Rietveld Refinement of Palladium immobilized on \( \text{Zn}_3[\text{Fe(CN)}_6]2.1.33\text{H}_2\text{O}19.22/\text{SiO}_2 \) Nanocomposite prepared by Coprecipitation Method.

Ankita Gupta\(^1\) and Sunil Rohilla\(^2\)*

\(^1\)Department of Physics, Shri jagdishprasad Jhabarmal Tibrewala University, Jhunjhunu-333001, India
\(^2\)*Department of Physics, BRCM College of Engineering and Technology, Bhiwani- 127028, India

E-mail: *sunil78rohilla@gmail.com

Abstract: This research article presents the synthesis and Rietveld Refinement of Palladium on the \( \text{SiO}_2 \) doped Prussian Blue compound i.e. \( \text{Pd}@\text{Zn}_3[\text{Fe(CN)}_6]_{2.1.33}\text{H}_2\text{O}19.22/\text{SiO}_2 \). Synthesis was carried out by wet chemical Coprecipitation method. The X-ray Diffraction (XRD) analysis was applied to study the structural parameters. The refinement of XRD data was done by using Fullprof suit software. For obtaining microstructural parameters, we had done the Rietveld Refinement. It provides parameters like interatomic distance, Wyckoff position etc. The Bragg R factor, \( R_p \) value, \( R_{exp} \) value were also calculated. The result of rietveld refinement reveals that the crystal had \( \text{Fm}3\text{m} \) space group geometry. Applications of Prussian blue were also mentioned in the presented paper.

1. INTRODUCTION

In the periodic table, Palladium belongs to group 10th. But its configuration is typically difficult on comparing with its group members like Ni, Pt, and Ds. The electrical configuration of palladium is 4d\(^{10}\) 5s\(^{0}\). Palladium has low melting point, it is low dense when compare with its other member of groups i.e. Ruthenium, Rhodium, Osmium, Iridium, platinum etc. Solubilized of Palladium is in nitric acid, and sulfuric acid (hot) is very slow. Cost of palladium is very high. Palladium shows good catalytic activity but its price limits to use it on a large scale.

Prussian Blue indicated by the common formula \( \text{KFeIII}[\text{FeII}(\text{CN})_6] \), prepared by mixing the colorless solutions of iron(III) in the form of ferric chloride in a stirred solution of iron(II) in the form of hexacyanoferrate(II). The Prussian blue compound fascinates the researchers because of their properties.\(^{[1]}\) These fascinating properties are catalysis property, shows electrochromic properties, easy method of synthesis, and most important its low cost. An easy and efficient method for preparation of palladium immobilized PB was done by Co-Precipitation method. Recently many research groups have reported on the study of the properties of Prussian blue and shows that due to its electrochemically active nature, high specific surface area, controllable structure, adjustable pore size and high thermal stability, photo-physical, and magnetic properties, ease of preparation and low-cost productivity, allow using in the development of sensors, solid batteries, secondary batteries, electrochromic devices, fuel cells, opto-magnetic devices, removal of cesium from water, photo-magnetism, seawater desalination \(^{[2-10]}\)

In this work, we fabricate Palladium on the \( \text{SiO}_2 \) doped Prussian Blue compound i.e. \( \text{Pd}@\text{Zn}_3[\text{FeC}_8\text{N}_6]_{2.1.33}\text{H}_2\text{O}19.22/\text{SiO}_2 \) and report the particle size characterization of composites by XRD and Rietveld refinement of the sample. In order to investigate the phase, crystal structure of the sample, we apply X-Ray Diffraction analysis. The Refinement from Fullprof Suit Software is adopted in this work for obtained various parameters of the structures in range of nanometers. Refinement is a treatment of XRD powder to obtain some particular parameters of the achieved sample.
2. EXPERIMENTAL DETAILS

Here we used a wet chemical Coprecipitation approach for the synthesis of Pd@Zn$_3$[Fe(CN)$_6$]$_2$.1.33H$_2$O19.22/SiO$_2$.

2.1 Chemical Used
The high purity used chemicals: KFeC$_6$N$_6$ (99.99% pure from the Sigma Aldrich company), Zinc Sulphate heptahydrate (99.99% pure from the Sigma Aldrich company), KCl (99.99% pure from the Sigma Aldrich company), HCl (37%), and Deionized water.

2.2 Method of Preparation
Step1 For synthesis of Zn$_3$[Fe(CN)$_6$]$_2$.1.33H$_2$O19.22:- The nanoparticle was synthesized by dropping the solution of K$_3$[FeC$_6$N$_6$] (25 mmol concentration, 50 ml deionized water) in a solution of 25 mmol ZnSO$_4$.7H$_2$O which was stirred in 50 ml DI water with the help of magnetic stirrer. The Pale green precipitate was filtered and washed many times with water which was deionized.

Step2 For synthesis of amorphous SiO$_2$: The suspension of amorphous of silica oxide was formed according to method given in the literature. [11]

Step3 for obtaining resultant suspension, step1 was doped in the suspension of step2 and was mixed smoothly with the help of stirrer for 7h at a constant speed.

Step4 To this mixture, Palladium-diacetate of 0.25 g was mixed in the existence of acetone of 380 ml and again agitated for 36 hours. The solid was parted by magnetic decantation again and again. At room temperature, we washed the obtained magnetic catalyst again and again with acetone and dried in vacuum overnight in order to get palladium catalyst immobilized on superparamagnetic nanoparticles.

3. RESULT AND DISCUSSION

3.1 XRD Analysis
In order to obtain the crystal parameters of the nanoparticles before Pd immobilized on Prussian blue composite nanoparticles and after immobilization of palladium on the Prussian blue composite, we used X-Ray Diffraction. XRD pattern with and without Pd was shown in figure 1 & 2 and shows cubic type structure. Figure 1 & 2 shows that the XRD patterns of as-prepared (with and without palladium), both shows hump at around 21° corresponding to the amorphous matrix of silica oxide. Figure 1 & 2 shows a very strong diffraction peak at 17.194(002), and the other peaks occurred at 14.876(111), 24.40(022), 34.79(004), 39.054(024), 42.958(224), 50.023(044), and 53.288(244). These peaks show the prepared sample was of Zn$_3$[Fe(CN)$_6$]$_2$.1.33H$_2$O19.22 and matched with JCPDF No:-751257. The (hkl) value, intensity, 2θ, value of d-spacing, FWHM, value of dislocation density, Size of crystal, correlated phase and microstrain value of the above ready sample was obtained from XRD as shown in Table 1.

| No. | 2Theta | d-spacing | Int. | (hkl) | FWHM | Crystallite Size (nm) |
|-----|--------|-----------|------|-------|------|----------------------|
| 1   | 14.876 | 5.9503    | 125.01 | (111) | 1.21 | 6.92                 |
| 2   | 17.194 | 5.1531    | 1270.29 | (002) | 0.36 | 23.32                |
| 3   | 24.409 | 3.6438    | 803.50 | (022) | 5.74 | 1.48                 |
| 4   | 34.791 | 2.5766    | 664.49 | (004) | 3.57 | 2.44                 |
| 5   | 39.054 | 2.3045    | 530.07 | (024) | 3.82 | 2.31                 |
| 6   | 42.958 | 2.1037    | 190.21 | (224) | 6.46 | 1.38                 |
| 7   | 50.023 | 1.8219    | 406.95 | (044) | 2.8  | 3.27                 |
| 8   | 53.288 | 1.7177    | 146.81 | (244) | 15.4 | 0.60                 |

Table1: Structural parameters of Zn$_3$[Fe (CN)$_6$]$_2$.1.33 H$_2$O19.22/SiO$_2$ Achieved from X-ray Diffraction Pattern.
Size of the crystal was determined by the Scherrer’s formula which is given below:

\[
\text{Size of Crystal} = \frac{0.9 \times \lambda}{FWHM \times \cos \theta}
\]  

From table 1, the size of crystal was calculated on average of most intense peak in xrd pattern i.e. at 2θ - 17.194, 24.409, and 34.791 degree value. The calculated average crystal size was 9.08 in order of nm.

### 3.2 Rietveld Refinement Analysis

This refinement is that refinement which performed on the pattern of X-ray diffraction. We can’t do this refinement without having xrd pattern of the powder. The obtained XRD pattern was then undergoes in a set of adjustment for obtaining that XRD pattern data which provides the structural and diffraction profiles of super paramagnetic nanoparticles. In this method of refinement of powder, least square refinements were carried out until we got best fit. This method helps to achieve all crystal structural information from the 2θ data of powder diffraction [12]. In rietveld refinement, we have to adjust cell and some other parameters like positions of atoms, occupancy, orientation etc. Main parameters like scale factor, orientation, lattice parameter, position of atoms are refined in rietveld refinement process. Chebyshev polynomial was used for background correction. Pseudo-Voigt having asymmetry function was used for modelling the peak profile function. These things are repeated until we get chi square factor. The profile of XRD data is fitted with the Rietveld Refinement and
obtained spectra of Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22/SiO$_2$, Pd@Zn$_3$[Fe (CN) $_6$)$_2$1.33 H$_2$O19.22/SiO$_2$ was shown in Figure 3 and Figure 4 respectively. This also allows finding Wyckoff position and occupancy. These values are shown in below Table 2 for Zn$_3$[Fe (CN) $_6$)$_2$1.33 H$_2$O19.22.

Table 2: Parameter of different atoms achieved from refinement of Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22

| Atom | Occ. | Wyck. |
|------|------|-------|
| O1   | 0.04166 | 24e   |
| O2   | 0.01400 | 32f   |
| O3   | 0.02833 | 32f   |
| N4   | 0.08334 | 24e   |
| C5   | 0.08334 | 24e   |
| Fe6  | 0.01389 | 4a    |
| O7   | 0.01421 | 8c    |
| Zn8  | 0.02083 | 4b    |
| O9   | 0.00192 | 4a    |

Figure 3: Refinement of Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22/SiO$_2$ XRD pattern

Figure 4: Refinement of Pd@Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22/SiO$_2$ XRD pattern

The refined parameters from Rietveld Refinement of Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22,Pd@Zn$_3$[FeC$_6$N$_6$)$_2$1.33 H$_2$O19.22 was shown in table no. 3 and 4 respectively.

Table 3: Results obtained from refined parameters of Zn$_3$[Fe (CN) $_6$)$_2$1.33 H$_2$O19.22/SiO$_2$ of cubic crystal structure of space group Fm-3m.

| S.No. | $\chi^2$ | $R_p$ | $R_{wp}$ | $R_{exp}$ |
|-------|----------|-------|----------|-----------|
| 1     | 1.80     | 20.5  | 21.8     | 16.23     |

Table 4: Results obtained from refined parameters of Pd@ Zn$_3$[Fe (CN) $_6$)$_2$1.33 H$_2$O19.22/SiO$_2$ of cubic crystal structure of space group Fm-3m.

| S.No. | $\chi^2$ | $R_p$ % | $R_{wp}$ % | $R_{exp}$ % |
|-------|----------|---------|-----------|------------|
| 1     | 0.417    | 0.64    | 0.29      | 0.45       |
4. CONCLUSION

The Coprecipitation approach was used for synthesized the sample of Zn₃[Fe(CN)₆]₂·1.33 H₂O₁₉.₂₂/SiO₂ and Pd@Zn₃[Fe(CN)₆]₂·1.33 H₂O₁₉.₂₂/SiO₂. The prepared sample was found to be of cubic crystal structure with Fm-3m space group. The refinement of samples was successfully done by Fullprof Software. Obtained values of all R-Factor were of low value. Hence, there was good agreement amongst the data.

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