

Synthesis of NiO nanoparticles by water-in-oil microemulsion technique

Abstract

NiO nanoparticles were synthesized by water-in-oil microemulsion technique using Aerosol-OT as a surfactant. The study aims to understand the nanoparticle size and distribution synthesized with the surfactant and co-precipitated without surfactant. Nanoparticles were synthesized with different R-ratios (molar ratio of water to surfactant). It was found that particle size distribution is narrow within the microemulsion forming regime while the particles were polydispersed when synthesized outside the microemulsion forming regime at high R-ratio. In addition, co-precipitated nanoparticles were found to have a wide size distribution that was comparable to the nanoparticles synthesized at high R-ratio. Phase identification and particle size analysis were carried out using X-ray diffraction (XRD) and Transmission electron microscope (TEM).

Key words: Water-in-oil microemulsion; nanoparticles; XRD; TEM; Size distribution

1. Introduction

Synthesis and characterization of nanoparticles has received much attention in the last few decades because of the unique physical and chemical properties observed in the nanoscale regime. Due to the interesting properties, they have the potential to be used in various applications including coatings [1], pharmaceuticals [2], catalysis [3], superconductors [4] and optical devices [5]. Many techniques have been used to synthesize nanoparticles, for example, sol-gel [6], co-precipitation [7], solvothermal process [8], laser ablation [9], and microemulsion method [10]. In the above-mentioned methods, microemulsion synthesis offers the advantage of controlling the particle size.

Nanoparticles of oxides [11], sulphides [12], pure metals [13], and polymers [14] have been synthesized using the water-in-oil microemulsion technique. Important surfactants that have been used include cetyl-trimethyl-ammonium bromide (CTAB), dioctyl sulfosuccinate sodium salt (AOT), sucrose fatty acid ester, polyisobutene butanedimide and rhamnolipids [15, 16]. Sometimes, a co-surfactant was also used along with the surfactant. Therefore a wide variety of microemulsions have been developed for synthesizing nanoparticles.

Microemulsion technique has been used to synthesize nanoparticles of CdS [17], CdS-Ag₂S core-shell/composite [18], MoS_x [19], Pt [20], TiO₂ [21], ZnS [22] and gold [23]. It has been shown that this synthesis technique has a good control over the particle size.

Microemulsion is prepared by dispersion of an aqueous phase in the hydrocarbon oil phase with the presence of a surfactant that give rise to a stable dispersion of aqueous phase, and the size of the nanoreactor formed inside the microemulsion is given by [24]

$$W (\text{\AA}) = 1.5 * R \text{ -----} 1$$

Where W is the water pool radius in Å and R is the molar ratio of water to surfactant. The particle size can be controlled by varying the R-ratio. The most widely used surfactant is the sodium bis (2-ethylhexyl) sulfosuccinate (called as Aerosol-OT) and it is found that the Aerosol-OT has good water solubilizing capacity because of its structure [25]. Recently, it has been shown that nanoparticles can be synthesized using rhamnolipids, a biosurfactant [15, 16].

Nickel oxide is one of the widely studied oxide material because of its anomalous magnetic behavior due to surface anisotropy [26] and electronic behavior [27]. It has also been used as a support catalyst for anatase [28]. Zhan *et al.* [29] synthesized NiO nanowires using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and NaCl in cyclohexane using Poly(oxyethylene)₅nonylphenyl ether and Poly(oxyethylene)₉nonylphenyl ether as surfactant. Lin *et al.* [30] synthesized ordered NiO nanowires in an electrochemical deposition process using an anodic alumina membrane and found that the nanowires were continuous and dense. Ichianagi *et al.* [31] synthesized NiO by chemically precipitating $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. Richardson *et al.* [32] prepared colloidal NiO particles by chemically precipitating $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NaOH at a pH of 12 to study the

magnetic properties. Han *et al.* [33] synthesized NiO nanoparticles through water-in-oil microemulsion technique using TritonX-100 / n-hexanol / cyclohexane / water system. It was found that with increase in R value and calcination temperature the particle size increases. Dharmaraj *et al.* [34] synthesized NiO nanoparticles of around 40 - 50nm using Nickel acetate and poly (vinyl acetate) as precursor. Nickel acetate was dissolved in 2-methoxy ethanol by heating to a temperature 343 K under constant stirring. Poly vinyl acetate was mixed with the nickel acetate at room temperature and stirred for 3 hrs. The solid mixture was then heated to 723 K to obtain NiO nanoparticles. The average particle size obtained is around 44 nm. The resultant formed mixture was heated at 723 K for 3 hrs to obtain NiO nanoparticles. Tao *et al.* [35] prepared NiO nanoparticles of 30 nm using nickel acetate, which was mixed with PVP. The mixture was evaporated to remove water. The resultant solid mixture was then calcined at 400 °C for 2 hrs. The average particle size was around 30nm.

In the present study, an attempt has been made to synthesize NiO nanoparticles through the water / AOT / n-heptane system. The composition of the microemulsion was selected based on the AOT-n-heptane-water phase diagram [36] and the microemulsion composition $R=25$ fall within the microemulsion forming regime and for all the other compositions it falls outside the regime. The study aims at understanding the effect of varying the R-ratio (i.e. molar ratio of water to AOT) on the particle size, distribution and crystallinity of the NiO nanoparticles. Co-precipitation of NiO nanoparticles has also been carried out for comparison purpose.

2. Experimental

2.1 Materials

Nickel (II) chloride hexahydrate (99% pure) (S. D. Fine-Chem, India), ammonia solution (25 wt.%) (Ranbaxy Fine Chemicals, India), n-heptane (Qualigens Fine Chemicals, India) and sulfosuccinic acid bis[2-ethylhexyl ester] (AOT: 97% pure from Sigma Aldrich) were used in the as-received condition.

2.2 Microemulsion

In the microemulsion technique, AOT was used as a surfactant and n-heptane as the oil phase. One microemulsion was prepared using 1 M nickel chloride and the second microemulsion was prepared using 10 M ammonia solution. The molar ratio of water to surfactant (R-ratio) was varied from 25 to 100 i.e., the amount of surfactant was reduced. Table.1 gives the details of the microemulsion composition. Two microemulsions were stirred separately before they were mixed. Stirring was continued for a few minutes after mixing both the microemulsions. The precipitated nickel hydroxide were then centrifuged at 5000 rpm for 30 min. and then washed 3-4 times with n-heptane and methanol in order to remove the surfactant. The washed product was dried in an oven for 100°C for 5 hrs. Thermo Gravimetric Analysis (TGA) was carried out on the hydroxide samples and found that the complete hydroxide decomposition occurs at a temperature of approximately 600°C to produce a highly crystalline NiO. TGA graph is given in Fig. 1 and the hydroxide particles obtained from microemulsion was calcined at a temperature of 600°C for 3 hrs.

Nickel oxide nanoparticles were also prepared by bulk co-precipitation method. In the co-precipitation method, ammonia solution was slowly added to 10 ml solution of nickel chloride until the pH was raised to about 9. The precipitates were filtered and dried in an oven at about 100 °C for 5 hours and calcined to a temperature of 600°C for 3 hrs.

2.3 Characterization

NiO nanoparticles obtained after calcination were characterized by X-Ray diffraction (JEOL - JDX 8030) using Cu-K α radiation (1.5418 Å) for phase identification and crystallite size measurement. TEM analysis was done using JEOL 200CX microscope operating at an accelerating voltage of 160 kV for measuring the particle size and distribution, and to check the crystallinity. The sample for TEM analysis was prepared by dissolving small amount of NiO nanoparticles in acetone and ultrasonication for a period of 5 min in order to disperse the agglomerated particles and a droplet of the nanoparticle mixture was deposited in the copper grid coated with carbon and allowed to dry for a few seconds.

3. Results and Discussion

Fig. 2 shows the X-Ray powder diffraction pattern of the NiO nanoparticles corresponding to R values of 25, 50, 75, 100 and for co-precipitated sample. From the peak broadening it is evident that the crystallites are nanosize and the average crystallite size determined using Scherrer formula [37] gave 8, 12, 12 and 15nm for R values of 25, 50, 75 and 100, respectively and for bulk co-precipitated sample it is 15nm. Table.2 shows the crystallite size determined using XRD.

The lattice parameter calculated at a higher angle gave a value of 4.1736 Å that is consistent for NiO and is matched with the JCPDS card No. 75-0197 for 100R and 50R, for 25R, 75R and for co-precipitated sample it is matched with the JCPDS card No. 78-0423.

Fig. 3 shows the TEM micrographs of NiO nanoparticles synthesized using microemulsion technique as well as for the co-precipitated sample. The Selected Area Electron Diffraction (SAED) pattern (inset in the TEM micrographs) shows that the nanoparticles are highly crystalline. The size controlling feature is one of the advantages of the microemulsion technique for nanoparticle synthesis that is evident from the particle size measured from the TEM micrographs for various R values (Fig. 4). The particle size distribution was measured using the Sigma scan pro 4.0 software, and the number of particles taken under the study was 60. The particle size distribution histogram is given below the TEM micrographs. The size distribution was narrow for the particles synthesized in the microemulsion region and a wide distribution was observed for the nanoparticles synthesized outside the microemulsion regime. The size distribution was wider in the case of high R values attributed due to swelling of the nanoreactor due to less coverage of the capping agent. It is found that particle size and distribution for high R value is comparable to the conventional co-precipitated sample with no surfactant. The co-precipitated nanoparticle has unconstrained growth and is consistent with the observed wide particle size distribution.

The particle size measured from the TEM micrographs for different R-values and for co-precipitated sample is given in Table. 2. Consistent with the eqn. 1, particle size increases

proportionally with R-value and this shows that microemulsion is a good technique for size controlled synthesis of nanoparticles. Significant difference in the crystallite size estimates by XRD technique and as measured by TEM was attributed due to strain, defects and inherent instrumental broadening that adds to the error in nanoparticle size estimate by XRD technique [37].

Conclusions

NiO nanoparticles were successfully synthesized by microemulsion technique using Aerosol-OT as a surfactant. It is found that particle size distribution was narrow for the synthesis within the microemulsion regime and a wide size distribution for high R ratio outside the microemulsion regime attributed due to the swelling of the nanoreactor due to less surfactant coverage. The constrained nanoreactor is stable when the surfactant concentration is high and the particle size proportionally increases with R-values. In addition, the co-precipitated nanoparticles found to have a wide size distribution due to the unconstrained growth in the absence of the capping agent.

References

- 1) Q. H. Powell, G. P. Fotou, T. T. Kodas, B. M. Anderson, *Chem. Mater.* 9 (1997) 685.
- 2) S. K. Sahoo, T. K. De, P. K. Ghosh, A. Maitra. *J. Colloids and Inter. Sci.* 206 (1998) 361.
- 3) S. Eriksson, U. Nylen, S. Rojas, M. Boutonett. *Appl. Catal. A: Gen.* 265 (2004) 207.

- 4) V. Pillai, P. Kumar, M. J. Hou, P. Ayyub, D. O. Shah. *Adv. Colloid. Interfac.* 55 (1995) 241.
- 5) A. Ekimov. *J. Lumin.* 70 (1996) 1.
- 6) A. Chatterjee, D. Das, S. K. Pradhan, D. Chakravorty. *J. Mag. and Magn. Mater.* 127 (1993) 214.
- 7) Y. Kim, D. Kim, C. S. Lee. *Phys B.* 337 (2003) 42.
- 8) K. Tang, Y. Qian, J. Zeng, X. Yang. *Adv. Mater.* 15 (2003) 448.
- 9) T. Tsuji, K. Iryo, N. Watanabe, M. Tsuji. *Appl. Surf. Sci.* 202 (2002) 80.
- 10) M. P. Pileni. *Langmuir.* 13 (1997) 3266.
- 11) K. Y. Kim, S. B. Park. *Mater. Chem. and Phys.* 86 (2004) 210.
- 12) P. S. Khiew, N. M. Huang, S. Radiman, M. Ahmad. *Mater. Lett.* 58 (2004) 762.
- 13) I. Capek. *Adv. Colloid. Interfac.* 110 (2004) 49.
- 14) X. Xiangling, G. Xuwu, Y. Qiang, Z. Zhicheng, Z. Ju, N. Aizhen, Z. Manwei. *Rad. Phys. and Chem.* 54 (1999) 279.
- 15) P. Palanisamy, A. M. Raichur. *Mater. Sci. and Engg: C.* 29 (2009) 199.
- 16) P. Palanisamy, A. M. Raichur. *Mater. Lett.* 29 (2008) 743.
- 17) E. Caponetti, L. Pedone, D. C. Martino, V. Panto, V. T. Liveri. *Mater. Sci. and Eng. C.* 23 (2003) 531.
- 18) G. Hota, S. Jain, K. C. Khilar. *Coll. and Surf A: Physicochem.Eng. Aspects.* 232 (2004) 119.
- 19) K. E. Marchand, M. Tarret, J. P. Lecharie, L. Normand, S. Kasztelan, T. Cseri. *Colloids Surf A: Physicochem.Eng. Asp.* 214 (2003) 239.

- 20) O. P. Yadav, A. Palmqvist, N. Cruise, K. Holmberg. *Coll. and Surf A: Physicochem.Eng. Aspects*. 221 (2003) 131.
- 21) R. Zhang, L. Gao. *Mater. Res. Bull.* 37 (2002) 1659.
- 22) J. Xu, Y. Li. *J. Colloid Interf. Sci.* 259 (2003) 275.
- 23) F. Chen, G. Q. Xu, T. S. A. Hor. *Mater. Lett.* 57 (2003) 3282.
- 24) M. Zulaf, H. F. Eicke. *J. of Phys. Chem.* 1979 (83) 480.
- 25) S. Nave, J. Eastoe, R. K. Heenan, D. Steytler, I. Grillo. *Langmuir*. 2000 (16) 8741.
- 26) A. E. Berkowitz, R. H. Kodama, S. A. Makhlof, F. T. Parker, F. E. Spada, E. J. McNiff Jr, S. Foner. *J. of Mag. and Mag. Mater.* 196- 197 (1997) 591
- 27) A. B. Kunz. *J. Phys. C: Solid State Phys.* 14 (1981) L 455.
- 28) B. Xu, L. Dong, Y. Fan, Y. Chen. *J. of Catal.* 193 (2000) 88.
- 29) Y. Zhan, C. Zheng, Y. Liu, G. Wang. *Mater. Lett.* 57 (2003) 3265.
- 30) Y. Lin, T. Xie, B. Cheng, B. Geng, L. Zhang. *Chem. Phys. Lett.* 380 (2003) 521.
- 31) Y. Ichiyanagi, N. Wakabayashi, J. Yamazaki, S. Yamada, Y. Kimishima, E. Komatsu, H. Tajima. *Phys. B.* 329-333 (2003) 862.
- 32) J. T. Richardson, D. I. Yiagas, B. Turk, K. Forster, M. V. Twigg. *J. Appl. Phys.* 11 (1991) 70.
- 33) D.Y. Han, H.Y. Yang, C.B. Shen, X. Zhou, F.H. Wang, *Powder Technol.* 147 (2004) 113.
- 34) N. Dharmaraj, P. Prabu, S. Nagarajan, C. H. Kim, H. S. Park, H. Y. Kim. *Mat. Sci. Engg. B.* 128 (2006) 111.
- 35) D. Tao, F. Wei. *Mat. Lett.* 58 (2004) 3226.

- 36) Ph. Monnoyer, A. Fonseca, J. B. Nagy. *Colloids Surf A: Physicochem. Eng. Asp.* 100 (1995) 233.
- 37) B. D. Cullity. *Elements of X-ray Diffraction*. 2nd Edition. Addison-Wesley Publishing Inc.

Table.1 Composition of the microemulsion

R Value	25	50	75	100
AOT Wt %	10.51	9.50	8.67	7.97
Aqueous Wt%	10.639	19.22	26.32	32.25
Oil Wt%	78.846	71.27	65	51.76

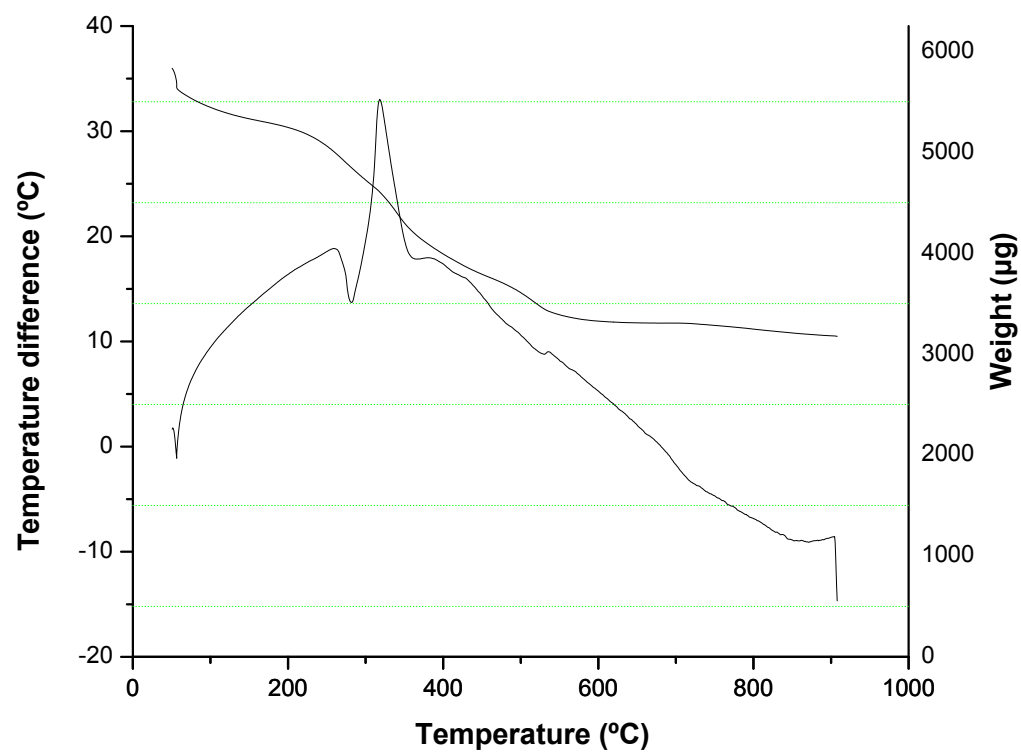


Fig-1. TGA and DTA curves for the microemulsion synthesized sample.

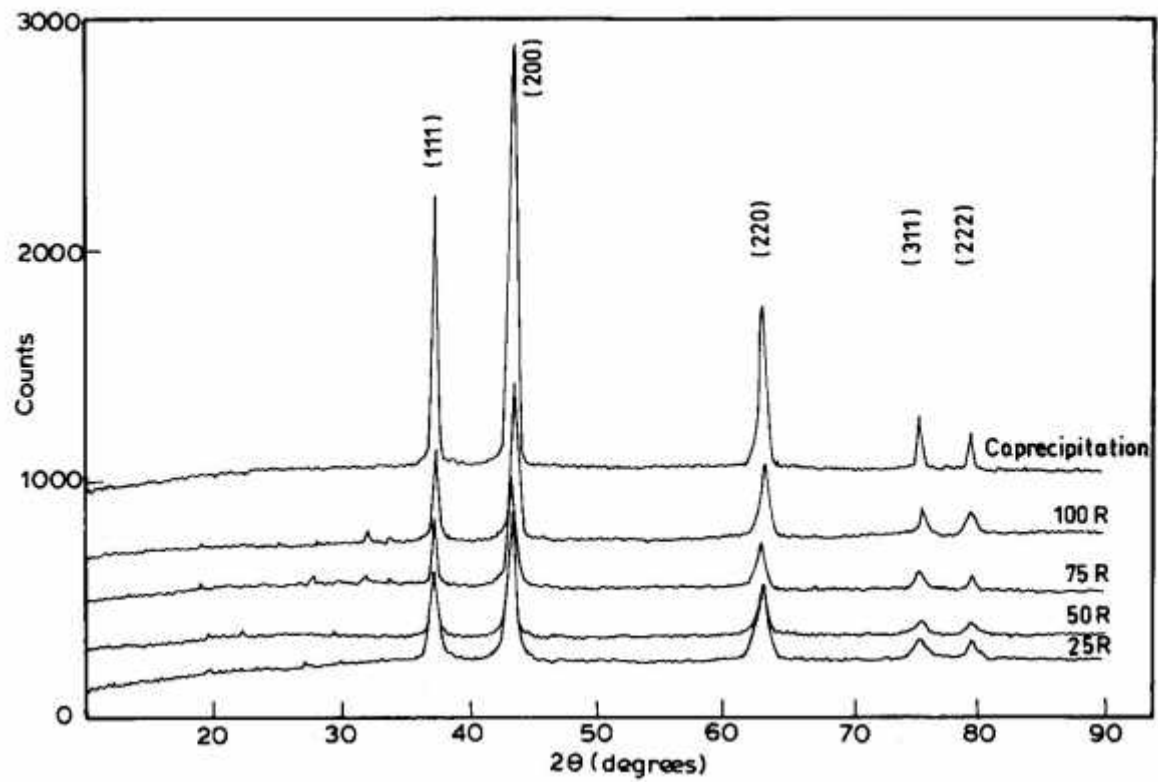
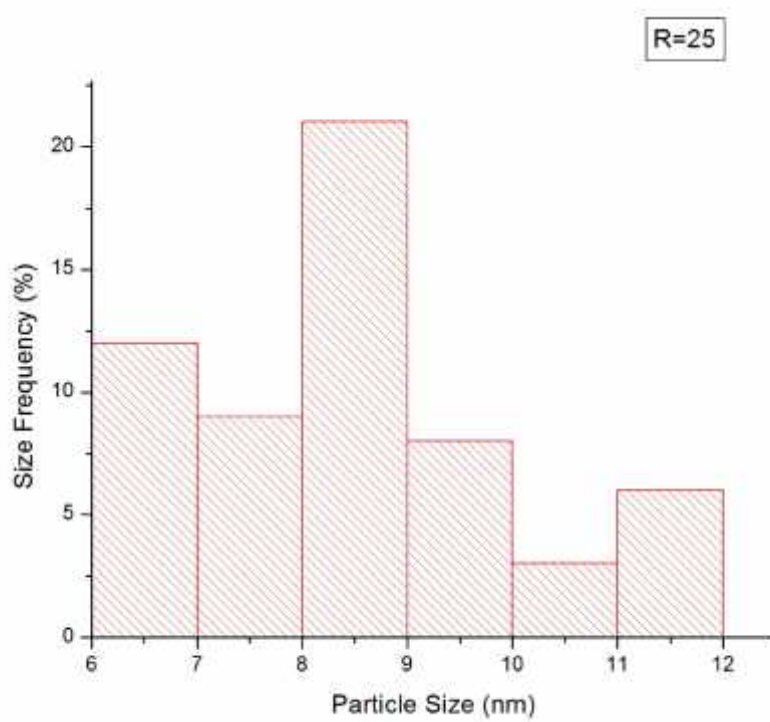
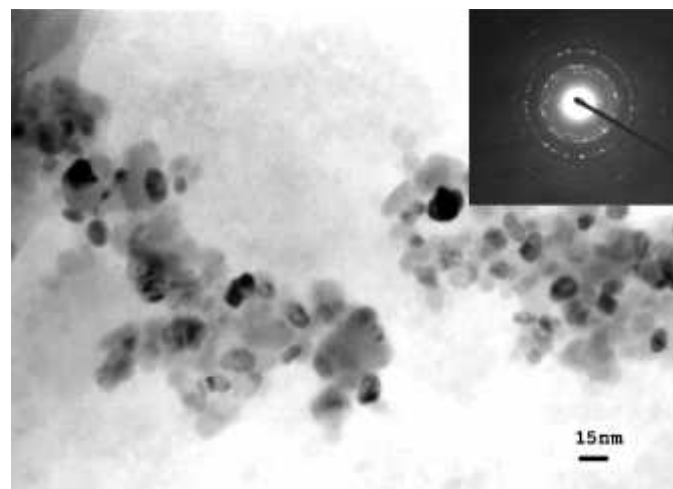
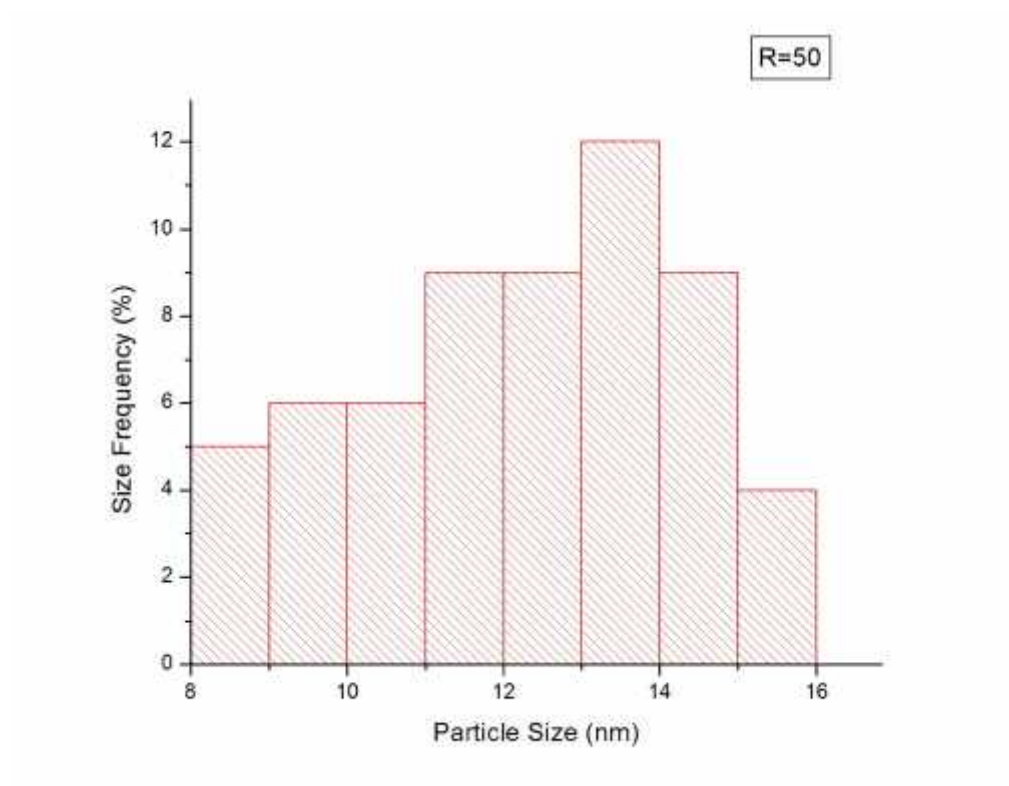
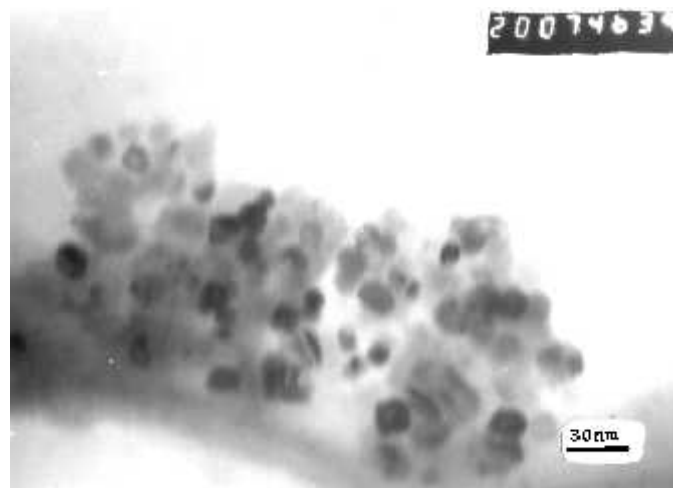


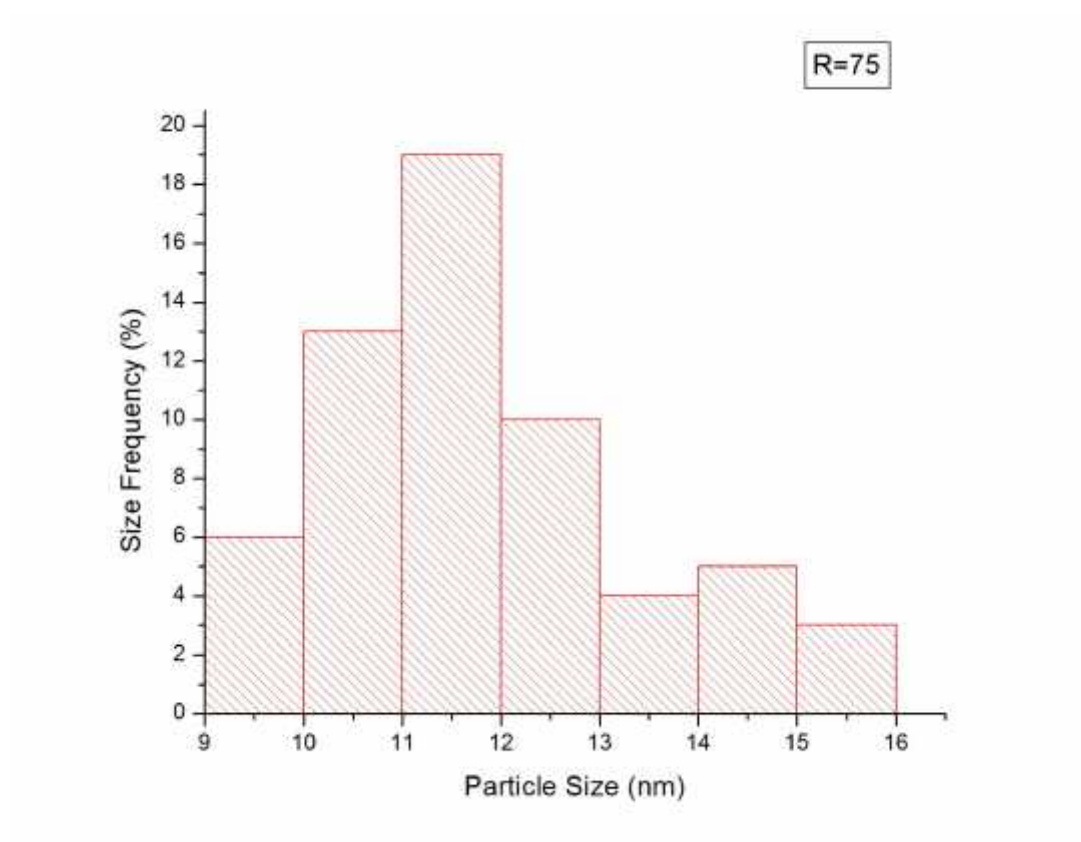
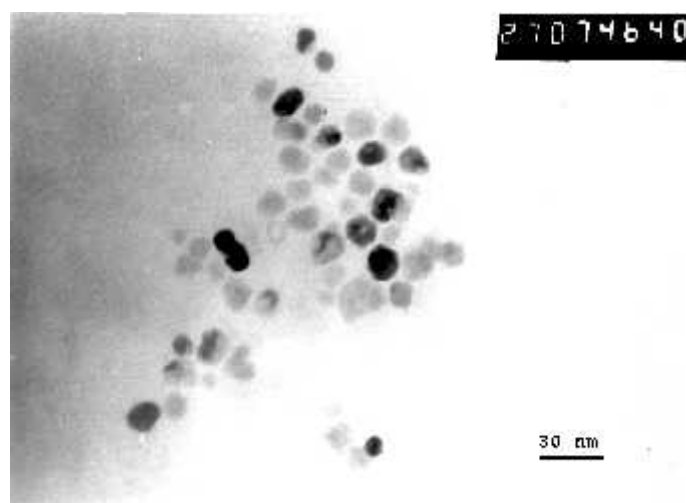
Fig. 2. X-ray diffraction pattern of nanoparticles synthesized for different R-values and co-precipitated sample.



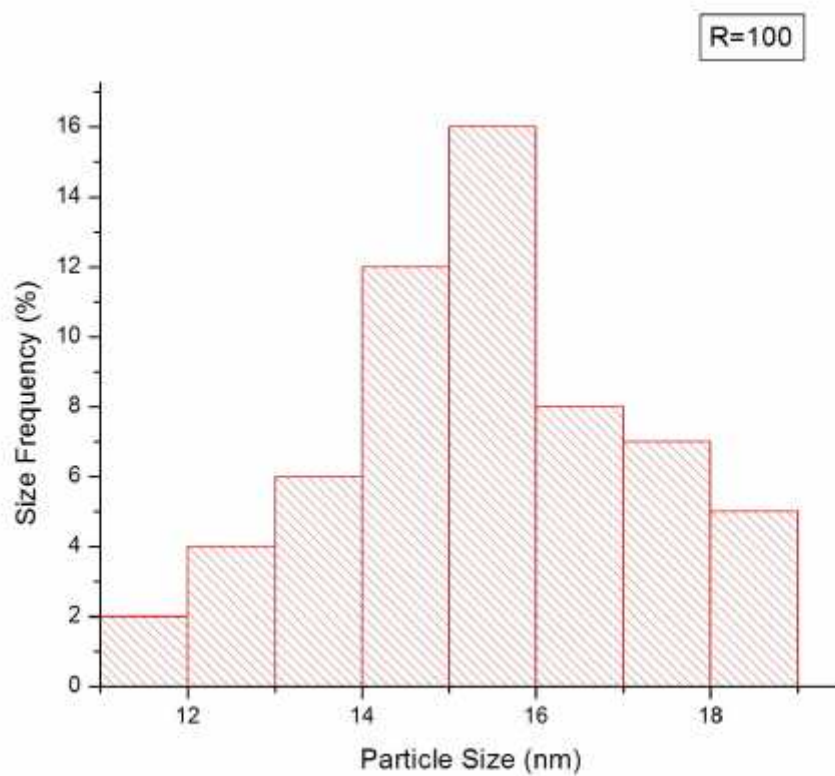
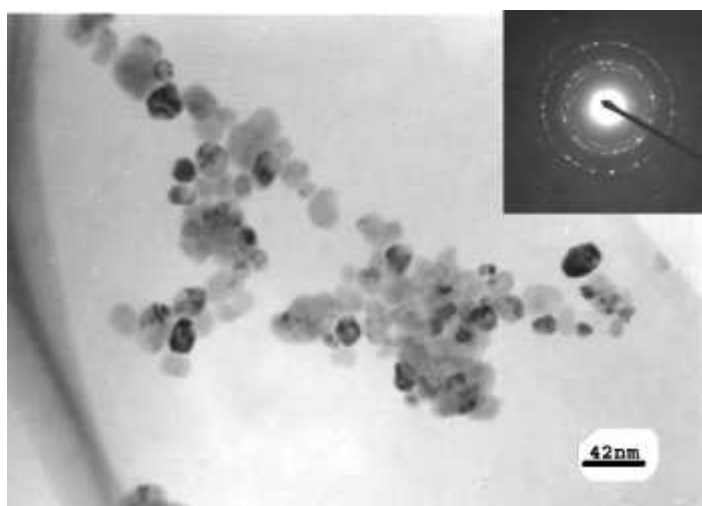
(a)



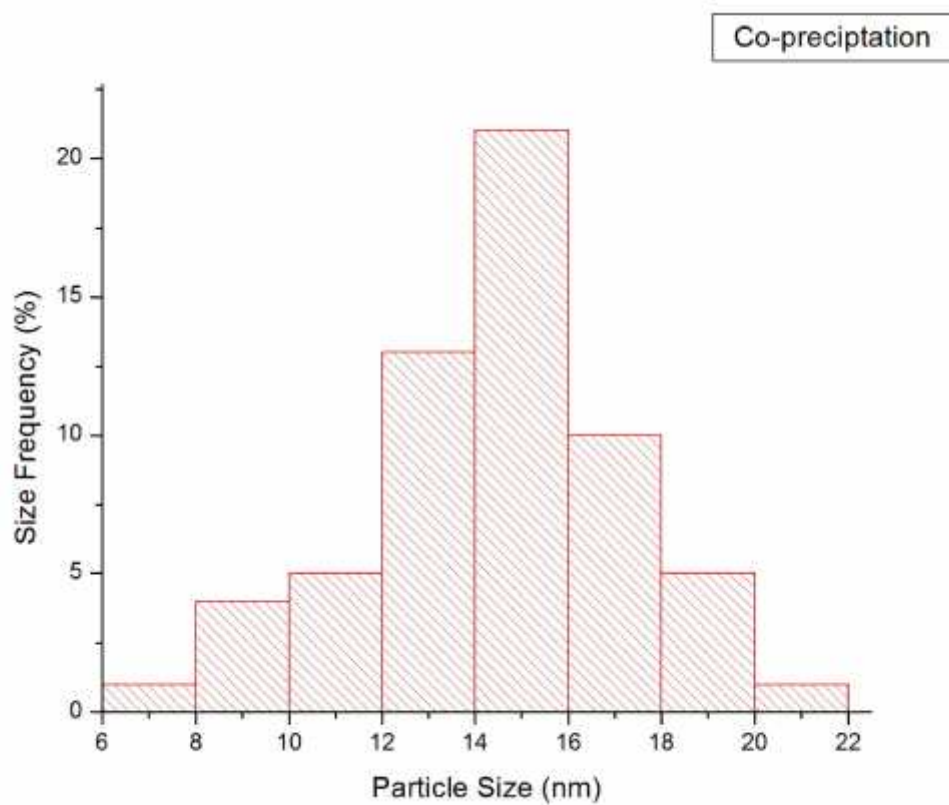
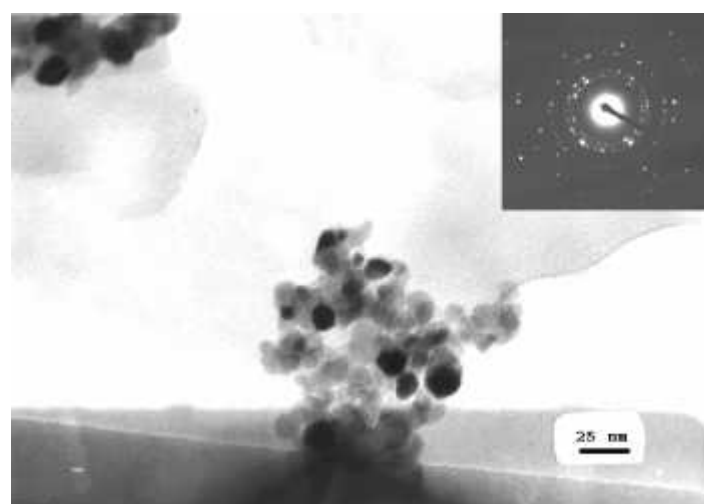
(b)



(c)



(d)



(e)

Fig. 3. TEM micrographs and histogram showing the nanoparticle size distribution. Inset shows the electron-diffraction pattern.

a) R=25 b) R= 50 c) R= 75 d) R= 100 e) Co-precipitated.

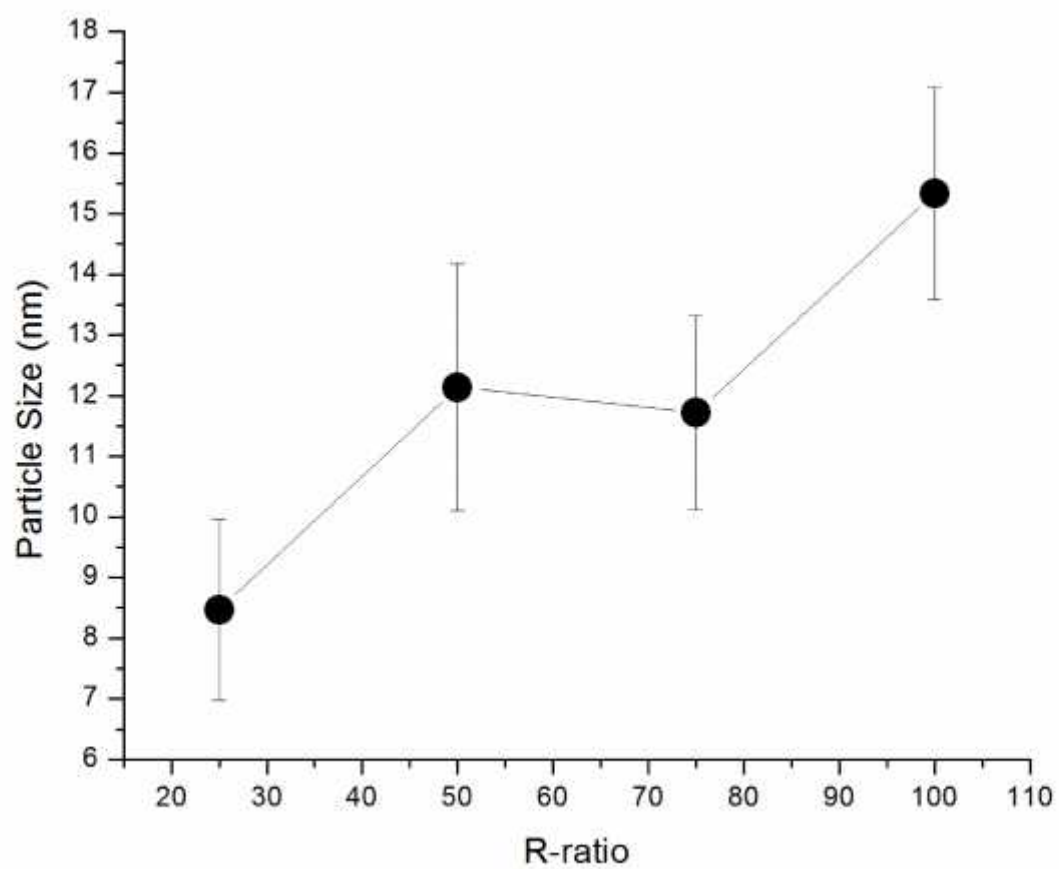


Fig. 4. Average NiO nanoparticle size (nm) vs. R-ratio.

R value	X-ray diffraction (Average crystallite size) (nm)	Transmission electron microscopy (Average particle size) (nm)
25	7.2	8.47±1.5
50	8.6	12.14±2.0
75	11	11.72±1.6
100	13	15.33±1.75
Co-precipitation	23	14.35±2.84

Table. 2. Particle size determined by XRD and Transmission Electron Microscopy.