Research and Application of Prussian Blue in Modern Science

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Abstract. Recently, the attention to Prussian Blue has been aroused in the next generation applications in many areas, due to its specific advantages. However, the development of Prussian blue remains significant challenges. For example, nowadays, it can effectively improve the electrochemical performance of ions batteries. Herein, we summarize the recent advances and applications materials on the progress of the study and application of Prussian Blue in several area, including storage, electrochemistry, photochemical, medical. Special attentions were given on the following items: Prussian Blue Sensor, Ionic batteries and Hydrogen storage. The superior chemical nature of Prussian Blue makes Prussian Blue important in many areas.

1. Introduction

Prussian blue (PB), which people also call it ferric ferrocyanide, has a long history of using from 18th century. For a long time, it has been used in lots of area, as it is stable in light. This material can be used in the industrial production of coatings, baking varnishes, ink colorants and additives of detergent. It is also widely used as a kind of catalyst in some chemical reaction, or can help to hydrogen storage and photochemistry, even can be chemical sensors, biosensor monitoring and clinical medicine. It is well known in electrochromic, electrochemical, photochemistry, magnetic properties, and potential analytical application.

In recent years, a large number of progress were made in Prussian blue in all kinds of area. For example, in 2014, transition metal hexacyanoferrates in electrocatalysis of H₂O₂ reduction was produced, which is an exclusive property of Prussian Blue [1]. Another research results in 2010 on the structure of porous copper Prussian blue analogues and the properties of high H₂ storage capacity [2]. In ionic batteries area, a high crystalline Prussian blue analogue for the cathode of sodium ion batteries appeared in recent years. The synthesis methods were used in sodium ion batteries [3]. And in photochemistry, scientists explored a series of photoinduced magnetism in Prussian blue analog heterostructures, which was a marvelous progress [4]. Also, Prussian Blue has its long history in biological area. As early as 1995, researchers had developed the first-generation Prussian blue biosensor, a sensitive amperometry electrode for glucose, which was continuously updated and developed in the following time [5]. In clinical medicine, Prussian Blue can be used as a routine dye to detect the content of hemosiderin, which has an accurate diagnostic role for some kidney diseases [6]. In recent years, due to its unique physical and chemical characteristics, Prussian Blue has gradually emerged in the field of cancer medicine research. This paper will review the research and application of PB in the storage, electrochemistry and photochemical fields [7] [8].
2. Synthesis of Prussian Blue

2.1. Coprecipitation
People mostly using coprecipitation method to prepare Prussian blue. The method has a variety of advantages such as the simple preparation process, low energy consumption, and easy to get pure phase products [9][10]. The core technology of preparing Prussian blue by coprecipitation is the control of reaction conditions.[11] There are some factors affecting crystalline morphology of Prussian blue including stock solution concentration, type of precipitator, feeding ways, reaction temperature, aging time and pH value. Although it has such superiority, there are still two inferiors in the preparation: First is the preparation time is long, and second is output, which is very low. Therefore, with the development of study, we know that it is necessary on the premise of guarantee the integrity of crystal morphology, also pay attention to shortening the reaction time and increasing the yield.

Table 1. The parameter range of coprecipitation reaction

| Parameter          | Range         | Parameter          | Range                        |
|--------------------|---------------|--------------------|------------------------------|
| Reaction Temperature (°C) | 25 ~ 100      | reducing agent     | ascorbic acid, sodium citrate |
| reaction time (h)  | 0. 2~20       | atmosphere         | N2, air                      |
| aging time (h)     | 8~24          | drying temperature | 25~120                      |
| pH                 | 3. 6~7. 0     | drying time (h)    | 6~30                        |
| chelating agent    | PVP, poly (allylamine), citric acid | others | vacuum drying, atmosphere protection, ultrasonic |

2.2. Hydrothermal synthesis
Hydrothermal synthesis and coprecipitation has many similarities. This method needs shorter reaction time and uniform particle distribution. But it also has obvious drawbacks: We cannot monitor this reaction directly because it has the closed system. It also needs a high temperature and high-pressure condition during reaction so we need a strong equipment. So, this process is suitable for industrial production but not in the lab. The morphology of PB cathode materials prepared by hydrothermal method is generally crystalline and difficult to obtain special morphologies.

It is useful for improving its electrochemical performance by optimization of material morphology. Therefore, continuing studies can develop hydrothermal synthesis conditions to better crystalline materials.

3. Application

3.1. Applications in catalysis
One way of improving catalytic performance is using bimetallic catalysts, which also called synergistic catalysis. This is the beginning of widespread concern for water oxidation catalysts (WOC). [12] Using copper iron Prussian blue as a precursor to prepare bimetallic Fe\textsubscript{3}O\textsubscript{4}/CuO by situ preparation is a typical catalyst structure. The principle is synergistic effects of Fe\textsubscript{3}O\textsubscript{4} and CuO in the complex hydroxide reaction (WOR) process has a high oxygen evolution rate. Designing new metal bimetallic catalysts for WOR will compliance this principle.
In other fields, noble metal-free oxygen reduction reaction catalysts (ORR) can lead to other complexes which consist polyaniline (PANI) and Prussian blue analogues. [13] Similarly, high-performance Fenton catalysts can use morphologically evolved Prussian blue microcrystals to synthesis, and it can be used in photocatalytic degradation of organic matter, increasing attentions in improving the stability and recyclability of catalysts [14]. In 1983, Isamu Uchida et al found that oxidized Prussian blue could be used to catalyze the oxidation of hydrogen peroxide [15]. There are two electron transfer channels in Prussian blue crystals, which is respectively of the high-spin ions in Fe$^{3+/2+}$, and the low-spin iron ions in Fe$^{III/II}$, help to reduction and oxidation of hydrogen peroxide. The results show that molecular sieve characteristics and the metal centers in Prussian blue crystals may be important in catalysts.

Prussian blue was widely used in the reduction of H$_2$O$_2$, and it can be a unique feature through reduction which is called Prussian white (PW), and it catalyzes the electrochemical reduction of H$_2$O$_2$ at a low potential. Generally, it is regarded as an "artificial enzyme peroxidase", which has been widely used in electrochemical biosensors productions. And in 2007, chemically active Prussian blue modified gold nanoparticles were firstly synthesized by researchers. We choose the LbL (layer-by-layer) method to synthesize PB-coated Au nanoparticles by mixing ferric chloride and ferricyanide in order to synthesize ferric chloride and ferricyanide chloride under ultrasonic conditions. A good electrocatalytic activity is appeared assembled PB@Au nanoparticle films in the reduction of hydrogen peroxide. [22] In addition, Prussian blue modified Fe$_3$O$_4$ catalyzes the reaction. The product remains superparamagnetic, and the dipole-dipole interaction is weakened between nanoparticles because of the blocking temperature, moreover, reduces nanoparticles’ aggregation rate, and let it lower than that of pure iron oxide nanoparticles that extend the lifetime of nanoparticles. This material gives a new application view to Fe$_3$O$_4$ and Prussian blue nondielectric biosensors. [23] Correspondingly, scientists have proposed a new method for the synthesis of Prussian Blue/hollow polypyrrole (PB/H-PPy) nanocomposites, hoping that can enhance the electrochemical determination of H$_2$O$_2$. Using Fe$_3$O$_4$ balls as a source of template and Fe$^{3+}$ is a simple method to prepare PB/H-PPy nanocomposite. [24]

A major challenge in artificial photosynthetic apparatus development is the water oxidation catalyst (WOC). And the catalytic activity of Cobalt Hexacyanoferrate (CoHCF) Prussian Blue coordination polymer was found by José Ramón Galán-Mascarós et al, and says that CoHCF adds typical properties of molecular materials, namely transparency, porosity, flexibility, workability, and low-density visible light, which make CoHCF a good WOC candidate for the advancement of solar fuel production. [25] And we can prepare CoHCF by mature electrochemical method that on a fluorinated doped tin oxide (FTO) coated glass electrode.

Figure 1. Kinetics of O$_2$ evolution of the catalytic system using 2.0 mg of different catalysts (a): CuFe-2 (black); Fe$_3$O$_4$ (red); CuO (blue); CuO +Fe$_3$O$_4$ (pink).
3.2. Application in Energy Storage

Prussian blue has a wide variety of storage conditions, and its most common storage conditions are high hydrogen storage, sodium storage, and coordination of hydrogen atoms and copper atoms. Porous Prussian blue analogues can absorb hydrogen, which means there are some direct interaction between the copper atom and the hydrogen molecule. The hydrogen molecule’s antibonding σ* orbital can be affected by large availability of electron density on copper through its interaction. Electrons removed from the t₂g orbit are compensated by H₂ (donation) through lateral σ interaction. From these principles, we know that H₂ is a receptor-donor ligand of copper, so we can explain why hex-cyanogen-based copper metals have such a high capacity of hydrogen storage. [16] When we see a sodium ion battery, it has a kinetic problem, which is associated with the solid diffusion, thus its specific capacity and degraded rate performance is lower. In recent years, Liqiang Mai et al. developed a controlled selective etching method for synthesizing Prussian blue analogs (PBA) with enhanced sodium storage activity. [17] Cube units are often used in solving crystal structure of Prussian blue analogues, and it is corresponding to random vacancy distribution. However, the X-ray diffraction pattern of the copper containing component was carefully evaluated, and the deviation from the structural model was clarified, which we get that the highest hydrogen storage capacity was observed in porous Prussian blue for copper. This behavior was found in the crystal structure for Cu₃[Fe(CN)₆]₂ with M=Fe, Co or Ir. [2]

![Hydrogen adsorption isotherms at 75 K for Cu₃₋ₓMnₓ[Co(CN)₆]₂ and Cu₃[Ir(CN)₆]₂. Solid symbols: adsorption; open symbols: desorption.](image)

However, in 2004, the detection limit of nanophotus array of Prussian blue in the flow injection analysis mode was 1 billion (1×10⁻⁸ M), and it was accurately detected and exceeded in linear calibration. And the order of H₂O₂ size, which is 1×10⁻⁴ to 1×10⁻² M, is the most favorable analytical performance in the analysis of electroanalytical H₂O₂. Additionally, the results show that in electrochemical kinetics, reaction can be improved by Prussian blue during discharge / charging of polysulfide adsorbents lithium-sulfur batteries, but this may inhibit dissolution of polysulfide and shuttle. Other than this, in 2016, researchers put forward a zinc ion secondary battery with metal zinc anode, bio-ionic liquid electrolyte and nanostructured Prussian blue analog (PBA) cathode. There is good compatibility between Zinc anodes and PBA cathodes, among bio-ionic liquid electrolytes, electrochemical deposition/dissolution of zinc-to-zinc anodes, and reversible insertion /extraction of zinc ions. [18]
Figure 3. Electrochemical characterization of the FeFe(CN)$_6$ electrode in 1.0 M Zn(OAc)$_2$/([Ch]OAc + 30 wt % water mixtures). (a) Ten successive CV curves. Scan rate: 0.1 mVs$^{-1}$. (b) Charge and discharge profiles at a current of 10 mA g$^{-1}$ for 10 cycles. (c) Rate capability of the battery. (d) Cycling behavior at different current.

Prussian blue analogues can also be a kind of raw materials for secondary batteries, which includes several solvents such as non-aqueous solution of Ca(CF$_3$SO$_3$)$_2$, and Ca anode made to a primary cell which working voltage is about 2.0 V. We use magnesium plate as the anode, and CF$_3$SO$_3^-$ which formed on the surface of the magnesium plate is the negative electrode active material. As this theory, scientist made a new type of secondary battery which was prepared by consisting negative electrode active material. The cathode is transported by Ca$^{2+}$ and the anode is transported by CF$_3$SO$_3^-$ Dual ions. This battery prove the theory that this kind of battery is rechargeable. [19] The PB electrode is also used in a rocking chair type desalination battery, and this capacitive seawater desalination system is based on Prussian blue material consists of sodium nickel hexacyanoferrate (NaNiHCF) and sodium iron hexacyanoferrate (NaFeHCF) electrodes. Not only by the charging process are ions removed, but by the discharge process. The Prussian blue material can be used to treat the seawater, because it has a reversible charge and it is reversible in reaction of alkaline cations. And this kind of rocking chair desalination battery shows that this system has a high desalting capacity (59.9 mg / g) and high energy consumption (40% sodium ion removal efficiency is 0.34 Wh / L). [20] This kind of battery can be very useful in industrial field, had has a very wide application.
Figure 4. Principle of a rocking chair desalination battery. In the charging step, the cations in the negative compartment solution are captured by a chemical reaction with the negative electrode, whereas cations intercalated into the positive electrode are released into the positive compartment solution. Anions in the negative compartment solution pass through the anion-exchange membrane by diffusion. After exchange of the treated water with the source water, the solutions are diluted and concentrated by the reverse movement of ions.

3.3. Application in Sensor
The key of the preparation of chemical sensors is preparation of sensor surface sensitive membranes, and Prussian blue sensitive membranes can consist Prussian blue sensitive sensors, and chemically and electrochemically be used to prepare it. We traditionally synthesize Prussian blue powder and then fix it to the sensor surface in an appropriate manner, this is chemical method. And a new way is mixed graphite powder into [Fe(CN)$_6$]$^{3-}$ solution followed by addition of FeCl$_3$ to form Prussian blue on the surface of graphite powder. And Electrochemical methods also have a wide range of applications in the preparation of modified electrodes. Generally, PB is electrodeposited on the electrode surface by cyclic voltammetry, constant current method and constant potential method.

Also, many of inorganic polymers have been used for the research of chemically modified electrodes. Particularly, multicore transition metal cyanide is an important material, and Prussian blue is a typical representative of the multicore transition metal material. There are four categories applications of Prussian blue modified electrodes: detection of non-electroactive cations, application of oxidizable compounds, biosensors and optical sensors. [26]

During the redox process of Prussian blue, the positive ion M$^+$ enters the crystal lattice and maintains the charge balance of the PB film:

$$\text{Fe}^{4+}(\text{Fe (CN)}_6)^{4-} + 4\text{M}^+ + 4e^- \rightarrow \text{M}_4\text{Fe}_4^{4+}(\text{Fe (CN)}_6)^{3-}$$

This is the basis of Prussian blue modified membranes as sensitive membranes of non-electroactive cationic sensor. Prussian blue has a unique molecular sieve structure, which has preferential permeability and different cation selectivity for the cation in solution, especially for alkali metal ions, such as NH$_4^+$, H$^+$. And there are sensors which can be used to detect various cations. They can be applied to K$^+$, Na$^+$, Rb$^+$, Li$^+$, Cs$^+$, NH$_4^+$, in which selectivity Li$^+ < $ Na$^+ < $ K$^+ < $ Rb$^+ < $ Cs$^+$. 

When Prussian blue is oxidatively reduced the surface of the electrode, two pairs of reversible redox peaks may occur at near 0.8 V and 0.1 V. If the oxidizable and reducible substance on the surface of the electrode is changeable, the peak height changes accordingly. The half width of the reversible voltammogram was found to be greatly changed by the nature of the injected cations. [31] Other readily reduced compounds determined by the PB modified electrode include NO, cytochrome C, SO$_2$, acetylcysteine, and glutathione.

As for biosensor, the first-generation biosensor is based on oxygen reduction current, and it can directly use electrochemical methods to detect enzyme reactive substances or products. With an oxidant, oxygen can catalyze the oxidation of the substrate while releasing hydrogen peroxide. And we use a platinum electrode (or other noble metal electrode) to measure oxygen consumption (compared to AgCl) at -0.6 V to indirectly determine the substrate content. So, Halloran et al. developed a method for using Prussian blue modified carbon screen printed electrodes to detect hydrogen peroxide current. The detection limit of hydrogen peroxide was 0.4 mmol/L, the linear range was 0.4 to 100 mmol/L, and the sensitivity was 137 mA·(mmol·L)$^{-1}$·cm$^{-1}$.

Prussian blue film has a deep blue color, and its spectrum is compatible with low cost infrared light sources, such as diode laser and light emitting diode light source. The change of optical properties of Prussian blue film can be used as a basis for various chemical recognition. This makes PB a sensitive element of optical sensor. Lenarczuk reported a practical glucose sensor. The biosensor consists of chemically linked glucose oxidase with Prussian blue. Before the test, we use ascorbic acid to reduced Prussian blue to colorless Prussian white. During the assay, the enzyme catalyzes the oxidation of Prussian white to Prussian Blue by hydrogen peroxide. The maximum absorption peak was detected at 720 nm.

3.4. Application in Photochemistry

Photomagnetic is one of the attractive material property for its apparent technical applications in areas such as memory, and an important component of charge transfer induced spin transfer material (CTIST) is the Prussian blue analogue (PBA) syste, where long lifetime photo induced magnetic (PPIM) can coexist with long-range magnetic circuits. The photoinduced structural strain in CoFe PBA lattice results in the random magnetic anisotropy of the MCR PBA component, this is because the tight coupling of two crystal gratings by heterostructure geometry. Tokio Yamabe et al. reported that Co (III) can be generated from Fe(II) by irradiation of visible light irradiation, and it effectively enhanced the magnetization. Since this electron transfer is not a D-D transition on the same metal ion, so it can’t apply the law of Laplace, or if applicable, the rule may be relaxed with (CO, Fe) Prussian blue. [27]

Since there are more and more materials are available, the magnetic response optical switch is a growing field. Persistent photoinduced magnetism (PPIM) is an important example. If it has a long exposure, the long-term magnetization change does not occur over several weeks. [28] At first, synthetic heterostructure film consisting of two different Prussian blue analogues (one of which has a high TC and another is a photo active) was prepared by Daniel R. Talham et al. This arrangement results in a sustained photoinduced change of magnetization at high temperatures, which greatly inhibits the amount of Co-Fe material, and it is bistable.

Erkang Wang et al. [29] proposed a highly efficient fluorescence switching system based on a closed bipolar electrode (C-BPE) system, which has previously modified Au nanocluster (Au-NCs) on BPE monopole. Used as a fluorescent donor. Fluorescence quenching caused by the internal filtering effect was observed on the basis of the overlap of the Prussian blue absorption spectrum and the gold NCS fluorescence spectrum. In comparison with traditional three electrode systems, the introduction of BPE provides a simpler and more controllable fluorescence switch, which provides new ideas for the design of electron induced fluorescence switches, especially the integration of microdevices.
4. Conclusion
As an ancient dyestuff, Prussian blue still has many uses in modern chemistry, biology and medicine. Prussian blue can be used as electrode material, high quality catalyst or electron transport medium material in the field of electrochemistry, photochemistry and magnetism. Biologically, Prussian blue is often used as a raw material for biosensors. Molecular magnetic switches based on Prussian blue are also hot spots in current research. It is mainly used for hydrogen storage materials. Prussian blue is also used in the diagnosis and treatment of cancer. To sum up, the research and application of Prussian blue is still in the developing stage. It can be predicted that its application will be more and more in the future.

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