180 mg/dL, Ascorbic acid: 0.25 to 4.0 mmol/L	Glucose and vitamin analysis
[105]	PB solution stamped on polyester	Polyester	Bacteria (E. coli, S. aureus)	Color shift used for detection	Color change from PB to PB White	Bacteria detection in textiles

Prussian Blue can also be used to synthesize organometallic magnets based on hexacynaometalate and a Lewis acid. The dark blue solid is prepared by mixing $V[Cr(CN)_6]$. 2.8 H_2O with aqueous solution of potassium hexacyanochromate (III) and Tutton salt. The formed precipitate is filtered, washed with water and stored under oxygen free environment. The magnetization properties can be understood from the spectroscopic and structural data. Low saturation magnetization at a temperature of 10 K implies that Cr^{+3} and V^{+2} and V^{+3} have their spins at antiparallel which shows there is a short-range antiferromagnetic interaction between them [108].

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