Electronic Supplementary Information (ESI)

Beneficial Synergy of Adsorption-Intercalation-Conversion Mechanisms in Nb₂O₅@Nitrogen-Doped Carbon Frameworks for Promoted Removal of Metal Ions via Hybrid Capacitive Deionization

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Table of contents

Experiments	S4
Materials	S4
Structural characterization	S4
Electrochemical characterization	S5
CDI test	S6
Figure S1	S9
Figure S2	S10
Figure S3	S11
Figure S4	S12
Figure S5	S13
Figure S6	S14
Figure S7	S15
Figure S8	S16
Figure S9	S17
Figure S10	S18
Figure S11	S19
Figure S12	

Figure S13	
Figure S14	
Figure S15	
Figure S16	
Figure S17	
Figure S18	
Figure S19	
Figure S20	
Figure S21	
Figure S22	
Table S1	
Table S2	
Table S3	
Table S4	

Experiments

Materials

Niobium pentachloride (NbCl₅) and 2-Methylimidazole (2-MeIM, 99%) were purchased from Aladdin. Melamine, methanol (CH₃OH), ethanol (CH₃CH₂OH), acetylene black, polytetrafluoroethylene (PTFE) and activated carbon (AC) were purchased from Sinopharm Chemical Reagent Co. Ltd. in China. All the chemicals were used without further purification.

Structural characterization

X-ray diffraction (XRD) were tested with a Rigaku D/MAX-RB X-ray diffractometer (Cu K α , 40 kV, 20 mA). Raman spectra were conducted on a spectrometer (JY H800UV). Nitrogen adsorption/desorption isotherms were tested with an ASAP 2020 (Micromeritics) at 77 K. The specific surface areas were recorded by Brunauer–Emmett–Teller (BET) method and the pore size distributions were obtained from the desorption branches of the isotherms by the Barrett–Joyner–Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) spectra were measured on a Perkin-Elmer PHI 5000C ESCA system accompanied with a twin anode Mg K α (1253.6 eV) X-ray radiation. The Zeta potential of GO/g-C₃N₄ complex (10 mg dispersed in 50 ml deionized water) was tested by STABINO PMX 400. The morphology of products was viewed by scanning electron microscope (SEM, JEOL JEM-700F), transmission electron microscope (TEM, JEOL JEM-200CX), and high-resolution transmission electron

microscopy (HRTEM, JEOL JEM-2010F). The hydrophilicity of the electrode surface was analyzed the dynamic contact angle (Kruss DSA100).

Electrochemical characterization

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) were tested in a 0.5 M NaCl solution by electrochemical workstations of CHI 760D (Shanghai Chen Hua, China). The working electrode was with a size of 2 cm \times 2 cm \times 0.01 cm and the mass was about 5 mg. Besides, the counter electrode was a graphite sheet, and the reference electrode was the saturated calomel electrode. The frequency of EIS was from 100000 to 0.01 HZ. CV curves were tested from 1, 5, 10, 20, 50 to 100 mV s⁻¹ at the voltage window from -0.5 to 0.5 V. The current density of GCD was accepted at 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 A g⁻¹. The specific capacitance (C_m: F g⁻¹) was calculated by the following equation

$$C_m = \left(\int I dV\right) / 2v\Delta V m \tag{S1}$$

where I is the current density, ΔV is the voltage change, v is the scan rate, and m is the weight of the working electrode.

The contributions of the capacitive charge and the diffusion-controlled charge were obtained by the following equation

$$i(v) = k_1 v + k_2 v^{05}$$
(S2)

where i is the current, v is the scanning rate, k_1 and k_2 are the constant values at a fixed potential, k_1v corresponds to the capacitive current, and k_2v is related to the diffusioncontrolled charge. The diffusion coefficient $(D_{Na}^+: cm^2 s^{-1})$ was calculated by the following equation

$$D_{Na^{+}} = \frac{R^2 T^2}{2n^4 c^2 F^4 A^2 \sigma^2}$$
(S3)
$$Z_{re} = \sigma \overline{\omega}^{-1/2}$$
(S4)

where R is the gas constant, T is the absolute temperature, n is the electrons per molecule in intercalation process, c is the concentration of Na⁺ in the material, F is the Faraday constant, A is the surface area of the electrode, σ is the Warburg factor, and Z_{re} is the real part impedance.

CDI test

The CDI electrodes were obtained by combining active materials with acetylene black and PTFE with the weight ratio of 8 : 1 : 1 and then casting into a graphite sheet with a size of 5 cm \times 5 cm \times 0.01 cm. After that, the electrode was dried at 80 °C overnight. The weight of active materials was about 0.072 g. The counter electrode was obtained by the same procedure with activated carbon (AC). Finally, the electrodes (Nb₂O₅@N-C-1//AC) were assembled into a home-made desalination device to test ion adsorption performance. The two CDI electrodes were separated by a spacer. A 50 mL NaCl solution was driven cyclically through the electrodes via a peristaltic pump. A conductivity meter (SevenMulti, METTLER TOLEDO, America) was used to monitor the conductivity of the NaCl solution instantly. The applied voltage was from 0.8, 1.0 to 1.2 V and the initial concentration of NaCl solution was from 100, 300 to 500 mg L⁻¹. The flow rate was kept at 40 mL min⁻¹. The testing temperature in the capacitive

deionization experiment was maintained at 25 °C. The ion adsorption capacity (IAC) of electrodes was calculated by the following equation

$$IAC = (C_0 - C_t)V/m \tag{S5}$$

where C_0 is the initial concentration, C_t is the final concentration, V is the volume of NaCl solution, and m is the total weight of active materials.

The ion adsorption rate (IAR) was calculated as:

$$IAR = IAC / t$$
 (S6)

where t is the desalination time.

The average ion adsorption rate (AIAR) was calculated by averaging the whole IAR among the capacitive deionization time.

The concentration reduction (CR) could be calculated as:

$$CR = \frac{C_o - C_t}{M} \tag{S7}$$

where M is the mole weight of NaCl.

The deionization rate (DR%) was calculated as:

$$DR\% = (C_0 - C_t) / C_0 \times 100\%$$
(S8)

The charge efficiency $(\Lambda, \%)$ was calculated by the following equation

$$\Lambda = \frac{\Gamma \times F}{\Sigma} \tag{S9}$$

where Γ is the removal capacity, *F* is the Faraday constant, and Σ is obtained by integrating current curves.

The specific energy consumption (SEC⁻¹) in the constant-voltage CDI system could be calculated by the following equation

$$SEC^{-1} = \frac{(C_0 - C_t)V}{V_d \int_0^t Idt}$$
(S10)

where V_d is the applied voltage, and I is the time-dependent current.

The water recovery (WR) could be calculated by the following equation

$$WR = \frac{V_1 t_1}{V_1 t_1 + V_2 t_2}$$
(S11)

where V_1 is the volume of initial NaCl solution, t_1 is the desalination time in one cycle, V_2 is the volume of NaCl solution recover to the initial level, t_2 is the recovery time in one cycle. In the system, the ions removal/regeneration was kept in a constant volume, $V_1=V_2$. The energy consumption (EC) could be calculated as:

$$EC = \frac{V_d \int_0^t Idt}{m}$$
(S12)

The deionized product water-specific Gibbs free energy $(\Box g)$ was given by the following equation

$$\Box g = vRT \left\{ \frac{C_0}{WR} \ln \left[\frac{C_0 - C_t WR}{C_0 (1 - WR)} \right] - C_t \ln \left[\frac{C_0 - C_t WR}{C_t (1 - WR)} \right] \right\}$$
(S13)

where v is a van't Hoff factor, R is the ideal gas constant, and T is the absolute temperature. The energy efficiency (EE) could be given by the following equation

$$EE = \frac{\Box g}{EC} \tag{S14}$$



Figure S1. (a) SEM image and (b) TEM image of Nb/2MeIM/g- C_3N_4 /GO precursors.



Figure S2. SEM image, TEM image, and particle size distribution of Nb₂O₅@N-C-0.5 (a, b, c), Nb₂O₅@N-C-1 (d, e, f) and Nb₂O₅@N-C-2 (g, h, i).



Figure S3. SAED pattern of Nb₂O₅@N-C-1.



Figure S4. The corresponding EDS elemental mapping of C, N, O and Nb of $Nb_2O_5@N-C-1$.



Figure S5. XRD patterns of bare Nb_2O_5 , Nb_2O_5 @N-C-0.5 and Nb_2O_5 @N-C-2.



Figure S6. (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distribution plots of Nb₂O₅@N-C-0.5, Nb₂O₅@N-C-1, and Nb₂O₅@N-C-2.

Obviously, these obtained materials demonstrated hysteresis loops in the P/P_0 range of 0.4-1.0, which proved the mesoporous properties.



Figure S7. XPS survey spectra of Nb₂O₅@N-C-0.5, Nb₂O₅@N-C-1 and Nb₂O₅@N-C-2.



Figure S8. XPS spectra for C 1s of (a) Nb₂O₅@N-C-0.5, (b) Nb₂O₅@N-C-1, and (c) Nb₂O₅@N-C-2.

The high-resolution C 1s spectra could be divided into three peaks at around 284.4, 286.3, and 288.5 eV, corresponding to C-C/C-H, C-N/C-O, and O-C=O.



Figure S9. XPS spectra for N 1s of (a) $Nb_2O_5@N-C-0.5$, (b) $Nb_2O_5@N-C-1$, and (c) $Nb_2O_5@N-C-2$.

The high-resolution N 1s spectra could be deconvoluted into four peaks at around 397.9, 399.9, 401.1, and 402.8 eV, corresponding to pyridinic N, pyrrolic N, graphitic N, and oxide N.



Figure S10. XPS spectra for O 1s of (a) Nb₂O₅@N-C-0.5, (b) Nb₂O₅@N-C-1, and (c) Nb₂O₅@N-C-2.

The high-resolution O 1s spectra could be divided into three peaks at around 530.4, 531.0, and 532.2 eV, corresponding to Nb-O, C-O and C=O. Additionally, the apparent shift to the low binding energy of Nb₂O₅@N-C-2 was due to the more Nb element affecting the O binding information.



Figure S11. Dynamic water contact angle analysis from 0, 30, 60, 90 to 120 s of $Nb_2O_5@N-C-0.5$, $Nb_2O_5@N-C-1$, and $Nb_2O_5@N-C-2$.

When the water droplet first went close to the surface of electrodes, the contact angle of Nb₂O₅@N-C-1 (86.83°) was smaller than Nb₂O₅@N-C-0.5 (91.49°) and Nb₂O₅@N-C-2 (93.16°). With the test going on, the contact angle of Nb₂O₅@N-C-1 decreased quickly compared to Nb₂O₅@N-C-0.5 and Nb₂O₅@N-C-2. After 120 s, the Nb₂O₅@N-C-1 electrode reached the smallest contact angle.



Figure S12. CV curves of (a) Nb₂O₅@N-C-1, (b) Nb₂O₅@N-C-0.5, and (c) Nb₂O₅@N-C-2 at scan rates from 1, 5, 10, 20, 50 to 100 mV s⁻¹ and (d) Specific capacitance of Nb₂O₅@N-C-1, Nb₂O₅@N-C-0.5, and Nb₂O₅@N-C-2 at different scan rates.

It was clear that the specific capacitance gradually decreased with scan rate increasing from 1, 5, 10, 20, 50 to 100 mV s⁻¹. The specific capacitance of Nb₂O₅@N-C-1 was 127.26 (1 mV s⁻¹), 80.32 (5 mV s⁻¹), 57.65 (10 mV s⁻¹), 43.13 (20 mV s⁻¹), 28.04 (50 mV s⁻¹), and 19.98 F g⁻¹ (100 mV s⁻¹), higher than Nb₂O₅@N-C-0.5 (98.96, 55.71, 39.98, 29.7, 20.42, and 14.27 F g⁻¹) and Nb₂O₅@N-C-2 (89.44, 55.47, 37.39, 26.03, 16.45, and 10.94 F g⁻¹) at any corresponding scan rate.



Figure S13. CV curves of Nb₂O₅@N-C-1 at scan rates from 0.1, 0.2, 0.5 1, 5, 10, 20, 50 to 100 mV s⁻¹ (Pt foil as counter electrode).

We tested the CV measurement by a three-electrode system in a 0.5 M NaCl solution consisting of Nb₂O₅@N-C-1 (working electrode), Pt foil (counter electrode) and a calomel electrode (reference electrode) at scanning rates from 0.1, 0.2, 0.5, 1, 5, 10, 20, 50 to 100 mV s⁻¹. Obviously, redox peaks were appeared at the voltage range and the peak intensity was increased with the raise of scan rates, which demonstrated a faradaic reaction of Na⁺ ions inserting into the Nb₂O₅@N-C-1 electrode.



Figure S14. GCD curves of (a) Nb₂O₅@N-C-1, (b) Nb₂O₅@N-C-0.5, and (c) Nb₂O₅@N-C-2 at current densities from 0.2, 0.4, 0.6, 0.8, 1.0 to 1.2 A g^{-1} and (d) IR drop of Nb₂O₅@N-C-1, Nb₂O₅@N-C-0.5, and Nb₂O₅@N-C-2 at different current density.

The iR drop increased linearly with the increase of current density from 0.2, 0.4, 0.6, 0.8, 1.0 to 1.2 A g⁻¹. The iR drop value of Nb₂O₅@N-C-1 was 7 (0.2 A g⁻¹), 14 (0.4 A g⁻¹), 21 (0.6 A g⁻¹), 29 (0.8 A g⁻¹), 36 (1.0 A g⁻¹), and 43 mV (1.2 A g⁻¹), much smaller than Nb₂O₅@N-C-0.5 (9, 17, 26, 34, 42, and 51 mV) and Nb₂O₅@N-C-2 (11, 22, 33, 44, 56, and 66 mV) at any corresponding current density.



Figure S15. (a) Plots of IAC vs. deionization time of Nb₂O₅@N-C-1, N-C and AC electrodes in a 500 mg L⁻¹ NaCl solution with a working voltage of 1.2 V and flow rate of 40 mL min⁻¹, (b) Ragone plots of IAR vs. IAC of Nb₂O₅@N-C-1, N-C and AC electrodes in a 500 mg L⁻¹ NaCl solution with a working voltage of 1.2 V and flow rate of 40 mL min⁻¹.

We compared Nb₂O₅@N-C-1//AC electrodes with N-C//AC and AC//AC to prove the outstanding composite to combine Nb₂O₅ with a nitrogen-doped carbon matrix. The Nb₂O₅@N-C-1//AC composites demonstrated the best removal performance of 35.4 mg g⁻¹ in 120 min measurement. Nevertheless, the IAC of N-C//AC and AC//AC was merely 20.9 and 15.8 mg g⁻¹, respectively. Moreover, the Ragone plots of Nb₂O₅@N-C-1//AC also located the most upper and right region compared to other samples, indicating the fastest IAR and the largest IAC.



Figure S16. Comparison of AIAR and CR of different electrode materials in a 500 mg L^{-1} NaCl solution with working voltage of 1.2 V and flow rate of 40 mL min⁻¹.

The Nb₂O₅@N-C-1//AC indicated the biggest concentration reduction (0.88 mM) and average ion adsorption rate (0.50 mg g⁻¹ min⁻¹) in the comparison of Nb₂O₅@N-C-0.5//AC (0.72 mM, 0.44 mg g⁻¹ min⁻¹), Nb₂O₅@N-C-2//AC (0.48 mM, 0.29 mg g⁻¹ min⁻¹), Nb₂O₅//AC (0.26 mM, 0.12 mg g⁻¹ min⁻¹), N-C//AC (0.52 mM, 0.33 mg g⁻¹ min⁻¹) and AC//AC (0.40 mM, 0.22 mg g⁻¹ min⁻¹).



Figure S17. (a) Ragone plots of IAR vs. IAC of Nb₂O₅@N-C-1 in different initial concentrations of NaCl solution, (b) Ragone plots of IAR vs. IAC of Nb₂O₅@N-C-1 with different working voltages.



Figure S18. Comparison of AIAR and CR of Nb₂O₅@N-C-1 in different applied voltage and initial concentration.

Different measuring parameters led to different desalination results. The Nb₂O₅@N-C-1//AC was tested in a 500 mg L⁻¹ NaCl solution at 1.2 V (1.2 V, 500 ppm) indicated the biggest concentration reduction (0.88 mM) and average ion adsorption rate (0.50 mg g⁻¹ min⁻¹) in the comparison of 1.2 V, 300 ppm (0.68 mM, 0.35 mg g⁻¹ min⁻¹), 1.2 V, 100 ppm (0.45 mM, 0.29 mg g⁻¹ min⁻¹), 1.0 V, 500 ppm (0.48 mM, 0.27 mg g⁻¹ min⁻¹), and 0.8 V, 500 ppm (0.12 mM, 0.09 mg g⁻¹ min⁻¹).



Figure S19. Deionization stability of Fe-N-C electrode of 20 adsorption-desorption cycles in a 100 mg L⁻¹ NaCl solution at charge/discharge voltage of 1.2-0 V and flow rate of 40 mL min⁻¹.

From the results of desalination tests in Figure 4, we could get the conclusion that the ion adsorption occurred quickly in the first 10 min. After that, it became slowly and mildly increasing. Based on that, we accepted the ion adsorption time of 10 min and ion desorption time of 20 min.



Figure S20. (a) SEM image, (b) TEM image, and (c) particle size distribution of $Nb_2O_5@N-C-1$ after regeneration test.



Figure S21. CV curves of Nb₂O₅@N-C-1 at 0.1 mV s⁻¹ in different stages of discharge/charge for in-situ Raman tests.



Figure S22. Ex-situ XPS measurements of Nb 3d peaks in different stages of pristine, adsorption, and desorption process.

Samples	Nb ₂ O ₅ @N-C-1	Nb ₂ O ₅ @N-C-0.5	Nb ₂ O ₅ @N-C-2
$S_{BET}(m^2 g^{-1})$	34.1	78.6	29.5
V _{pore} (cm ³ g ⁻¹)	0.13	0.17	0.07

Table S1. Specific surface area and pore volume of Nb₂O₅@N-C-0.5, Nb₂O₅@N-C-1, and Nb₂O₅@N-C-2.

Samples	С	Ν	Ο	Nb
Nb ₂ O ₅ @N-C-0.5	55.37	2.63	36.87	5.13
$Nh_0.@N_0.1$	52.07	1 71	35.21	<u> </u>
10205@11-C-1	52.07	7./1	55.21	0.01
Nb ₂ O ₅ @N-C-2	43.22	4.05	42.79	9.95
2 3 ()				

Table S2. Elemental quantification analyzed by XPS of Nb2O5@N-C-0.5, Nb2O5@N-C-1, and Nb2O5@N-C-2.

Samples	Nb ₂ O ₅ @N-C-1	Nb ₂ O ₅ @N-C-0.5	Nb ₂ O ₅ @N-C-2
R _s	0.76	0.68	0.87
R _{ct}	14.66	18.52	23.94

Table S3. The typical fitted parameters in the electrochemical impedance spectroscopyof Nb₂O₅@N-C-0.5, Nb₂O₅@N-C-1, and Nb₂O₅@N-C-2.

		Initial NaCl		
Electrode materials	Voltage	concentration	IAC	Reference
	(V)	(mg/L)	(mg/g)	
Na ₄ Mn ₉ O ₁₈	1.2	580	31.2	S1
Na ₂ FeP ₂ O ₇	1.2	580	30.2	S2
MnO ₂	1.4	500	14.9	S3
AC-Ti-S	1.2	500	10	S4
Hybrid-MnO ₂	1.2	870	27.3	S5
Ag coated carbon	1.2	585	15.6	S6
$MoS_2/g-C_3N_4$	1.6	250	24.2	S7
Ti ₃ C ₂ -MXene	1.2	300	15.0	S8
5 wt% CeO2@GNFs	1.4	50	7.2	S9
rGO/Co ₃ O ₄	1.6	500	20.2	S10
2D MXeneTi ₃ C ₂ T _x nanosheets	1.4	500	26.8	S11
ACP/TiO ₂ /SO ₃ -	1.0	500	22	S12
Nb ₂ O ₅ @N-C-1	1.2	100	18.1	This work
Nb ₂ O ₅ @N-C-1	1.2	300	27.4	This work
Nb ₂ O ₅ @N-C-1	1.2	500	35.4	This work

Table S4. Comparison of IAC of Nb₂O₅@N-C-1 with another metal-based electrode materials from the literature.

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