

# Electrochromic properties of one-dimensional tungsten oxide nanobundles

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Received 21 November 2006; accepted 15 December 2006

Available online 19 September 2007

## Abstract

In this study, one-dimensional (1D) tungsten oxide nanobundles (TNB) were synthesized via a simple solvothermal method. The phase of 1D tungsten oxide was  $W_{18}O_{49}$ , and the diameter and length of the building units (nanowires) were about 7 and 800 nm, respectively. TNB films were fabricated by the Langmuir–Blodgett (LB) method. The locally arranged domains of the long nanobundles form the LB films, but it is difficult for them to align perfectly owing to the inter-nanobundle interaction and dispersion problems. The electrochromic (EC) property of the TNB LB films was characterized by electrochemical potential cycling tests and *in situ* transmittance measurement. The deposition condition of the LB films influenced their EC property. The heat treatment and surface pressure of the TNB LB films plays an important role in the response time and transmittance of the TNBs.

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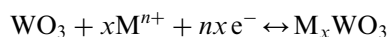
**Keywords:** Electrochromic; Tungsten oxide nanobundle; Langmuir–Blodgett method

## 1. Introduction

An electrochromic (EC) material is able to change its optical properties when a voltage is applied to it. Its optical properties should be reversible, i.e., the original state should be recoverable if the polarity of the voltage is changed. That is, EC properties are defined as a persistent and reversible change of color induced by electrochemical oxidation or reduction [1]. These properties make EC materials of considerable interest for optical devices of several different types, such as elements for smart windows, information displays, sunroofs and variable reflection mirrors [1–5]. EC automotive mirrors have already been commercialized. Thus, the remaining technology challenge in this field is to construct low-cost, large-area EC devices [1,2].

Tungsten oxide, one of the important semiconducting metal oxides, exhibits good EC properties, so it is the most

suitable candidate for EC devices [1,3]. The EC mechanism involves the simultaneous injection of electrons and metal ions into the tungsten oxide film forming a tungsten bronze,



The  $M^{n+}$  ions which can be used in this case have so far been restricted to the monovalent ions,  $H^+$ ,  $Li^+$  and  $Na^+$ . The reversible electrochemical injection of a material into a solid matrix has a number of areas of technology and scientific interest, in addition to EC applications [4].

Over the past few years, there has been a great deal of interest in the synthesis and application of low-dimensional nanostructured materials [6–9]. Especially, semiconductor oxides such as  $ZnO$ ,  $TiO_2$ ,  $SiO_2$ ,  $SnO_2$  and  $WO_x$  have been intensively investigated because of their potential applications in photonics, optics, electronics, sensing materials and catalysis. In these research trends, one-dimensional (1D) tungsten oxides are of special interest due to their low dimensionality and good properties [10–14]. Although there have been some reports on the synthesis of tungsten

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oxide nanostructures, insufficient research has been conducted into their unique properties.

In this study, 1D nanostructure tungsten oxide bundles with a new morphology were synthesized via the solvothermal reaction method. The Langmuir–Blodgett (LB) method is considered to be one of the most versatile techniques for fabricating thin films with a well-controlled composition, structure and thickness. Due to these features, the LB method has been widely used to handle and assemble different functional molecules in a predefined manner [15–17]. Hence, we applied the LB technique to produce arrays of synthesized 1D nanostructure tungsten oxide bundles on a large scale, and the EC properties of the tungsten oxide nanobundles (TNB) LB films were characterized by electrochemical potential cycling tests and *in situ* transmittance measurement.

## 2. Experimental

1D nanostructure tungsten oxide bundles were synthesized via a simple solvothermal method. Tungsten hexachloride (98%,  $\text{WCl}_6$ , Aldrich) was used as the starting material.  $\text{WCl}_6$  is easily decomposed by moist air and water and was therefore handled in a glove box.  $\text{WCl}_6$  is soluble in organic solvents including ligroin, ethanol, so 8.1 g of  $\text{WCl}_6$  was dissolved in 200 mL of 1-propanol. For the solvothermal reaction, 10.0 mL of the  $\text{WCl}_6$  solution was further diluted in 60.0 mL of 1-propanol, so that the concentration of the final solution was 0.014 M. The prepared solution was transferred to a 100 mL Teflon-lined acid digestion bomb, and the solvothermal reaction was conducted at 200 °C for 10 h in an electric oven. After the reactions, the resulting particles were obtained by centrifugation and through washing with ethanol.

The LB trough model was KSV5000 system (KSV Chemicals, Finland) which had double baths and programmable dipping arms allowing alternate deposition. Since the surface of the TNB should be hydrophobic for LB experimental, TNB were dispersed in chloroform through ultrasonification. The solution was diluted in order to control the volatilization speed, immediately before spreading of the solution on the subphase of deionized water (DI) water. After spreading a short period of time (approximately 2–3 min) it is allowed for the chloroform to evaporate from the layer. Substrate to transfer LB films was ITO glass. ITO (Samsung Corning Co, Ltd.)-coated transparent glass, with a resistivity of 10–12  $\Omega/\text{cm}$ , was used as the substrate. The ITO/glass substrate used consisted of ITO,  $\text{SiO}_2$  (30 nm) and soda lime glass, where the  $\text{SiO}_2$  layer blocks the diffusion of Na from the glass into the ITO. The ITO glasses were cleaned by sonication in a surfactant solution, acetone and ethanol, and then thoroughly washed with DI water, and dried under a stream of dry  $\text{N}_2$  gas.

The morphology and phase of the TNBs were characterized using X-ray diffraction (XRD, Cu  $\text{K}\alpha$  radiation, Rigaku D/max-IIIc, Japan) and scanning electron micro-

scopy (SEM, JEOL JSM-6700F, Japan). SEM was also used to visualize the orientation of the LB film. The phase of the nanobundles was matched with monoclinic  $\text{W}_{18}\text{O}_{49}$  (JCPDS no. 05-0392), which is the same result as that obtained in the case of a similar study using ethanol as the solvent in the previous study [14], and the peak intensities of the (0 1 0) and (0 2 0) were also higher than those of the other peaks.

All of the electrochemical potential cycling tests were performed for an individual half-cell using an Autolab PGSTAT30 Potentiostat/Galvanostat. Pt and Ag/AgCl (sat. KCl) were used as the counter and reference electrodes, respectively. Continuous potential cycling (or linear-sweep potential cycling) was carried out for up to 100th cycles in the range of –0.5 to 1.8 V at a scan rate of 50 mV/s in the 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte. The EC response time was measured by applying a pulse potential wave between –0.5 and 1.8 V with a duration of 30 s. The transmittance was simultaneously measured *in situ* during all of the experiments using a He–Ne laser (633 nm). The *in situ* transmittance measurement technique allows the optical behavior to be evaluated as a function of time during the coloring/bleaching process of the EC active film and provides a better understanding of the differences in the optical performance between the samples. In the half-cell test, the transmittance of the (glass)/(ITO) with the electrolyte and cell window was assumed to be 100%.

## 3. Results and discussion

Fig. 1 shows the SEM images of the TNB LB films. The TNBs were deposited uniformly over a large area, and the maximum surface pressure of the LB film was much higher and its deposition state was more uniform. As shown in Fig. 1, a partially assembled domain of nanobundles forms the LB film. Some of the nanobundles were gathered into small clusters in several places. This suggests that the non-dispersed nanobundles became agglomerated before the monolayer was compressed and formed an assembled structure. Kim et al. [15] proposed that nanorods tend to align in roughly the same direction, and form a monolayer with a partially nematic arrangement at the initial pressure. When the monolayer is further compressed, it showed a smectic (2D smectic) arrangement and, finally, a transition from a monolayer to a multilayer with a nematic (3D nematic) configuration was obtained. When increased surface pressure was applied, greater compaction among the nanobundles was observed in the SEM image, but their state was nearly 3D nematic instead of 2D smectic. This is due to the shape of the nanobundles rather than that of the individual nanowires or nanorods, the interaction among the nanobundles, the size distribution of the nanobundles, the problem of dispersion and the deposition conditions.

The cyclic voltammograms of the TNB LB films as a function of the heat treatment temperature are shown in Fig. 2. As the temperature increased, the current density was lowered. In the case of the heat treatment at 60 °C, a

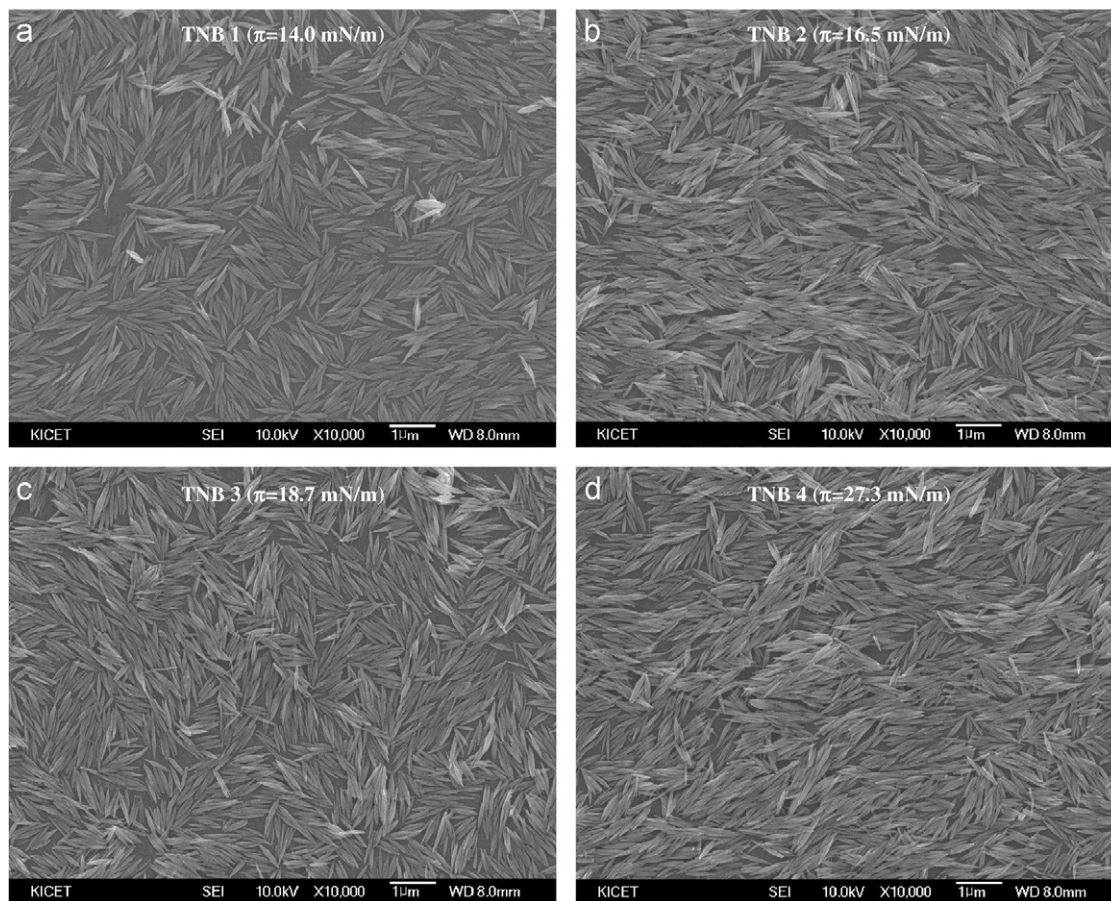


Fig. 1. SEM images of 1D nanostructure tungsten oxide deposited on ITO glass by LB method as a function of the maximum surface pressure ( $\pi$ ): (a)  $\pi = 14.0$  mN/m, (b)  $\pi = 16.5$  mN/m, (c)  $\pi = 18.7$  mN/m and (d)  $\pi = 27.3$  mN/m.

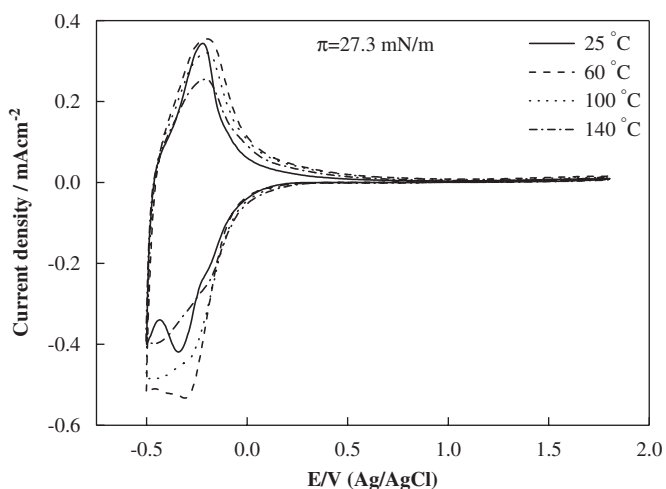


Fig. 2. Cyclic voltammogram of the TNB LB films as a function of the temperature. The heat treatment was done at (a) 25 °C, (b) 60 °C, (c) 100 °C and (d) 140 °C.

broad cathodic current peak occurred in the applied potential range of about  $-0.5$  to  $-0.25$  V and an anodic current peak appeared at about  $-0.2$  V. The cathodic current peak is associated with the evolution of the protons on the electrode and their insertion into the TNB LB films.

The cathodic current density of the TNB at 60 °C was the largest, and decreased when the temperature went up (Fig. 2). This is due to the influence of the substrate—ITO glass. The resistance of ITO glass becomes higher as the temperature is increased. The substrate also has a significant effect on the EC properties, so it is preferable to conduct the heat treatment at low temperature. 60 °C is quite a low temperature as compared to that used in the sol-gel method in which the heat treatment is generally conducted at 200–500 °C. In addition, not applying heat treatment might result in impurities remaining in the film and to the inter-particle gap problem, so proper heat treatment is needed.

Fig. 3 shows the cyclic voltammety curves for the TNB LB films as a function of the maximum surface pressure ( $\pi$ ) during the LB method. The heat treatment of all the LB films was conducted at 60 °C for 12 h. With the voltage increased, the current goes from a negative value, passes through a broad maximum, and approaches zero at the highest voltage. This part of the curve corresponds to ion deintercalation (bleaching). The current is related to ion intercalation/deintercalation. The current density shows a tendency to increase with increasing surface pressure. However, the charge density of  $\pi = 16.5$  is the best among those of the various TNB LB samples. The surface pressure



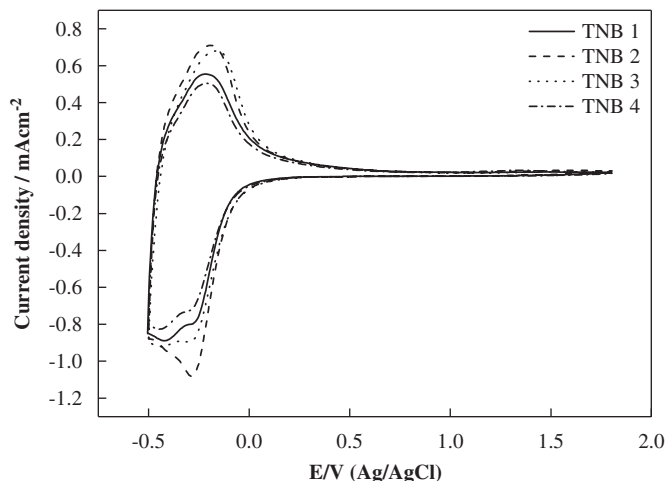


Fig. 3. Cyclic voltammogram of the TNB LB films as a function of the maximum surface pressure.

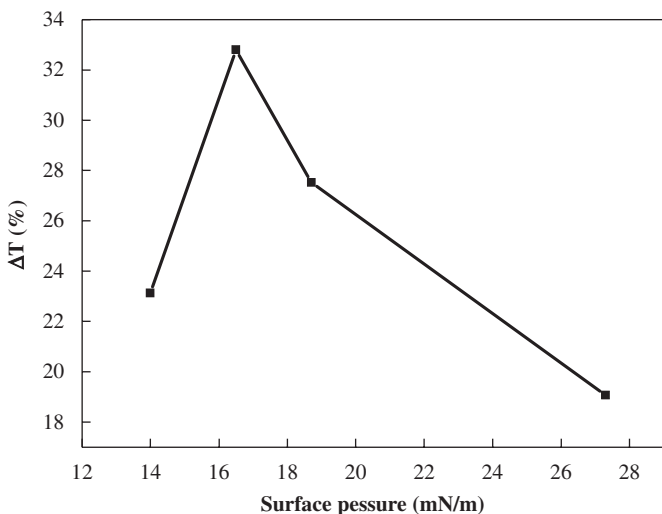


Fig. 4. Transmittance difference of the TNB LB films as a function of the maximum surface pressure.

indicates the relative state of the nanobundles, so it can explain the state of the film deposition to a certain extent. This means that it is possible for the EC property to be affected by the surface pressure; however, other factors might also be involved. Since the cyclic voltammetric behavior of the films ( $\pi = 16.5$ ) is good,  $\Delta T$  shows a relatively high value (Fig. 4). In general, the transmittance of an EC material is related to the injected charge per unit area, the film thickness, and the linear absorption coefficient. The transmittance difference of the TNB LB films was relatively good, whereas their thickness is very low. Since these LB films were composed of nearly a monolayer of nanobundles, their thickness is relatively smaller than that of other tungsten oxide films fabricated by sputter method or sol-gel method. When the 100th cycle was performed, the LB film showed a very stable state. Since the electrolyte is strong acid ( $\text{H}_2\text{SO}_4$ ), it is easy for the tungsten oxide film to be peeled off, like sputtered films

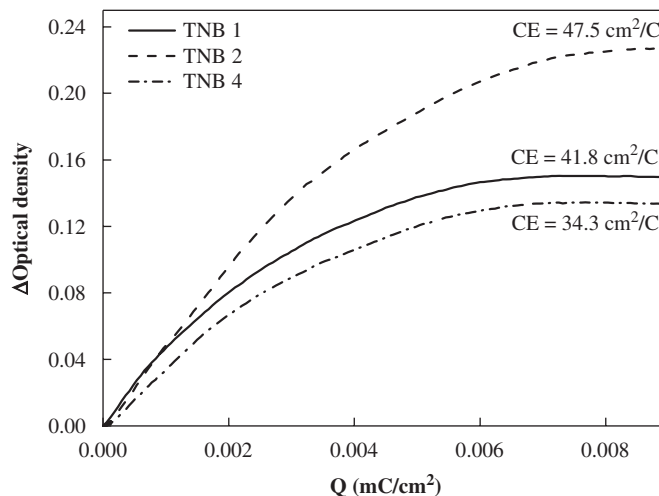


Fig. 5. Coloration efficiency of the TNB LB films as a function of the maximum surface pressure.

in general. However, these nanobundle LB films were more stable than other similar types of tungsten oxide film.

Fig. 5 shows the optical density difference ( $\Delta\text{OD} = \log(T_{\text{bleached}}/T_{\text{colored}})$ ) and coloration efficiency ( $\text{CE} = \Delta\text{OD}/Q$ ) as a function of the maximum surface pressure, where  $Q$  is the charge per unit area during the coloring process. The electrochemical cells, TNB 1, TNB 2 and TNB 4 had CE values of about 41.8, 47.5 and  $34.3 \text{ cm}^2/\text{C}$ , respectively, which are comparable to those reported for sputter deposited  $\text{WO}_3$  films [1,18]. The observed improved coloration efficiency is due to the high surface area and short diffusion length for the  $\text{H}^+$  ions at the nanobundle electrode. 1D nanostructure TNB film is extremely favorable to  $\text{H}^+$  intercalation and deintercalation, since the surface oxidation and reduction reactions occur along the side surface of the 1D nanostructure and the solid-state diffusion distance is very small. The 1D nanostructure would enhance the  $\text{H}^+$  diffusion through the electrolyte. Although more detailed studies of the TNB film are required, we expect that it will be useful as an EC material with a high CE.

#### 4. Conclusion

1D nanostructure tungsten oxide bundles with a new morphology were synthesized via the solvothermal reaction method. The as-synthesized nanobundles with a small size distribution were deposited by the LB method. Locally assembled domains of the nanobundles formed the LB films, but it was difficult for them to align perfectly due to the inter-nanobundle intercalation and dispersion problems. The EC properties of the TNB LB films were characterized by the electrochemical potential cycling test and *in situ* transmittance measurement. The deposition conditions of the TNB LB films influenced their EC properties. As the heat treatment temperature increased, the current density was lowered. The current density showed a tendency to increase with increasing surface

pressure, but the charge density, transmittance difference and coloration efficiency of  $\pi = 16.5$  were the best among the TNB LB samples. Further study is needed to investigate the relation between the low-dimensional tungsten oxide and its EC properties.

### Acknowledgments

Financial support from Korean Science and Engineering Foundation (Grant no. R01-2004-000-10143) are gratefully acknowledged. Do Kyung Kim thanks the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Korean Ministry of Science and Technology and Brain Korea 21 Program from Korean Ministry of Education for the financial support.

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