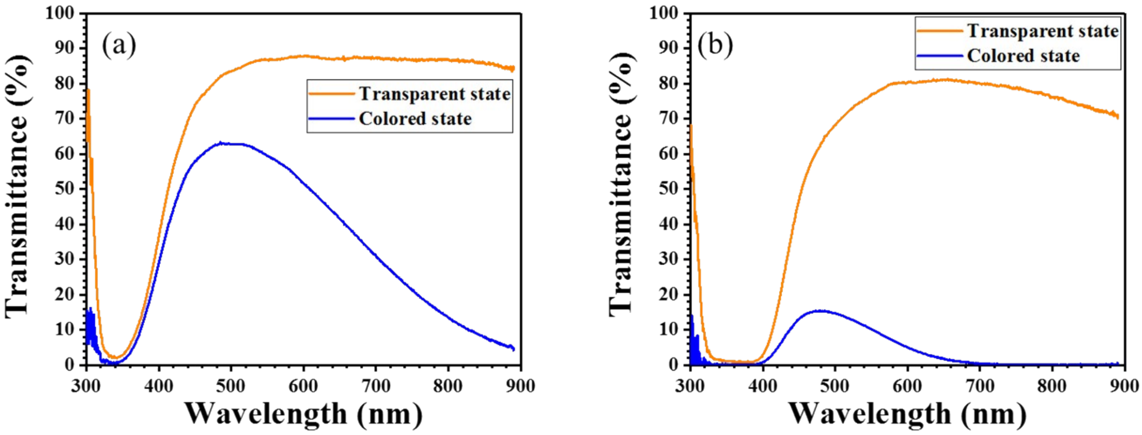
Supplementary information

Green fabrication of a complementary electrochromic device using water-based ink containing nanoparticles of WO_3 and Prussian blue

Kazuki Tajima*[a], Hiroshi Watanabe[a], Mizuka Nishino[a], and Tohru Kawamoto*[a]

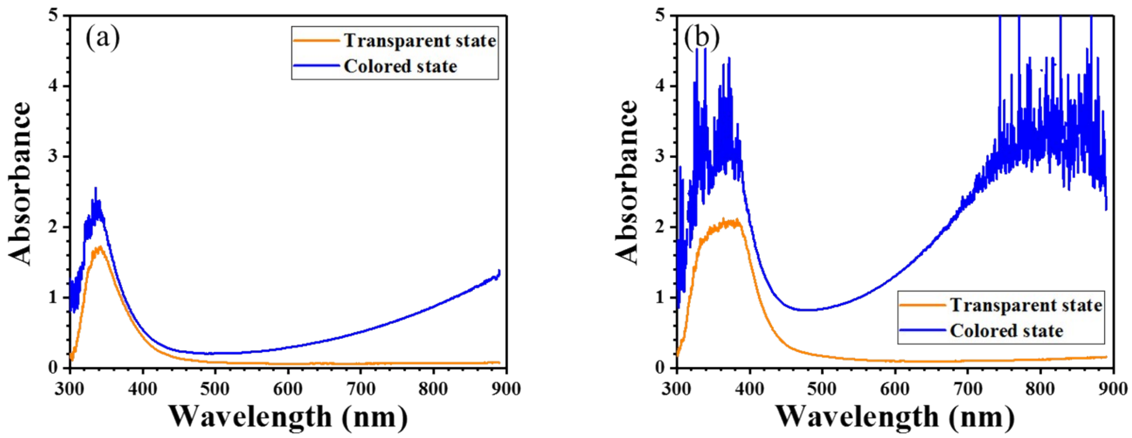
a.Nanomaterial Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565, Japan

*Corresponding Author:
E-mail: k-tajima@aist.go.jp, tohru.kawamoto@aist.go.jp



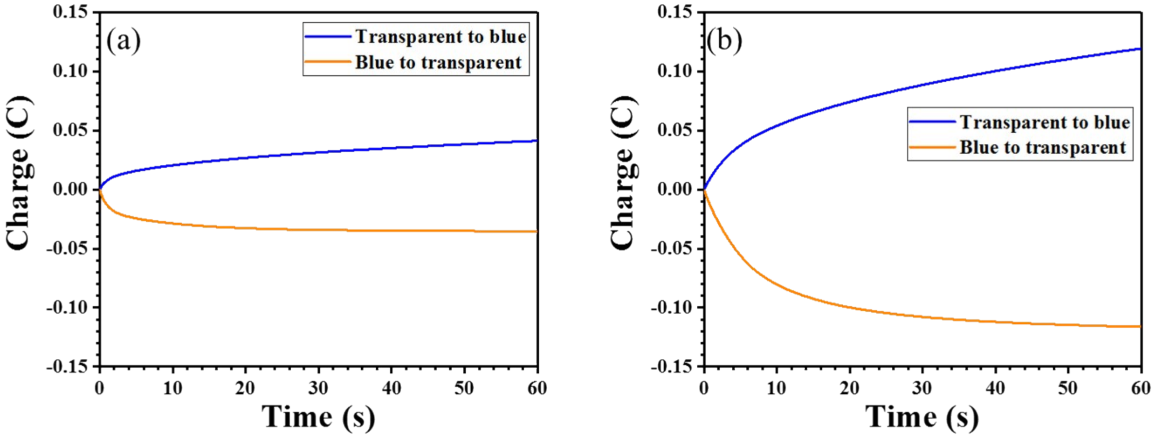
[Figure S1]

Figure S1 Change in electrochromic transmittance of WO_3 film on ITO/glass.
(a) Thin film deposited by spin-coating at 500 rpm for 30 s, and (b) thick film generated in this work after thermal treatment at 500 °C for 1 h.



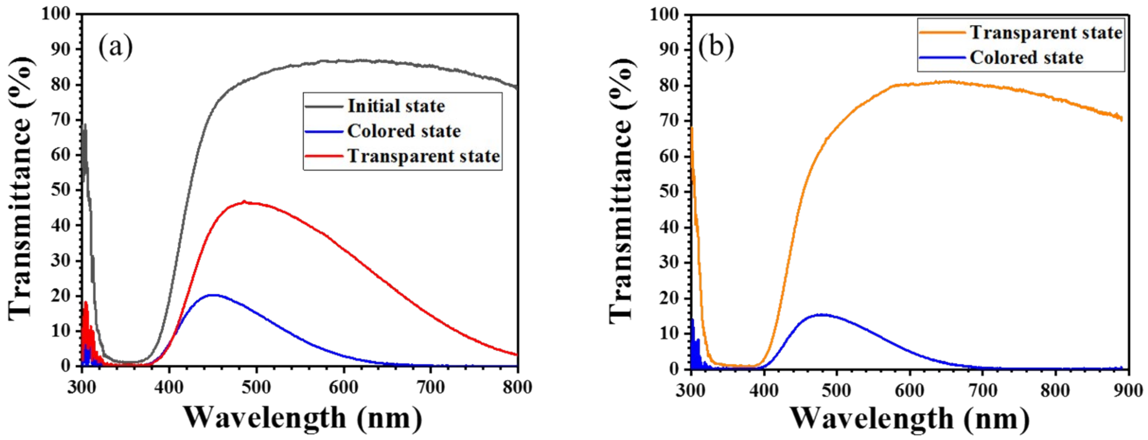
[Figure S2]

Figure S2 Change in electrochromic absorbance of WO_3 film on ITO/glass.
(a) Thin film deposited by spin-coating at 500 rpm for 30 s, and (b) thick film generated in this work after thermal treatment at 500 °C for 1 h.



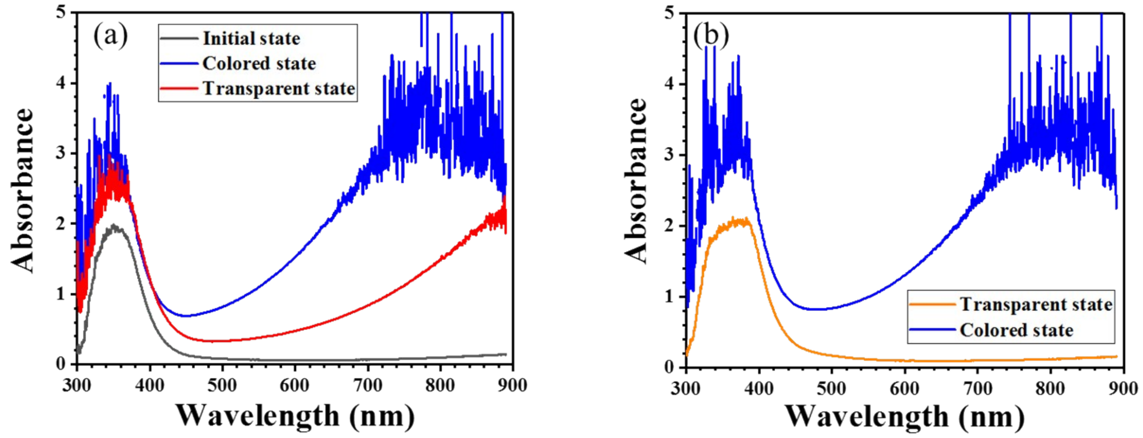
[Figure S3]

Figure S3 Multiple potential step measurements of WO_3 film on ITO/glass.
(a) Thin film deposited by spin-coating at 500 rpm for 30 s, and (b) thick film generated in this work after thermal treatment at 500 °C for 1 h.



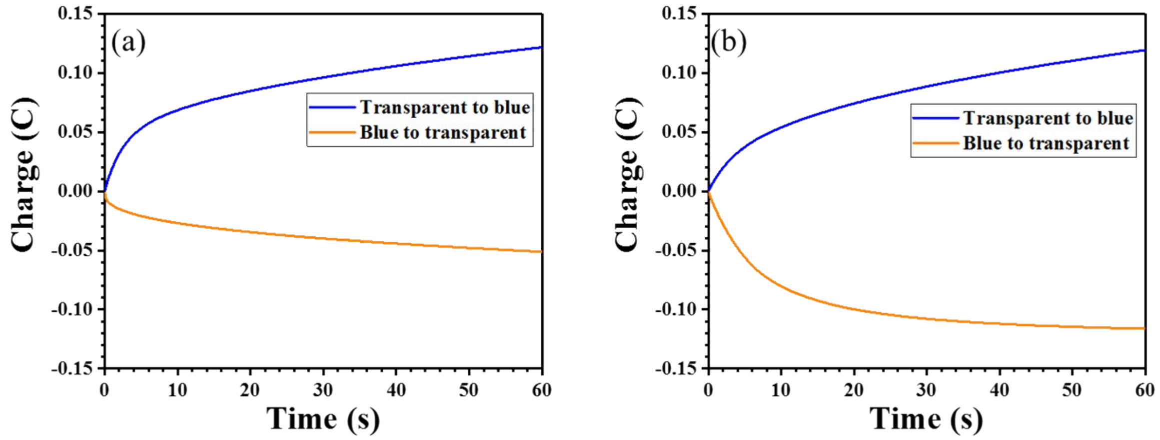
[Figure S4]

Figure S4 Change in electrochromic transmittance of WO_3 thick film on ITO/glass. (a) As-prepared (not thermally treated), and (b) after thermal treatment at 500 °C for 1 h.



[Figure S5]

Figure S5 Change in electrochromic absorbance of WO_3 thick film on ITO/glass.
(a) As-prepared (not thermally treated), and (b) after thermal treatment at 500 °C for 1 h.



[Figure S6]

Figure S6 Multiple potential step measurements of WO_3 thick film on ITO/glass. (a) As-prepared (not thermally treated), and (b) after thermal treatment at 500 °C for 1 h.

Table S1 Parameters for multiple potential step measurements.

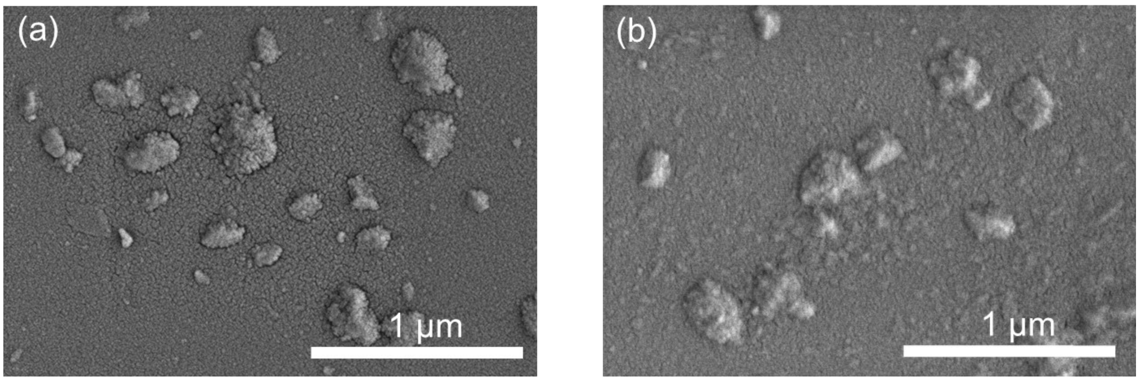
First step potential (V)	-1.2
First step Time (S)	60
Second step potential (V)	1.0
Second step Time (S)	60
Quiet time (S)	10

Table S2 Coloration efficiency of WO_3 film on ITO/glass.

WO_3 film conditions		Coloration efficency
Thickness (nm)	Treatment	Δ Abs (670nm) / Charge (C)
500	500 °C for 1 h	8.91
2300	room temperature	18.53
1200	500 °C for 1 h	15.86

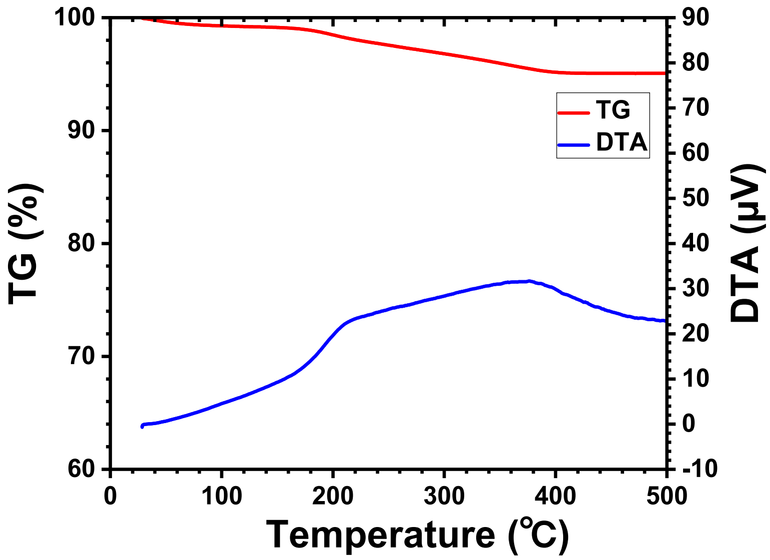
[Figure S7]

Figure S7 FE-SEM images of WO_3 films on ITO/glass substrates. (a) and (b): surface images before and after thermal treatment.



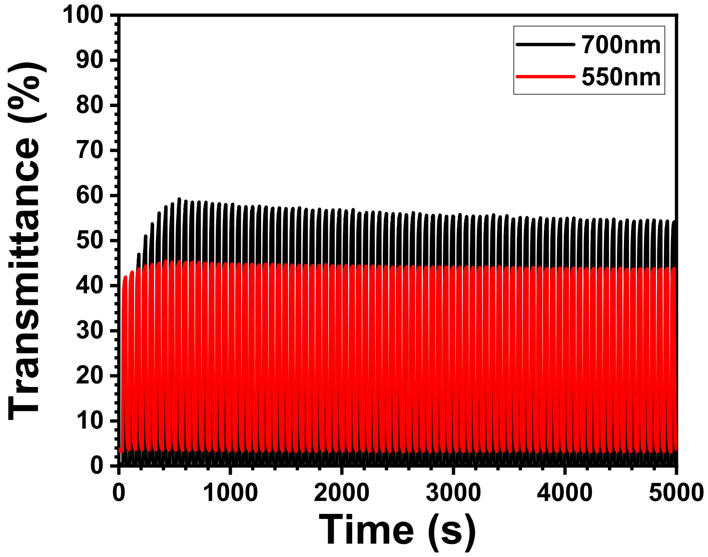
[Figure S8]

Figure S8 TG-DTA analysis of WO_3 slurry with PVA (5%).
Percentage relative to the total solid content, WO_3 : PVA : H_2O = 26.5 : 1.3 : 72.2



[Figure S9]

Figure S9 The durability of the electrochromic device.



[Figure S10]

(a) without PVA (44°) (b) with PVA (24°)

Figure S10 Wettability of the WO_3 ink on ITO/glass substrate.
The wettability was evaluated by contact angle of the ink on the substrate.

Table S3 Comparison of characteristics of various WO_3 fabrication methods and performance of ECDs with WO_3 and PB.

				Transmittance (%)		Response time (s)	
Starting materials	Process / Synthesis	Product	Coating method	Transparent state	Coloured state	Transparent to colloerd	
W	plasma process in vacuum condition under Ar/O_2 gasses	WO_3 NP	spin-coating	64(at 670nm) 40(at 500nm)	0.1(at 670nm) 10(at 500nm)	3	In this work
WO_3	thermal evaporation	WO_3	vacuum-deposition	22(at 670nm) 61(at 500nm)	> 1(at 670nm) 25(at 500nm)	45	ref.37
WCl_6	Solvothermal	$W_{18}O_{49}$ nanowire	immersed into the reaction solution	59(at 670nm) 68(at 500nm)	> 1(at 670nm) 28(at 500nm)	100	ref.38
W	electrodeposition in H_2O_2 solution	WO_3	electrodeposition in H_2O_2 solution	N.D.	N.D.	N.D.	ref.39
$Na_2WO_4{\cdot}2H_2O$	immersed into the reaction solution	$WO_3{\cdot}H_2O$ nanosheets	immersed into the reaction solution	70(at 670nm) 71(at 500nm)	12(at 670nm) 34(at 500nm)	2	ref.40