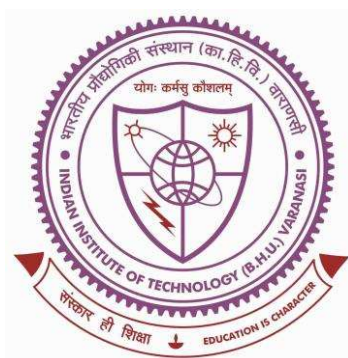


Alkoxysilane Mediated Synthesis of Prussian Blue Nanoparticles and its Catalytic Applications



**Thesis submitted in partial fulfillment for the
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By

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SUMMARY

The thesis entitled “Functional Alkoxysilane Mediated Synthesis of Prussian Blue Nanoparticles and its Catalytic Applications” is divided into five chapters.

- General Introduction.
- Functional Alkoxysilane Mediated Controlled Synthesis of Prussian blue nanoparticles, Enabling Silica-Alginate Bead Development; Nanomaterial for Selective Electrochemical Sensing.
- Synthesis and Application of Functional Prussian Blue Nanoparticles for Toxic Dye Degradation.
- Synthesis of Prussian Blue Nanoparticles-Embedded Heterogeneous Catalyst for Hydrogen Peroxide Detection.
- Palladium-Prussian Blue Nanoparticles; As Homogeneous and Heterogeneous Electrocatalysts.

Chapter I

This section gives a brief overview of synthesis, properties and applications of the Prussian blue nanoparticles (PBN). Different methods available for the synthesis of PBN have been described with its well-known advantages in this section. The significant characteristics (electrochemical, electrochromic, electro-catalysis, photo-physical, magnetic, ion exchange, etc.) and sustainable applications of PBN (viz. electrochemical sensors, biosensors, transducer, and photo-Fenton catalyst, etc.) have been conferred briefly. The control synthesis and the significance of nano-geometry over material's catalytic activity have been correspondingly focused. Thus, the origin, objective and the work plan of the current research have been itemized precisely.

Chapter II

Since the synthesis of PB often encountered many obstacles associated with their practical functionality, it directed to systematic search on the control synthetic protocol and appliance of the same to eliminate the problems associated to practical applications of this pigment. A novel and flexible synthetic approach for PBN preparation via 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (EETMSi) and tetrahydrofuran-hydroperoxide (THF-HPO) has been illustrated in this chapter. It is established that EETMSi act as a reducing agent as well as a stabilizing agent, which controls the dimension and crystallinity of as-synthesized PBN. EETMSi emerged as a promising solution during this investigation which regulates the particle size as a function of its molar concentration followed by stabilization of the same. The resultant nanoparticles are utilized as competent peroxidase candidate, which proposes the size-dependent catalytic efficiencies towards H_2O_2 and attained lower K_m value concerning smaller-sized PBN. The absorption maxima of the resulting PBN is found to be dependent upon nano-dimension of particle. These chemical reduction processes result into a hydrophobic reaction product that controls the dispersibility of resulting PBN in both aqueous and several organic solvents. The fabricated nanostructures demonstrated as the suitable material for the development of stable mesoporous silica-alginate beads with controlled pores (9-26 nm), intended for successful encapsulation of even smaller-sized PBN within the complex matrix. The developed bead represented the potentiality towards selective electrochemical sensing of pyrogallol.

The experimental finding demonstrates that EETMSi could tune the dimension of PBN on employing desired alkoxy silanes (EETMSi) content. Consequently, as-synthesize PBN displays the size-dependent electrochemical and catalytic activity towards hydrogen peroxide (H_2O_2) at nanoparticles modified electrodes. Besides the EETMSi also allows the fabrication of PBN doped calcium-alginate beads via successful encapsulation of nanoscale particles within porous silica-alginate beads, which allocates selective electrochemical oxidation of pyrogallol (Py). EETMSi emerges here as a promising finding throughout the investigation which also stabilizes nanoparticles via a resultant hydrophobic reaction product and enhances the dispersibility in various solvents (water, methanol, acetone, tetrahydrofuran, dimethyl sulfoxide, *etc.*).

Chapter III

This section describes a facile chemical reduction method using EETMSi and cyclohexanone to synthesize nanoparticles of different sizes and morphology, viz. nano-cubes and nano-sphere. Here, EETMSi and cyclohexanone facilitate the formation of PBN of controlled nanogeometry, dependent upon the elected alkoxy silane concentration. The effect of alkoxy silane concentration over the size of PBN was monitored, which established that increase in nano-dimension and morphology of PBN was noticeably transforming from large-sized nano-cubes to tiny spherical particles, as a result of the increasing EETMSi concentration. The flexibility in this methodology allows the manufacturing of PBN of desired size at elected EETMSi and Cyclohexanone concentration. Moreover, synthesized PBN has been applied as a photo-Fenton catalyst and similarly, their photodegradation ability has been attempted by several means like RT, UV-radiation, solar light and heating conditions. The advanced photo-Fenton process accomplished with different nanostructured simplified better performance of smaller-sized than the larger ones under solar radiation. The nanoparticles degradation ability was also observed to influence via H_2O_2 concentration variation. However, individually PBN or H_2O_2 shows the negligible amount of degradation, while attempted in similar solar irradiation.

In particular, the photodegradation method attempted individually with PBN or H_2O_2 in solar irradiation shows a quiet extent of degradation. Out of all the nanostructures, the smaller-sized PBN possessed high catalytic activity towards the targeted dye. The outcomes indicate that the degradation efficiency for RhB are as follows; $(PBN_4-H_2O_2) > (PBN_3-H_2O_2) > (PBN_2-H_2O_2) > (PBN_1-H_2O_2) > H_2O_2$. In addition, it was observed that PBN possesses superior and favourable photo-Fenton catalytic ability at low pH (3). The kinetics of the degradation process was evaluated with different parameters and it was found to follow a pseudo-first-order kinetics. LC-MS analysis has been performed to determine the extent of mineralization and non-toxic impact of the degradation process. The finding also emphasized on the recyclability of the material after the degradation process. In addition, characterization of the catalyst by ATR, and TEM techniques was performed to observe the consequences of degradation process over it.

The outcomes indicate that EETMSi influences both the morphology and the diameter of nanoparticles in the collaboration of cyclohexanone. The catalytic ability of nanomaterials has been examined towards toxicant which elucidates a promising approach of functional PBN / H₂O₂ combination towards Rhodamine B (RhB) degradation via in-situ generated free radical, depending on the preferred reaction conditions (acidic/basic). This work confers and invent the functional PBN as a very effective photo-Fenton recyclable catalyst for dye degradation, which follows the pseudo-first-order kinetics and endeavors a higher rate constant (0.9353 min⁻¹) as compared to others previous reports.

Chapter IV

A novel and simple approach has been attempted to develop PBN@SiO₂ using EETMSi and cyclohexanone from single precursor potassium ferricyanide. The chemical reduction method productively conquered the cubic and spherical shaped nanoparticles over SiO₂. The fabricated heterogeneous matrix PBN@SiO₂ has been characterized by different methods that exhibit the successful modulation of crystalline PBN over amorphous PBN@SiO₂. The obtained nanostructure demonstrated the peroxidase mimetic ability and catalytic activity regarding H₂O₂. The absorption maxima for the oxidized peroxidase substrate is found to be dependent of the elected H₂O₂ concentration. Besides, the differential pulse voltammogram investigation anticipated a sequential change in the redox peak current of PBN, dependent upon the analyte concentration variation.

Here, a novel approach has been explored for the heterogeneous modulation, via successfully incorporating these homogeneous nanodispersion of PBN within and over the designated suspension matrix; silica (SiO₂) while retaining its catalytic ability. The nanostructured heterogeneous matrix PBN@SiO₂ similarly displays the peroxidase mimetic like catalytic activity towards H₂O₂ molecule.

Chapter V

Appliance of THF-HPO along with 3-APTMS during the synthesis of palladium nanoparticles (PdNP), and a comparative study on the role of nano-size of palladium over PBN's catalytic ability was investigated in this section. This study proposes a facile and effective methodology that involves the active participation of 3-APTMS and THF-HPO to fabricate the PB-PdNP. Here, THF-HPO allows the conversion of potassium ferricyanide into PBN and 3-APTMS capped palladium ion to PdNP. The possibility of mixing of PBN and palladium nanoparticles of variable nano-geometry enables the formation of nano-dispersion, which possess the catalytic activity as a function of palladium nano-dimension in both homogeneous and heterogeneous phases. The PdNP (PdNP₁ and PdNP₂) differs from each other in many aspects such as catalytic ability and stability. These 3-APTMS capped nanomaterials show functional ability to form homogeneous nano-suspension to perform as a homogeneous catalyst with PBN for specific applications. The as-fabricated PB-PdNP₁ and PdNP₂ have been introduced into graphitic material to explore heterogeneous catalysis. The outcomes reveal that, among the different systems, one with smaller sized PdNP (PdNP₂) was found to be highly active materials, illuminating the enhancement in analytical performances of these PBN materials as a function of palladium nano-dimension. Observations based on cyclic voltammetry, amperometry, peroxidase mimetic and electrocatalytic activity indicate the improved electrochemical property as a function of nano-geometry. The advanced system, PB-PdNP₂ modified enzyme electrode, was developed and examined for in-situ generated H₂O₂ from the GOx-glucose system. Both mimetic and electrocatalytic ability, discovered for probing glucose oxidase catalyzed reactions, justifying the potential sustainability of nanomaterials in biomedical applications.

Chapter V study about the possibility of noble metal influence over PBN catalytic ability through fabricating Pd-PBN system by opting THF-HPO mediated synthesize PBN in combination with 3-APTMS capped PdNP. The as-synthesized PB-PdNP₁ and PB-PdNP₂ own

potential to use as homogeneous and heterogeneous matrix and reveal the improvement in analytical performances of these nanomaterials as a function of palladium nano-dimension. The resulting nanomaterials suspensions efficiently probe the glucose oxidase catalysed reaction based on peroxidase mimetic ability and also display excellent electrocatalytic activity during the electrochemical sensing of H_2O_2 .

FUTURE PROJECTION

The thesis addresses the challenges accompanying the amalgamation of processable Prussian blue nanoparticles (PBN) based materials having a large variety of applications. Current study deals with the synthesis of functionalized PBN involving the active participation of EETMSi and several other reducing agents, including THF-H₂O₂ and cyclohexanone. Depending upon the reducing agent used, these nanoparticles differ in their morphology, size and catalytic activities. Accordingly, a variety of other reducing agents could also be exploited with EETMSi, which remained unexplored so far, to attain more tuned nano-geometry. Moreover, the appliance of current work reflects the electro-catalysis and mimetic potentiality of PBN, which was found worth of chemical sensing of biologically significant analytes viz. hydrogen peroxide, dopamine and pyrogallol. However, the properties concerned with the optical, magnetic and secondary cells of these PBN based materials have not been considered herein, which could be advantageous for the innovation of practical devices.

Prussian blue analogues (PBAs) has reportedly demonstrated a better peroxidase mimetic activity compared to PBN. Subsequently, such mixed metal analogues (PBAs) could also be derived from the current methodology and may be explored during the electro-catalytic process. Besides, the synthesis of nanocomposites materials could also be attempted to reflect the material's possibility in sensor development with improved sensing ability towards analytes. Functional alkoxy silanes have been exploited for the development of thin-film in different chemical and biosensors. Consequently these PBN, derived through novel methodology, can further be investigated for in-situ encapsulation within a nanostructured matrix having potentiality in electro-catalysis and bio-catalysis. Alkoxy silane has been used to fabricate mesoporous silica nanoparticles with viability for biomedical applications since such nanomaterials are non-toxic. The current methodology can support incorporating PBN and other biocompatible metal nanoparticles within mesoporous silica nanoparticles and could be specifically applied in drug delivery, bio-imaging, etc. due to the unique merits of as-derived materials. Since, synthesized PBN has also been explored as a photo-Fenton reagent and being proficient in dye degradation process at the fastest rate and possessing recyclability, accordingly catalytic ability of

nanomaterials can be investigated for the treatment of other persistent toxicants. Thus, considering the advantages of EETMSi during the chemical synthesis routes, acceleration in properties of PBN and subsequent novel applications in various significant fields needs to be considered in the future.