



Research Article

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Synthesis and characterization of NiO nanoparticles by sol-gel route with various additives

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ABSTRACT

NiO nanoparticles with various additives have been successfully synthesized by sol-gel route. The synthesis was accomplished by using nickel acetate tetrahydrate was used as the non-alkoxyde precursor, methanol as the solvent. The effect of additives such as urea, sodium hydroxide (NaOH 5 M) and ammonia (NH₃) on the NiO nanoparticles formation were investigated. The synthesized powders were calcined at $\pm 500^{\circ}\text{C}$ for ± 1.5 hours. XRD and SEM were used as to characterize the structure and microstructure of NiO. The formation of the nanoparticles NiO and their structure were greatly dependent on the additives. The XRD patterns showed NiO nanoparticles were produced in cubic shape with average crystalline size in the range of 38-51nm. SEM images show various morphological changes of NiO nanoparticles. SEM results depict that rodlike shape of NiO nanoparticle were formed by using urea+NaOH as additive.

Keywords: additives, cubic, nanoparticle, NiO, rodlike.

INTRODUCTION

NiO is attracting tremendous attention due to its interesting properties. NiO is a well studied material among various transition metal oxides. NiO has unique advantage in terms of properties and application. The application of NiO nanoparticles are p-type transparent conducting film, gas sensors, catalyst, dye-sensitized solar cells, solid oxide fuel cells anode, cathode in alkaline batteries and electrochromic device [1-3]. NiO nanoparticles also have excellent thermal stability, a p-type semiconductor with a wide band gap (3.6-4.0 eV) [4-6] and conduction band energy 1.8 eV. NiO has been considered as a promising material for optical, electronic and catalytic application.

A variety of techniques like solvothermal method, sonochemical method [10], thermal treatment, chemical precipitation [4] [7] dan [10] [14], microemulsion [12], soft chemical synthesis route [13] have been widely used in the synthesis of nanomaterials and nanostructures. Soft chemical synthesis route involved solid - liquid separation, washing and drying process have previously been investigated for preparation of nickel oxide nanoparticles. Another process were microwave irradiation method [7] and [8], thermo chemical processing [14], liquid phase process, spray pyrolysis process, electroplating of nickel particle [7], metal organic chemical vapor deposition (MOCVD) [8] has a number disadvantages such as quite expensive, uses volatile compound and need complicated reactor. Many of the reported methods are limited to laboratory scale due to specific condition requires [14], low-yield, high cost, and complex apparatus.

In this study, the author presents the results of an investigation into the well dispersed NiO nanoparticles by sol-gel route with various additives. The various additives that used in this research were urea, NH₃ and NaOH. Nickel acetate tetrahydrate (Merck) was used as precursor and methanol (p.a) as the solvent. The sol-gel route has a number of advantages over other methods, such as inexpensive equipment, easily in processing and produce homogeny nanoparticles. We investigated the effect of additives on the microstructure of NiO nanoparticles.

EXPERIMENTAL SECTION

All the chemical reagents used in this experiment were of analytical grade and without further purification. The precursor used in this study was nickel acetate tetrahydrate (Merck) and methanol as solvent. Urea, NH_3 , and NaOH were used as various precipitation agents (additives).

In a typical procedure, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (4.976 g), was dissolved in 20 mL methanol, stirred at room temperature for 60 minutes. To synthesize nickel oxide nanocrystalline, urea+NaOH, NH_3 +NaOH and NaOH was added drop wise 20 mL of 1.0 M $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution which were stirred by magnetic stirring apparatus, under vigorous stirring the solution for ± 2 hours at room temperature. Light green suspension was produced. It was then dried at 100-110 °C for ± 1 hour, the green powders were produced. The product then transferred to porcelain crucible and put in furnace at ± 500 °C for 1.5 hours, and finally black powders produced. The results were characterized including crystal structure and morphology.

This research used some instruments, including X-ray Diffraction (XRD) with a diffractometer by using monochromatic $\text{CuK}\alpha$ with $\lambda = 1.54060$ was used for determination of crystal structure and morphological study was carried out by Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

There are different methods to synthesis NiO materials reported in the literature, hydrothermal synthesis [15], microemulsion assisted sol-gel method [16]. In this research, NiO nanoparticles were prepared from nickel acetate tetrahydrate and methanol as a solvent. The synthesis involves sol-gel process at low temperature. Sol of nickel oxide with various additives that produced by sol-gel route with NaOH as precipitation agent dried at 100-110 °C for 1 hour in oven. The color of sol of nickel oxide with urea+ NaOH additive was light green (Fig. 1a) and blue color by using NH_3 + NaOH additive (Figure 1b). The morphology of $\text{Ni}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ was homogenous. Gel of NiO produced after heating process in oven at 100-110 °C for 1 hour (Fig 2).

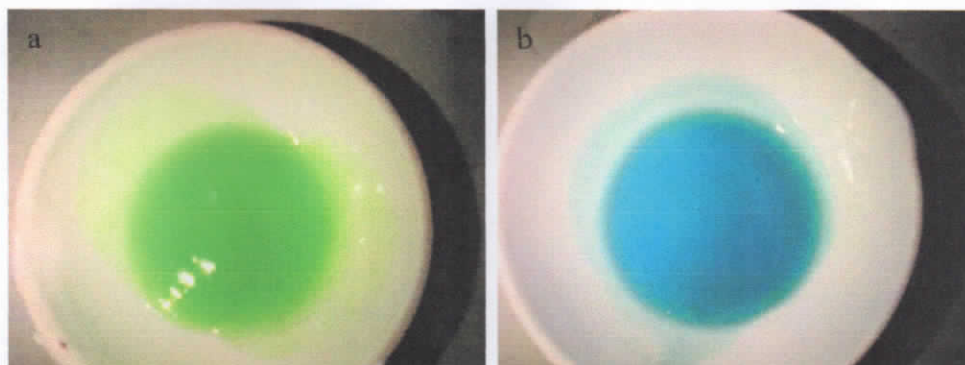
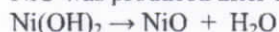


Figure 1 a) sol of NiO by using urea+NaOH additive, b) sol of NiO by using NH_3 + NaOH additive

The reaction can be seen below:



NiO was produced after calcination at 500 °C for 1.5 hours in furnace, the reaction can be seen below:



The black powder produced after calcination process with 500 °C for 1.5 hours. The powder in visual was homogenous and the particle size was very small.

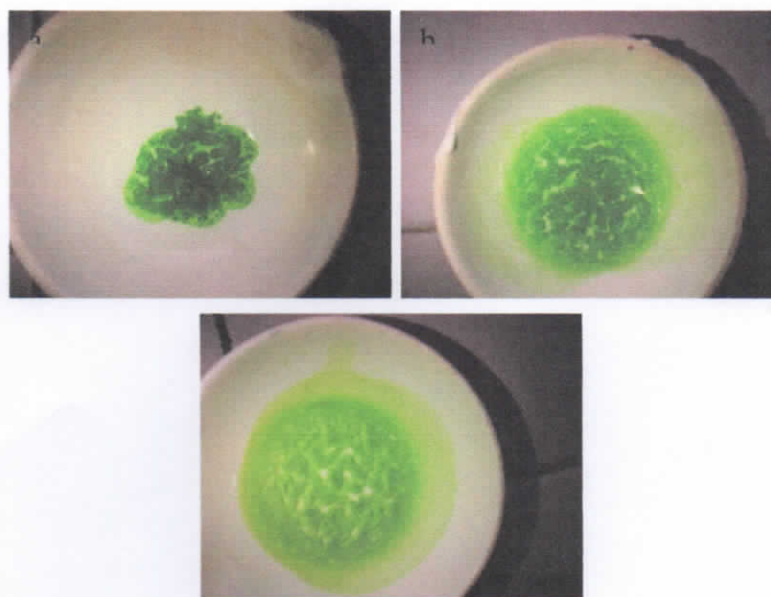


Figure 2 a) gel of NiO by using NaOH additive, b) gel of NiO by using urea + additive, c) gel of NiO by using NH_3 + NaOH additive

3.1 X-ray diffraction (XRD) study

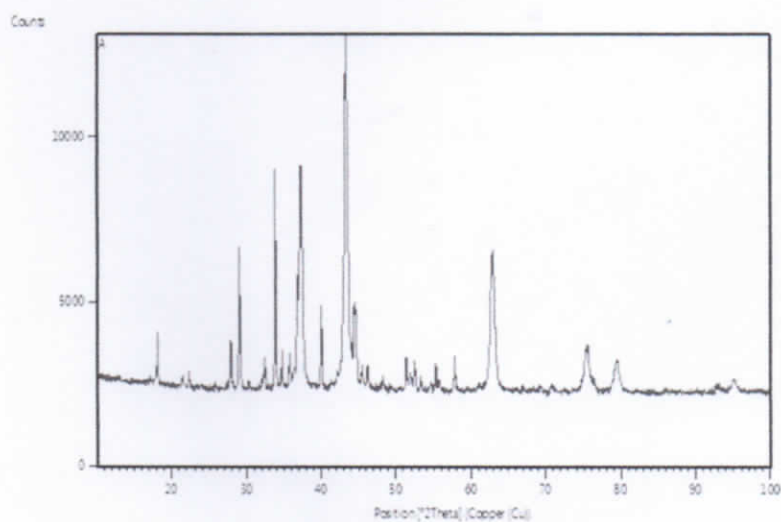


Figure 3 X-ray diffraction pattern for NiO with urea + NaOH additive

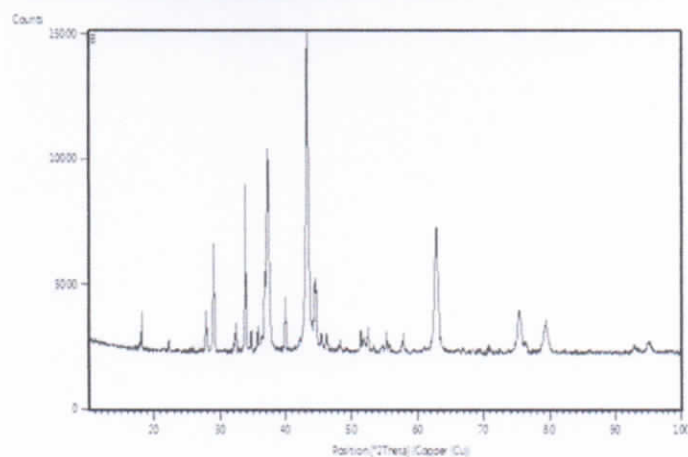


Figure 4 X-ray diffraction pattern for NiO with NaOH additive

The phase structure of the NiO samples were characterized by X-ray diffraction technique with CuK α with $\lambda = 1.54060$. The data have been collected in the range $(2\theta) = 0-100$. Fig. 3 shows the XRD pattern of the black powder formed via sol-gel route by using urea+ NaOH as additive. XRD pattern of NiO powder shows the highest intensity with typical peak at $2\theta = 43.3$. XRD analysis depicted that this substance is a typical cubic NiO (ICSD No. 01-078-0643). The final product appeared in black color. Fig. 3 indicates high crystallinity of NiO nanoparticle. All diffraction peaks can be indexed as the cubic phase of NiO with space group Fm-3m.

Figure 4 depicts the X-ray diffraction (CuK α radiation) pattern of the NiO sample prepared by sol-gel route with NaOH as additive. XRD pattern of NiO powder at temperature 500°C shows the highest intensity with typical peak at $2\theta = 43.2$. XRD analysis showed that this substance is a typical cubic NiO (ICSD No. 01-071-4751). Fig. 4 indicates high crystallinity of NiO nanoparticle.

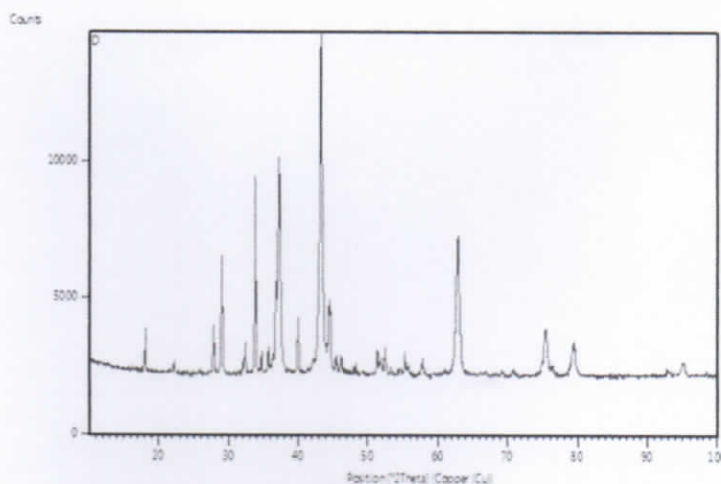


Figure 5 X-ray diffraction pattern for NiO with NH₃+ NaOH additive

Figure 5 illustrates the XRD pattern of the calcined product at 500 °C for via sol-gel process with NH₃+ NaOH as additive. XRD pattern of NiO powder shows the highest intensity with typical peak at $2\theta = 43.2$. XRD analysis showed that this substance is a typical a cubic NiO (ICSD No. 01-078-0423). Figure 5 indicates high crystalline of NiO nanoparticle.

The grain sizes of the synthesized NiO have been calculated by using Scherer formula. According to Scherer equation, crystallite size generally decreases with broadening the longest XRD peaks. The mean crystallite size was calculated by the application of the Scherer equation:

$$D = \frac{K \cdot \lambda}{\beta \cos \theta}$$

where:

D is the mean crystallite size of the powder,

λ is 0.15406 nm is the wavelength of CuK α ,

β is the *Full Width at Half Maximum* (FWHM) intensity of $2\theta \times (\pi/180)$,

θ is Bragg's diffraction angle, and

K is a constant usually equal to 0.89

The crystalline size of NiO calculated by Scherer formula, were 50.91 nm, 40.73 and 38.63 nm for the various additives (Table 1).

Table 1. The crystalline size of NiO nanoparticles

Additives	2 θ	FWHM	The crystallite size(L/nm)
Urea + NaOH	43.2	0.2558	50.91
NH ₃ + NaOH	43.2	0.3149	40.73
NaOH	43.2	0.3346	38.63

3.2 Morphological investigation by SEM

Typical SEM images of different NiO samples prepared by sol-gel route have been shown in Fig. 6-8. SEM analysis was carried out to determination of morphology, size and crystalline properties of NiO samples. It can be estimated that the average size of NiO lie nearly around 30 nm (from Fig.6). From this figure shows the structure and size of NiO nanoparticle was changed.

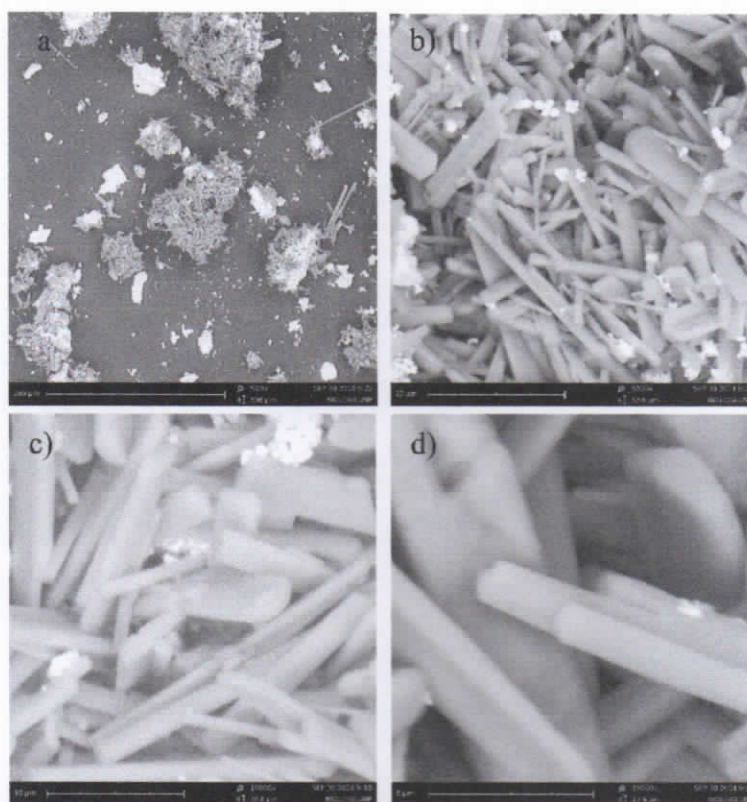


Figure 6. SEM photograph of NiO particles produced with urea + NaOH as additive a) 500x, b) 5000x, c) 10000x, d) 15000x

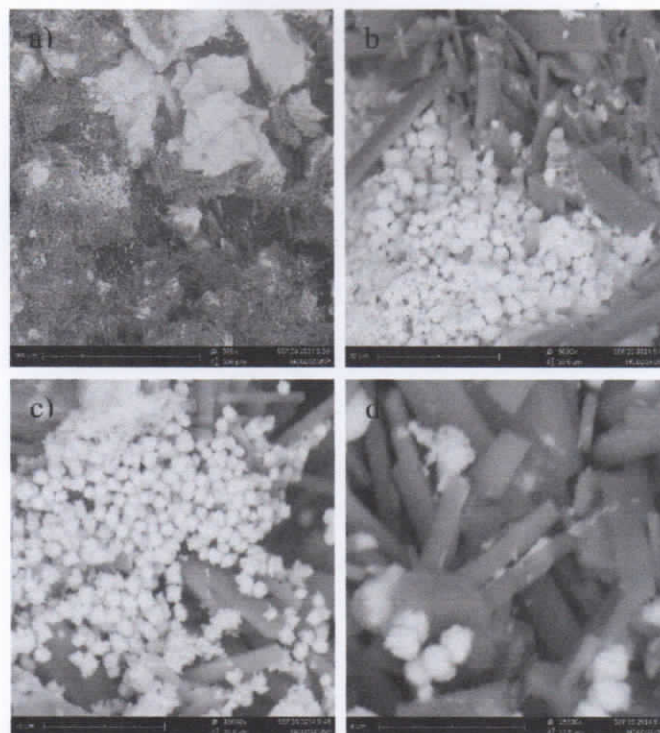


Figure 7 SEM micrograph of agglomerated nanopowders NiO particles produced with NaOH as additive a). 500x, b) 5000x, c) 10000, d) 15000x

Figure 6 shows the micrograph of SEM of NiO nanoparticle that characterized by using sol-gel method with urea+ NaOH as additive. From the image of NiO, it is clearly seen that the NiO nanoparticle are mostly regular shaped. The range particle size vary between 50-60 nm are observable in the Figure 6. From the SEM analysis, the microstructure of NiO nanopowder was produced in rodlike shape. Fig.6a-d shows the highest aggregated rod-like nanoparticles.

Figure 7 depicts the photo SEM of NiO nanoparticle that characterized by using sol-gel route with NaOH as additive. It is clear that in all cases, NiO nanoparticle was succesfull synthesized by sol-gel process. The range particle size vary between 50-70 nm are observable in the Figure 7 From the SEM analysis, the microstructure of NiO nanopowder was produced in spherical form combined with rod like shapes. Figure 7a-d shows the highly agregated spherical and rod-like nanoparticles.

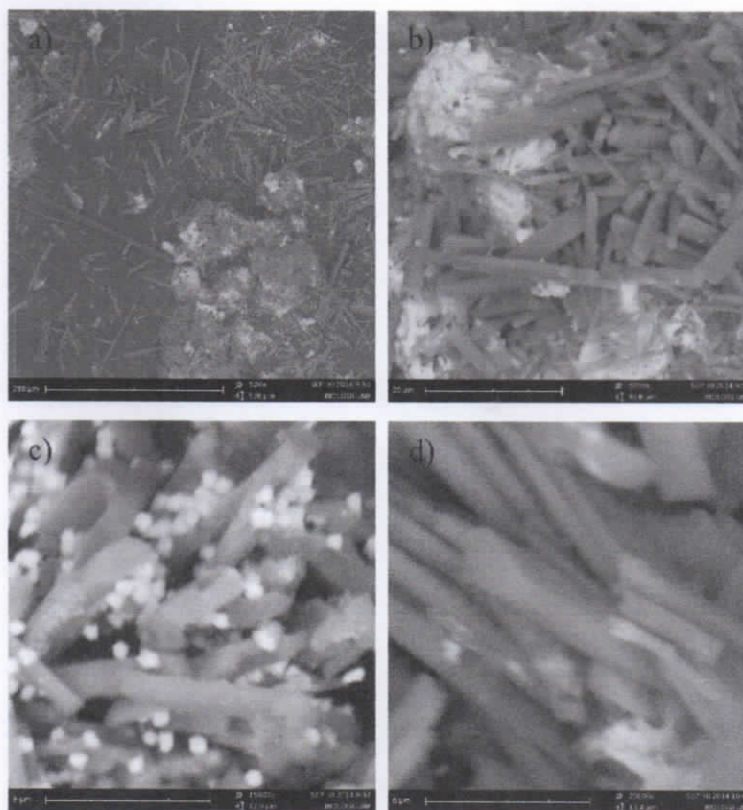


Figure 8 SEM photograph of NiO nanoparticle produced with NH_3 + NaOH as additive, a) 500x, b) 5000x, c) 15000x, d) 20000x

SEM images recorded for the NH_3 + NaOH additive is shown in Fig. 8. In the case of additive sample (Fig. 8), the particles look agglomerated and the morphology is regular, the particles posses agglomerated rod-like morphology. The range particle size vary between 40-60 nm are observable in the Fig.8. From the SEM analysis, the microstructure of NiO nanopowder was produced in spherical form. Fig.8a-d shows the highly aggregated rod-like shape.

CONCLUSION

The choice of additives in sol-gel prepared of NiO nanoparticles influence very much the properties of the final NiO nanoparticles. We studied three additives: urea+ NaOH.; NH_3 +NaOH; NaOH. The NiO nanopowders were produced by calcination in furnace at 500 °C for 1.5 hours. The crystalliine size of NiO nanoparticle were 32.63 nm with NaOH additive, 40.73 nm by using NH_3 +NaOH as additive and 50.91nm with urea + NaOH as additive. The structure of NiO nanoparticles were cubic type. Micrograph SEM of NiO nanoparticles were rod like shape for urea+NaOH as additive; spherical shape for NaOH as additive and rod-like shape for NH_3 + NaOH as additive.

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