Electronic Supplementary Material (ESI) for Materials Advances.

The discovery of conductive ionic bond in NiO/Ni transparent counter electrode for electrochromic smart windows of ultra-long cycle life

Qi Zhao,[1] Jinkai Wang,[1] Yuanyuan Cui,[1] Xinghui Ai,[1] Zhang Chen,[1] Chuanxiang Cao,[1] Feng Xu,[2]* Yanfeng Gao[1]*

1 School of Materials Science and Engineering, Shanghai University, 99 Shangda Rd., Shanghai, 200444 China

2 Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083 China

*Corresponding author: Feng Xu, Email: xfx315@bjfu.edu.cn; Yanfeng Gao, Email: yfgao@shu.edu.cn

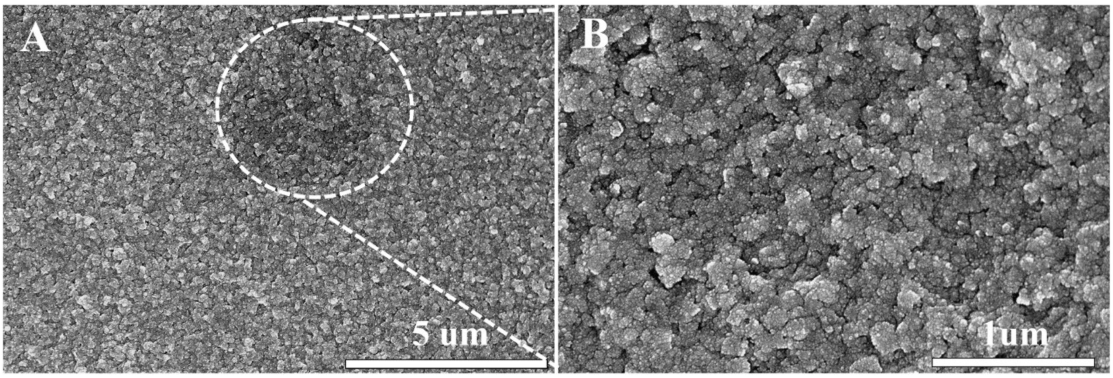

Fig. S1. (A) SEM image of NiO/Ni films with low magnification. (B) Corresponding high magnification.

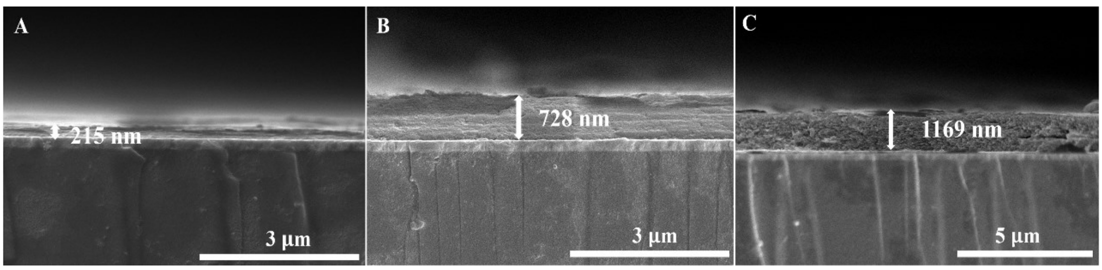

Fig. S2. Cross sectional SEM images of the as-prepared NiO/ Ni-1 (a), NiO/ Ni-2 (b), NiO/ Ni-3 (c) films.

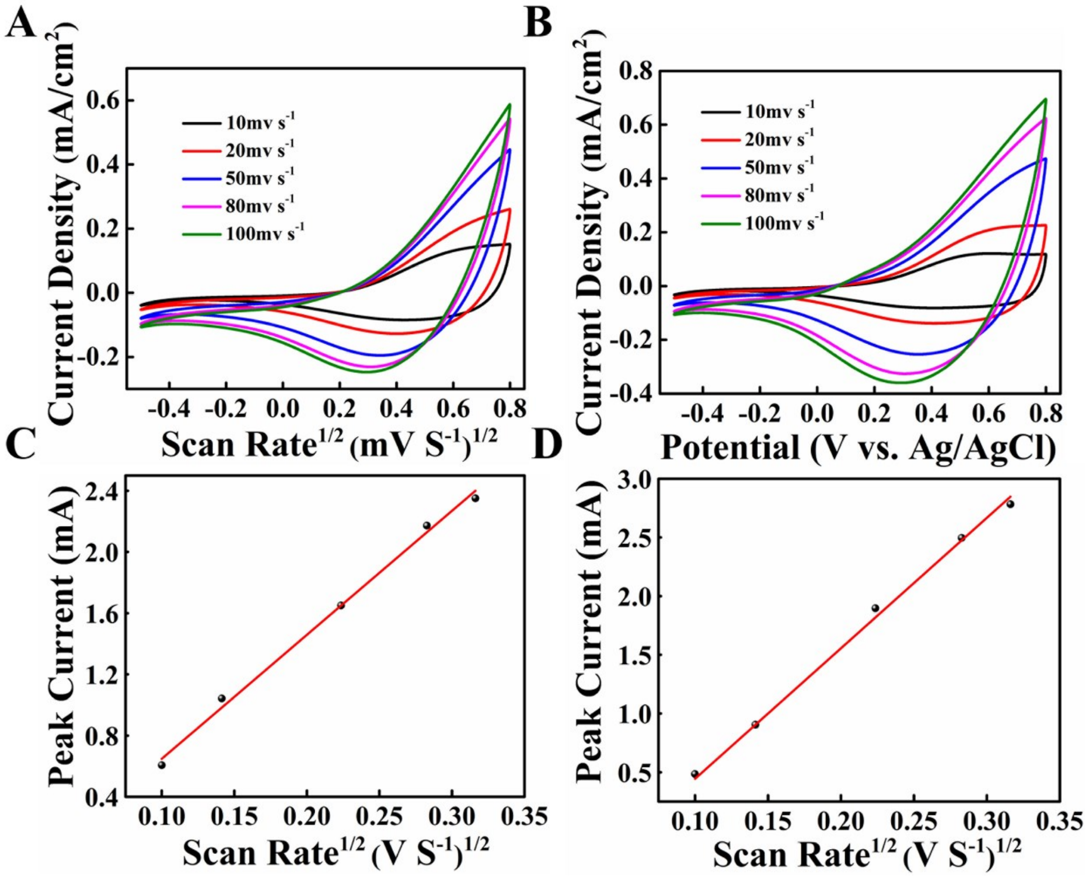

Fig. S3. Cyclic voltammograms of (A) NiO/Ni-2 and (B) NiO/Ni-3 films at different scan rates (10 mV s^{-1},20 mV s^{-1}, 50 mV s^{-1}, 80 mV s^{-1}, 100 mV s^{-1}) in the voltage windows of -0.5V to +0.8V. The ion diffusion coefficient of (C) NiO/Ni-2 and (D) NiO/Ni-3calculated by the Randles-Sevcik law.

S4. Diffusion coefficient.

The ion diffusion coefficient (D) obeys the Randles-Sevcik law:

$$I_p = 2.72\times10^5 \times n^{3/2} \times A \times D^{1/2} \times C_0 \times V^{1/2}$$

where I_p is the peak current (A), *n is* the number of electrons (1), *A* is the working electrode area (cm^2), C_0 is the concentration of electrolyte ($mol\ cm^{-3}$) and *V* is the scan rate ($mV\ s^{-1}$).

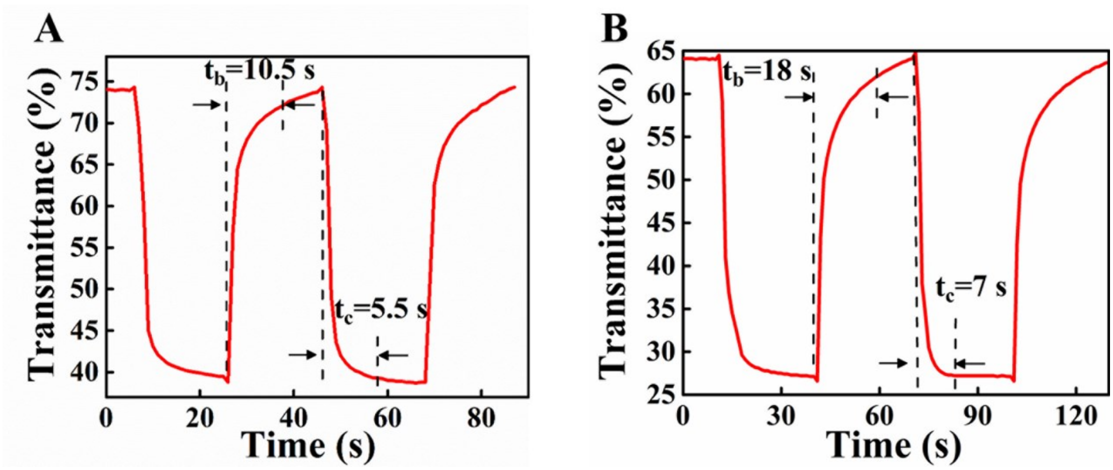

Fig. S5. Real-time transmittance spectra at 550 nm in the -0.5/+0.8 V voltage window (with time interval of 20 s and 30 s for NiO/ Ni-2 (A) and NiO/ Ni-3 (B), respectively).

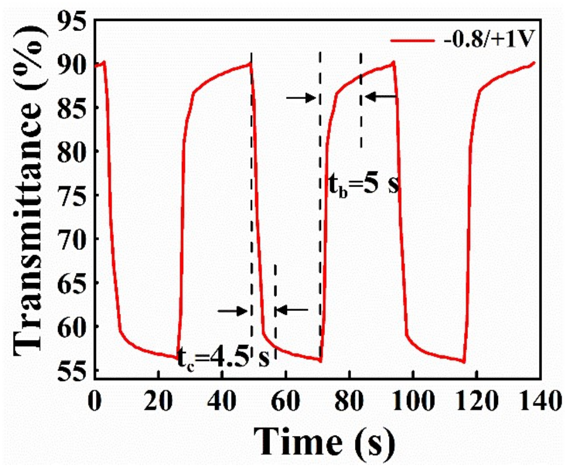

Fig. S6. Real-time transmittance spectra at 550 nm in the -0.8/+1 V voltage window for NiO/Ni-1 flims.

S7. The calculation of coloration efficiency (CE)

It can be calculated by the following equation:

$$CE = \triangle OD/\triangle Q = [\log (T_b/T_c)]/ (Q/A)$$

where A is the surface area, and T_b and T_c refer to the transmittance of film in the bleached and colored states, respectively.

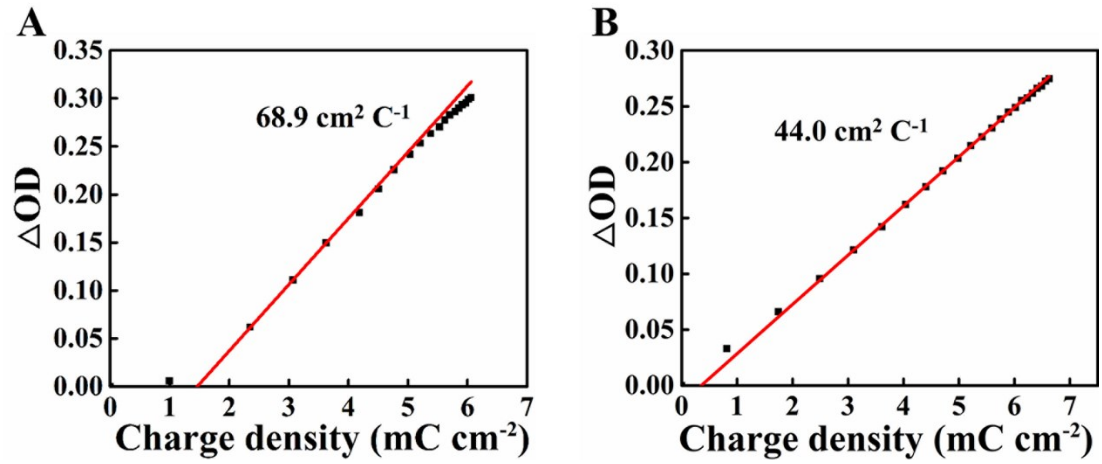

Fig. S8. Changes in optical density (at 550nm) with respect to the injected charge density for NiO/ Ni-2 (A) and NiO/ Ni-3 (B).

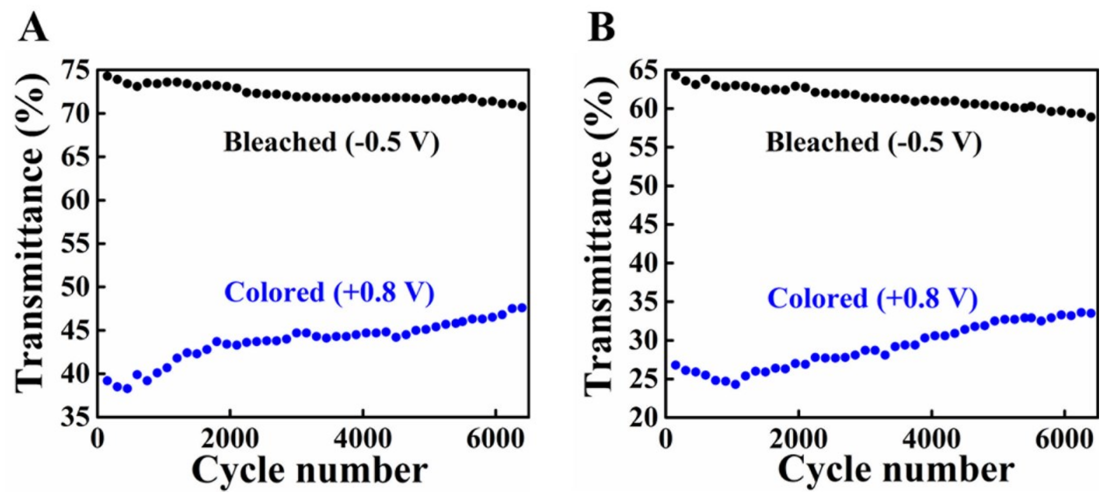

Fig. S9. Cycle performance recorded in situ changes of transmittance at 550 nm for the samples of NiO/ Ni-2 (A) and NiO/Ni-3 (B).

Table S1. Other types of electrochromic films from literature

Materials	**Film preparation method**	**Cycle Times**
WO_3 (nanowire)[1]	Hydrothermal	1000
WO_3 (mesoporous)[2]	Sputtering	2000
WO_3 (quantum dots)[3]	Spin-coating	50
$W_{18}O_{49}$ [4]	Spin-coating	2000
WO_3/PEDOT[5]	Inkjet-printing	1000
TiO_{2-x}[6]	Spin-coating	2000
PANI[7]	Electrodeposition	500
P3HT[8]	Roll-to roll	2000

Table S2 Summary of the EC properties obtained from all the samples at 550 nm, including transmittance modulation (△T), coloration time (t_c), bleaching time (t_b) and coloration efficiency (CE), and T_b represents the transmittance in bleached states.

Samples	**Cycle Times**	**T_b (%)**	**△T (%)**	**t_c (s)**	**t_b (s)**	**CE (cm^2 C^{-1})**
NiO/Ni-1	10000 (retain 87.0%)	90.1	32.2	4.5	5	88.1
NiO/Ni-2	6400 (retain 66.1%)	74.3	35.5	10.5	5.5	68.9
NiO/Ni-3	6400 (retain 67.6%)	64.5	37.9	18	7	44.0

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