

PREFACE

Extensive employ of nanoscale material “Prussian blue nanoparticles (PBN)” in the discipline of sensing, catalysis, and electrochromic device development is reasonable to the distinctive physical and chemical characteristics they possess, which has been directed to a surge in its synthesis protocols. Fabricating these chemical sensors, prominent to high catalytic efficiency with selectivity and sensitivity, is one of the foremost challenges of the current research. Meanwhile, several techniques viz. chemical and electrochemical procedures are avail for the Prussian blue (PB) synthesis and often deals with some limitations; (i) Chemical synthesis procured PBN often deals with instantaneous nucleation and leads to the formation of an unstable, agglomerated and large-sized nanoparticles; (ii) PBN, fabricated through electrochemical techniques, possess the disadvantages of their large-scale producibility and meanwhile covering a limited range of applicability; (iii) The PBN, synthesized through conventional procedures, restricts the dispersibility of these nanomaterials in various solvents and accordingly decline their obvious utility for the practical means; (iv) Modulation of homogeneous nano-suspension of PBN to the stable heterogeneous nanomatrix over solid support by retaining its catalytic potentiality. The synthesis of PB often encountered many obstacles associated with their practical functionality, directed to systematic search on the control synthetic protocol and appliance of the same to eliminate the problems. Thus, there is a need to devise a method that can produce stable, less agglomerated colloidal dispersion of PBN with intrinsic characteristics and enhanced catalytic property, along with the ability to convert the homogeneous nano-suspension to heterogeneous system endeavouring similar catalytic efficiency. This constitutes the theme of the current research program integrated with the active participation of functional alkoxy silane to resolve with the stringent issues and develop an effective mechanism for yielding novel nanostructured PBN materials.

Functional alkoxy silane like 3-aminopropyltrimethoxysilane (3-APTMS), 3-glycidoxypropyltrimethoxysilane (3-GPTMS), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (EETMSi), trimethoxysilane (TMS), etc., have been applied for the amalgamation of nanomaterials through sol-gel techniques. Some of these functional alkoxy silanes like; 3-APTMS, 3-GPTMS, and EETMSi have the potential to perform as a reducing agent during the

palladium nanoparticles (PdNP) synthesis, and simultaneously allows the introduction of Pd within a nanostructured complex of organically modified silicates through interacting with PdCl₂. Such finding established EETMSi as a reducing agent for noble metal ion and directed to examine the functionality of alkoxy silane during PBN synthesis and its heterogeneous fabrication, which remained concealed before the current research.

The present study describes utility of functional EETMSi for synthesis of PBN from a single-source potassium ferricyanide in the presence of organic reducing agents such as tetrahydrofuran-hydroperoxide (THF-HPO) and cyclohexanone. Besides, these protocols have been attempted with variation in EETMSi content to switch the nano-dimensions and, in turn, to its catalytic performance. EETMSi here stabilizes nanoparticles via a resultant hydrophobic reaction product and enhances the dispersibility in various solvents (water, methanol, acetone, tetrahydrofuran, dimethyl sulfoxide, etc.). The process was extensively explored for the heterogeneous modulation, as EETMSi correspondingly allow the successful incorporation of homogeneous nanodispersion over and within the designated suspension matrix; silica (SiO₂) via retaining its catalytic ability. The study has been further extended with the noble metal impact over peroxidase mimetic activity of PBN, which was examined through fabricated Pd-PBN system by opting THF-HPO mediated synthesis of PBN in combination with 3-APTMS capped PdNP.

This work has been organized into five chapters with Summary and Future Projection where the influential role of EETMSi has been investigated and discussed from different perspectives in an elementary means. Chapter (I) 'General Introduction' incorporates with reviews of the present status of the subject, included with the outcome of earlier studies performed on the PB and its analogues and validate the reason for embarking upon the current study, along with a precise interpretation of the origin, objectives, and work design to the corresponding research program. Chapter (II) deals with the synthetic strategy for PBN formation using EETMSi in the presence of THF-HPO. The dimension of PBN was found to be the function of EETMSi concentration variation which displays size-dependent electrochemical and catalytic activity towards hydrogen peroxide (H₂O₂).

Apart from that, fabrication of PBN doped calcium alginate beads was attempted, allocating selective electrochemical oxidation of pyrogallol. The EETMSi here emerged as a promising finding that controls the size of PBN, followed by stabilizing and enhancing its dispersibility in both aqueous and various organic solvent. Chapter (III) describe the strategic ability of functional EETMSi with organic agent cyclohexanone in the course of PBN synthesis of different size and morphology. Functional PBN/H₂O₂ combination elucidates a promising approach for treating toxicant dye Rhodamine B (RhB) by in-situ generated free radicals through the photo-Fenton process. The degradation process has been observed to be influence by each parameters and attempting a higher rate constant in the acidic condition. The photo-Fenton process simplified the better performance of smaller-sized particles and conferred the functional PBN as an inexpensive, eco-friendly, recyclable, and more effective photo-Fenton catalyst. Chapter (IV) deals with a method that can produce stable and less agglomerated colloidal dispersion of PBN along with the ability to convert the homogeneous nano-suspension to heterogeneous systems endeavouring similar catalytic property towards H₂O₂ molecules. Further synergistic interactions between noble metal components with PBN have been studied in chapter (V) by fabricating the Pd-PBN system by opting THF-HPO mediated synthesise PBN in amalgamation of 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-dimensions. The resulting nanomaterial suspensions efficiently probe the glucose oxidase catalysed reaction based on peroxidase mimetic ability and display an excellent electrocatalytic activity during the electrochemical sensing of H₂O₂.

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