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Structure Investigations of $NiO/Al_2O_3/B_2O_3/SiO_2$ Composite Based on PVA Using Sol-Gel Processing and the Electrospinning Technique

FATIH SEVIM* and ESMA SEVIMLI

Department of Chemical Engineering, Engineering Faculty, Atatürk University, 25240 Erzurum, Turkey

*Corresponding author: Fax: +90 4422314544; Tel: +90 4422314555; E-mail: fsevim@atauni.edu.tr

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Nickel oxides are well-studied materials due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as battery materials, electrochromic layers, catalysis materials, *etc*. Among them electrochromic device using as NiO anodic material are recognized for their durability compared with other anodic EC materials, colouration efficiency and low material cost. Therefore it is well suitable in conjunction with electro chromic tungsten oxide as colouring electrode. Important information regarding dynamics, structure and exchange rates between different spin groups that might exist in a system can be extracted from their NMR signals. To accomplish this, one often needs to decompose different NMR signal components within the final spectrum.

Keywords: Nanofibers, $NiO/Al_2O_3/B_2O_3/SiO_2$ composite, Industrial minerals, NMR.

INTRODUCTION

Nickel oxides are well-studied materials due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as battery materials, electrochromic layers, catalysis materials, *etc*. Among them electrochromic device using as NiO anodic material are recognized for their durability compared with other anodic EC materials, colouration efficiency and low material cost. Therefore it is well suitable in conjunction with electro chromic tungsten oxide as colouring electrode[1].

Important information regarding dynamics, structure and exchange rates between different spin groups that might exist in a system can be extracted from their NMR signals. To accomplish this, one often needs to decompose different NMR signal components within the final spectrum[2].

The introduction of further elements (such as boron or aluminum) into the preceramic polymers can increase the high temperature stability, creep and oxidation resistance, which featured directly correlated to the nanostructure of the ceramics[3].

This work reports an easily applicable and inexpensive approach to the fabrication of $NiO/Al_2O_3/B_2O_3/SiO_2$ composite nanofibers in PVA by using sol-gel processing and the electrospinning technique. ^{1}H NMR (nuclear magnetic rezonans) is used to investigate a porous material consisting of nano-sized NiO composite fibers by sol-gel processing and electrospinning technique. In addition, the fibers were characterized by FT-IR (Fourier transform-infrared spectroscopy), SEM (scanning electron microscopy) and BET surface area analyses. The SEM results show that the morphology of the fibers was affected perfectly by the temperature of calcination. The obtained fibers were composed of many different composite ceramics.

EXPERIMENTAL

In the experiments $NiO/Al_2O_3/B_2O_3/SiO_2$ composite nanofibers were prepared using the sol gel technique and electrospinning method. Nanofiber production was carried out in three stages. The first step is the preparation of electrospinning solution using sol gel method, the second step the creation nanofibers by the method of electrospinning and finally nanofiber production by thermal treatment.

Raw materials used to prepare the electrospinning solution: Tetraethyl orthosilicate (TEOS, 98 %), boric acid (99 %), nickel nitrate hexahydrate (97 %), aluminum isopropoxide (97 %), hydrochloric acid, absolute ethanol (99.5 %) and absolute isopropyl alcohol. Distilled water was also used for the hydrolysis reaction.

In experiments, in first stage, three different (A, B and C) solutions were prepared. In second stage, to prepare for electrospinning solution, B and C solutions added to A.

PVA which was in form of powder was stirred for 1 h in distilled water at 80 ºC and then continued to stirring at room temperature for 24 h by the way PVA solution was prepared. Combinations of these solutions are given in Table-1.

TABLE-1
COMPOSITION USED SOLUTIONS IN THE ELECTROSPINNING METHOD

Solution - A	TEOS:EtOH:H_2O:HCl	1:10:2:0.01(Molar)
Solution - B	$Ni(NO_3)_2.6H_2O$:EtOH:HCl	1:10:8 (Molar)
	($Ni(NO_3)_2.6H_2O$:EtOH:HCl):PVA	1:1 (Weight)
	H_3BO_3:EtOH:HCl	1:10:8 (Molar)
	(H_3BO_3:EtOH:HCl):PVA	1:1 (Weight)
Solution - C	$Al(C_3H_7O)_3$:i-PrOH:HCl	0.1:2:0.8(Molar)
	($Al(C_3H_7O)_3$:i-PrOH:HCl):PVA	1:1 (Weight)

The electrospinning solution obtained was filled to syringe and was placed into syringe pump. A positive electrode to the tip of the syringe, a negative electrode to collector is connected and set up the potential difference between the tip of the syringe tip and collector.

When high voltage was applied to the solution of the tip of the syringe, nanofibers were collected on the surface of the collector. To be affected by environmental conditions, nanofiber electrospinning experiment was carried out in a closed cell.

At the final stage, PVA nanofiber structure obtained and the organic structures were removed by heat treatment and then pure nanofibers were obtained.

RESULTS AND DISCUSSION

BET surface area: The BET surface areas of nanofibers before and after calcination were determined as 440 and 626 m^2/g, respectively. The sol-gel reaction of TEOS in the presence of nickel nitrate and organic additives with coordinating abilities is also effective for the high dispersion of Ni metal particles, probably leading to the highest BET values obtained for Si-based material[4]. For the alumina, a larger variation of the area is expected due to its low thermal stability, characteristic of this type of materials. As expected, when the nanofiber was calcined, the BET surface area increased due to removal of the PVA in the nanofiber structure.

NMR analysis results: Composite nanofibers that prepared in this study were also characterized by ^1H NMR analysis. Both pure PVA and alumina supported nickel borosilicate/PVA composites were dissolved in DMSO and analyzed by H NMR. NMR spectra's of these samples are shown in Figs. 1 and 2, respectively. As can be seen from the figure, signals in 3.2-3.4 ppm's , composite structure of Al-O-C, Si-O-C, Ni-O-C and B-C-O indicate the presence of protons. In ^1H NMR spectrum (Fig. 1), the observed signals in 3.5- 4.0 ppm indicate hydroxyl groups of PVA. While some of the hydroxyl groups creates the composite structure by a sol gel method, other hydroxyl groups were not united with Al, B, Si and Ni atoms. This intensity of peak in PVA the spectrum is more than the spectrum of nanofiber composite.

Decreasing of the hydroxyl groups in the structure of PVA and a new peak is present in 3.2-3.4 ppm in the composite nano-fiber spectrum confirmed that Al, Ni, B, Si and PVA complex reaction has been occurred. The peaks observed in 1.75-1.85 and 1.4-1.5 ppm solutions were shown protons connected with carbon bond in the composite structure.

In addition, the signals 1.0-1.5 and 3.8-4.2 ppm solutions, the composite during the formation indicate some by-products arising from the methyl and methylene groups. For example

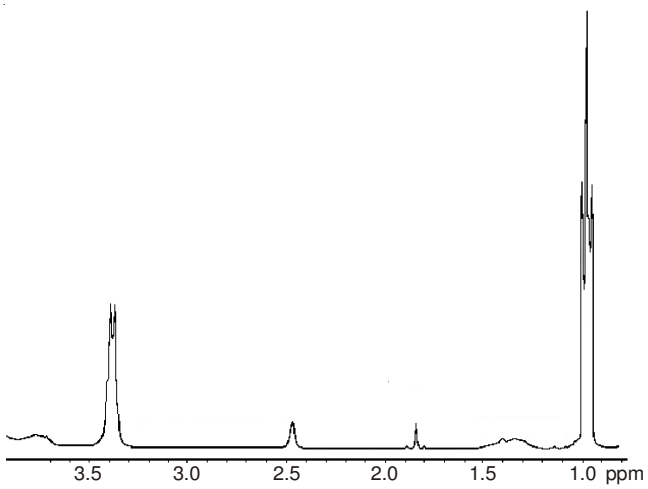


Fig. 1. ^2H NMR spectra of PVA solutions

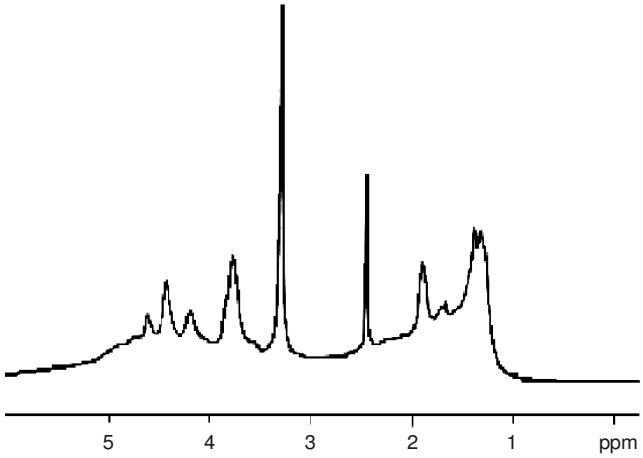


Fig. 2. ^2H NMR spectra of $NiO/Al_2O_3/B_2O_3/SiO_2$ composite with PVA

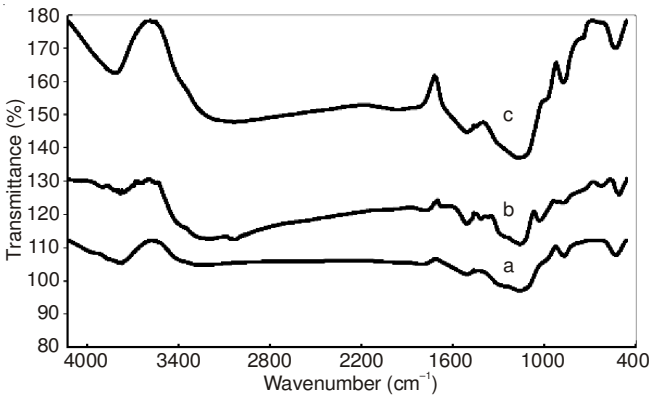
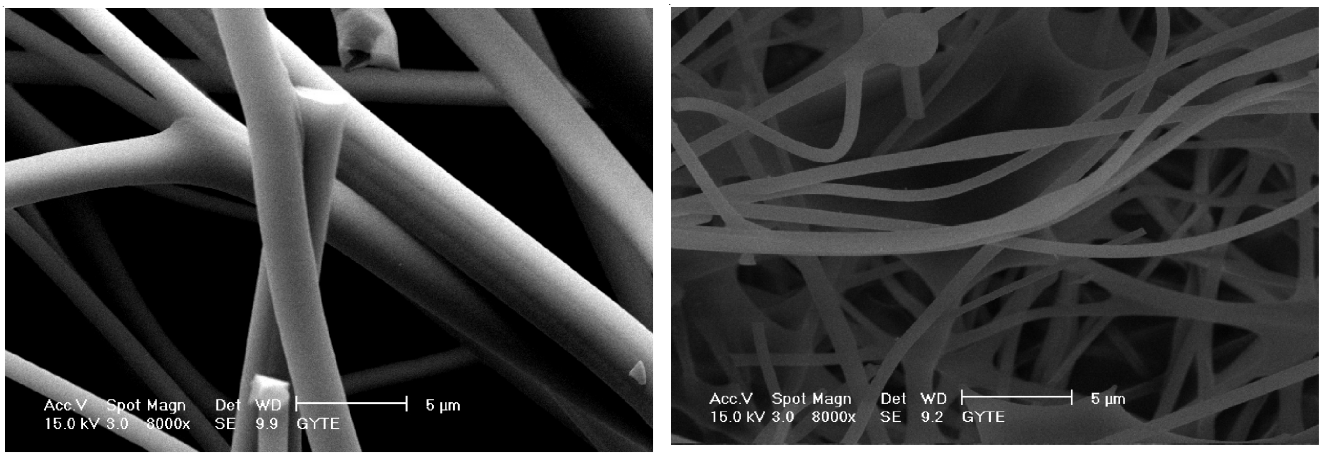


Fig. 3. FT-IR spectra for (a) calcined at 1000 ºC; (b) calcined at 750 ºC; (c) before applied the thermal treatment PVA/nickel nitrate/tetraethyl orthosilicate/aluminum izopropoxide/boric acid composite fibers

ethanol occurs with reaction between TEOS and PVA. The peak in the spectrum at around 2.5 ppm, is stemmed from the DMSO used as the solvent[5].

FT-IR Spectra: Fig. 3 displays the FT-IR spectra of the nanofibers of PVA/nickel nitrate/silicate/aluminum isopropoxide/boric acid composite and after the fiber composites calcined at different temperatures between 750 and 1000 ºC. Fig. 3 shows the FT-IR spectra for (a) before applying the



(a) (b)

Fig. 4. (a) SEM images of the $NiO/Al_2O_3/B_2O_3/SiO_2$ nanofibers at 400 ºC (b) SEM images of the $NiO/Al_2O_3/B_2O_3/SiO_2$ nanofibers at 750 ºC

thermal treatment PVA/nickel nitrate/tetraethyl orthosilicate/aluminum izopropoxide/boric acid composite fibers; (b) calcined at 750 ºC; (c) calcined at 1000 ºC. The peaks are shown especially as Al-O-Si and Si-O-Si at around 1050 and 1091 cm^{-1} respectively[6]. When the calcinations were at 750 and 1000 ºC (Fig. 3), all the peaks corresponding to the organic groups of PVA and other components disappeared and a new peak at 467 cm^{-1} is assigned to the Ni-O bond[7]. Formation of the anticipated B-O-Si linkage is confirmed by Fourier Transform infrared (FT-IR). The FT-IR spectrum of nanofibers indicates the presence of the B-O bonds at around 1430 cm^{-1}, especially this distinct band assigns the asymmetric stretching of BO_3 unit[8]. Besides, in all of the FT-IR spectra, the peaks at around 800 cm^{-1} are assigned to Al-O-Si bending[9]. Furthermore, the peak at 1331 cm^{-1} which is assigned to Si-OEt or ethanol normally disappeared[10].

Scanning electron microscopy (SEM): SEM photographs of PVA/nickel nitrate/tetraethyl orthosilicate/aluminium isopropoxide composite bers 10 kV, capillary tip to metal collector distance of 10 cm, 10 % PVA concentration, 3 mL/h flow rate of solution are shown in Fig. 4. As shown in Fig. 4a, the fibers obtained after calcinations at 400 ºC, the nickel nitrate/tetraethyl orthosilicate/aluminum isopropoxide composite nanobers demonstrated a uniform morphology. After calcination at 750 ºC (Fig. 4b), the diameters of the fibers became smaller. The diameter of nanofibers before and after calcination was determined as on average 886 and 254 nm, respectively. It was thought to be due to the complete removal of organic molecules and the development of $NiO/Al_2O_3/B_2O_3/SiO_2$ composite fibers smaller than 500 nm[11,12].

Conclusion

Nanofibers of PVA/nickel nitrate/tetraethyl orthosilicate/aluminum isopropoxide/boric acid composite have been successfully prepared by using sol-gel processing and the electrospinning technique and then, by calcination at a certain temperature (750 ºC) of the obtained nanofibers with this way, $NiO/Al_2O_3/B_2O_3/SiO_2$ nanofiber was obtained. These nanofibers demonstrated a uniform morphology and also have large BET surface areas (629 m^2/g). This value is very important for uses in place of nanofibers. The obtained composite nanofiber could be suggested for catalysis and ceramic application. This route is simple and effective to produce nanofibers of mixed inorganic oxide composite. Future research will be aimed at the production of finer fibers, of diameters smaller than 50 nm, with more uniformly and densely distributed nanoparticles.

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