Electronic Supplementary Information

Regulation of carbon content in MOF-derived hierarchical-porous NiO@C films for high-performance electrochromic

Hao Liang,[a] Ran Li,[a] Ce Li,[c] Chengyi Hou,*[a] Yaogang Li,*[b] Qinghong Zhang[b] and Hongzhi Wang[a]

[a.] *State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China. E-mail: hcy@dhu.edu.cn*

[b.] *Engineering Research Center of Advanced Glasses Manufacturing Technology, Ministry of Education, Donghua University, Shanghai 201620, P. R. China. E-mail: yaogang_li@dhu.edu.cn*

[c.] *College of Mechanical Engineering, Donghua University, Shanghai 201620, P. R. China.*

Keywords: electrochromic, metal-organic framework, nickel oxide, thermolysis, carbon

Contents

Supplementary discussion

S1. Thermogravimetric analysis：

As shown in Fig. S1, the TGA trace of Ni@C shows a trend of increases initially and decreases afterwards. The weight gain from 290 °C to 390 °C owing to the process of metal oxidation; The followed weight loss after 390 °C because of the carbon decomposition.

For Ni-MOF: The first weight loss (about 5%) before 200 °C due to the volatilization of embedded solvent molecules; Then the second weight loss (about 50%) from 340 °C to 390 °C related to the rapid decomposition of Ni-MOF.

S2. Calculation process of D_w and D_{CV}:

Calculation process for D_w according to the equation S1 (Fick's law).

$$D_w = R^2T^2 / 2S^2n^4F^4C^2\sigma^2 \quad \text{(S1)}$$

Where R is the gas constant, T is the absolute temperature, S is the effective working area, F is the Faraday constant, n is the number of electrons, C is molar concentrations of ions and σ represents the Warburg constant.

Calculation process for D_{cv} according to the equation S2 (Randles–Sevcik equation).

$$i_p = 2.687 \times 10^5 \times n^{3/2} \times D_{cv}^{1/2} \times C \times S \times v^{1/2} \quad \text{(S2)}$$

In the above equation, i_p is the peak current density, n is the number of electrons, C is the concentration of active OH^- ions, S is the surface area and v is the potential sweep rate.

Supplementary Figures

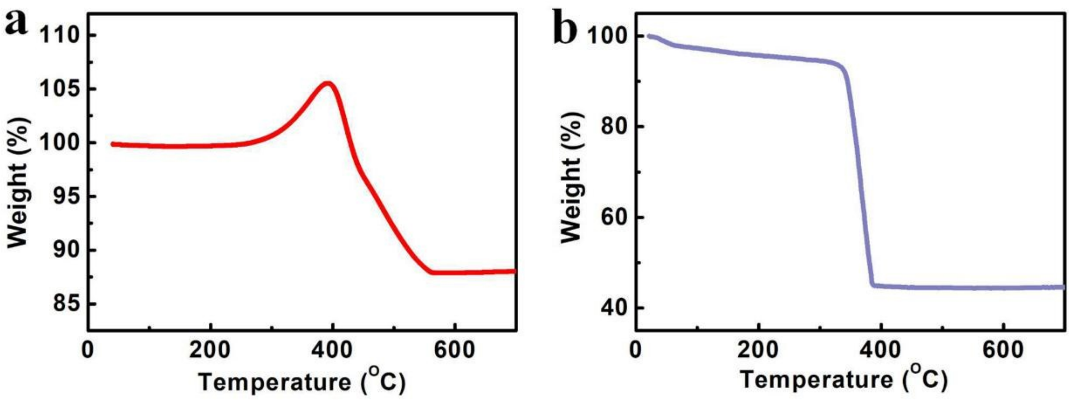

Fig. S1 TGA traces of (a) Ni@C powder, (b) Ni-MOF powder at the heating rate of 10 °C/ min in air atmosphere.

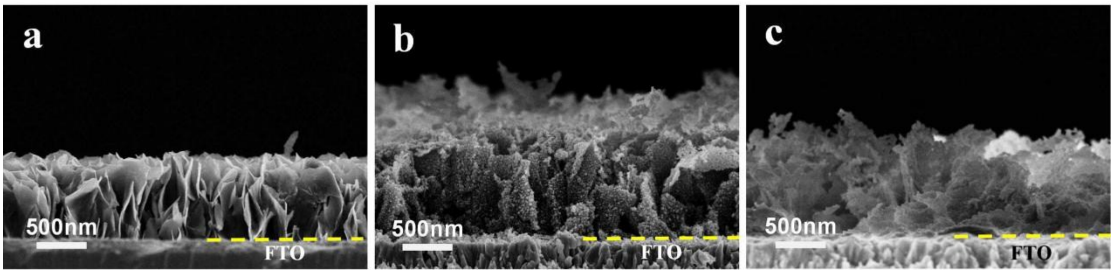

Fig. S2 Cross-sectional SEM images of (a) Ni-MOF, (b) Ni@C and (c) hierarchical-porous NiO@C layer on FTO glass.

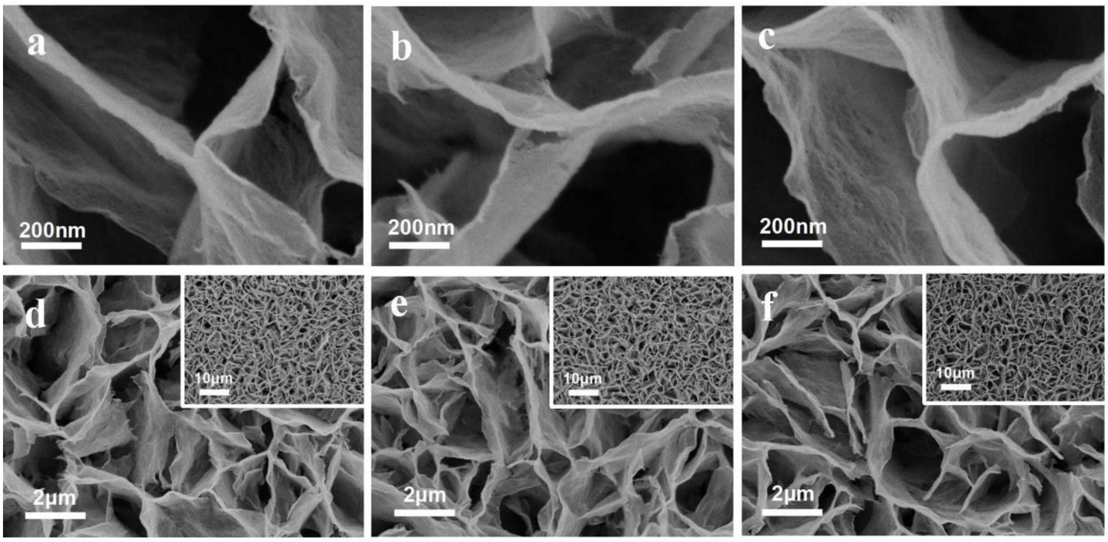

Fig. S3 SEM images of (a, d) A-10, (b, e) A-30 and (c, f) A-60 films.

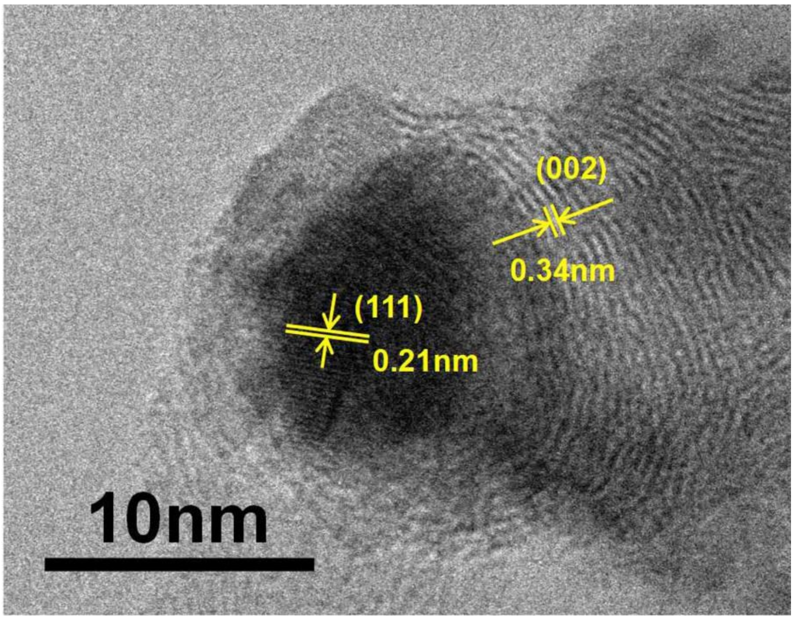

Fig. S4 HRTEM image of Ni@C.

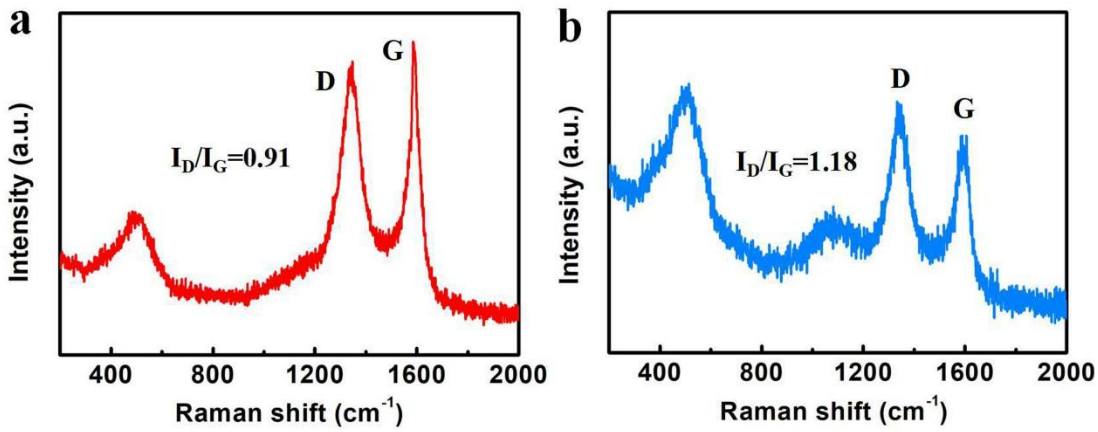

Fig. S5 Raman spectrum of (a) Ni@C and (b) hierarchical-porous NiO@C.

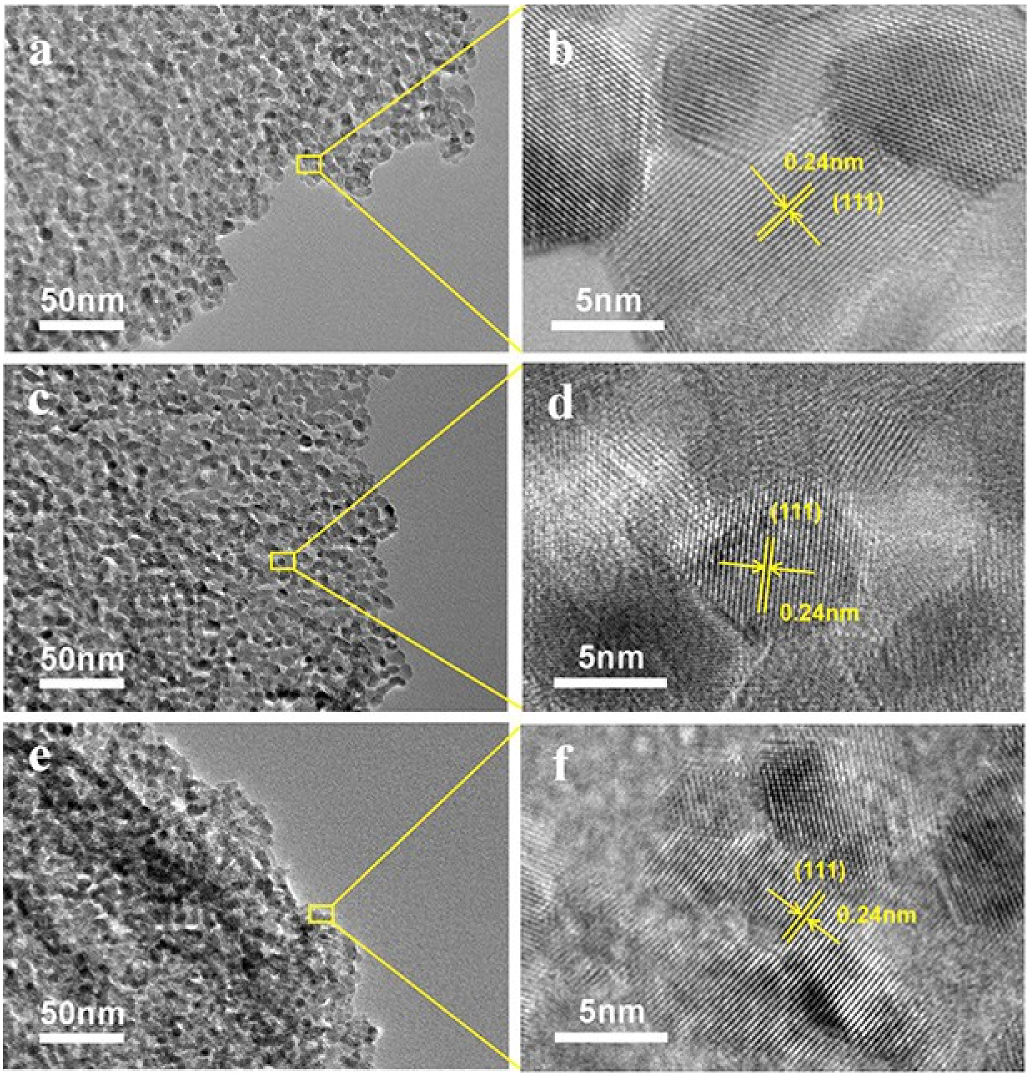

Fig. S6 TEM images of (a, b) A-10, (c, d) A-30 and (e, f) A-60.

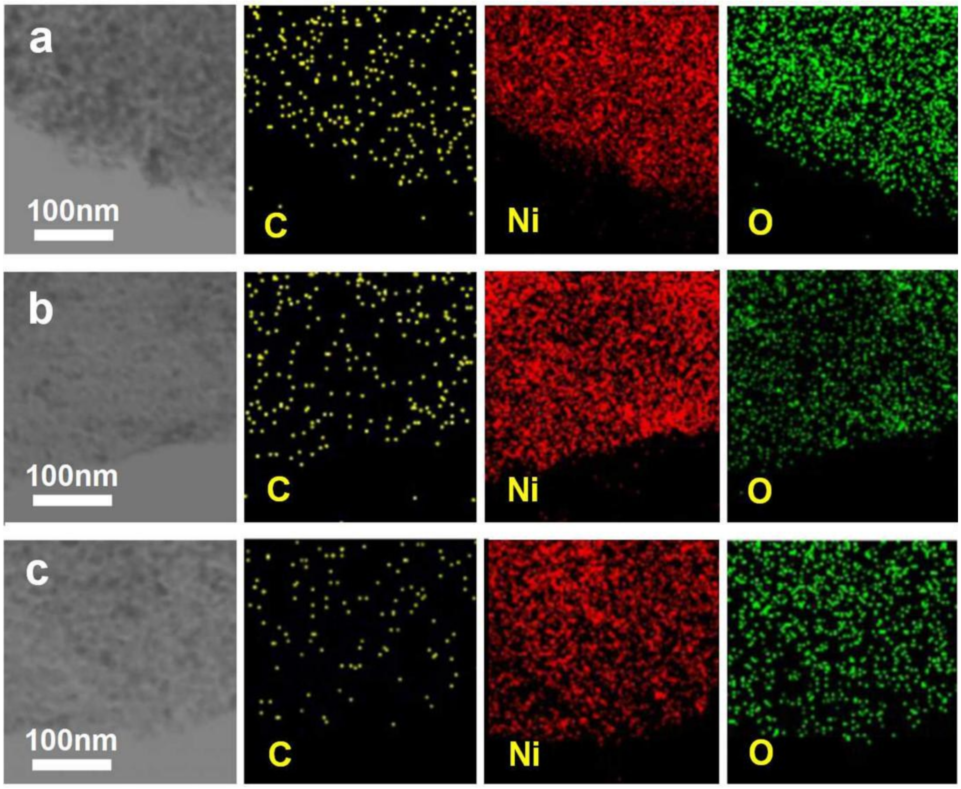

Fig. S7 Elemental mapping of (a) A-10, (b) A-30 and (c) A-60.

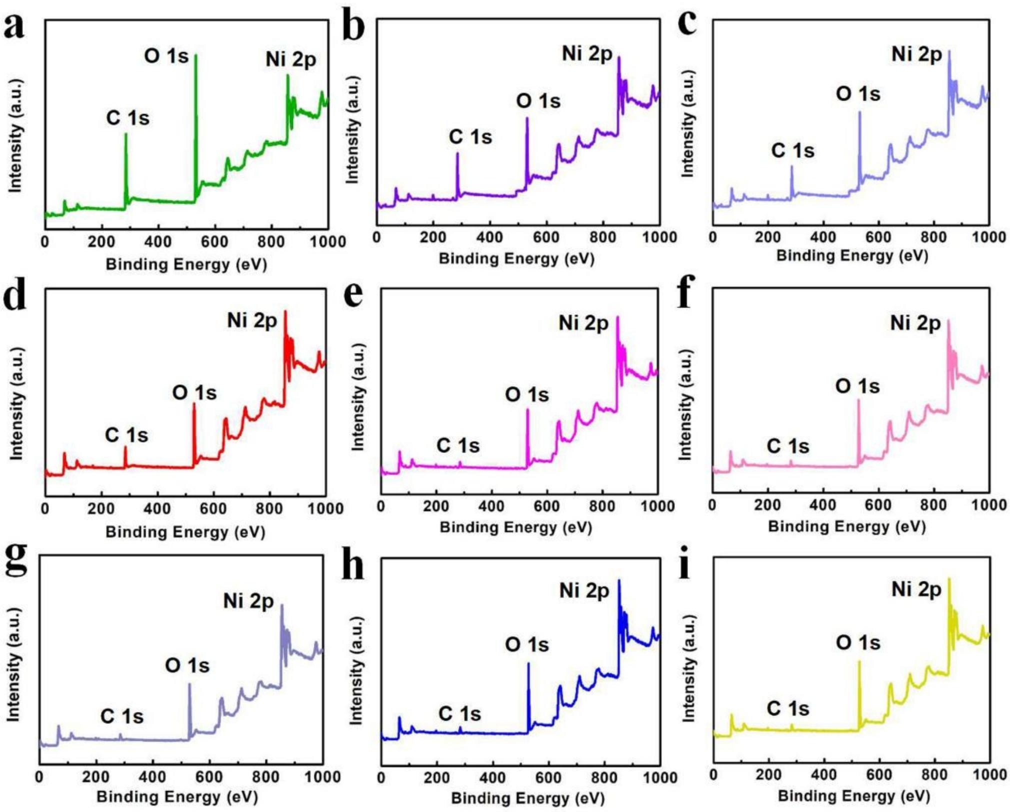

Fig. S8 X-ray photoelectron spectroscopy (XPS) of (a) PTA-Ni-MOF; (b) HA-15; (c) HA-20; (d) HA-25; (e) HA-30; (f) HA-60; (g) A-10; (h) A-30 and (i) A-60.

Fig. S9 Digital photographs of HA-25 film electrode at (a) bleached state and (b) colored state.

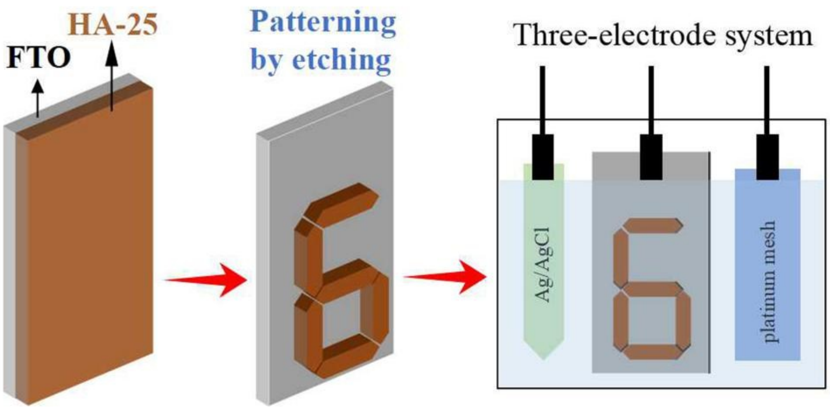

Fig. S10 Schematic illustration for HA-25-based number "6" film.

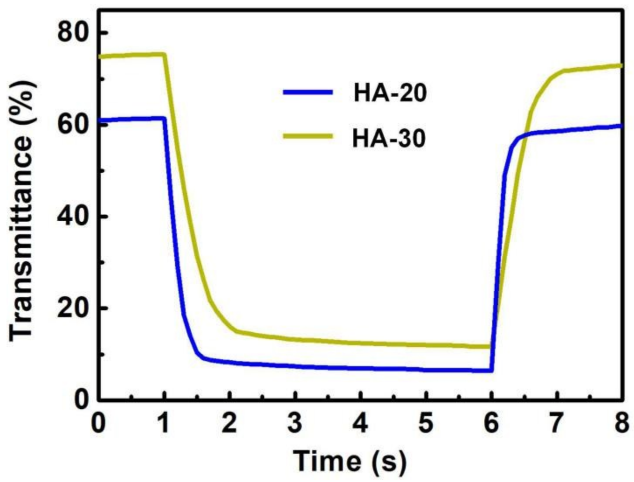

Fig. S11 In situ transmittance responses (at 550 nm) for HA-20 and HA-30 films in 1 M KOH solution measured between 0 and 0.6 V bias.

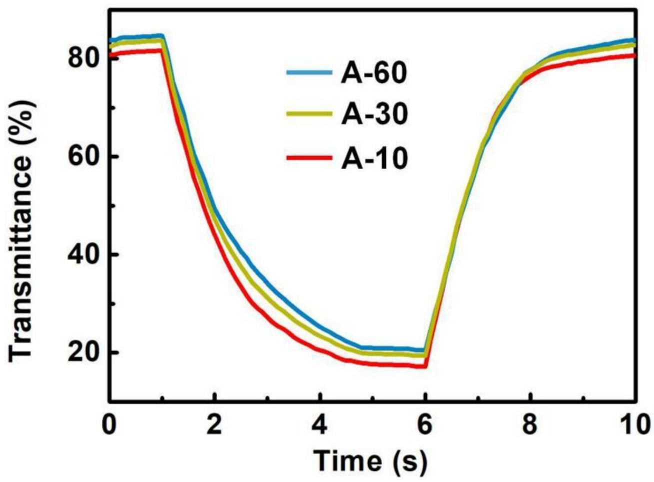

Fig. S12 In situ transmittance responses (at 550 nm) for A-10, A-30 and A-60 films in 1 M KOH solution measured between 0 and 0.6 V bias.

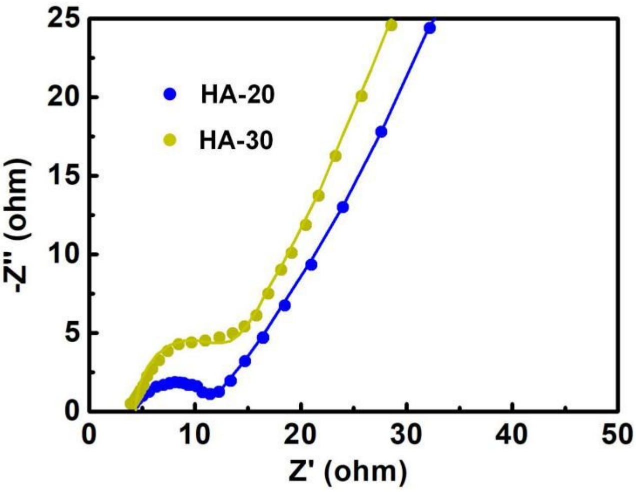

Fig. S13 The Nyquist plots and corresponding simulation results (fitting lines) for HA-20 and HA-30 films measured in 1 M KOH solution.

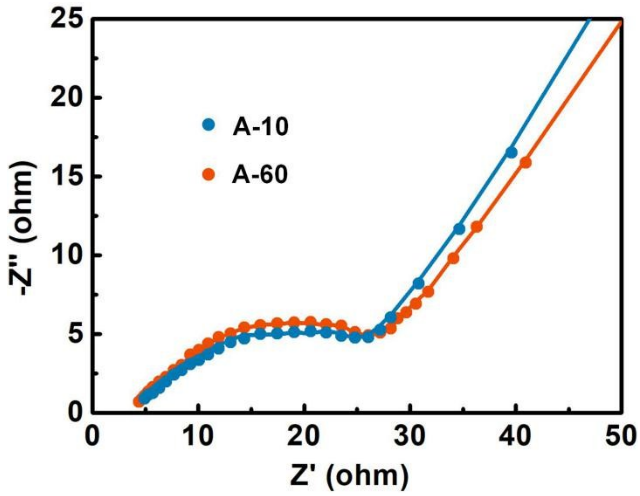

Fig. S14 The Nyquist plots and corresponding simulation results (fitting lines) for A-10 and A-30 films measured in 1 M KOH solution.

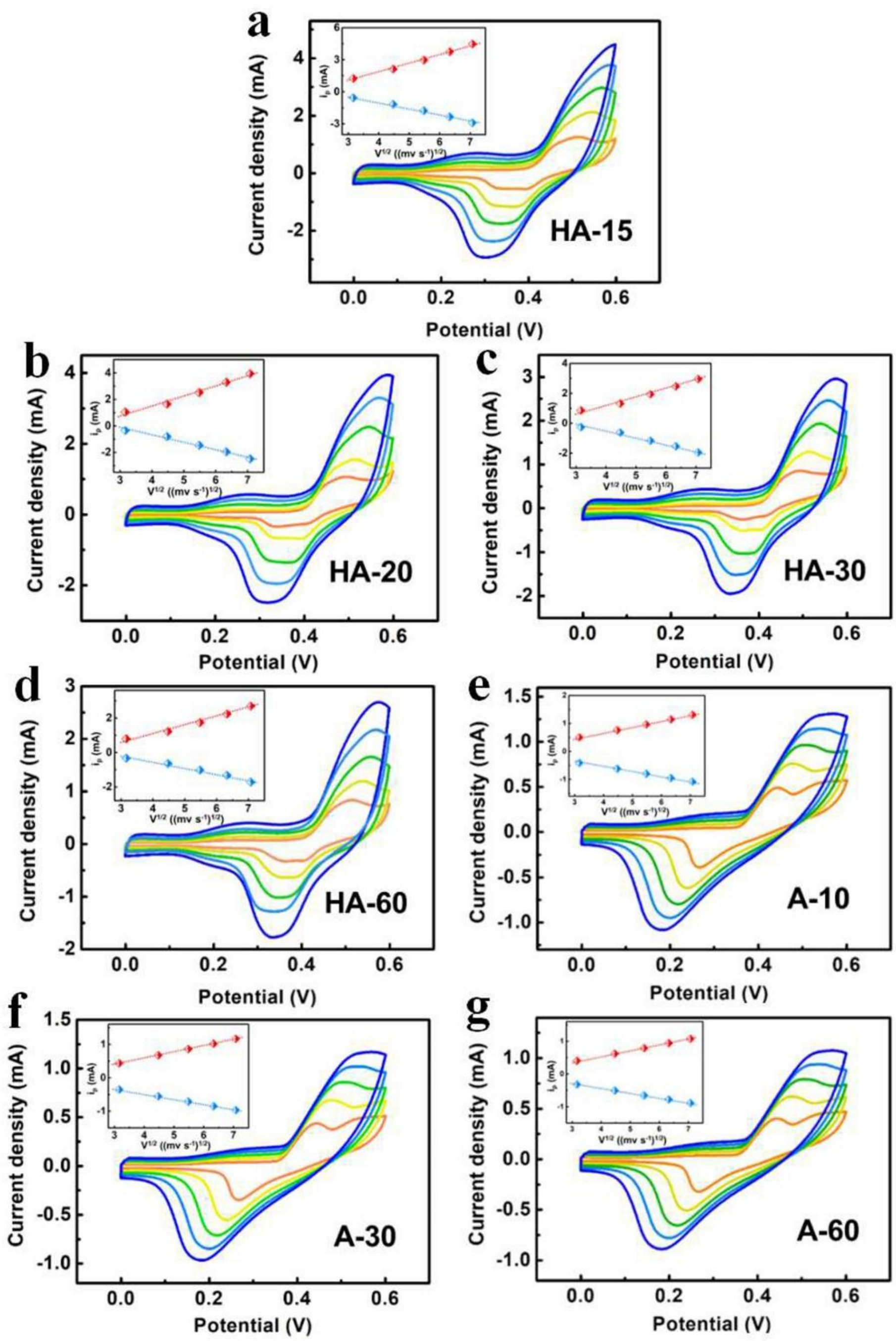

Fig. S15 Cyclic voltammogram curves of (a) HA-15; (b) HA-20; (c) HA-30; (d) HA-60; (e) A-10; (f) A-30 and (g) A-60 films measured in 1M KOH solution. Scan rates: 10, 20, 30, 40 and 50 mV/s.

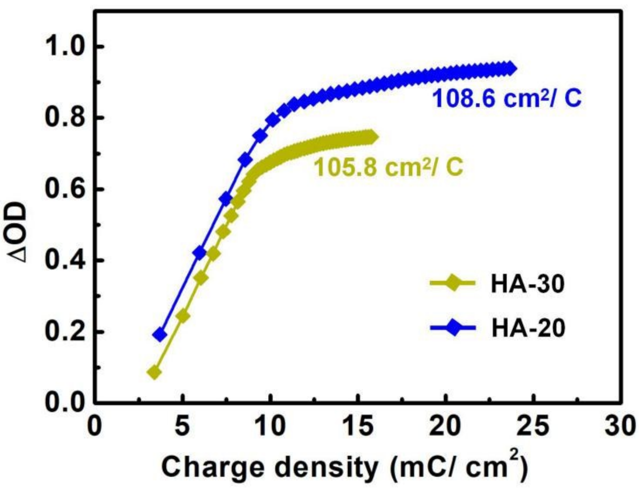

Fig. S16 Coloration efficiency of HA-20 and HA-30 films in 1 M KOH solution.

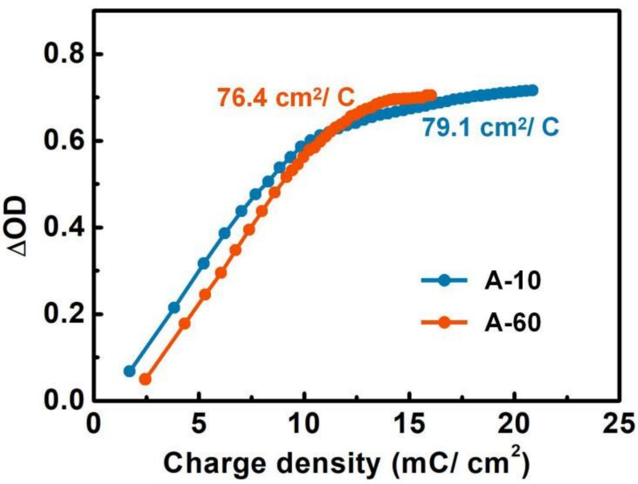

Fig. S17 Coloration efficiency of A-10 and A-30 films in 1 M KOH solution.

Supplementary Tables

Table S1 Percentage of each element of different NiO@C films from X-ray photoelectron spectroscopy (XPS).

Films	Atomic% (C)	Atomic% (O)	Atomic% (Ni)
HA-15	29.74	39.51	30.75
HA-20	19.15	43.59	37.26
HA-25	11.42	46.44	42.13
HA-30	6.01	47.97	46.02
HA-60	3.96	48.54	47.5
A-10	5.05	47.36	47.59
A-30	4.42	48.03	47.55
A-60	3.77	48.62	47.61

Table S2 Fitted parameters according to electrochemical impedance spectroscopy of different NiO@C films.

Films	R_s (Ω)	R_{ct} (Ω)	σ (Ω×s$^{-1/2}$)
HA-15	4.03	4.24	38.65
HA-20	4.11	6.82	42.50
HA-25	4.26	7.59	45.90
HA-30	4.40	12.51	48.16
HA-60	4.49	15.36	51.09

A-10	4.67	42.65	113.53
A-30	4.75	45.14	118.69
A-60	4.81	45.78	123.04

Table S3 Comparison of D_w of different NiO@C films calculated from Fick's law and D_{cv} calculated from Randles–Sevcik equation.

Films	D_w calculated from Fick's law (cm^2/s)	D_{cv} calculated from R–S equation (cm^2/s)
HA-15	1.85×10^{-7}	$1.37\times10^{-7}/2.94\times10^{-8}$
HA-20	1.53×10^{-7}	$1.08\times10^{-7}/2.55\times10^{-8}$
HA-25	1.31×10^{-7}	$9.72\times10^{-8}/1.76\times10^{-8}$
HA-30	1.19×10^{-7}	$9.55\times10^{-8}/1.57\times10^{-8}$
HA-60	1.06×10^{-7}	$9.08\times10^{-8}/1.44\times10^{-8}$
A-10	2.14×10^{-8}	$1.21\times10^{-8}/7.73\times10^{-9}$
A-30	1.97×10^{-8}	$9.93\times10^{-9}/7.12\times10^{-9}$
A-60	1.82×10^{-8}	$9.64\times10^{-9}/6.89\times10^{-9}$

Table S4 Comparison of EC performances of NiO and other inorganic EC materials.

EC materials	Coloring/bleaching time	CE	Cycling stability	References
NiO	7.2/6.7 s	76 cm^2 C^{-1}	2200 cycles	1

NiO	~5 s	88 $cm^2\ C^{-1}$	NA	2
NiO	< 0.1 s	~45 $cm^2\ C^{-1}$	1000 cycles	3
WO_3	5.8/1 s	51.4 $cm^2\ C^{-1}$	81.6% after 1000 cycles	4
WO_3	0.93/1.27s	71.8 $cm^2\ C^{-1}$	450 cycles	5
WO_{3-X}	0.9/1 s	154 $cm^2\ C^{-1}$	NA	6
Ni/Mg-NDISA	~7 s	~100 $cm^2\ C^{-1}$	NA	7
This work	**0.46/0.25 s**	**113.5 $cm^2\ C^{-1}$**	**90.1% after 20000 cycles**	

Supplementary Movies

Movie S1 HA-25 film measured in three electrode system powered by electrochemical workstation.

Movie S2 Digital display device powered by commercial batteries.

Supplementary References

1 G.-F. Cai, J.-P. Tu, J. Zhang, Y.-J. Mai, Y. Lu, C.-D. Gu and X.-L. Wang, *Nanoscale,* 2012, **4**, 5724-5730.
2 D. S. Dalavi, R. S. Devan, R. S. Patil, Y. R. Ma, M. G. Kang, J. H. Kim and P. S. Patil, *J. Mater. Chem. A.,* 2013, **1**, 1035-1039.
3 M. R. J. Scherer and U. Steiner, *Nano Lett*., 2013, **13**, 3005-3010.
4 B.-R. Koo and H.-J. Ahn, *Nanoscale,* 2017, **9**, 17788-17793.
5 Z. Q. Xie, Q. Q. Zhang, Q. Q. Liu, J. Zhai and X. G. Diao, *Thin Solid Films,* 2018, **653**, 188-193.
6 S. Cong, Y. Y. Tian, Q. W. Li, Z. G. Zhao, F. X. Geng, *Adv. Mater*., 2014, **26**, 4260-4267.
7 K. AlKaabi, C. R. Wade and M. Dincă, *Chem*., 2016, **1**, 264-272.