Prussian Blue based materials: Structure, functional properties and multifunctional Application-A Review

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***Abstract* - Prussian Blue (iron (III) hexacyanoferrate (II)) is a famous mixed-valence coordination compound with multi-functional properties. It has an open-framework cubic structure, a moderate band gap (~1.5-2.0 eV) and interesting redox activity. Due to its unique electronic, optical and ion-exchange properties, it can be used in energy storage, electrochromic devices, biosensors, catalysis, environmental remediation and biomedicine. Functionalisation of Prussian Blue into various nanostructures including nanoparticles, nanocubes, thin films and hierarchical frameworks bring about a significant enhancement of its electrochemical and catalytic performances. This review summarises the recent progress of Prussian Blue materials, synthesis methods and functional device applications. It highlights the key strategies such as defect engineering, composite formation, heterostructure design, and hybrid systems with conductive materials. Critical discussions are made on the challenges of structural vacancies, water content, low conductivity and long-term stability. Future work includes scalable synthesis, improved material design and the development of smart, multifunctional and sustainable Prussian Blue based technologies.**

***Keywords:* Prussian Blue, electrochromic devices, biosensors, energy storage, biomedical applications.**

I. INTRODUCTION

Prussian blue (PB), also known as iron (III) hexacyanoferrate (II), is one of the oldest synthetic coordination compounds and still draws considerable research interest because of its unique structure and wide applications [1]. It has a face-centered cubic structure with cyanide (-CN-) bridges linking alternating Fe^{2+} and Fe^{3+} ions to form a strong three-dimensional network [2]. Its open structure contains interstitial sites for water molecules and alkali metal ions such as K+ and Na+, allowing for efficient ion diffusion and reversible redox reactions [3]. The deep blue colour and the unique electrochemical properties of PB are attributed to the strong intervalence charge transfer originating from the mixed-valence nature of iron ions [4]. Due to these features, Prussian Blue and its analogues exhibit excellent ionic conductivity, structural stability and biocompability [5]. Such properties make them promising candidates for energy storage technologies such as supercapacitors and rechargeable batteries [6]. Recent progress in the field of nanotechnology has enabled the synthesis of PB in different nanostructured morphologies such as nanoparticles, nanocubes, nanowires and thin films. The nanostructures also increase the surface area and enhance the reactivity, which in turn enhances their functional performance [7]. Therefore, PB-based materials have been studied for different applications including environmental remediation, drug delivery systems, electrochemical sensors, electrochromic devices and photothermal therapy [8]. Prussian blue based materials have developed as an important class of multifunctional materials due to their structural flexibility and wide variety of applications. The review provides a comprehensive summary of their composition, functional properties, and applications, recent advances and future research directions.

II. SYNTHESIS METHODS OF PRUSSIAN BLUE

2.1 Co-precipitation Method

This is the most prevalent and easy method. PB is produced by combining iron salts such as $FeCl_3$ with potassium ferrocyanide in aqueous solution. It provides bulk or nanoparticle PB with facile compositional control [9].

This approach employs elevated temperature and pressure within a confined container. It yields precisely defined nanostructures such as nanocubes and nanorods. The control over crystallinity and particle size has been improved [10].

2.3. Sol-Gel Method

PB is generated via the gel-like properties network derived from precursor solutions. The product provides consistent distribution and a refined particle size.

Valuable for the production of thin films and coatings.

2.4 Electrodeposition Method

PB thin films are directly grown on conductive substrates.

This method is widely used for sensors and electrochromic devices.

Film thickness and morphology can be controlled by voltage and time [11].

2.5. Green Synthesis Method

Eco-friendly methods use plant extracts or mild conditions.

They reduce toxic chemicals and are safer for large-scale use.

III. FUNDAMENTAL PROPERTIES OF PRUSSIAN BLUE

3.1. Structure and Chemical Composition

One of the coordination polymers, called Prussian Blue analogues (PBAs), is Prussian Blue (Fe4[Fe(CN)6]3·xH2O). It has a face-centered cubic (fcc) lattice, where Fe^{3+} and Fe^{2+} ions are linked via cyanide (–CN–) bridges [12]. The open framework contains interstitial water molecules and vacancies, which are known to play an important role in its physicochemical behaviours.

3.2. Electronic and Optical Properties

One of the most characteristic properties of Prussian Blue is its intense deep blue colour, which comes from the intervalence charge transfer between Fe^{2+} and Fe^{3+} through the cyanide ligand. It means:

- Absorption in the visible region is broad
- Electrochromic behaviours (reversible colour change under the applied voltage)
- Semiconducting character with a moderate band gap (~1.5–2.0 eV) [13]

3.3. The Redox Activity

Prussian Blue is very redox-active and can be reversibly electron-transferred between Fe(II) and Fe(III) states [14]. This gives rise to a number of redox forms:

- Less Prussian White
- Neutral form of Prussian Blue
- Berlin Green (oxidised form)

This redox flexibility is crucial for applications in electrochemical energy storage and sensing.

3.4. Magnetics

Prussian Blue displays interesting magnetic behaviours due to super exchange interactions between Fe ions: Can show ferromagnetic or ferrimagnetic ordering at low temperatures

Concentration of vacancies and the level of hydration dependence of magnetic properties [15].

3.5 Thermal and Chemical Stability

Stable at room temperature, decomposes at high temperature Sensitive to strong acids & bases Water content (xH2O) affects stability and conductivity.

3.6. Electrical Conductivity

Prussian Blue is normally a poor conductor but can show: Mixed ion-electron conductivity better conductivity when nanostructured or combined with conductive materials (such as polymers, carbon) [16]

3.7. Biocompatibility and Low Toxicity

Biocompatibility of Prussian Blue, which is FDA-approved for the treatment of radioactive poisoning (eg, Cs and Tl exposure) and possesses ion-trapping ability.

IV. APPLICATION OF PRUSSIAN BLUE

4.1 Energy Storage Applications

4.1.1 Sodium-Ion and Potassium-Ion Batteries

PBAs have been widely studied as cathode materials for sodium-ion batteries (SIBs) due to their large interstitial sites which are favourable to rapid Na+ diffusion.

They show:

- High specific capacity (~120-170mAh/g)
- Good rate performance
- Long term cycling stability

PB also has good compatibility with K + ions in potassium-ion batteries [17].

4.2 Supercapacitors

Electrodes based on PB exhibit pseudocapacitive behaviours:

- Rapid kinetics of redox
- High power density.
- Improved performance by hybridisation with carbon materials or conductive polymers [18].

4.3 Electrochromic Devices

PB is a well-known electrochromic material. It can reversibly change colour between blue and colourless states. Applications include:

- Efficient display
- Optical Switch Equipment

Advantages include high colouration efficiency, fast switching speed and long cycling stability [19].

4.4. Sensors and Biosensors

PB shows high catalytic activity in electrocatalysis for the reduction of hydrogen peroxide and thus is a key material in biosensing:

- Glucose biosensors (via enzyme-coupled reactions)
- Detection of H_2O_2, dopamine, and other biomolecules
- High sensitivity, low detection limits, and rapid response

Recent work has concentrated on nanostructured PB and PB–polymer composites for improved sensing performance [20].

4.5. Magnetic and Electronic Applications
PB exhibits tunable magnetic properties due to Fe^{2+}–CN–Fe^{3+} interactions: Molecular magnetism, Spintronic devices and Data storage applications [21].

V. CHALLENGES AND FUTURE PERSPECTIVES

5.1 Challenges
5.1.1 Structural Defects and Vacancies
Prussian Blue commonly contains $[Fe(CN)_6]^{4-}$ vacancies, which: Reduce electrochemical capacity, affect structural stability and Create inconsistency in performance. Controlling vacancy concentration remains a major challenge for reproducible material quality.
5.1.2 Low Electrical Conductivity
PB is intrinsically a poor electronic conductor, which limits: Charge transfer kinetics,
Rate capability in batteries and supercapacitors. This necessitates integration with conductive additives (carbon, graphene, conducting polymers).
5.1.3 Particle Aggregation and Morphology Control
Nanostructured PB tends to: Aggregate during synthesis and exhibit non-uniform particle size distribution. This affects surface area, electrochemical activity, and reproducibility.
5.1.4 Selectivity and Efficiency in Environmental Applications
Although PB is excellent for Cs^+ removal: Selectivity may decrease in complex real wastewater systems. Competing ions can reduce adsorption efficiency.
5.1.5 Scalability and Cost-Effective Production
Large-scale, defect-controlled synthesis is still challenging.
5. 2. Future Perspectives
5.2.1 Defect Engineering
Controlled synthesis to minimize vacancies
Tailoring defect density to optimize electrochemical performance
5.2.2 Composite and Hybrid Materials
Combining PB with conductive materials can significantly enhance performance:
PB/carbon, PB/conducting polymers (e.g., PANI, PEDOT), PB/metal oxides
These hybrids improve conductivity, stability, and mechanical strength.
5.2.3 Nanostructure Engineering
Designing advanced morphologies such as: Nanocubes, nanorods, hollow structures and Core–shell architectures. These improve surface area, ion diffusion, and catalytic activity.
5.2.4 Advanced Energy Storage Systems
Future research is focusing on: High-performance sodium-ion and potassium-ion batteries
And Hybrid supercapacitors. Flexible and wearable energy devices
5.2.5 Environmental and Sustainable Applications
Development of PB-based materials for selective ion removal in real wastewater
Integration into membrane filtration systems. Sustainable and green synthesis approaches.
5.2.6 Artificial Intelligence and Material Design
Use of machine learning and computational modelling to design optimized PB structures
Predictive control of defects, morphology, and performance

VI. CONCLUSION

Prussian Blue remains a highly promising multifunctional material; however, challenges such as structural defects, low conductivity, and stability limitations hinder its full potential. Future advancements focusing on defect engineering, nanostructured design, and hybrid material development are expected to unlock its capabilities for next-generation energy, environmental, and biomedical applications.

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