Sonochemical Synthesis of Nickel Oxide Nano-particle

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Abstract: Nickel oxide (NiO) nanopowder was obtained during a sonochemical method. Nickel hydroxide precursor, prepared by addition of sodium hydroxide (NaOH) to nickel nitrate $Ni(NO_3)_2$ solution and vigorously stirring until the pH becomes 7.2. Ultrasounds waves were applied during precipitation period and after drying in oven nanopowder NiO was achieved. Transient and scanning electron microscopy showed that the synthesized nanopowder NiO had dimensions about 20 nm. The X-ray diffraction pattern revealed that the produced well-crystallized and high purity nickel oxide nanostructure.

Keywords: Nickel oxide; Sonochemical rout; Nanopowder; Characterization.

Introduction

Nickel oxide (NiO) is a p-type oxide semiconductor with a wide band gap (3.6–4.0 eV) and ~1.8 eV conduction band energy [1-2] which has been considered as a promising materials for optical, electronic and catalytic applications. NiO nanoparticles also may have many applications such as in the manufacture of superparamagnetic materials, p-type transparent conducting films, gas sensors, catalyst, alkaline batteries cathode, dye-sensitized solar cells, and solid oxide fuel cells anode [3–6].

Various methods such as sol–gel, hydrothermal synthesis, electrochemical methods, metal evaporation and spray pyrolysis, have been used and developed to produce nonopowder materials [3,7-8]. Recently, the sonochemical methods have been acknowledged as a promising route for preparation of a variety of materials with nanometer dimensions, including metallic and ceramic nanoparticles [9-11].

Ultrasonic waves consist compression and rarefaction cycles. Cavitation is the origin of sonochemical effects and takes place in rarefaction cycles where negative acoustic pressure is enough to pull water molecules from each other to create tiny microbubbles (cavities). On the other hand in compression cycle of wave, acoustic pressure is positive. Finally microbubbles collapse violently during compression cycles and act as a localized microreactor which produces instantaneous temperatures of several thousand degrees (>5000 °C) and pressure in excess of several hundred atmospheres (>500 atm) [12]. Thus, such extreme temperatures and pressures within a small reactor can induce many changes in the morphology nano-particles during preparation. The actual mechanism of cavitation is still incompletely understood, and in different cases almost certainly involves shock waves, imploding liquid jets, and the high temperatures and pressures associated with bubble collapse [12].

In this work, nickel hydroxide was prepared sonochemically and by post heat treatment converted to nickel oxide nano-particles. Also morphological and structural characterizations were carried out on NiO nano-particles.

Experimental

Sonochemical preparation of NiO nanostructure is composed of three stages: first, the formation of nickel hydroxide precursor precipitate, second, ultrasonic irradiation and subsequent transformation to NiO by heat treatment. Nickel hydroxide precursor, prepared by slow drop wise addition of 0.1M sodium hydroxide NaOH to 0.1M nickel nitrate $Ni(NO_3)_2$ solution was kept vigorously stirred until the pH becomes 7.2. In sonochemical method high frequency ultrasounds waves used for exciting nucleation and then to remove byproducts, precursor was filtered and washed repeatedly with distilled water for three times and final washing is carried out by using alcohol. Wet cake obtained after filtration was oven dried for 70 ºC overnight. After determining the reaction temperature of conversion nickel hydroxide to nickel oxide by thermal analysis, the oven-dried cake was heated at 320ºC for 1h to form nanoparticle NiO.

Simultaneous thermal analysis (Netzsch STA 409, DE) was carried out to determination of $Ni(OH)_2$ to NiO reaction temperature in air atmosphere. STA measurement conditions was: hold for 1 min at 30 °C, heat from 30 °C to 600 °C at the rate 10 °C/min and then hold for 10 min at 600 °C.

X-ray diffraction (Unisantic XMD300, GmbH) was used for structural study and characterization of powders before and after heating them in furnace. Phase purity of the initial powder also was characterized by XRD. Morphological study also carried out using scanning electron microscope (Cambridge-S360 20kV, UK). Transmission electron microscopy (LEO 912AB, DE) also corroborated formation of well crystalline shaped NiO nanoparticle.

Results and Discussion

Fig. 1.a shows X-ray diffraction pattern of powder before calcinations procedure. After sonochemical treatment and drying of powder in the oven, green powder was obtained. This green powder identified as Nickel hydroxide by XRD. This is a typical α-type $Ni(OH)_2$. All the diffraction peaks can be indexed to the diffraction data of the $Ni(OH)_2.6H_2O$ (JCPDS card No. 38-0715). All peaks are broad; in general, the broadening of XRD diffraction peaks may result from small grain sizes or structural micro-distortions in crystal. Under the present experimental conditions, the extremely small particle-like structure results in a significant broadening of some diffraction peaks in $Ni(OH)_2$ XRD patterns. Also, these “saw-tooth” reflections are typical of turbostratic phases which are ordered in two dimensions, but whose layers are orientationally disordered [13].

Reaction procedure to form $Ni(OH)_2$ is:

$$2NaOH\ (aq.) + Ni(NO_3)_2.6H_2O\ (aq.) \rightarrow 2NaNO_3\ (aq.) + Ni(OH)_2.6H_2O\ (aq.) \quad (1)$$

According to this reaction, sodium nitrate was produced as byproduct. Because of high solubility of this byproduct in water, for removing it, wet cake washed with distilled water repeatedly.

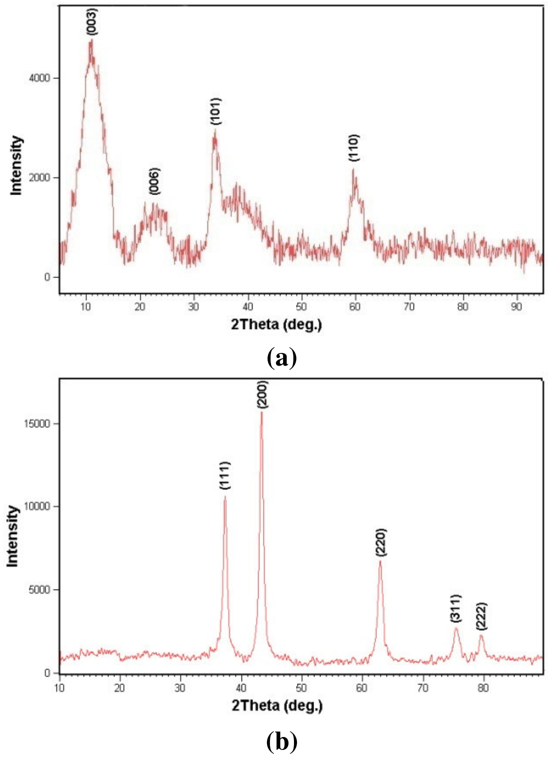

Fig. 1. X-ray pattern of nickel hydroxide powder (a) before and (b) after calcination.

From STA graphs (Fig. 2) can be concluded that two endothermic reactions occurred on heating cycle of $Ni(OH)_2$ powders from room temperature to 600°C. In both reactions mass was decreased which related to removing H_2O molecule from powders and include:

$$Ni(OH)_2.6H_2O \rightarrow Ni(OH)_2 + 6H_2O \quad (2)$$

$$Ni(OH)_2 \rightarrow NiO + H_2O \quad (3)$$

As shown in Fig. 2 the reactions start about 220°C and finish around 310°C. XRD result (Fig. 1.b) confirms formation of black nickel oxide after calcination treatment (JCPDS card No. 22-1189). Other components are not detected in final powders. In nickel oxide this non-stoichiometry is accompanied by a color change, with the stoichiometrically correct NiO being green and the non-stoichiometric NiO being black.

Because of suppression of grain growth, minimum heat treatment temperature was chosen. Therefore, the oven-dried cake was heated at 320ºC for 1h to form nanoparticle NiO.

Figs. 1.a & b illustrate, $Ni(OH)_2$ with poor crystallinity and NiO nano-powder with high crystallinity were obtained. According to Scherer equation, when maximum peak broadens, the crystalline size will decrease. The width and the intensity of maximum peak for NiO nanoparticle produced via sonochemical method and conventional sol-gel have been shown in table 1. Crystalline size has been calculated by using Scherer equation:

$$D = \frac{K\lambda}{\beta\ Cos\theta} \quad (4)$$

where D is the mean crystallite size of the powder, k is the wavelength of Cu kα equal to 1.54056Å, β is the full width at half-maximum (FWHM) intensity of the (200) peak in radian, θ is Bragg’s diffraction angle and k is a constant usually equal to 0.9). Thus crystalline size of nickel oxide powder (D= 17.6 nm) confirms that nano-crystalline powder has been formed.

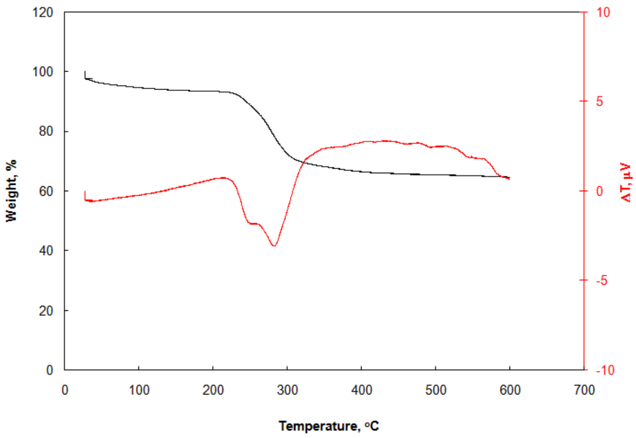

Fig. 2. STA (TG/DTA) graphs of nickel hydroxide; Conditions: hold for 1 min at 30 °C; heat from 30 °C to 600 °C at the rate 10 °C/min; hold for 10 min at 600 °C.

Table 1- XRD parameters of NiO nanoparticle obtained from sonochemical and conventional sol- gel rout.

Procedure	θ_{max} (°)	Full width at half maximum (FWHM)	Crystalline size (nm)
Conventional sol-gel	**43.355**	**0.486**	**21.8**
Sonochemically synthesised	**43.346**	**0.393**	**17.6**

Results show sonochemical treatment decrease the crystalline size of synthesized powders. Micrograph which showed in Fig. 4 depicted aggregated spherical particles with diameter about 50 to 300 nm. They might form due to an interparticle magnetic intraction.

TEM investigations (Fig. 5.a) exhibit the NiO nanoparticles with an average particle size of ~20 nm. Morphology of powders is qubic particles due to NaCl structure of NiO. The crystallite NiO were shown in this figure are not perfect, because effect of ultrasonic waves.

In Fig. 5.b, it is obvious that these primary nanoparticles form larger agglomerated particles due to both effect of collisions caused by ultrasonic shock waves and magnetic interaction. These secondary particles formed morphologies observed in SEM images (Fig. 4).

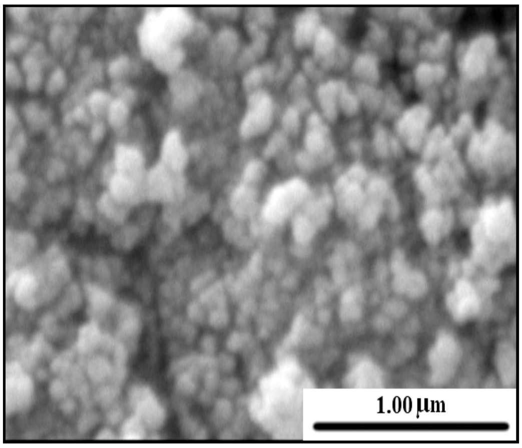

Fig. 4 Micrograph of nickel oxide nano-powder.

Conclusion

Pure high crystallinity nickel oxide nano-particle with average crystallite size of about 20 nm was synthesized by a novel sonochemical approach. Morphology of resulted powder is qubic particles due to NaCl structure of NiO. Ultrasonic irradiation resulted in cavitation phenomenon and leads to decrease crystalline size of the NiO particles. Nickel oxide which is produced in this method is non-stoichiometry and this non-stoichiometry is accompanied by a color change from green to black.

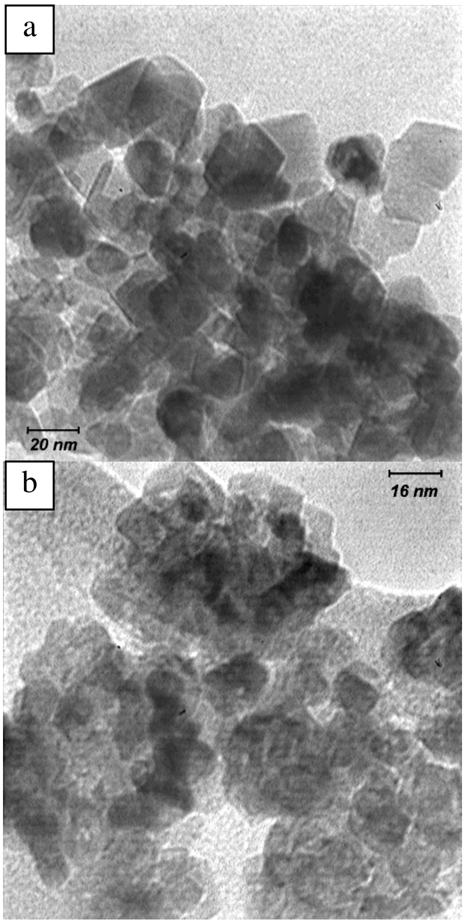

Fig. 5 Transmission electron micrograph of nickel oxide nano-powder.

References

[1] A. B. Kunz, "Electronic structure of NiO", *J. Phys. C: Solid State Phys.* 14 (1981) L455-L460.

[2] H. Sato, T. Minami, S. Takata, T. Yamada, "Transparent conducting p-type NiO thin films prepared by magnetron sputtering", *Thin Solid Films*, 236 (1993) 27.

[3] Y. Bahari Molla Mahaleh, S. K. Sadrnezhaad, D. Hosseini, "NiO Nanoparticles Synthesis by Chemical Precipitation and Effect of Applied Surfactant on Distribution of Particle Size", *J. Nanomat.*, 1(2008) 1-4.

[4] C. Luyo, R. Ionescu, L.F. Reyes, Z. Topalian, W. Estrada, E. Llobet, C.G. Granqvist, P. Heszler, "Gas sensing response of NiO nanoparticle films made by reactive gas deposition", *Sensors and Actuators B: Chemical*, 138 (2009) 14-20.

[5] S. A. Needham, G. X. Wang, and H. K. Liu, "Synthesis of NiO nanotubes for use as negative electrodes in lithium ion batteries", *J. Power Sources*, 159 (2006) 254–257.

[6] G. Boschloo, J. He, S. Lindquist, A. Hagfeldt, "Dye Sensitization of Nanostructured NiO", Proceedings of the 12th Workshop on Quantum Solar Energy Conversion - (QUANTSOL 2000), Wolkenstein, Südtirol, Italy, March

11-18, 2000.

[7] M. Ghosh, K. Biswas, A. Sundaresan, C. N. R. Rao, “MnO and NiO nanoparticles: synthesis and magnetic properties”, *Journal of Materials Chemistry,* 16 (2006) 106–111.

[8] Y. Wu, Y. He, T. Wu, T. Chen, W. Weng, and H. Wan, “Influence of some parameters on the synthesis of nanosized NiO material by modified sol-gel method,” *Materials Letters*, 61 (2007) 3174–3178.

[9] Mahyar Mazloumi, Saeid Zanganeh, Amir Kajbafvala, Parisa Ghariniyat, Shadi Taghavi, Aidin Lak, Matin Mohajerani, S.K. Sadrnezhaad, “Ultrasonic induced photoluminescence decay in sonochemically obtained cauliflower-like ZnO nanostructures with surface 1D nanoarrays”, *Ultrasonics Sonochemistry*, 16 (2009) 11–14.

[10] Hamed Arami, Mahyar Mazloumi, Razieh Khalifehzadeh, S.K. Sadrnezhaad, “Sonochemical preparation of TiO2 nanoparticles”, *Materials Letters*, 61 (2007) 4559–4561.

[11] B. Neppolian, Q. Wang, H. Jung, H. Choi, “Ultrasonic-assisted sol-gel method of preparation of TiO2 nano-particles: Characterization, properties and 4-chlorophenol removal application”, *Ultrasonics Sonochemistry* 15 (2008) 649–658.

[12] J. David, N. Cheeke, *Fundamentals and Applications of Ultrasonic Waves*, 2002, CRC Press.

[13] G. Fu, Zh. Hu, L. Xie, X. Jin, Y. Xie,Y. Wang, Z. Zhang, Y. Yang, H. Wu, “Electrodeposition of Nickel Hydroxide Films on Nickel Foil and Its Electrochemical Performances for Supercapacitor”, *Int. J. Electrochem. Sci.,* 4 (2009) 1052 – 1062.