Supporting information

Enhancing aqueous zinc-ion battery performance through dual-mechanism strategy

Experimental section

Synthesis of MoG Precursors: 0.3 mmol of ammonium molybdate tetrahydrate was dissolved in 72 ml of a mixed solvent (18 ml of water, 42 ml of isopropanol (IPA), and 12 ml of glycerol). The solution was stirred magnetically at 400 rpm for 30 minutes, resulting in a clear, transparent solution. Then transfer solution into a 100 ml Teflon-lined autoclave and subjected to a hydrothermal reaction at 190°C for 3 hours. The resulting brown powder was washed three times with water and ethanol, respectively, and then dried in an oven at 60 °C for 12 hours.

Synthesis of N-MoS_x: A solution was prepared by dissolving 1 g of sulfur powder in 10 ml of ammonium sulfide solution (30%) and stirring it at 400 rpm using a magnetic stirrer for 6 hours, resulting in a reddish-brown polysulfide ammonium solution for subsequent use. Subsequently, 0.2 g of MoG was weighed and thoroughly dispersed in 20 ml of a mixed solvent (12 ml of ammonia water and 8 ml of water). The polysulfide ammonium solution was then added, and the mixture was stirred at 400 rpm for 30 minutes using a magnetic stirrer. The resulting mixture was transferred into a 50 ml Teflon-lined autoclave and subjected to a hydrothermal reaction at 180 °C for 6 hours. The resulting product was washed three times with water and ethanol, respectively, and then carefully dried in an oven at 60 °C for 12 hours before being collected. In a parallel synthesis, MoS_2 was prepared by replacing the sulfur source with thiourea and the solvent with 30 ml of water, while maintaining the other reaction conditions unchanged.

Synthesis of MoS_2 nanospheres： Subsequently, 0.2 g of MoG was weighed and thoroughly dispersed in 30 ml of water. Then added 0.5 g of thiourea, and the mixture was stirred at 400 rpm for 30 minutes using a magnetic stirrer. The resulting mixture was transferred into a 50 ml Teflon-lined autoclave and subjected to a hydrothermal reaction at 180°C for 6 hours. The resulting product was washed three times with water and ethanol, respectively, and then carefully dried in an oven at 60°C for 12 hours before being collected.

Preparation of Mn-MIL: Solution A was prepared by dissolving 60 mg $Mn(NO_3)_3 \cdot 4H_2O$ and 1.35 g lauric acid in 15 mL methanol under magnetic stirring for 15 min. Solution B was prepared by dissolving 200 mg 1,3,5-Benzenetricarboxylic acid in 10 mL methanol. Solution B was then added to solution A under continuous stirring for 5 min at room temperature. The resulting mixture was transferred into a Teflon-lined autoclave and reacted at 125 °C for 6 h.

Synthesis of Mn_2O_3: The Mn-MIL precursor was annealed in a muffle furnace at 600 °C for 4 h with a heating rate of 2 °C/min.

Materials characterization

The synthesized material was characterized through X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Electrochemical Measurements: The electrochemical evaluation was conducted by assembling a CR2032-type coin cell, using Zn foil and fiberglass filter paper as the anode and separator, 80 μL 2 M $Zn(CF_3SO_3)_2$ mixed with 2M LiTFSI serving as the composite electrolyte. Galvanostatic charge/discharge (GCD) measurements of the coin cells were conducted using the Neware battery tester (BTS-4000) within a potential range of 0-1.0 V (*vs.* Zn^{2+}/Zn). The Galvanostatic Intermittent Titration Technique (GITT) was finished through a sequence of galvanostatic discharge pulses lasting 5 minutes at a current density of 100 mAh g^{-1}, succeeded by a 20 minutes rest period. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) tests were carried out on a CHI 760E electrochemical workstation.

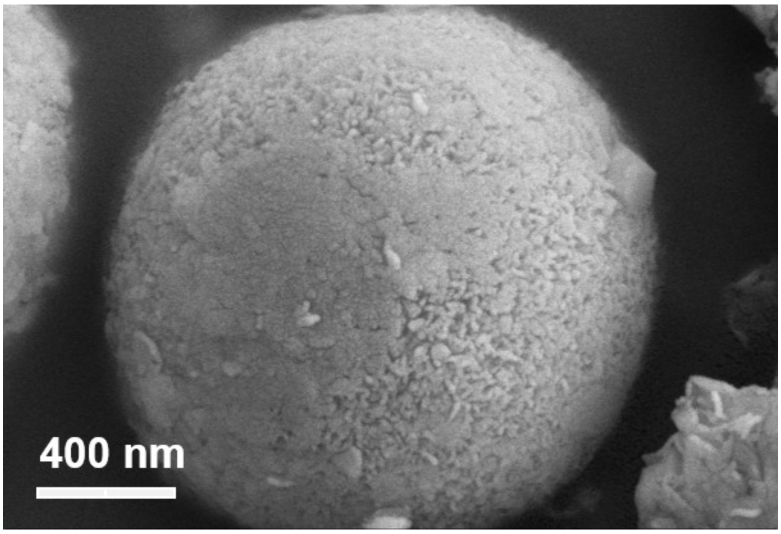

Figure S1. SEM image of MoS_2.

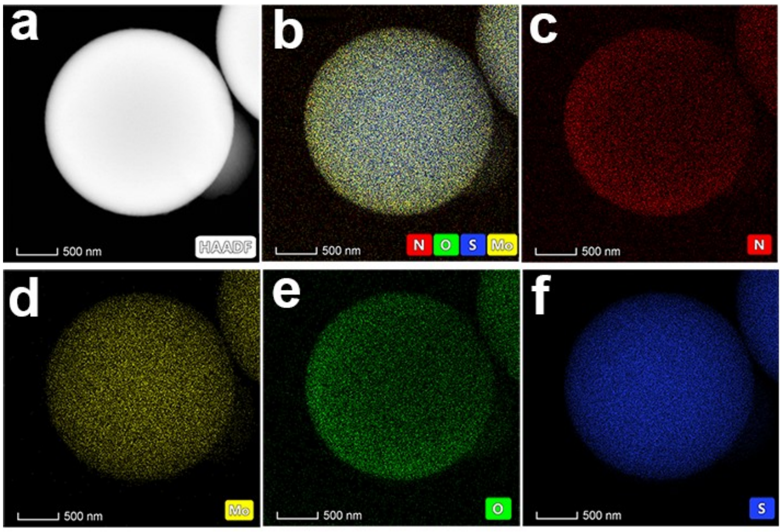

Figure S2. The element mappings of N-MoS_x.

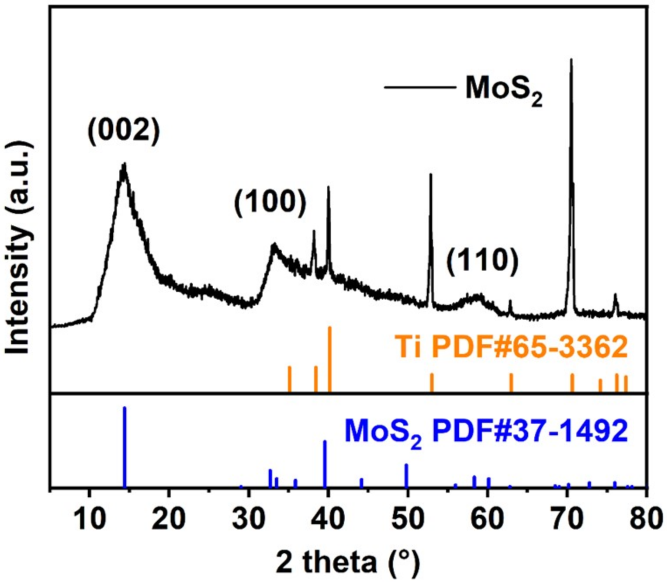

Figure S3. XRD spectra of MoS_2.

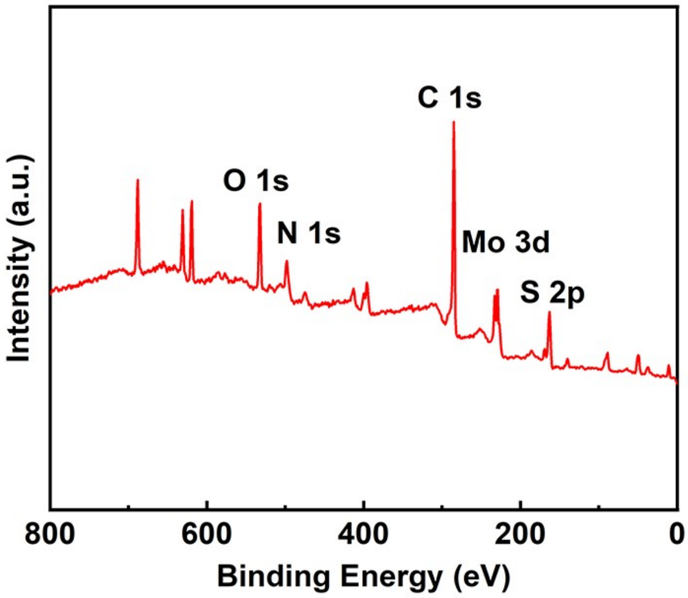

Figure S4. XPS survey spectra of N-MoS_x.

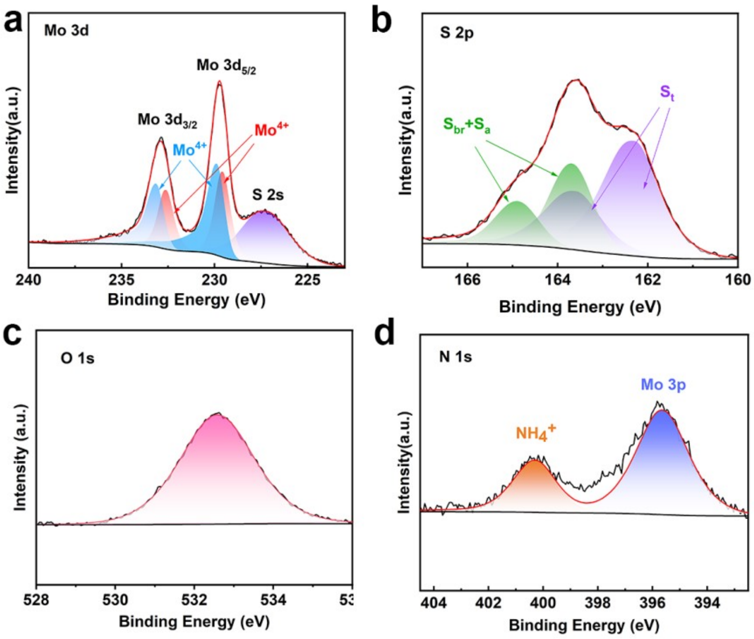

Figure S5. (a) Mo 3d XPS spectra of N-MoS_x. (b) S 2p XPS spectra of N-MoS_x. (c) O 1s of N-MoS_x. (d) N 1s spectra of N-MoS_x.

In the N 2p high resolution spectrum, the peak at 400.33 eV was attributed to NH_4^+ ions, while the peak at 395.63 eV corresponded to the Mo 3d.

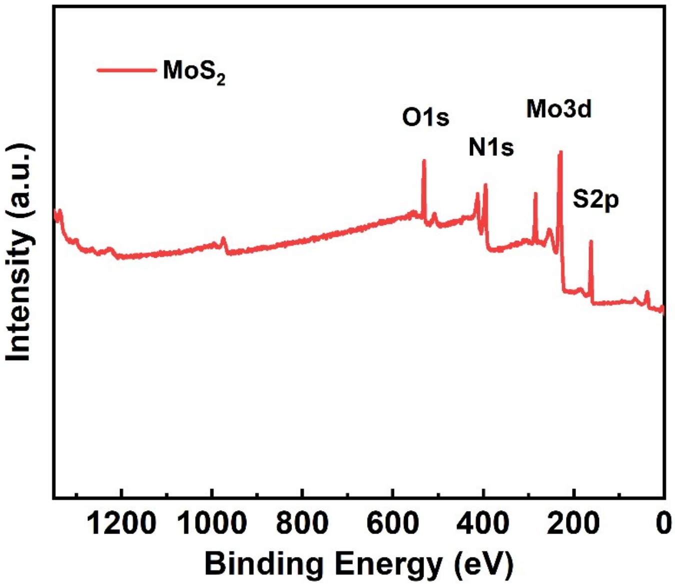

Figure S6. XPS survey spectra of MoS_2.

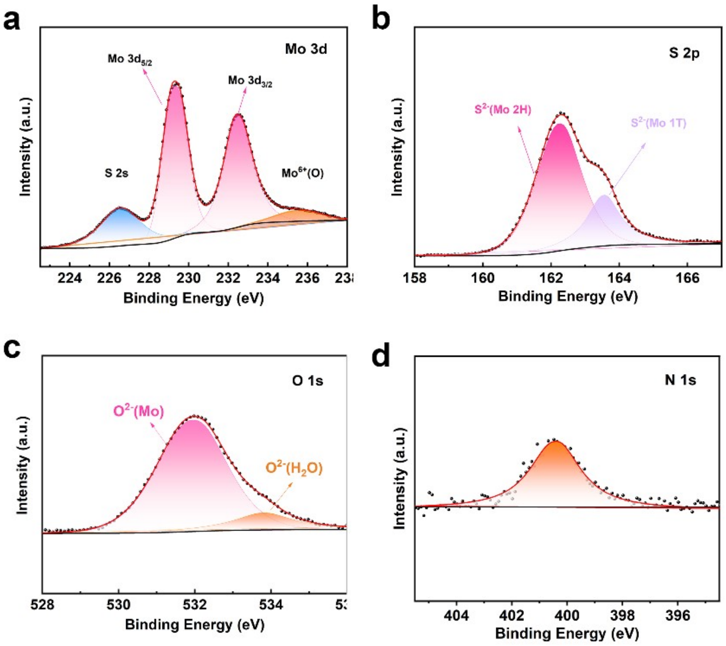

Figure S7. (a) Mo 3d XPS spectra of MoS_2. (b) S 2p XPS spectra of MoS_2. (c) O 1s of MoS_2. (d) N 1s spectra of MoS_2.

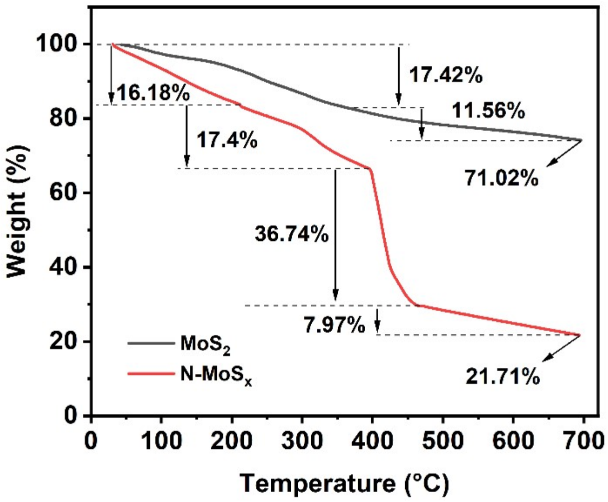

Figure S8. TGA of N-MoS$_x$ and MoS$_2$.

The initial weight loss of 17.42% observed in MoS$_2$ from room temperature to 370°C is attributed to the removal of adsorbed water and water of crystallization. Subsequently, the second weight loss of 11.56% occurring between 370°C and 700°C corresponds to the oxidation of MoS$_2$ to MoO$_3$. The initial weight loss of 16.18% observed in N-MoS$_x$ from room temperature to 200°C was attributed to the removal of adsorbed water and water of crystallization. The subsequent weight loss of 17.4% occurring between 200°C and 400°C resulted from the simultaneous release of H_2S and ammonia NH_3:

$$(NH_4)_2Mo_3S_{13} \rightarrow 2NH_3 + H_2S + Mo_3S_{12}$$

The third weight loss of 36.74% occurring between 400°C to 465°C corresponds to the Mo$_3$S$_{12}$ to MoS$_2$. The final weight loss of 7.97% occurring between 465°C to 700°C corresponds to the oxidation of MoS$_2$ to MoO$_3$.

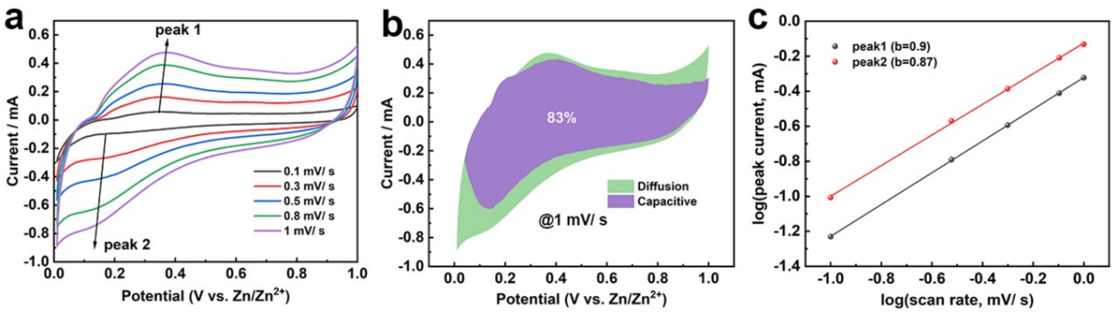

Figure S9. (a) CV curves of N-MoS$_x$ from 0.1 to 1 mV s^{-1}. (b) Linear relationship between logi and logv. (c) Capacitive contribution at 1 mV s^{-1}.

To investigate the energy storage kinetics of the N-MoS$_x$ electrode, CV tests were conducted (Figure S7a). At 0.1 mV s^{-1}, the oxidation/reduction peaks appeared at 0.2 V and 0.368 V, with slight shifts observed as the scan rate increased, maintaining a consistent curve shape. To further assess its electrochemical kinetics, the following calculations were performed [36]:

$$i = av^b \qquad (1)$$

Where i represents peak current, v denotes scan rate; a and b are adjustable parameters. Typically, the magnitude of b can be used to evaluate the process of electrochemical charge storage reactions. b value of 0.5 indicates a diffusion-controlled process, while the b value of 1.0 suggests a capacitance-controlled process. The b values calculated for reduction (peak 1) and oxidation (peak 2) peaks were 0.9 and 0.87, respectively (Figure S7b), indicating that the electrochemical reaction process is primarily governed by capacitive characteristics. To quantitatively analyze the contributions of capacitance and diffusion, the equation $i= av^b$ can be divided into two parts, as follows:

$$i=k_1v+k_2v^{1/2} \qquad (2)$$

Here, k_1 and k_2 are constants specific to particular potentials. k_1v represents the capacitive contribution, while $k_2v^{1/2}$ represents the diffusion contribution. At a scan rate of 0.1 mV s^{-1}, the capacitive contribution is 62%. When the scan rate reaches 1 mV s^{-1}, the capacitive contribution reaches 83% (Figure S7c). Subsequently, ion diffusion kinetics of N-MoS$_x$ and MoS$_2$ were studied using galvanostatic intermittent titration technique (GITT) (Figure 4e). The calculation formula is as follows [37]:

$$D = \frac{4L^2}{\pi\tau}\left(\frac{E_s}{Et}\right)^2 \qquad (3)$$

Where τ is the relaxation time, L is the electrode thickness, E_s is the total voltage change induced by the pulse, and E_t is the voltage change during GCD.

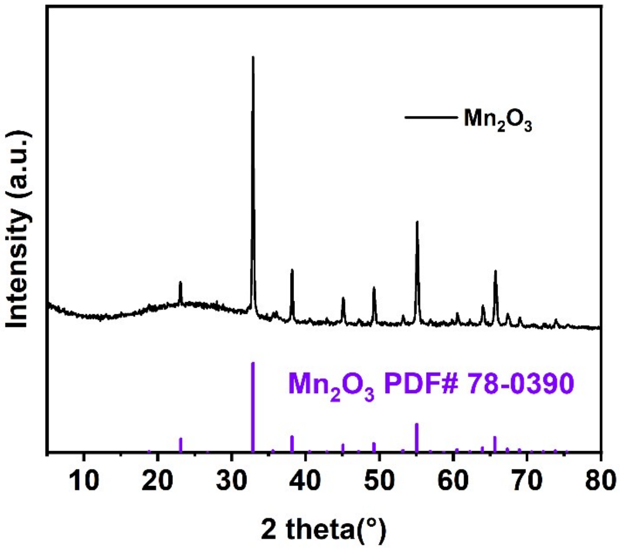

Figure S10. XRD spectra of Mn_2O_3.

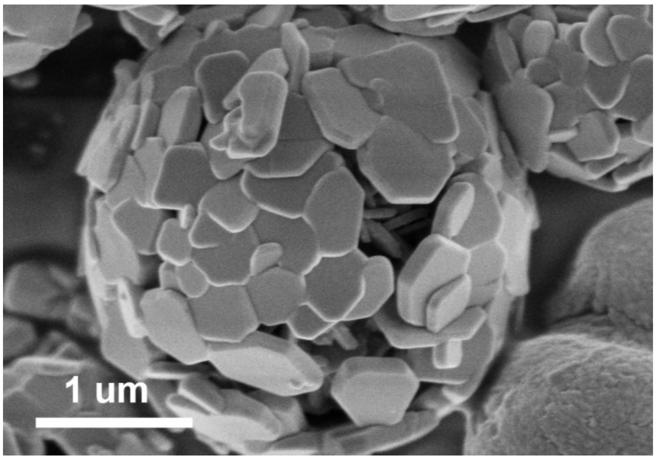

Figure S11. SEM image of Mn_2O_3.

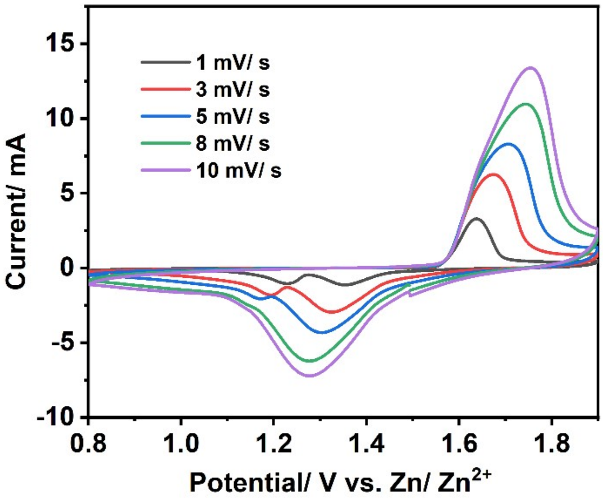

Figure S11. CV curves of Mn_2O_3.

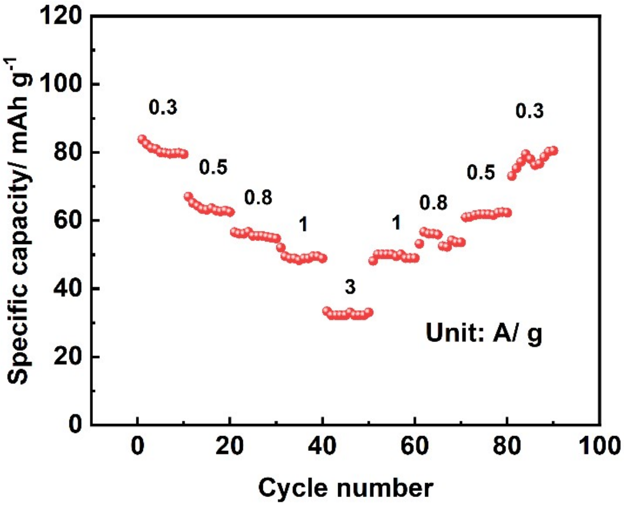

Figure S12. Rate performance of N-MoS_x@Mn_2O_3 full cell.