

Supporting Information

CrN Thin Film Prepared by Reactive DC Magnetron Sputtering for Symmetric Supercapacitors

Binbin Wei,^a Hanfeng Liang,^{*a,b} Dongfang Zhang,^a Zhengtao Wu,^a Zhengbing Qi,^c and
Zhoucheng Wang^{*a}

^aDepartment of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^bMaterials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

^cCollege of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, China

*E-mails: hanfeng.liang@kaust.edu.sa (H. Liang); zcwang@xmu.edu.cn (Z. Wang)

Calculations

For single electrode

The areal specific capacitance based on GCD curves was calculated from the following equation (1):

$$C_a = I\Delta t / (S \times \Delta U) \quad (1)$$

where C_a (mF cm⁻²) is the areal specific capacitance of the electrode, I (mA) is the discharge current, Δt (s) is the discharge time, ΔU (V) is the potential window, and S (cm²) is the surface area of the working electrode.

The areal specific capacitance based on CV curves was calculated using the following equation (2):

$$C_a = \int_{U_a}^{U_b} I(V)dV / [2 \times v \times S \times (U_b - U_a)] \quad (2)$$

where C_a (mF cm⁻²) is the areal specific capacitance of the electrode, $\int IdV$ is the integrated area of one CV cycle, v (mV s⁻¹) is the potential sweep rate, S (cm²) is the surface area of the working electrode, and U_a (V) and U_b (V) are the lowest and the highest potentials, respectively.

For symmetric supercapacitor device

The areal cell capacitance (C_a , mF cm⁻²) based on GCD curves was calculated according to the following equation (3):

$$C_a = I\Delta t / (S \times \Delta U) \quad (3)$$

Where I (mA) is the discharge current, Δt (s) is the discharge time, ΔU (V) is the potential window, and S (cm²) is the total surface area of both electrodes.

The energy density and power density were concluded by the following equations (4) and (5):

$$E = \frac{1}{2} C_a \times \Delta U^2 \quad (4)$$

$$P = E / \Delta t \quad (5)$$

where E (Wh cm⁻³) is the specific energy density, P (W cm⁻³) is the specific power density, C_a (mF cm⁻³) is the specific capacitance of symmetric supercapacitor device, ΔU (V) is the potential window, and Δt (s) is the discharge time.

Additional Figures and Data

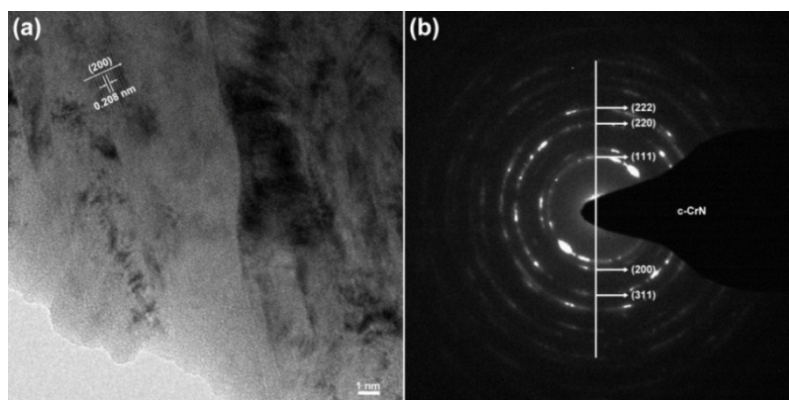


Fig. S1 (a) The HRTEM image and (b) the corresponding SEAD pattern of T5 thin film.

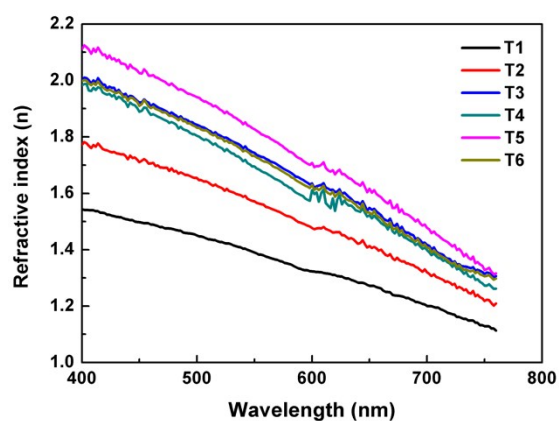


Fig. S2 Refractive index versus the wavelength of the CrN thin films under different pressures.

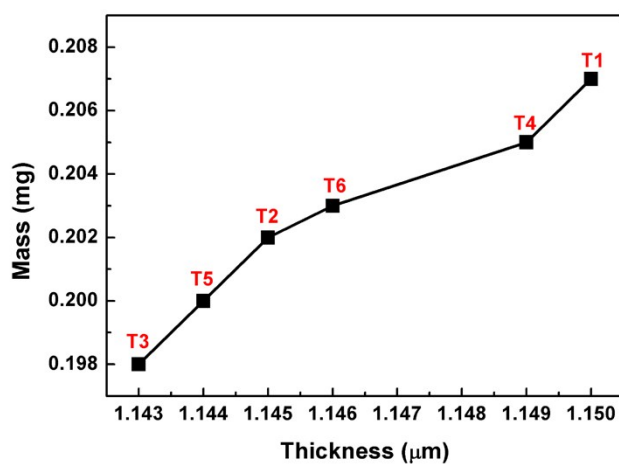


Fig. S3 The mass plotted against the thickness of the CrN thin films fabricated under different pressures.

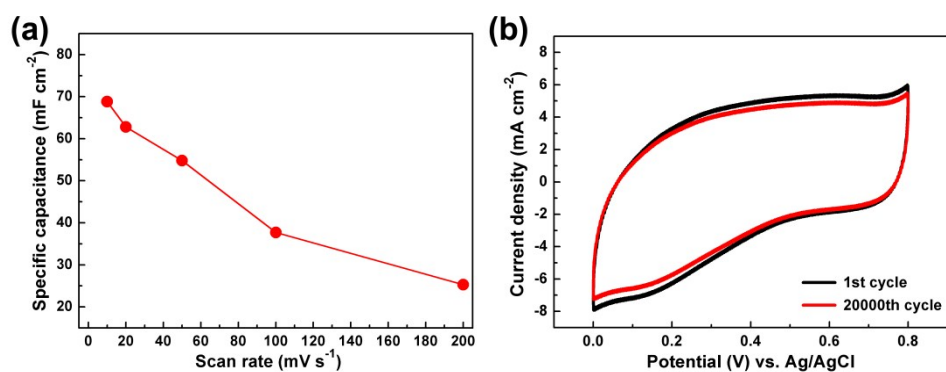


Fig. S4 (a) Specific capacitance as a function of scan rate and (b) CV curves of the 1st and 20000th cycles at a scan rate of 200 mV s⁻¹ of T5 thin film.

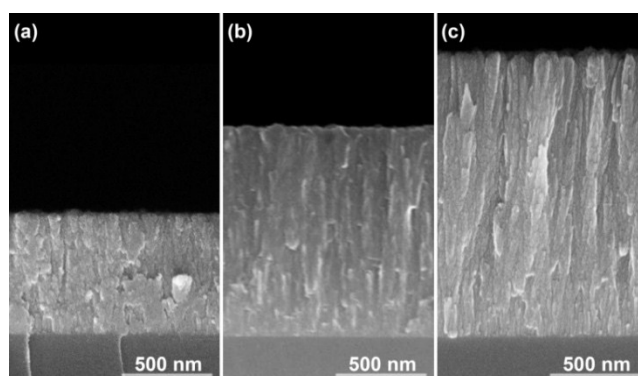


Fig. S5 The cross-sectional SEM images of CrN thin films with different deposition times: (a) 15, (b) 30, and (c) 45 min.

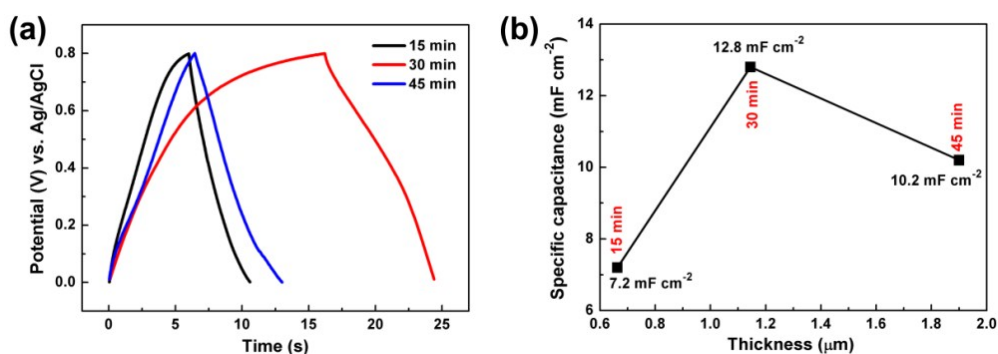


Fig. S6 (a) GCD curves at 1.0 mA cm⁻² and (b) the corresponding areal capacitances of CrN thin films fabricated for different deposition times.

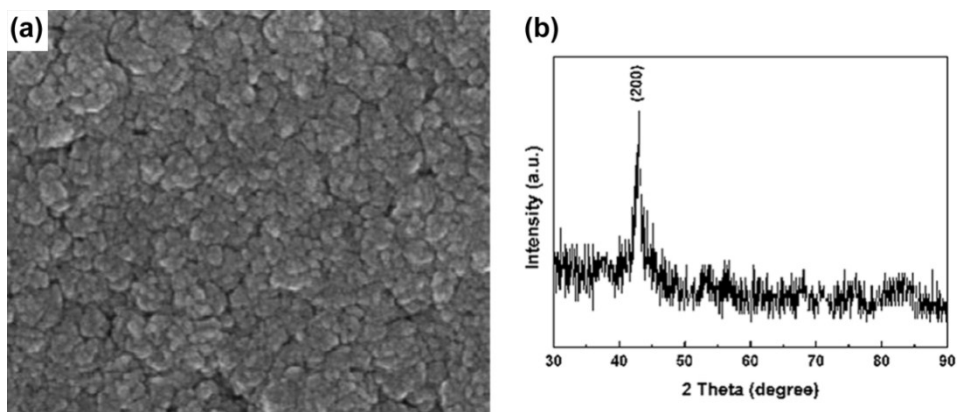


Fig. S7 (a) SEM image and (b) XRD pattern of T5 thin film after 20000 cycles.

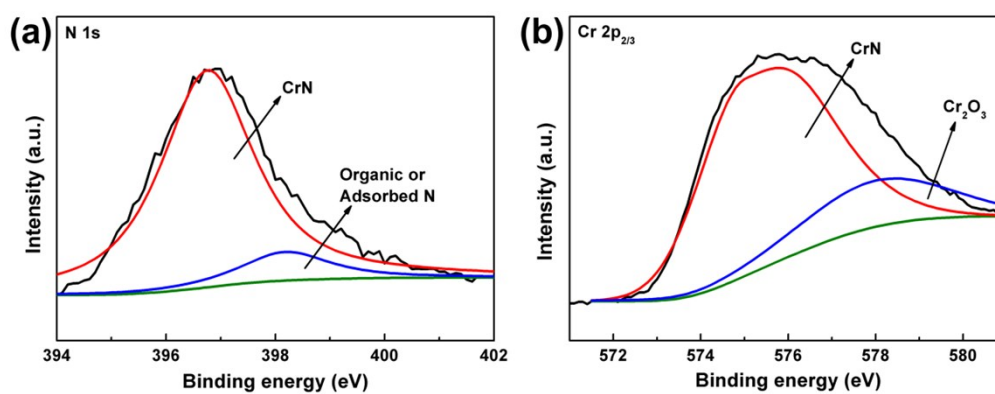


Fig. S8 The N 1s and the Cr 2p_{2/3} high resolution XPS spectra for T5 thin film after 20000 cycles.

Supplementary Tables

Table S1. The thicknesses, mass loading, and gravimetric capacitance of CrN thin films fabricated under different pressures.

Sample	T1	T2	T3	T4	T5	T6
Thickness (μm)	1.150	1.145	1.143	1.149	1.144	1.146
Mass loading (mg cm^{-2})	0.207	0.202	0.198	0.205	0.200	0.203
Gravimetric capacitance (F g^{-1})	20.3	28.7	43.4	48.8	64.0	36.0

Table S2. The areal specific capacitance of CrN thin films.

Sample	T1	T2	T3	T4	T5	T6
Discharge time (s)	2.7	3.7	5.5	6.4	8.2	4.7
Areal specific capacitance (mF cm^{-2})	4.2	5.8	8.6	10.0	12.8	7.3

Table S3. The electrical conductivity of CrN thin films.

Sample	T1	T2	T3	T4	T5	T6
Electrical conductivity (S cm^{-1})	2008	2063	4961	5068	6202	2485

Table S4. The capacitance of T5 thin film at different scan rates.

Scan rate (mV s^{-1})	10	20	50	100	200
Integrated area ($\times 10^{-4}$)	8.8	16.1	35.1	48.3	64.8
Areal specific capacitance (mF cm^{-2})	68.8	62.8	54.8	37.7	25.3
Volumetric capacitance (F cm^{-3})	601.4	549.0	479.0	329.5	221.2
Gravimetric capacitance (F g^{-1})	343.7	313.7	273.7	188.3	126.4

Table S5. Comparison of the electrochemical performance of CrN thin films in this work with other metal nitrides.

Nitrides	Specific capacitance	Rate capability	Cycling performance	Reference
CrN (T5) thin film	12.8 mF cm ⁻² at 1.0 mA cm ⁻² 37.7 mF cm ⁻² (188.3 F g ⁻¹) at 100 mV s ⁻¹ 25.3 mF cm ⁻² (126.4 F g ⁻¹) at 200 mV s ⁻¹	61% (0.5-10 mA cm ⁻²) 54.8% (10-100 mV s ⁻¹)	92.1% after 20000 cycles	This work
TiN thin film	8.8 mF cm ⁻² at 100 mV s ⁻¹	58.6% (10-100 mV s ⁻¹)		<i>J. Power Sources</i> , 2015, 300 , 525-532.
VN power	5.4 mF cm ⁻² at 100 mV s ⁻¹		64.8% after 400 cycles	<i>J. Phys. Chem., solids</i> , 2009, 70 , 495-500.
VN film	22.8 mF cm ⁻² at 100 mV s ⁻¹	54.2% (10-100 mV s ⁻¹)	67.2% after 1000 cycles	<i>Electrochim. Acta</i> , 2014, 141 , 203-211.
RuN thin film	6 mF cm ⁻² at 200 mV s ⁻¹			<i>Scripta Mater.</i> , 2013, 68 , 659-662.
TiN/CNT	25.5 mF cm ⁻² at 100 mV s ⁻¹		90.9% after 20000 cycles	<i>Nano Energy</i> , 2014, 7 , 104-113.
WN	13 F g ⁻¹ at 100 mV s ⁻¹	52.1% (10-100 mV s ⁻¹)	80% after 500 cycles	<i>J. Am. Ceram. Soc.</i> , 2007, 90 , 3113-3120.
MoN _x power	27.2 F g ⁻¹ at 100 mV s ⁻¹	24.5% (10-100 mV s ⁻¹)	60% after 500 cycles	<i>J. Am. Ceram. Soc.</i> , 2011, 94 , 2371-2378.
NbN _x power	10.5 F g ⁻¹ at 100 mV s ⁻¹	18.2% (10-100 mV s ⁻¹)	103.2% after 500 cycles	<i>J. Am. Ceram. Soc.</i> , 2011, 94 , 2371-2378.
TiN power	52.3 F g ⁻¹ at 100 mV s ⁻¹	22.2% (10-100 mV s ⁻¹)	27.6% after 400 cycles	<i>J. Electrochem. Soc.</i> , 2006, 153 , A2298-A2303.
Porous NbN	67.2 F g ⁻¹ at 0.1 A g ⁻¹	30.8% (0.1-5 A g ⁻¹)	97.9% after 15000 cycles	<i>J. Mater. Chem. A</i> , 2016, 4 , 9760-9766.
Nb ₄ N ₅	225.8 mF cm ⁻² at 0.5 mA cm ⁻²	60.8% (0.5-10 mA cm ⁻²)	70.9% after 2000 cycles	<i>Adv. Sci.</i> , 2015, 2 , 1500126.
G/TiN NTA	25.2 mF cm ⁻² at 100 mV s ⁻¹	54.5% (10-100 mV s ⁻¹)	86.1% after 1000 cycles	<i>RSC Adv.</i> , 2014, 4 , 41856-41863.
Nb ₄ N ₅ NBAs	30.2 mF cm ⁻² at 1.0 mA cm ⁻²		80% after 1000 cycles	<i>Appl. Surf. Sci.</i> , 2016, 383 , 57-63.

Table S6. Cell capacitance, energy density, and power density of the CrN-based symmetric supercapacitor at different current densities.

Current density (mA cm ⁻²)	0.2	0.5	1.0	2.0
Areal specific capacitance (mF cm ⁻²)	10.6	7.7	6.5	5.0
Volumetric capacitance (F cm ⁻³)	92.7	67.3	56.8	43.7
Specific energy density (mWh cm ⁻³)	8.2	6.0	5.0	3.9
Specific power density (W cm ⁻³)	0.7	1.8	3.5	7.0