Nanostructured nickel oxide (NiO) was synthesized by a facile urea-based hydrothermal route followed by subsequent heat treatment. The influence of nickel precursors, nickel acetate, chloride, nitrate, and sulphate was investigated on the formation of morphology of NiO nanostructures. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transformed infra-red (FT-IR) spectroscopy and Raman spectroscopy. The XRD patterns confirmed the presence of cubic NiO phase in all the heat-treated samples. It was observed that the samples obtained from nickel acetate and sulphate resulted in agglomerated shapeless grains while those obtained from nickel chloride and nitrate resulted in nanospheres made up of nanoflakes. The difference in the nucleation process seemed to be responsible for formation of varying NiO morphology.

**Key words:** Hydrothermal route, Urea; Nickel oxide, Nanospheres, Nanoflakes.

**1. Introduction**

Nanostructured materials exhibit unique and different properties in comparison to those of the bulk materials mainly due to high surface area (SA), surface-to-volume ratio (S/V) and changes in density of states (DOS) [1-2]. The increased SA and S/V had strong influence on catalytic activity which encouraged researchers in worldwide to generate wide range of nanostructured materials. Among the various oxide-based nanomaterials, NiO is one of the functional ceramic materials which has been used in several applications such as, Li-ion battery anode, ultracapacitors, electrocatalyst, automobile gas sensors, solar cells etc [3-10].

Over the past decade, several methods such as microwave hydrothermal, hydrothermal, sol-gel etc. have been employed for the synthesis of nanostructured NiO. Among the various methods, hydrothermal method is known to offer attractive morphologies ranging from nanospheres, nanorods, nanosheets etc. Hydrothermal is one of the wet chemical routes in which water is used as solvent, leading to almost green process for obtaining nanostructured materials. Recently, hydrothermal process has been explored for synthesizing NiO nanostructures by various groups and the obtained NiO was used in several applications [11-15]. For example, A. K. Mondal et al., prepared urchin-like NiO nanospheres and utilized it for Li-ion battery anode as well as electrochemical capacitors which resulted in enhanced electrochemical performances [12]. M. Zhou et al., synthesized graphene nanosheets-NiO composite for supercapacitor application [13]. M. S Wu et al., prepared mesoporous NiO nanosheets applied for electrocatalytic oxidation of urea [15]. P. Rai et al., utilized glucose-assisted hydrothermal method for designing the Au@NiO yolk-shell nanoreactors which exhibited high sensitivity and selectivity to H$_2$S gas [17]. H. T. Wang et al., utilized flower-like NiO morphology obtained by microwave-assisted hydrothermal route and used as photocathode for dye-sensitized solar cell application [19]. J. Zhao et al., synthesized NiO nanosheets and examined its temperature dependent paramagnetic behaviors [20]. In most of the above reports, randomly, a nickel salt was used as precursor. To the best of our knowledge, there were no reports on the influence of different nickel precursors on the formation of NiO morphology in hydrothermal process.

Thus, in the present work, NiO nanostructures were synthesized by urea-based hydrothermal route by using four different nickel precursors, nickel acetate, nickel chloride, nickel nitrate, and nickel sulphate. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transformed infra-red spectroscopy and Raman
spectroscopy. It was observed that the use of different precursors had strong influence on the formation of NiO nanostructures. The detailed hydrothermal process and characterization of the samples are presented here.

2. Materials and Methods

2.1 Synthesis of nanostructured NiO by urea-based hydrothermal method

Nanostructured nickel oxide has been prepared by means of urea-based hydrothermal route. Chemicals such as, Ni(CH₃COO)₂·4H₂O, NiCl₂·6H₂O, Ni(NO₃)₂·6H₂O, NiSO₄·6H₂O and urea ((NH₂)₂CO) were of analytical grade (Fisher Scientific, 99%), and utilized as received. Deionized water was used throughout the experiment. An appropriate amount of each of nickel precursors was dissolved in deionized water and stirred well for complete dissolution for about 30 mins. Urea solution (1 M) was added to the above metal-ion solution in dropwise until pH attains 8.0. Then it was stirred well for about 30 min and the solution was transferred into 50 ml Teflon-lined autoclave vessel, and kept inside the hot air oven at 160°C for 6 h. After the reaction, the content was cooled to room temperature to obtain the precipitate. The obtained precipitate was centrifuged and washed well with the mixture of ethanol and deionized water, and dried at 120°C overnight. Finally, obtained precipitate was subjected to calcination in a furnace at 400°C for 3 h in air. Figure 1 shows the schematic view of the hydrothermal route adopted here.

![Fig. 1. Schematic view of the hydrothermal route adopted for the synthesis of NiO nanostructures](image)

2.2 Characterization of synthesized NiO nanostructures

The crystal structure and phase identification of assynthesized and heat-treated hydrothermal products were characterized by powder X-ray diffraction (XRD) analysis by using diffractometer (Bruker D8 Advanced) equipped with Cu Kα radiation (wavelength, λ=1.5418 Å). Fourier transformed infra-red spectroscopy data were obtained by using FT-IR spectroscopy (Thermo Nicolet 6700) in the frequency range of 500-4000 cm⁻¹. The surface morphology and elemental analysis of the samples were carried out by using scanning-electron microscope equipped with elemental microanalysis system (SEM/EDX - Hitachi S3400N). Raman spectra were obtained by Laser Confocal Raman spectroscopy with RENISHAW using the 488 nm line of an Argon laser source.

3. Results

In the urea-based hydrothermal process, the following reactions are proposed for the formation of NiO [21]. Urea undergoes hydrolysis producing ammonium ions and NCO⁻ (Eqn. 1). The formed NCO⁻ reacts with water to produce OH⁻ (Eqn. 2). The formation of OH⁻ is associated with increase of pH (above 7) which resulted in the formation of green precipitate, oxonium nickel oxide ((H₂O)₂NiO)₂ (Eqn. 3).

\[
\text{CO(NH}_2\text{)}_2 \rightarrow \text{NH}_4^+ + \text{NCO}^- \quad (1)
\]

\[
\text{NCO}^- + 3\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{NH}_4^+ + \text{OH}^- \quad (2)
\]

\[
\text{Ni}^{2+} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_2\text{NiO}_2^- \quad (3)
\]

The formation of oxonium nickel oxide in as-synthesized hydrothermal product is confirmed by XRD patterns shown in Fig. 2(a). The observed Bragg peaks were indexed to the standard pattern of (H₂O)₂NiO₂ as per JCPDS # 732408 in all cases, except in the nickel sulphate precursor. In the case of nickel sulphate precursor, NiS (JCPDS # 781886) has resulted instead of (H₂O)₂NiO₂. The following reactions are seemed to be responsible for formation of NiS.

\[
\text{SO}_4^{2-} \rightarrow \text{S}^2^- + 2\text{O}_2 \quad (4)
\]

\[
\text{Ni}^{2+} + \text{S}^2^- \rightarrow \text{NiS} \quad (5)
\]

Upon heat treatment of oxonium nickel oxide or NiS at 400°C, the following decomposition reactions are expected to take place, leading to formation of NiO.

\[
(\text{H}_2\text{O})_2\text{NiO}_2 \rightarrow \text{NiO} + 3\text{H}_2\text{O} \quad (6)
\]

\[
\text{NiS} + 3/2 \text{O}_2 \rightarrow \text{NiO} + \text{SO}_2 \quad (7)
\]

It was observed that while the colours of oxonium nickel oxide and NiS were green, all the heat-treated samples were black. In case of nickel sulphate precursor, NiS has precipitated which may be due to the lower solubility product of NiS over oxonium nickel oxide.

4. Discussion

Figure 2(b), shows the XRD patterns of the heat-treated hydrothermal samples obtained from each of different Ni precursors. In all samples, the distinct Bragg peaks appeared in the XRD pattern indicates that the samples are crystalline in nature. For all the samples, the set of Bragg peaks observed at 37.4, 43.3, 62.9, 75.62 and 79.5° could be assigned to cubic phase of NiO as per JCPDS # 731519. No other impurity peaks were observed. Thus, it confirms the formation of NiO from each nickel precursors upon heat
Fig. 2. XRD patterns of as-synthesized (a) and 400°C-heat-treated (b) samples obtained from each of different nickel precursors by hydrothermal method.

treatment. It is noted that the width of Bragg peaks in all samples are very broad which is characteristic for nanograin. The average crystallite size of NiO was calculated using Scherer formula given below.

\[ L_{hkl} = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where, \( L_{hkl} \) denotes crystallite size, \( \lambda \) is X-ray wavelength (1.5418 Å), \( \beta \) is the full width at half maximum (FWHM) of the Bragg peak (in radians), and \( \theta \) is the Bragg angle. The obtained NiO crystallite sizes from each of nickel acetate, chloride, nitrate and sulphate are 60, 40, 55 and 65 nm, respectively.

Figure 3 shows the FT-IR spectra of heat-treated hydrothermal samples obtained from each of different Ni precursors. In all cases, the strong peak appeared at about 600 cm\(^{-1}\) confirms the presence of nickel-oxygen (Ni-O) bond. The peak observed at about 1000 cm\(^{-1}\) is due to the presence of C-H bond. The broad peak appeared at about 3400 cm\(^{-1}\) in all the samples is characteristic for OH group of adsorbed water molecules which could have come either by decomposition of oxonium nickel oxide or from the atmosphere. In all the samples, the peak observed at about 1400 and 1600 cm\(^{-1}\) are characteristics for CO bond which could have been resulted from atmosphere or partial decomposition of acetate precursor.

Fig. 3. FT-IR spectra of the heat-treated samples obtained from each of different nickel precursors by hydrothermal method.

Figure 4 shows the surface morphology of the samples obtained from each of different nickel precursors. In case of samples obtained from acetate (a) and sulphate (d), the matrix consisted of agglomerated shapeless nanograins, while the samples obtained from chloride (b) and nitrate (c) precursors resulted in attractive giant look ball-shaped nanograins. It is interesting to note that the sample from chloride precursor yielded attractive nanosphere which are made up of fine nanoflakes (Fig. 4 (b) inset). The surface of this sample is highly porous where as in the case of the sample obtained from nitrate precursor, the matrix had dense spherical grains. The average NiO grain sizes resulted from each of acetate, chloride, nitrate and sulphate precursors are about 50, 70, 80 and 65 nm, respectively. The elemental analysis carried out by EDX (not shown) confirmed the presence of Ni as the only metallic element in each matrix. The Raman spectra (Fig. 5) had a peak at about 518 cm\(^{-1}\) which is characteristics of Ni-O bond in all the samples.

Based on the aforesaid data, the type of nickel precursor played an influential role on the formation of NiO nanostructures in urea-based hydrothermal method. The nickel chloride precursor offered attractive NiO nanospheres consisting of nanoflakes. It is believed that differences in the nucleation process would have led to formation of varying NiO morphology. It is known that homogenous nucleation results in smaller size and uniform
Fig. 4. SEM images on surface of NiO samples obtained from each of nickel precursors, (a) nickel acetate, (b) nickel chloride, (c) nickel nitrate and (d) nickel sulphate by hydrothermal method. Inset: High Magnification.

Fig. 5. Raman spectra of the heat-treated samples obtained from each of different nickel precursors by hydrothermal method.

shape grains, while random nucleation results in larger size and irregular shape grains [1-2]. In NiCl₂ precursor, homogenous nucleation seems to be taking place, while in other, random nucleation was taken place. Works are under progress using the above generated NiO nano-spheres as electrode material for yttria-stabilized zirconia (YSZ) high-temperature gas sensor, supercapacitor, Li-ion battery applications.

5. Conclusions

NiO nanostructures were synthesized by a facile hydrothermal route using different nickel precursors. The XRD, FT-IR and Raman studies confirmed that heat-treated samples resulted in nanostructured NiO irrespective of nickel precursors. The sample obtained from nickel chloride precursor resulted in attractive NiO nanospheres made of highly porous nanoflakes, while from other precursors had dense nanospheres or no shape. The type of metal precursors seems to control the formation of NiO morphologies in urea-based hydrothermal route.

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