

***In Operando* X-ray Absorption Fine Structure on Local Structure and Electronic State of Tungsten Oxide Nanoparticles under Electrochromism**

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1 Introduction

Tungsten oxide (WO_{3-x}) is one of the most well-known electrochromic (EC) materials. Recently, in order to make flexible EC film, printing techniques using nanoparticles (NPs) as an ink has attracted attention.¹ Although it is known that the crystal structure and morphology of WO_{3-x} NPs influences EC performance, the underlying mechanisms of the color deterioration have not yet been clarified. Therefore, in this study, we performed *in operando* XAFS measurement for EC films composed of two different crystal structured WO_{3-x} NPs during coloration and bleaching cycles.

2 Experiment

Two different WO_{3-x} NPs, namely monoclinic $\text{W}_{18}\text{O}_{49}$ NPs and hexagonal $(\text{NH}_4)_{0.75}\text{W}_3\text{O}_9$ NPs, were synthesized by wet chemical synthesis. Those NPs were then coated onto an ITO-PET film. The film was set in a tailor-made cell. Using LiPF_6 as an electrolyte, +3 V was applied for coloring and -3 V was applied for bleaching. During the alternate voltage applications, XANES measurements at W L_{3} -edge were conducted in BL-9C and photos were taken of the film at each step. EXAFS spectra were obtained before applying the voltage and after the color of the film deteriorated. The color of the film was analyzed based on the CIE1976 $L^*a^*b^*$ color space.

3 Results and Discussion

As synthesized NPs were found to have rod shape based on TEM images. XRD patterns showed that the produced NPs were either monoclinic or hexagonal phase. Fig. 1a,b show photos of monoclinic or hexagonal NP-loaded films (m-Film and h-Film respectively) under repeating voltage application. The plot of b^* value shows the cyclic dependence of chromaticity (Fig. 1c) where a more negative value means a darker blue. Color deterioration was observed after 8 cycles for the m-Film and 7 cycles for the h-Film. Here, one cycle corresponds to applying +3 V for 52 min followed by -3 V for 52 min.

XANES spectra obtained from the m-Film and the h-Film under 0 V are shown in Fig. 1d. Since WO_{3-x}

has a WO_6 octahedron unit in the crystal structure, the ligand field splits the 5d orbital level into the t_{2g} and e_g levels. Based on simultaneous fitting of the XANES spectrum and its second derivative, the energy levels of t_{2g} and e_g were determined as shown in Fig. 1e. A periodic change was clearly observed in the e_g levels until the color deteriorated (8 cycles for m-Film and 7 cycles for h-Film). Because the e_g level was formed by the on-axis alignment of the 5d orbital and ligand field, they were more sensitive to the change of the ligand field than the t_{2g} . The gradual increase of the e_g level in the m-Film was considered to be due to the formation of distortions.² Analyses of EXAFS spectra revealed that W-O bonds in the m-Film increased after color deterioration while no bond change was observed in the h-Film, suggesting that different crystal structures have different coloration deterioration mechanisms. In the case of the m-Film, the accumulation of distortions stopped the reversible color change. On the other hand, the reason for the color deterioration in the h-Film was explained by the trapping of Li^+ in the optically inactive trigonal cavities during repeated voltage application. A detailed discussion was written in the published paper.

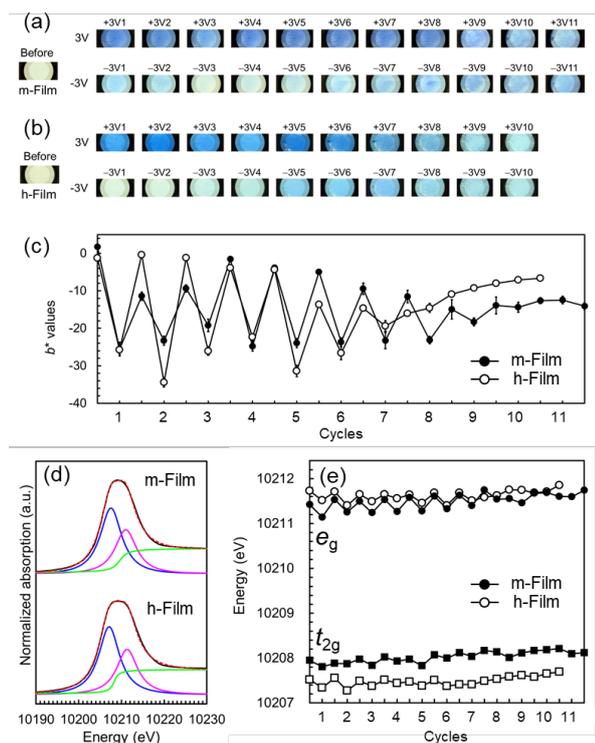


Fig. 1 Photos of the (a) m-Film and (b) h-Film under either +3 V or -3 V. (c) The plot of the b^* values at each step. (d) XANES spectra of W L_3 -edge. The blue, pink, green and red lines are t_{2g} , e_g , background and the sum of the components respectively. (e) Variation of t_{2g} and e_g energy positions with respect to each step.

References

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Research Achievements

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