

Effect of surfactants in the synthesis of NiO nanoparticles by colloidal thermal assisted reflux condensation method

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Received: 29 August 2013, revised: 26 December 2013, accepted: 27 December 2013

Abstract

Nickel oxide (NiO) nanoparticles were prepared by colloidal thermal assisted reflux condensation method using nickel acetate (precursor salt) and N, N - Dimethylformamide - DMF (solvent) with or without the addition of surfactants such as cetyl trimethyl ammonium bromide (CTAB), polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and sodium monododecyl sulphate (SDS) respectively. Finally, the prepared samples products were calcined at different temperatures systematically such as at 200°C, 400°C, 600°C, 800°C for 2 hrs each to get the phase pure product. The calcined nanoparticles were characterized by X-Ray Diffraction (XRD), Energy Dispersive X-ray Analysis (EDAX), Fourier Transform Infrared (FTIR) Spectroscopy, Particle Size Analysis, Scanning Electron Microscopy (SEM), Diffuse Reflectance Spectroscopy (DRS) and Photo Luminescence (PL) Spectroscopy techniques. All the samples were crystallized in cubic structure. Effect of surfactants in the synthesis of nickel oxide (NiO) particles is discussed and reported.

Keywords: Thermal assisted reflux condensation method; NiO nanoparticles; Effect of surfactants

1. Introduction

Metal oxide nanoparticles have been studied world-wide for potential applications now-a-days. NiO is a p-type semiconductor oxide material owing to its defect structure and it has a wide band gap energy range from 3.4 - 4 eV [1, 2]. NiO has been studied various groups since it has an excellent durability and electrochemical stability as well due to its good optical, magnetic and electrical characteristics[3-5]. Further, NiO is a potential candidate for various applications such as electronic devices [6-8], catalysts [9-11], smart windows [12], battery electrodes [13], dye-sensitized solar cell devices [14,15], electro chromic display devices and films [16,17], gas sensor materials [18], electrochemical super capacitors [19], antiferro-magnetic films [20], fuel cell electrodes [21,22], energy efficient automobile mirrors [23], building glazing materials [24] and hetero junction solar cells [25]. Several reports showed an amazing level of its performance as a candidate material for various other applications also [26-27]. NiO

nanoparticles were prepared by various routes such as, sputtering [28-31], electrochemical deposition [32-34], thermal decomposition [35-37], electron beam evaporation[38], vacuum evaporation[39], solvothermal[40], polymer-matrix assisted synthesis[41], spray pyrolysis[42,43], surfactant-mediated synthesis[44], sol-gel technique[45-50], chemical method[51], chemical precipitation [52,53], micro emulsion [54], reactive pulsed laser ablation technique [55], hydrothermal method [56-58] microwave method [59], etc. In this research work, we report a simple way of synthesizing NiO nanoparticles by a colloidal thermal assisted reflux condensation method in presence of surfactants. The prepared materials were characterized systematically by XRD, EDAX, FTIR, Particle Size Analysis, SEM, DRS and PL techniques. The effect of surfactants in the synthesis of NiO nanoparticles is discussed and reported.

2. Experimental procedure

The analytical grade chemicals such as nickel acetate (Merck, India), N, N-Dimethylformamide (Merck, India), cetyl trimethyl ammonium bromide (Merck, India), polyvinyl pyrrolidone (Merck, India), polyvinyl alcohol (Merck, India) and sodium monododecyl sulphate (Merck, India), ethanol (Merck, India) were used. Deionized water was used throughout the experiment. The NiO nanoparticles were prepared by colloidal thermal assisted reflux condensation method as shown in Fig. 1. In the typical experiment, the nickel acetate solution (1M) was prepared by dissolving it in 100 ml DMF. The above solution mixture was taken in a RB flask and stirred well at room temperature for about 10 minutes. After stirring, a reflux condenser was connected with the RB flask and the solution was refluxed at 90° C for 6 h in a magnetic stirring apparatus (1200 rpm). A colloidal precipitate was resulted. It was cooled down and the precipitate was separated by centrifugation. The separated precipitate was washed thoroughly with 9:1 water ethanol mixture and then dried at 85° C for 2 h. The resultant material was heat treated at temperatures such as, 200, 400, 600 and 800°C for 2 h each to get a phase pure product. The above experiment was repeated with the addition of surfactant (1 %) such as CTAB, PVP, PVA and SDS each at the initial stage itself to study the effect of surfactants in the preparation of NiO nanoparticles. The reaction and mechanism involved in the synthesis of NiO nanoparticles are indicated in Fig. 2.

The powder XRD studies were carried out with a Shimadzu XRD6000 X-ray diffractometer using CuK α radiation ($\lambda = 0.154059$ nm) radiation with a nickel filter. The applied current and voltage were 30 mA and 40 kV respectively. The 2θ scanning range was 10° to 90° with a scan rate of 10°/min⁻¹. The crystallite sizes of nickel oxide were estimated using the Debye-Scherrer equation. The chemical structure information of NiO nano powder were recorded by Fourier transform infrared spectra (SHIMADZU Spectrophotometer) using KBr pellet technique in the range from 4000cm⁻¹ to 400cm⁻¹ (spectral resolution was 4 cm⁻¹ and number of scans was 20). The average particle size of the NiO nano powder was measured with a Zetasizer Ver. 6.32 manufactured by the Malvern Instruments Ltd. The surface morphology, size of particles and elemental compositions of NiO nano powder was characterized by scanning electron microscope (SEM JEOL JSM-6610) equipped with an energy dispersive X-ray (EDAX) spectrophotometer and operated at 20kV. Absorbance spectra of the NiO nano powder were recorded by UV-Visible Double Beam Spectrophotometer (Shimadzu 1800), equipped with a diffuse reflectance sphere using Teflon was employed as a reference material. Powder samples were loaded into a quartz cell and spectra were recorded range between 200 nm to 600 nm by using

diffused reflectance method. Photoluminescence spectrum of the NiO nano powder was measured by Spectrofluorophotometer (FLUOROLOG, HORIBA YVON) with Xe laser as the excitation light source at room temperature.

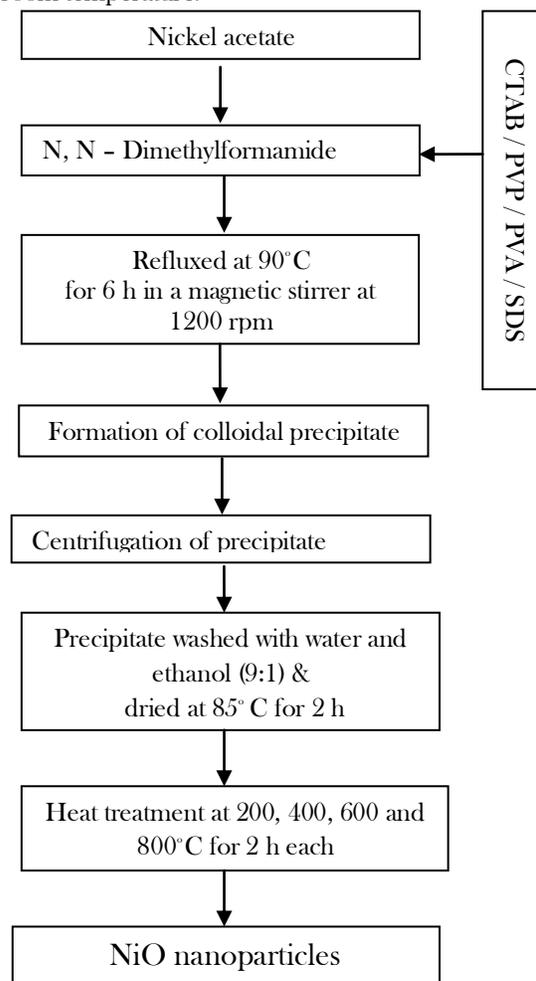


Figure 1. Flow chart to prepare NiO nanoparticles by colloidal thermal assisted reflux condensation method

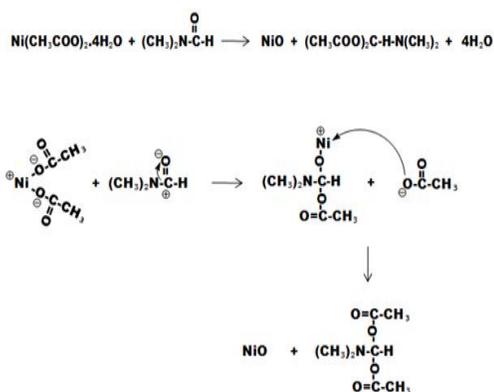


Figure 2. Reaction and mechanism involved in the synthesis of NiO nanoparticles by colloidal thermal assisted reflux condensation method

3. Results & Discussion

3.1. X-Ray Diffraction Studies

The powder XRD patterns obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method are indicated in Fig. 3. The XRD peaks are found to be very sharp indicating the highly crystalline nature of the sample. The product is identified as NiO using JCPDS pattern No. 01-1239. The diffraction peaks found in all the samples can be exactly indexed to a cubic structure of NiO. The lattice parameters were calculated from 2θ values in the X-ray diffraction patterns. No characteristic peaks of impurity were observed. The crystal size (D_x) was calculated using the Debye-Scherrer formula [60].

$$D_x = 0.91 \lambda / \beta \cos\theta \quad (1)$$

Where ' λ ' is the X-ray wavelength ($\lambda = 0.154059$ nm for CuK α), ' β ' is the FWHM (full width at half maximum intensity) and ' θ ' is the Bragg's angle.

The theoretical density (D_p) was calculated using the formula [61].

$$D_p = (Z * M) / (N * a^3) \text{ g.cm}^{-3} \quad (2)$$

Where ' Z ' is the number of chemical species in the unit cell, ' M ' is the molecular mass of the sample (g/mol), ' N ' is the Avogadro's number (6.022×10^{23}) and ' a ' is the lattice constant (cm). The crystallographic parameters obtained on the NiO nanoparticles are given in the Table 1.

Table 1. The crystallographic parameters obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method

Sample	Crystal structure	Unit cell lattice parameter 'a' (Å)	Unit cell volume (Å) ³	Theoretical density (g/cc)	Crystallite size (nm)
Standard XRD data for NiO powder (JCPDS No. 01-1239)	Cubic	4.171	72.56	6.838	--
NiO (prepared without any surfactant)	Cubic	4.1786	72.9613	6.7999	.30
NiO (prepared with CTAB)	Cubic	4.1714	72.5848	6.8352	5.17
NiO (prepared with PVP)	Cubic	4.1538	71.6699	6.9225	5.12
NiO (prepared with PVA)	Cubic	4.1600	71.9913	6.8916	4.87
NiO (prepared with SDS)	Cubic	4.1534	71.6492	6.9245	4.55

3.2 Energy dispersive X- ray spectroscopy (EDAX) analysis

The EDAX spectra of NiO nanoparticles synthesized by colloidal thermal assisted reflux condensation method are reported in Fig. 4. EDAX spectra of the samples show peaks for Ni and O only and not for any other impurities in the samples. The chemical composition data obtained on NiO by EDAX analysis is given in Table 2. The data confirmed the presence of nickel and oxygen in all the samples. From the EDAX data, it was found that the weight percentage of nickel is varied between 53.0-57.46 % and for oxygen is 42.54 - 47.0%. The variation in the percentage of elements (Ni and O) may be due to the reaction conditions during the preparation of nickel oxide nanoparticles. EDAX shows that samples 'a' and 'b' are substoichiometric and samples 'c', 'd' and 'e' have an oxygen excess (or a deficit on Ni) which is the case for thermodynamically stable NiO (the departure from stoichiometry in Ni_{1-x}O

is due to nickel vacancies). All these compounds are far from equilibrium. The lattice parameters of samples 'c', 'd' and 'e' are less than samples 'a' and 'b' which also describes the above effect.

3.3 FTIR spectroscopic studies

Fig. 5 shows the FTIR spectra obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method. FTIR studies were carried out to understand the presence of functional group of any organic molecule. Generally, any metal oxide may show absorption bands below 1000 cm⁻¹ due to inter atomic vibrations. The wide band at 3620 and 1640 cm⁻¹ present in all the samples is mainly due to the stretching vibration mode O-H group, which are associated with the adsorbed water on the products [62]. The broad absorption band in the region of 600 - 700 cm⁻¹ is assigned to Ni-O stretching vibration mode; the broadness of the absorption band indicates that the NiO powers are nanocrystals [63].

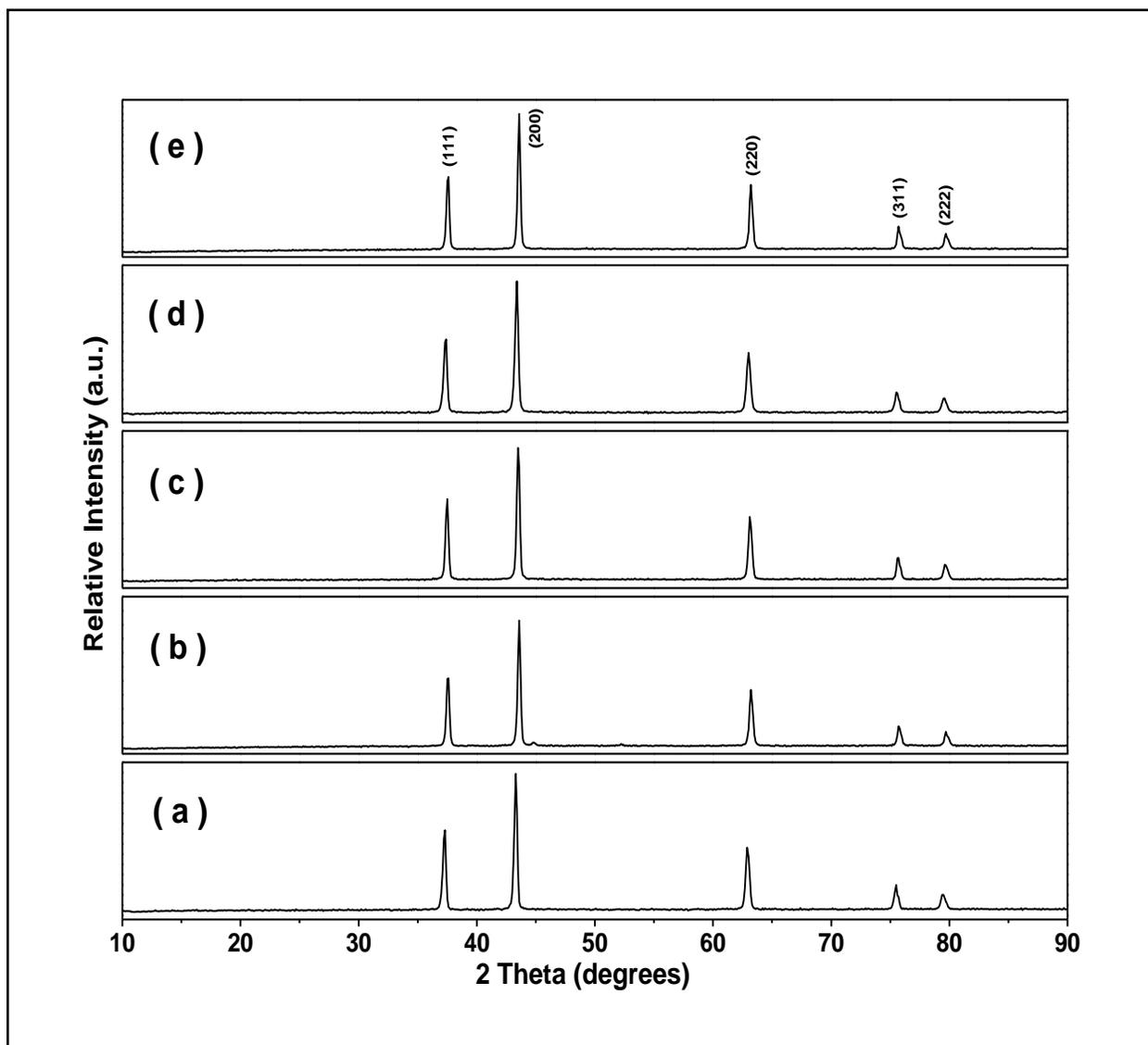


Figure 3. Powder XRD patterns obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) prepared with SDS

3.4 Particle size analysis

The particle size distribution curves obtained with NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method are shown in Fig.6. The particle characteristics data obtained on NiO nanoparticles particles is indicated in Table 3. From the particle size distribution data (Table 3), it was found the sample prepared with SDS as a surfactant resulted in very low particle size (78.98 nm). The presence of bigger particles (> 500 nm) in the samples may be due to high temperature treatment. It was reported that the higher temperature caused agglomeration to occur more readily[24]. However,

the results obtained through laser scattering analysis are less reliable than microstructural studies.

3.5 SEM studies

The SEM images of the NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method are indicated in Fig.7. Presence of nanostructural homogeneity in all the samples was confirmed by the SEM photographs. The images indicate that the samples have monodisperse and polycrystalline particles. The particles were spherical in shape and it was observed that some of the particles were agglomerated with each other due to large surface energy and large surface tension of the ultrafine particles. Smaller size grains were present in

the sample prepared with SDS as a surfactant which is in accordance with the particle characteristics data. The samples 'c' and 'e' whose SEM images show large differences in aggregates size and size distributions (Fig. 6) but similar compositions and lattice

parameters. The above difference in the particle characteristics of samples 'c' and 'e' is due to the departure from stoichiometry in Ni_xO and which may be due to nickel vacancies.

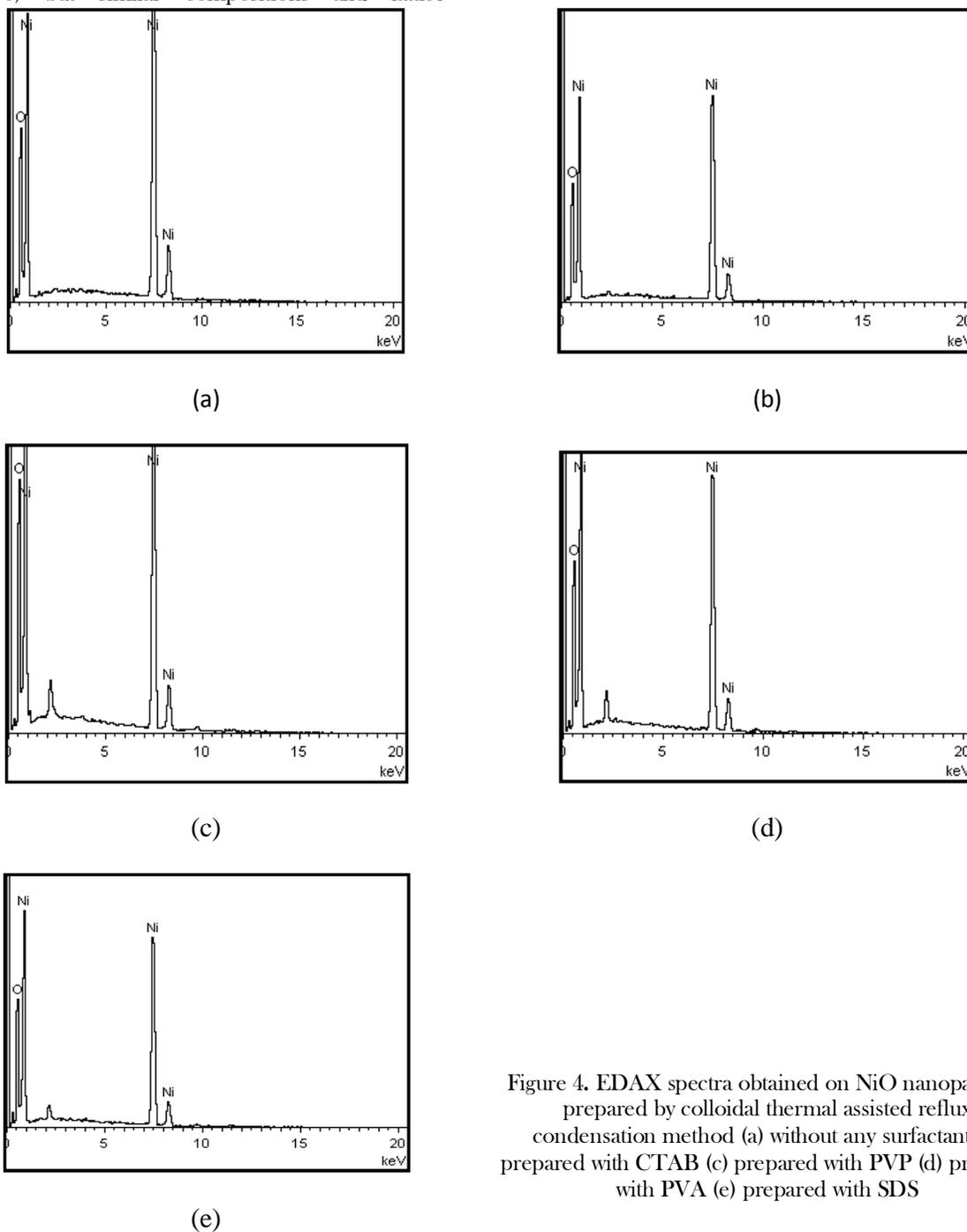


Figure 4. EDAX spectra obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) prepared with SDS

3.6. DRS studies

The DRS spectra obtained in all the samples are indicated in Fig.8. The absorption wavelengths of 343, 342, 339, 337 and 336 nm were obtained for NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method without any

surfactants and with surfactants, CTAB, PVP, PVA and SDS respectively. Energy band gap values for all the samples were calculated by using Tauc relation [64].

$$(\alpha h\nu)^n = A (h\nu - E_g) \quad (3)$$

Where ' α ' is the absorption coefficient, ' $h\nu$ ' is the photo energy, ' E_g ' is the optical band gap, ' A ' is a constant relative to the material and ' n ' is either 2 for direct transition, or $\frac{1}{2}$ for an indirect transition. The optical band gap value for the direct transition was obtained from Fig. 9. The calculated band gap values for the NiO nanoparticles were 3.45, 3.52, 3.57, 3.64 and 3.69 eV for the samples prepared without any

surfactant and with surfactants, CTAB, PVP, PVA and SDS respectively. The reported band gap values for the NiO sample are in the range 3.4 - 4.0 eV[2]. Hence, the band gap values calculated for the NiO particles are in agreement with the reported data. The obtained band gap values of NiO nanoparticles may cause a blue shift in their absorption spectra due to quantum confinement effects.

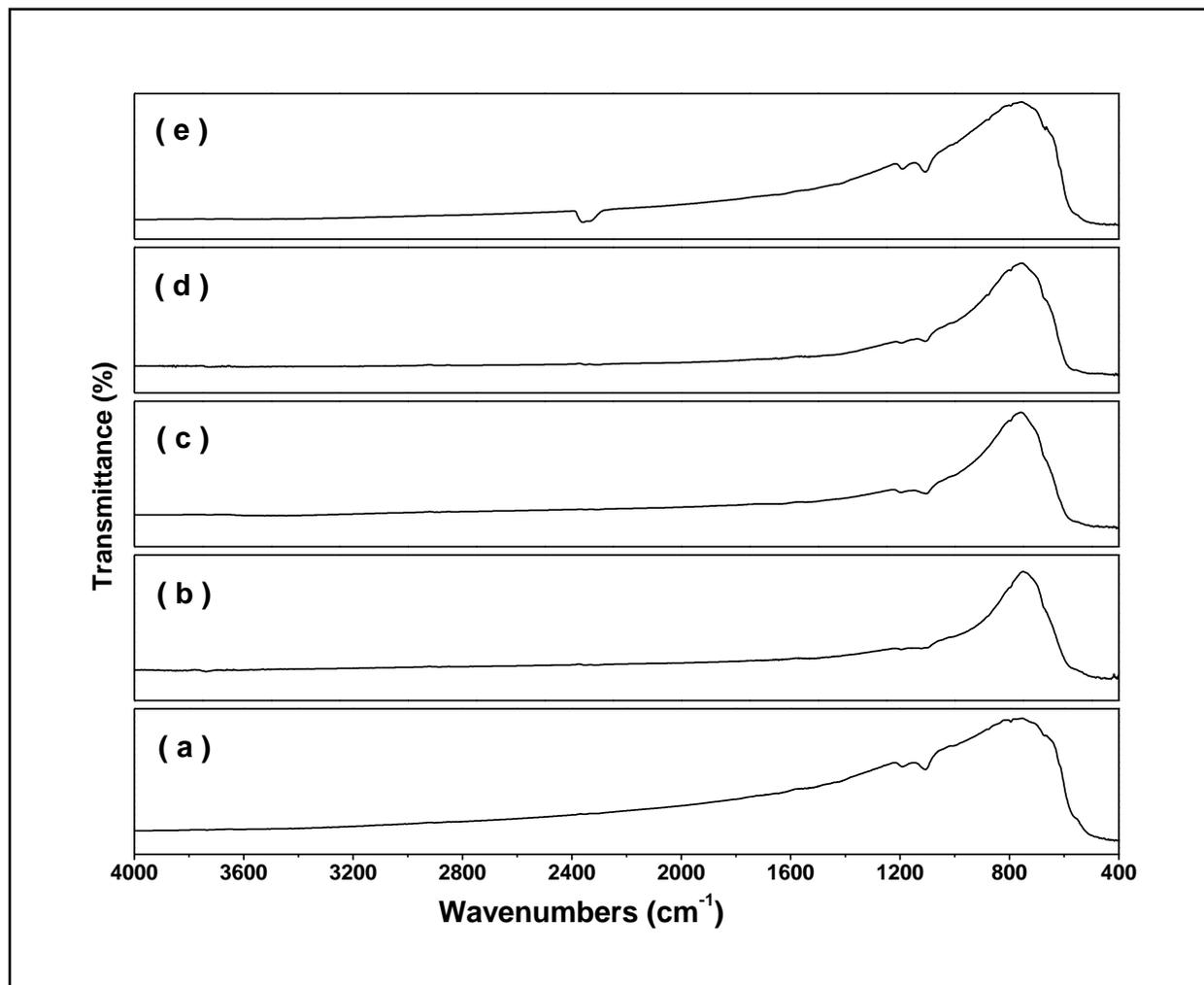


Figure 5. FTIR spectra obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) prepared with SDS

3.7. PL emission spectra studies

The PL Emission spectra obtained in all the samples are indicated in Fig.10. The excitation wavelength is 340 nm. A strong PL emission peak was found at 410 nm (3.03 eV) which is corresponding to near emission band edge in all the samples due to the recombination of excitons. The strong PL emission peak is attributed to the high purity and perfect

crystallinity of the NiO nanoparticles. The above result also in accordance with the reported data.

4. Conclusions

NiO nanoparticles are prepared by Colloidal thermal assisted reflux condensation method using various surfactants (CTAB, PVP, PVA and SDS) and the results are reported. The XRD data obtained on NiO nanoparticles shows that all samples crystallized as cubic. The EDAX data confirmed the presence of

nickel and oxygen in all the samples. From the FTIR data, it is shown that all samples exhibited characteristic peaks for NiO and the samples have moisture due to their less size. The particulate properties obtained on NiO powder suggest that the particles are present in the nanometer range. The SEM images exhibit that the samples prepared with the addition of SDS (surfactant) during the preparation of NiO resulted in smaller particle size

than other samples. Optical studies were carried out by DRS spectra and PL emission spectra.

5. Acknowledgment

The authors thank DST Nanomission, Government of India for the financial support. Also, they thank Karunya University for providing all the facilities to carryout nanotechnology research activity in the University campus.

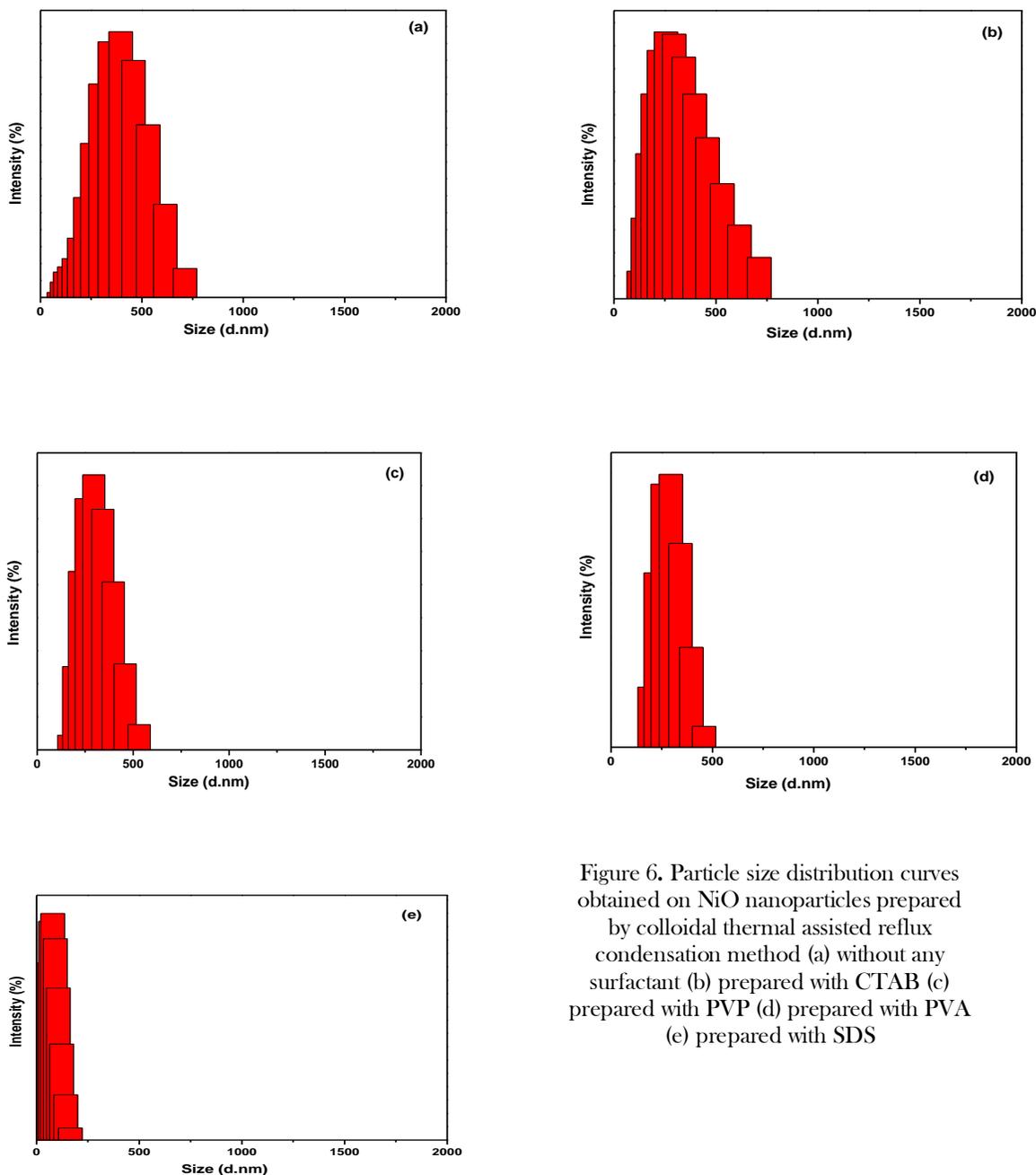


Figure 6. Particle size distribution curves obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) prepared with SDS

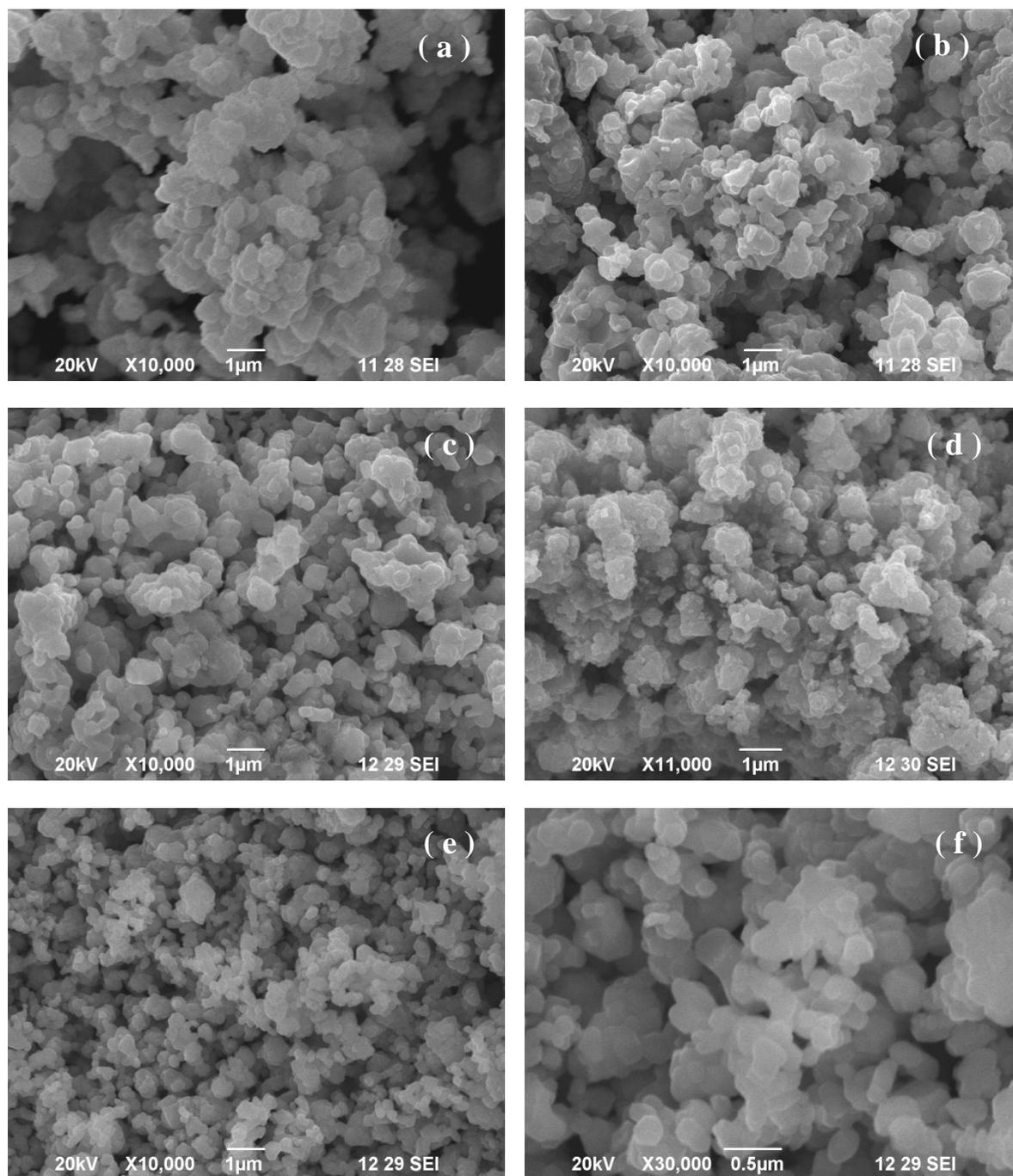


Figure 7. SEM image obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) & (f) prepared with SDS

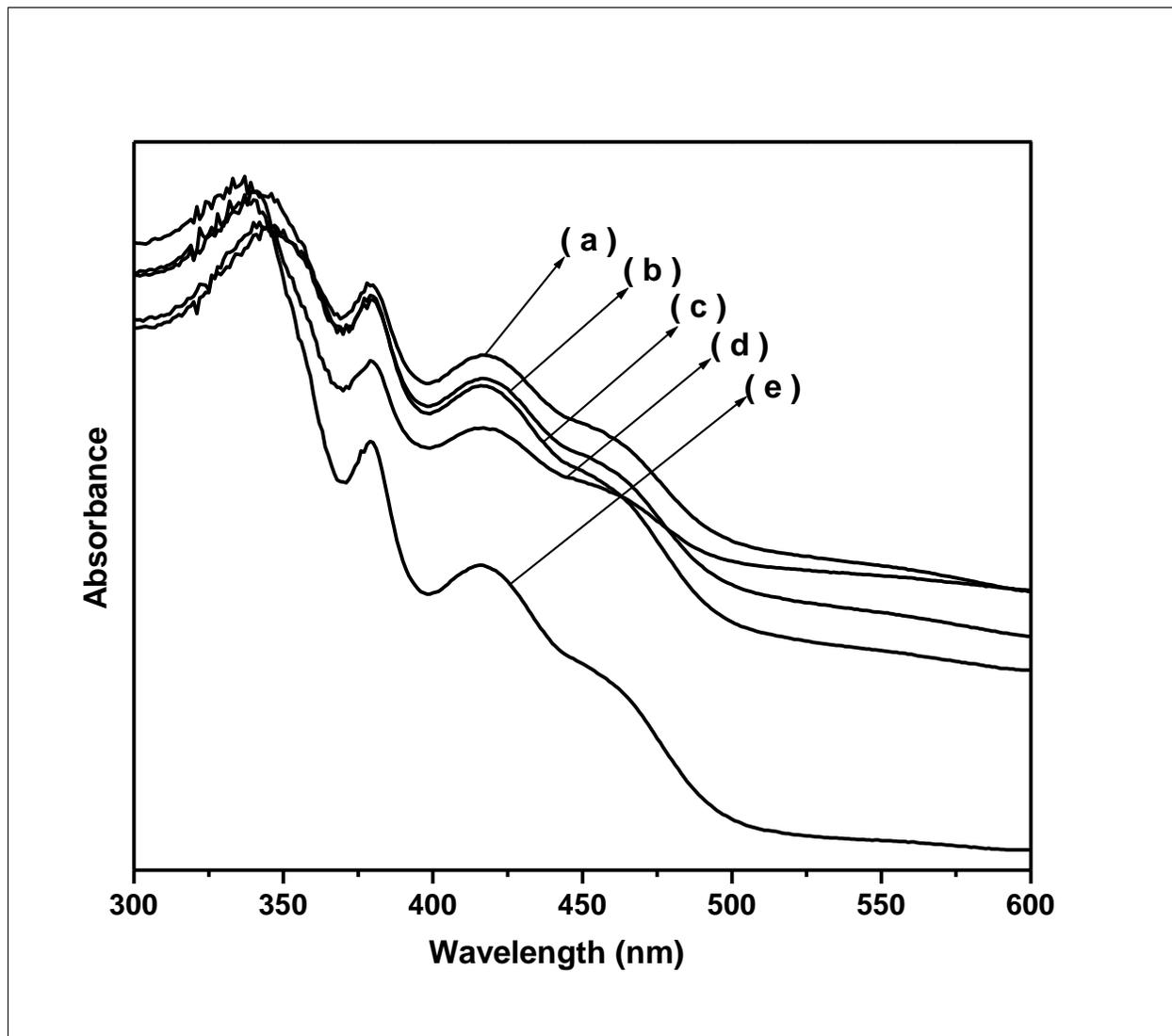


Figure 8. DRS spectra obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) & (f) prepared with SDS

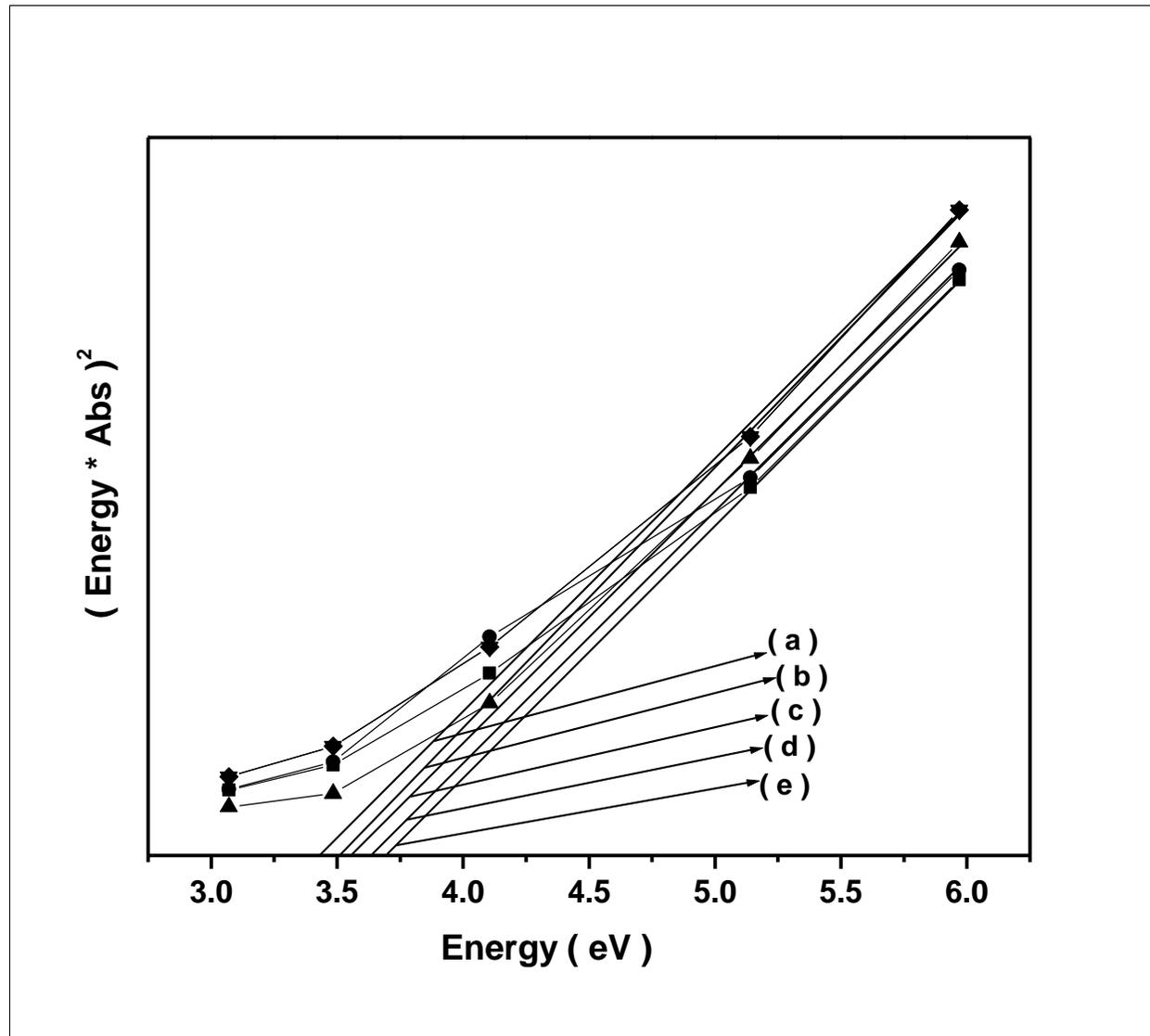


Figure 9. Band gap energy of NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method
(a) without any surfactant (b) prepared with CTAB (c) prepared with PVP
(d) prepared with PVA (e) & (f) prepared with SDS

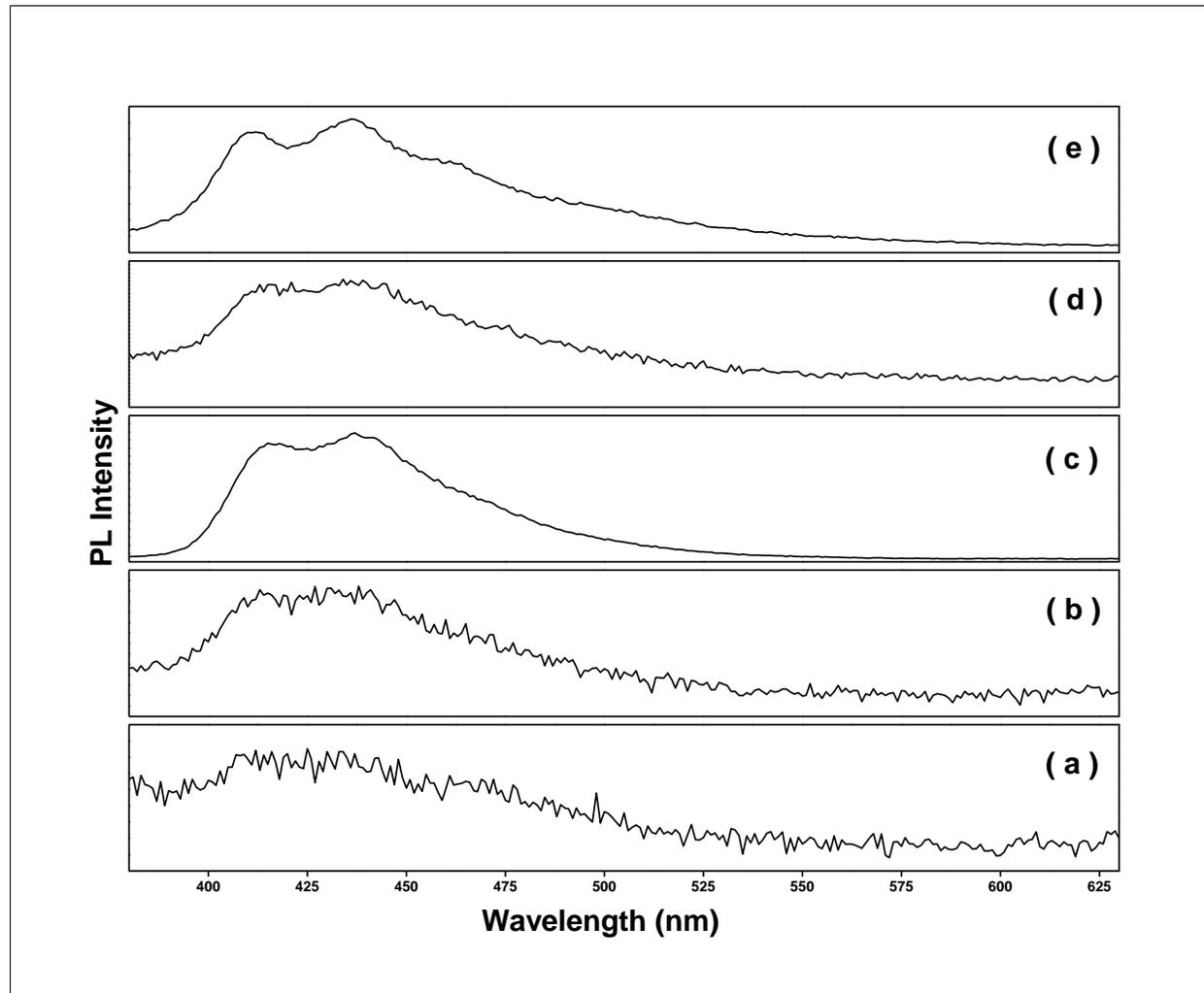


Figure 10. PL Emission spectra of NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method (a) without any surfactant (b) prepared with CTAB (c) prepared with PVP (d) prepared with PVA (e) & (f) prepared with SDS

Table 2. Chemical composition data obtained on NiO (prepared by colloidal thermal assisted reflux condensation method) by EDAX analysis

Process	Atomic weight % of elements
Without any surfactant	Ni - 57.46 O - 42.54
CTAB	Ni - 53.0 O - 47.0
PVP	Ni - 45.91 O - 54.09
PVA	Ni - 46.07 O - 53.93
SDS	Ni - 45.91 O - 54.09

Table 3. Particle characteristics data obtained on NiO nanoparticles prepared by colloidal thermal assisted reflux condensation method

Process	Peak 1		Peak 2		Average particle size (nm)
	% Intensity	Diameter (nm)	% Intensity	Diameter (nm)	
Without any surfactant	91.1	319.5	8.9%	4830	329.4
CTAB	100	367.1	--	--	452.0
PVP	100	305.8	--	--	320.7
PVA	100	288.9	--	--	314.1
SDS	96.7	81.88	3.3	4760	78.98

6. References

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