ACERP: Vol. 2, No. 4, (Fall 2016) 13-17

Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Nb_2O_5 Nanoparticles Synthesis by Chemical Surfactant-Free Methods: ltrasonic Assisted Approach

M. Mohammadifar, A. Massoudi*, N. Naderi, M.J. Eshraghi

Department of Semiconductors, Materials and Energy Research Center, Karaj, Iran

PAPER INFO

Paper history:
Received 25 October 2016
Accepted in revised form 29 January 2017

Keywords:
Nb_2O_5
Nanoparticles
Surfactant-Free
Ultrasonic
Concentration Effect
Metal Oxides

ABSTRACT

In this study, spherical Nb_2O_5 nanoparticles were synthesized by a novel chemical method as a simple, robust, surfactant-free, non-toxic and widely applicable approach. In order to investigate the effect of initial concentration on particle sizes, nanoparticles with different initial concentration were synthesized. Ultrasonic assisted method was applied and the effects of ultrasonic treatment and concentration on particle sizes have been investigated. The structure and morphology of Nb_2O_5 nanoparticles were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy (FE-SEM). Particle size measurement was estimated by Digimizer software and particle size distribution was plotted. The results showed that ultrasonic treatment and different suspension concentration impact on particle sizes. Nanoparticles with average particle size of 41 nm in diameter were achieved by using 2 gr/L of Nb_2O_5 in initial suspension with ultrasonic assist.

1. INTRODUCTION

Nb_2O_5 is a highly applicable metal oxide which attracted much attention in 1940, when the Nb_2O_5 polymorphs were introduced [1]. Nb_2O_5 is a felicitous choice among the candidates for catalysis [2-4], sensors [5-7] and electrochromic devices [7-9]. Furthermore, thin films and nanostructures of Nb_2O_5 were applied in batteries, solar cells, and electronic devices [10-13].

Nb_2O_5 nanoparticles with high surface area to volume ratio result in physical and chemical properties different from its bulk state [14]. Nb_2O_5 nanostructures were synthesized by different methods such as solvothermal [15], hydrothermal [16, 17], sol-gel [18] and chemical surfactant-free method [19]. In comparison to surfactant-directed methods, solvent-controlled approaches are more robust, simple and widely applicable synthesis protocols. Furthermore, good accessibility of nanoparticle surface, non-toxicity and safety are provided through this method [20].

The studies about sonochemical synthesis indicate that ultrasonic treatment exerts an influence on morphology and particle sizes [21]

Ultrasonication leads to cavitation phenomenon that burst cavities in water to break particles in smaller sizes. Cavitation produces high energy which causes breaking of the particles into smaller ones. The energy released by cavitation is about 10 to 100 kJ/mol which is in the range of hydrogen bonding [22].

In this research we are aiming to synthesize Nb_2O_5 nanoparticles from micropowders. This approach can be applied for other ceramic oxides, so we are introducing a novel, robust, cost effective and reliable method to construct nanostructures from micropowders. In addition to synthesizing Nb_2O_5 nanoparticles, the effect of different concentrations has also been discussed. Due to the increased demand for smaller particle sizes in different applications, a physical approach to minimize the particle sizes was applied.

2. EXPERIMENTAL

2.1. Materials

Nb_2O_5 micro powders, Ammonia (NH_3) and hydrofluoric acid (HF) (40%) were purchased from MERCK. Deionized water was used during experiments.

2.2. Preparation of Nb_2O_5 nanoparticles

Nb_2O_5 nanoparticles were synthesized in two different methods. In the first method, initially Nb_2O_5 powder was dissolved in HF (40%) at 100°C in a Teflon beaker. After dissolving Nb_2O_5 in HF, a colorless solution was obtained which was diluted with deionized water until the corresponding concentration of Nb_2O_5 changed to 4

*Corresponding Author's Email: massoudi@merc.ac.ir (A. Massoudi)

gr/lit. Similar processes were used to produce 3 gr/lit and 2 gr/lit concentrations. After that, ammonia solution was added to the solution until the pH of the solution tuned to 9 and a white precipitate of niobic acid ($Nb_2O_5.nH_2O$) was obtained. The white precipitate was washed with ethanol and DI water to remove F^- ion completely. Then the solution was filtered by paper. $Nb_2O_5.nH_2O$ precipitate was dried in an oven at 80°C for 6h. In the following, to change amorphous $Nb_2O_5.nH_2O$ to crystallized Nb_2O_5, amorphous Nb_2O_5 was calcinated at 580°C for 30 min. The heating rate was 10°C/min.

2.3. Chemical Formula and Mechanism of Nanoparticles Formation In this section, the chemical formula and mechanisms corresponding to each levels of formation is discussed. Initially, Nb_2O_5 micro powders were dissolved in HF and Nb-fluorocomplex compound was obtained (1):

$$Nb_2O_5 + 12HF \rightarrow 2HNbF_6 + 5H_2O \quad (1)$$

After that, by adding ammonia solution to Nb-fluorocomplex, nucleation was occurred and a white precipitate of $Nb_2O_5.nH_2O$ was obtained (2):

$$2HNbF_6 + 12NH_3 + 6H_2O \rightarrow Nb_2O_5.nH_2O + 12NH_4F(NH^{4+}F^-) \quad (2)$$

At last, in order to remove fluorine ions (2), the white precipitate was washed by ethanol and deionized water (3). This process removed the fluorine ions from the structure and the fluorine ions were converted to HF which was dissolved and eliminated completely. Finally, $Nb_2O_5.nH_2O$ was heated at 80 °C for 6h to obtain amorphous Nb_2O_5 (4) and it was subsequently calcinated at 580°C for 30min to convert it into crystalline form (5).

$$Nb_2O_5.nH_2O \xrightarrow{80℃-6h} Nb_2O_5(amorphous) \quad (3)$$

$$F^- + C_2H_6OH \rightarrow CH_2CH_2OH \rightarrow HF \quad (4)$$

$$Nb_2O_5(amorphous) \xrightarrow{580℃-30min} Nb_2O_5(crystalline) \quad (5)$$

2.4. Preparation of Nb_2O_5 Nanoparticles Via Ultrasonic Assisted Method In the second method, Nb_2O_5 powder was dissolved in hydrofluoric acid at 100°C and stirred for 1h to obtain a colorless solution. The solution was diluted with deionized water until concentration changed to 4gr/lit. Similar processes were carried out to obtain 2 gr/lit and 3 gr/lit concentrations. The solution was ultrasonicated for one hour and aqueous ammonia solution was simultaneously added until the pH ofsolution was tuned to 9 and the white precipitate was obtained. Then the white precipitate was washed with ethanol and DI water to remove F^- ion completely until the pH was tuned to 7. Afterwards, the solution was filtered by paper and dried at 80°C for 6h to obtain amorphous Nb_2O_5.The white precipitate was calcinated at 580°C for 30 min while heating rate was fixed on 10 °C/min.

2.5. Characterization X-ray powder diffraction (XRD) analysis of the samples was carried out with Philips (pw 3710) X-ray diffractometer system with graphite monochromatized Co kα irradiation ($\lambda_{k\alpha}$ (Co) = 1.78901 A˚). Field emission scanning electron microscopy (FESEM) was employed with Mira 3-XMU. Average particle sizes and standard derivation (SD) of nanoparticles were measured by Digimizer software. FT-IR spectra were measured by Pekin-Elmer (model: spectrum 400).

3. RESULT AND DISCUSSION

3.1. XRD analysis Fig. 1 shows X-ray powder diffraction analysis of Nb_2O_5 after calcination at 580°C. Nb_2O_5 crystal structure is hexagonal and major peaks can be indexed as (100), (001), (101), (002), (102), (110), (111), (200) and (201), respectively. No characteristic peaks arising from possible impurities were detected. Considering the sharp peaks, Nb_2O_5 nanoparticles have high crystallinity. The crystalline size for 4gr/lit concentration has been calculated by Scherer formula,

$$D = \frac{k\lambda}{\beta Cos\theta} \quad (6)$$

where k = 0.9 and $\lambda_{k\alpha}$ (Co) = 1.78901. Major peaks were indexed as (100), (001), (101) and (102) which were referred to average crystalline size of 30.2, 33.0, 22.9, and 20.4 nm, respectively.

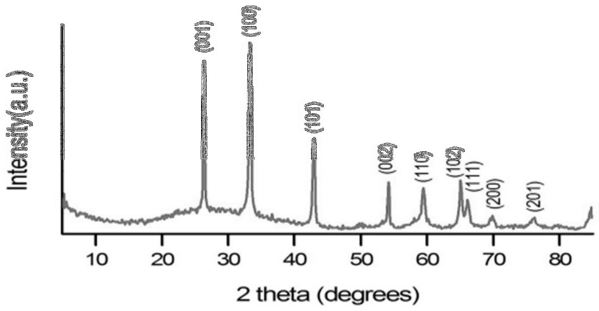

Figure 1. XRD pattern of Nb_2O_5 nanoparticles with 4gr/lit concentration without ultrasonication

3.2. FT-IR Analysis FTIR (Fourier transform infrared) spectra were obtained in order to evaluate chemical composition of Nb_2O_5. The bands at wave number of 3431 and 1626 cm^{-1} [23, 24] support the presence of OH^- group and it is due to the absorption of water from atmosphere during sample preparation. The strong band at 887 cm^{-1} is attributed to Nb-O

stretching vibration [25]. The band observed at 587 cm^{-1} can be correlated to Nb-O-Nb vibrations [26]

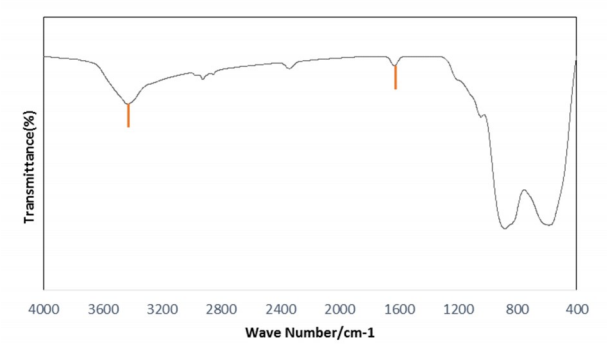

Figure 2. Transmittion FT-IR spectra of Nb_2O_5 nanoparicle synthesized at 2 gr/lit

3.3. Effect of Concentration on Nb_2O_5 Nanoparticle Size

The crystallization behavior of Nb_2O_5 is influenced by the starting materials, the crystallization time, the impurities and their interaction with other compounds; so any changes in these factors may result in different grain size, average particle size and morphologies [19, 26]. In this research, the concentration was considered as optimization parameter, which results in different average particle sizes. Table 1 shows average particle sizes achieved by using suspension with different concentrations. Fig.3 illustrates FESEM images of Nb_2O_5 nanoparticles synthesized with different initial concentrations. Fig.3 (a), 3(b), and 3(c) are related to Nb_2O_5 nanoparticles synthesized in 4, 3 and 2 gr/lit, respectively, without ultrasonic assisted method. FE-SEM images demonstrate that synthesized Nb_2O_5 nanoparticles have spherical morphology and no sign of pores, sharpness or edge are visible on nanoparticle surfaces. Moreover, Nb_2O_5 nanoparticles are distributed homogeneously and they are uniform in size and shape.

TABLE 1. Average particle size of Nb_2O_5 in different concentrations, calcinated at 580^0c, calculated at room temperature

Concentrations	Average particle sizes without ultrasonication assisted method	Average particle sizes with ultrasonication assisted method
4gr/lit	70	68
3gr/lit	57	52
2gr/lit	49	41

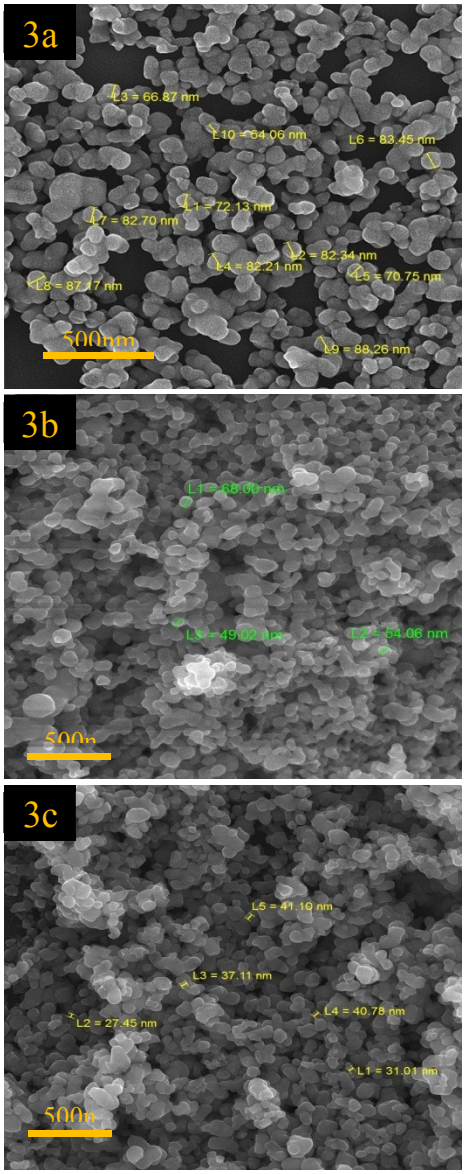

Figure 3. a) Nb_2O_5 nanoparticles with 4gr/lit concentration without ultrasonication assisted, b) Nb_2O_5 nanoparticles with 3gr/lit concentration without ultrasonication assisted c) Nb_2O_5 nanoparticles with 2gr/lit concentration without ultrasonication assisted

3.4. Effects of Ultrasonic Assisted Method on Nb_2O_5 Nanoparticle Size

Ultrasonic energy during the nucleation processes leads to cavitation, growth of the cavity and cavity bursting [22]. Therefore, due to the cavitation process, nucleation follows a different route and it may have an effect on nuclei. In order to investigate the sort of effects on particle sizes, FESEM images were considered. Figs. 4(a), 4(b), and 4(c) illustrate Nb_2O_5 nanoparticles synthesized in 4 gr/lit, 3 gr/lit, and 2 gr/lit suspensions through sonochemical method. As it can be seen, nanoparticles are entirely spherical, the boarders are clearly distinguishable and they have been distributed

homogeneously. Average particle size of Nb_2O_5 nanoparticles synthesized by sonochemical method is decreased. Fig. 5 illustrates average particle sizes corresponding to various concentrations. Figures show that for 2, 3 and 4 gr/lit concentrations, the average particle sizes are 41, 52, and 68 nm, respectively.

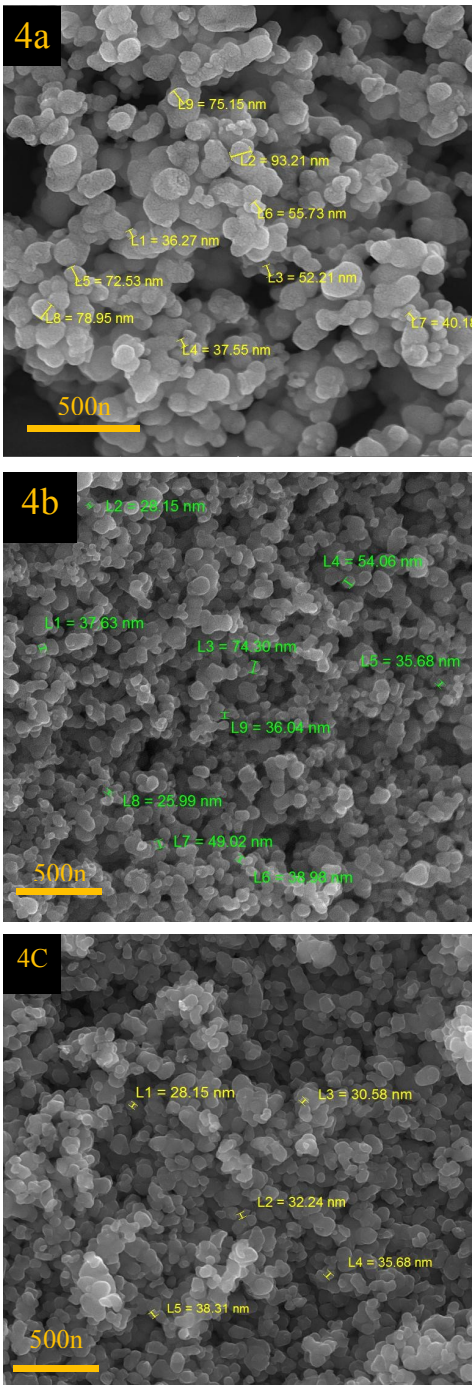

Figure 4. a) Nb_2O_5 nanoparticles with 4gr/lit concentration with ultrasonication assisted b) Nb_2O_5 nanoparticles with 3gr/lit concentration with ultrasonication assisted c) Nb_2O_5

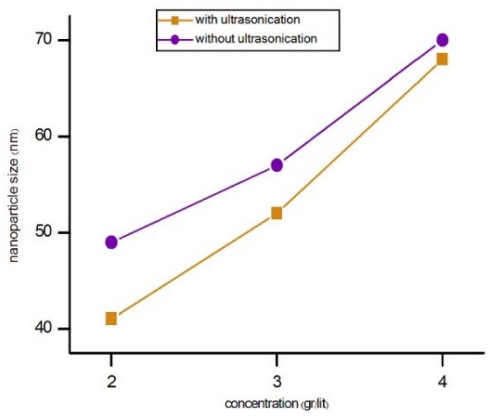

Figure 5. Nanoparticle size changes correspond to concentration

3.5. Particle Size Distribution

Particle sizes for the samples prepared in 2 gr/lit concentration with and without ultrasonic assisted reaction, are calculated by Digimizer software. Particle size distribution is illustrated in Fig. 6 As one can see in Fig. 6, ultrasonic assisting decrease the particle sizes. Standard derivation (SD) was calculated separately for each sample. SDs for 2 gr/lit with and without ultrasonic assisting are 10 and 9, respectively.

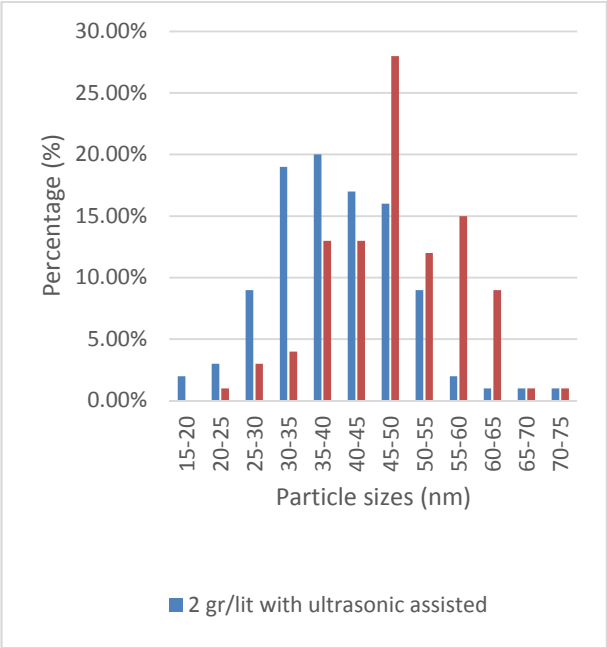

Figure 6. Particle size distribution for 2 gr/lit with and without ultrasonic assist

4. CONCLUSION

Nb_2O_5 nanoparticles were synthesized by chemical surfactant-free approach. The effect of ultrasonic

assistance and concentration on nanoparticle sizes were examined. Nb_2O_5 nanoparticles were characterized by FE-SEM, FT-IR and XRD analyses. Particle size distribution plot was presented and it decrease in particle sizes was validated. Synthesized nanoparticles are totally spherical and without pores, edges or sharpness. By decreasing initial concentration and using ultrasonic assisted approach, the particle size was decreased. It was shown that concentration value and ultrasonic energy play important roles in determining the final phase of the nanoparticles validating the decrease in particle sizes.

5. ACKNOWLEDGMENTS

The authors would like to thank Materials and Energy Research Center for supporting this research

REFERENCES

1. Frederic, H., Reisman, A., Berry, M. and Berkenblit, M., "Chemistry of the group VB pentoxides. VI. The polymorphism of Nb_2O_5", ***Journal of the American Chemical Society,*** Vol. 79, No. 9, (1957), 2039-2043.
2. Zhao, W., Zhao, W., Zhu, G., Lin, T., Xu, F. and Huang, F., "Black Nb_2O_5 Nanorods with Improved Solar Absorption and Enhanced Photocatalytic Activity", ***Dalton Transactions,*** Vol. 45, (2016), 3888-3894.
3. Machida, N., Tatsumisago, M. and Minami, T., "Electrochromic Properties of Sputtered Amorphous Films in the Systems WO_3-Nb_2O_5 and Li_2O-WO_3-Nb_2O_5", ***Journal of the Electrochemical Society,*** Vol. 133, No. 9, (1986), 1963-1966.
4. Stranick, M.A., Houalla, m. and Hercules, D.M., "Spectroscopic characterization of $TiO_2Al_2O_3$ and $CoAl_2O_3$ TiO_2 catalysts", ***Journal of Catalysis,*** Vol. 106, No. 2, (1987), 362-368.
5. Abdul Rani, R., "Anodized Nb_2O_5: application for gas sensors, lithium-ion batteries and dye-sensitized solar cells", (2014).
6. Chadwick, A.V., Zhou, W. and Thomas, J.M., "A New Oxygen Sensor Based on the Thermoelectric Power of Solid Solutions of Nb_2O_5 and Bi_2O_3", ***Angewandte Chemie International Edition in English,*** Vol. 28, No. 1, (1989), 75-76.
7. Rosenfeld, D., Schmid, P.E., Szeles, S., Levy, F., Demarne, V. and Grisel, A., "Electrical transport properties of thin-film metal-oxide-metal Nb_2O_5 oxygen sensors", ***Sensors and Actuators B: Chemical,*** Vol. 37, No. 1, (1996), 83-89.
8. Gomes, M.A.B., Bulhões, L.O.S., De Castro, S.C. and Damião, A.J., "The Electrochromic Process at Nb_2O_5 Electrodes Prepared by Thermal Oxidation of Niobium", ***Journal of the Electrochemical Society,*** Vol. 137, No. 10, (1990), 3067-3070.
9. Aegerter, M.A., Schmitt, M. and Guo, Y., "Sol-gel niobium pentoxide coatings: Applications to photovoltaic energy conversion and electrochromism", ***International Journal of Photoenergy,*** Vol. 4, No. 1, (2002), 1-10.
10. Ghosh, R., Brennaman, M.K., Uher, T., Ok, M.-R., Samulski, E.T., McNeil, L.E., Meyer, T.J. and Lopez, R., "Nanoforest Nb_2O_5 photoanodes for dye-sensitized solar cells by pulsed laser deposition", ***ACS Applied Materials & Interfaces,*** Vol. 3, No. 10, (2011), 3929-3935.
11. Aegerter, M.A., "Sol–gel niobium pentoxide: a promising material for electrochromic coatings, batteries, nanocrystalline solar cells and catalysis", ***Solar Energy Materials and Solar Cells,*** Vol. 68, No. 3, (2001), 401-422.
12. Hota, M.K., Bera, M.K., Verma, S. and Maiti, C.K., "Studies on switching mechanisms in Pd-nanodot embedded Nb_2O_5 memristors using scanning tunneling microscopy", ***Thin Solid Films,*** Vol. 520, No. 21, (2012), 6648-6652.
13. Viet, A.L., Reddy, M.V., Jose, R., Chowdari, B.V.R. and Ramakrishna, S., "Nanostructured Nb_2O_5 polymorphs by electrospinning for rechargeable lithium batteries", ***The Journal of Physical Chemistry,*** Vol. 114, No. 1, (2009), 664-671.
14. Rani, R.A., Zoolfakar, A.S., O'Mullane, A.P., Austin, M.A. and Kalantar-Zadeh, K., "Thin films and nanostructures of niobium pentoxide: fundamental properties, synthesis methods and applications" ***Journal of Materials Chemistry,*** Vol. 2, No. 38, (2014), 15683-15703.
15. Yun, Z., Eley, C., Hu, J., Foord, J.S., Ye, L., He, H. and Tsang, S.C.T., "Shape-Dependent Acidity and Photocatalytic Activity of Nb_2O_5 Nanocrystals with an Active TT (001) Surface", ***Angewandte Chemie International Edition,*** Vol. 51, No. 16, (2012), 3846-3849.
16. Luo, H., Wei, M. and Wei, K., "Synthesis of Nb_2O_5 nanosheets and its electrochemical measurements", ***Materials Chemistry and Physics,*** Vol. 120, No. 1, (2010), 6-9.
17. Li, G., Wang, X. and Ma, X., "Nb_2O_5-carbon core-shell nanocomposite as anode material for lithium ion battery", ***Journal of Energy Chemistry,*** Vol. 22, No. 3, (2013), 357-362.
18. Olding, T., Sayer, M. and Barrow, D., "Ceramic sol–gel composite coatings for electrical insulation", ***Thin Solid Films,*** Vol. 398, (2001), 581-586.
19. Zhou, Y., Qiu, Z., Lü, M., Zhang, A. and Ma, Q., "Preparation and characterization of porous Nb_2O_5 nanoparticles", ***Materials Research Bulletin,*** Vol. 43, No. 6, (2008), 1363-1368.
20. Pinna, N., and Niederberger, M., "Surfactant-Free Nonaqueous Synthesis of Metal Oxide nanostructures", ***Agnewandte Chemie International Edition,*** Vol. 47, No. 29, (2008), 5292-5304.
21. Kianpour, G., Salavati-Niasari, M. and Emadi, H., "Sonochemical synthesis and characterization of NiMoO 4 nanorods", ***Ultrasonics sonochemistry,*** Vol. 20, No. 1, (2013), 418-424.
22. Kim, H.Y., Han, J.H., Kweon, D.K., Park, J.D. and Lim, S.T., "Effect of ultrasonic treatments on nanoparticle preparation of acid-hydrolyzed waxy maize starch", ***Carbohydrate polymers,*** Vol. 93, No. 2, (2013), 582-588.
23. Athar, T., Hashmi, A., Al-Hajry, A., Ansari, Z.A. and Ansari, S.G., "One-Pot Synthesis and Characterization of Nb_2O_5 Nanopowder", ***Journal of nanoscience and nanotechnology,*** Vol. 12, No. 10, (2012), 7922-7926.
24. Madadi, Z. and T.Bagheri Lotfabad. " Aqueous Extract of Acanthophyllum laxiusculum Roots as a Renewable Resource for Green synthesis of nano-sized titanium dioxide using Sol-gel Method", ***Advanced Ceramics Progress,*** Vol. 2, No. 1, (2016), 26-31.
25. Saddeek, Y.B., Shaaban, E.R., Abdel-Rahim, F.M. and Mahmoud, K.H., "Thermal analysis and infrared study of Nb_2O_5–TeO_2 glasses", ***Philosophical Magazine,*** Vol. 88, No. 25, (2008), 3059-3073.
26. Maurer, S.M., and Ko, E.I., "Structural and acidic characterization of niobia aerogels", ***Journal of Catalysis,*** Vol. 135, No. 1, (1992), 125-134.