STUDENT EDITORIAL

HYDROTHERMAL GROWTH OF NIOBIUM OXIDE MICRORODS IN AMMONIUM FLUORIDE FOR ELECTROCHROMIC APPLICATION

Abstract

Nowadays, high energy consumption and climate-change greenhouse gas emission are found to be a pressing issue in the world. Thus, the study of electrochromic is imperative. Niobium oxide (Nb_2O_5) is an electrochromic material with the ability to change its colour with an applied potential. In this work, the optimum temperature and hydrothermal solution concentration were determined. The Nb_2O_5 microrods were synthesized by a hydrothermal process using niobium (Nb) metal foil as substrate and ammonium fluoride (NH_4F) as precursor. This research found that Nb_2O_5 fabricated at 150 °C for 24 h using 0.3 M NH_4F hydrothermal solution, followed by annealing treatment at 400 °C for 30 minutes had small microrods diameter and no impurity was formed. Results for X-ray diffraction (XRD) indicates that the microrods were orthorhombic Nb_2O_5 and grew toward (001) direction. Cyclic voltammetry analysis proves that the microrods enhanced the electrochromic performance.

Objectives

- To determine the optimum precursor concentration and hydrothermal synthesis temperature for producing niobium oxide microrods.
- To examine the morphological and structural properties of niobium oxide microrods.
- To correlate the morphological and structural properties of niobium oxide microrods with the electrochromic properties.

Methodology

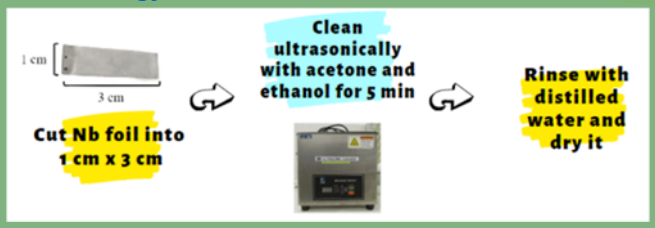

***Figure 1**: Flowchart of Nb Foil Preparation*

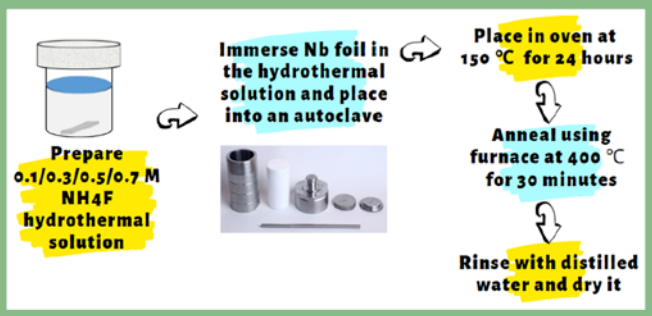

***Figure 2**: Flowchart of Hydrothermal Synthesis Process*

Results and Discussion

Morphological Analysis: Scanning Electron Microscopy (SEM)

As can be seen from Figure 3 (a), no microrods could be observed when the NH_4F hydrothermal solution concentration used was 0.1 M. In fact, the compact oxide layer was made up of cube-like shape microstructures with 0.5–2.5 µm side length. As the NH_4F hydrothermal solution concentration increased to 0.3 M, the rounded shape microrods with a diameter of 0.6–1.6 µm were formed, as shown in Figure 3 (b). According to Figure 3 (c), the sample obtained at 0.5 M NH_4F hydrothermal solution consisted of larger diameter microrods, ranging from 4.8 to 5.7 µm. It can be observed that the diameters became larger (4.7–7.3 µm) when the concentration of NH_4F was increased from 0.5 to 0.7 M. The sample with a smaller microrod diameter (0.3 M sample) would provide more surface area for ion intercalation to occur, resulting in better utilization of charge [1-2].

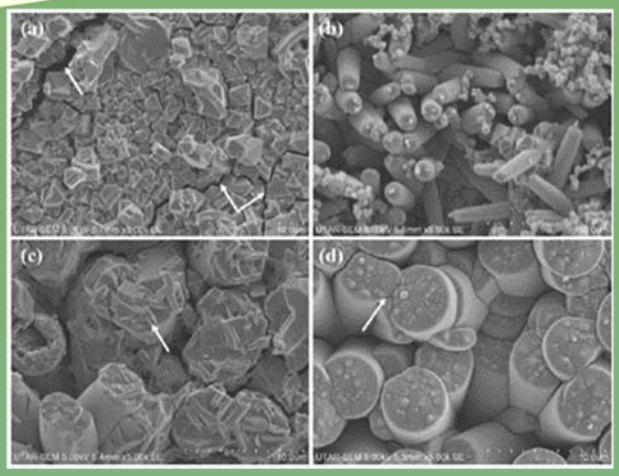

***Figure 3:** SEM Images of Annealed Microstructures Synthesized at Different NH_4F Hydrothermal Solution Concentrations: (a) 0.1, (b) 0.3, (c) 0.5, and (d) 0.7 M*

Structural Analysis: X-Ray Diffraction Analysis (XRD)

The XRD pattern of the bare Nb foil sample shows two distinct peaks at 55.67° (200) and 69.72° (211), which are attributed to the columbium/cubic Nb according to ICDD No. 34-0370, as shown in Figure 4. An extra peak at 29.49° of the XRD pattern of the bare Nb foil is matched with the Nb_2O_5 peak. It could be an existing oxide layer on the bare foil. For the 0.1 M sample, two small oxide peaks were present at 22.70° and 28.85°, indicating that the reaction was incomplete and the surface layer was not crystalized [3-4]. Therefore, it is possible to speculate that the NH_4F hydrothermal solution concentration at 0.1 M was not sufficient to form niobium oxide microrods.

For 0.3 and 0.5 M samples, the oxide peaks became visible and they are attributed to the orthorhombic T-Nb_2O_5 according to ICDD No. 27-1003, as shown in Figure 4, which is consistent with the work done by Wen et al. (2011) [4]. Also, it is readily apparent that the diffraction peak at (001) was much dominant than other peaks of Nb_2O_5, in which the samples are therefore highly *c*-axis oriented [5]. Moreover, the XRD patterns for 0.3 and 0.5 M consist of sharp peaks, which imply that the fabricated samples were crystallized. On the other hand, with the increasing NH_4F concentrations from 0.3 to 0.5 M, it can be noticed that the (001) diffraction peak is significantly higher, which could be due to the higher Nb_2O_5 growth rate at a higher concentration of NH_4F hydrothermal solution [6]. It is important not to neglect that there are weak intensity (180) and (181) peaks appear at XRD patterns of sample fabricated with 0.1, 0.3, and 0.5 M NH_4F hydrothermal solution, which could be due to the disordering of the microstructures, as well as the crystallized oxide layer at the bottom of the microstructures [4]. Besides that, no impurity phases were detected by XRD, indicating that pure Nb_2O_5 microrods were grown on the Nb foil substrate, as shown in 0.3 and 0.5 M samples [7]. In short, the crystallized orthorhombic T-Nb_2O_5 microrods were produced.

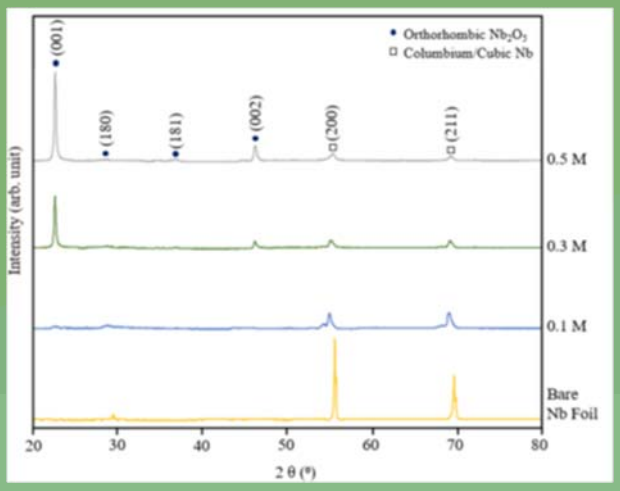

***Figure 4**: XRD Patterns of Bare Nb Foil and Annealed Samples After Synthesized at Different NH_4F Hydrothermal Solution Concentrations of 0.1, 0.3, and 0.5 M*

Electrochromic Analysis: Cyclic Voltammetry (CV)

The 0.3 M sample possessed reversible changes of optical properties when the potential difference was applied to the foil, which demonstrated the characteristics of electrochromic materials, as shown in Figure 5 (a) and Figure 5 (b). This is due to the intercalation of H^+ (from H_2SO_4 electrolyte) into the niobium oxide lattice, accompanied by the reduction of Nb_2O_5, which is expressed in Equation 4.1 [8]. On the other hand, the de-intercalation of H^+ from Nb_2O_5 lattice, accompanied by the oxidation of Nb_2O_5, caused the bleaching of optical property [5]. This led to the reversible redox reaction between Nb^{5+} and Nb^{4+}, with the oxidation state of +5 and +4, respectively [7].

$$Nb_2O_5 + xH+ + xe- \rightleftarrows HxNb_2O_5$$

(Equation 4.1)

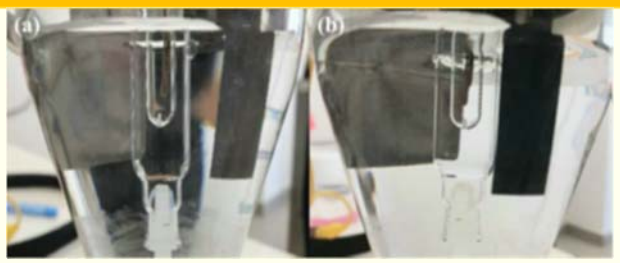

***Figure 5:** Reversible Changes of Optical Properties When Voltage was Applied to 0.3 M Sample: (a) Bleached and (b) Coloured States*

The results for CV analysis are illustrated in Figure 6, in which the dotted line and solid line represent the results for bare Nb foil and annealed 0.3 M sample, respectively. The amount of H^+ from H_2SO_4 electrolyte intercalated into and de-intercalated from Nb_2O_5 represents by the integrated cathodic and anodic current densities, respectively [9]. The 0.3 M microrod layer consists of cathodic and anodic current densities at –21.6333 and +17.9034 mA cm^{-2} during the cycle, which are significantly higher than that of bare Nb foil at –3.0969 and +0.1582 mA cm^{-2}. According to Ng, Abdul Razak and Lockman (2015) [9], the sample with higher cathodic and anodic current densities indicates more intercalation of H^+ ions into the microrod layer. This is because the presence of the microrod layer on the 0.3 M sample created a larger surface area that was contacted with the H_2SO_4 electrolyte, allowing more H^+ ions to be inserted in and extracted out from the layer. Therefore, the higher current density values indicate that the intercalation of H^+ ions within the Nb_2O_5 layer is easier, causing fast switching times, high colouration efficiency, and high optical modulation [7].

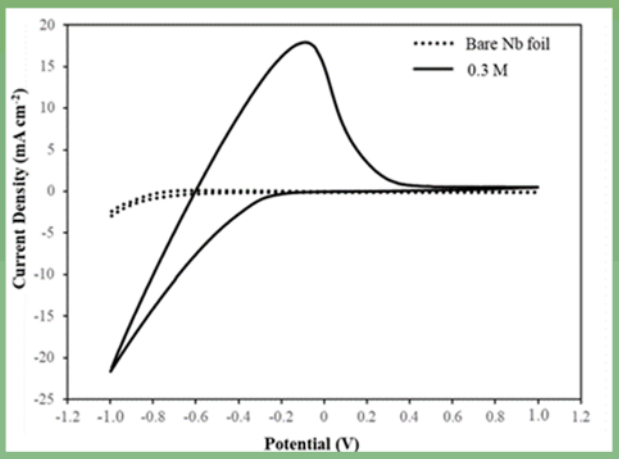

***Figure 6:** Cyclic Voltammograms of Bare Nb Foil and Annealed Sample Fabricated with 0.3 M NH_4F Hydrothermal Solution at 150 °C for 24 h*

Conclusion

⇒ Optimal hydrothermal parameters:
- NH_4F hydrothermal solution
- concentration: 0.3 M
- Temperature: 150 °C
- Time: 24 hours

⇒ Orthorhombic T-Nb_2O_5 layer was produced using the optimal hydrothermal synthesis parameters

⇒ Larger diameter microrods were formed with increasing NH_4F concentration

⇒ The presence of the Nb_2O_5 microrods layer enhanced the electrochromic property

Reported and edited by:

Liew Son Qian, IMM-UTAR Student Chapter (Postgraduate Student)

References

[1] Granqvist, C.G., Avendaño, E. and Azens, A. 2003. Electrochromic coatings and devices: Survey of some recent advances. *Thin Solid Films*, 442(1), pp.201-211.

[2] Zhang, J., Tu, J.P., Cai, G.F., Du, G.H., Wang, X.L. and Liu, P.C. 2013. Enhanced electrochromic performance of highly ordered, macroporous WO3 arrays electrodeposited using polystyrene colloidal crystals as template. *Electrochimica Acta*, 99, pp.1-8.

[3] Wei, M., Qi, Z.-m., Ichihara, M. and Zhou, H. 2008. Synthesis of single-crystal niobium pentoxide nanobelts. *Acta Materialia*, 56(11), pp.2488-2494.

[5] Ong, G.K., Saez Cabezas, C.A., Dominguez, M.N., Skjærvø, S.L., Heo, S. and Milliron, D.J. 2020. Electrochromic niobium oxide nanorods. *Chemistry of Materials*, 32(1), pp.468-475.

[6] He, J., Hu, Y., Wang, Z., Lu, W., Yang, S., Wu, G., Wang, Y., Wang, S., Gu, H. and Wang, J. 2014. Hydrothermal growth and optical properties of Nb_2O_5 nanorod arrays. *Journal of Materials Chemistry C*, 2(38), pp.8185-8190.

[7] Yu, C., Ma, D., Wang, Z., Zhu, L., Guo, H., Zhu, X. and Wang, J. 2021. Solvothermal growth of Nb_2O_5 films on FTO coated glasses and their electrochromic properties. *Ceramics International*, 47(7, Part A), pp.9651-9658.

[8] Reichman, B. and Bard, A.J. 1980. Electrochromism at niobium pentoxide electrodes in aqueous and acetonitrile solutions. *Journal of The Electrochemical Society*, 127(1), pp.241-242.

[9] Ng, C.Y., Abdul Razak, K. and Lockman, Z. 2015. Thermal oxidation of seeds for the hydrothermal growth of WO3 nanorods on ITO glass substrate. *Thin Solid Films*, 595, pp.73-78.

A quarterly magazine PP18691/01/2018(034114)/ISSN2289-9030

MATERIALS MIND

Issue 32

October 2021

www.iomm.org.my

Institute of Materials, Malaysia

HIGHLIGHTS

IMM Student Chapter

Addressing the Issues of Significant Figures for Degree of Similarity and Specific FTIR Fingerprint Regions for Paints: A Pilot Study

Predicting the Whiteness Index of Cotton Fabric with a Least Squares Model

TABLE OF CONTENTS

INSTITUTE OF MATERIALS, MALAYSIA

Suite 515, Level 5, Block A, Kelana Centre Point (Lobby B), No. 3 Jalan SS 7/19, Kelana Jaya, 47301 Petaling Jaya, Selangor.
Tel: +603-76611591

secretariat@iomm.org.my
www.iomm.org.my
+60 18-911 3480
Institute of Materials, Malaysia

OCTOBER 2021 Issue 32