†Electronic Supplementary Information

Ultrathin Sputtered NiO Films for Enhanced Electrochromic Performance in Smart Windows

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Tables:

Table S1 Oxygen percentage ratio from the flux inputs of oxygen and argon gases into the deposition chamber.

O_2/Ar	Ar (sccm)	O_2 (sccm)	Oxygen percentage
0.3	40	12	23
0.4	35	14	28
0.5	34	17	33
0.6	30	18	38
0.7	28	19	40

Table S2 XRD parameters estimated for NiO films deposited at different O_2/Ar ratios.

sample	2θ (degree)	FWHM (degree)	Crystallite size D, (nm)	Strain, ε (in×10^{-3})	Lattice parameter, a (Å)
0.3	37.33	1.05	8.4	4.3	4.17
0.4	37.20	0.88	10.0	3.6	4.18
0.5	37.35	0.93	9.4	3.8	4.16
0.6	37.25	0.93	9.4	3.8	4.17
0.7	37.24	0.97	9.0	4.0	4.18

Table S3 Roughness of the NiO films deposited at different O_2/Ar ratios using AFM measurements.

Sample	R_a (nm)	R_q (nm)
0.3	1.0	1.3
0.4	1.3	1.6
0.5	0.3	0.5
0.6	0.3	0.4
0.7	0.7	1.1

Table S4 Peak fitting parameters obtained from XPS for NiO films 0.3, 0.4, 0.5, 0.6, and 0.7, respectively.

	Binding energy (eV)	FWHM (eV)	Peak split (eV)	Assignment	Area ratio
O1s	529.82	1.611	1.56	Ni^{+2}	0.84
	531.38	2.04		Ni^{+3}	
Ni2p	852.6	1.48		Ni	
	854.03	1.6	2	Ni^{+2}	1.22
	856.03	3.33		Ni^{+3}	
	861.11	4.41		sat. peak	
	864.83	3			
	871.53	3.55	2.22	Ni^{+2}	0.84
	873.75	3.58		Ni^{+3}	
	880.12	5.77		sat. peak	

	Binding energy (eV)	FWHM (eV)	Peak split (eV)	Assignment	Area ratio
O1s	529.66	1.71	1.44	Ni^{+2}	0.74
	531.1	2.18		Ni^{+3}	
Ni2p	852.41	1.26		Ni	
	853.70	1.99	2.46	Ni^{+2}	1.04
	856.16	3.73		Ni^{+3}	
	861.15	4.51		sat. peak	
	864.38	2.84			
	871.60	3.39	2.47	Ni^{+2}	0.98
	874.07	4.14		Ni^{+3}	
	880.09	5.76		sat. peak	

	Position	FWHM	Peak split	Assignment	Area ratio
O1s	529.66	1.63	1.57	Ni^{+2}	0.42
	531.23	1.48		Ni^{+3}	
Ni2p	852.36	0.93		Ni	
	853.57	2.35	2.44	Ni^{+2}	0.95
	856.01	3.17		Ni^{+3}	
	860.93	4.44		sat. peak	
	864.25	1.9			
	870.62	2.95	2.81	Ni^{+2}	0.98
	873.43	4.12		Ni^{+3}	
	880.07	5.77		sat. peak	

	Binding energy (eV)	FWHM (eV)	Peak split (eV)	Assignment	Area ratio
O1s	529.61	1.66	1.58	Ni^{+2}	0.55
	531.19	1.68		Ni^{+3}	
Ni2p	852.36	0.88		Ni	
	853.27	2.41	2.64	Ni^{+2}	0.76
	855.91	3.24		Ni^{+3}	
	861.07	4.7		sat. peak	
	864.34	1.98			
	870.34	2.82	3.32	Ni^{+2}	0.99
	873.66	3.95		Ni^{+3}	
	879.66	5.86		sat. peak	

	Binding energy (eV)	FWHM (eV)	Peak split (eV)	Assignment	Area ratio
O1s	529.71	1.52	1.65	Ni^{+2}	0.38
	531.36	1.45		Ni^{+3}	
Ni2p	852.57	0.66		Ni	
	853.46	2.42	2.64	Ni^{+2}	0.77
	856.1	3.12		Ni^{+3}	
	861.03	4.58		sat. peak	
	864.44	2.13			
	870.87	3.3	2.95	Ni^{+2}	0.82
	873.82	3.77		Ni^{+3}	
	880.13	6.01		sat. peak	

Table S5 Transmittance at 550 nm for as deposited NiO films.

Sample	T (%) at 550 nm
0.3	76
0.4	75
0.5	76
0.6	74
0.7	75

Table S6 Areal capacitance (mF/cm^2) calculated for NiO films at 25 mV/cm^2 in electrolytes of 1 M LiOH and 1 M KOH.

Sample	Areal capacitance (mF/cm^2)	
	LiOH	KOH
0.3	6.83	4.73
0.4	4.80	4.77
0.5	5.63	5.00
0.6	3.67	5.00
0.7	4.15	3.50

Table S7 Diffusion coefficients obtained from Randles model for various NiO films in LiOH and KOH electrolytes.

Sample	LiOH		KOH	
	cathodic	anodic	cathodic	anodic
0.3	7.80×10^{-11}	1.14×10^{-10}	2.94×10^{-11}	4.21×10^{-11}
0.4	2.50×10^{-11}	3.14×10^{-11}	2.67×10^{-11}	3.93×10^{-11}
0.5	5.39×10^{-11}	6.72×10^{-11}	3.39×10^{-11}	4.60×10^{-11}
0.6	4.33×10^{-11}	3.08×10^{-11}	3.64×10^{-11}	5.13×10^{-11}
0.7	2.37×10^{-11}	3.89×10^{-11}	1.37×10^{-11}	2.49×10^{-11}

Table S8 Extracted values of b parameter from the $\ln(i_p)$ vs $\ln(v)$ graph in LiOH and KOH electrolytes from cathodic (pc) and anodic (pa) peaks.

Sample	LiOH		KOH	
	Cathodic (i_{pc})	anodic (i_{pa})	Cathodic (i_{pc})	anodic (i_{pa})
0.3	0.79	0.62	0.55	0.45
0.4	0.63	0.53	0.54	0.46
0.5	0.66	0.48	0.58	0.49
0.6	0.62	0.49	0.57	0.48
0.7	0.65	0.6	0.52	0.48

Table S9 Coloring (t_c) and bleaching (t_b) response time obtained from in-situ transmittance, 550 nm response time (LiOH) for NiO films.

Sample	t_c (s)	t_b (s)
0.3	5.13	2.32
0.4	4.9	2.1
0.5	4.94	2.66
0.6	7.51	2.17
0.7	9.74	1.64

Table S10 Coloring (t_c) and bleaching (t_b) response time obtained from chronoamperometry curves for NiO films in LiOH and KOH electrolytes.

Sample	In LiOH		In KOH	
	t_c (s)	t_b (s)	t_c (s)	t_b (s)
0.3	2.31	1.32	2.60	1.20
0.4	3.78	1.68	2.51	1.28
0.5	3.72	1.77	3.89	1.59
0.6	6.22	2.86	3.75	1.56
0.7	4.72	1.89	3.53	1.86

Table S11 XRD parameters extracted for NiO sample 0.4 deposited at different thicknesses.

Thickness (nm)	2θ (degree)	FWHM (degree)	Crystallite size D, (nm)	Strain, ε (in$\times 10^{-3}$)	Lattice parameter, a (Å)
80	37.38	1.00	8.8	4.13	4.16
120	37.34	0.93	9.4	3.84	4.17
150	37.35	0.98	8.9	4.05	4.16

Table S12 Roughness values obtained for the different thick NiO films.

Thickness (nm)	R_a (nm)	R_q (nm)
80	0.5	0.6
120	0.7	0.8
150	0.5	0.6

Table S13 Transmittance for NiO thin films with different thicknesses.

Thickness (nm)	Transmittance (%)
50	75
80	66
120	59
150	57

Table S14 Bleaching and coloring response time with thickness from in-situ transmittance measurements (LiOH).

Thickness (nm)	Bleaching time (s)	Coloring time(s)
80	3.65	8.78
120	4.2	9.2
150	7.8	19.53

Figures:

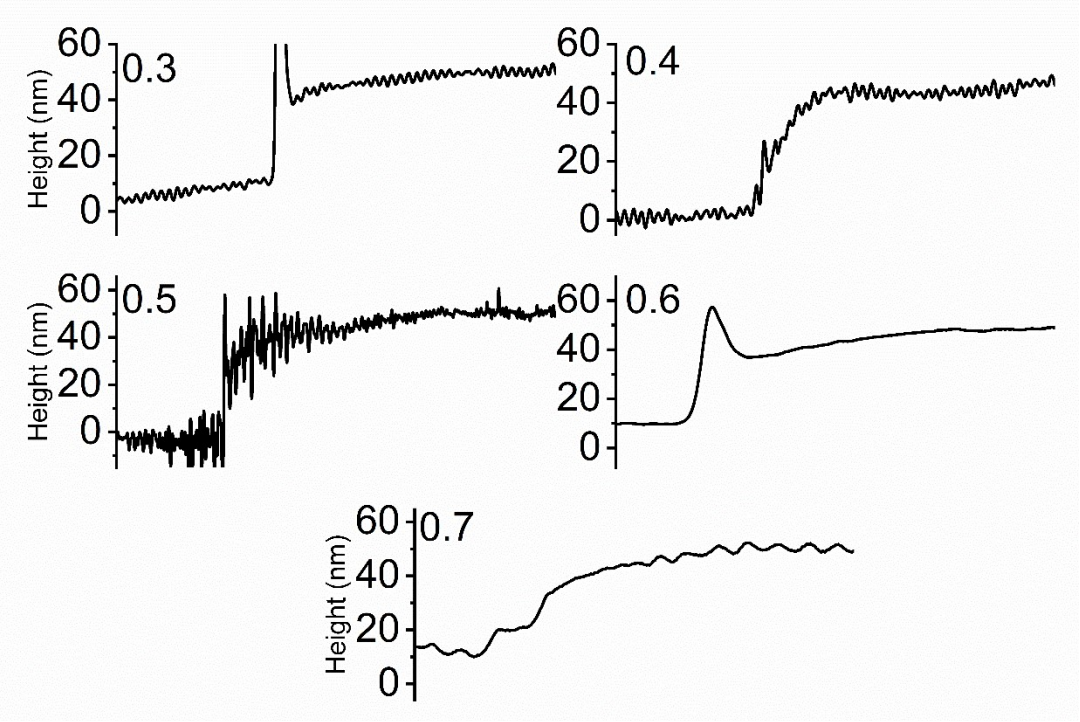

Figure S1 Thickness profiles for various NiO thin films obtained from stylus profilometer.

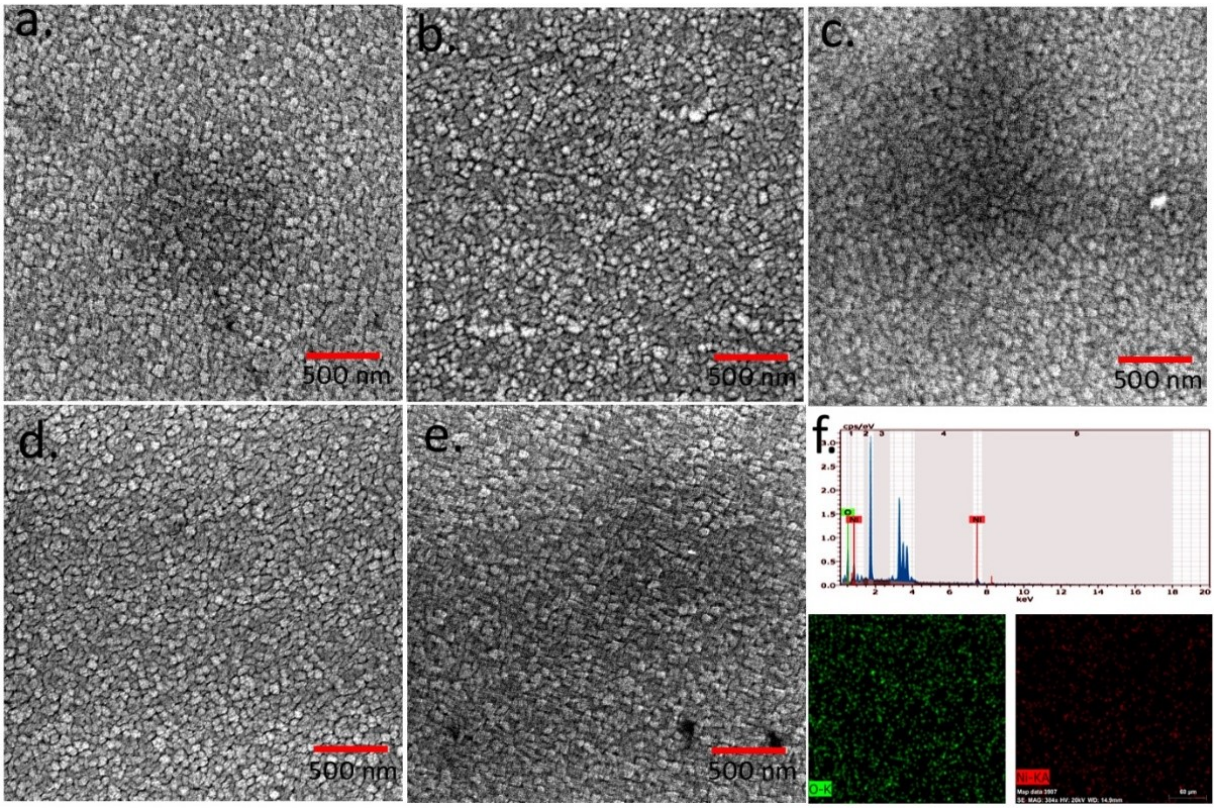

Figure S2 SEM micrographs of NiO thin films: a) 0.3, b) 0.4, c) 0.5, d) 0.6, e) 0.7, f) representative EDS and mapping for 0.4 sample.

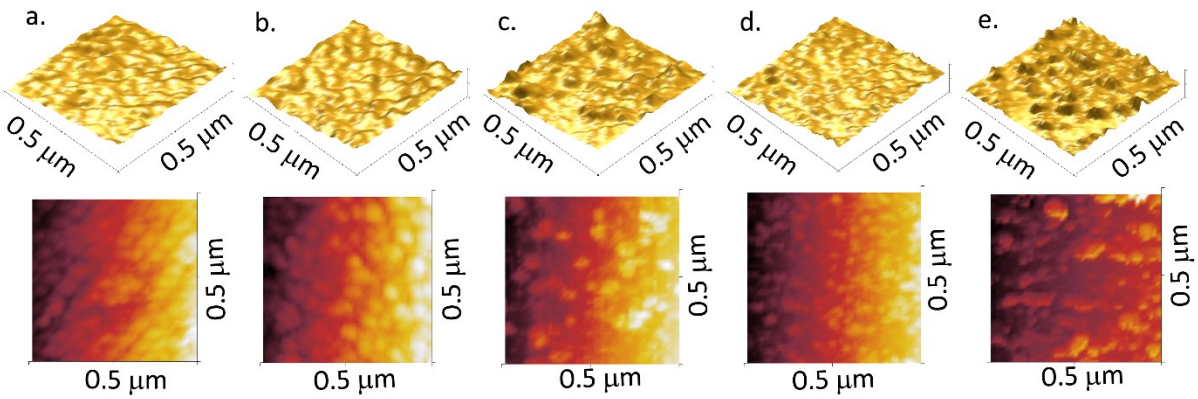

Figure S3 Atomic force micrographs for NiO thin films: a) 0.3, b) 0.4, c) 0.5, d) 0.6, and e) 0.7.

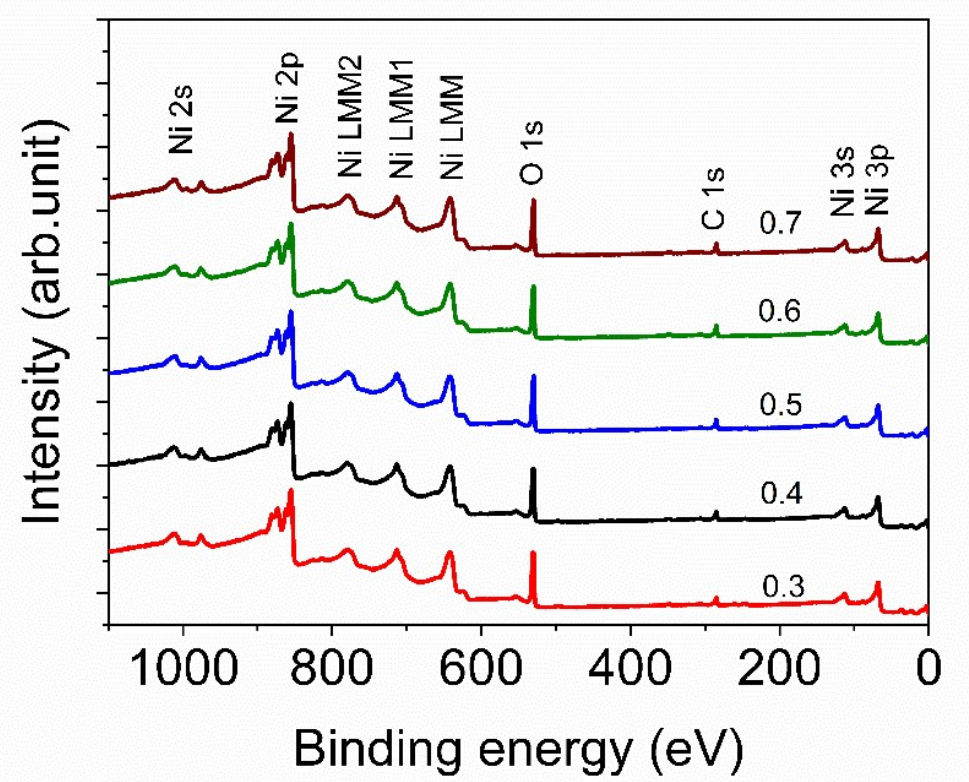

Figure S4 XPS survey spectra of NiO films.

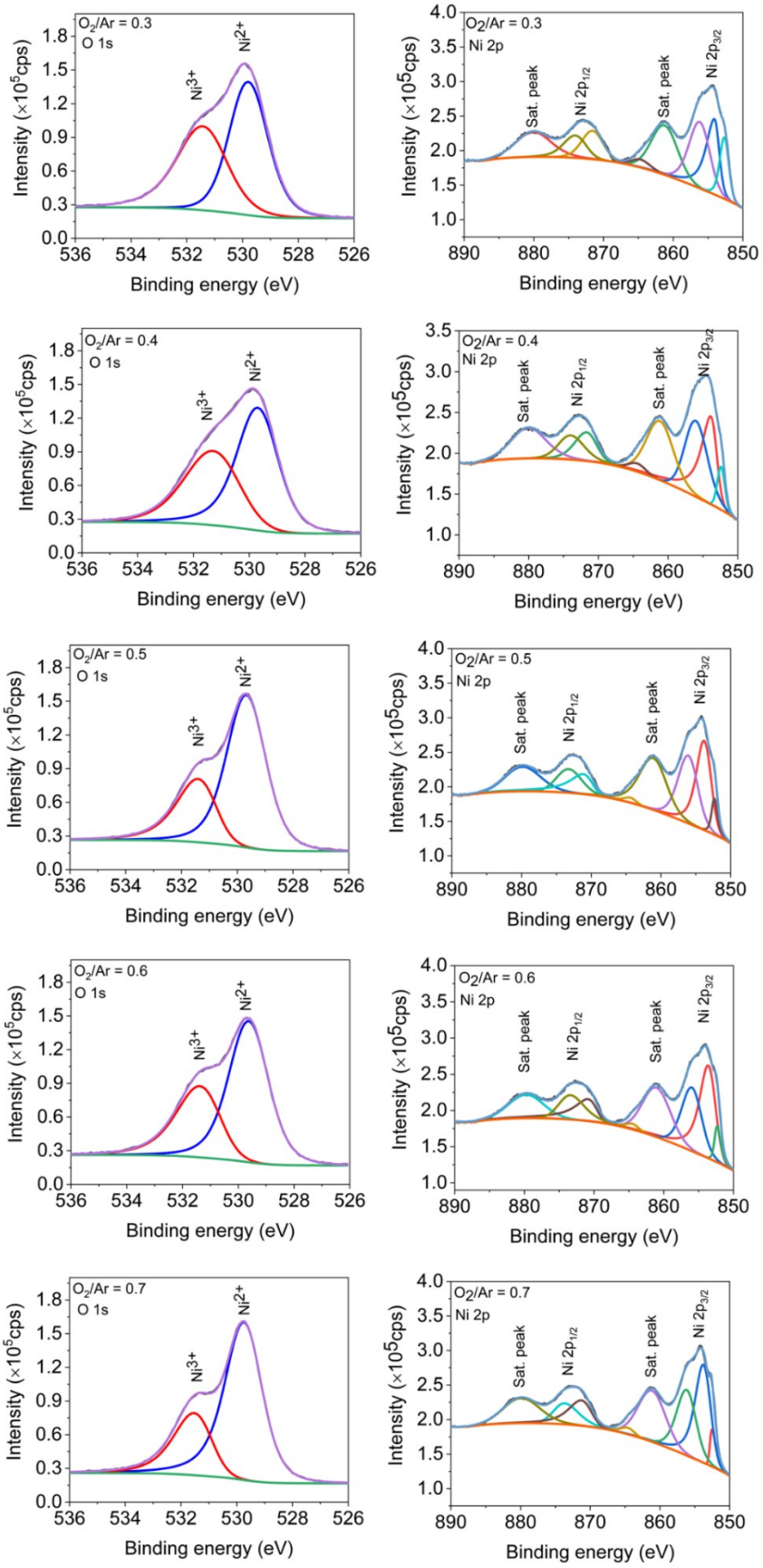

Figure S5 XPS peak fitting data consisting of O1s and Ni 2p core level spectra for NiO films.

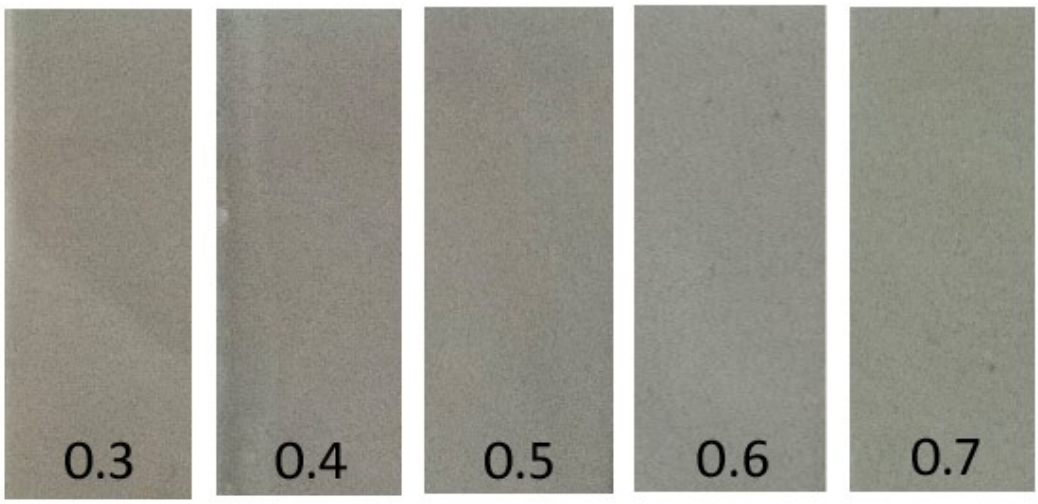

Figure S6 Photographic image of NiO films.

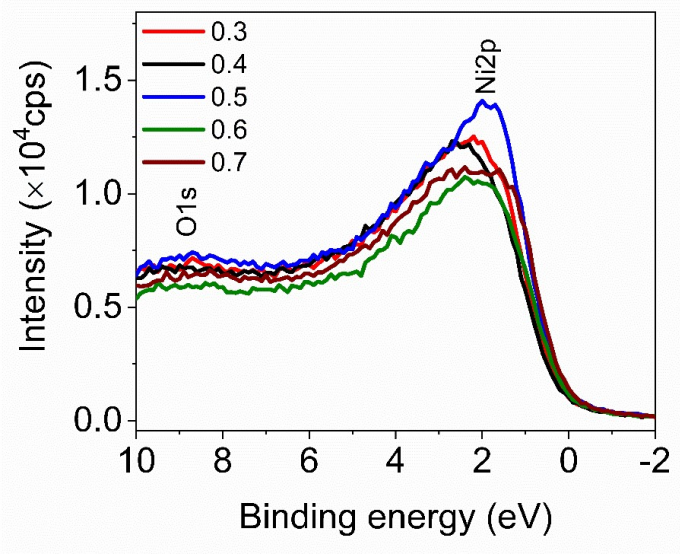

Figure S7 Valence band spectra for NiO films.

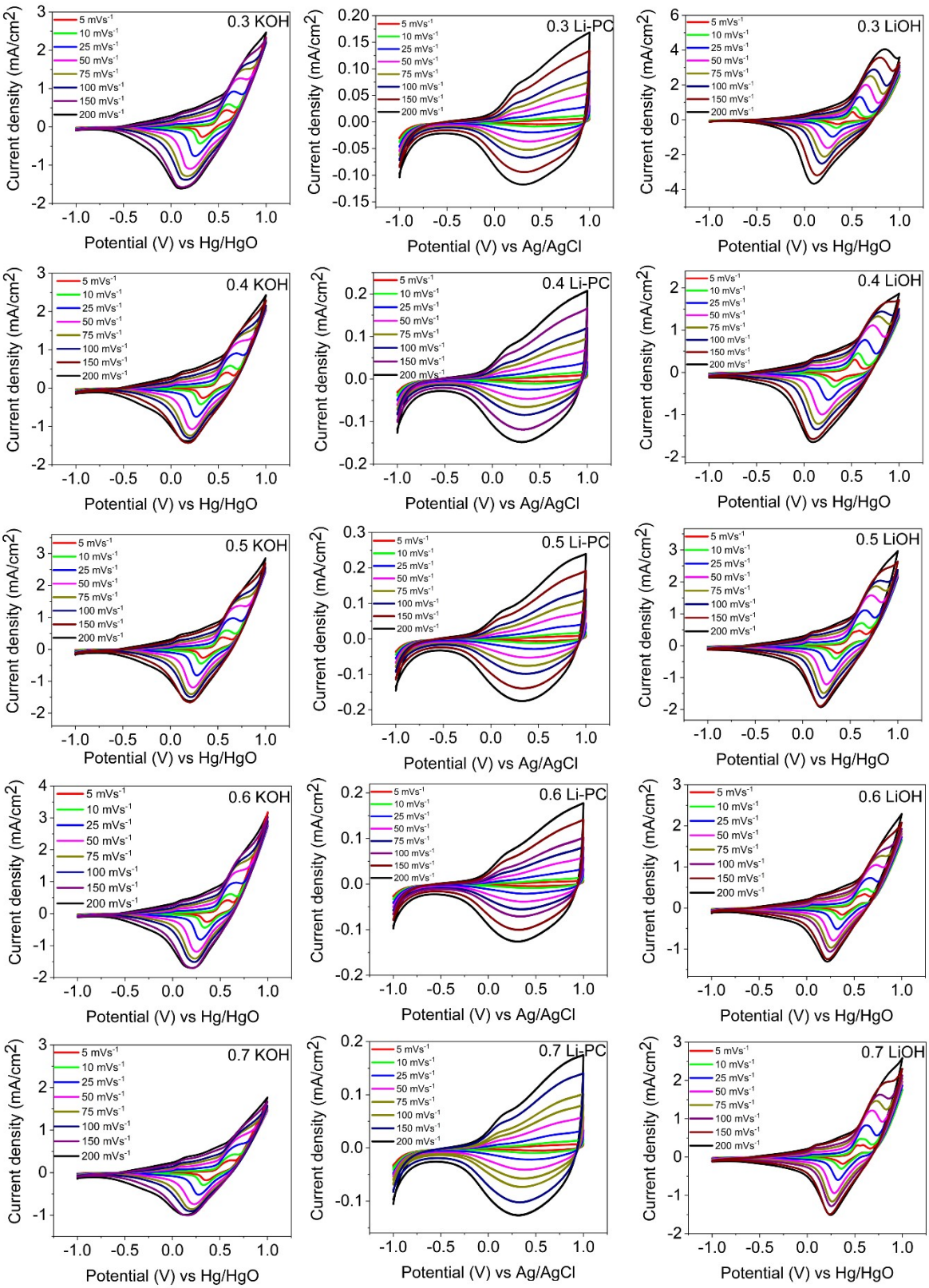

Figure S8 Cyclic voltammetry curves (plot of potential vs current density at different scan rates) for NiO samples (0.3, 0.4, 0.5, 0.6, and 0.7) in different electrolytes (1 M aq. KOH, 1 M $LiClO_4$ in PC, 1 M aq. LiOH), image code consists of two words, first is the sample name followed by electrolyte used.

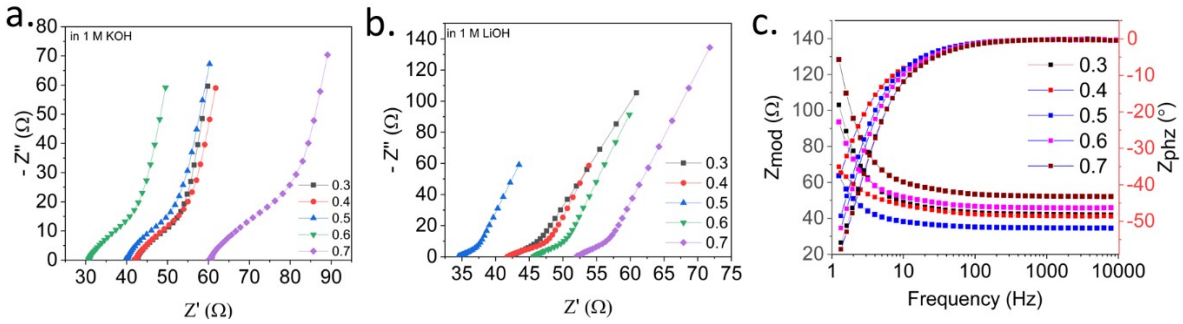

Figure S9 Nyquist plot a) in 1 M KOH, b) in 1 M LiOH, c) Bode plot for NiO films in LiOH.

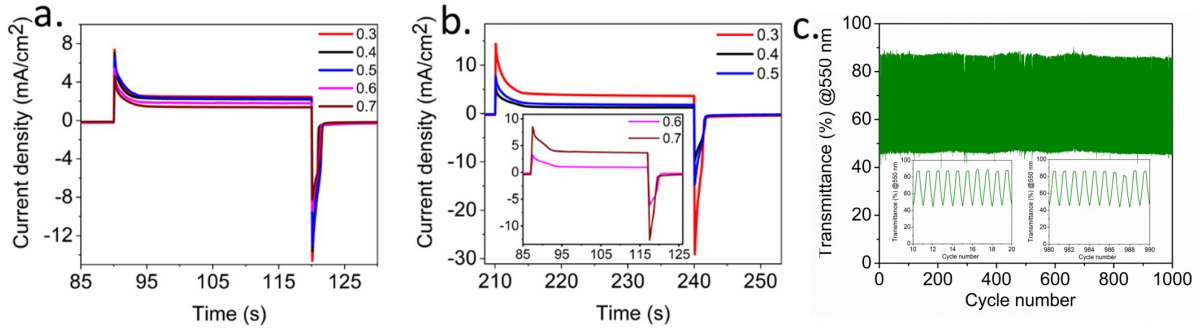

Figure S10 Chronoamperometric curves for NiO films in a) 1 M LiOH and b) 1 M KOH electrolytes c) Cyclic stability of the NiO film (0.4) in terms of transmittance with time, at 550 nm and and insets show the transmittance modulation at selected intervals.

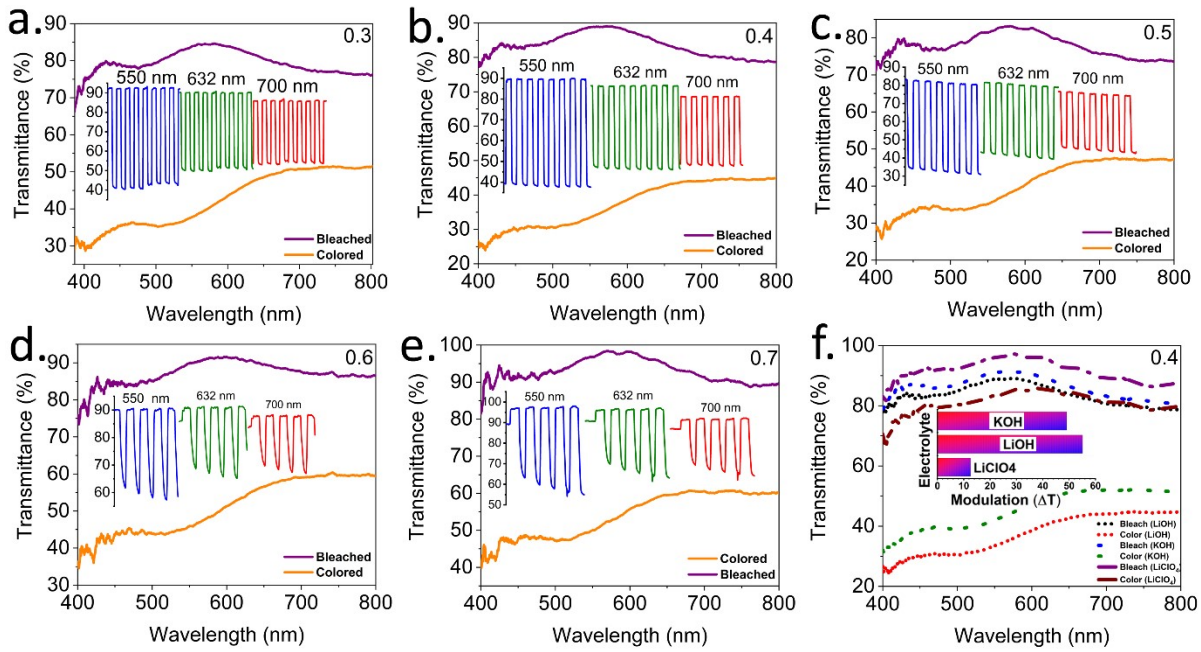

Figure S11 In-situ transmittance plot (wavelength vs transmittance) showing the colored/bleached states for various NiO films a) 0.3, b) 0.4, c) 0.5, d) 0.6 e) 0.7, f) Comparison of bleached and colored transmittance of NiO sample (0.4) in different electrolytes.

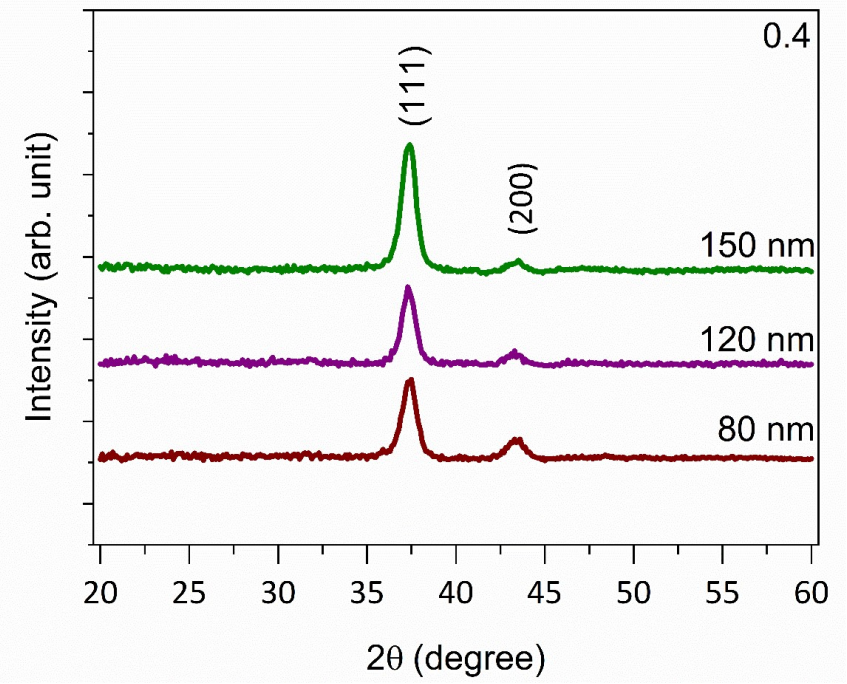

Figure S12 XRD for NiO thin film samples (0.4) with different thicknesses.

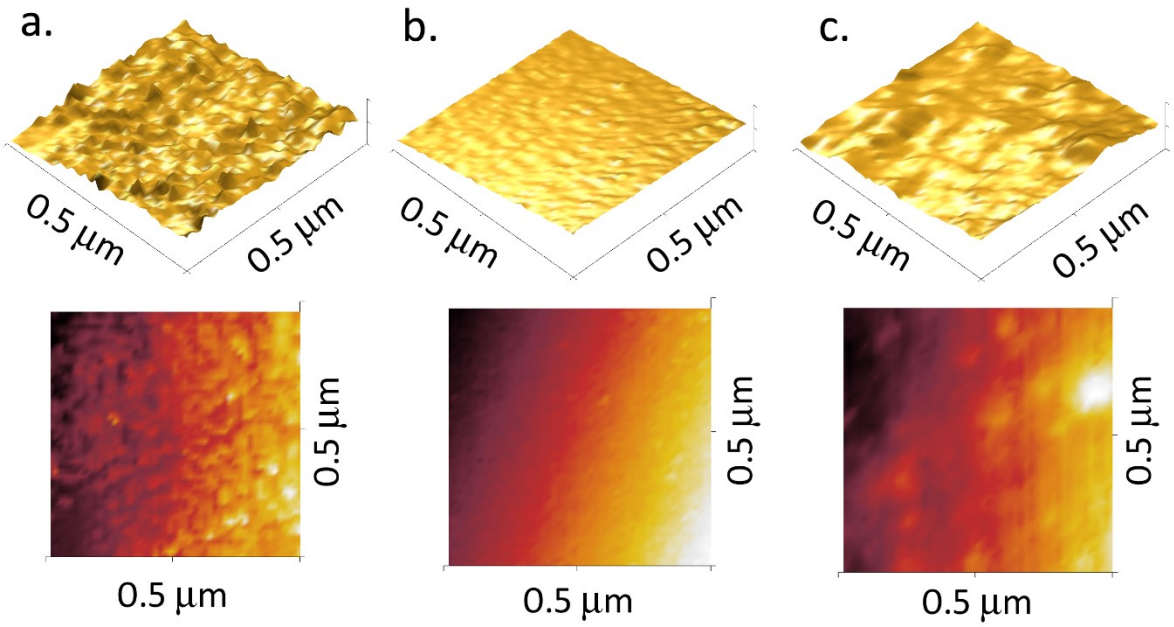

Figure S13 AFM for NiO films (0.4) at different thickness a) 80 nm, b) 120 nm, and c) 150 nm.

Figure S14 Photographs of NiO films (0.4) at different thicknesses

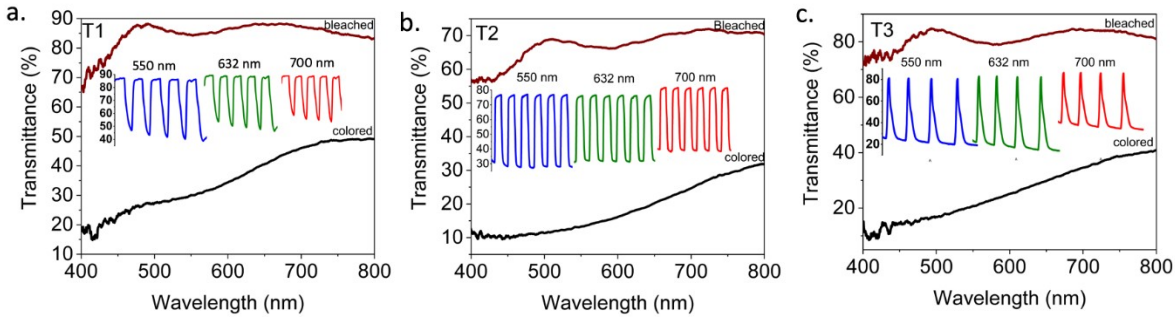

Figure S15 In-situ transmittance curves for 0.4 NiO film at different thicknesses: a) 80 nm, b) 120 nm, c) 150 nm.

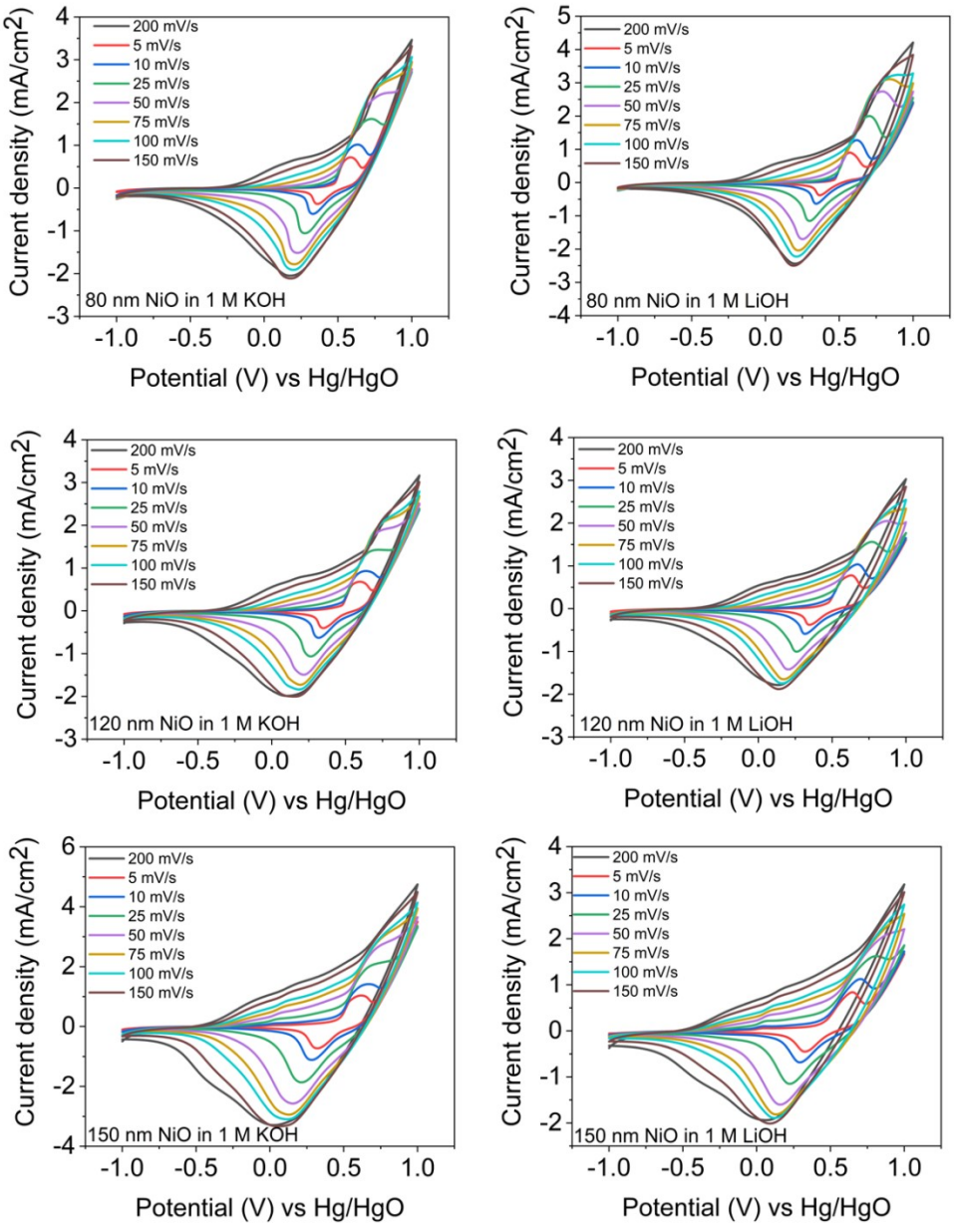

Figure S16 CV curves for NiO films with different thicknesses and in different electrolytes.

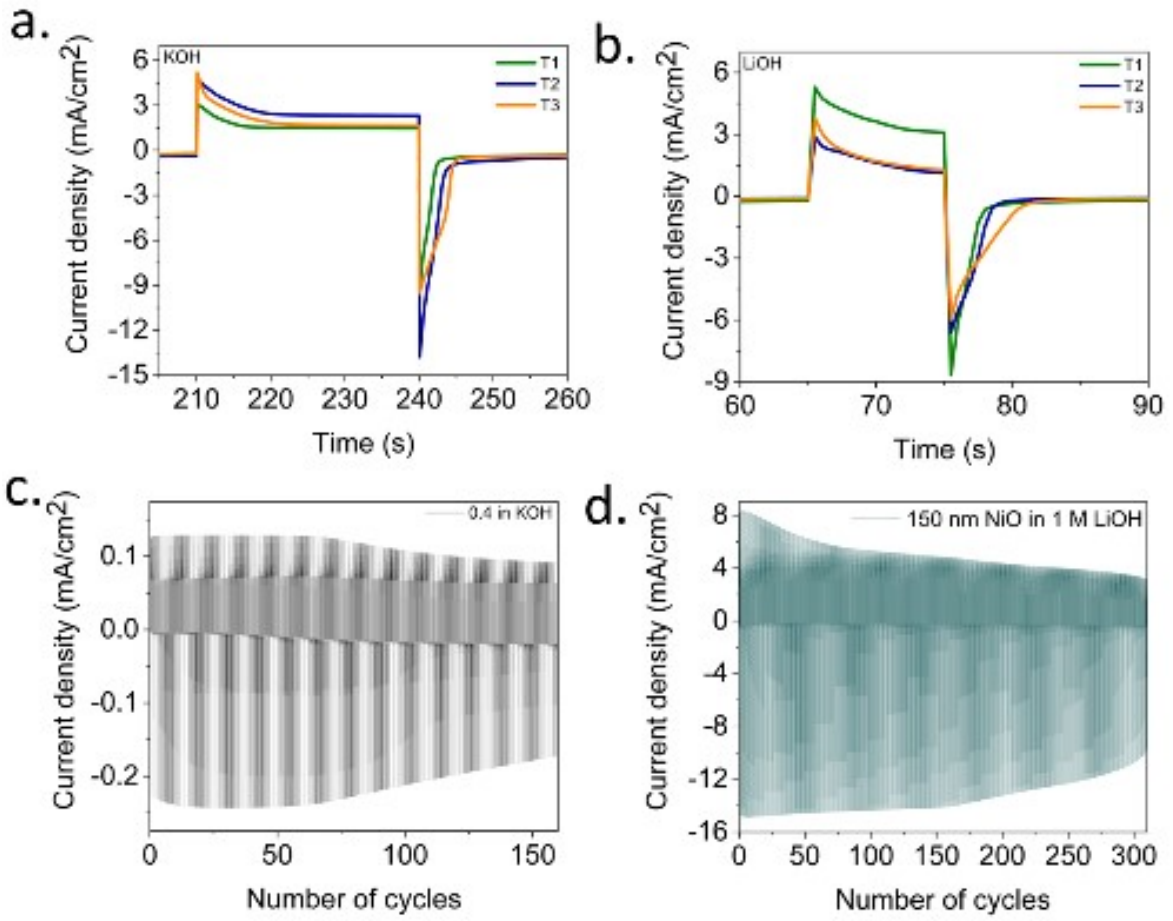

Figure S17 Chronoamperometric curves for different thickness 0.4 NiO thin film samples a) in 1 M KOH, b) 1 M LiOH. c) Cyclic stability of NiO sample (0.4, 50 nm) in 1 M aq. KOH, d) 150 nm NiO in 1 M LiOH.

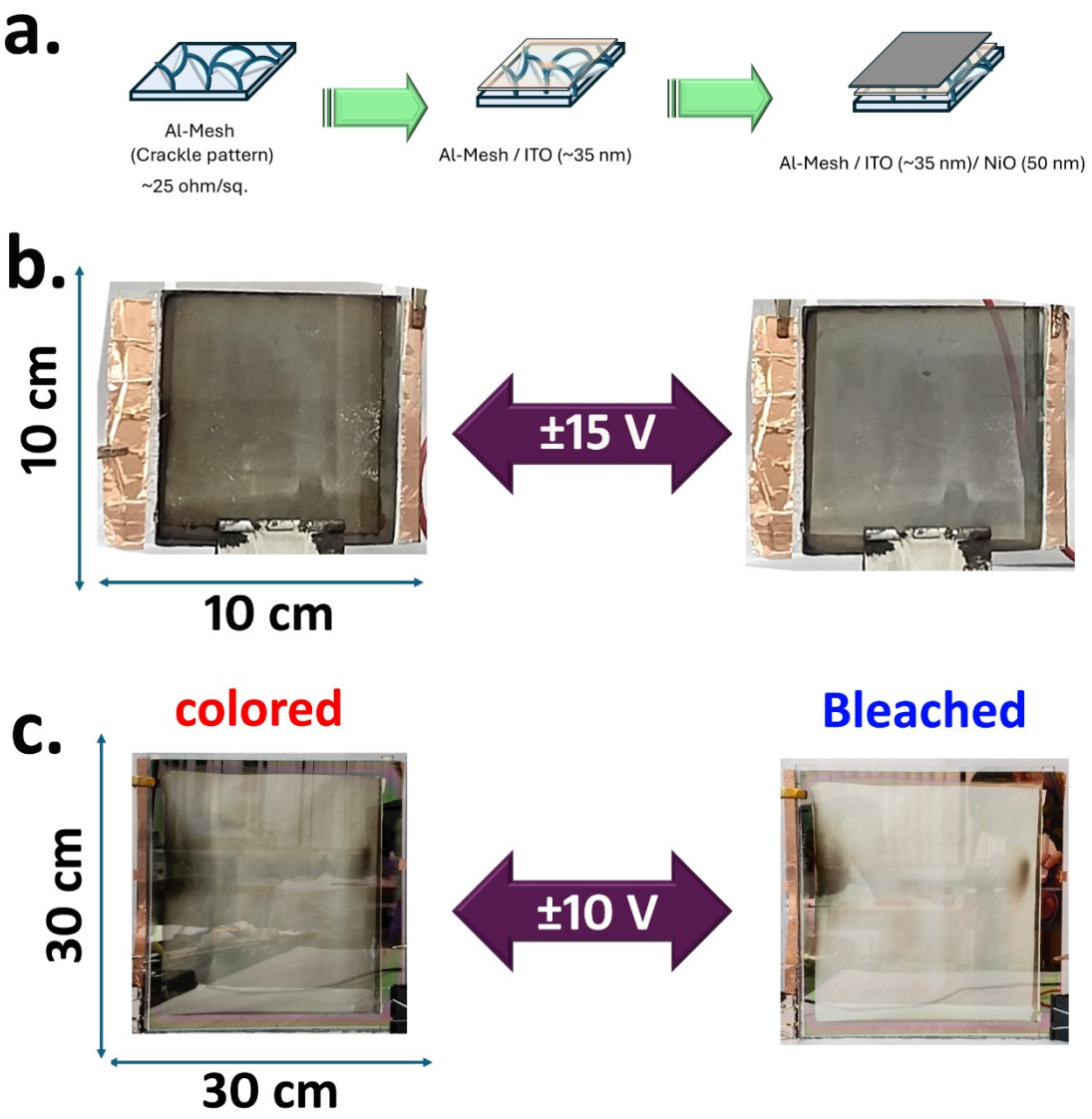

Figure S18 a) Block diagram representing the preparation of Al-mesh/ITO (35 nm)/NiO (50 nm), b) colored and bleached states of Al-mesh/ITO/NiO/aq.LiOH/ITO/Al-mesh (10 cm^2), c) colored and bleached states of 30 cm^2 ITO (250 nm)/NiO (50 nm)/aq.LiOH/ITO (250 nm).