



Hierarchical polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$ architectures enabling high-rate and stable aqueous zinc storage

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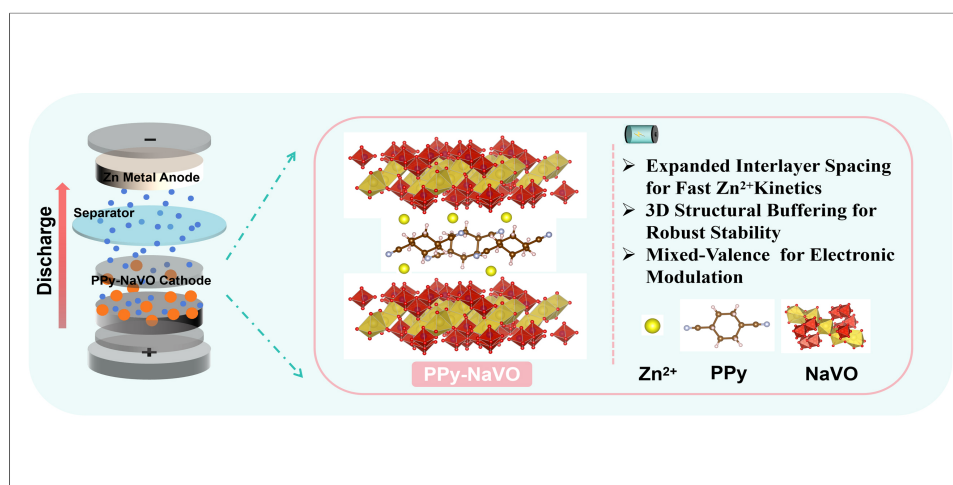
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Abstract

While aqueous Zn-ion batteries represent highly attractive technologies for large-scale grid storage, their practical implementation remains bottlenecked by severe structural degradation and sluggish ion diffusion kinetics in transition-metal oxide cathodes. Herein, a structural buffering hierarchical assembly strategy is proposed to construct a polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$ (PPy-NaVO) 3D nanoflower cathode. Structural and morphological analyses reveal that *in situ* intercalated PPy molecules act as soft pillars to significantly expand the interlayer spacing, which lowers the steric hindrance for ion diffusion and concurrently drives the anisotropic assembly of 1D nanorods into a 3D interconnected porous architecture. This cross-scale structural engineering endows the cathode with intrinsic structural buffering properties to buffer volumetric strain during continuous cycling. Furthermore, the strong interfacial charge transfer between the PPy network and

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the V-O framework induces a mixed V^{4+}/V^{5+} valence state. This optimized electronic structure is favorable for interfacial charge transfer and Zn^{2+} diffusion, minimizing the interfacial resistance and enabling ultrafast Zn^{2+}/H^+ co-intercalation kinetics. Consequently, the PPy-NaVO electrode exhibits an impressive reversible capacity (382.2 mAh g^{-1}). This structural engineering approach enables highly stable and kinetically accelerated cathodes for aqueous zinc batteries.

INTRODUCTION

The increasing global requirement for clean energy solutions and grid-scale energy has accelerated the search for post-lithium-ion battery technology that balances safety, cost-effectiveness, and high performance^[1-4]. Although the portable electronics sector is dominated by lithium-ion batteries (LIBs), the extensive application of LIBs in large-scale grid storage is severely impeded by both the uneven spatial distribution of lithium reserves and the inherent fire risks associated with combustible organic electrolytes^[5-7]. Because of the exceptional theoretical capacity (820 mAh g^{-1}) and inherent safety of metallic zinc anodes, aqueous rechargeable zinc-ion batteries (ARZIBs) have become a very attractive option^[8-10]. However, the commercialization of ARZIBs is fundamentally impeded by the lack of ideal cathode materials capable of sustaining rapid and reversible multivalent ion insertion/extraction.

Vanadium-based oxides have garnered a lot of attention from researchers among different potential systems because of their structural variety, tunable coordination environments, and the ability to participate in multi-electron redox reactions, which translate into high theoretical capacities^[11,12]. Specifically, layered sodium vanadates, such as $Na_2V_6O_{16}$ (NaVO), possess an open two-dimensional framework that is theoretically conducive to Zn^{2+} diffusion. Nevertheless, the practical performance of NaVO is severely limited by several intrinsic bottlenecks: (i) the strong electrostatic interactions that cause slow diffusion kinetics between the host framework and the high-charge-density Zn^{2+} ions^[13]; (ii) the poor intrinsic electronic conductivity of the vanadium oxide lattice^[14]; and (iii) the severe structural instability resulting from periodic lattice strain and active material dissolution during long-term cycling^[15]. These issues become even more pronounced under high-rate conditions or mechanical deformation, leading to rapid capacity fading and structural collapse. To overcome these issues, “interlayer engineering” has been extensively investigated as a primary strategy to control the physical and chemical characteristics of layered host materials^[16,17]. For example, using Na^+ /Polyethylene glycol (PEG) co-intercalation, Guo *et al.* demonstrated an interlayer-engineered ammonium vanadate cathode for rapid and effective Zn-ion storage^[18]. Han *et al.* showed that Ca/F co-doping effectively modifies the layered structure of sodium vanadate, leading to significantly enhanced energy storage performance^[19]. However, metal ion pillars often provide limited expansion and may introduce additional electrostatic repulsion, which is insufficient to overcome the high migration barrier of Zn^{2+} ^[20]. A more advanced strategy in this regard is the intercalation of conducting polymers such as polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), and polyaniline (PANI)^[21-23]. These organic molecules can act as robust molecular pillars to achieve substantial interlayer expansion far beyond that of metal ions, while simultaneously providing continuous pathways for electronic transport and acting as mechanical buffers to accommodate lattice strain. In practice, achieving both fast reaction kinetics and long-term structural stability remains a persistent challenge. Current strategies typically address electronic conductivity or interlayer expansion in isolation, largely overlooking the anisotropic lattice strain and localized stress accumulation during high-rate Zn^{2+} cycling^[24,25]. This oversight inevitably leads to premature structural degradation. Overcoming this limitation requires a hierarchical engineering approach that couples

atomic-scale lattice modification with a mesoscale structural buffering architecture.

In this work, a 3D polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$ nanoflower architecture (designated as PPy-NaVO) was successfully fabricated via a facile one-step hydrothermal approach for high-rate zinc storage. In this design, the *in situ* intercalated PPy serves a dual function. Structurally, it acts as molecular pillars to expand the interlayer spacing and directs the self-assembly of 1D nanorods into a 3D structural buffering framework. This hierarchical architecture lowers the steric hindrance for ion diffusion and effectively accommodates anisotropic volume fluctuations. Electronically, strong interfacial charge transfer between the conjugated PPy and the vanadate host induces a $\text{V}^{4+}/\text{V}^{5+}$ mixed-valence state, which minimizes the activation energy for electron hopping. Benefiting from the simultaneously optimized ionic and electronic transport, the PPy-NaVO cathode facilitates rapid $\text{Zn}^{2+}/\text{H}^+$ co-intercalation kinetics, delivering high-rate capability and extended cycling stability. This study offers an effective structural design strategy toward the development of highly stable intercalation cathodes.

EXPERIMENTAL

Materials

All chemical reagents were of analytical grade and were used as received without further purification. Vanadium pentoxide (V_2O_5), hydrogen peroxide (H_2O_2 , 30%), zinc trifluoromethanesulfonate [$\text{Zn}(\text{CF}_3\text{SO}_3)_2$], N-methyl-2-pyrrolidone (NMP), and polyvinylidene fluoride (PVDF) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium hydroxide (NaOH) and anhydrous ethanol were obtained from Tianjin Yongda Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) was supplied by Sinopharm Chemical Reagent Co., Ltd. Pyrrole (Py) was purchased from Macklin Reagent. Super P carbon black was obtained from Lion Specialty Chemicals Co., Ltd.

Synthesis of NaVO and PPy-NaVO

First, 45 mL of deionized water was mixed with 1.1 g of V_2O_5 and 5 mL of 30% H_2O_2 , and the mixture was stirred at 400 rpm for 30 min at 25 °C. After that, 0.32 g of NaOH was added, and stirring was continued at 400 rpm for another 30 min. By adding 0.5 M HCl, the pH of the mixture was adjusted to close to 2. Approximately 40 mL of the prepared yellow suspension was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated to 180 °C for 30 h. The dark-red product was collected after cooling to room temperature, repeatedly cleaned with ethanol and deionized water, and then vacuum-dried for 12 h at 60 °C to produce $\text{Na}_2\text{V}_6\text{O}_{16}$ (NaVO) nanorods. The PPy- $\text{Na}_2\text{V}_6\text{O}_{16}$ (denoted as PPy-NaVO) composite with a 3D mesoporous nanoflower architecture was prepared using a similar procedure, except that 120 μL of Py was introduced into the pale yellow solution and stirred for an additional 30 min before the hydrothermal treatment, ultimately yielding a dark green product.

Characterization

X-ray diffraction (XRD; Bruker D8 AXS, Germany) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) was used to measure the materials' phase compositions and crystallographic structures. The surface morphologies and elemental distributions were examined using a scanning electron microscope (SEM; Hitachi SU1080, Hitachi, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. Transmission electron microscopy (TEM; JEM 2100, JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM) were used to examine the microstructures and lattice fringes. The chemical states and valence variations of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, Thermo Fisher Scientific, USA) using monochromatic Al K α radiation. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Tensor II spectrometer (FTIR; Bruker Tensor II, Bruker Corporation, Germany) in the range of 400–4,000 cm^{-1} using KBr pellets. Raman spectra were collected on a LabRAM HR Evolution Raman spectrometer (Raman; LabRAM HR Evolution, HORIBA, Japan). The

specific surface area and pore structure were characterized using an automated surface area and porosity analyzer [Brunauer-Emmett-Teller (BET); Autosorb IQ-Mp, Quantachrome Instruments, USA].

Electrochemical measurements

CR2032 coin cells were assembled for electrochemical testing. The working electrodes were prepared by mixing the active material (NaVO or PPy-NaVO), Super P carbon black, and PVDF binder in NMP at a mass ratio of 7:2:1. The resulting slurry was coated onto a current collector and dried in a vacuum drying oven (DHG-9246A; Shanghai Yiheng Scientific Instrument Co., Ltd.). The mass loading of the active material was approximately $1.5\text{--}2.0\text{ mg cm}^{-2}$, as determined using an electronic analytical balance (Sartorius SQP series; Sartorius Scientific Instruments Co., Ltd.). The cells were assembled using a Zn foil anode, a Whatman glass fiber separator, and a 3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ aqueous electrolyte, and the assembly was completed with a coin cell crimping machine (MSK-110; Shenzhen Kejing Star Technology Co., Ltd.). All electrochemical measurements were conducted within a voltage window of 0–1.8 V (vs. Zn^{2+}/Zn). Cyclic voltammetry (CV; $0.2\text{--}1.0\text{ mV s}^{-1}$), electrochemical impedance spectroscopy (EIS; $100\text{ mHz--}100\text{ kHz}$, $\pm 5\text{ mV}$), and galvanostatic intermittent titration technique (GITT) were recorded on a Bio-Logic VMP3 electrochemical workstation (VMP3; Bio-Logic, France). Galvanostatic charge-discharge (GCD) cycling was evaluated using a NEWARE battery testing system (NEWARE; Shenzhen Neware Electronics Co., Ltd.).

RESULTS AND DISCUSSION

The synthesis and structural characteristics of the PPy-NaVO composite are illustrated schematically in [Figure 1](#). Fabricated via a hydrothermal process coupled with *in situ* polymerization, the composite self-assembles into a unique 3D mesoporous nanoflower architecture. This process enables an effective structural modification of the pristine NaVO host through the bulk intercalation of PPy. The intercalated PPy chains effectively expand the vanadate interlayer spacing, which significantly lowers the migration barrier for solid-state Zn^{2+} diffusion. Consequently, this structural optimization intrinsically accelerates ionic kinetics, enabling exceptional high-rate zinc storage. SEM and TEM were used to examine the samples' morphology and microstructure. As seen in [Figure 2A](#) and [Supplementary Figure 1A and B](#), the PPy-NaVO composite features a 3D hierarchical nanoflower architecture assembled from interconnected nanorods. In contrast, the pristine NaVO consists of densely aggregated 1D nanorods [[Supplementary Figure 1C and D](#)] with corresponding elemental mapping confirming the distribution of Na, V, and O [[Supplementary Figure 2](#)]. During synthesis, the *in situ* polymerized PPy acts as a structure-directing agent through interfacial coordination, driving the anisotropic self-assembly of the nanorods into a 3D mesoporous network. EDS mapping confirms the homogeneous spatial distribution of C, N, Na, V, and O elements throughout the nanoflower structure [[Figure 2B–F](#)]. Additionally, the EDS spectra [[Supplementary Figure 3](#)] quantitatively verify the substantial incorporation of C and N in the composite, which are absent in the pristine NaVO. The successful incorporation of PPy into the vanadate framework is consistent with a uniform distribution of C and N. The pristine NaVO exhibits lattice fringes with a *d*-spacing of $1.542\text{ \AA}$, corresponding to the (431) plane [[Figure 2G and H](#)]. For PPy-NaVO, lattice fringes with a *d*-spacing of $1.804\text{ \AA}$ are observed, corresponding to the (411) plane [[Figure 2I and J](#)]. These observations indicate that PPy incorporation alters the local lattice structure of the vanadate framework. Furthermore, the interconnected 3D architecture and intrinsic mesoporosity act as mechanical buffers to accommodate localized stress. This configuration accommodates the anisotropic volume changes during continuous Zn^{2+} (de)intercalation, consequently maintaining the electrode's structural stability throughout extended cycling.

The crystalline structures and phase compositions were further determined by XRD. The pure layered phase (PDF#22-1412) has been identified from the pristine NaVO diffraction pattern [[Figure 3A](#)]. After PPy intercalation, the characteristic (001) diffraction peak shifts from 11.2° to 9.88° [[Figure 3B](#)]. This shift corresponds to an increase in the interlayer distance from 0.79 nm to 0.89 nm , according to Bragg's equation.

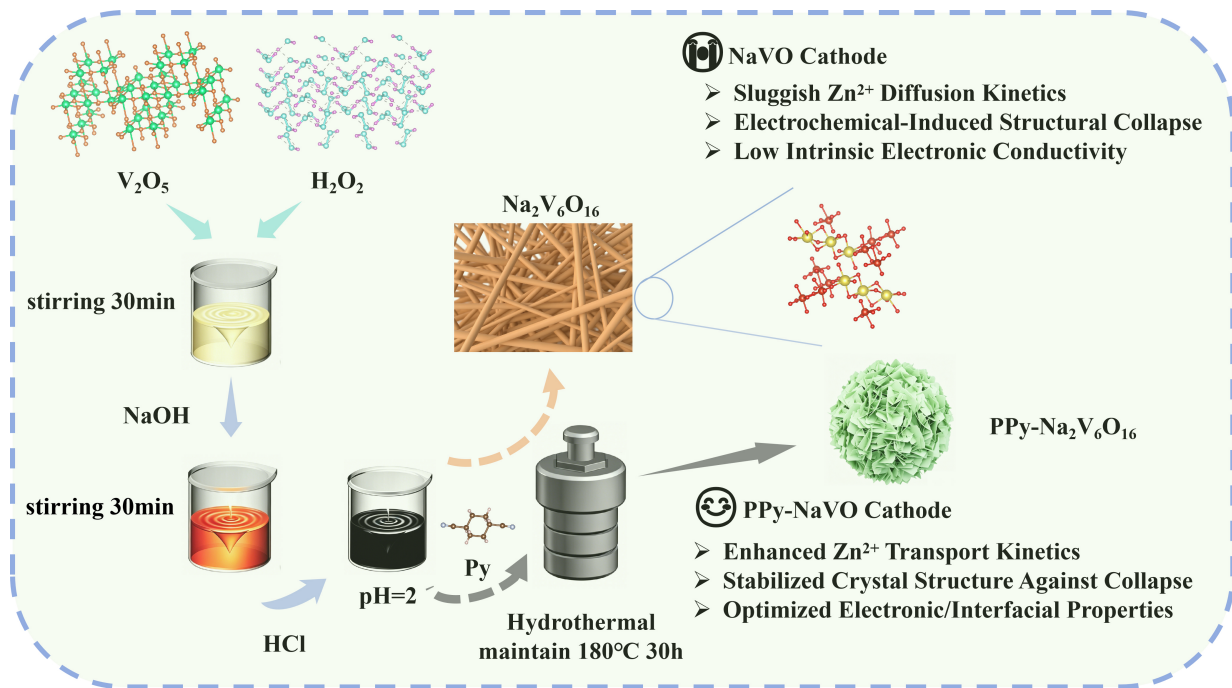


Figure 1. Schematic diagram of the synthesis pathway for the PPy-NaVO composite. PPy-NaVO: Polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$.

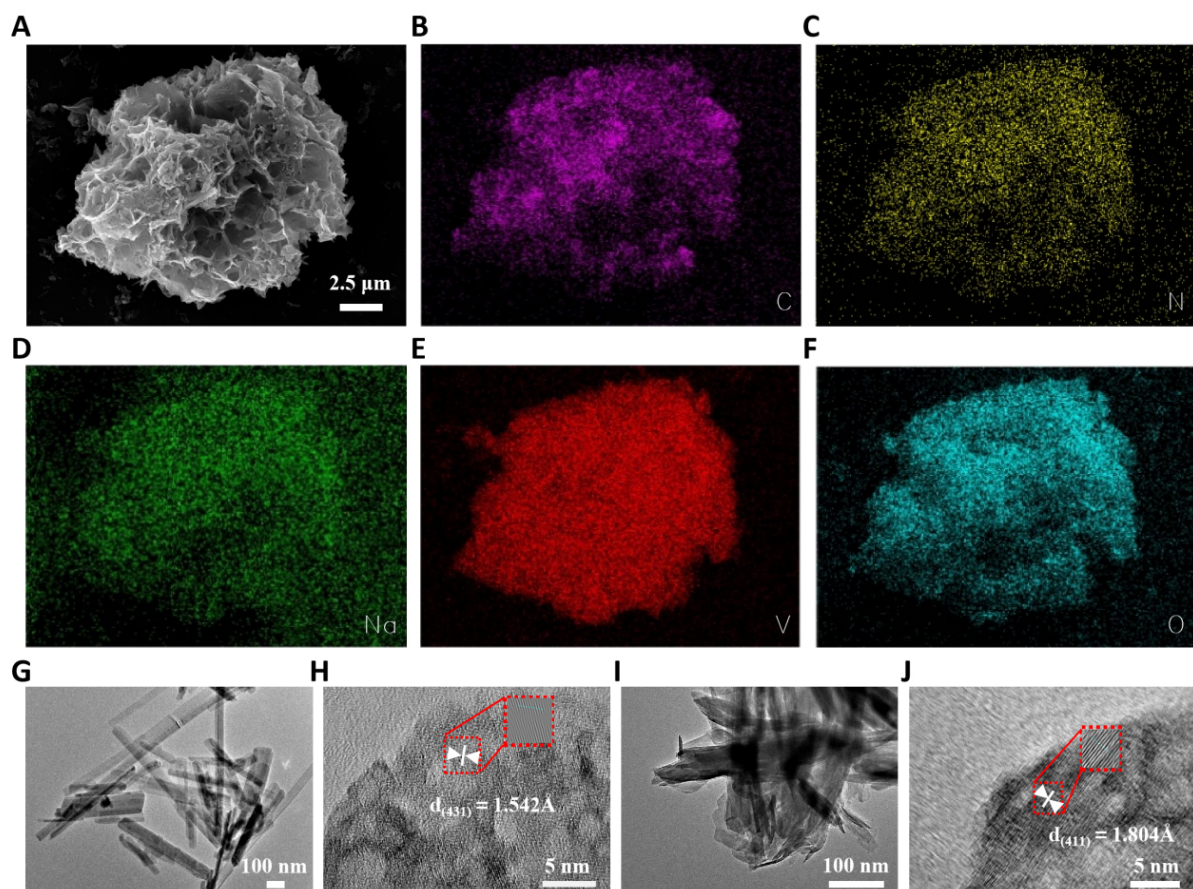


Figure 2. (A) SEM image of PPy-NaVO; (B-F) EDS mapping images of (A); (G) TEM image of NaVO; (H) HRTEM image of NaVO; (I) TEM image of PPy-NaVO; (J) HRTEM image of PPy-NaVO. EDS: Energy-dispersive X-ray spectroscopy; TEM: transmission electron microscopy; HRTEM: high-resolution transmission electron microscopy; SEM: scanning electron microscope; PPy-NaVO: polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$.

This expanded interlayer spacing lowers the migration barrier for solid-state Zn^{2+} diffusion and provides additional free volume to accommodate the intercalated ions and volume changes during cycling. The chemical composition was examined using FTIR spectroscopy [Figure 3C]. The low-wavenumber V-O vibrations in PPy-NaVO are preserved, indicating that the basic vanadate framework is maintained after intercalation. Additionally, other absorption bands appear at 1,410 and 765 cm^{-1} , which are attributed to the pyrrole ring's C-N stretching and C-H out-of-plane bending vibrations, respectively^[26]. The broad band near 1,600 cm^{-1} is attributed to the overlapping signals of the intercalated water bending vibration and the PPy C=C skeletal stretching^[27]. To elucidate the interfacial electronic structure and chemical states of the composite, XPS was employed. Na, V, O, C, and N are present in the survey spectrum [Supplementary Figure 4], with no identified impurities. The high-resolution C 1s spectrum of PPy-NaVO [Figure 3D] displays three peaks at 284.7, 285.8, and 287.9 eV, which are assigned to C-C, C-N, and C-O bonds, respectively^[28]. Three peaks can be seen in the N 1s spectra [Figure 3E] at 399.7, 400.7, and 402.1 eV, which correspond to the pyrrole ring's -NH-, $-\text{N}^+\text{H}-$, and $=\text{N}^+$ - species^[29]. The existence of positively charged nitrogen species suggests that the intercalated PPy is in an oxidatively doped state, which enhances the composite's electrical conductivity. The V 2p high-resolution spectra [Figure 3F] further verify the interfacial charge transfer. Pristine NaVO exhibits a typical spin-orbit doublet at 517.3 eV ($\text{V } 2\text{p}_{3/2}$) and 524.7 eV ($\text{V } 2\text{p}_{1/2}$), characteristic of the V^{5+} oxidation state^[30,31]. After PPy intercalation, the deconvoluted V 2p spectrum of PPy-NaVO reveals a mixed-valence feature: the V^{5+} components located at 517.4 eV ($\text{V } 2\text{p}_{3/2}$) and 524.8 eV ($\text{V } 2\text{p}_{1/2}$) with a spin-orbit splitting of 7.4 eV account for approximately 57.36% of the total vanadium, while the V^{4+} components at 516.1 eV ($\text{V } 2\text{p}_{3/2}$) and 523.4 eV ($\text{V } 2\text{p}_{1/2}$) with a spin-orbit splitting of 7.3 eV account for approximately 42.64%. Such partial reduction of V^{5+} to V^{4+} is attributed to electron transfer from the PPy network to the vanadate framework. The resulting $\text{V}^{4+}/\text{V}^{5+}$ mixed-valence state is expected to reduce the activation energy for intervalence small-polaron hopping, thereby improving the intrinsic electronic conductivity and facilitating rapid charge-transfer kinetics of the cathode^[32]. To better understand the local structural environment and host-guest interactions, Raman spectroscopy was used in Figure 3G. For pristine NaVO, the spectrum exhibits distinct vanadate framework vibrations. In particular, the $(\text{V}_2\text{O}_2)_n$ stretching and $\text{V}=\text{O}$ bending vibrations are attributed to the peaks at 125 and 287 cm^{-1} , respectively. The V3-O bond of the triply coordinated oxygen in the edge-sharing VO_x polyhedra is indicated by the signal at 510 cm^{-1} ^[33]. Furthermore, the V-O-V and $\text{V}=\text{O}$ stretching modes are illustrated by the bands at 698 and 764 cm^{-1} . Following PPy intercalation, these intrinsic peaks undergo frequency shifts, reflecting an altered local coordination environment induced by interfacial interactions and localized stress from the intercalated PPy molecules. Concurrently, the intensity of the vanadate peaks decreases significantly, which is attributed to the optical absorption of the conjugated PPy network^[34]. Also, a strong broad band appears in the range 1,300–1,700 cm^{-1} , which includes the stretching vibrations of the pyrrole rings C-C ($\sim 1,320 \text{ cm}^{-1}$), C-N ($\sim 1,400 \text{ cm}^{-1}$) and C=C ($\sim 1,589 \text{ cm}^{-1}$). These results indicate the successful intercalation of PPy and its structural interaction with the vanadate framework^[35]. As shown in [Figure 3H], both pure NaVO and PPy-NaVO composite show the nitrogen adsorption-desorption isotherms of type IV with H3 hysteresis loops. After the intercalation of PPy, the specific surface area and the total pore volume are significantly increased from 29.9 $\text{m}^2 \text{ g}^{-1}$ and 0.203 $\text{cm}^3 \text{ g}^{-1}$ to 39.8 $\text{m}^2 \text{ g}^{-1}$ and 0.277 $\text{cm}^3 \text{ g}^{-1}$, respectively, while the average size of mesopores is maintained at 28 nm. As a result, this optimized porous architecture promotes electrolyte absorption and provides more reactive sites for capacitive charge accumulation.

To evaluate the electrochemical zinc storage potential, CV was performed, and the profiles obtained at 0.8 mV s^{-1} clearly display well-defined anodic and cathodic peaks, indicating the occurrence of Zn^{2+} insertion/extraction redox reactions [Figure 4A]. Compared to pristine NaVO, the PPy-NaVO electrode exhibits a larger integrated area and higher peak currents, indicating enhanced charge storage capacity. This reversibility is further corroborated by the initial three CV cycles at a scan rate of 0.2 mV s^{-1} [Supplementary Figures 5 and 6]. The PPy-NaVO electrode undergoes a rapid initial electrochemical activation, after which

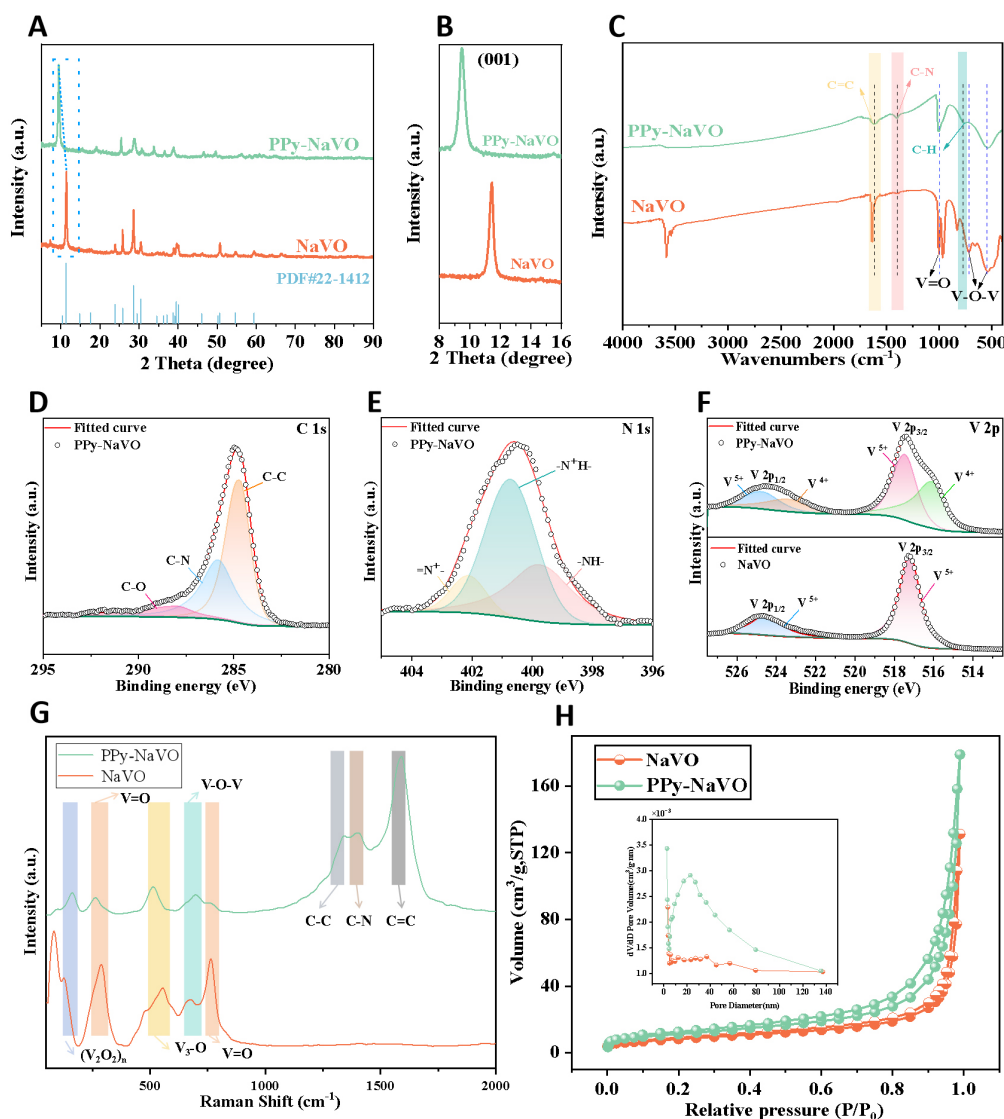


Figure 3. Chemical structure characterization of PPy-NaVO. (A) Full XRD patterns; (B) Enlarged view of the (001) diffraction peak; (C) FTIR spectra; (D–F) High-resolution XPS spectra; (G) Raman spectra; (H) Pore size distribution curves (inset) and N₂ adsorption-desorption isotherm curves. XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy; FTIR: Fourier transform infrared spectroscopy; PPy-NaVO: polypyrrole-pillared Na₂V₆O₁₆.

the subsequent CV curves overlap almost completely, confirming its highly reversible electrochemical kinetics. The CV results are in agreement with the GCD profiles at 0.5 A g^{−1} [Figure 4B], where PPy-NaVO offers a high specific capacity (382.2 mAh g^{−1}), much beyond that of the pure NaVO (223.2 mAh g^{−1}). The kinetic advantages of PPy-NaVO are further highlighted by its rate capability [Figure 4C]. The electrode delivers highly reversible capacities of 382.2, 359.8, 310.6, 281.3, 254.6, and 219.8 mAh g^{−1} at current densities of 0.5, 1, 3, 5, 7, and 10 A g^{−1}, respectively [Supplementary Figures 7 and 8]. The capacity recovers to approximately 95.4% of the initial value upon returning to 0.5 A g^{−1}, indicating excellent electrochemical reversibility and structural stability at high rates. This rate performance compares favorably with recently reported vanadium-based cathodes [Figure 4D; Supplementary Table 1]. At a high current density of 5.0 A g^{−1}, the prolonged cycling performance of both electrodes was measured [Figure 4E]. The pristine NaVO cathode has poor cycling stability with a capacity retention of just ~80% after 250 cycles. In contrast, the PPy-NaVO composite exhibits increased cyclability, able to retain ~80% of its original capacity after 500 charge/discharge cycles. To further examine the electrochemical reaction kinetics, EIS experiments were

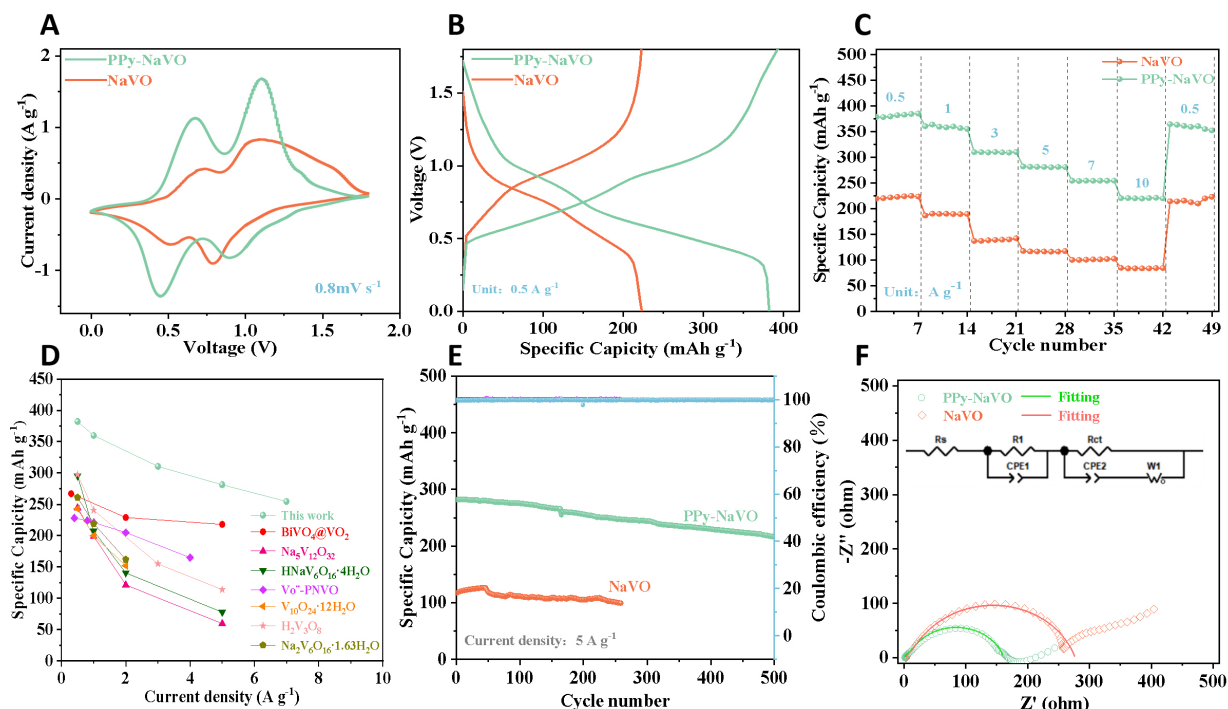


Figure 4. (A) CV curves; (B) GCD curves; (C) Rate performance; (D) Capacity comparison with reported vanadium-based AZIB cathodes; (E) Cycling stability at 5 A g⁻¹; (F) Nyquist plots (EIS). CV: Cyclic voltammetry; GCD: galvanostatic charge-discharge; EIS: electrochemical impedance spectroscopy; AZIB: aqueous zinc-ion battery; PPy-NaVO: polypyrrole-pillared Na₂V₆O₁₆.

carried out [Figure 4F]. The high-frequency semicircle of PPy-NaVO is substantially smaller than that of pristine NaVO, according to the Nyquist plots. As determined from the Nyquist plots and equivalent circuit fitting, the Rct values are 153.7 Ω for PPy-NaVO and 268.8 Ω for pristine NaVO with corresponding χ^2 values of 1.61×10^{-3} and 6.175×10^{-3} , respectively [Supplementary Table 2]. This reduced Rct indicates that the integrated PPy network effectively accelerates interfacial charge-transfer kinetics^[36].

The Zn²⁺ storage kinetics were investigated using CV at different scan rates [Figure 5A]. The peak shapes are retained at all scan rates, indicating reversible redox processes. The four redox peaks of PPy-NaVO have b values of 0.88, 0.64, 0.78, and 0.71 when the peak current (i) versus scan rate (ν) is analyzed using $i = a\nu^b$ [Figure 5B]. These b values exceed those of the pristine NaVO [Supplementary Figures 9 and 10], indicating a charge storage mechanism comprising both diffusion-controlled intercalation and surface-controlled capacitive processes. The capacitive contribution of PPy-NaVO [Figure 5C] increases from 53.86% at 0.2 mV s⁻¹ to 71.61% at 1.0 mV s⁻¹. For pristine NaVO, the capacitive ratio ranges from 46.41% to 66.37% at the same scan rates [Supplementary Figures 11 and 12]. As PPy-NaVO has more sites for surface-controlled charge transfer owing to its larger specific surface area, it has a more significant capacitive contribution. GITT was used to calculate solid-state Zn²⁺ diffusion coefficients [Figure 5D]. The V⁴⁺/V⁵⁺ mixed-valence state in PPy-NaVO effectively lowers the Zn²⁺ transport barrier, ensuring robust D_{Zn} values [Figure 5E]. The PPy-NaVO//Zn cell exhibits an energy density of 278.99 Wh kg⁻¹ with a power density of 365.07 W kg⁻¹, illustrated in the Ragone plot [Figure 5F]. To demonstrate practical applicability, a series connection of two PPy-NaVO//Zn coin cells was utilized to power an electric fan [Supplementary Figure 13], while three cells connected in series successfully illuminated an Light-Emitting Diode (LED) display [Supplementary Figure 14]. The structural evolution and charge storage mechanism of the PPy-NaVO cathode were investigated using *ex-situ* characterizations [Figure 6A]. During the discharge process, the (001) diffraction peak shifts to a smaller angle in the *ex-situ* XRD patterns [Figure 6B and C]. This shift corresponds to the increase in interlayer space due to hydrated Zn²⁺ intercalation. The (001) peak recovers to the initial state after charging

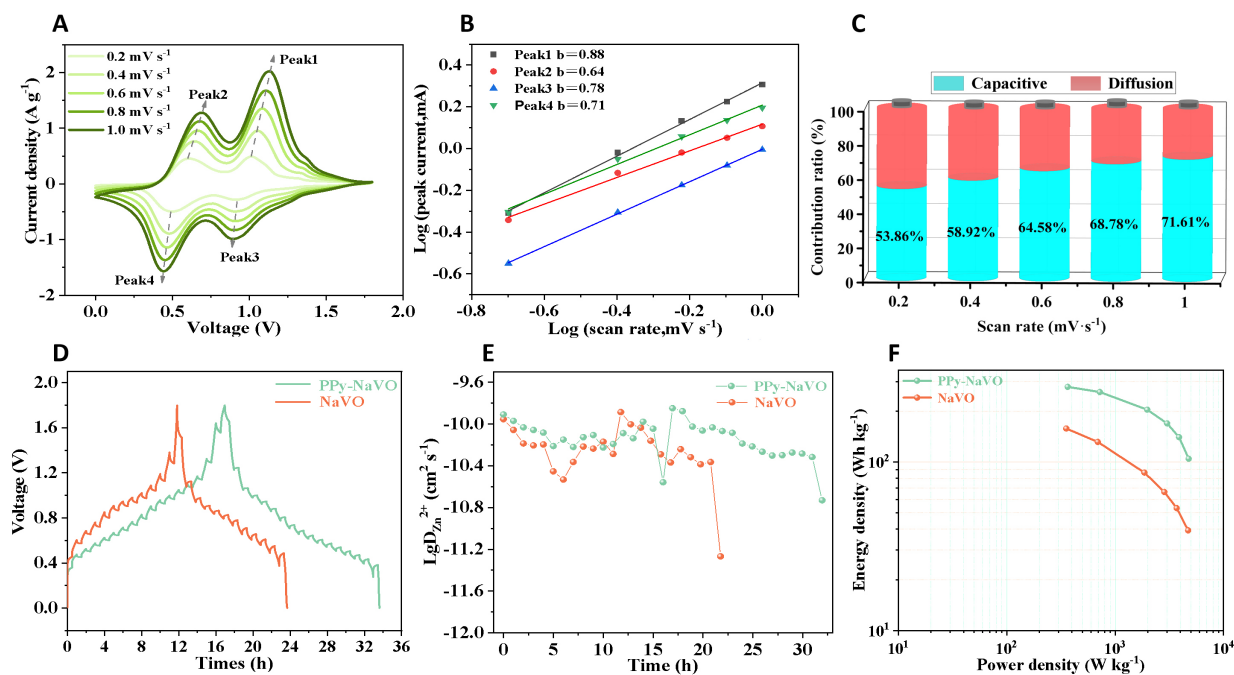


Figure 5. (A) CV curves; (B) Log(*i*) versus log(*v*) fitting plot; (C) Capacitive contribution of PPy-NaVO at different scan rates; (D) GITT charge-discharge comparison curves; (E) Comparison of Zn²⁺ diffusion coefficients; (F) Ragone plot of NaVO and PPy-NaVO. CV: Cyclic voltammetry; GITT: galvanostatic intermittent titration technique; PPy-NaVO: polypyrrole-pillared Na₂V₆O₁₆.

to 1.15 V, indicating reversible lattice variation. Additionally, new diffraction peaks emerge during discharge, corresponding to Zn₃(OH)₂V₂O₇·2H₂O (ZVO) and a basic zinc salt (BZS)^[37,38]. Upon fully charging the electrode, the intensity of these diffraction peaks decreases significantly, although weak residual signals remain. This highly reversible precipitation-dissolution behavior suggests a co-insertion mechanism^[39]. The chemical state evolution was examined using *ex-situ* XPS. The high-resolution Zn 2p spectrum [Figure 6D] reveals no initial zinc signal. After discharging to 0 V, the Zn 2p doublet appears at 1,023.0 eV and 1,046.2 eV, confirming Zn²⁺ intercalation. Following the charge process, the Zn 2p signal intensity decreases, indicating Zn²⁺ extraction. The weak residual signal is attributed to trapped Zn²⁺ or residual precipitates^[40]. The V 2p_{3/2} spectrum [Figure 6E] tracks the vanadium valence states. The pristine PPy-NaVO electrode presents a V⁴⁺/V⁵⁺ mixed-valence state. A V³⁺ peak emerges, and the V⁵⁺ component decreases during discharge, reflecting a steady reduction via V⁵⁺ to V⁴⁺ and then to V³⁺. Upon full charging, the V 2p_{3/2} spectrum returns to the initial mixed-valence state^[41]. The PPy-NaVO cathode's electrochemical mechanism is shown in Figure 6F. In addition to structural expansion/contraction and multielectron vanadium redox reactions, the process includes a reversible Zn²⁺/H⁺ co-intercalation. The intercalated PPy network and the mesoporous architecture provide continuous electron and ion transport pathways. Furthermore, this structural configuration acts as a mechanical buffer to accommodate localized stress caused by lattice volume changes, keeping the structural stability of the cathode during repeated cycling.

CONCLUSIONS

In conclusion, a PPy-NaVO composite was developed via a hydrothermal process and used as a cathode. The structural and electronic properties of the vanadate host are intrinsically optimized through polymer intercalation and the induction of a V⁴⁺/V⁵⁺ mixed-valence state. Structural analyses confirm that the intercalated PPy chains increase the interlayer distance from 0.79 nm to 0.89 nm. This expanded coordination environment, coupled with the formation of V⁴⁺ species, facilitates multi-electron redox reactions at the vanadium active centers. *Ex-situ* characterizations demonstrate that charge storage proceeds

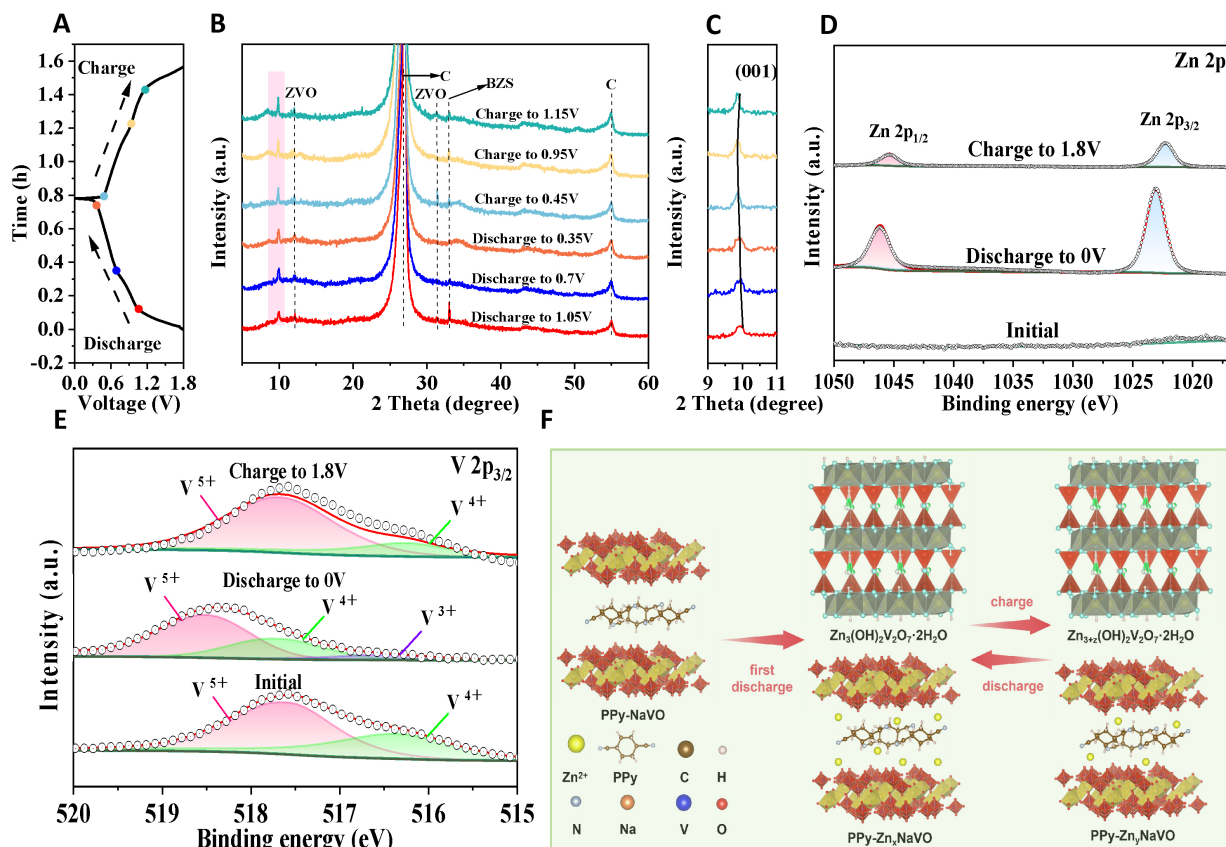


Figure 6. (A) Typical GCD profile of the electrode; *Ex-situ* analyses of XRD patterns at the selected points of (B) PPy-NaVO; (C) Enlarged view of the (001) diffraction peak; (D and E) *Ex-situ* XPS analyses; (F) Schematic illustration of the electrochemical storage process. GCD: Galvanostatic charge-discharge; XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy; ZVO: $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$; BZS: basic zinc salt; PPy-NaVO: polypyrrole-pillared $\text{Na}_2\text{V}_6\text{O}_{16}$.

via a highly reversible $\text{Zn}^{2+}/\text{H}^+$ co-intercalation mechanism. During continuous cycling, the expanded interlayer spacing provides sufficient free volume to accommodate anisotropic lattice strain, while the continuous electronic pathways of the PPy network and the structural buffering framework help mitigate the structural collapse typically induced by the high charge density of Zn^{2+} . This work provides an effective structural engineering method for building stable vanadium-based cathodes for aqueous energy storage.

DECLARATIONS

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Authors' contributions

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Availability of data and materials

The original contributions presented in this study are included in the article/[Supplementary Materials](#). Further inquiries can be directed to the corresponding author(s).

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

Zhang, S. is the Guest Editor of the special topic "Interfacial and Composite Material Design for Advanced Batteries, Photocatalysis, and Electrocatalysis" of the journal *Energy Materials*, but was not involved in any steps of editorial processing, notably including reviewer selection, manuscript handling, and decision-making, while the other authors have declared that they have no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

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