

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

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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

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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]

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

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 [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 NiCl₂·6H₂O, Na₂S·9H₂O and NaCl in cyclohexane using Poly(oxyethylene)₅nonylphenyl ether and Poly(oxyethylene)₉nonylphenyl 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 NiCl₂·6H₂O and Na₂SiO₃·9H₂O. Richardson *et al.* [31] prepared colloidal NiO particles by chemically precipitating Ni(NO₃)₂·6H₂O 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.

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].

Table.1 Composition of the microemulsion

R Value	25	50	75	100
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

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139 **2.3 Characterization**

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

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149 **3. RESULTS AND DISCUSSION**

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151 Fig. 2 shows the X-Ray powder diffraction pattern of the NiO nanoparticles corresponding to
152 R values of 25, 50, 75, 100 and for co-precipitated sample. From the peak broadening it is
153 evident that the crystallites are nanosize and the average crystallite size determined using
154 Scherrer formula [36] gave 7.0, 8.0, 11.0 and 13.0nm for R values of 25, 50, 75 and 100,

155 respectively and for bulk co-precipitated sample it is 15nm. Table.2 shows the crystallite size
156 determined using XRD.

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158 The lattice parameter calculated at a higher angle gave a value of 4.1736 Å that is
159 consistent for NiO and is matched with the JCPDS card No. 75-0197 for 100R and 50R, for
160 25R ,75R and for co-precipitated sample it is matched with the JCPDS card No. 78-0423.

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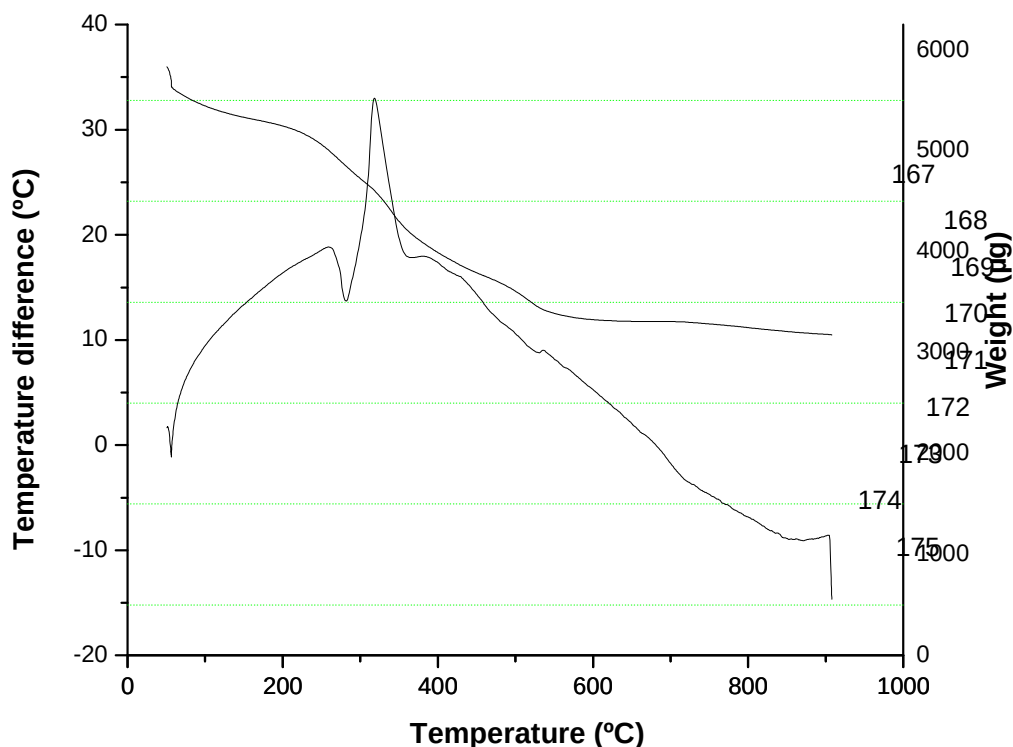
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Fig. 1. TGA and DTA curves for the microemulsion synthesized sample.

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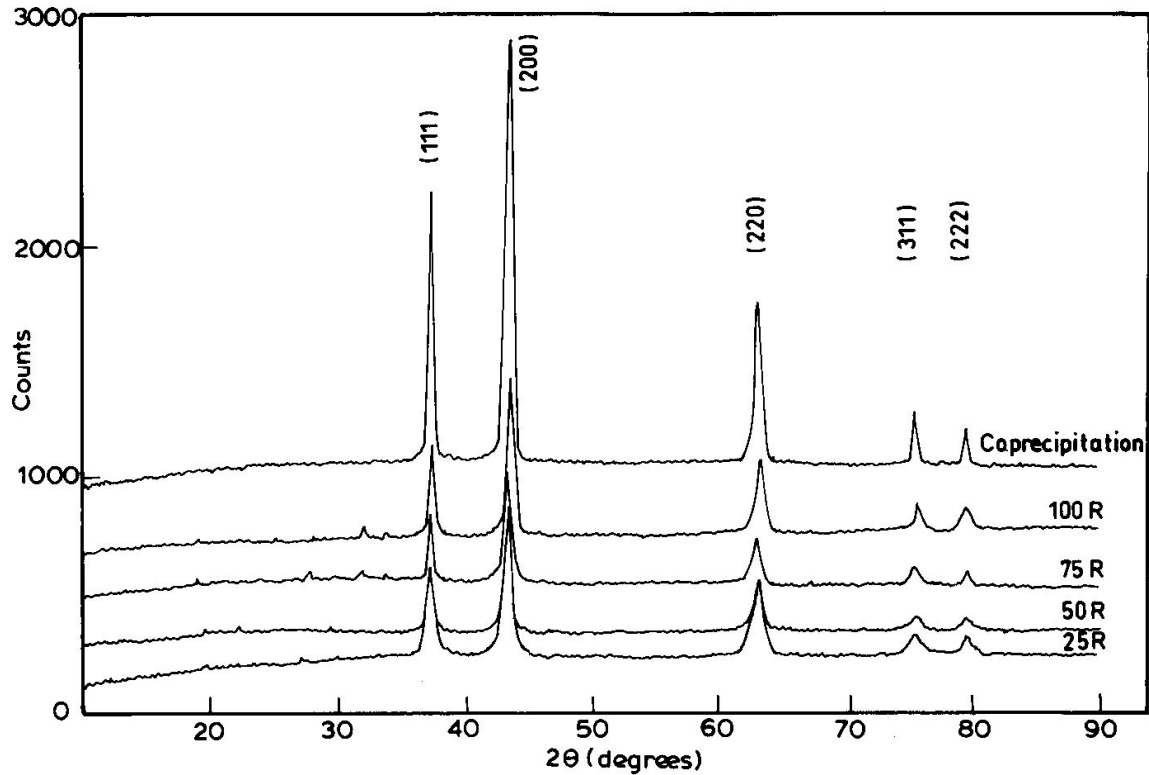
181 Fig. 3 shows the TEM micrographs of NiO nanoparticles synthesized using microemulsion
182 technique as well as for the co-precipitated sample. The Selected Area Electron Diffraction
183 (SAD) pattern (inset in the TEM micrographs) shows that the nanoparticles are highly
184 crystalline. The size controlling feature is one of the advantages of the microemulsion
185 technique for nanoparticle synthesis that is evident from the particle size measured from the
186 TEM micrographs for various R values (Fig. 4). The particle size distribution was measured
187 using the Sigma scan pro 4.0 software, and the number of particles taken under the study
188 was 60. The particle size distribution histogram is given below the TEM micrographs. The
189 size distribution was narrow for the particles synthesized in the microemulsion region and a
190 wide distribution was observed for the nanoparticles synthesized outside the microemulsion
191 regime. The size distribution was wider in the case of high R values attributed due to
192 swelling of the nanoreactor due to less coverage of the capping agent. It is found that

193 particle size and distribution for high R value is comparable to the conventional co-
194 precipitated sample with no surfactant. The co-precipitated nanoparticle has unconstrained
195 growth and is consistent with the observed wide particle size distribution.

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197 The particle size measured from the TEM micrographs for different R-values and for co-
198 precipitated sample is given in Table. 2. Consistent with the eqn. 1, particle size increases
199 proportionally with R-value and this shows that microemulsion is a good technique for size

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

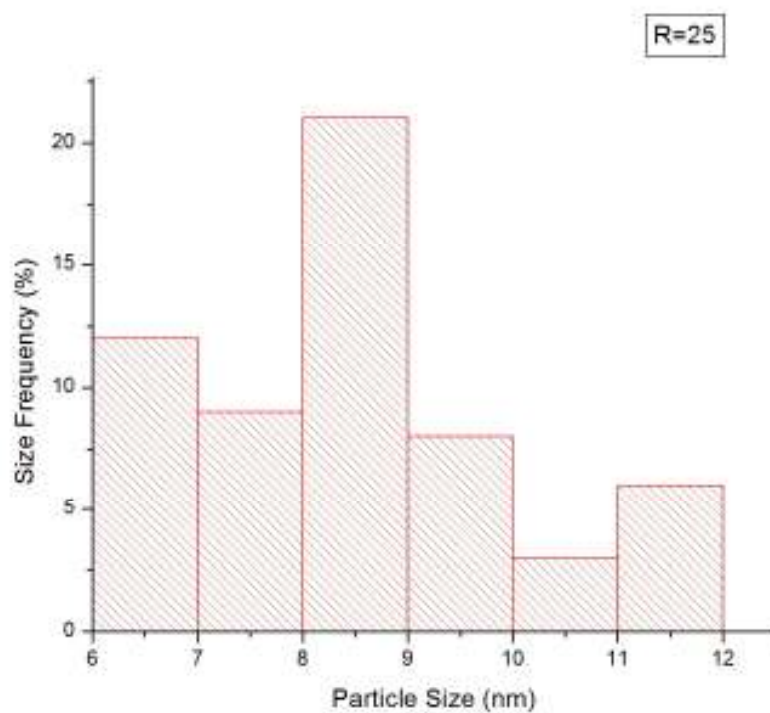
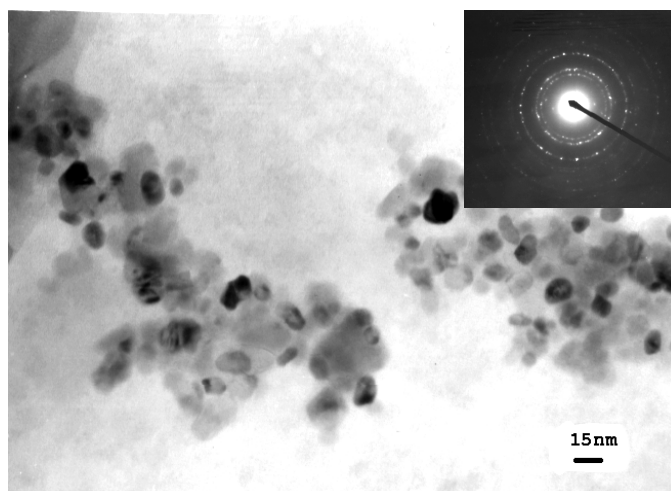
202 controlled synthesis of nanoparticles. Significant difference in the crystallite size estimates
203 by XRD technique and as measured by TEM was attributed due to strain, defects and
204 inherent instrumental broadening that adds to the error in nanoparticle size estimate by XRD
205 technique [36].

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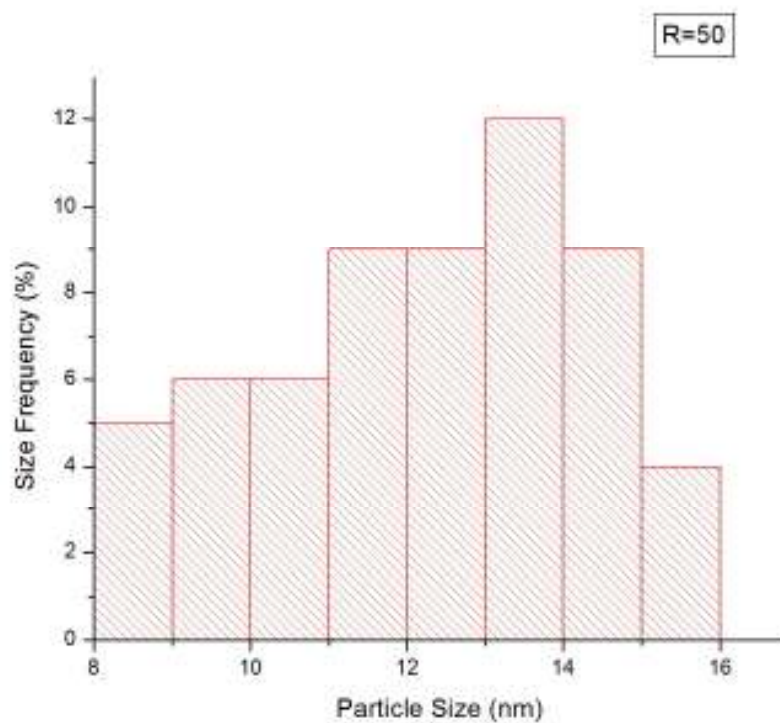
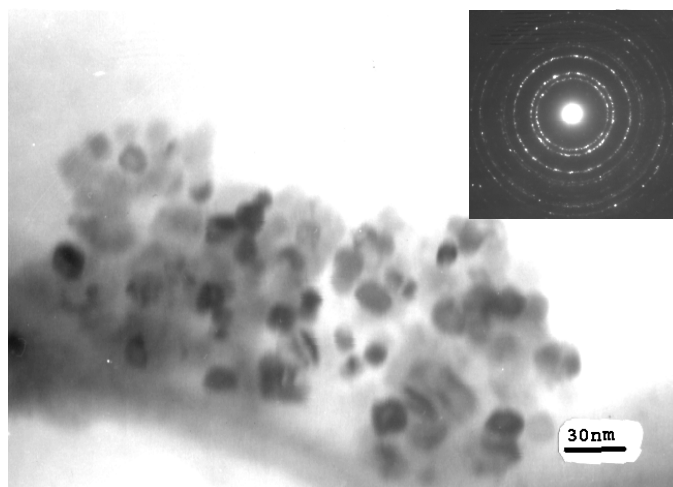
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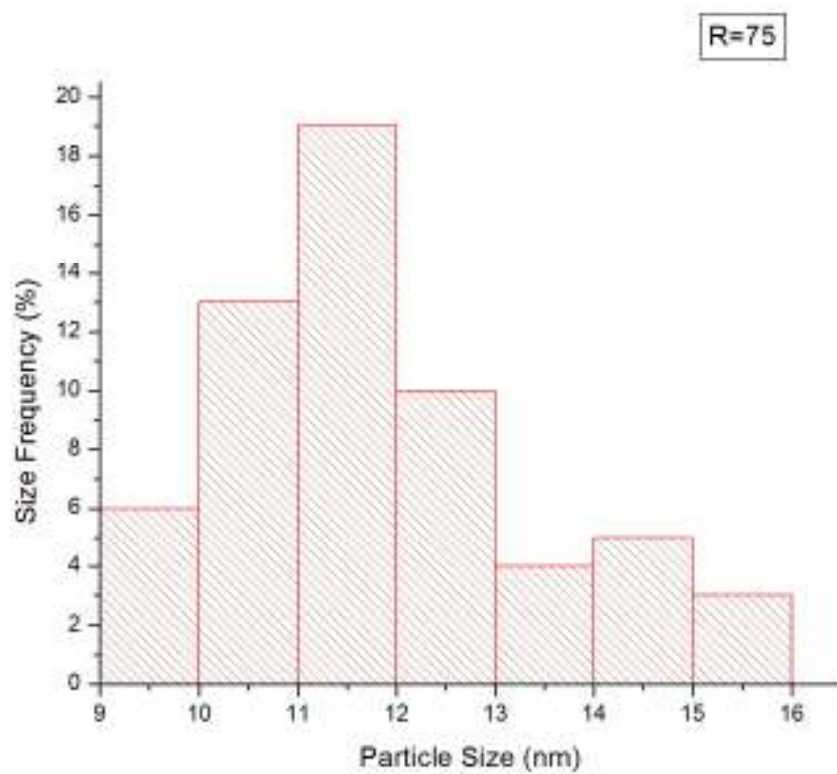
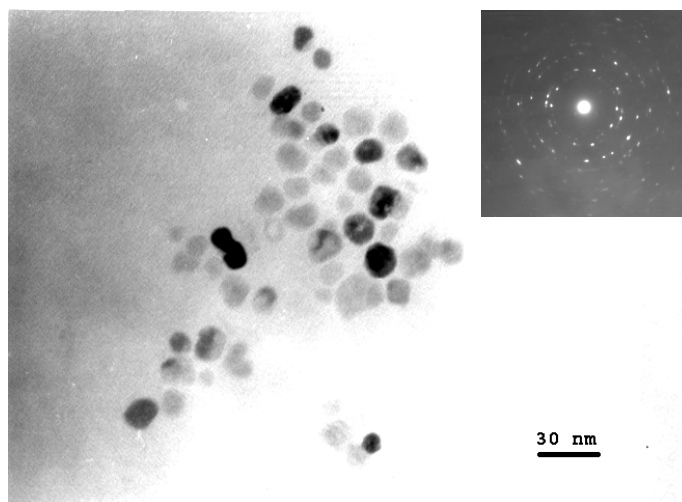
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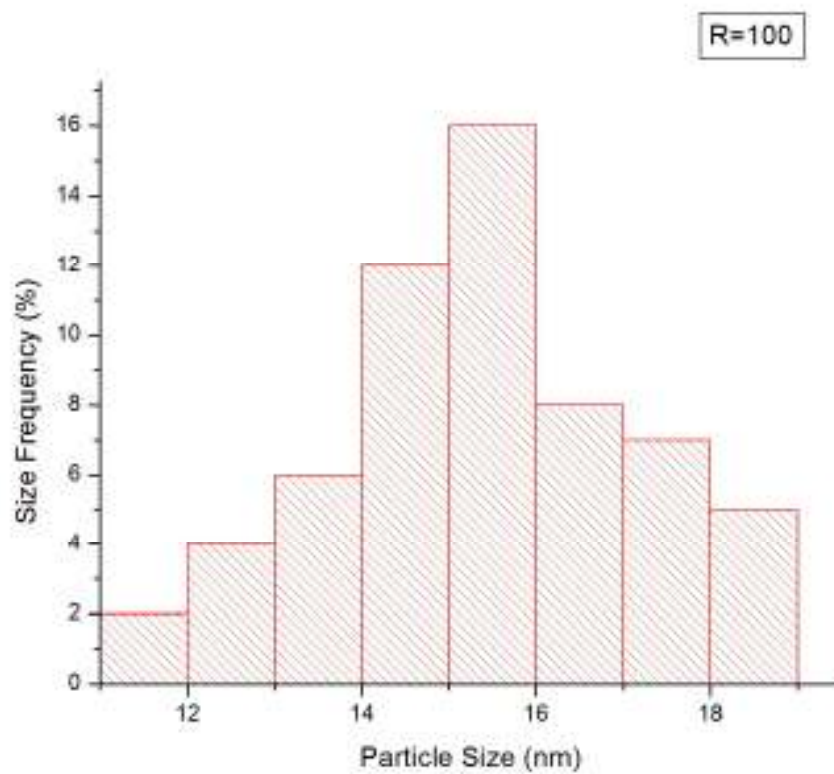
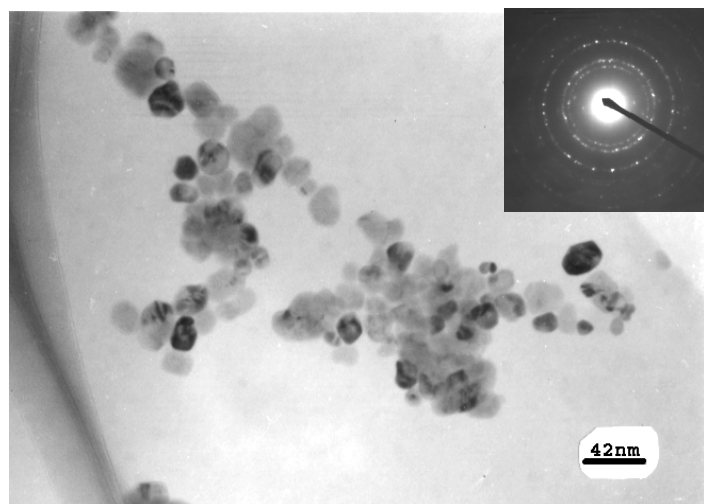


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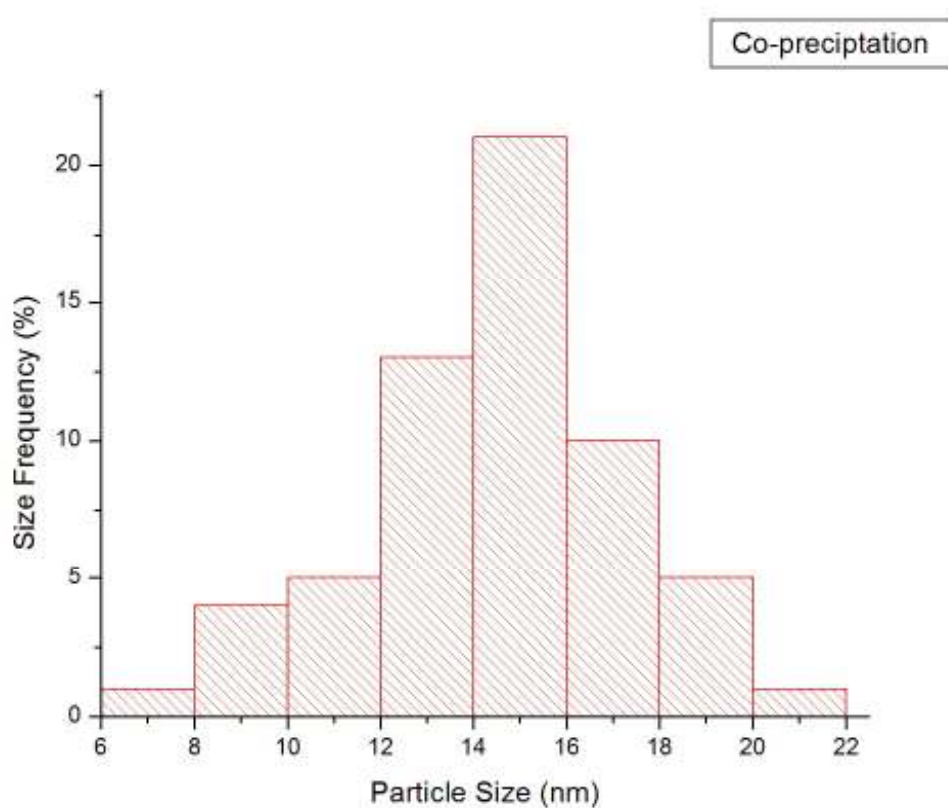
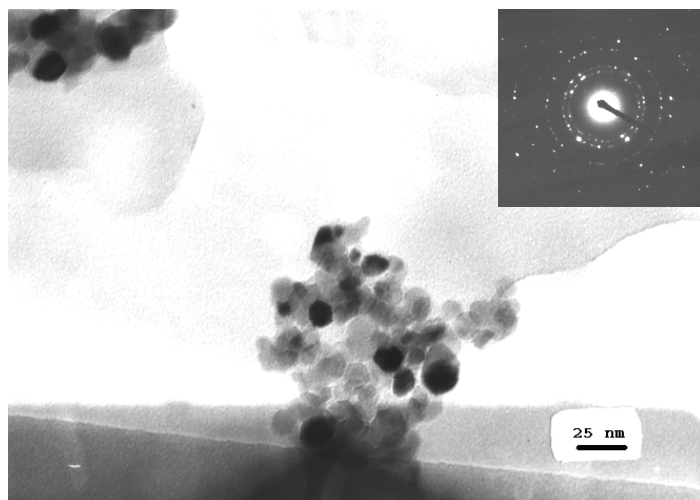


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Fig. 3. TEM micrographs and histogram showing the nanoparticle size distribution. Inset shows the electron-diffraction pattern.

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

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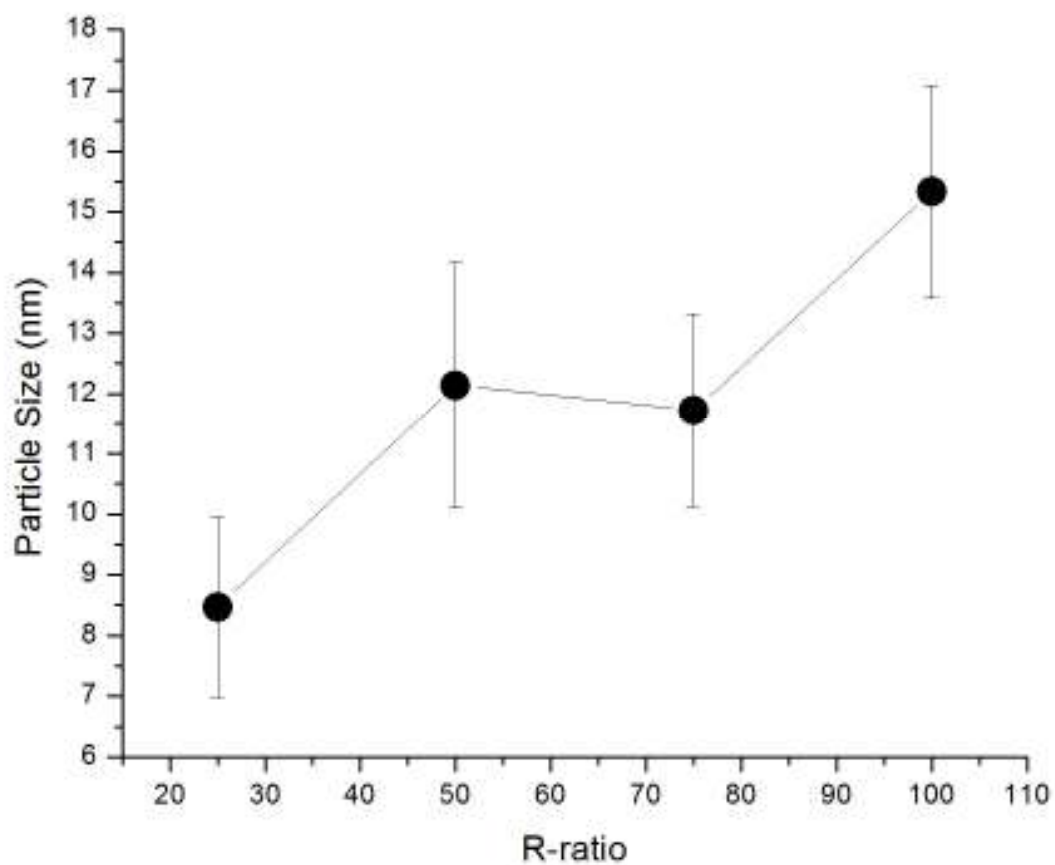


Fig. 4. Average NiO nanoparticle size (nm) vs. R-ratio.

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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

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

4. CONCLUSION

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

457 **COMPETING INTERESTS**

458

459 Authors have declared that no competing interests exist.

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462 **REFERENCES**

463

- 464 1) H. Cui, S. Pillai, P. Campbell, M. Green. A novel silver nanoparticle assisted texture as
465 broadband antireflection coating for solar cell applications. *Solar Energy Materials and*
466 *Solar Cells*. 109 (2013) 233.
- 467 2) L. Zhao, A. Seth, N. Wibowo, C-X. Zhao, N. Mitter, C. Yu, A. P. J. Middelberg.
468 Nanoparticles vaccines. *Vaccine*. 32 (2014) 327.
- 469 3) S. St. John, A. P. Angelopoulos. In situ analysis of optimum surface atom coordination for
470 Pt nanoparticle oxygen reduction electrocatalysts. *Electrochim. Acta*. 112 (2013) 258.
- 471 4) V. Pillai, P. Kumar, M. J. Hou, P. Ayyub, D. O. Shah. Preparation of nanoparticles of silver
472 halides, superconductors and magnetic materials using water-in-oil microemulsions as
473 nano-reactors. *Adv. Colloid. Interfac.* 55 (1995) 241.
- 474 5) A. Ekimov. Growth and optical properties of semiconductor nanocrystals in a glass matrix.
475 *J. Lumin.* 70 (1996) 1.
- 476 6) H. Mangal, A. Saxena, A. S. Rawat, V. Kumar, P. K. Rai, M. Datta. Adsorption of
477 nitrobenzene on zero valent iron loaded metal oxide nanoparticles under static conditions.
478 *Microporous and Mesoporous Mater.* 168 (2013) 247.
- 479 7) H-H. Ko, C-S. Hsi, M-C. Wang, X. Zhao. Crystallite growth kinetics of TiO₂ surface
480 modification with 9 mol% ZnO prepared by a coprecipitation process. *J. Alloy. Comp.* 588
481 (2014) 428.
- 482 8) K. Tang, Y. Qian, J. Zeng, X. Yang. Solvothermal route to semiconductor nanowires. *Adv.*
483 *Mater.* 15 (2003) 448.
- 484 9) L. Franzel, M. F. Bertino, Z. J. Huba, E. E. Carpenter. Synthesis of magnetic
485 nanoparticles by pulsed laser ablation. *Appl. Surf. Sci.* 261 (2012) 332.
- 486 10) T. Lu, J. Wang, J. Yin, A. Wang, X. Wang, T. Zhang . Surfactant effects on the
487 microstructures of Fe₃O₄ nanoparticles synthesized by microemulsion method. *Colloids*
488 *Surf A: Physicochem. Eng. Asp.* 436 (2013) 675.
- 489 11) D. Sarkar, S. Tikku, V. Thapar, R. S. Srinivasa, K. C. Khilar. Formation of zinc
490 oxide nanoparticles of different shapes in water-in-oil microemulsion. *Coll. and Surf A:*
491 *Physicochem.Eng. Aspects*. 381 (2011) 123.
- 492 12) J. N. Solanki, R. Sengupta, Z.V.P. Murthy. Synthesis of copper sulphide and copper
493 nanoparticles with microemulsion method. *Solid State Electronics*. 12 (2011) 1560.
- 494 13) I. Capek. Preparation of metal nanoparticles in water-in-oil microemulsions. *Adv. Colloid.*
495 *Interfac.* 110 (2004) 49.
- 496 14) N. M. B. Smeets, T. F. L. McKenna. The synthesis of translucent polymer nanolatexes via
497 microemulsion polymerization . *J. Colloid Interf. Sci.* 383 (2012) 28.
- 498 15) P. Palanisamy, A. M. Raichur. Synthesis of spherical NiO nanoparticles through a novel
499 biosurfactant mediated emulsion technique. *Mater. Sci. and Engg: C*. 29 (2009) 199.
- 500 16) P. Palanisamy, A. M. Raichur. Biosurfactant mediated synthesis of NiO nanorods. *Mater.*
501 *Lett.* 29 (2008) 743.
- 502 17) Y. Liang, M. Shao, W. Cui, L. Liu, J. G. McEvoy. Photocatalytic degradation of
503 Rhodamine B by CdS-loaded K₄Nb₆O₁₇ nanocomposites prepared via reverse
504 microemulsion. *J. Molec. Catal. A: Chem.* 370 (2013) 87
- 505 18) G. Hota, S. Jain, K. C. Khilar. Synthesis of CdS–Ag₂S core-shell/composite nanoparticles
506 using AOT/*n*-heptane/water microemulsions. *Coll. and Surf A: Physicochem.Eng.*
507 *Aspects*. 232 (2004) 119.
- 508 19) K. E. Marchand, M. Tarret, J. P. Lecharie, L. Normand, S. Kasztelan, T. Cseri.
509 Investigation of AOT-based microemulsions for the controlled synthesis of

- 510 MoS_x nanoparticles: an electron microscopy study. *Colloids Surf A: Physicochem. Eng.*
 511 *Asp.* 214 (2003) 239.
- 512 20) O. P. Yadav, A. Palmqvist, N. Cruise, K. Holmberg. Synthesis of platinum nanoparticles in
 513 microemulsions and their catalytic activity for the oxidation of carbon monoxide. *Coll. and*
 514 *Surf A: Physicochem. Eng. Aspects.* 221 (2003) 131.
- 515 21) C. E. Zubieta, J. F. A. Soltero - Martínez, C. V. Luengo, P. C. Schulz. Preparation,
 516 characterization and photoactivity of TiO₂ obtained by a reverse microemulsion route.
 517 *Powder Technology.* 212 (2011) 410.
- 518 22) Y. Li, C. Cao, Z. Chen. Magnetic and optical properties of Fe doped ZnS nanoparticles
 519 synthesized by microemulsion method. *Chem. Phys. Lett.* 517 (2011) 55.
- 520 23) K. Lemke, C. Prietzel, J. Koetz. Fluorescent gold clusters synthesized in a
 521 poly(ethyleneimine) modified reverse microemulsion. *J. Colloid Interf. Sci.* 394 (2013)
 522 141.
- 523 24) S. Nave, J. Eastoe, R. K. Heenan, D. Steytler, I. Grillo. What is special about Aerosol-
 524 OT?. *Langmuir.* 16 (2000) 8741.
- 525 25) A. E. Berkowitz, R. H. Kodama, S. A. Makhlof, F. T. Parker, F. E. Spada, E. J. McNiff Jr,
 526 S. Foner. Anomalous properties of magnetic nanoparticles. *J. of Mag. and Mag. Mater.*
 527 196- 197 (1997) 591
- 528 26) A. B. Kunz. Electronic structure of NiO. *J. Phys. C: Solid State Phys.* 14 (1981) L 455.
- 529 27) B. Xu, L. Dong, Y. Fan, Y. Chen. A study on the dispersion of NiO and/or WO₃ on
 530 anatase. *J. of Catal.* 193 (2000) 88.
- 531 28) Y. Zhan, C. Zheng, Y. Liu, G. Wang. Synthesis of NiO nanowires by an oxidation route.
 532 *Mater. Lett.* 57 (2003) 3265.
- 533 29) Y. Du, W. Wang, X. Li, J. Zhao, J. Ma, Y. Liu, G. Lu. Preparation of NiO nanoparticles in
 534 microemulsion and its gas sensing performance. *Mater. Lett.* 68 (2012) 168.
- 535 30) Y. Ichiyanagi, N. Wakabayashi, J. Yamazaki, S. Yamada, Y. Kimishima, E. Komatsu, H.
 536 Tajima. Magnetic properties of NiO nanoparticles. *Phys. B.* 329-333 (2003) 862.
- 537 31) J. T. Richardson, D. I. Yiagas, B. Turk, K. Forster, M. V. Twigg. Origin of
 538 superparamagnetism in Nickel oxide. *J. Appl. Phys.* 11 (1991) 70.
- 539 32) D.Y. Han, H.Y. Yang, C.B. Shen, X. Zhou, F.H. Wang. Synthesis and size control of NiO
 540 nanoparticles by water-in-oil microemulsion. *Powder Technol.* 147 (2004) 113.
- 541 33) N. Dharmaraj, P. Prabhu, S. Nagarajan, C. H. Kim, H. S. Park, H. Y. Kim. Synthesis and
 542 nickel oxide nanoparticles using nickel acetate and poly(vinyl acetate) precursor. *Mat. Sci.*
 543 *Engg. B.* 128 (2006) 111.
- 544 34) D. Tao, F. Wei. New procedure towards size-homogeneous and well-dispersed nickel
 545 oxide nanoparticles of 30 nm. *Mat. Lett.* 58 (2004) 3226.
- 546 35) Ph. Monnoyer, A. Fonseca, J. B. Nagy. Preparation of colloidal AgBr particles from
 547 microemulsions. *Colloids Surf A: Physicochem. Eng. Asp.* 100 (1995) 233.
- 548 36) B. D. Cullity. Elements of X-ray Diffraction. 2nd Edition. Addison-Wesley Publishing Inc.
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550 **AUTHORS' CONTRIBUTIONS**

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