In-operando Raman Spectroscopic Studies of the Coloring and Bleaching Mechanism of Self-powered Photoelectrochromic Devices

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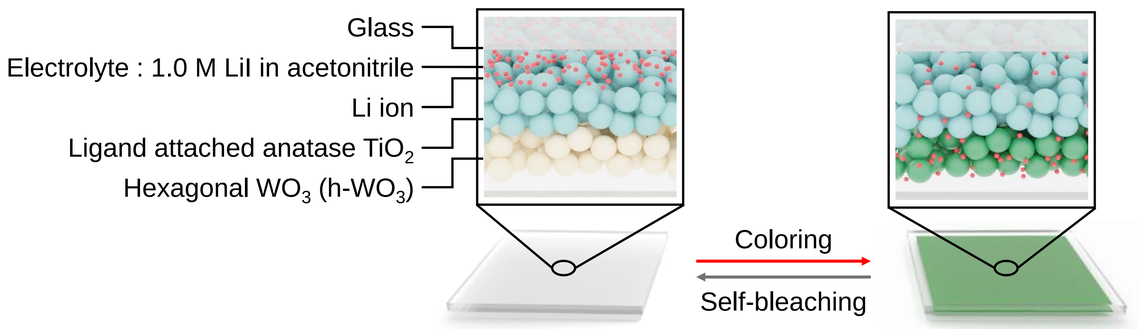
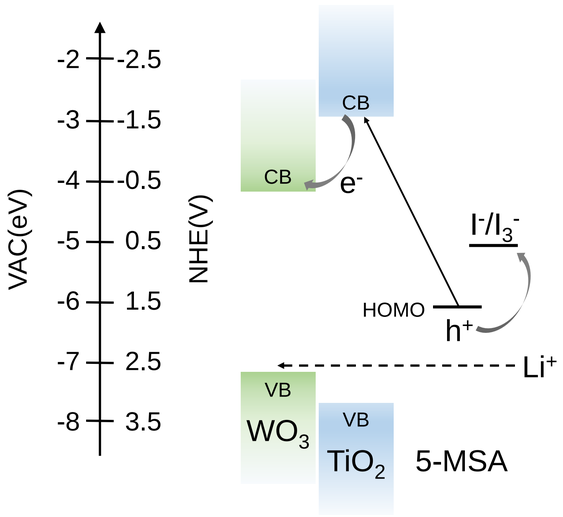
Abstract

The chromogenic material, which have various applications in smart windows and glasses, reversibly change their color when electrons and cations are injected by applied voltage or absorption of light. Especially, electrochromic devices (ECDs) have been studied in many studies to utilize as switchable windows, however, it is difficult to make them on a large scale due to the technical requirements for ECDs. This problem does not occur in photochromic devices (PCDs), but the studies on the mechanism of PCDs are still insufficient. In a PCD, the intercalation/deintercalation of Li ions during the coloring/bleaching process plays an important role in the device's color-switching performance. In this study, we propose a plausible mechanism for the PCD using in-operando Raman spectroscopy. The time resolved Raman spectra of PCD was measured under illumination and in the dark. Through the spectral shift of characteristic peaks of WO_3, we propose a Li^+ insertion/extraction mechanism into specific sites within the tunnels that exist in the hexagonal WO_3 units during PCDs coloring/self-bleaching.

Introduction to PCDs



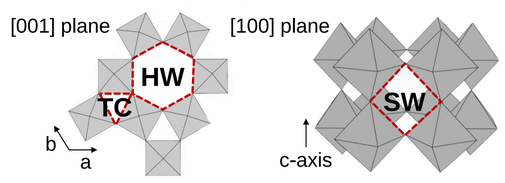
Working mechanism of PCDs



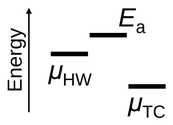
Clear — Dark green~blue

- $WO_3 + xLi^+ + xe^-$ (5-MSA) ↔ Li_xWO_3
- $3I^- + 2h^+$ (5-MSA) ↔ I_3^-

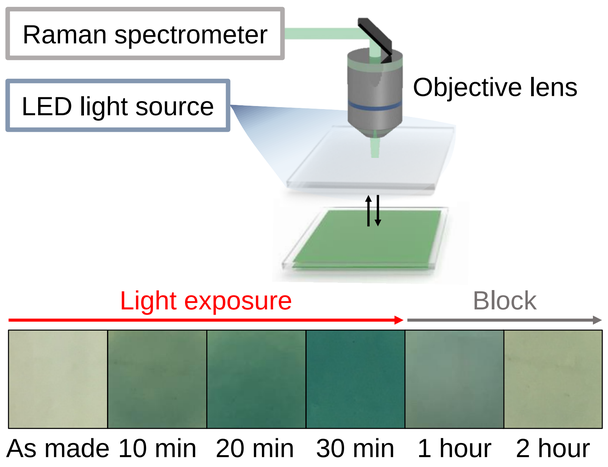
h-Li_xWO_3 structure

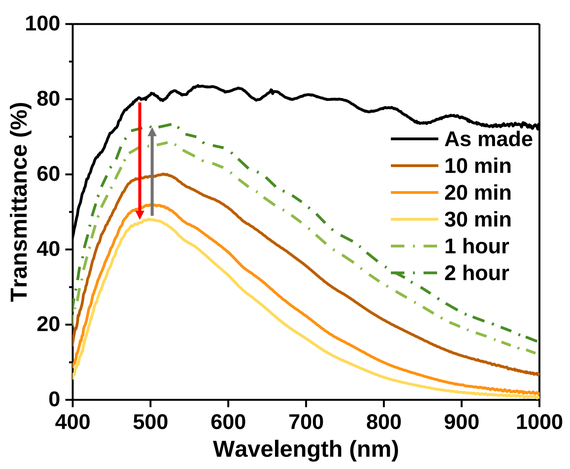


- Trigonal cavity (TC)
- Hexagonal window (HW)
- Square window (SW)

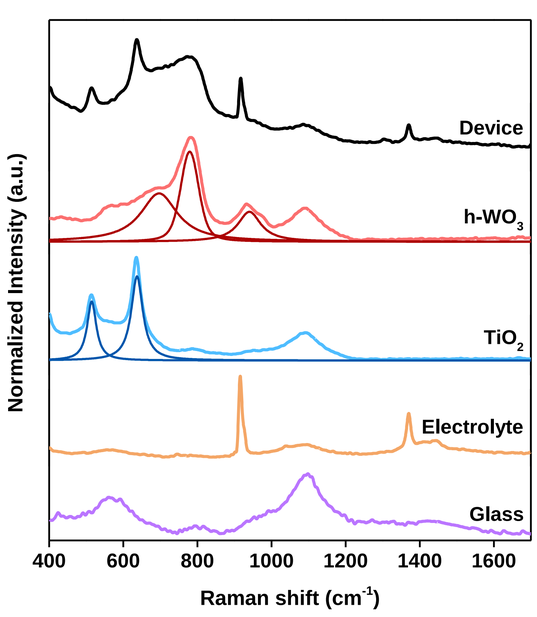


In-operando Raman studies of PCDs



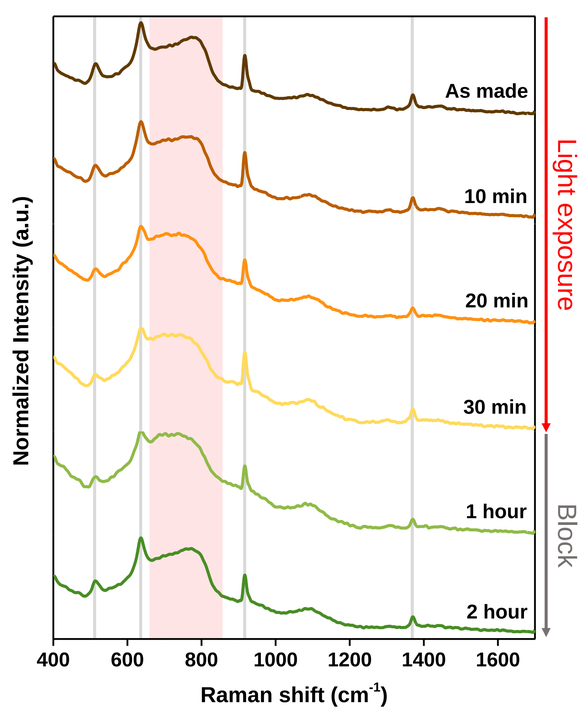


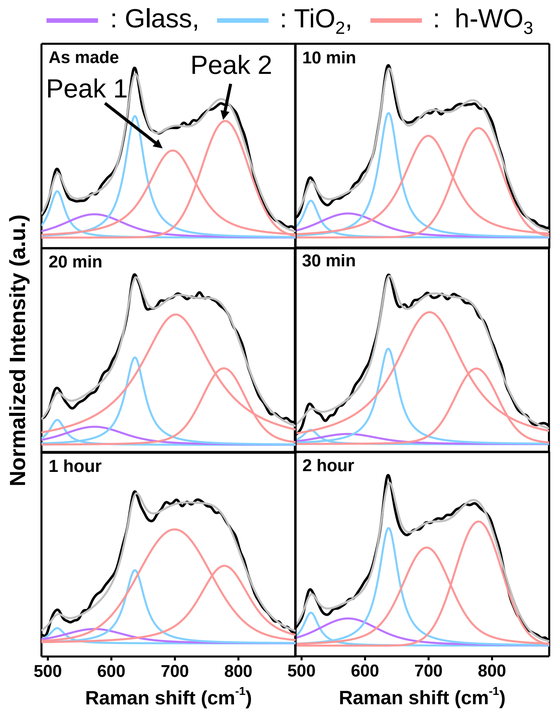
Raman spectrum of each layer constituting the device



	Raman shift (cm^{-1})	Mode
h-WO_3	697	ν_s(O–W–O)$_a$ (axial)
	779	ν_s(O–W–O)$_e$ (equatorial)
	940	$\nu_s n_s$(W=O)
TiO_2	515	δ_a(O–Ti–O)
	637	ν_s(O–Ti–O)
Electrolyte	916	ν(CC)
	1371	$\delta_d(CH_3)$
Glass	573	δ_s(Si–O–Si)
	1092	ν_s(Si–O–Si)

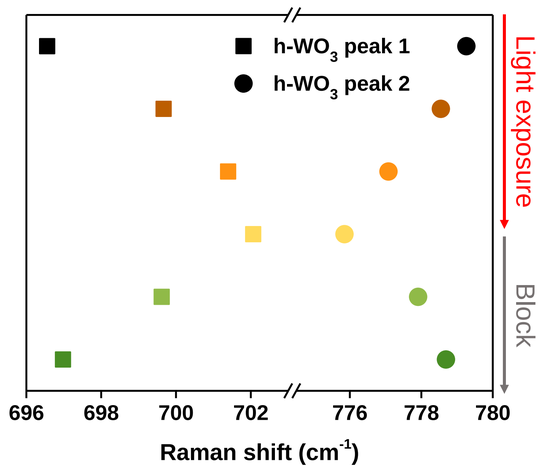
Time-resolved Raman spectra of the PCDs

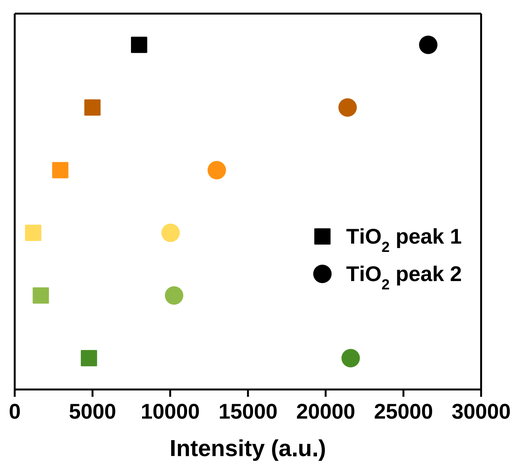




➢ Asymmetric band of h-WO_3 has shifted. ➔ Deconvoluted using Voigt function.

Spectral shift of characteristic peaks of h-WO_3



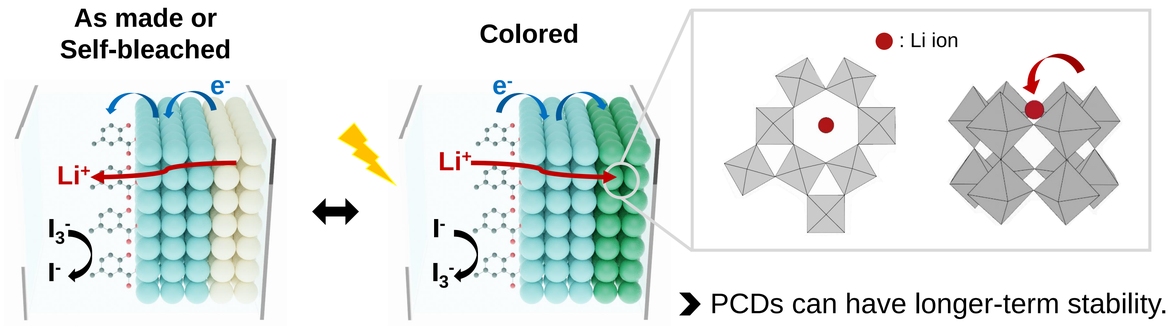


➢ Coloring state : peaks shifted to another trend and did not disappear during coloring.
➔ Li^+ was inserted up to x < 0.4. ➔ Lattice parameter a↑ , c↓
➔ SW site was not occupied.

➢ Self-bleaching state : peaks showed excellent reversibility.
➔ Complete deintercalation of Li^+ occurred as no TC site was occupied during coloring.
➔ Only HW site was occupied with Li^+ by LED illumination.

➢ Raman modes of TiO_2 did not shifted but the intensity had changed.
➔ Li^+ was partially inserted into TiO_2.

Mechanism of operating PCDs



➢ PCDs can have longer-term stability.

Conclusion

The analysis of WO_3 layer is important since performance of PCD depends on the microstructure, crystallinity, porosity, reversibility and guest ion (Li^+) capacity of the WO_3 layer. We proposed a plausible mechanism for describing coloring and self-bleaching of the PCD using in-operando Raman spectroscopy. Homogenous coloring and self-bleaching processes in PCD was enabled by the Li^+ insertion into the WO_3 layer. Our experiments revealed that the Li^+ passes through the HW in the h-WO_3 lattice and partially inserted into the TiO_2 layer during the coloration process, thus the PCDs showed longer-term stability. The reaction mechanism proposed in this study is expected to be of great help in understanding the homogenous coloring/self-bleeding process in a large-scale smart windows and fabricating the most-effective PC device.