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Two-dimensional Nanosheets of Bimetallic Chalcogenide-Tagged Nitrogen-Doped Carbon as a Cathode for High-Performance and Durable Zinc-Ion Capacitor

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Experimental details

Synthesis of $NbMo_6S_8$/NC

Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), and thiourea ($NH_2CSNH_2$) were purchased from Sigma-Aldrich and used as received without any further purifications. Initially, 1 g of CS, $(C_6H_{11}NO_4)_n$) were dissolved in 50 mL of 1% HCl aqueous solution (A) under constant stirring for 2 h. Next, 1 mmol of $NbCl_5$ dissolved in previous solution and stirred it next 2 h to obtain the milky solution, noted as A. Meanwhile, solution B was prepared in 50 mL distilled water with adding 2mmol of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Finally, solution B added dropwise to the above CS-containing solution A and stirred for 2 h. Then, a desired amount of thiourea was added to the above milky white suspension and dissolved by stirring vigorously for 1 h. Then the final solution was transferred into a stainless-steel autoclave and heated at 180 °C for 12 h and then after completing reaction it keeps for natural cooling. The resulting blackish colored suspension was then centrifuged for 10 min under 7000 rpm. The obtained suspension was filtered and dried at 60° C under vacuum for 6h to acquire nanosheets. Finally, the obtained product annealed at 700°C under N_2 atmosphere for 2h to obtain the of $NbMo_6S_8$/NC phase. Nitrogen and carbon undoped $NbMo_6S_8$ material were obtained using the same hydrothermal process with use of CS.

Material characterizations

Powder X-ray diffraction (XRD) patterns of the prepared samples were recorded on a PANalytical X'Pert Pro Multi-Purpose X-ray diffractometer by using the Cu Kα radiation source (λ = 0.15406 nm) with a scan step size 2θ is 0.001°. The morphologies of the prepared samples were seen using a scanning electron microscope (SEM) SU800 and Filed emission-transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Japan) equipped with an energy dispersive X-ray detector (EDS) at an acceleration voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) measurement were performed with a Thermo Scientific with an Al K-alpha X-ray source. The Raman spectra (FEX, NOST, Republic of Korea) were employed for the prepared samples with a 532 nm excitation laser. The Brunauer-Emmett-Teller surface area were calculated by the BET method.

Electrochemical Measurements

The water in salt $NbMo_8S_6$/NC ZIC was fabricated with a zinc foil acting as counter electrode and reference electrodes. The aqueous electrolyte consisted of 0.2 M $ZnClO_4$ and 17 M $NaClO_4$ additive salt. The cyclic voltammetry (CV) testing and galvanostatic charge/discharge (GCD) measurements were conducted with a Wonatech measurement system (WonATech, South Korea), conducted in the potential range of 0–1.5 V (vs Zn^{2+}/Zn). Electrochemical impedance spectra (EIS) experiments were carried out with 10 mV amplitude in the frequency from 1 MHz to 10 mHz. All electrochemical parameter values are calculated without taking the Zn-electrode mass into consideration.

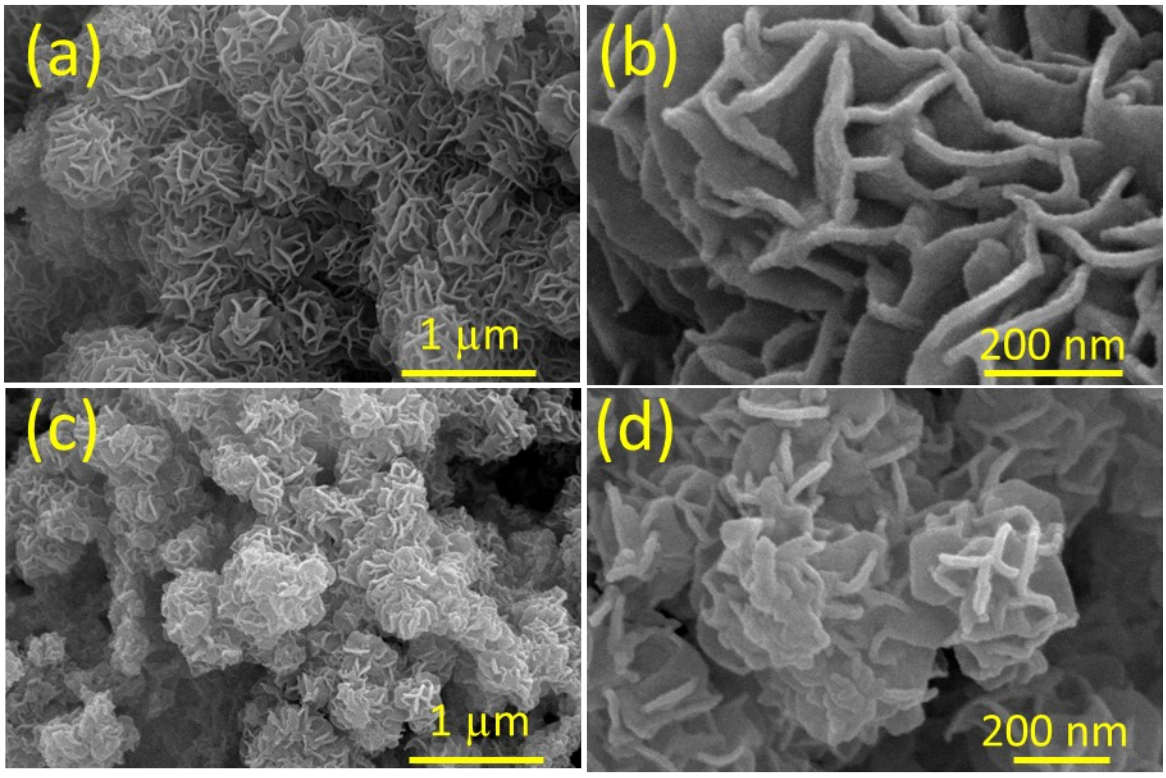

Figure S1 The surface morphologies of (a, b) $NbMo_6S_8$ and (c, d) $NbMo_6S_8$/NC materials.

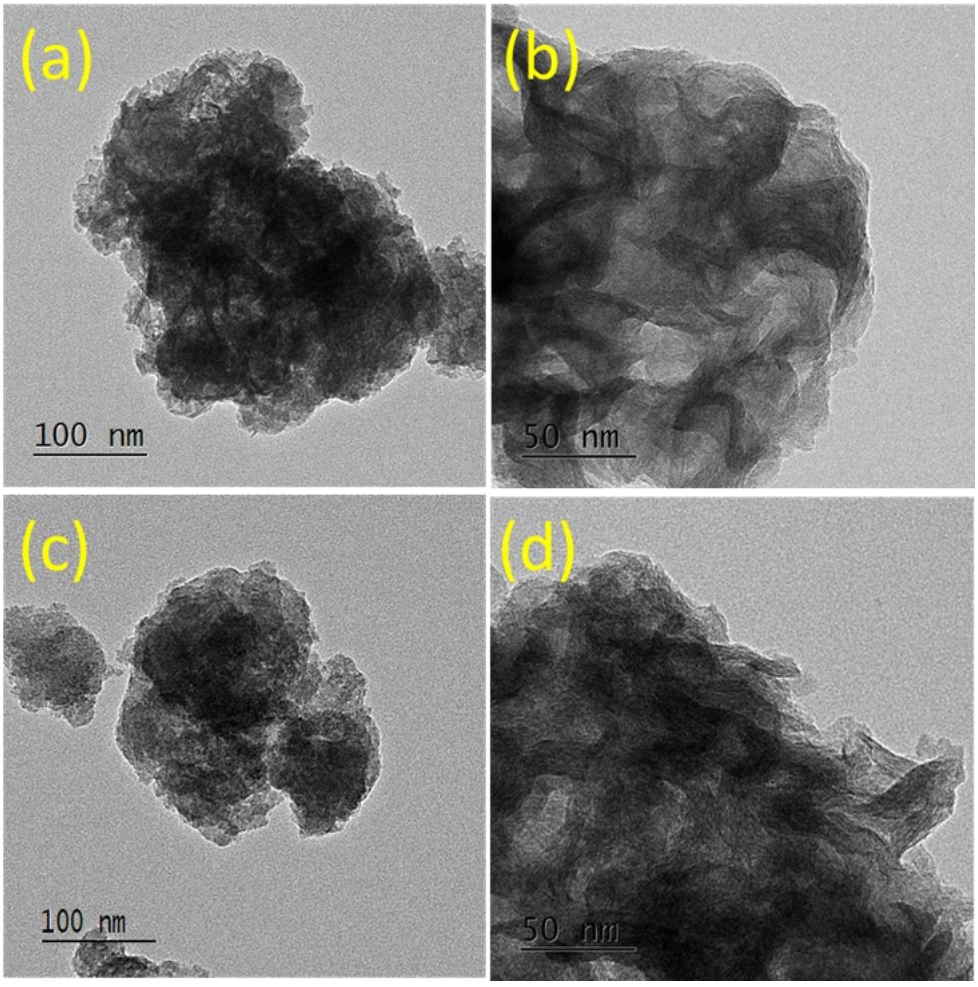

Figure S2 TEM images of (a, b) $NbMo_6S_8$ and (c, d) $NbMo_6S_8$/NC materials at low and high magnifications.

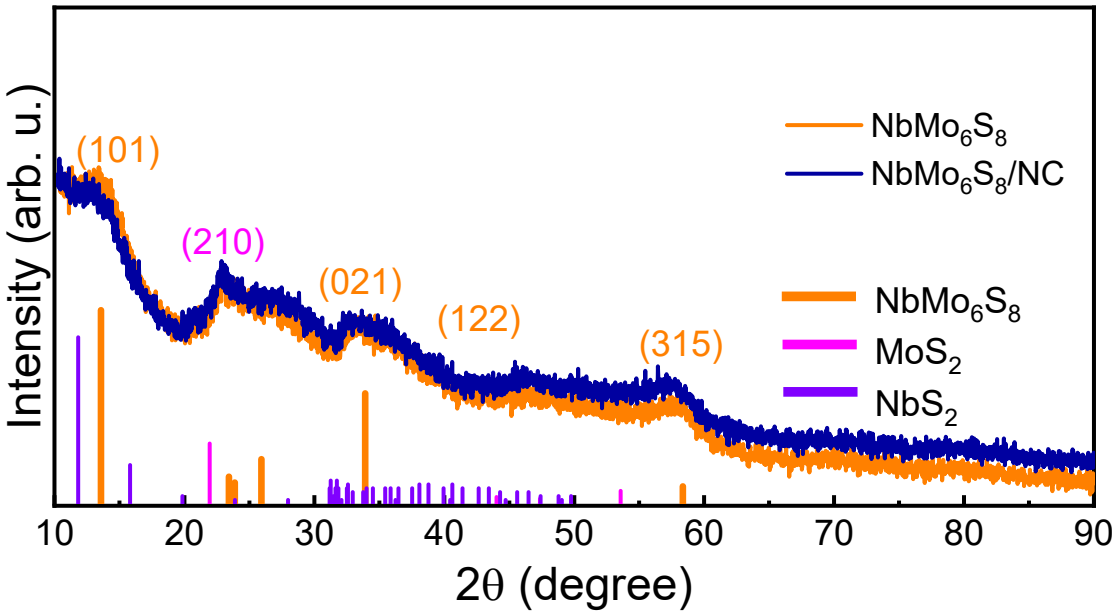

Figure S3 The XRD patterns of $NbMo_6S_8$ and $NbMo_6S_8$/NC materials.

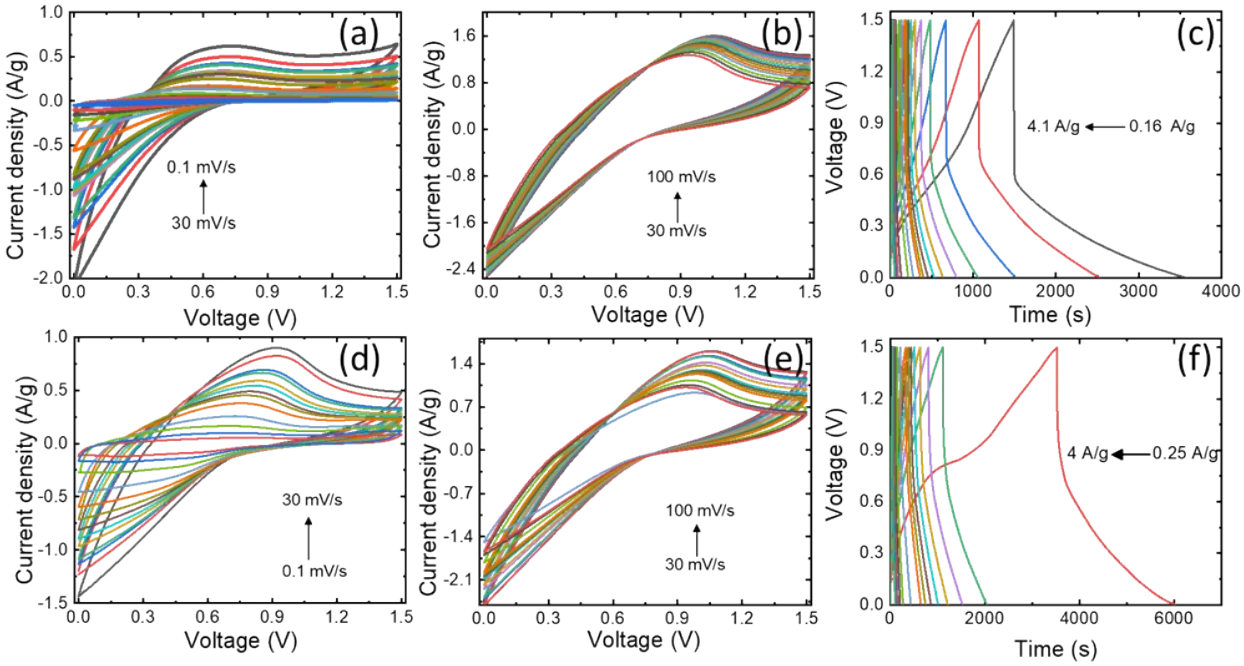

Figure S4 Electrochemical behavior of the $NbMo_6S_8$ and $NbMo_6S_8$/NC ZICs in aqueous electrolyte. Cyclic voltammograms of the $NbMo_6S_8$ (a) at low and (b) high scan rates. Cyclic voltammograms of the $NbMo_6S_8$/NC (d) at low and (e) high scan rates. The galvanostatic charge-discharge profiles of (c) $NbMo_6S_8$/NC and (f) $NbMo_6S_8$/NC ZICs at different current densities.

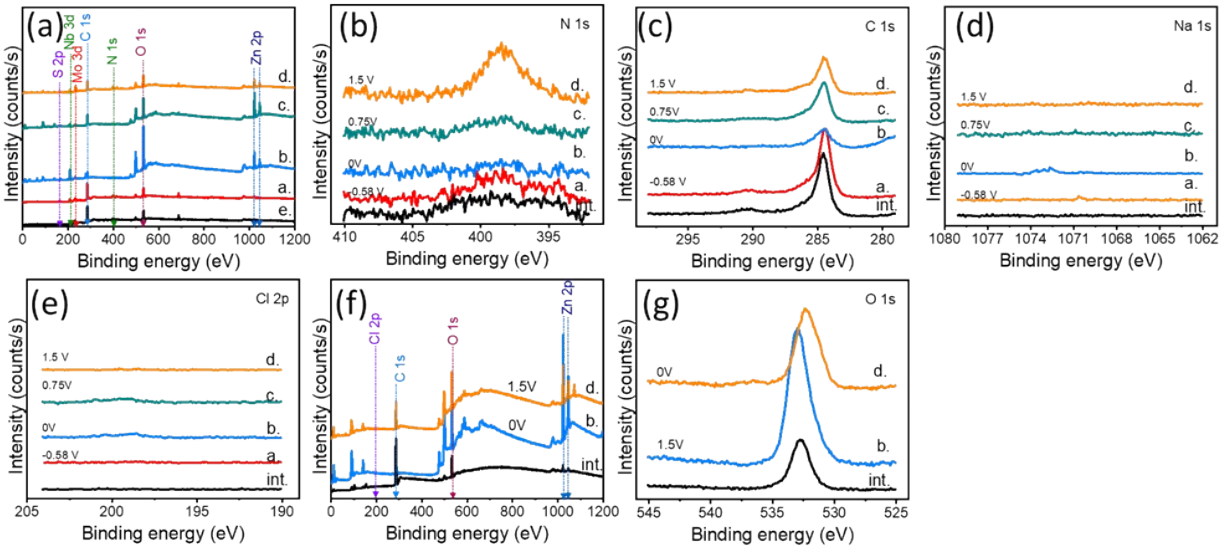

Figure S5 XPS studies: (a) wide scan spectra of $NbMo_6S_8$/NC cathode during charge/discharge process. Core-level spectra for (b) N 1s, (c) C 1s, (d) Na 1s and (e) Cl 2p. The wide scan spectra of Zn-anode during charge, discharge, and initial state. Core-level spectra for (g) O 1s.

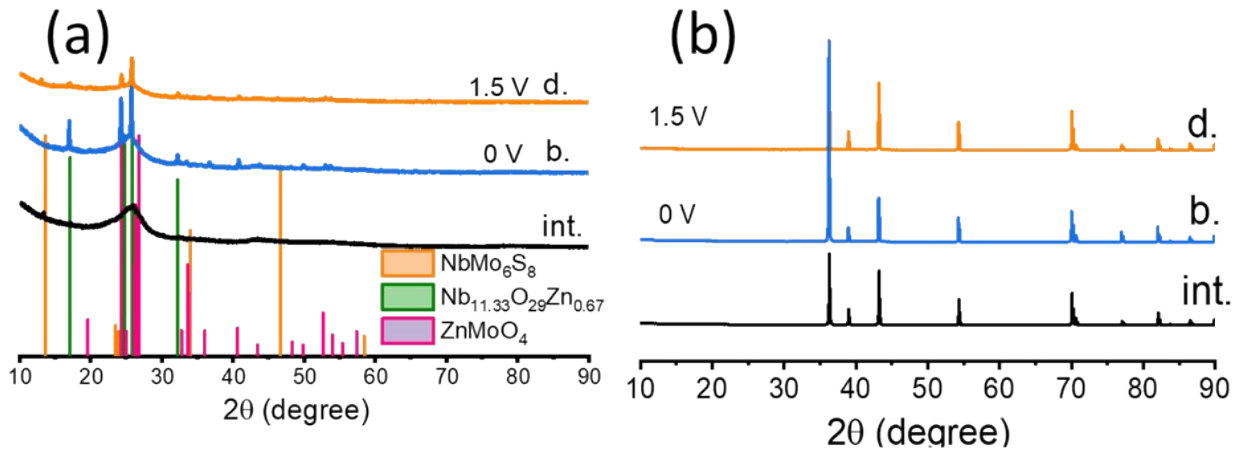

Figure S6 XRD patterns of the (a) $NbMo_6S_8$/NC cathode and (b) Zn anode at original, full charge and discharge state.

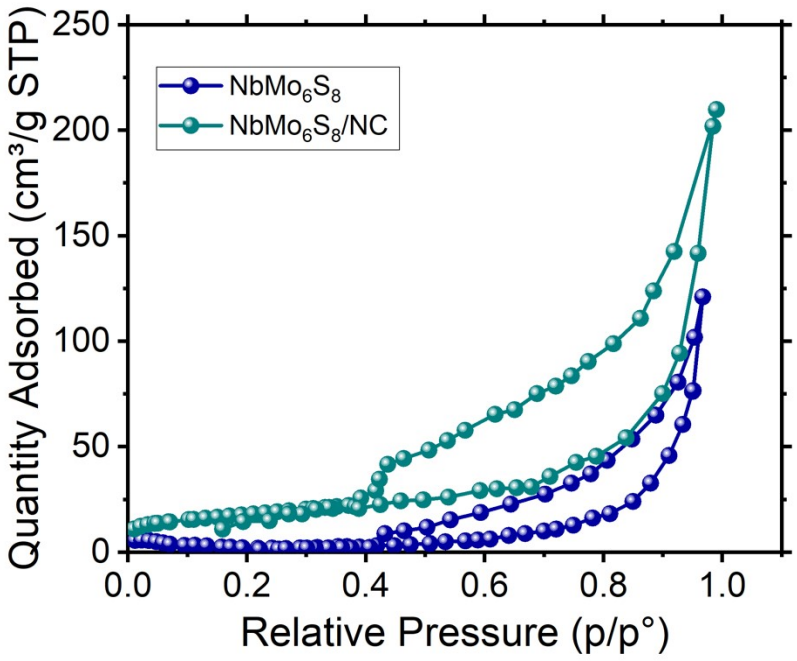

Figure S7 N_2 adsorption–desorption isotherms of $NbMo_6S_8$/NC, and $NbMo_6S_8$.

Table S1 The parameter values of the $NbMo_6S_8$ and $NbMo_6S_8$/NC cathode in diluted and MHCZE.

Electrode	R_s (Ω/cm)	R_{ct} (Ω/cm)
$NbMo_6S_8$	22.87	32.87
$NbMo_6S_8$/NC	20.18	27.75
$NbMo_6S_8$/NC MHCZE	4.80	7.12

Table S2 The performance evaluation of $NbMo_6S_8$/NC ZICs device with past reported metal-ion capacitors.

Material	**Electrolyte**	**Capacity**	**Energy density**	**Power density**	**Stability**	**Ref.**
$NbMo_6S_8$/NC	0.1M $ZnClO_4$/ 15M $NaClO_4$	167.89	188.87	250	87.60 % (15000)	PW
MoS_2-160	3M $Zn(CF_3SO_3)_2$	168				[1]
TiO_2/MoS_2@NC	1M $NaClO_4$		148	200		
3D-IEMoS_2@G	1M $NaClO_4$	580	140	630	(10000)	[2]
E-MoS_2	2M $ZnSO_4$	202.6	148.2	70.5	98.6% (600)	[3]
MoS_{2-x}	3M $Zn(CF_3SO_3)_2$	138.6			87.8% (1000)	[4]
MoPO/MoS_2	3M KCl	---	52.6	746.9	90% (26000)	[5]
MoS2/Graphene	$Zn(CF_3SO_3)_2$	141.6	157.5		88.2% (1800)	[6]
MoS_2@C	1M $LiPF_6$	433.6	78.98	11250	72.12% 3000	[7]
N-doped 1T MoS_2	3M $Zn(CF_3SO_3)_2$	149.6			89.1% (1000)	[8]
D-MoS_2-O	3M $Zn(CF_3SO_3)_2$	203.8	161.3		90.5 % (1000)	[9]

MoS_2	1M $LiPF_6$	241.5 F/g	69.56	150	78.0% (5000)	[10]
MoS_2–SnS@g-C_3N_4	1M $NaClO_4$		193.1	90	76.3% (5000)	[11]
MoS_2/N-NPCM	1M $LiPF_6$		120	100	85.5% (4000)	[12]
Gr-Nb_2O_5	1M $NaClO_4$		112.9	80.1	97.1% (1500)	[13]
E-MoS2/NG	1M $NaClO_4$	201	150	35	78.1 (1500)	[14]
P-MoS_2/PANI/rGO	1M Li_2SO_4		56	450	93.5% (30000)	[15]

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