LOW TEMPERATURE CONDITION FOR NIO NANOPARTICLES PREPARATION VIA SOL-GEL METHOD

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Abstract—Nickel oxide (NiO) nanoparticles had been widely used in semiconductor, magnetic and fields due to its high surface area, adsorptive and diffusivities properties. In this study, NiO was prepared via sol-gel method under low temperature operating condition. The properties of NiO nanoparticles were investigated by XRD, FTIR, TEM and TGA analysis. TGA had confirmed the organic compound decomposed at $400^{o}C$ and NiO nanoparticles were formed at this temperature. The structure of NiO nanoparticles obtained was cubic structure. The spherical shape of NiO nanoparticles was observed by TEM with average particle size of 18.11 nm which was close to the average particle size calculated using XRD analysis of 22.78 nm. The sol-gel method showed an easier way to produce smaller size of NiO nanoparticles at low temperature.

Index Terms— Nickel Oxide, Nanoparticles, sol-gel method, low temperature

I. INTRODUCTION

Recently, nickel oxide (NiO) nanoparticles had received much attention due to its excellent properties in semiconductor, magnetic and catalytic fields [1] . It had been widely used as lithium ion batteries, magnetic materials, electrochromic, catalysis, optical and electrochemical properties [2-5]. Small size particle was required for better performance in all these applications.

NiO had been synthesized by using precipitation method, thermal decomposition, heat treatment, solvothermal, sol gel and so on [6-11]. Sol gel preparation method has gain more popularity due its simplicity, inexpensive technique and its ability to produce high surface area [12].

In the present work, NiO nanoparticles were prepared via low temperature condition via sol-gel method in the presence of surfactant. The aim of this work was to develop a simpler way to synthesis NiO nanoparticles at low temperature condition using citric acid as precursor and ethylene glycol as a surfactant. The performance of the NiO nanoparticles was based on surface morphology characterization test.

II. MATERIALS AND METHOD

A. Materials

NiO nanoparticles were synthesized via low temperature sol-gel method. Analytical grade of nickel nitrate salt ($Ni(NO)_3.6H_2O$)(Merck, Germany), ethylene glycol ($C_2H_6O_7$)(Merck, Germany), absolute ethanol (C_2H_5OH)(Systerm, India), and citric acid ($C_6H_8O_7.H_2O$, J. Kollin Chemicals) were used in this study without further purification.

B. Preparation of NiO nanoparticles

First, 1 g of $Ni(NO)_3.6H_2O$ and $C_6H_8O_7.H_2O$ were dissolved in 50 ml of ethanol in two different beakers under stirred at the rotation speed of 300 rpm. 0.5 ml of $C_2H_6O_7$ was then slowly added to the mixture of $Ni(NO)_3.6H_2O$ and C_2H_5OH. After the chemicals had completely dissolved, both solutions were mixed together and continued stirring for 1 hour to allowed complete reaction. The reaction was carried out under room temperature. After the reaction had completed, the solutions will dry in oven at $80^{o}C$ for overnight. The resulting gel will undergo heat treatment of $400^{o}C$ for 2 hours in furnace. The powder formed after heat treatment was NiO nanoparticles which was dark green in colour. A simple illustration on the processing steps for NiO nanoparticles preparation was shown in Fig. 1.

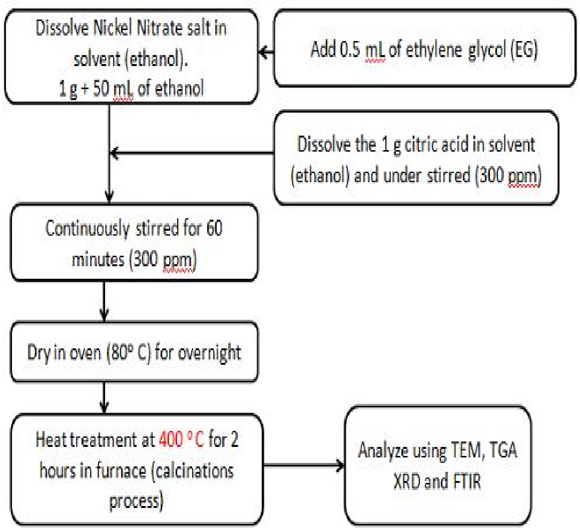

Fig. 1. Processing steps for NiO nanoparticles preparation

C. Nanoparticles Characterization

Properties of NiO nanoparticles were characterized by using X-ray Diffraction (XRD)(Brukur D8 Advance AXS, Germany) with CuKα radiation (1.5406Å) in the 2θ scan range of 5-80^o, Transmission Electron Microscope (TEM)(JEOL, JEM-2010, Netherland), Thermogravimetric Analysis (TGA/DSC)(Netzsch, STA 449 F3 Jupiter, Germany) and Fourier Transform Infrared Spectroscopy (FTIR) (Thermoscientific Nicolet 6700, USA). X-ray diffraction was employed to calculate the average particle size by using Scherrer equation as shown in equation (1),

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

where β is the peak width at half maximum, K is the Scherer constant (K=0.89), λ is the X-ray wavelength (λ=0.154056 nm), θ is the Bragg diffraction angle. TEM analysis was to confirm the shape of the produced nanoparticles and to compare the average particle size with the XRD analysis. TGA test was carried out to check the decomposition of the substances. FTIR analysis was used to determine the functional groups or chemical bonding that presence.

D. Chemical Mechanism of the Reaction

Formation of NiO nanoparticles can be explained by using three stages. First stage of the mechanism was the reaction between $Ni(NO)_3.6H_2O$ and $C_6H_8O_7.H_2O$ with the present of $C_2H_6O_7$ as surfactant. First stage reaction happened at room temperature under stirred. The next stage was the dehydration of nickel (II) oxalate dihydrate ($NiC_2O_4.2H_2O$) to nickel (II) oxalate (NiC_2O_4) at temperature around 200-300^{o}C. Final stage would be the decomposition of the NiC_2O_4 to NiO at the range of temperature between 300-400^{o}C. All the stages of the reaction were shown in the equation below:

Stage 1

$$3Ni(NO_3)_2.6H_2O + C_6H_8O_7.H_2O \rightarrow 3NiC_2O_4.2H_2O + 6HNO_3 + 8H_2O + 6H_2 \quad (2)$$

Stage 2

$$NiC_2O_4.2H_2O \xrightarrow{200-300^o C} NiC_2O_4 + 2H_2O \quad (3)$$

Stage 3

$$NiC_2O_4 \xrightarrow{300-400^o C} NiO + CO + CO_2 \quad (4)$$

E. Material and Parameter Condition

Selection of the material and parameter condition was crucial to produce high purity and smaller size of NiO nanoparticles. In this study, $C_6H_8O_7.H_2O$ and $C_2H_6O_7$ material was selected to prepare NiO nanoparticles. $C_6H_8O_7.H_2O$ was selected because of its chemical structure that enable it to supplied 3 $^-$O-C=O bond to the formation of $NiC_2O_4.2H_2O$. The supplied of $^-$O-C=O bond was sufficient to the formation of $NiC_2O_4.2H_2O$ as it only needed 2 $^-$O-C=O bond. Formation of $NiC_2O_4.2H_2O$ is necessary because heat treatment of $NiC_2O_4.2H_2O$ will resulted to the NiO product. Therefore, $C_6H_8O_7.H_2O$ was one of the best precursors to be used. The chemical structure of $C_6H_8O_7.H_2O$ and $NiC_2O_4.2H_2O$ was presented at Fig. 2. The presence of surfactant in this study was to enhance the particles stability by introducing high solubility surfactant. This will reduce the particle agglomeration and could lead in smaller size of nanoparticles produced [13]. $C_2H_6O_7$ was selected in this study because it had shown good solubility effect [14].

Parameter condition that was selected in this study was the heat treatment at 400^{o}C. Heat treatment at 400^{o}C was selected according to the temperature of decomposition of nickel oxalate to nickel oxide occurs at 400^{o}C [15-16]. Heat treatment has a linear relationship with the particle size [17]. As the heat treatment temperature used is higher, the particle size produce will be larger.

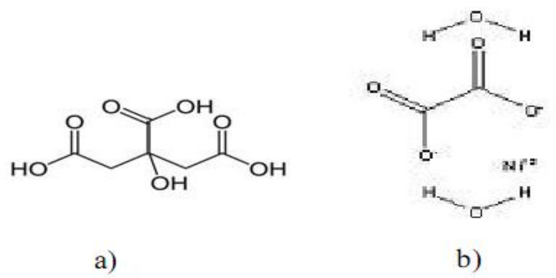

Fig. 2. Chemical structure of a) $C_6H_8O_7.H_2O$ and b) $NiC_2O_4.2H_2O$

III. RESULTS AND DISCUSSION

The dehydration of $NiC_2O_4.2H_2O$ to NiC_2O_4 and decomposition of NiC_2O_4 to NiO can be explained by using the thermal gravimetric analysis and differential scanning calorimetry (TGA/DSC) as shown in Fig. 3. From Fig. 3, stage 1 product was referred to the temperature before 100^{o}C. It can be observed that when the temperature was below 100^{o}C, the percentage of weight loss was low and most of the organic substance was still remain in the solution. Start from 100^{o}C onwards, the percentage of weight loss become significant. DSC endothermic peak found at 186.5^{o}C was referred to the dehydration of water as shown in equation (2). The percentage of weight lost was around 16.42% at the range of 100-200^{o}C.

The second stage reaction as described by equation (3) occurred at the range of 200 to 300^{o}C. The DSC endothermic peak found at 236.8^{o}C was best described by the dehydration of $NiC_2O_4.2H_2O$ to NiC_2O_4. At this range of temperature, the percentage of weight lost was around 26.98%. Decomposition process occurred at the third stage of reaction at the temperature range of 300-400^{o}C and was indicated by the DSC endothermic peak at 352.2°C. The percentage of weight lost at this temperature range was 26.89%. The weight percentages remain after 400°C was less than 8% and this prove that most of the organic and water compound had been removed from the final product. The summary of the TGA/DSC curve with respect to the reactions stages were shown at Table I.

Table I: Summary of TGA/DSC curve with respect to the reaction stages

Temperature Range (°C)	DSC peak (°C)	Percentage of weight loss (%)	Remarks
100-200	186.5	16.42	Removal of water
200-300	236.8	26.98	Dehydration of $NiC_2O_4.2H_2O$ to NiC_2O_4
300-400	352.2	26.89	Decomposition of NiC_2O_4 to NiO

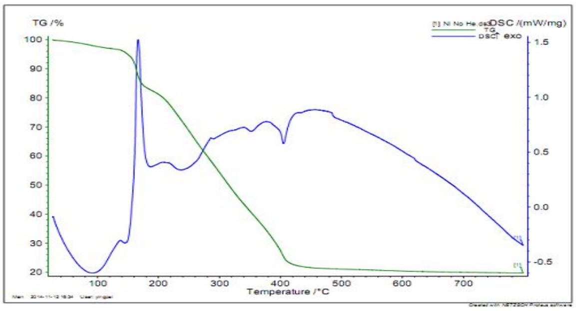

Fig. 3. TGA analysis of NiO nanoparticles

Table II shows the comparison between the dehydration and decomposition steps of this study with other literature studies done previously. It can be seen that the results of this study was close to the literature studies. As a conclusion, the equation (3) to (4) [15-16] was proved to be valid and NiO nanoparticles can be produced according to the reaction.

Table II: Comparison of TGA result with other studies

No.	Temperature Range (°C)	DSC peak (°C)	Percentage of weight loss (%)	Reference
1	196-284 316-400	258 365	19.73 39.85	Zhan et al. (2005)
2	175-300 300-360	250 340	18 41.8	Mansour et al. (1993)
3	200-300 300-400	236.8 352.2	26.98 26.89	This work

The XRD pattern of NiO nanoparticles was shown in Fig. 4. The peaks position appearing at 2θ is 37.04°, 43.16°, 62.70°, 75.25° and 79.24°. The locations of the diffraction peaks were referred to the diffraction data of face-centered cubic (FCC) crystalline structure according to the structure in JCPDS card (No. 04-0835) [18-19]. The obtained crystal planes from results were close to the literature value as shown in Table III. The average particle size predicted by the Scherrer equation as shown in equation (1) was 22.78 nm.

Table III: Comparison of XRD result with other study

No.	Peak location (θ)	Reference
1	37.21°, 43.22°, 63.10°, 75.20° 79.39°	Sharanabasava et al. (2012)
2	37.04°, 43.16°, 62.70°, 75.25° 79.24°	This work

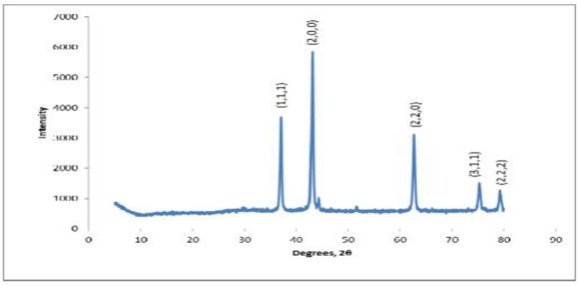

Fig. 4. XRD pattern of NiO nanoparticles

The average particle size of the NiO nanoparticles was also investigated by TEM photograph which was shown in Fig. 5. The average particles sizes given by TEM analysis was 18.11 nm which was close to the average particle size predicted from XRD analysis. The TEM analysis revealed that the NiO particle obtained was spherical.

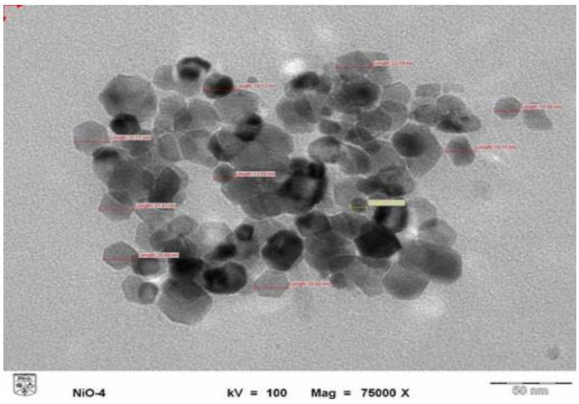

Fig. 5. TEM diagram of NiO nanoparticles

FTIR was used to investigate the presence of functional group in all stages. The FTIR analysis was carried out before and after the heat treatment and the results are shown in Fig. 6 and Fig. 7 respectively. According to equation (1) to (3), there are several functional group exists in the chemical compounds at different reaction stages and they were summarized in Table 1. From Fig. 6., hydroxide (OH^-) groups was found at the broader band of 3436.2 cm^{-1}, C-H stretch at sharp band of 2983.9 cm^{-1}, C≡C groups at band 2362.4 cm^{-1}, C=O groups at band 1733.3 cm^{-1}, C-H bending groups at 1375.9 cm^{-1},NO groups at 1348.6 cm^{-1} and C=O groups at 1198.1 cm^{-1}. All these results leads to a conclusion where all the functional groups presented at Table IV were exist except Ni-O groups. The reason behind this behavior was that Ni-O groups will only appear after heat treatment. This can be proven from Fig. 7, where the peak at 436.6 cm^{-1} gave clear evidence that Ni-O groups were presence while there was no sign of any Ni-O functional groups shown in Fig. 6. The peak value reported in this study was in good agreement with others studies as reported in reference which was shown in Table V. This result also gave a conclusion where heat treatment was necessary for production of NiO nanoparticles. This also proves that the mechanism suggested in this experiment was in line with the results.

Table IV: Functional group at particular stage Reaction at Stage N, Functional Group

Reaction at Stage N, N=1,2,3	Functional Group
Stage 1	OH^-, C=O, C-O, C-H, NO
Stage 2	OH^-, C=O, C-O
Stage 3	Ni-O, C=O, C≡O

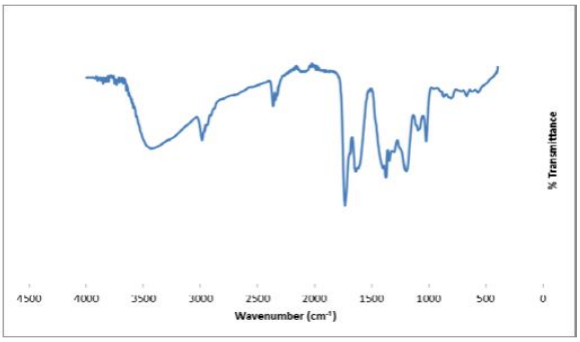

Fig. 6 FTIR of NiO before heat treatment

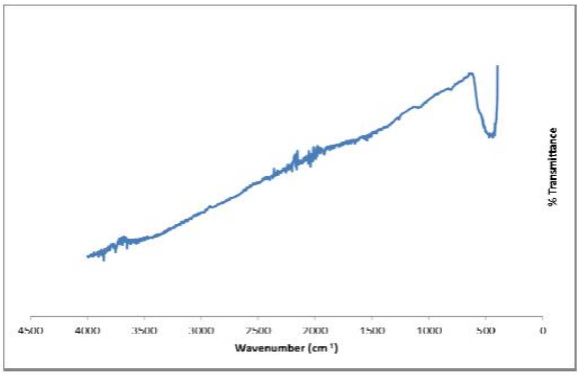

Fig. 7. FTIR of NiO after heat treatment

Table V: Comparison of Ni-O wavenumber with other

No.	Ni-O wavenumber (cm^{-1})	Reference
1	455	Salavati-Niasari (2010)
2	445	Dharmaraj et al. (2006)
3	436.6	This work

CONCLUSIONS

NiO nanoparticles were successfully produced via sol-gel method at low temperature condition using citric acid and ethylene glycol as a precursor and surfactant respectively. The effect of thermal stability was investigated by TGA and it showed that the NiO nanoparticle was formed at 400oC. From the analysis of XRD and TEM, the average particle size of NiO obtained was small which was 22.78 nm and 18.11 nm from XRD and TEM analysis respectively. FTIR analysis confirmed that heat treatment was necessary for formation of Ni-O functional groups. Attribute to the small particle size of NiO, large surface to volume ratio make it an ideal candidate for highly specific applications. The result shows that this method has good characteristics to be used for NiO synthesis such as nontoxic, simple, inexpensive and easily scale up. Although the particle size of the NiO nanoparticles produced was small, further research should be carried out in the future to investigate the factors of high temperature reaction condition, pH and molar ratio to find the optimal condition to produce minimal size of NiO nanoparticles.

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