

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 $0.5\text{--}2.5\ \mu\text{m}$ side length. As the NH_4F hydrothermal solution concentration increased to 0.3 M, the rounded shape microrods with a diameter of $0.6\text{--}1.6\ \mu\text{m}$ 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 $5.7\ \mu\text{m}$. It can be observed that the diameters became larger ($4.7\text{--}7.3\ \mu\text{m}$) 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].

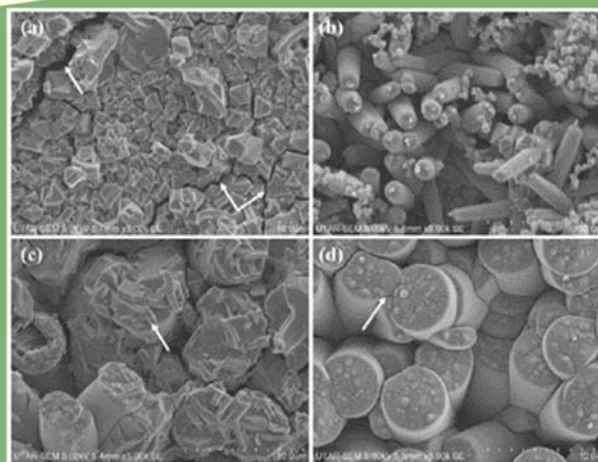


Figure 3: SEM Images of Annealed Microstructures Synthesized at Different NH_4F Hydrothermal Solution Concentrations: (a) 0.1, (b) 0.3, (c) 0.5, and (d) 0.7 M

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 crystallized [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-Nb₂O₅ 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 Nb₂O₅, 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 NH₄F 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 Nb₂O₅ growth rate at a higher concentration of NH₄F 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 NH₄F 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 Nb₂O₅ 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-Nb₂O₅ microrods were produced.

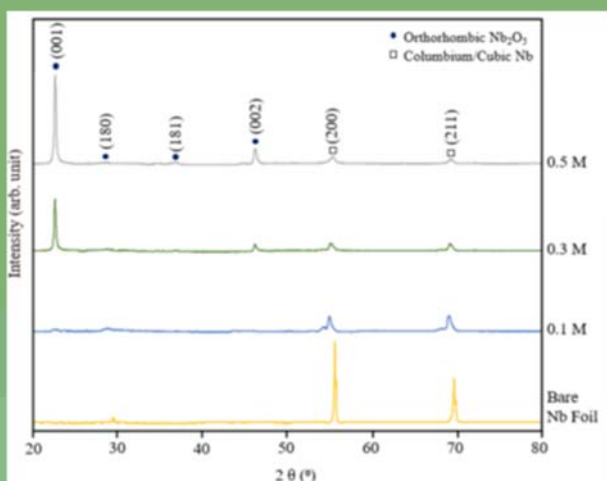


Figure 4: XRD Patterns of Bare Nb Foil and Annealed Samples After Synthesized at Different NH₄F Hydrothermal Solution Concentrations of 0.1, 0.3, and 0.5 M

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 H₂SO₄ electrolyte) into the niobium oxide lattice, accompanied by the reduction of Nb₂O₅, which is expressed in Equation 4.1 [8]. On the other hand, the de-intercalation of H⁺ from Nb₂O₅ lattice, accompanied by the oxidation of Nb₂O₅, caused the bleaching of optical property [5]. This led to the reversible redox reaction between Nb⁵⁺ and Nb⁴⁺, with the oxidation state of +5 and +4, respectively [7].

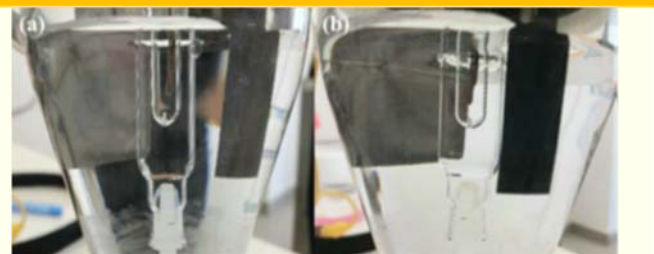
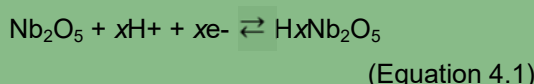


Figure 5: Reversible Changes of Optical Properties When Voltage was Applied to 0.3 M Sample: (a) Bleached and (b) Coloured States

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 H₂SO₄ electrolyte intercalated into and de-intercalated from Nb₂O₅ 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 H₂SO₄ 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 Nb₂O₅ layer is easier, causing fast switching times, high colouration efficiency, and high optical modulation [7].

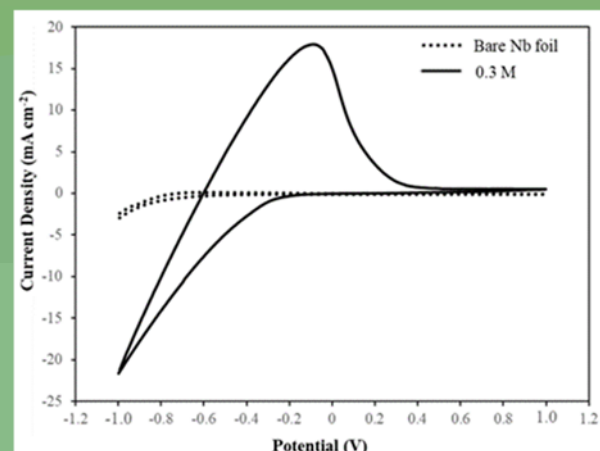


Figure 6: Cyclic Voltammograms of Bare Nb Foil and Annealed Sample Fabricated with 0.3 M NH₄F Hydrothermal Solution at 150 °C for 24 h

Conclusion

- ⇒ Optimal hydrothermal parameters:
 - ◆ NH₄F hydrothermal solution
 - ◆ concentration: 0.3 M
 - ◆ Temperature: 150 °C
 - ◆ Time: 24 hours
- ⇒ Orthorhombic T-Nb₂O₅ layer was produced using the optimal hydrothermal synthesis parameters
- ⇒ Larger diameter microrods were formed with increasing NH₄F concentration
- ⇒ The presence of the Nb₂O₅ microrods layer enhanced the electrochromic property

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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



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