

## PREPARATION OF PVP MODIFIED $\text{CoFe}_2\text{O}_4$ NANOPARTICLES AND ITS DISPERSION IN ETHANOL

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### ABSTRACT

**In this paper  $\text{CoFe}_2\text{O}_4$  ultrafine particles of 2nm have been prepared by precipitation method and modified by Poly-vinyl pyrrolidone (PVP). Confirmation of the formation of PVP@  $\text{CoFe}_2\text{O}_4$  (PVP modified  $\text{CoFe}_2\text{O}_4$ ) was characterized by XRD, EDX and FTIR comprised analysis. And the size, shape, nature of sample was analyzed and discussed using TEM, XRD. Hydrodynamic size was characterized by PSD-DLS after the ultrasonic ton treatment on the dispersed PVP/ $\text{CoFe}_2\text{O}_4$  powder in an ethanol which has been compared to the TEM and XRD estimate. The zeta-potential and conductivity have been analyzed for the varying weight concentration of powder in ethanol dispersion. The nature of PVP@  $\text{CoFe}_2\text{O}_4$  powder in ethanol dispersion in term of shift was analyzed using the zeta potential and rendering this study to the stability and the nature for the negative and positive potential.**

**KEYWORDS :** PVP coating, Ethanol dispersion,  $\text{CoFe}_2\text{O}_4$

The assembly of Polyvinyl Pyrrolidone (PVP) on ultrafine  $\text{CoFe}_2\text{O}_4$  magnetic NPs depends on the dispersion solvent and the use of solvent which can stabilize the magnetic NP (Chowdhury, 2012). He has discussed the water dispersion of PVP/  $\text{CoFe}_2\text{O}_4$  will give longer chain assembly on application of unidirectional magnetic field and with toluene dispersion of PVP@  $\text{CoFe}_2\text{O}_4$  NPs few assemblies/no assembly on applying magnetic field. He has studied PVP@  $\text{CoFe}_2\text{O}_4$  using water, toluene and ethanol. According to (Katalin et. al., 2012) the nanoparticles were generally dispersed in ethanol and the number-weighted particle size distribution was detected by DLS. Water is avoided for the DLS measurements to avoid the aggregation of the particles in water. In a DLS analysis the size of Cobalt ferrite seems increasing from ethanol, water, CTAB and NaDS as 2X, 3X, 4X and 5X respectively compare to the size by SEM an SAX analysis. They have discussed bigger diameter of particles in water than in an ethanol solution was due to the larger dipole moment of water than ethanol and resulting in a stronger connection of solvent molecules to the particle surface. So many things like aggregation, agglomeration, surface modification/coating affect the sample's original size and results in larger particle size in a DLS output (indirect technique). Zeta potential measurements can be verifying the surface modification effect as a function of concentration of PVP@  $\text{CoFe}_2\text{O}_4$  in Ethanol. The particles which were well dispersed and size regulated according to the MNP group (Kang et. al., 2013) also affected the Zeta potential. After the powder dispersed in an ethanol by varying its concentration, the stability must be affected. Pre added PVP in precursor solvent have not observed. This could lead to coating of the just precipitated

Cobalt ferrite particle by nucleation and stop its growth give ultrafine monodispersed particles.

Therefore aim of this research work is to monitor the ultrafine PVP@  $\text{CoFe}_2\text{O}_4$  (synthesized with pre-added PVP in precursor) dispersed in ethanol of different concentrations using zeta potential and investigates its behavior in it.

### MATERIALS AND METHODS

#### Materials

All AR Grade reagents/chemicals are used for the synthesis of the PVP modified  $\text{CoFe}_2\text{O}_4$ . Those are Ferric Chloride Hexahydrated ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), Cobalt Sulfate Hydrated ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), Polyvinyl Pyrrolidone (PVP) average MW 10000,  $\text{NH}_3$ , Ethanol, Acetone (Emplura, 99% pure), Hexane (85%). All Chemicals were used without post purification. Double distilled water is used in a synthesis and characterization process.

#### Preparation of PVP Modified $\text{CoFe}_2\text{O}_4$

The 0.1M Stalk solution of Cobalt Chloride and Ferric Chloride hexahydrated were prepare separately in double distilled water and stirred after mixed in a proportion of 2:1 volume ratio. The 0.1M PVP solution in double distilled water have been prepared and stirred for 15 minutes.

PVP aqueous solution were added to previous precursor solution in w/w ratio 1:1 and stirred for 10 minutes. The aqueous solution of  $\text{NH}_3$  was suddenly added using syringe. Nucleation and growth have seen during the addition of Ammonium aqueous solution. This solution was

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rigorously stirred and increased its temperature to 70°C. After 30 minute of constant temperature treatment, the byproduct was cooled to room temperature and continued to stir for 2 hours. Through the synthesis process pH was maintained to 10. The yield product was then washed, rinsed using hot water and by decantation. Then again rinse using dispersion medium of Acetone. The powder was re-dispersed in Hexane and Ethanol mixture and centrifuged at high speed and dried in an oven at 80°C. Higher reaction temperature and post-treatment temperature were avoided. This PVP modified surface of the CoFe<sub>2</sub>O<sub>4</sub> particles. Samples C1, C2, C3 and C4 with the weight concentration of 1.0, 0.5, 0.2 and 0.125 gram per liter (g/l) of this powder in an ethanol have been prepared after the duration of 10 days. For these 40 minutes of ultrasonication treatment had been given to C1.

### Characterization

XRD was performed from 20 to 80 degree with step size 0.05 using Panalytical instrument with Cu-K<sub>α</sub> 0.15406nm source and analyzed using Profex-3.70 (Dobelin and Kleeberg, 2015). Zeta potential and particle size detection were performed using Malvern DLS Instrument at 25°C temperature. Dynamic Light Scattering (DLS) was done for 15-20 runs, 4.50 measurement position, Attenuator-9, keeping count rate around 100kcps. Zeta dip cell is used for the investigation of ζ -potential in an ethanol solvent. Actual sizes were estimated from bright field micrograph using Philips CM200 Transmission Electron Microscope (TEM) operating at 200kV voltage with resolution of 0.24nm.

Transmission data from 450-1600 cm<sup>-1</sup> with resolution 2 have been recorded on Shimadzu 8400 FTIR Spectrometer for number of scan 45.

## RESULTS AND DISCUSSION

### Formation of PVP@ CoFe<sub>2</sub>O<sub>4</sub>

A XRD pattern (Fig.1 Error Reference source not found). is indicated the amorphous nature of the sample powder. Mounds shows high degree of polycrystallinity and limitation of the X-ray source. Therefore convolutions of peaks were dominated and predicted the particle size below 5nm. The observed data were indexed and fitted for different broadening parameters using the Crystallography Open Database's (COD) CIF file 5910063 in latest revision (Wyckoff, 1931). For the Rp=10.1% and 15 iteration steps the lattice parameter approximated to 8.34±0.14 Å. Size of

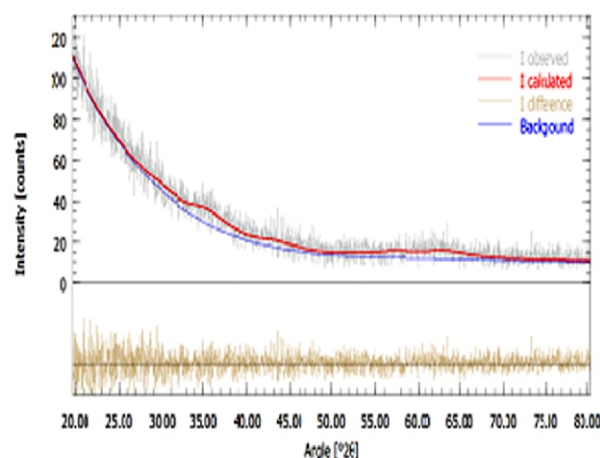


Figure 1: XRD data plot of PVP/CoFe<sub>2</sub>O<sub>4</sub> shows two mounds due to convolution of peaks

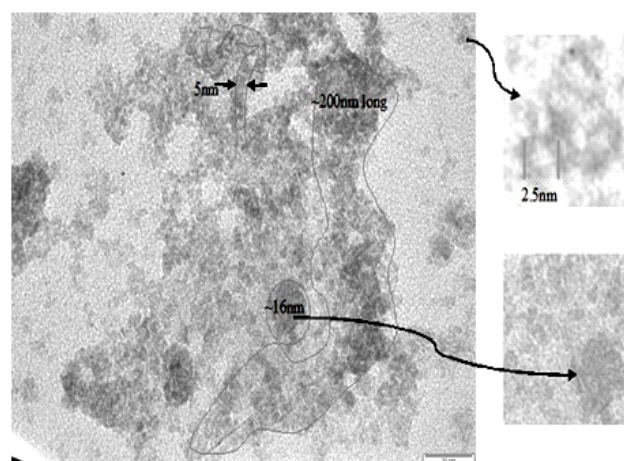


Figure 2: TEM bright field image

the crystallite particles were predicted as estimated by XRD i.e. 2.12±0.85 nm in (1,1,1) direction.

TEM image has confirmed the size, estimated around 1.5 to 2.5 nm as shown in Fig. 2. TEM bright field image and ED showing aggregated PVP coated CoFe<sub>2</sub>O<sub>4</sub> particles. For the scale of 20nm (shown right side bottom) of images, a spherical bigger grain-group 16nm in diameter, a chain shape of 2 to 3 particles 5nm wide in diameter and mixed/interconnected mega nanostructure approximate 200nm long have been illustrated. An isolated grain of few aggregated particles after analysis reveal the diameter of each PVP@ CoFe<sub>2</sub>O<sub>4</sub> estimated as around 1.5-2.5nm.

Simultaneously among many smaller grain-groups at top right corner has zoomed at right illustrated each particle with 2 to 2.5nm size and spherical shape.

On background subtraction, the first mound in XRD found for the convolution of (220) (311) (400) peaks and a second mound for the (422) (511) (440) peaks of JCPDS card no. 22-1086. The preference of Co<sup>2+</sup> in tetrahedral center for above T<sub>b</sub>. T<sub>b</sub> is below room temperature for this size. It has been confirmed that homogeneous nanoparticles with narrow-size distribution with big-deviation in grain-size and chain-size, compare to single particle, has been synthesized.

Uncertainties in phase and structure has solved by SAED and FTIR. The diffracting planes for CoFe<sub>2</sub>O<sub>4</sub> have been confirmed in a SAED ring pattern (Fig.3 (a)). For brightest (311) with 3.9nm<sup>-1</sup> radius estimated a=0.83nm with significant error. Broader and non-sharp rings suggested the higher order of polycrystallinity, randomly oriented particles and hence amorphous nature. Presence of tetrahedral and octahedral sub structure found in a Infrared probing Fig.3 (b).

S-type ferrites show absorption bands below 1000 cm<sup>-1</sup> (Arjunwadkar, 2005). In a fingerprint region for octahedral frequencies  $\nu_1$ , 553, 628, 702 cm<sup>-1</sup> small peaks in an absorption band with central frequency at 628 cm<sup>-1</sup> was obtained which shows presence of the Fe-O. This has also

confirmed that the particles are very small in size and in distribution so that all possible stretching and bending motions may be taken place. Tetrahedral frequency  $\nu_2$  absorption at left begin from 467 cm<sup>-1</sup> indicates presence of Co-O bonding. The characteristic absorption bands of the sample show Fe-O and Co-O stretching and bending vibration modes of CoFe<sub>2</sub>O<sub>4</sub>. The existence of strong absorption bands around 800 cm<sup>-1</sup> and 470 cm<sup>-1</sup> are due to stretching of metal oxygen (M-O) as it is close to (Raval, 2013), which attributed to the formation of the ferrite phase. P. In one paper it has been already predicted the large possibility of occurrence of severe interaction between  $\nu_1$  and  $\nu_2$  frequencies (Tarte, 1963). This implies the smaller to bigger size groups of the uniformed size particles are present. This information is complementary to the TEM and XRD result. The absorption peaks 1365, 1398, 1501, 1638 in cm<sup>-1</sup> have confirmed the modification of PVP on the surface of CoFe<sub>2</sub>O<sub>4</sub> particles as a spectrum of comprised of the conjunction of their individual particles. It has confirmed that the ultrafine CoFe<sub>2</sub>O<sub>4</sub> was successfully synthesized and surfaces were modified with a PVP.

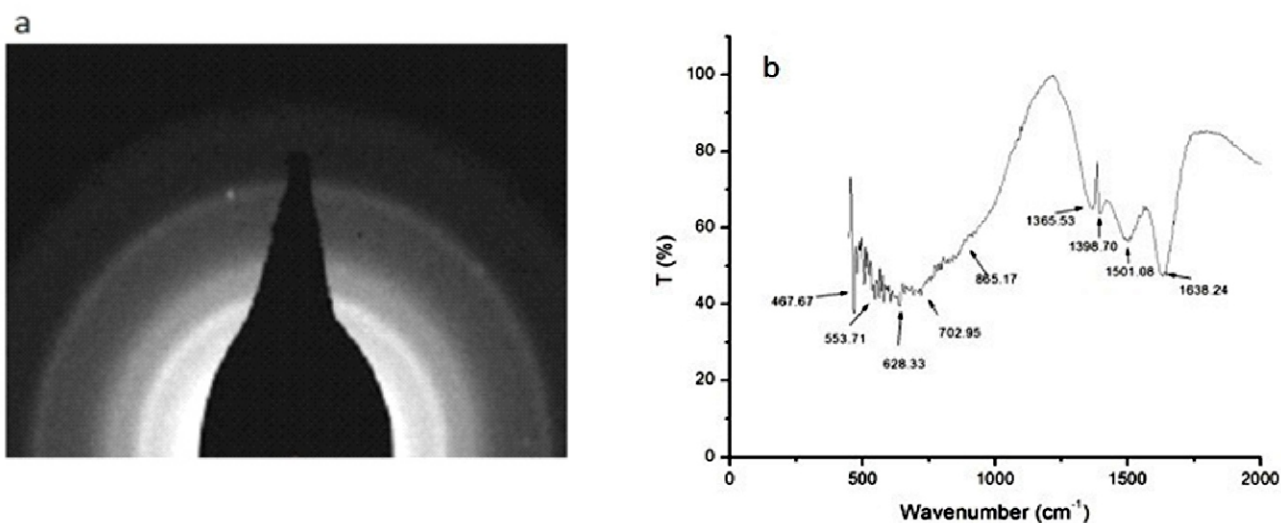
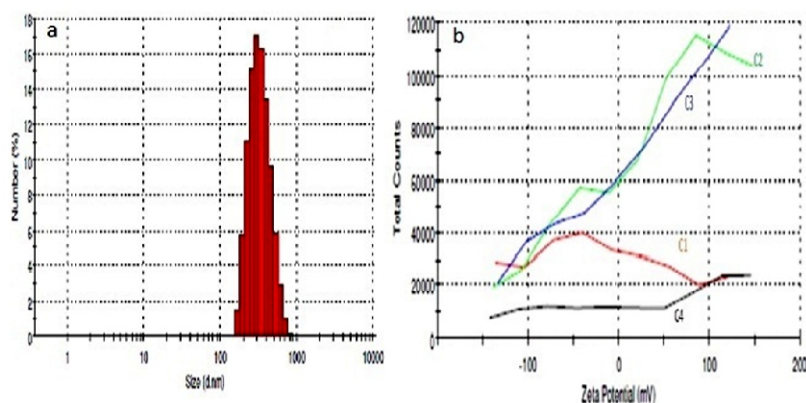


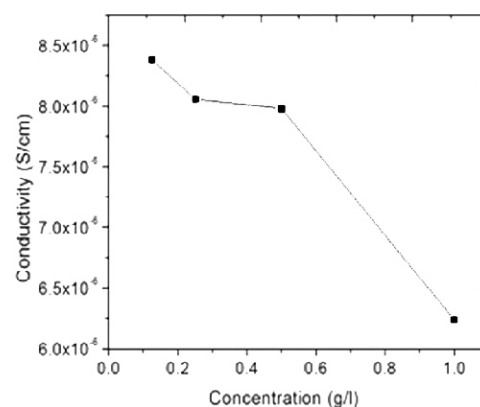
Figure 3: (a) SAED pattern of powder sample. (b) FTIR spectrum of ultrafine PVP@ CoFe<sub>2</sub>O<sub>4</sub>

### Particles In Ethanol Dispersion



**Figure 4: (a) Hydrodynamic size by PSD. (b) Zeta potential curve for different concentrations dispersion C1, C2, C3 and C4 as 1, 0.5, 0.25 and 0.125 mg/ml respectively**

In a C1 (see Fig.4(a)), the hydrodynamic size-distribution has observed from 164 to 712 nm and central maxima at 210nm with deviation 150nm which is very large with compare to the size-distribution obtained from the TEM image. But bigger grains, chains and mixed meganano-size-structure are comparable to the PSD-DLS data. This result could be justified up to some extend using the finding of (Kang et. al., 2013). Relative size distribution of separated MNP groups in aqueous solution measured by DLS which's result was correlated with the TEM and clearly showed hydrodynamic size is nearly double to triple of the TEM size. In present case, aggregation found in TEM was significantly large and suspected due to PVP modification. The first opinion is that the PVP modification however stopped the growth during synthesis and formed smaller particles with monodispersivity. After washing and heating and due to the atmospheric thermal fluctuation the PVP causes the formation of grains with actual particles size left unchanged. And the other opinion is that the hydrodynamic size of so small particles shows nearly ten to twenty times larger may be the cause of influence of chain or big shape formed due to stickiness which has been justified by TEM analysis. Nanoparticle dispersion or aggregation is mainly associated with the Van der Waals attraction and electrostatic double-layer repulsion interaction between particles according to the



**Figure 5: Variation of conductivity of dispersion. (data point from left to right indicate C1, C2, C3, C4)**

Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Ramimoghadam et. al., 2015) which describes electrostatic and steric stabilization mechanism.

Z-potential curves (Fig.4 (b)) for the different concentration seems not an ideal for the monodispersed good quality data. For the run of 15 repetitive measurements (four times with same attenuator of 9 and one time for attenuator 6 were carried for each samples to resolve the issue and we found consistently the same nature of the curve. The conductivity was (see Fig.5) found higher for the lower concentration, implies that the ionic strength was increasing. In a highly conductive sample, the movement of the conductive ions can lead to electrode polarization and degradation. To minimize these, Malvern instrument didn't recommend conductivity higher than  $5 \times 10^{-3}$  S/cm<sup>-1</sup>. PVP has dielectric nature but reported  $7.42 \times 10^{-8}$  S/cm<sup>-1</sup> (Ravi, 2013). Ethanol is non-conducting but adulteration of salt causes conduction. In present work, conductivity has found below  $8.38 \times 10^{-6}$  S/cm<sup>-1</sup> for all samples. This very small number indicates the repulsive forces were merely caused by  $\zeta$ -potential. This has confirmed the absence of residual reactants, large non-analytic organic molecules and dissolved ions. Figure4 support aggregate nature of sample to TEM and presence of dispersed small grains. Ultrasonication have loosen aggregation strength and it dispersion in ethanol provided mobility.



From C1 to C4 the increase in gradient of gray columns in a Figure4 showed increase in the magnitude of  $\zeta$ -potential at both negative and positive side. Large size of aggregation still contained in a sample revealed from the plots between 10 to -10 mV. But main peaks were started beyond 25mV and -25mV reveal the presence of larger numbers of weakly aggregated and well dispersed grain-groups and particles. This has been tested for all samples by keeping for 24 hour under observation which confirmed those were well suspended for long time after initial 15-30 minutes at the cost of settling of the nominal particles. Study has pointed out: i) Peaks were shifting towards larger  $\zeta$ -potential from C1 to C4 and ii) Counts of negative  $\zeta$ -potential diminishing and counts towards positive  $\zeta$ -potential increasing relatively from C1 to C2 for each sample.

Finally  $\zeta$ -potential and conductivity found inversely proportional to concentration of PVP@CoFe<sub>2</sub>O<sub>4</sub> in Ethanol. Lowering aggregation due to increasing mobility as an effect of decrease of concentration provided better stabilized dispersion in our samples. This may be the reason for first observation. Therefore 'ultrasonication for 40 minutes are not sufficient and the time more than that' has been recommended. Ethanol was slightly basic (7.3 pH) and PVP vary from 3 to 7 (5% sol). Therefore 'the PVP bound to CoFe<sub>2</sub>O<sub>4</sub> possesses inhomogeneous thickness of coating' has been predicted. However suspension became stabilized with increasing its strength, the counts of negative  $\zeta$ -potential diminishing can be explainable by losing pH effect. And dominating peak shifted from negative to positive potential with increasing pH crossed isoelectric point. As CoFe<sub>2</sub>O<sub>4</sub> is nanosize (2nm) magnetic particles are superparamagnetic which are affected by thermal fluctuation. Domination of this phenomenon may cause also shifting of zeta potential from negative to positive value and its domination.

## CONCLUSIONS

Ultrafine PVP@CoFe<sub>2</sub>O<sub>4</sub> monodispersed particles of size 2nm with smaller-bigger grains and chain aggregates were synthesized using pre-added PVP. These have shown good stability at both side of  $\zeta$ -potential which has predicted the repulsive forces for higher concentration dominated due

to negative ions and for lower concentration dominated due to positive ions. Pre-addition of PVP before precipitation did not work for highly yield suspended particles in a dispersion but succeeded to form high yield monodispersed 2nm PVP@CoFe<sub>2</sub>O<sub>4</sub> and hence recommended it with requirement of time consuming ultrasonication treatment. It also shows good stability. This work has been directed the possibility of the effect of superparamagnetism on  $\zeta$ -potential for ultrafine scale of PVP@CoFe<sub>2</sub>O<sub>4</sub> at ambient temperature.

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