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A simple and effective method of the synthesis of single phase nanosized $NiFe_2O_4$ particles

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Abstract:

Nanosized spinel nickel ferrite $NiFe_2O_4$ has been synthesized by precipitation method. X-ray diffraction (XRD), transmission electron microscopy (TEM) and Vibrating sample magnetometer (VSM) are used to characterize the structural, morphological and magnetic properties. XRD studies show that nickel ferrite was formed as cubic $NiFe_2O_4$. The small hysteresis loop with low remanence and coercivity at 300K indicate the ferromagnetic character in the nanocrystalline $NiFe_2O_4$ ferrite materials. The particle size of the synthesized $NiFe_2O_4$ was determined by TEM. TEM images show very fine nanoparticles of synthesized ferrite. Size of particles of $NiFe_2O_4$ varied from 10nm to 28nm with average particle size of ~20nm. Ms value was observed to be 15emu/g at 300K.

Key words: Nanaomaterial, $NiFe_2O_4$, TEM, Nickel ferrite, XRD analysis

1. Introduction:

Spinel ferrites are magnetic materials and have wide applications in magnetic devices and switching devices [1-3]. Nickel ferrite ($NiFe_2O_4$) is of interest as it has wide applications in RF/ microwave because of its high Neel temperature, low microwave loss, low magnetic anisotropy [4-8]. Nanosized nickel ferrite possesses attractive properties for the application as soft magnets, core materials in power transformers and low loss materials at high frequencies [9]. Ni ferrites are technologically important material. Nickel ferrite has inverse spinel structure. The crystal structure is face centered cubic with the unit cell containing 32 O^{2-}, 8 Ni^{2+} and 16 Fe^{3+} ions. The oxygen ions form 64 tetrahedral and 32 octahedral sites, where 24 cations are distributed. The eight Ni^{2+} and eight Fe^{3+} cations occupy half of the octahedral sites and the other eight Fe^{3+} ions occupy eight tetrahedral sites (10-11). Ferrimagnetic property of the material arises from magnetic moments of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} and Fe^{3+} ions at octahedral sites (12). The properties of ferrite nanoparticles are influenced by the composition and microstructure which are sensitive to the preparation methodology used. Ni ferrites as well as Ni-based mixed ferrites are extensively investigated by various researchers [13-16]. Different methods have been reported for the synthesis of $NiFe_2O_4$. Nickel ferrite particles have been prepared by using hydrothermal method [17]. Samples were prepared in presence of Glycerol and Sodium dodecyl sulfate and inhibition effect of surfactant on $NiFe_2O_4$ particles growth has been studied. Nickel ferrite $NiFe_2O_4$ particles of high crystallinity have been synthesized by forced hydrolysis of ionic iron (III) and nickel (II) solutions in 2-hydroxyethyl ether [18]. $NiFe_2O_4$ nanoparticles have been prepared by the sol-gel method using polyacrylic acid (PAA) as a chelating agent [19]. Nickel ferrite nanoparicles with various grain sizes are synthesized using annealing treatment followed by ball milling of its bulk component materials and their magnetic properties have been studied [20]. $NiFe_2O_4$ particle/organic hybrid were synthesized in situ from iron-organic and nickel organic compounds below 100 °C and the remanent magnetization and coercive field of the hybrid were evaluated as 7.4 emu/g and 460 Oe, respectively, at 5 K [21]. Solvothermal synthesis of size controlled nickel

ferrite particles has been carried out and their magnetic properties have been studied [22]. $NiFe_2O_4$ have been synthesized by citrate precursor gel formation of average size 55.4 nm and their magnetic behavior has been studied [23]. Synthesis of chromium-substituted nickel ferrites has been carried out by aerosol route and cation distribution along with magnetic properties has been studied [24]. Oxidative stress mediated apoptosis induced by nickel ferrite nanoparticles in cultured A549 cells has been studied and it has been observed that nickel ferrite nanoparticles induced dose-dependent cytotoxicity in A549 cells demonstrated by MTT, NRU and LDH assays [25]. In the present manuscript, synthesis of $NiFe_2O_4$ nanoparticles has been reported by simple aqueous precipitation method using aqueous ammonia as precipitating agent. This method involves a simple, cheap and one step process for synthesis of very fine $NiFe_2O_4$ nanaoparticles as compared to other methods of synthesis like ultrasonic radiation, sol-gel approach, Fe implantation thermal decomposition of metal-surfactant complexes, colloid mill, mechanical milling etc. The obtained particles of $NiFe_2O_4$ have size from 10-28 nm. The synthesized nanoparticles were characterized by XRD, TEM and VSM studies.

2. Methods and materials

2.1 Chemicals:

All chemicals used in the experiment are analytic reagent grade. Ferric nitrate Fe $(NO_3)_3$, Ni $(NO_3)_2$ was purchased from Merck, India. Ammonium hydroxide (liquor ammonia) was purchased from SRL. Deionized water was used throughout the experiment.

2.2 Synthesis of $NiFe_2O_4$:

Fe $(NO_3)_3$ and Ni $(NO_3)_2$ were taken in equal mass ratio and were dissolved in 500 mL of water. Aqueous ammonia (2M) was added drop wise with constant stirring until the pH of the solution reached to 10. The precipitates thus obtained were filtered by Buckner funnel and was washed several times with distilled water. The precipitates were dried in oven at 70°C for 24 hrs and were calcined at 600°C in a muffle furnace for 5 hrs. Obtained material was ground and sieved through 100 mesh size sieve.

2.3 Characterization techniques:

The microstructure of the particles was characterized by X-ray diffraction (XRD), Philips PW 11/90 diffractometer using nickel filtered CuKα (l = 1.5405 Å) radiations. The average diameter (D) of the ferrite nanocrystals has been calculated from the broadening of the XRD peak intensity after $K\alpha_2$ corrections using the Debye-scherrer equation. Transmission electron microscopy (TEM) measurements of the sample were taken on Hitachi H7500 with a 70 kV accelerating voltage. The dispersions of nanoparticles in water were placed on carbon-coated 400 mesh copper grids, allowed to dry at room temperature before taking measurement. The obtained micrographs were then examined for particle size and shape. The magnetic properties of the solid was measured at 300K using a Vibrating sample Magnetometer Model 155.

3. Results and discussions:

3.1. X-ray studies:

X-ray diffraction of synthesized $NiFe_2O_4$ is shown in Figure (1). X-ray diffraction pattern of $NiFe_2O_4$ pure indicated that Nickel ferrite is in the form of $NiFe_2O_4$. In X-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with the standard i.e. JCPDS file No. 74-2081 (Table-1). X-ray diffraction shows that metal oxide is pure $NiFe_2O_4$ having cubic spinel structure. The peaks indexed to (220), (311), (400), (422), (511) and (440) planes of a cubic unit cell, corresponds to single phase spinal crystal structure. Sharpness of the peaks shows good crystal growth of the ferrite particles. Average particle size (t) of the particles have been calculated using from high intensity peak (311) using the Debye-Scherrer equation

$$t = K\lambda / B \cos\theta$$

Where t is the average crystallite size of the phase under investigation, K is the Scherrer constant (0.89), λ is the wave length of X – ray beam used, B is the full-with half maximum(FWHM) of diffraction (in radians) and θ is the Bragg's angle

The average crystallite size calculated is 23nm which is in close agreement with the TEM results. Lattice constant of ferrite nanocrystals are computed using the d value (interplaner spacing) and their respective lattice (h k l) parameters. Lattice constant for ferrite nanocrystals has been found to be $8.31915A^0$. The actual (X-ray) density of $NiFe_2O_4$ nanoparticles is calculated using the formula Px = 8*M/Na*3 (26) and is given in Table 2. Where *M* is the molecular weight (kg) of the sample, *N* the Avogadro's number (per mol) and *a* the lattice constant (Å). Value of Px was calculated as 5.40707 (g/cc).

3.1. Magnetic measurements:

Magnetic measurements were carried out to find out the magnetic behavior of synthesized Nickel ferrite. The magnetic measurement of $NiFe_2O_4$ was carried out at room temperature and it has been observed that $NiFe_2O_4$ shows ferromagnetic behavior in nanocrystaline form as there is no hysteresis observed. It showed very small Ms value (15 emu/g) obtained [Fig.2].

Previously reported values of *M*s for Nickel ferrite nanoparticles prepared by various methods have been reported in Table2. The value of *M*s ranging from 30-55.56 $emug^{-1}$ shows that *M*s strongly depends on the synthesis method used [27-29]. This Ms Value of 15 emu/g at room temperature is comparable with earlier synthesized nanoparticles.

3.2 TEM studies

TEM studies were carried to find out exact particle size of synthesized $NiFe_2O_4$. Figure 3 shows the TEM image of the synthesized $NiFe_2O_4$ nanoparticles. The single crystal nature of the $NiFe_2O_4$ is revealed by TEM analysis. A very fine spherical $NiFe_2O_4$ nanoparticle in the range of 10-28 nm with average size of ~20nm is obtained. The size distribution histograms for nanoparticles provided their respective sizes as 23.4 ± 5.2 nm [Fig. 3a], 22 ± 5.6 nm [Fig. 3b], 20.5 ± 5.7 nm [Fig. 3c], 19.6 ± 4.6 nm [Fig. 3d], 17.9 ± 5.8 nm [Fig. 3e], 22.7 ± 3.4 nm [Fig. 3f], respectively.

The average crystallite size $D_{XRD,}$ D_{TEM}, and the lattice constant (a) of the sample obtained are summarized in Table 2.

4. Conclusion:

$NiFe_2O_4$ nanoparticles with cubic structure are synthesized successfully by aqueous precipitation method. TEM study show very fine nanoparticles of diameter 10-28 nm with average size of 20nm. VSM studies show ferromagnetic behavior of synthesized nanoparticles. This method is advantageous over the existing methods of synthesis of nanoparticles because other methods require specialized instrumentation, highly skilled labour, expensive materials and methods. Therefore, the proposed precipitation method is very promising and may have extensive applications.

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Table-1 X-RAY DIFFRACTION DATA FOR $NiFe_2O_4$

S. No.	d=λ / 2sinθ (Observed)	d=λ / 2sinθ (Reported)	I/I_0X100% (Observed)	I/I_0X100% (Reported)
1.	2.50832	2.5139	100	100
2.	2.95501	2.9478	41	30
3.	2.40448	2.4069	21	7
4.	2.09075	2.0844	35	20
5.	1.70883	1.7019	16	08
6.	1.60606	1.6046	38	26
7.	4.82418	4.8138	19	11
8.	1.47254	1.4739	60	33

74-2081 Wavelength= 1.54060

NiFe2O4

Nickel Iron Oxide

Rad.: CuKa1 λ: 1.54060 Filter: d-sp: Calculated

Cut off: 17.7 Int.: Calculated I/Icor.: 4.83

Ref: Calculated from ICSD using POWD-12++, (1997)

Ref: Subramanyam, K.N., J. Phys. C: Solid State Phys., 4, 2266 (1971)

Sys.: Cubic S.G.: Fd3m (227)

a: 8.3379(3) b: c: A: C:

α: β: γ: Z: 8 mp:

Ref: Ibid.

Dx: 5.372 Dm: ICSD # : 028108

Peak height intensity. R-factor: 0.163. PSC: cF56. Mwt: 234.39. Volume[CD]: 579.66.

d(A)	Int	h	k	l
4.8138	114	1	1	1
2.9478	299	2	2	0
2.5139	999*	3	1	1
2.4069	74	2	2	2
2.0844	202	4	0	0
1.9128	5	3	3	1
1.7019	81	4	2	2
1.6046	261	5	1	1
1.4739	331	4	4	0
1.4093	8	5	3	1
1.3896	1	4	4	2
1.3183	24	6	2	0
1.2715	59	5	3	3
1.2569	23	6	2	2
1.2034	19	4	4	4
1.1675	4	7	1	1
1.1142	23	6	4	2

Table 2

Size and Magnetic parameters for as synthesized Nickel Ferrite

Particle size D_{TEM}(nm)	Particle size D_{XRD}(nm)	Lattice constant[A^0]	X- ray density(Px)	Magnetization M(emu/g)
20nm	23nm	8.31915	5.40707	15

Table 3

Nickel ferrite	Ms (emu/g)	Temp	Size	Synthesis method	Ref Number
$NiFe_2O_4$	15	600	10-30	Precipitation	This work
$NiFe_2O_4$	38	478K	4.4	Forced hydrolysis	27
$NiFe_2O_4$	55.56	-	20-30	Thermal Plasma	28
$NiFe_2O_4$	31.62	600	16.7	Sol gel	29
$NiFe_2O_4$	30.8990	600	15.009	Precipitation	29

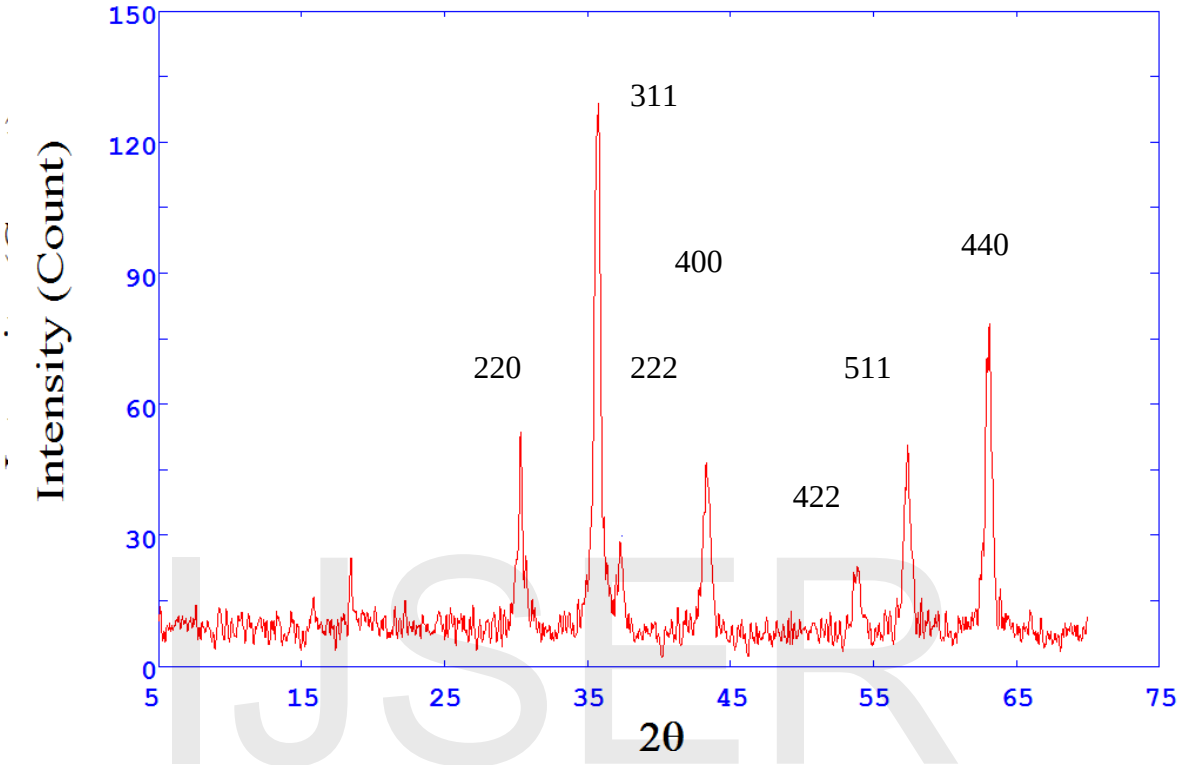


Figure 1 XRD spectra of Nickel Ferrite

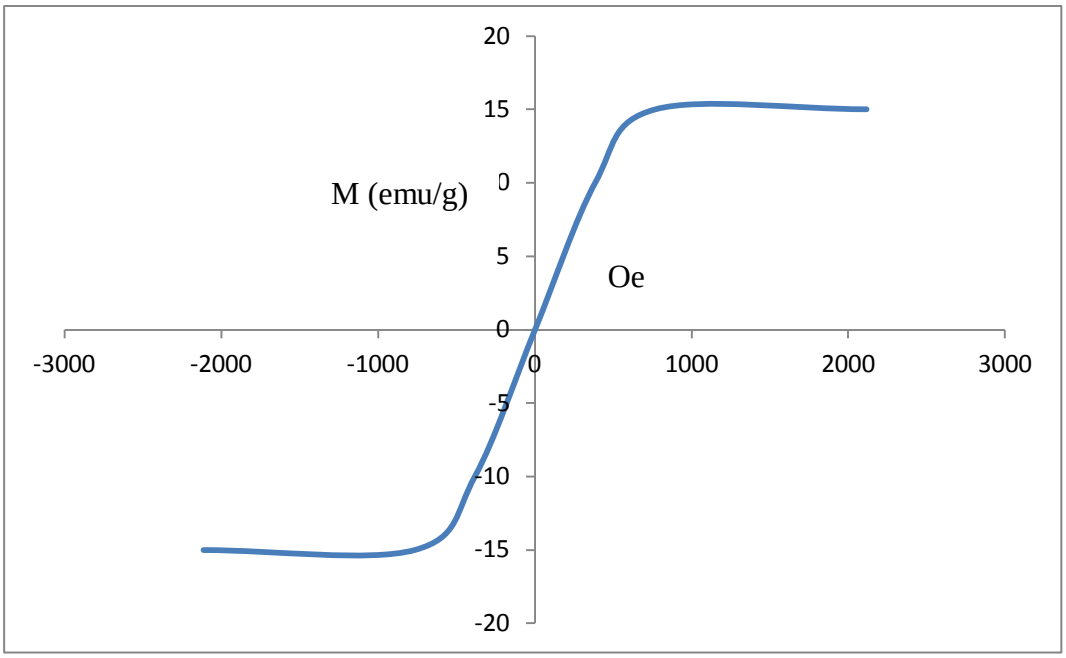


Figure 2: Magnetic measurement of synthesized Nickel ferrite

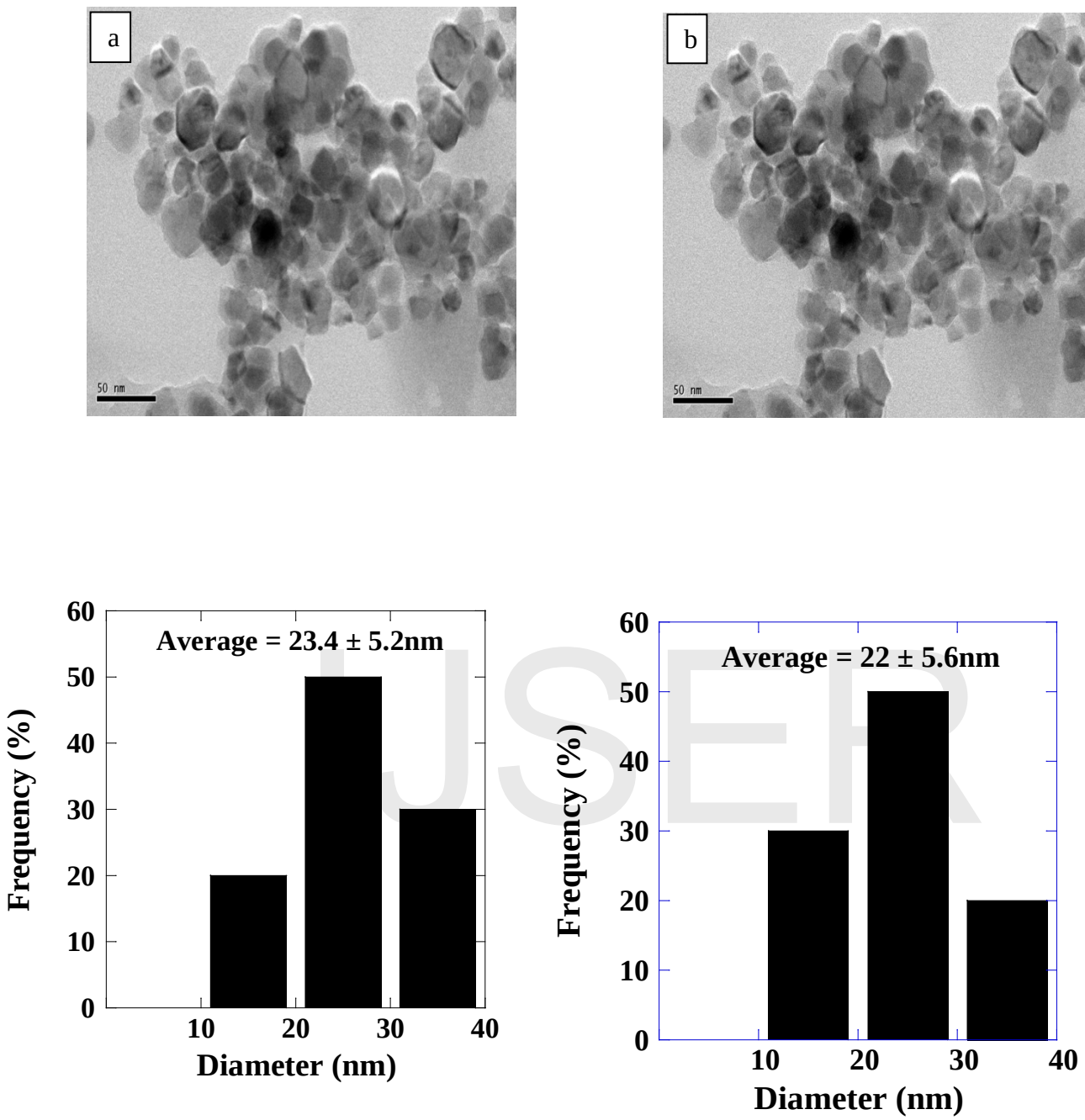
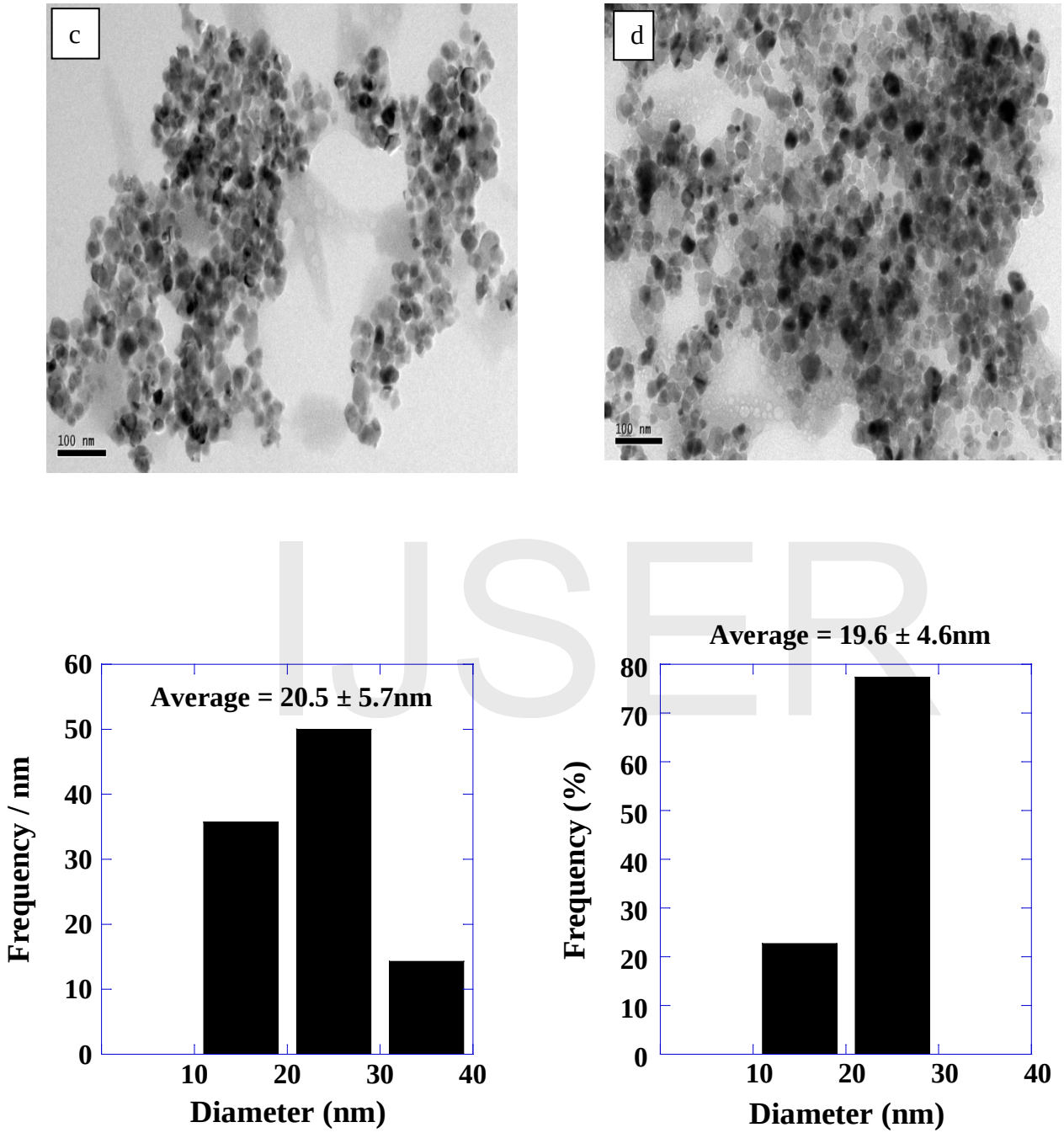


Figure 3 TEM images of Nickel Ferrite nanoparticles



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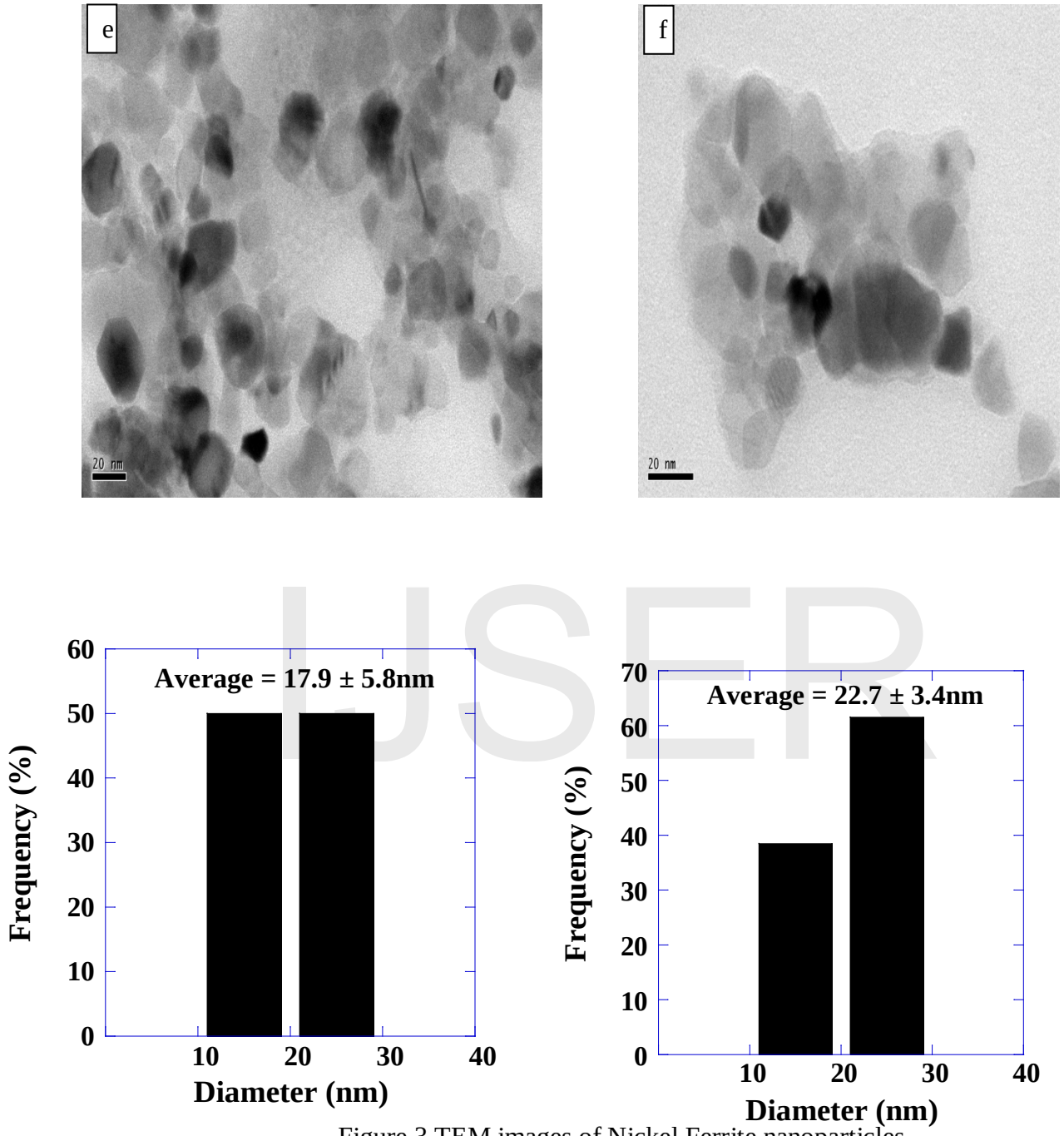

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