ORIGINAL RESEARCH PAPER

Hydrothermal Synthesis of Nickel Hydroxide Nanostructures and Flame Retardant Poly Vinyl Alcohol and Cellulose Acetate Nanocomposites

S.R. Yousefi¹, D. Ghanbari², M. Salavati-Niasari^{1*}

¹ Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, I. R.

Iran

² Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran.

ARTICLE INFO.

Received 28/10/2015 Accepted 24/12/2015 Published online 01/01/2016

KEYWORDS

Flame Retardancy Nanocomposite Nanoparticles PVA

ABSTRACT

Nickel hydroxide nanostructures were synthesized by a hydrothermal reaction. The effect of different precursors and surfactants on the morphology of nickel hydroxide nanostructures was investigated. Nanostructures were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy. The influence of Ni(OH)₂ nanostructures on the thermal stability and flame retardancy of the poly vinyl alcohol and cellulose acetate matrix was studied using UL-94 analysis. The enhancement of thermal stability and flame retardancy of nanocomposites is due to the endothermic decomposition of Ni(OH), and release of water which dilutes combustible gases.

INTRODUCTION

Among transition metal oxides and hydroxides, NiO and Ni(OH), have been studied due to their natural abundance and lowcost which render them as promising candidates to replace the very expensive RuO₂ [1-3]. There is a challenge to fabricate threedimensional nanoporous Ni(OH), directly on metal substrates to produce components for additive-free super capacitors. The fabricated nanoporous Ni(OH), thin-film delivers promising ECs performance in both three electrode testing and asymmetric two electrode super capacitor devices [4-7]. Nickel hydroxide is a material with important applications in energy conversion and energy storage devices. It is the active component of the positive electrode in alkaline rechargeable batteries (With Cd, Zn, and Fe) and is also used as a precursor for the preparation of porous and composite nickel electrodes for solid-oxide fuel cells and molten carbonate fuel cells. The performances of the devices are strongly dependent on size,

*Corresponding author Email address: salavati@kashanu.ac.ir

Tel.: +98361 591 2383

morphology, and crystal structure of Ni(OH),[6-8]. Two polymorphic forms of nickel hydroxide, α and β , exist. The hexagonal β phase has a brucite like hexagonal structure with a = 3.12 Å and c = 4.60 Å consisting of the ordered stacking of Ni(OH), layers with a Ni-Ni distance of 4.60 Å. Whereas α -Ni(OH), is iso structural with hydrotalcite and consists of hydroxyl-deficient Ni(OH), host layers and interlayer species, such as anions and water molecules. Inorganic structures with well defined size and morphology, often originated by self-assembly of nano building blocks, can be obtained in the presence of suitable organic molecules. However, the use of organic additives to direct the morphogenesis of Ni(OH), has received little attention [9-12]. Nickel hydroxide represents a technologically important material with distinctive structural and physical properties and wide applications in catalysts, batteries, and electrochromic devices. The large inter layer spacing of α -Ni(OH), enables high mobility of the inter layer ions and little structural rearrangement during the electrochemical cycles. Taking into account that α -Ni(OH), exhibits a superior theoretical specific capacity of 433 mAh/g, compared to 289 mAh/g of α -Ni(OH)₂. It is not surprising that the research and development of α -Ni(OH), materials for high performance electrochemical devices are of great interest. Template-free methods, such as hydrothermal or solvothermal synthesis where the nucleation and growth of materials can be performed at relatively high temperatures and high pressures, have also been developed to prepare 1D Ni(OH), nano-materials. The products of the hydrothermal or solvothermal synthesis are dependent on the reaction medium, temperature, pH value, reaction time. It is important to point out that the hydrothermal or solvothermal approaches are very promising for a large-scale production of Ni(OH), nanomaterials at relatively simple and mild conditions, which represents an important factor for their practical applications .Obviously, an improved understanding of the physical properties of 1D Paraotwayite-type α -Ni(OH), nanomaterials is interesting and important for their applications in photo electrochemical devices. It is also worth pointing out that, in addition to the possible size effect that is typical for nanomaterials with small featured sizes and large surface areas. There are several studies indicating that high specific capacitance can be achieved using Ni(OH), electrodes. α -Ni(OH), has been extensively studied. Despite being a meta stable phase, α -Ni(OH), presents itself as a promising material for secondary battery and electrochemical capacitor applications [10-15].

One the main commonly used mineral flame retardants are metal hydroxide. As the temperature rises some metal hydroxide shows an endothermic decomposes and absorbs energy. Moreover, they release nonflammable water which dilutes combustible gases. Residual nickel oxide also provides heat insulation by reflecting heat when it accumulates on the surface. Nickel hydroxide can be used as halogenfree flame-retardant for polymers. Ni(OH), can act as a reinforcing agent and flame retardant suppressant additive with low or zero emissions of toxic or hazardous substances. The main advantages of polymer materials over many metal compounds are high toughness, corrosion resistance, low density and thermal insulation. Improvement of the flame retardancy and thermal stability of polymers is a major challenge for extending their use for most applications. The use of halogen-free flame retardants is widespread due to the increasing concern about the health and environmental risks. One of the main disadvantages of metal hydroxide is that for effective flame retardancy tests high loading levels are required to achieve the appropriate fire retardancy. Increasing the loading of inorganic metal hydroxides will result in a significant decrease in physical properties. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion [16-20]. Poly vinyl alcohol has been widely used in a wide range of applications due to its particular advantages. It is a water soluble biodegradable polymer with applications in paper coating, packaging films and adhesives. The scientific literature contains very diverse strategies for improving fire resistance of PVA [21-25]. In this work a facile hydrothermal method for preparation of nickel hydroxide is used. Nickel hydroxide was then added to the poly vinyl alcohol and cellulose acetate in order to increase the thermal stability and flame retardant properties.

MATERIALS AND METHODS

Ni(NO3)2 6H2O, NiSO4, NiBr2, ammonia, sodium dodecyl sulfonate (SDS), cetyl tri-methyl ammonium bromide (CTAB), poly vinyl alcohol (PVA MW:20000-30000) and poly ethylene glycol (MW: 6000) were purchased from Merck. All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered CuK_a radiation. A multiwave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation. In UL-94 a bar shape specimen of plastic $130 \times 13 \times 1.6$ mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each).

Synthesis of Ni(OH), nanoparticles

 $1 \text{g Ni}(\text{NO}_3)_2$ and 0.25 g of surfactant(CTAB, SDBS, PEG6000) were dissolved in water. 2 mL of ammonia (12M) was slowly added into the solution. The solution

was put in autoclave at 180° C for 5h. The green precipitate was centrifuged and washed with distilled water to removing the surfactant, and later dried at 70°C for 24h in a vacuum dryer. These stages carried out for other surfactant materials as synergetic additives including PEG, CTAB and SDBS.

Synthesis of polymer-Ni(OH), nanocomposite

4 g of PVA was dissolved in 10 mL of water and then Ni(OH)₂ (1 g) was dispersed in 5 mL of water with ultrasonic waves (60W, 30 min). For preparation of cellulose acetate nanocomposite at the same condition water solvent was replaced by acetone. The dispersion of Ni(OH)₂ was then added slowly to the polymer solution. The solution was mixed under stirring for 6 h. For preparation of samples for UL-94 test after stirring, the product was casted on a template with dimension 130×13 mm and after about 48 h of solvent evaporation; the nanocomposite was placed in the vacuum oven for another 6 h for removal of residual traces of water. The final sheets for the test are $130 \times 13 \times 1.6$ mm in dimension (stay at oven 90 °C for 48 h).

RESULTS AND DISCUSSION

XRD pattern of $Ni(OH)_2$ nanoparticles is shown in Fig. 1. It is indexed as a pure hexagonal structure with suitable agreement to literature value (reference peaks are also depicted in the XRD pattern, JCPDS card no. 73-1520, Space group: P-3m1).

The crystallite size measurements were carried out using the Scherrer equation (Eq. 1),

$Dc=0.9\lambda/\beta cos\theta$

(1)

 β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK_a radiation, 0.154 nm). The estimated crystallite size is about 6 nm.

SEM images of $Ni(OH)_2$ synthesized by different surfactants cationic, anionic and neutral are shown in Fig. 2-6 respectively. By using cetyl tri-methyl ammonium bromide (CTAB: as a cationic surfactant) and nickel sulfate, rod-like agglomerated and bulk product were obtained (Fig. 2).

It seems CTAB remained on the surface of particles and growth stage overcomes to nucleation stage and bulk products were obtained.

Fig. 3 illustrates product which was synthesized by poly ethylene glycol 6000 and nickel nitrate. Interestingly PEG as a neutral capping agent lead to



Fig. 1. XRD pattern of Ni(OH), nanoparticles



Fig. 2. SEM image of $Ni(OH)_2$ nanoparticles obtained by $NiSO_4$ -CTAB



Fig. 3. SEM images of nanoparticles synthesized by $NiNO_3$ -PEG

mono-disperse nanoparticles with average diameter less than 15 nm.

Fig. 4 shows nickel hydroxide prepared by sodium dodecyl benzene sulfonate and nickel sulfate. With SDBS as an anionic surfactant nanoparticles with average diameter around 50 nm were synthesized.



Fig. 4. SEM images achieved by NiSO₄-SDBS

Fig. 5 shows products which was obtained by poly ethylene glycol (MW:6000) and NiBr₂. By using PEG 6000 and nickel bromide also nanoparticles with average diameter around 50 nm were achieved. Nanoparticles present on the surface of nano-plate and it seems they formed nano-plate via preferential growth.



Fig. 5. SEM images obtained by NiBr₂-PEG

Fig. 6 shows products which were prepared by triplex and $NiSO_4$. In this condition nano-plate with average thickness less than 100 nm were synthesized that confirmed preferential growth of nanostructure at hydrothermal procedure.



Fig. 6. SEM images synthesized by $NiSO_4$ -Triplex



Fig. 7. SEM images of PVA-Ni(OH)₂ nanocomposite

SEM images of PVA-Ni(OH)₂ nanocomposite are shown in Fig. 7 that approve presence of nanoparticles in the poly vinyl alcohol matrix.

FT-IR spectrum of the Ni(OH)₂ is shown in Fig. 8; Sharp peak at 3645 cm⁻¹ is attributed to the O–H bond stretching vibration in the crystal structure of nickel hydroxide. Broad peak at 3450 to 3550 cm⁻¹ is attributed to the O–H bonds adsorbed on the surface of the nickel hydroxide. Absorption at around 613 cm⁻¹ is assigned to the Ni–O stretching vibration in Ni(OH), [21-25].

Energy dispersive X-ray spectroscopy of nickel hydroxide nanoparticles is depicted in Fig. 9. EDS graph confirm presence the elements of Ni and O. No other peak related to impurities was observed.



Fig. 9. EDS analysis of Ni(OH), nanoparticles

In the polymer matrices (PVA,CA)-Ni(OH)₂, nanoparticles have been distributed in PVA matrix and

because of hydrogen bonds between them a suitable barrier layer of nanoparticles was formed.

The effect of nanostructure on flame retardant properties has been considered using UL-94 test. In UL-94 a bar shape specimen of plastic $130 \times 13 \times 1.6$ mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles allowed as long as they are not inflamed. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when slow burning on a horizontal specimen; burning rate < 76 mm/min. A V-1 classification is received by a sample with maximum combustion time < 30 s, drips of particles allowed as long as they are not inflamed. The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed [20-25]. UL-94 tests for PVA and PVA-Ni(OH), nanocomposites are HB and V-0 respectively. Also UL-94 tests for CA and CA-Ni(OH), nanocomposites are HB and V-2 respectively. The results show that the Ni(OH), nanostructure can enhance the flame retardant property of the PVA matrix.

The enhancement of flame retardancy of nanocomposites is due to decomposition of $Ni(OH)_2$ that absorbs energy and simultaneously release of water which dilutes combustible gases. Exfoliated $Ni(OH)_2$ have also a barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. Adsorption of polymer chains onto the surface of $Ni(OH)_2$ nanoparticles results in a restriction of the segmental mobility and suppress chain-transfer reactions [22-25].

CONCLUSION

Various morphologies of Ni(OH)₂ nanostructures were prepared by a hydrothermal method. The effect of various nickel precursor and surfactants such as SDBS, CTAB, triplex and PEG on the morphology of nickel hydroxide nanostructures was investigated. Ni(OH)₂ nanoparticles were then added to cellulose acetate and poly vinyl alcohol matrixes. The enhancement of flame retardancy of the nanocomposites is due to endothermic decomposition of Ni(OH)₂ and release of water which dilutes combustible gases. Ni(OH)₂ have also barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

- A.S. Aricò, P. Bruce, B. Scrosati, J.M. Tarascon, W. Schalkwijk, NatMater. 4 (2005) 366–377.
- [2] C. Yuan, X. Zhang, L. Su, B. Gao, L. Shen, J Mater Chem. 19 (2009) 5772–5777.
- [3] H. Wang, H.S. Casalongue, Y. Liang, H. Dai, J Am Chem Soc. 132 (2010) 7472–7477.
- [4] Y. Yang , L. Li, G. Ruan, H. Fei, C. Xiang, X. Fan, J.M. Tour , ACS Nano . 2014
- [5] M. Winter, R. Brodd, J ChemReV. 104 (2004) 4245
- [6] P. Holtappels, U. Vogt, T. Graule, AdVEng Mater. 7 (2005) 292.
- [7] X.L. Li, J.F. Liu, Y.D. Li, Mater ChemPhys. 80 (2003) 222.
- [8] M. Meyer, A. Be'e, D. Talbot, V. Cabuil, J.M. Boyer, B. Re'petti, R. Garrigos, J Colloid Interface Sci. 277 (2004) 309.
- [9] Z.H. Liang, Y.J. Zhu, X.L. Hu, JPhysChem B . 108 (2004) 3488.
- [10] D. Chen, L. Gao, ChemPhysLett. 405 (2005) 159.
- [11] X. Wang, L. Li, Y. Zhang, S. Wang, Z. Zhang, L. Fei, Y. Qian, Cryst Growth Des. 6 (2006) 2163.

- [12] D. Wang, R. Xu, X. Wang, Y. Li, Nanotechnology.17 (2006) 979.
- [13] H.B. Liu, L. Xiang, Y. Jin, Cryst Growth Des.6 (2006) 283.
- [14] R. Yang, L. Gao, J Colloid Interface Sci. 297 (2006) 134.
- [15] J. Zhu, Z. Gui, Y. Ding, Z. Wang, Y. Hu, M. Zou, JPhys Chem. C 111 (2007) 5622.
- [16] D. Ghanbari, M. Salavati-Niasari, M. Sabet, J Clust Sci. 23, (2012) 1081-1095.
- [17] F. Gholamian, M. Salavati-Niasari, D. Ghanbari, M. Sabet, J Clust Sci 24 (2013) 73–84.
- [18] AB. Morgan, CA. Wilkie, Flame retardant polymer nanocomposite. John Wiley & Sons; New Jersey 2007.
- [19] H.R. Momenian, S. Gholamrezaei, M. Salavati-Niasari, B. Pedram, F. Mozaffar, D. Ghanbari, J Clust Sci 24 (2013) 1031-1042
- [20] D. Ghanbari, M. Salavati-Niasari, High Temp Mater Proc. 31(2012) 133-138.
- [21] D. Ghanbari, M. Salavati-Niasari High Temp Mater Proc. 31(2012) 769-773.
- [22] M. Yousefi, M. Salavati-Niasari, F. Gholamian, D. Ghanbari, A. Aminifazl, Inorg Chem Acta. 371(2011) 1-5.
- [23] D. Ghanbari, M. Salavati-Niasari, S. Karimzadeh, S. Gholamrezaei J Nano Struc. 4, (2014) 227-232
- [24] P. Jamshidi, D. Ghanbari, M. Salavati-Niasari, J Ind Eng Chem, 20 (2014) 3507-3512.
- [25] D. Ghanbari, M. Salavati-Niasari M. Sabet. Composites: Part B 45 (2013) 550–555.

AUTHOR (S) BIOSKETCHES

Yousefi, S.R., M.Sc, Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, I. R. Iran. Email: S.R.Yosefi93@gmail.com

Ghanbari, D., Ph.D., Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran. Email: ghanbarichemist@gmail.com

Salavati-Niasari, M., Ph.D., Professor, Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, I. R. Iran. Email: Salavati@kashanu.ac.ir

How to cite this article:

Yousefi S.R, Ghanbari D, Salavati-Niasari M. Hydrothermal Synthesis of Nickel Hydroxide Nanostructures and Flame Retardant Poly Vinyl Alcohol and Cellulose Acetate Nanocomposites. J. Nanostruct. 2016; 6(1):77-82.

DOI: 10.7508/jns.2016.01.00* URL: http://jns.kashanu.ac.ir/article 13649 2332.html