

# Transforming Prussian Blue Analogues: The Future-Centric Pathway to Rise of Thin Layered Double Hydroxides for Superior Water Oxidation. An Overview

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## Abstract:

Prussian blue analogues (PBAs)[1–5] have exhibited great performance towards electrochemical water oxidation because of their high activity and stability. However, there were some challenges because of their limited surface area and less accessible active sites. Herein this work, we have explored the synthesis of a Prussian blue analogue-based thin layered double hydroxide (PBA-TLDH)<sup>[6–9]</sup> through a reconstruction method. The (PBA-TLDH) possessed high surface area and a large number of active sites for enhanced electrochemical water oxidation. These PBA-LDH materials were well characterized by X-ray diffraction, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and electrochemical techniques<sup>[1,7,10–12]</sup>. The PBA-TLDH materials had a well-defined thin layered structure with the PBAs uniformly distributed in the interlayer spaces of the LDHs. The PBA-LDH catalyst showed enhanced electrocatalytic activity towards water oxidation, with a very low overpotentials up to 240 mV and current density of 10 mA cm<sup>-2</sup>,<sup>[9,13–16]</sup> have been achieved which is significantly lower than that of the pristine PBAs. Moreover, these thin layered double hydroxides material showed excellent stability over large electrochemical cycle. This work provides a new strategy for the design and synthesis of highly active and stable electrocatalysts for water oxidation.

**Keywords:** PBAs, LDHs, PBA-LDHs, Electrocatalyst, Water oxidation, Reconstruction, etc.

## Introduction:

Prussian blue analogues (PBAs) are very important class of co-ordination compound which is also known as Prussian blue substitutes or iron cyanides<sup>[17]</sup>. These (PBAs) compounds have a similar crystal structure and colour as Prussian blue but these compounds can be made using different chemical process. PBAs can be synthesized by combining different metal ions with cyanide ions, resulting in a range of colours from blue to green and even purple<sup>[18]</sup>.

One of the very important and famous Prussian blue analogues is copper hexacyanoferrate which exhibited blue-green colour and is extensively used as a pigment in paints and inks. Another renowned example of PBA is manganese hexacyanoferrate which has a purple colour and is sometimes used as a catalyst in chemical reactions.

The Prussian blue analogues were well explored having some similarities with Prussian blue, as well as

they may possess different chemical and physical properties. The PBAs having different physical and chemical properties rolled it out for a variety of extremely useful applications beyond traditional uses of Prussian blue. Prussian Blue analogues (PBAs) have recently attracted researchers' attention as promising catalysts for electrochemical water oxidation[19–22]. Layered double hydroxides (LDHs) are another important class of clay material that has been peculiar for its catalytic activity towards electrochemical water oxidation. Combining the properties of these two materials, PBAs and LDHs, to create a Prussian Blue analogue based layered double hydroxide (PBA-LDH) may offer advantages such as improved catalytic activity and stability.

### **The Role of Thin Layered Double Hydroxides (TLDHs)**

Thin Layered Double Hydroxides (TLDHs) represent a ground-breaking advancement in the field of catalysis, particularly in the context of water oxidation[23–25]. These materials, characterized by their unique layered structure, consist of positively charged metal hydroxide layers interleaved with anions and water molecules. This architectural configuration not only enhances their stability but also facilitates the efficient transfer of charge and mass, which are crucial for catalytic processes[13,23,26].

One of the most significant attributes of TLDHs is their tunability[9,27–29]. By varying the metal constituents and the interlayer anions, researchers can tailor the electronic and catalytic properties of these compounds to optimize their performance in specific reactions. For water oxidation, this tunability is particularly beneficial, as it allows for the fine-tuning of the active sites responsible for the catalysis. Metals such as nickel, cobalt, and manganese can be incorporated into the TLDH structure, each contributing unique properties that enhance the overall catalytic efficiency[9,21,30–33].

Moreover, TLDHs have shown remarkable stability under reaction conditions, a critical factor for any catalytic material. Their layered structure provides a protective environment that minimizes degradation, ensuring prolonged activity during water oxidation processes. This stability is complemented by their ability to form well-defined active sites, which are essential for driving the water-splitting reaction efficiently[16,30].

Recent studies have demonstrated that TLDHs can achieve high turnover frequencies while maintaining low overpotentials, making them highly efficient catalysts compared to traditional materials. Their ability to facilitate electron transfer while simultaneously promoting the adsorption of reactants makes them ideal candidates for integration into photoelectrochemical cells and other renewable energy technologies.

In summary, the rise of Thin Layered Double Hydroxides marks a significant turning point in the quest for effective water oxidation catalysts[9,24,27,28,34]. Their unique structural properties, coupled with their tunability and stability, position them as frontrunners in the development of next-generation catalytic systems aimed at sustainable energy solutions. As research continues to unravel the potential of TLDHs, their impact on the field of catalysis is poised to grow, paving the way for innovative applications in energy conversion and storage.

### **Structural Characteristics**

Prussian blue analogue (PBA) derived layered double hydroxides (LDH) can be prepared through a co-precipitation method[5,21,35–41]. In co-precipitation method Prussian blue analogues and layered double hydroxides are mixed together in solution and these two materials allowed to form a solid material through a precipitation reaction. In this way the resulting PBA-LDH material has a layered structure with the PBAs incorporated into the layers of the LDHs.

The PBA-LDHs showed enhanced electrochemical water oxidation activity which has been well studied by cyclic voltammetry and chronoamperometry technique. These types of catalysts have shown the high catalytic activity towards electrochemical water oxidation, having quite low overpotentials for the oxidation reaction taking place. The additional characteristics of these PBA-LDHs are high stability towards long time electrochemical cycle, which making them excellent materials for use in electrochemical water oxidation applications.

**Reconstruction of PBA in to thin Layered Double Hydroxide.**

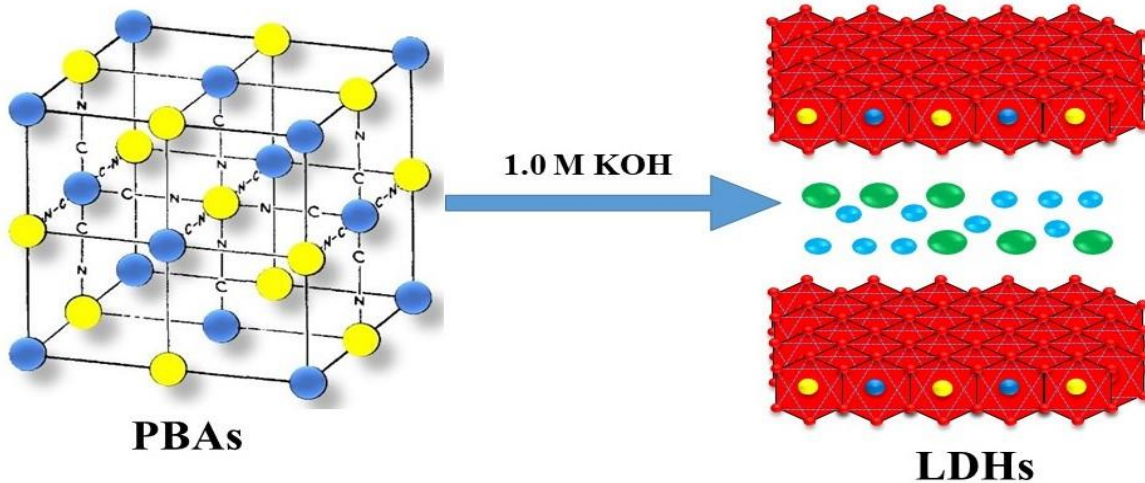


Fig- Schematic structural reconstruction of Prussian blue analogue into thin layered double hydroxide[42] The structural, compositional and other properties of these two material Prussian blue analogues and layered double hydroxides are different. However thin layered double hydroxide can be easily prepared by utilising Prussian blue analogues as a precursor material.

Prussian blue analogues (PBAs) are polymers of co-ordination Compounds[43] these co-ordination compound contains transition metal ions (such as Fe, Co, Ni) which are co-ordinated with cyanide ligands[43,44]. Prussian Blue Analogues have a cubical morphology or tetragonal crystal structure. In cubic morphology consist of corner-sharing octahedral units. When we look forward for structural pattern of layered double hydroxides (LDHs) then these are anionic clays that consist of positively charged metal hydroxide layers stacked with interlayer anions, such as carbonate or nitrate ions. Layered Doubled Hydroxides have a layered structure with a brucite-like arrangement of cations and hydroxide anions.

**Result and Discussion**

When PBA is dissolves in suitable solvent and in alkaline then its transformed by subsequent reconstruction into Layered Double Hydroxides. One of the most renowned methods involves the use of hydrazine to reduce the metal ions in PBAs to their lower oxidation states and create metal hydroxide species, which is then reconstructed in to LDHs.[27,45]

The process of structural reconstruction of PBAs into thin LDHs can be summarized as follows:

- The Prussian Blue Analogues precursor is dissolved in a suitable solvent, such as water or ethanol[22,46–48].
- The reducing agent added, such as hydrazine or sodium borohydride, to the solution to reduce the metal ions to their lower oxidation states[43,49,50].
- The pH of the solution is adjusted to promote the formation of metal hydroxide species[29].

- Now solution is allowed to age or undergo hydrothermal treatment to allow for the reassembly of the metal hydroxide species into Thin Layered Double Hydroxides[22,25,33,51].
- The resulting Thin Layered Double Hydroxides is collected by filtration or centrifugation, and wash and dry the product[22,23,39,52,53].

The Thin Layered Double Hydroxides thus formed possessed a layered structure with a brucite-like arrangement of cations and hydroxide anions, which resembles with natural LDHs[42,54] The actual structure and composition of the resulting material will depend on the specific PBA precursor used, the choice of solvent and reducing agent, and the reaction conditions.

### Conclusion:

Herein we conclude that the reconstruction of Prussian blue analogues (PBAs) into thin layered double hydroxides (TLDHs) can be achieved through a reconstruction method which has been shown to provide a promising approach for the development of efficient and stable electrocatalysts for electrochemical water oxidation[21,55]. The PBA-TLDH material form in this way exhibits a well-defined layered structure having a high surface area and a large number of accessible active sites, which showed enhanced electrochemical catalytic activity towards oxidation of water.

The demonstration of electrochemical measurements has revealed that PBA-TLDH has a very low overpotential than pristine PBAs, which indicated its higher electrochemical catalytic activity towards water oxidation. Further, the synthesized PBA-TLDH material shows excellent stability over extended electrochemical cycling, which making it a promising candidate for practical water oxidation applications. Overall, this work provides an approach for the design and synthesis of high-performance electrocatalysts for water oxidation by combining the unique properties of PBAs and TLDHs. Further studies can be conducted to explore the potential of PBA-TLDH in other electrocatalytic applications and to optimize the synthesis conditions for further improvements in performance.

Overall, the combination of PBAs and LDHs to form PBA-LDHs offers a promising approach for the development of efficient and stable catalysts for electrochemical water oxidation.

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