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Synthesis and Characterization of Nio Nanocrystals by using Sol-Gel Method with Various Precursors

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Abstrak

Nickel oxide (NiO) nanocrystals were synthesized by simple sol-gel method at low temperature by using methanol as the solvent and NaOH 5M as the precipitation agent. Nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate were used as the precursors. The crystals were formed by drying at 100-110 °C for ±1 hour, after which they were heated at ±450 °C for 1 hour. The resulting products were black powders. The as-prepared NiO nanocrystals were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns of the NiO nanocrystals showed that they are mostly cubic. The sizes of the NiO particles produced with nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate were 72.16, 38.63 and 32.84 nm, respectively. SEM images showed that the nanopowders produced by the precursors are spherical, rod-shaped and hexagonal shape with hollow, respectively.

Abstract

Sintesis dan Karakterisasi Nanopartikel Nio dengan menggunakan Metode Sol-Gel dengan Variasi Prekursor. Nanokristal Nikel oksida (NiO) telah disintesis menggunakan metoda sol-gel sederhana pada temperatur rendah dengan menggunakan metanol sebagai pelarut dan NaOH 5M sebagai zat pengendap. Nikel nitrat heksahidrat, nikel asetat tetrahidrat dan nikel sulfat heksahidrat digunakan sebagai prekursor. Kristal terbentuk setelah pengeringan pada suhu 100-110 °C selama ±1 jam dan setelah kalsinasi pada suhu ±450 °C selama 1 jam. Produk yang dihasilkan adalah berwarna hitam. Nanokristal NiO yang dihasilkan dikaraktersasi dengan menggunakan difraksi sinar-X (XRD) dan *Scanning Electron Microscopy* (SEM). Pola XRD NiO menunjukkan bahwa bentuk kristal NiO adalah kubik. Ukuran partikel NiO yang dihasilkan menggunakan nikel nitrat heksahidrat, nikel asetat tetrahidrat dan nikel sulfat heksahidrat adalah 72,16, 38,63 and 32,84 nm berturut-turut. Gambar SEM menunjukkan bahwa bubuk nano menggunakan precursor yakni sperik, seperti batang dan bentuk heksagonal dengan rongga, berturut-turut.

Keywords: nanocrystals, nickel oxide, precursors, rod like, sol-gel

Introduction

Nanoparticles have unique properties, such as high electrical conductivity, toughness, ductility and formability of ceramics. One of the most commonly used transition metal oxides with a wide range of applications is nickel oxide (NiO) [1]. NiO is a semitransparent [2] NaCl-type antiferromagnetic oxide semiconductor with p-type conductivity films due to its wide band gap energy range from 3.6 to 4.0 eV [3,4]. NiO shows electrochromic [5], thermoelectric [6] and attractive electric [7] properties. It can be used in electro-optical devices, antiferromagnetic film [1,8], catalytic reactions, superparamagetic devices [9], supercapacitors [10], sensors [11], the production of photodetectors [12], alkaline batteries cathode, solid oxide fuel cell anode and the manufacture of electrochromic displays [13]. NiO nanoparticles show many unique optical, electrical, magnetic and chemical properties [14].

Several approaches have been used to produce NiO nanocrystals, such as the sonochemical method [15], the microwave irradiation method [8,9], the solvothermal method [16], chemical precipitation [17], microwave pyrolysis, electroplating [12], precipitation-calcination [18], microemulsion [19] solid-liquid separation, the soft chemical synthesis route [16], the liquid-phase process, the spray pyrolysis process, metal organic chemical vapor deposition (MOCVD) [14] and the sol-

gel process [20]. Among these methods, the sol-gel process is the most cost-effective for producing large area particles.

Herein, the preparation of NiO nanocrystals by a sol-gel method at low temperature is reported. The effect of various precursors on the structure of NiO was studied by using XRD and SEM. The sol-gel process may be scaled up to synthesize NiO at a large scale at a relatively low cost. This method also offers other advantages such as high homogeneity, simple apparatus structure and ease of processing.
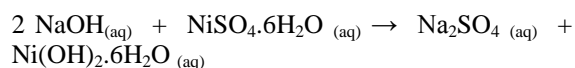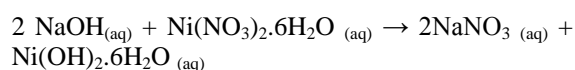
Materials and Methods

The NiO nanocrystals were synthesized by a sol-gel method at low temperature using NaOH as the precipitation agent with various precursors (nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate). All the chemical reagents used in this experiment were of analytical grade and without further purification. The solvent used in this study was methanol (p.a. grade).

Preparation of NiO Nanocrystals. In a typical procedure [20], $Ni(NO_3)_2.6H_2O$ (5.815g), $Ni(CH_3COO)_2.4H_2O$ (4.976 g), and $NiSO_4.6H_2O$ (5.257 g) were each dissolved in 20 mL of methanol and stirred at room temperature for 60 minutes. To synthesize NiO nanocrystals, 5.0 M NaOH was added dropwise to a 20 mL solution of 1.0 M $Ni(NO_3)_2.6H_2O$, 1.0 M $Ni(CH_3COO)_2.4H_2O$, and 1.0 M $NiSO_4.6H_2O$ which was vigorously stirred by magnetic stirring apparatus for ±120 minutes at room temperature. It was then dried at 100-110 °C for ±1 hour. Light green powders were produced. The product was then transferred to a porcelain crucible and put in a furnace at ±450 °C for 1 hour. At this stage, black powders were produced.

Characterization. NiO particle size was determined by analysis of the width of the X-ray diffraction (XRD) peaks according to the Debye-Scherrer equation. XRD was performed with a diffractometer using monochromatic $CuK\alpha$ with $\lambda = 1.54060$. XRD was also used for the determination of the crystal structure. The morphological study was carried out by scanning electron microscopy (SEM).

Results and Discussion

Nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate were used as the NiO sol-gel precursors. Methanol was used as the solvent, and NaOH of 5M was used as the precipitation agent. The reactions are as follows:

$$2\ NaOH_{(aq)} + Ni(NO_3)_2.6H_2O\ _{(aq)} \rightarrow 2NaNO_3\ _{(aq)} + Ni(OH)_2.6H_2O\ _{(aq)}$$

$$2\ NaOH_{(aq)} + Ni(CH_3COO)_2.4H_2O\ _{(aq)} \rightarrow 2NaCH_3COO\ _{(aq)} + Ni(OH)_2.4H_2O\ _{(aq)}$$

$$2\ NaOH_{(aq)} + NiSO_4.6H_2O\ _{(aq)} \rightarrow Na_2SO_4\ _{(aq)} + Ni(OH)_2.6H_2O\ _{(aq)}$$

Gel was produced by heating the crystals in an oven at 100-110 °C for 1 hour, with the following reaction:
$$Ni(OH)_2.6H_2O \rightarrow\ Ni(OH)_2 + 6H_2O$$
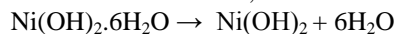
NiO was produced after calcination at 450 °C in a furnace, with the following reaction:
$$Ni(OH)_2 \rightarrow NiO\ +\ H_2O$$
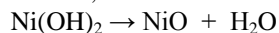
Visually, the powders were homogeneous, very small in particle size and light black in color.
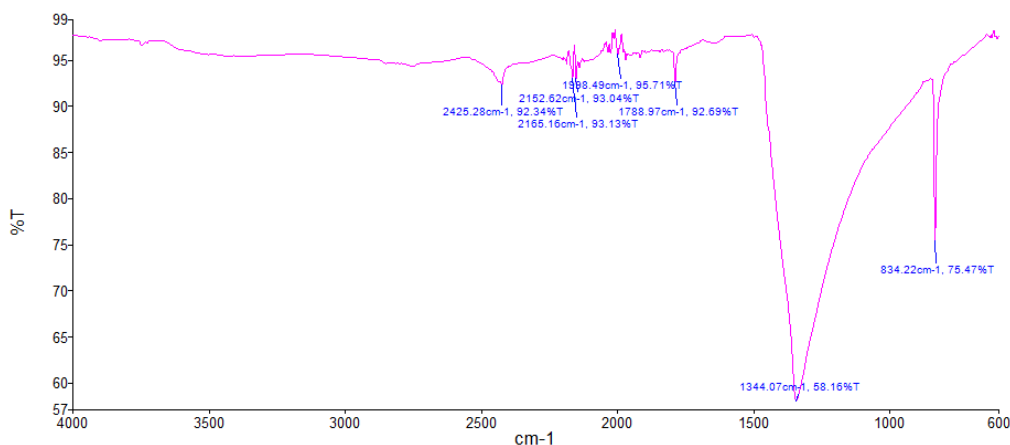
FTIR Analysis

Figure 1. FTIR Spectrum of NiO with Nickel Nitrate Hexahydrate as Precursor

In this study, FTIR was applied to identify the functional groups present in the sample of NiO. As can be seen in Figure 1, in general, the peak at 3323 cm^{-1} is assigned to O-H stretching vibration, the band at 1622 cm^{-1} is assigned to H–O–H bending vibration, and the band at 2328 cm^{-1} is assigned to C–H. The absorption band located at 1015 cm^{-1} is assigned to chloride, while the bands observed between 400-500 cm^{-1} are assigned to weak and strong stretching vibrations of Ni-O.

XRD analysis. The X-ray diffraction patterns of NiO nanocrystals were obtained after the NiO was heated at

450 °C for 1 hour. Figure 2a shows the X-ray diffraction pattern of NiO nanocrystals formed by a sol-gel method at low temperature with nickel nitrate hexahydrate as the precursor. From the XRD pattern of NiO powder calcined at 450 °C, it is clear that peaks appear at 2θ of 29.33, 37.10, 43.23, 47.86, 62.70, 63.02, 75.2, and 79.2°. The peak with the highest intensity is at 2θ of 29.33°. XRD analysis confirms that this substance is a typical cubic NiO (JCPDS No. 01-072-4521) [22] and suggests impurity of NaNO$_3$ (JCPDS No. 01-079-2056). Figure 2a indicates high crystallinity of NiO nanopowder.
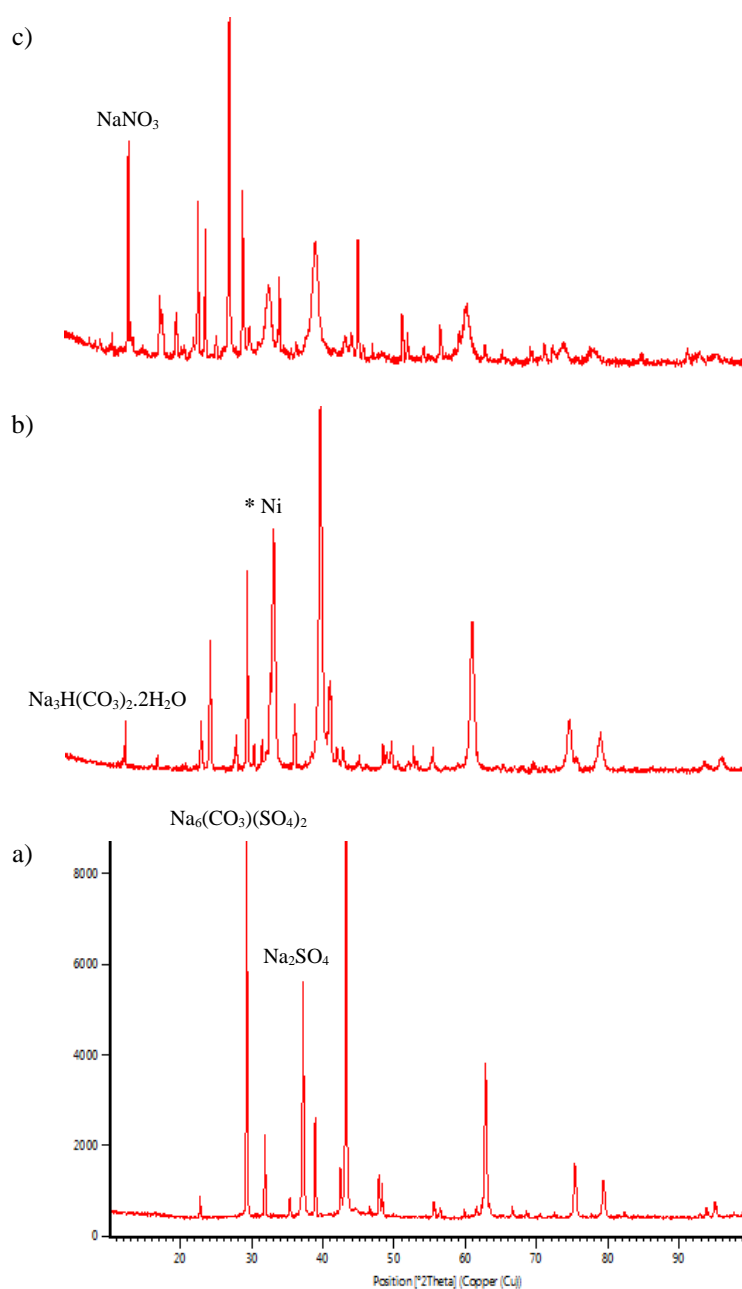

Figure 2. X-ray Diffraction Patterns of NiO Nanocrystals with Various Precursors a) Nickel Nitrate Hexahydrate, b) Nickel Acetate Tetrahydrate, c) Nickel Sulfate Hexahydrate

Figure 2b illustrates the X-ray diffraction pattern of NiO nanocrystals prepared by a sol-gel method at low temperature with nickel acetate tetrahydrate as the precursor. The XRD pattern of NiO powder calcined at 450 °C shows that peaks appear at 2θ of 27.8, 29.0, 33.8, 37.2, 39.9, 44.4, 62.7, and 75.3°. The peak with highest intensity is at 2θ of 43.2°. XRD analysis shows that this substance is a typical cubic NiO (JCPDS No. 01-071-4751) and suggests impurity of $Na_3H(CO_3)_2.2H_2O$ (JCPDS No. 00-029-1447) and nickel (Ni) metal (JCPDS No. 01-078-7533).

Figure 2c shows the X-ray diffraction pattern of NiO nanocrystals formed by a sol-gel process at low temperature with nickel sulfate hexahydrate as the precursor. The XRD pattern of NiO powder calcined 450 °C illustrates that the peak with the highest intensity is at 2θ of 28.0°, whereas other peaks are at 2θ of 29.0, 33.8, 37.1, 38.6, 43.2, 48.7, 45.5, 59.4, and 62.9°. XRD analysis shows that this substance is a typical monoclinic NiO (JCPDS No. 01-078-6794) [21] and suggests impurity of Na_2SO_4 (JCPDS No. 00-005-0631) and sodium carbonate sulfate ($Na_6(CO_3)(SO_4)_2$) (JCPDS No. 00-024-1134).

All XRD patterns show the existence of impurities in the NiO powder obtained. The reason for this is that the NiO powders produced in this synthesis were not washed with water. Also, for the NiO produced using nickel sulfate hexahydrate as the precursor, the volume of NaOH added was very high.

According to Scherrer equation, crystallite size generally decreases with broadening of the longest XRD peak. The mean crystallite size was calculated by using equation (1)

$$D = \frac{K.\lambda}{\beta \cos \theta} \qquad (1)$$

where:
D is the mean crystallite size of the powder,
λ is 0.15406 nm is the wavelength of CuKα,
β is the *Full Width at Half Maximum* (FWHM) intensity of 2θ x (π/180),
θ is Bragg's diffraction angle, and
K is a constant usually equal to 0.89

The mean sizes of the nanocrystals obtained are 72.16, 38.63, and 32.84 nm for the precursors nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate respectively, as presented in Table 1. The sharpest peak was at 2θ of 43.2°. This means that nickel sulfate hexahydrate is the best precursor in the preparation of NiO nanoparticles with a methanol solvent.

SEM analysis. The surface morphology of NiO nanocrystals was studied by scanning electron microscopy (SEM). Figure 3a-c depict SEM images of NiO nanocrystals prepared by using nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate, respectively. It is clear that in all cases, NiO nanopowder was successfully prepared by a simple sol-gel process. Figure 3a shows the micrograph SEM of NiO nanocrystals characterized by the sol-gel

Table 1. Mean Size of NiO Nanocrystals

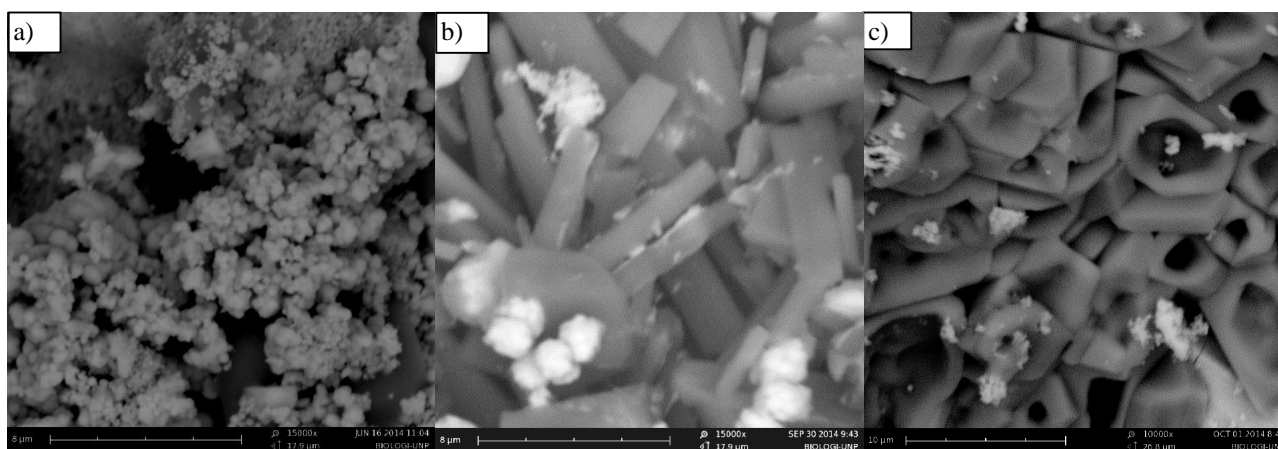| Precursors	2θ	FWHM	The crystal size(L/nm)
Nickel nitrate hexahydrate	43.2	0.1791	72.16
Nickel acetate tetrahydrate	43.2	0.3346	38.63
Nickel sulfate hexahydrate	43.2	0.3936	32.84

Figure 3. SEM Photographs of NiO Particles Produced with Various Precursors a) Nickel Nitrate Hexahydrate (15,000x), b) Nickel Acetate Tetrahydrate (15,000 x), c) Nickel Sulfate Hexahydrate (10,000x)

process with nickel nitrate hexahydrate as the precursor. From the SEM image, it is clearly seen that the NiO nanopowders in Figure 3a are mostly spherical in shape [21]. The SEM photo in Figure 3a shows the sizes of the particles, which range from 68 to90 nm. This image also shows that mono-dispersive and highly crystalline NiO nanocrystals are obtained. These NiO nanoparticles have the tendency to agglomerate due to their high surface energy. Figure 3b depicts the photo SEM of NiO nano-powder characterized by the sol-gel method with nickel acetate tetrahydrate as the precursor. As shown in Figure 3b, these particles range in size between 60-80 nm. From the SEM analysis shown in Figure3b, it is clear that the microstructure of NiO nanopowder was produced in rod-shaped form. Figure 3c shows the micrograph SEM of NiO nanopowder that was prepared by using a sol-gel process with nickel sulfate hexahydrate as the precursor. It is seen that the particle structure, as shown in Figure 3c, is hexagonal shape with hollow. Therefore, the SEM analysis shows that the crystal morphology of the obtained NiO nanocrystals varies with different precursors.

Conclusions

NiO nanocrystals were successfully synthesized by a sol-gel method at low temperature, using nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate as precursors. Methanol was used as the solvent and NaOH 5M was used as the precipitation agent. The sizes of the NiO nanocrystals obtained were 72.16 nm, 38.63 nm, and 32.84 nm for nickel nitrate hexahydrate, nickel acetate tetrahydrate and nickel sulfate hexahydrate, respectively. XRD analysis showed that the structure of NiO nanoparticles with nickel nitrate hexahydrate and nickel acetate tetrahydrate precursors was cubic, whereas the structure of NiO nanoparticles with nickel sulfate hexahydrate as the precursor was monoclinic. SEM photos of the NiO nanoparticles showed a spherical shape for nickel nitrate hexahydrate as precursor, a rod-like shape for nickel acetate tetrahydrate as precursor and a hexagonal shape with hollow for nickel sulfate hexahydrate as precursor. Based on these findings, it was determined that nickel sulfate hexahydrate is the best precursor for NiO nanocrystals synthesized via a sol-gel process, with the smallest particle size.

Acknowledgement

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