

---

# Synthesis of NiO Nanoparticles by Water-in-oil Microemulsion Technique

Prakash Palanisamy<sup>1\*</sup> and Ashok M. Raichur<sup>1,2</sup>

<sup>1</sup>Department of Materials Engineering Indian Institute of Science Bangalore, India.

<sup>2</sup>Department of Applied Chemistry University of Johannesburg Doornfontein, South Africa.

## Authors' contributions

This work was carried out in collaboration between both authors. Author PP performed the experimental and analytical study, wrote the protocol and first draft of the manuscript. Author AMR supervised the project. Both authors read and approved the final manuscript.

Original Research Article

Received 19<sup>th</sup> December 2013

Accepted 3<sup>rd</sup> February 2014

Published 7<sup>th</sup> May 2014

---

## 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).

*Keywords: 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

---

\*Corresponding author: Email: [palanisamy.prakash@gmail.com](mailto:palanisamy.prakash@gmail.com);

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 butanedimede 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-Ag<sub>2</sub>S core-shell/composite [18], MoS<sub>x</sub> [19], Pt [20], TiO<sub>2</sub> [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].

$$W (\text{Å}) = 1.5 * R$$

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 [24]. 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 [25] and electronic behavior [26]. It has also been used as a support catalyst for anatase [27]. Zhan et al. [28] synthesized NiO nanowires using NiCl<sub>2</sub>.6H<sub>2</sub>O, Na<sub>2</sub>S.9H<sub>2</sub>O and NaCl in cyclohexane using Poly (oxyethylene)<sub>5</sub> nonylphenyl ether and Poly (oxyethylene)<sub>9</sub> nonylphenyl ether as surfactant. Lin et al. [29] synthesized ordered NiO nanowires in an electrochemical deposition process using an anodic alumina membrane and found that the nanowires were continuous and dense. Ichiyanagi et al. [30] synthesized NiO by chemically precipitating NiCl<sub>2</sub>.6H<sub>2</sub>O and Na<sub>2</sub>SiO<sub>3</sub>.9H<sub>2</sub>O. Richardson et al. [31] prepared colloidal NiO particles by chemically precipitating Ni (NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O with NaOH at a pH of 12 to study the magnetic properties. Han et al. [32] 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. [33] 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. [34] 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 [35] 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 DETAILS

### 2.1 Materials and Reagents

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.

**Table 1. Composition of the microemulsion**

<b>R Value</b>	<b>25</b>	<b>50</b>	<b>75</b>	<b>100</b>
AOT Wt %	10.50	9.50	8.70	8.0
Aqueous Wt %	10.6	19.2	26.3	32.2
Oil Wt%	78.8	71.2	65.0	51.7

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 [33,34].

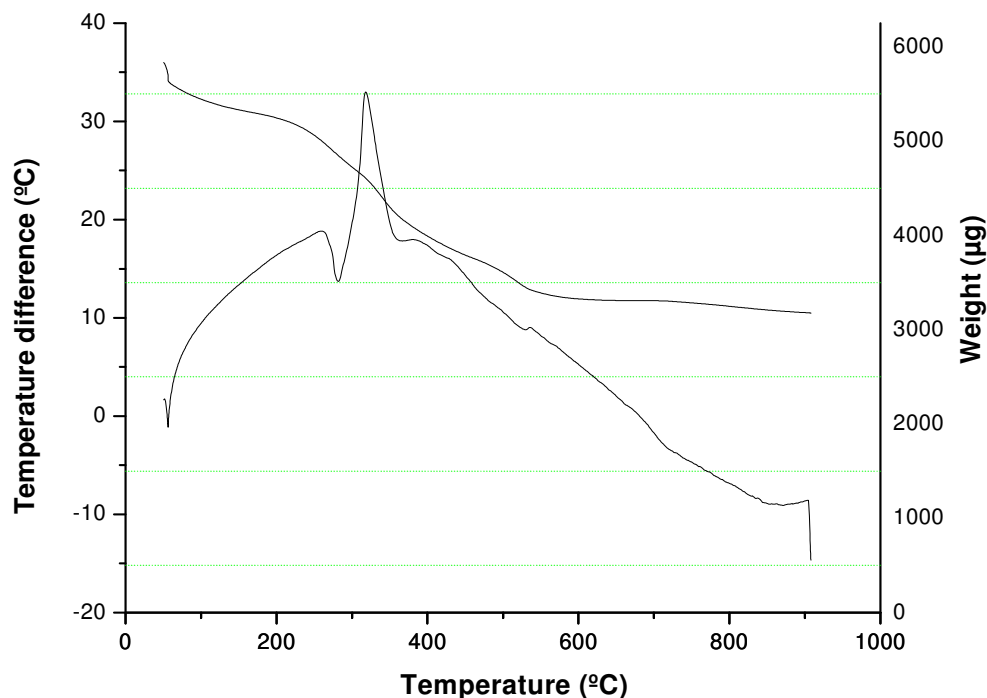


Fig. 1. TGA and DTA curves for the microemulsion synthesized sample

### 2.3 Characterization

NiO nanoparticles obtained after calcination were characterized by X-Ray diffraction (JEOL - JDX 8030) using Cu-K $\alpha$  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 [36] gave 7.0, 8.0, 11.0 and 13.0nm 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.

**Table 2. Particle size determined by XRD and transmission electron microscopy**

R value	X-ray diffraction (Average crystallite size) (nm)	Transmission electron microscopy (Average particle size) (nm)
25	7.0	8.5±1.5
50	8.0	12.1±2.0
75	11.0	11.7±1.6
100	13.0	15.33±1.7
Co-precipitation	23	14.3±2.8

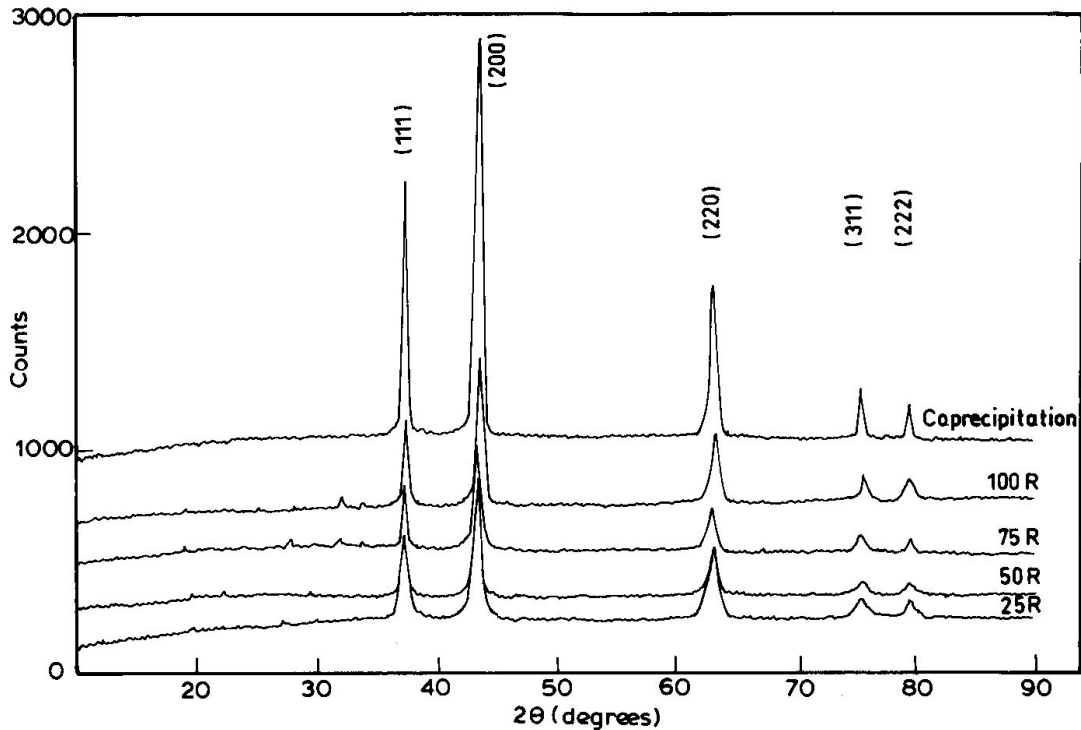
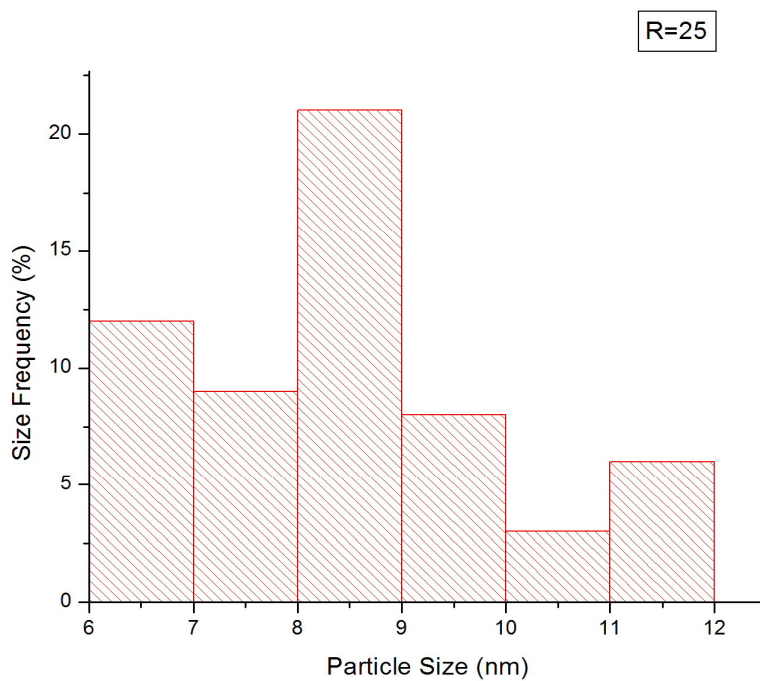
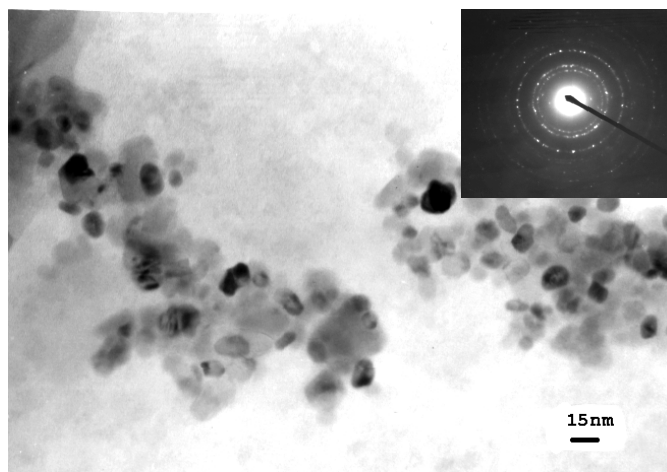
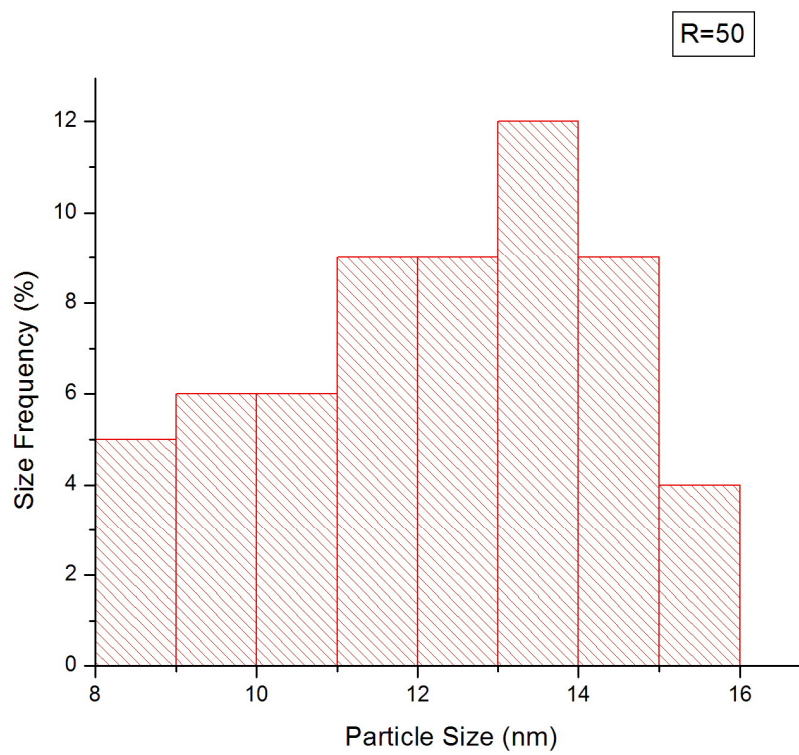
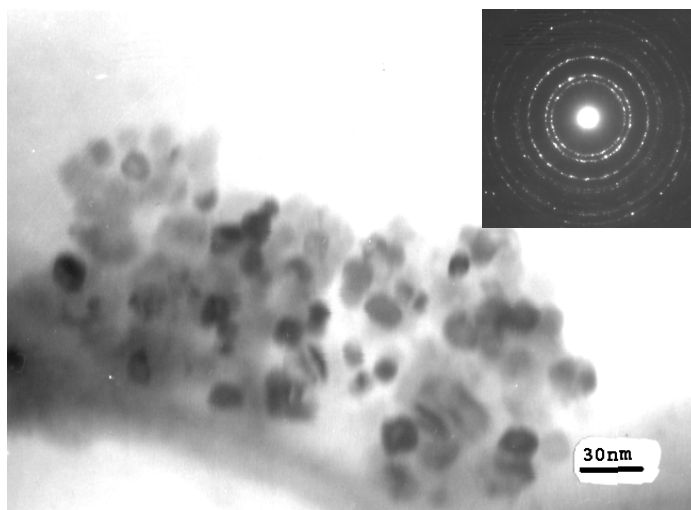
**Fig. 2. X-ray diffraction pattern of nanoparticles synthesized for different R-values and co-precipitated sample**

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 (SAD) 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-

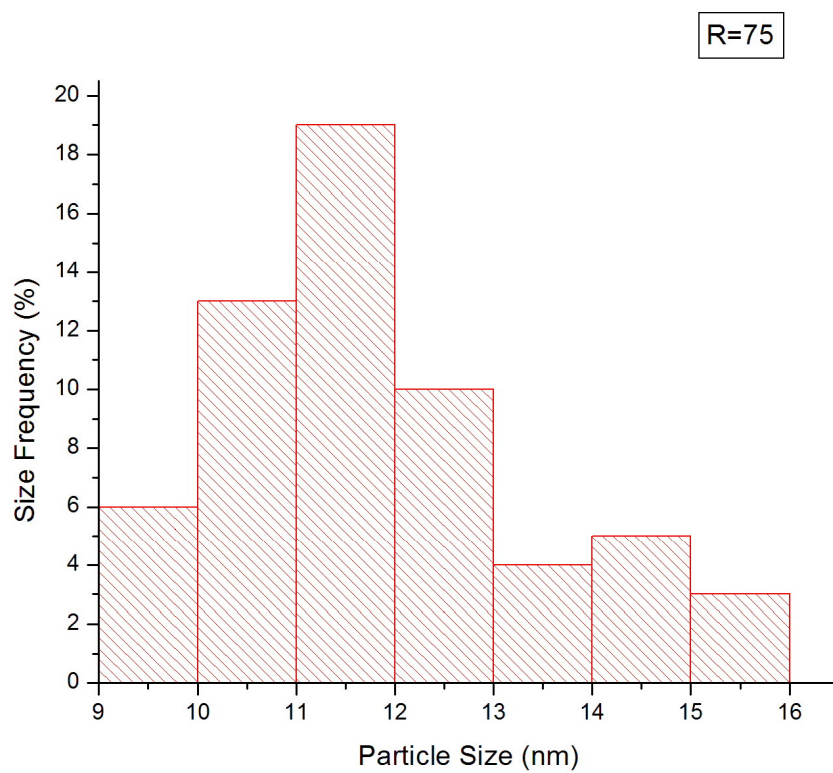
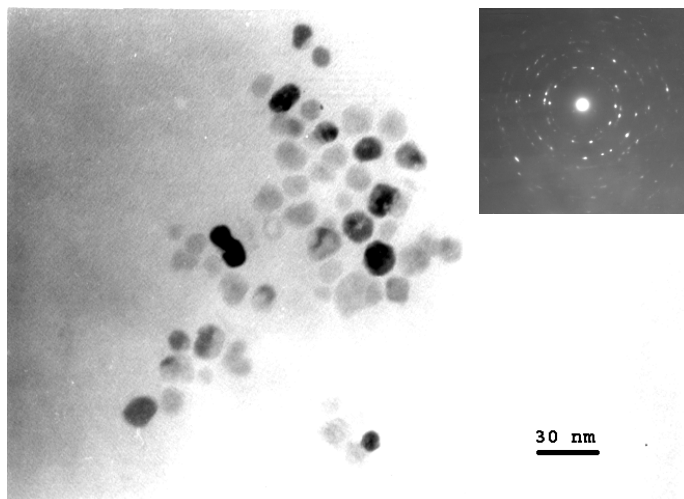
precipitated sample with no surfactant. The co-precipitated nanoparticle has unconstrained growth and is consistent with the observed wide particle size distribution.



(a)

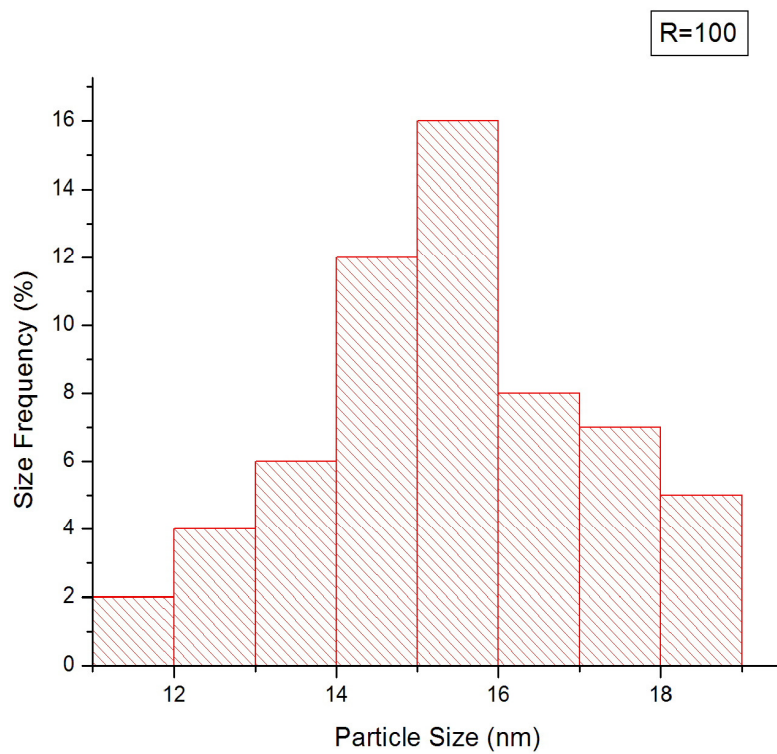
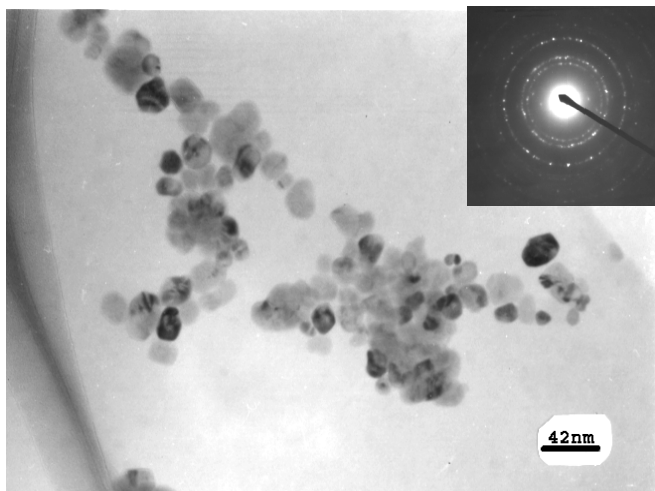


(b)

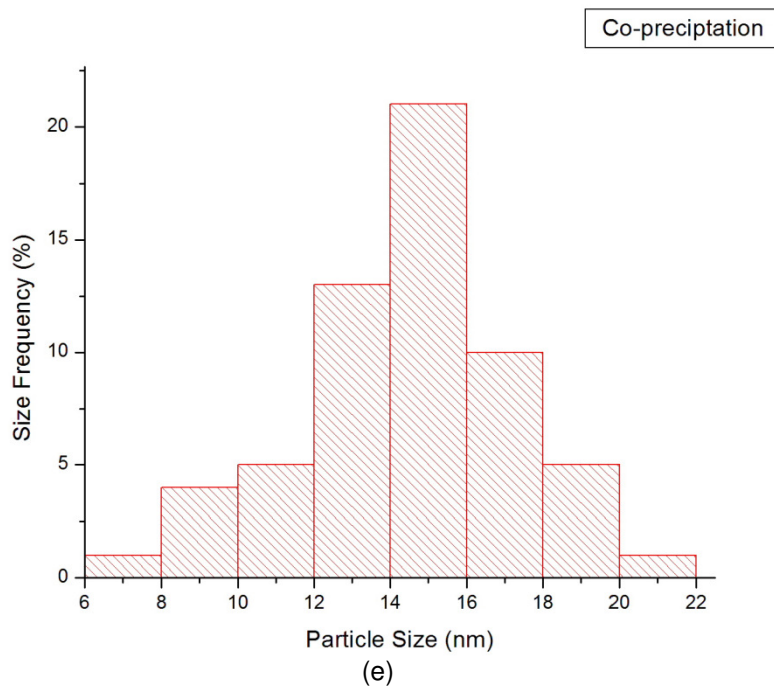
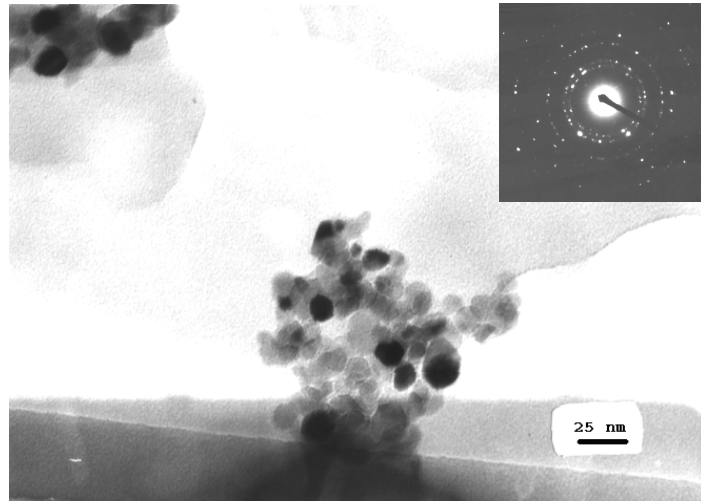


(C)





(d)



**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**

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 [36].

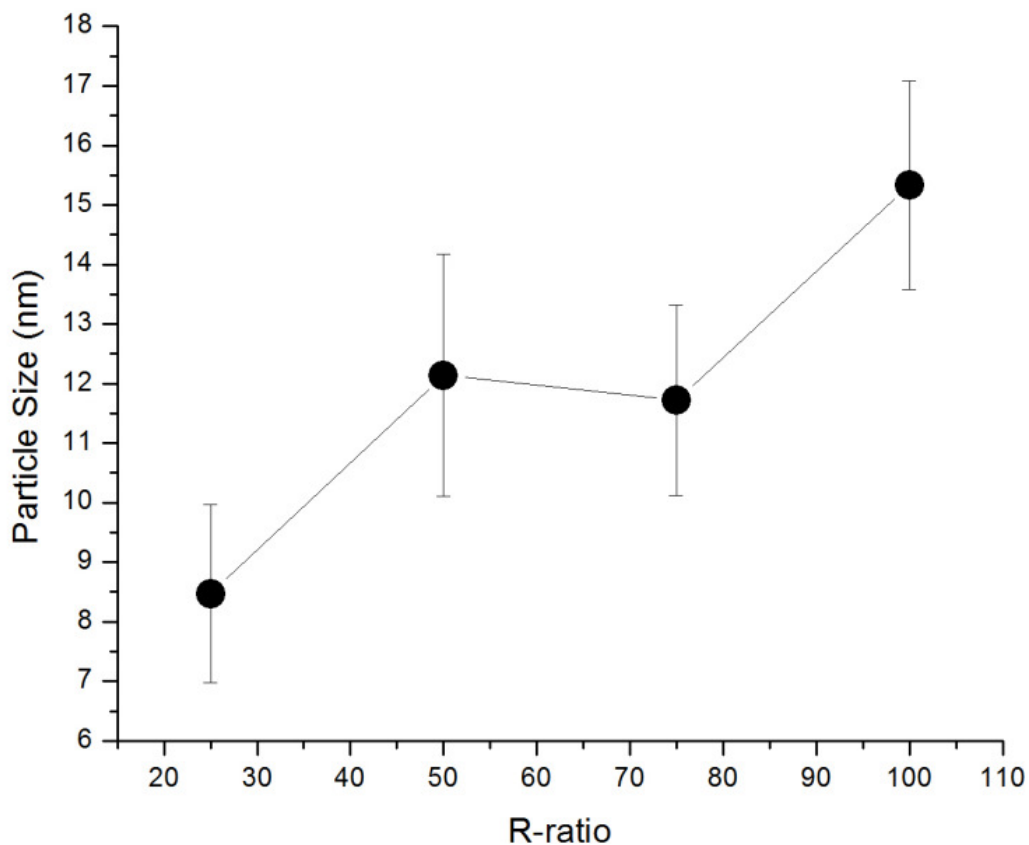


Fig. 4. Average NiO nanoparticle size (nm) vs. R-ratio

#### 4. CONCLUSION

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.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Cui H, Pillai S, Campbell P, Green M. A novel silver nanoparticle assisted texture as broadband antireflection coating for solar cell applications. *Solar Energy Materials and Solar Cells*. 2013;109:233.
2. Zhao L, Seth A, Wibowo N, Zhao CX, Mitter N, Yu C, Middelberg APJ. Nanoparticles vaccines. *Vaccine*. 2014;32:327.
3. St. John S, Angelopoulos AP. *In situ* analysis of optimum surface atom coordination for Pt nanoparticle oxygen reduction electrocatalysts. *Electrochim Acta*. 2013;112:258.
4. Pillai V, Kumar P, Hou MJ, Ayyub P, Shah DO. Preparation of nanoparticles of silver halides, superconductors and magnetic materials using water-in-oil microemulsions as nano-reactors. *Adv Colloid Interfac*. 1995;55:241.
5. Ekimov A. Growth and optical properties of semiconductor nanocrystals in a glass matrix. *J Lumin*. 1996;70:1.
6. Mangal H, Saxena A, Rawat AS, Kumar V, Rai PK, Datta M. Adsorption of nitrobenzene on zero valent iron loaded metal oxide nanoparticles under static conditions. *Microporous and Mesoporous Mater*. 2013;168:247.
7. Ko HH, Hsi CS, Wang MC, Zhao X. Crystallite growth kinetics of TiO<sub>2</sub> surface modification with 9 mol% ZnO prepared by a coprecipitation process. *J Alloy Comp*. 2014;588:428.
8. Tang K, Qian Y, Zeng J, Yang X. Solvothermal route to semiconductor nanowires. *Adv Mater*. 2003;15:448.
9. Franzel L, Bertino MF, Huba ZJ, Carpenter EE. Synthesis of magnetic nanoparticles by pulsed laser ablation. *Appl Surf Sci*. 2012;261:332.
10. Lu T, Wang J, Yin J, Wang A, Wang X, Zhang T. Surfactant effects on the microstructures of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by microemulsion method. *Colloids Surf A: Physicochem Eng Asp*. 2013;436:675.
11. Sarkar D, Tikku S, Thapar V, Srinivasa RS, Khilar KC. Formation of zinc oxide nanoparticles of different shapes in water-in-oil microemulsion. *Coll and Surf A: Physicochem Eng Aspects*. 2011;381:123.
12. Solanki JN, Sengupta R, Murthy ZVP. Synthesis of copper sulphide and copper nanoparticles with microemulsion method. *Solid State Electronics*. 2011;12:1560.
13. Capek I. Preparation of metal nanoparticles in water-in-oil microemulsions. *Adv Colloid Interfac*. 2004;110:49.
14. Smeets NMB, McKenna TFL. The synthesis of translucent polymer nanolatexes via microemulsion polymerization. *J Colloid Interf Sci*. 2012;383:28.
15. Palanisamy P, Raichur AM. Synthesis of spherical NiO nanoparticles through a novel biosurfactant mediated emulsion technique. *Mater Sci and Engg C*. 2009;29:199.
16. Palanisamy P, Raichur AM. Biosurfactant mediated synthesis of NiO nanorods. *Mater Lett*. 2008;29:743.
17. Liang Y, Shao M, Cui W, Liu L, McEvoy JG. Photocatalytic degradation of Rhodamine B by CdS-loaded K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> nanocomposites prepared via reverse microemulsion. *J Molec Catal A Chem*. 2013;370:87.
18. Hota G, Jain S, Khilar KC. Synthesis of CdS–Ag<sub>2</sub>S core-shell/composite nanoparticles using AOT/n-heptane/water microemulsions. *Coll and Surf A: Physicochem Eng Aspects*. 2004;232:119.
19. Marchand KE, Tarret M, Lecharie JP, Normand L, Kasztelan S, Cseri T. Investigation of AOT-based microemulsions for the controlled synthesis of MoS<sub>x</sub> nanoparticles: An electron microscopy study. *Colloids Surf A Physicochem Eng Asp*. 2003;214:239.

20. Yadav OP, Palmqvist A, Cruise N, Holmberg K. Synthesis of platinum nanoparticles in microemulsions and their catalytic activity for the oxidation of carbon monoxide. *Coll and Surf A: Physicochem Eng Aspects*. 2003;221:131.
21. Zubieta CE, Soltero-Martínez JFA, Luengo CV, Schulz PC. Preparation, characterization and photoactivity of TiO<sub>2</sub> obtained by a reverse microemulsion route. *Powder Technology*. 2011;212:410.
22. Li Y, Cao C, Chen Z. Magnetic and optical properties of Fe doped ZnS nanoparticles synthesized by microemulsion method. *Chem Phys Lett*. 2011;517:55.
23. Lemke K, Prietzel C, Koetz J. Fluorescent gold clusters synthesized in a poly(ethyleneimine) modified reverse microemulsion. *J Colloid Interf Sci*. 2013;394:141.
24. Nave S, Eastoe J, Heenan RK, Steytler D, Grillo I. What is special about Aerosol-OT? *Langmuir*. 2000;16:8741.
25. Berkowitz AE, Kodama RH, Makhlof SA, Parker FT, Spada FE, McNiff EJ Jr, Foner S. Anomalous properties of magnetic nanoparticles. *J of Mag and Mag Mater*. 1997;196-197:591.
26. Kunz AB. Electronic structure of NiO. *J Phys C: Solid State Phys*. 1981;14:455.
27. Xu B, Dong L, Fan Y, Chen Y. A study on the dispersion of NiO and/or WO<sub>3</sub> on anatase. *J of Catal*. 2000;193:88.
28. Zhan Y, Zheng C, Liu Y, Wang G. Synthesis of NiO nanowires by an oxidation route. *Mater Lett*. 2003;57:3265.
29. Du Y, Wang W, Li X, Zhao J, Ma J, Liu Y, Lu G. Preparation of NiO nanoparticles in microemulsion and its gas sensing performance. *Mater Lett*. 2012;68:168.
30. Ichiyanagi Y, Wakabayashi N, Yamazaki J, Yamada S, Kimishima Y, Komatsu E, Tajima H. Magnetic properties of NiO nanoparticles. *Phys B*. 2003;329-333:862.
31. Richardson JT, Yiagas DI, Turk B, Forster K, Twigg MV. Origin of superparamagnetism in Nickel oxide. *J Appl Phys*. 1991;11:70.
32. Han DY, Yang HY, Shen CB, Zhou X, Wang FH. Synthesis and size control of NiO nanoparticles by water-in-oil microemulsion. *Powder Technol*. 2004;147:113.
33. Dharmaraj N, Prabu P, Nagarajan S, Kim CH, Park HS, Kim HY. Synthesis and nickel oxide nanoparticles using nickel acetate and poly (vinyl acetate) precursor. *Mat Sci Engg B*. 2006;128:111.
34. Tao D, Wei F. New procedure towards size-homogeneous and well-dispersed nickel oxide nanoparticles of 30 nm. *Mat Lett*. 2004;58:3226.
35. Monnoyer PH, Fonseca A, Nagy JB. Preparation of colloidal AgBr particles from microemulsions. *Colloids Surf A: Physicochem Eng Asp*. 1995;100:233.
36. Cullity BD. *Elements of X-ray Diffraction*. 2<sup>nd</sup> Edition. Addison-Wesley Publishing Inc; 1978.

© 2014 Palanisamy and Raichur; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:*  
<http://www.sciencedomain.org/review-history.php?iid=500&id=7&aid=4509>