

Architecting $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ microflower cathodes with NaF-rich interfaces for ultrafast and ultrastable sodium-ion storage

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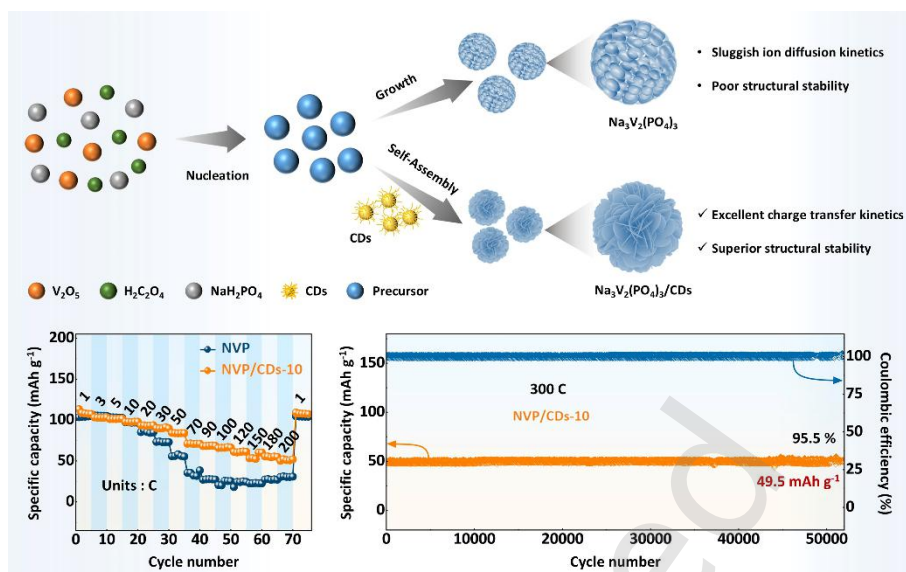
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Hydroxyl-functionalized carbon dots are employed as multifunctional regulators to direct $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ microflower construction and NaF-rich interfacial structure formation, enabling rapid ion/electron transport and stable interfacial chemistry toward ultrafast and durable sodium-ion storage.

Research Article

Architecting $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ microflower cathodes with NaF-rich interfaces for ultrafast and ultrastable sodium-ion storage

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Abstract

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with a NASICON framework stands out as a compelling cathode for sodium-ion batteries (SIBs) due to its open Na^+ transport channels and stable crystal framework. However, its fast-charging capability remains constrained by the poor electrical conductivity and uncontrolled growth of cathode-electrolyte interfacial layers under high rates. Herein, carbon dots (CDs) are employed to couple bulk architectural engineering with interfacial chemistry reconstruction in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, enabling the rapid ion/electron transport. First, the CDs can guide the self-assembly of two-dimensional nanosheet subunits into hierarchical nanoflower-like microspheres, thereby shortening Na^+ diffusion pathways. Second, the introduced CDs generate a thin carbon layer that effectively improves electrical conductivity with a limited carbon content. Third, the CDs-regulated surface chemistry promotes the formation of a thin, uniform, and NaF-rich CEI layer, which accelerates interfacial charge transfer. Consequently, the optimized cathode delivers 108.8 mAh g^{-1} at 1 C and 49.5 mAh g^{-1} at 300 C, while maintaining 95.5% capacity retention after 50000 cycles. Moreover, the corresponding full cell achieves a high energy density of 382.6 Wh kg^{-1} and retains 226.2 Wh kg^{-1} within a short charging time of approximately 102.2 s. Overall, these results highlight CDs-mediated structural and interfacial regulation as an effective route toward fast-charging SIBs.

Keywords: sodium-ion batteries, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode, carbon dots, fast charging

1 Introduction

The rapid expansion of grid-scale renewables and short-duration backup systems has intensified the need for fast-charging and ultra-long-life electrochemical energy storage beyond lithium-ion batteries[1-3]. Sodium-ion batteries (SIBs) are therefore considered a promising complementary technology, benefiting from abundant sodium resources and the potential for rapid charge storage [4-14]. However, their relatively low energy density and sluggish kinetics remain major obstacles to practical implementation. Therefore, cathode materials with high energy density, fast charging capability, and long cycle life are highly desirable for addressing the performance limitations of SIBs [15-22]. Various cathode materials have been explored, including transition metal oxides [23-25], Prussian blue compounds [26], and phosphates [27-29]. Among them, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) is regarded as a promising polyanionic cathode because of its NASICON three-dimensional framework, open Na^+ transport channels, and stable bulk crystal structure [30-35]. Nevertheless, the intrinsically low electrical conductivity and uncontrolled growth of cathode-electrolyte interfacial (CEI) layers give rise to sluggish kinetics, thereby limiting its rate capability and cycling durability [36, 37]. These issues indicate that both charge transport and interfacial chemistry should be simultaneously optimized to enable fast-charging and durable NVP cathodes.

To overcome these limitations, carbon-based modification and structural engineering have been widely developed to improve the electrochemical performance of NVP [38-41]. For example, hierarchically porous NVP cathodes with

nitrogen-doped carbon coatings [42] and NVP encapsulated in N-doped carbon nanocages [43] have been shown to enhance electronic conductivity, promote Na⁺ transport, and improve high-rate cycling stability. In addition, oxygen-containing functional groups in carbon precursors can provide binding sites for cathode precursors and promote uniform surface modification, thereby improving interfacial compatibility and structural integrity [44]. Nevertheless, existing strategies have largely emphasized conductivity enhancement or morphology optimization, whereas the suppression of resistive byproduct accumulation in the CEI and interfacial resistance growth during high-rate cycling remains insufficiently addressed. Therefore, a multifunctional strategy that integrates conductive modification, hierarchical architecture construction, and surface chemistry regulation is highly desirable for developing fast-charging and long-life NVP cathodes. Carbon dots (CDs), featuring nanoscale dimensions and abundant surface functional groups, are well suited for this purpose, as these characteristics have been demonstrated to regulate particle growth, facilitate Na⁺ migration, and modulate interfacial chemistry [45]. More importantly, although considerable efforts have been devoted to enhancing the bulk conductivity of NVP, fast-charging durability is not governed solely by bulk charge transport. The dynamic evolution of the CEI layer under high-rate cycling remains largely overlooked, despite its decisive role in regulating interfacial charge transfer, parasitic reactions, and cycling stability.

To address this challenge, hydroxyl-functionalized CDs are employed as multifunctional regulators to couple hierarchical architecture construction with

surface chemistry modulation in NVP. The introduced CDs promote the formation of hierarchical nanoflower-like NVP microspheres composed of nanosheet subunits, where the CD-derived thin carbon layer improves electron transport, while the nanosheet-assembled architecture shortens Na^+ diffusion pathways. Meanwhile, CDs-regulated surface chemistry is shown to facilitate the formation of a thin, uniform, and NaF-rich CEI layer, which suppresses interfacial side reactions and improves charge-transfer kinetics. As a result, the optimized cathode delivers 108.8 mAh g^{-1} at 1 C and 52.1 mAh g^{-1} at an ultrahigh rate of 200 C. When further assessed at 300 C, it still delivers 49.5 mAh g^{-1} and maintains 95.5% capacity retention after 50000 cycles, corresponding to an ultrashort charging time of approximately 4.7 s per charge. Moreover, its cycling stability was further validated over a wide range of rates from 1 to 300 C and mass loadings from 1 to 9.8 mg cm^{-2} . Furthermore, the full cells assembled with the optimized cathode and hard carbon anode deliver a high energy density of 382.6 Wh kg^{-1} under a power density of 324.3 W kg^{-1} and retain 226.2 Wh kg^{-1} under a high power density of 7965 W kg^{-1} with a short charging time of ≈ 102.2 s per charge. Remarkably, the full cells also exhibit excellent cycling stability, maintaining 96.1% capacity retention after 1500 cycles at 1 A g^{-1} .

2 Results and discussion

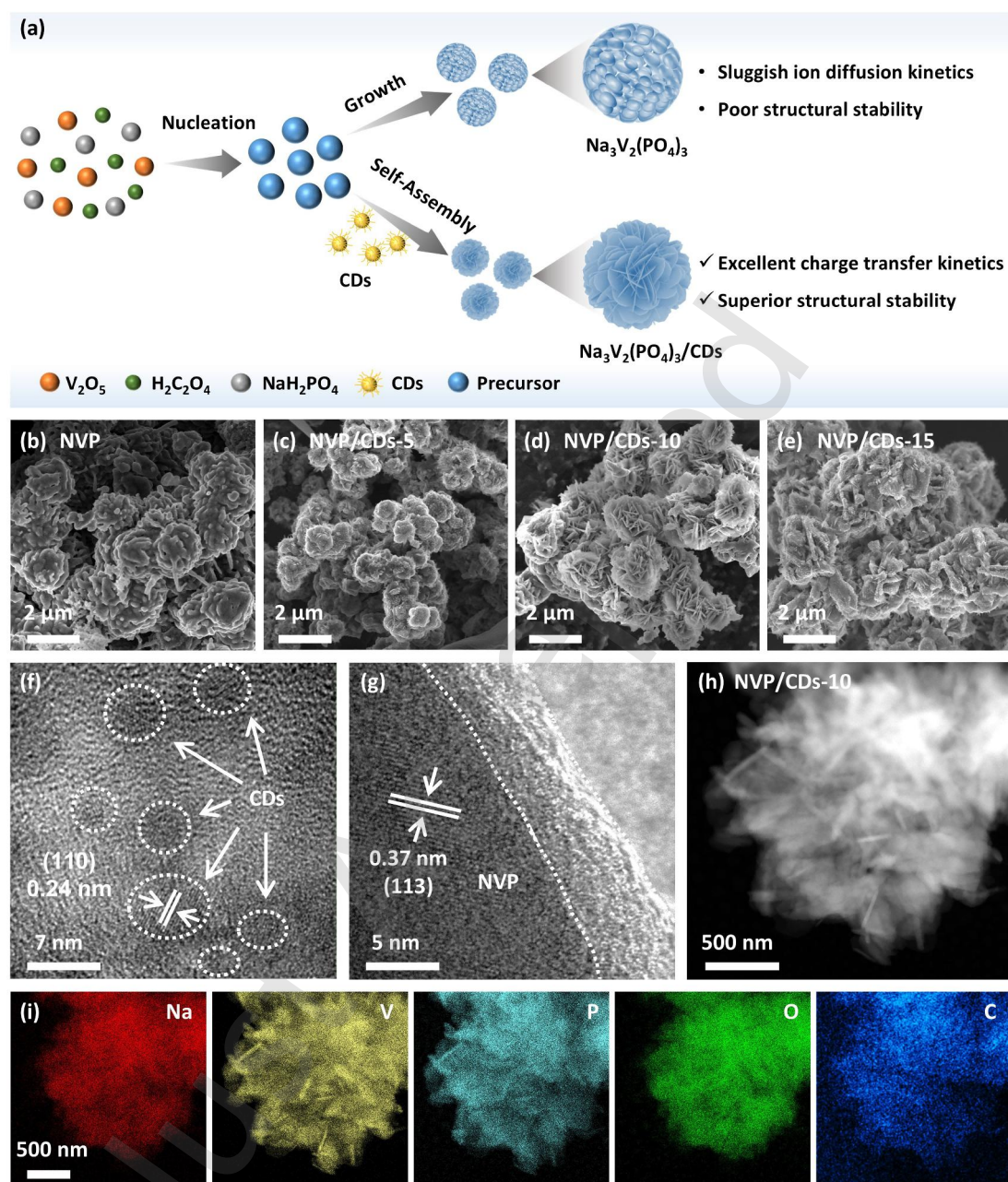


Figure 1 (a) Illustration of the optimization mechanism induced by CD incorporation in NVP. SEM of (b) NVP and (c-e) NVP/CDs-x, x = 5 ml, 10 ml, and 15 ml. HRTEM of (f) CDs and (g) NVP/CDs-10. (h) STEM of NVP/CDs-10 and (i) corresponding element mapping images.

NVP and NVP/CDs-x were synthesized via a co-precipitation method followed by heat treatment under an argon atmosphere, where x denotes the volume of the added CDs solution. Hydroxyl-functionalized CDs were introduced as a structure-directing

additive to modulate the growth behavior of NVP particles, favoring the formation of nanosheet subunits and their subsequent self-assembly into hierarchical flower-like microspheres (Fig. 1(a)). Scanning electron microscopy (SEM) was employed to investigate the influence of CDs introduction on NVP morphology (Fig. S1 in the ESM). As shown in Fig. 1(b) and Fig. S2 in the ESM, the NVP exhibits a spheroidal morphology with a rough surface. With the introduction of 5 mL of CDs solution, smaller microspheres are formed, and sparsely distributed nanosheets with a lateral size of approximately 1 μm are observed on their surfaces (Fig. 1(c)). Upon increasing the CDs content to 10 mL, well-defined flower-like microspheres with a diameter of approximately 2 μm are formed through the assembly of nanosheet subunits (Fig. 1(d)). This morphological evolution may originate from the structure-directing effect of hydroxyl-functionalized CDs. Their surface hydroxyl groups facilitate adsorption on the precursor species and promote heterogeneous nucleation, favoring anisotropic growth into thin nanosheets. [46] Moreover, the nanosheets may undergo secondary assembly to reduce the total surface free energy. The uniformly distributed CDs further regulate the interactions between adjacent nanosheets and suppress compact stacking, promoting the formation of flower-like microspheres. [47] During subsequent calcination, the anchored CDs are converted into a uniform residual carbon layer. This layer separates adjacent nanosheets and suppresses sintering-induced coalescence as well as grain growth. [48] Consequently, the microflower architecture is preserved after heat treatment. Moreover, the intimate

carbon coverage establishes conductive pathways, thereby facilitating electron transport. However, excessive CDs addition at 15 mL leads to pronounced agglomeration of the spherical particles (Fig. 1(e)). The particle agglomeration at an excessive CDs addition may originate from the strengthened interactions among the precursor nanosheets. At an appropriate dosage, the surface functional groups of the CDs facilitate their uniform adsorption on the NVP precursors and regulate nanosheet growth and assembly. However, when the CDs addition is increased to 15 mL, excess CDs may intensify the interactions between adjacent precursor nanosheets, promoting their stacking observed in NVP/CDs-15. Therefore, an appropriate CDs dosage is essential for balancing nanosheet formation with hierarchical microflower assembly. Transmission electron microscopy (TEM) further reveals a CDs-derived carbon layer with a thickness of approximately 5 nm on the surface of NVP/CDs-10 in Fig. 1(f) and 1(g), indicating successful surface modification by CDs-derived carbon. Scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) confirms the uniform distribution of elements in NVP/CDs-10 (Fig. 1(h) and 1(i)), while the corresponding elemental mapping of pristine NVP is shown in Fig. S2 in the ESM.

X-ray diffraction (XRD; Fig. 2(a)), and the refined analyses (Fig. 2(b) and Fig. S3 in the ESM), were analyzed to investigate the effect of carbon dot addition on the crystal structure of NVP. The NASICON structure is observed in all samples, with χ^2 values below 4 [49, 50], suggesting the unchanged phase structure of NVP after CDs

modification. In addition, the lattice parameters and cell volumes are similar for all samples (Tables S1-S3 in the ESM), further indicating the maintained phase structure of NVP. The N₂ adsorption-desorption isotherms indicate that all samples belong to type IV with mesoporous structures (Fig. 2(c) and Fig. S4 in the ESM). Compared to NVP (4.8 m² g⁻¹), NVP/CDs-5 (13.4 m² g⁻¹) and NVP/CDs-15 (10.0 m² g⁻¹), NVP/CDs-10 (23.73 m² g⁻¹) has a larger specific surface area. This enlarged surface area is attributed to the well-defined nanosheet-assembled flower-like architecture of NVP/CDs-10, which can provide accessible channels for Na⁺ transport.

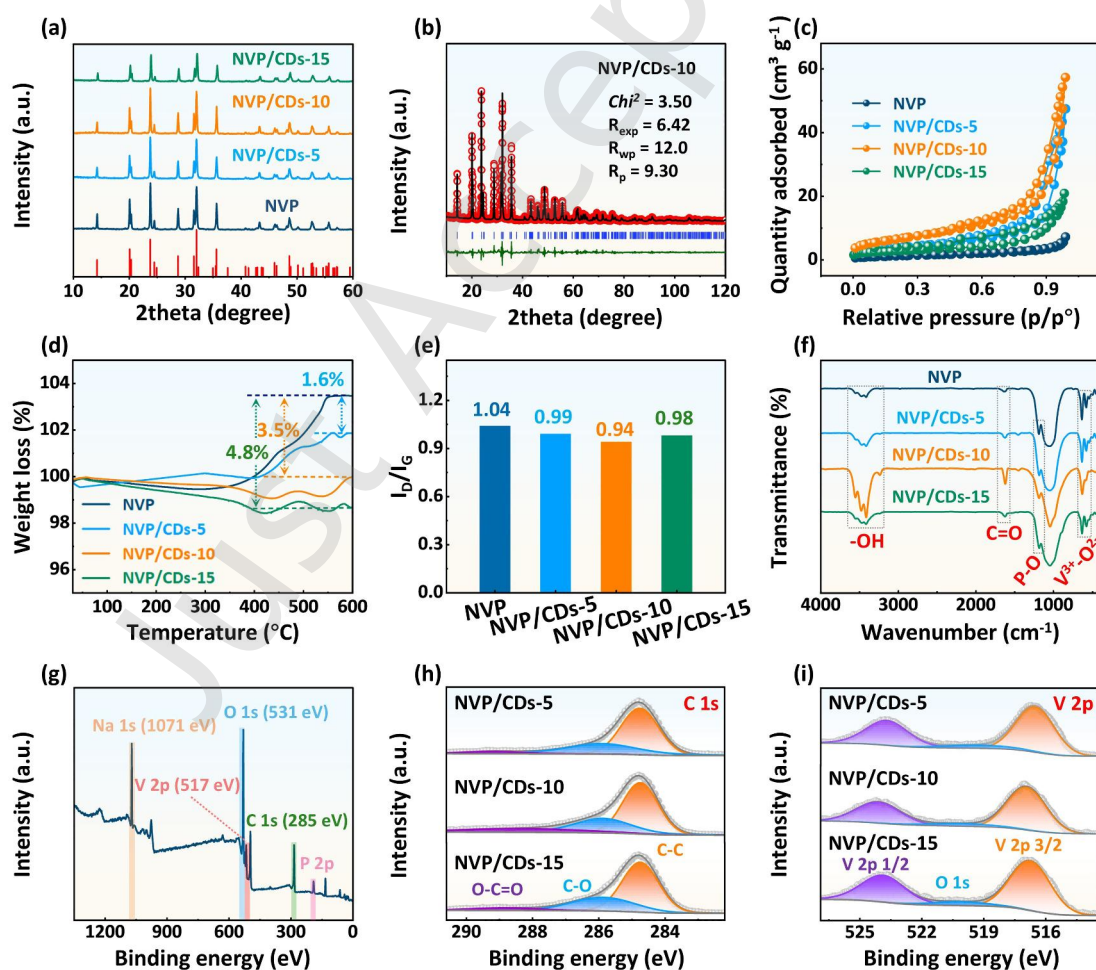


Figure 2 Structural and surface chemical characterizations. (a) XRD and (b) Rietveld refined XRD pattern of NVP/CDs-10. (c) The N₂ adsorption-desorption curve, (d) TGA, (e) Raman,

and (f) FT-IR spectra of all samples. (g) Full XPS spectrum of NVP/CDs-10 and the high-resolution XPS spectra of (h) C1s and (i) V 2p of the samples.

The carbon contents in NVP/CDs-5, NVP/CDs-10, and NVP/CDs-15 are determined to be 1.6, 3.5, and 4.8 wt.% through thermogravimetric analysis (TGA; Fig. 2(d)). A weight increase is observed in the TG curve after 450 °C, which is attributed to the oxidation of V^{3+} to V^{4+} and V^{5+} [51]. Subsequently, the carbon components of all samples were characterized by Raman spectroscopy (Fig. S5 in the ESM) [52], and NVP/CDs-10 shows the lowest I_D/I_G value, confirming a higher degree of graphitized carbon (Fig. 2(e)). Fourier transform infrared (FTIR) spectra were tested to analyze the surface functional groups (Fig. 2(f) and Fig. S6 in the ESM). The peaks at 634 cm^{-1} belong to the $V^{3+}\text{-O}^{2-}$ bonds, the signals at 1041 and 1180 cm^{-1} are related to the stretching bonds of the PO_4 tetrahedron, the peak at 1700 cm^{-1} corresponds to the surface -C=O , and the peak at 3440 cm^{-1} is related to the -OH stretching vibration [53]. The stronger O-H signal in NVP/CDs-10 suggests the enrichment of hydroxyl-related groups, which may participate in interfacial reactions and contribute to CEI chemistry regulation during cycling. Subsequently, X-ray photoelectron spectroscopy (XPS; Fig. 2(g) and Fig. S7 in the ESM) was further performed to analyze the surface chemical states of all samples. Characteristic signals assigned to Na, V, O, C, and P are detected in the XPS spectrum. In the high-resolution C 1s spectra, the stronger C signal of NVP/CDs-10 at 288.8 eV, assigned to O-C=O -related oxygenated carbon species, supports the presence of CDs-derived carbon and oxygen-containing surface groups, consistent with the FTIR

results (Fig. 2(h)). In the V 2p spectrum, the peaks at 523.9 and 516.9 eV are assigned to V 2p_{1/2} and V 2p_{3/2}, respectively (Fig. 2(i)) [54].

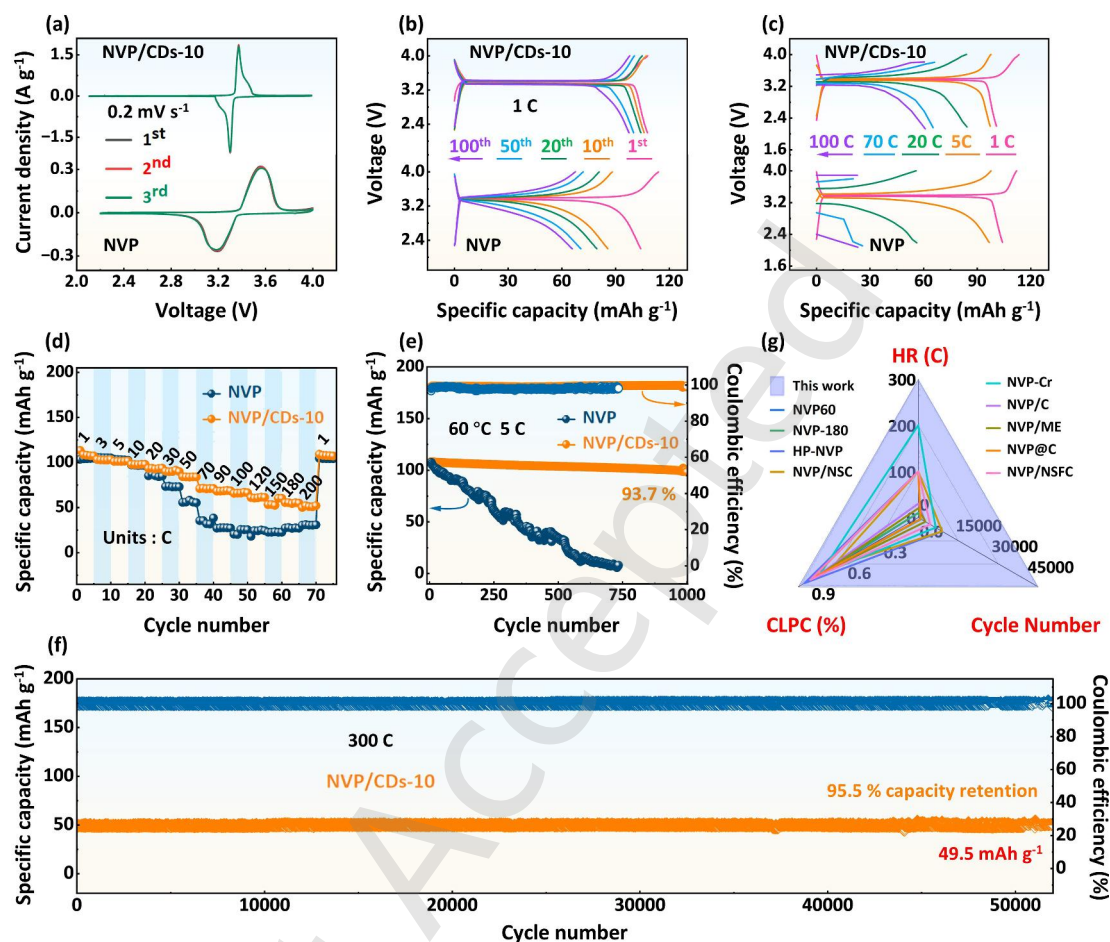


Figure 3 Electrochemical performance of NVP and NVP/CDs. (a) CV curves of NVP and NVP/CDs-10 at 0.2 mV s⁻¹. Charge and discharge profiles of NVP and NVP/CDs-10 at (b) 1 C and (c) other rates. (d) Rate performance of all samples. (e) Cycling performance of NVP/CDs-10 at 5 C and 60 °C. (f) Long-term cycling performance of NVP/CDs-10 at 300 C. (g) Performance comparison between NVP/CDs-10 and previously reported NVP-based cathodes. HR denotes the highest reported rate, and CLPC denotes the capacity loss per cycle.

Afterwards, the electrochemical performance of all samples was systematically investigated to evaluate Na⁺ storage behavior. The CV curves collected at 0.2 mV s⁻¹ exhibit a pair of well-defined redox peaks centered around 3.4 V, corresponding to the reversible Na⁺ extraction and insertion in the NVP framework (Fig. 3(a)). Compared

with pristine NVP, the NVP/CDs cathodes show sharper and more symmetric redox peaks with smaller peak separation, indicating reduced electrochemical polarization after CDs modification. This reduced polarization is also reflected in the charge and discharge profiles in Fig. 3(b) and 3(c). NVP/CDs-10 exhibits smaller voltage hysteresis than pristine NVP under the different rates, suggesting reduced polarization and improved reaction kinetics. The rate capability of all samples was further evaluated (Fig. 3(d) and Fig. S8 and S9 in the ESM). NVP/CDs-10 delivers the highest reversible capacities of 108.8, 101.2, 92.8, 83.8, 68.6, 60.9, and 52.1 mAh g⁻¹ at 1, 5, 20, 50, 90, 120, and 200 C, respectively, demonstrating superior high-rate Na⁺ storage capability. This performance is consistent with the well-defined nanosheet-assembled microflower morphology of NVP/CDs-10, which facilitate electrolyte penetration and shorten Na⁺ transport pathways. In contrast, excessive CDs addition in NVP/CDs-15 causes particle agglomeration and reduces the specific surface area, thereby impairing ion transport and rate capability. In addition, NVP/CDs-10 exhibits robust cycling stability, with capacity retentions of 83.4%, 94.6%, and 95.4% after 500, 1800, and 3000 cycles at 1, 50, and 100 C, respectively (Fig. S8 and S10 in the ESM). Notably, outstanding rate performance and long-term cycling stability are still retained with a high active material loading of 4.0 to 9.8 mg cm⁻², indicating the practical applicability of the optimized cathode (Fig. S11 in the ESM). Furthermore, NVP/CDs-10 maintains 93.7% capacity retention after 1000 cycles at 5 C and 60 °C, confirming its excellent high-temperature cycling stability (Fig. 3(e)) [55]. To further detect its ultrafast charge storage capability, NVP/CDs-10 delivers a highly reversible capacity of 49.5 mAh g⁻¹ with 95.5% capacity retention at

300 C after 50000 cycles, corresponding to a rapid charging time of approximately 4.7 s per charge (Fig. 3(f)). Remarkably, the electrochemical performance of NVP/CDs-10 surpasses that of the previously reported advanced NVP cathodes, particularly in terms of high-rate capability and cycling durability (Fig. 3(g) and Table S4 in the ESM) [49, 54, 56-62]. These results suggest that NVP/CDs-10 achieves a favorable balance between ultrahigh-rate capability and long-term cycling durability.

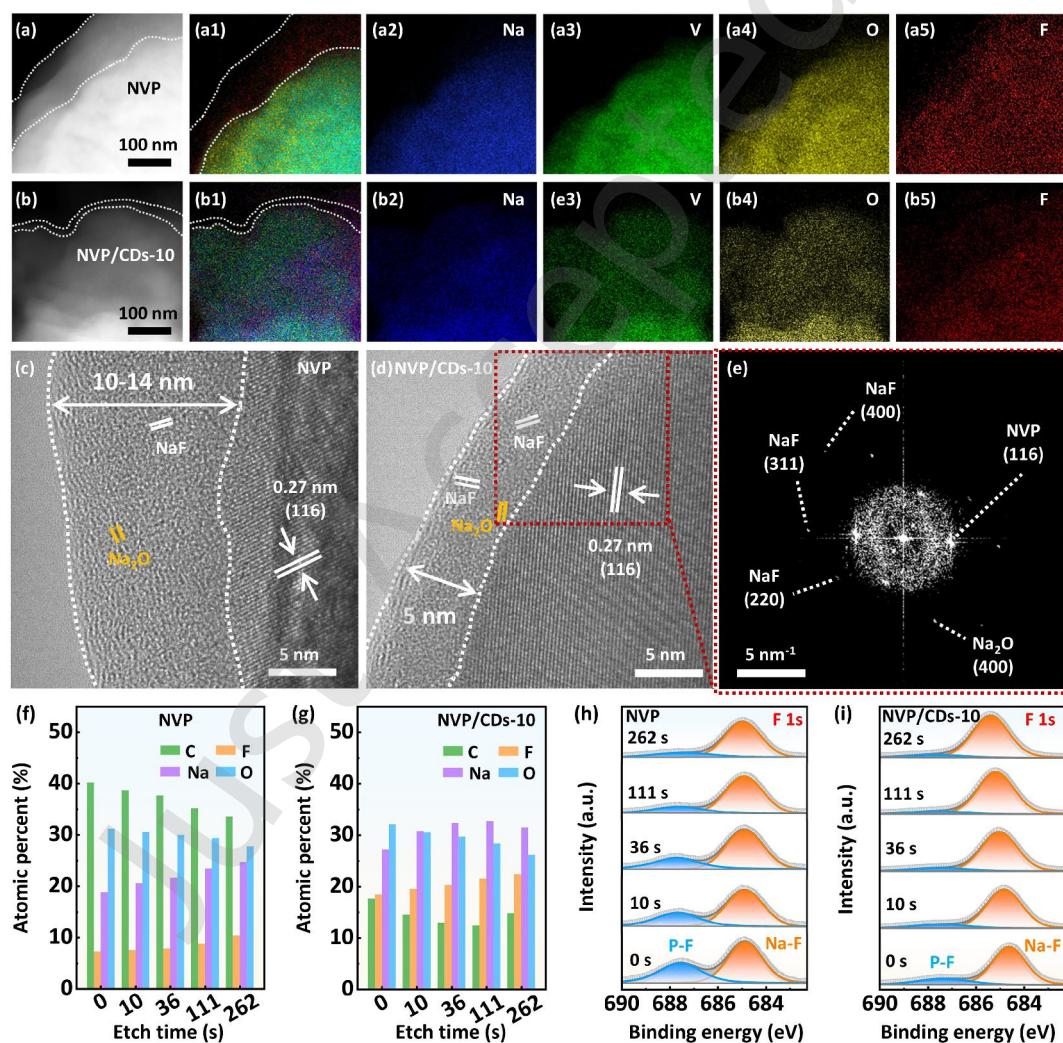


Figure 4 Interfacial characterization of NVP and NVP/CDs-10. TEM images and elemental mapping of (a) NVP and (b) NVP/CDs-10 after 1000 cycles. HRTEM of (c) NVP and (d) NVP/CDs-10 after 1000 cycles with the (e) corresponding FFT patterns. Atomic ratios of C, F, Na, and O at different sputtering times for (f) NVP and (g) NVP/CDs-10. F 1s spectra of (h) NVP and (i) NVP/CDs-10 at different sputtering times.

To investigate the dynamics of Na⁺ diffusion across the interface, the CEI layers formed on pristine NVP and NVP/CDs-10 after 1000 cycles were examined by post-cycling TEM and XPS depth profiling. As illustrated in Fig. 4(a) and 4(b), pristine NVP is covered by a thick and inhomogeneous CEI layer, whereas NVP/CDs-10 maintains a thin and uniform CEI layer of approximately 5 nm. Such a compact and homogeneous CEI film is expected to reduce interfacial resistance and facilitate Na⁺ transport across the electrode-electrolyte interface, which can effectively enhance the rate capability of NVP-CDs-10 [63-66]. To reveal the chemical composition and structural evolution of the interfacial film, the samples were characterized by HRTEM. Pristine NVP exhibits a 10-14 nm thick CEI layer containing NaF and Na₂O lattice fringes (Fig. S12 in the ESM), with a 0.27 nm lattice spacing corresponding to the (116) plane of NVP (Fig. 4 (c)). After modification with CDs, the thickness of the CEI layer in NVP/CDs-10 is significantly reduced to approximately 5 nm, while the phases of NaF and Na₂O are retained, and the structure of the (116) crystal plane of NVP remains intact (Fig. 4 (d)). The fast Fourier transform (FFT) pattern of NVP/CDs-10 (Fig. 4 (e)) further identifies diffraction signals assigned to NVP (116), NaF (220)/(311)/(400), and Na₂O (400), which corroborates the HRTEM results and confirms the successful construction of a stable CEI structure. The NaF lattice fringes in the CEI layer of NVP/CDs-10 facilitate the improvement of Na⁺ diffusion kinetics at the interface and enhance the mechanical performance of the CEI layer.

Subsequently, XPS depth profiling was further performed to analyze the CEI

composition at different sputtering times (Figs. 4(f) and 4(g)). The Na, F, C, and O signals were examined across various etching depths, and their respective atomic percentages were systematically compared. For pristine NVP, the continuous decrease in C and O contents, accompanied by gradual increases in Na and F, reflects the progressive removal of the organic-rich outer CEI and exposure of the Na/F-containing inorganic inner region. NVP/CDs-10 exhibits a similar depth-dependent trend from 0 to 111 s, indicating the gradual removal of its outer organic component and exposure of the inorganic-rich inner region. At 262 s, however, the slight increase in C content is attributed to the increasing contribution of the CDs-derived carbon layer, which becomes detectable due to the much thinner CEI on NVP/CDs-10. Meanwhile, the continued increase in F originates from the further exposure of the inner F-based compounds. Since the elemental contents are presented as normalized atomic percentages, the increased contributions from C and F result in a corresponding decrease in the relative Na fraction rather than substantial Na depletion. Moreover, the continued decrease in O confirms that the increased C signal primarily originates from the CDs-derived carbon layer rather than organic CEI species. Notably, the CEI layer on NVP/CDs-10 displays a lower C content and a higher F content than pristine NVP. The C signal detected in the CEI mainly arises from organic electrolyte decomposition products rather than the total carbon contained in the electrode material. Therefore, the lower C fraction of NVP/CDs-10 indicates reduced accumulation of organic CEI species and does not contradict its bulk carbon content derived from the introduced CDs. The increased F content indicates the

formation of more inorganic F-based compounds. This phenomenon indicates that the incorporation of CDs into NVP can promote the decomposition of NaPF_6 , leading to the formation of greater amounts of F-based compounds. Moreover, the high-resolution F 1s spectra further show two main components located at 684.7 and 687.4 eV, which are assigned to NaF and P-F-containing species such as PO_xF_y , respectively (Fig. 4(h) and 4(i)) [67, 68]. Notably, a higher NaF/ PO_xF_y ratio is observed for NVP/CDs-10 than for NVP at different sputtering depths, verifying the increased NaF fraction and its dominant contribution to the F-containing inorganic components. This NaF enrichment may be associated with the regulated surface environment by the hydroxyl-functionalized carbon layer, which may influence the local adsorption and decomposition behavior of electrolyte species and favor the formation of inorganic F-containing products. [69] Furthermore, the NaF-rich CEI facilitates interfacial kinetics through favorable Na^+ transport and effective electronic passivation. Nanoscale NaF domains and their associated defects provide accessible Na^+ migration pathways. [70] In addition, the electronically insulating and chemically stable NaF phase suppresses continuous electrolyte decomposition and organic byproduct accumulation. [71, 72] These features maintain a thin and uniform CEI, thereby prompting rapid interfacial charge transfer.

Subsequently, to further elucidate the effects of CDs-mediated structural and surface modulation on charge transport and interfacial kinetics, the electrochemical kinetics of all samples were systematically investigated. The cyclic voltammetry (CV) curves at different scan rates were first analyzed to evaluate reaction kinetics and Na^+

diffusion behavior (Fig. 5(a) and 5(b)). Compared with pristine NVP, all NVP/CDs electrodes exhibit reduced redox peak separation, indicating that CDs modification effectively alleviates electrochemical polarization. Among them, NVP/CDs-10 manifests the smallest peak separation, suggesting the most favorable reaction kinetics. Furthermore, the linear relationship between peak current and $\nu^{1/2}$ was used to estimate the apparent Na^+ diffusion coefficients (Fig. S13 in the ESM). As summarized in Fig. 5(c) and Table S5 in the ESM, NVP/CDs-10 delivers the highest apparent Na^+ diffusion coefficient among all samples, confirming the accelerated Na^+ diffusion kinetics.

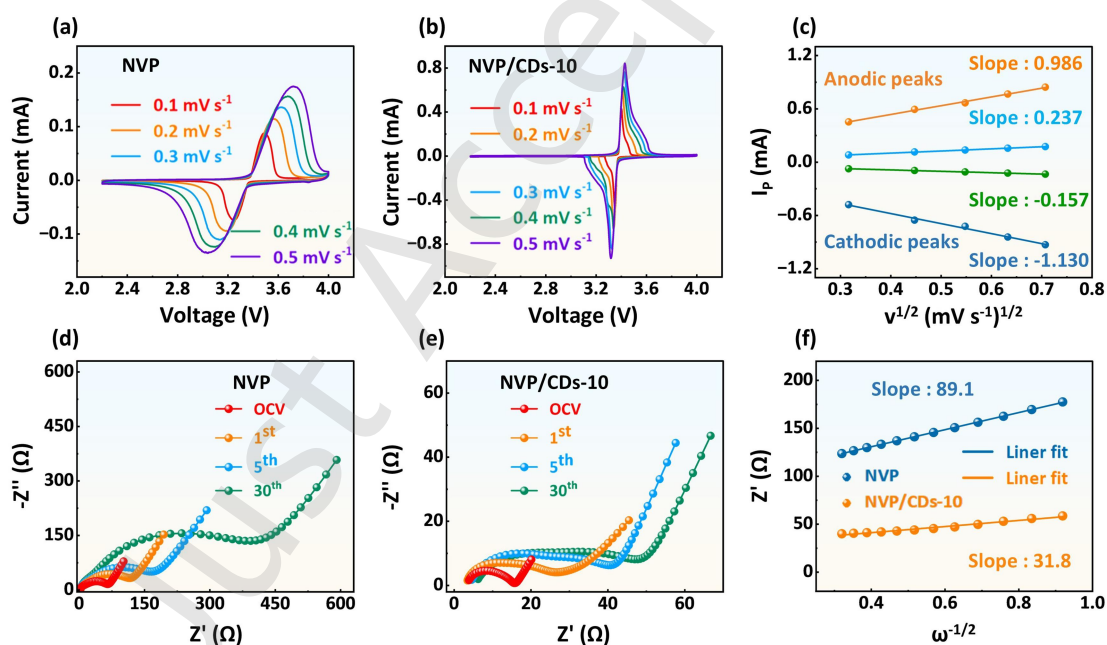


Figure 5 Kinetic analysis of NVP and NVP/CDs. (a, b) CV curves of (a) NVP and (b) NVP/CDs-10 at various scan rates. (c) Linear fitting of peak current (I_p) versus the square root of scan rate (ν). Nyquist plots of (d) NVP and (e) NVP/CDs-10 after different cycles. (f) Linear relationship between Z' and $\omega^{-1/2}$ in the low-frequency region for NVP and NVP/CDs-10.

Electrochemical impedance spectroscopy (EIS) was further performed at

different cycling stages, as illustrated in Fig. 5(d) and 5(e) and Fig. S14 in the ESM. Compared with pristine NVP and other CDs-modified samples, NVP/CDs-10 exhibits the lowest R_{CEI} and R_{ct} values (Table S6 in the ESM), demonstrating the greatly improved interfacial kinetics. Warburg analysis was subsequently performed to evaluate Na^+ diffusion behavior. In the low-frequency region, Z' presents a linear relationship with $\omega^{-1/2}$, where the slope corresponds to the Warburg factor σ (Fig. 5(f)). NVP/CDs-10 exhibits a much lower σ value of 31.8 than pristine NVP (89.1), indicating the reduced diffusion impedance and faster Na^+ diffusion kinetics. This result is consistent with the higher apparent Na^+ diffusion coefficient derived from the CV analysis. The enhanced electrochemical kinetics of NVP/CDs-10 arise from the regulation of morphology, carbon distribution, and interfacial chemistry by the CDs. The CDs-induced nanosheet-assembled microflower architecture shortens the transport distances for electrons and Na^+ . Meanwhile, the abundant surface functional groups of the CDs facilitate their uniform anchoring on the NVP precursors. Subsequent calcination converts the anchored CDs into a uniform carbon layer that covers the nanosheet surfaces, enabling efficient electron transport with only 3.5 wt.% carbon. In addition, the thin and NaF-rich CEI reduces interfacial resistance and facilitates charge transfer. These structural and interfacial effects account for the accelerated interfacial kinetics, outstanding high-rate capability, and long-term cycling stability of NVP/CDs-10.

To explore the influence of CDs modification on the structural evolution of NVP, *in situ* XRD patterns of NVP and NVP-CDs-10 during the initial cycle were

investigated within the voltage range from 2.0 V to 4.0 V. Fig. 6(a) and 6(b) exhibit the two-dimensional contour plots of *in situ* XRD patterns and the corresponding charge-discharge profiles (Fig. 6(c)), respectively. The reversible disappearance and reappearance of characteristic diffraction peaks during cycling indicate a highly reversible phase evolution and robust structural stability during Na⁺ (de)intercalation. In detail, diffraction peaks positioned at 23.8°, 28.9°, 32.9°, and 36.8° are assigned to the (113), (024), (116), and (300) crystal planes of NVP, respectively. During the initial stage of the charging process, the V³⁺/V⁴⁺ redox reaction occurs. This process causes the diffraction peaks of the (113), (024), (116), and (300) crystal planes to shift toward higher angles, accompanied by a gradual decline in intensity, which indicates the lattice contraction due to the extraction of Na⁺.

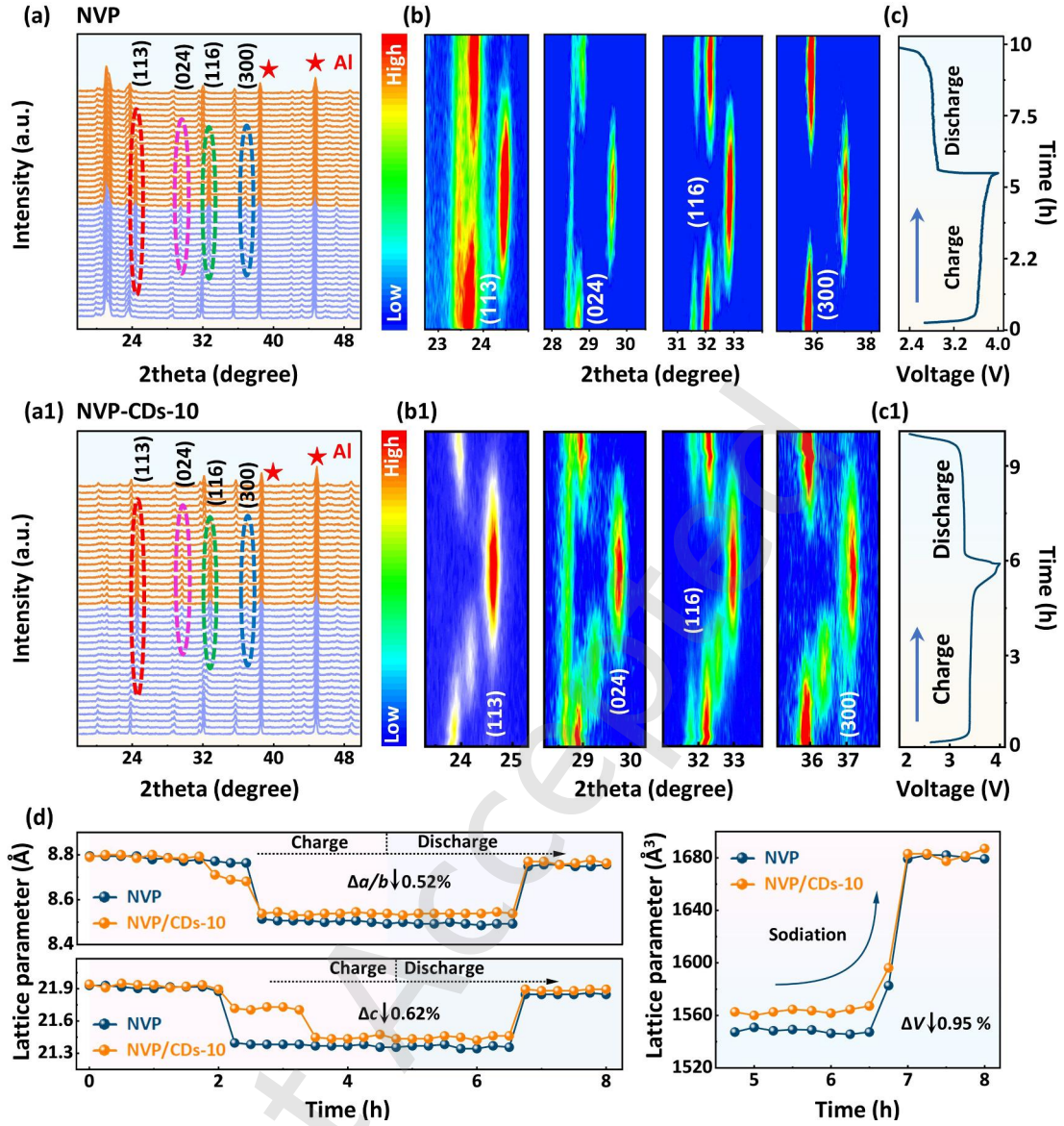


Figure 6 (a-b) 2D contour plot of *In situ* XRD patterns with (c) corresponding charge-discharge profiles of NVP and NVP-CDs-10. (d) *a*, *b*, *c* axes, and volume changes of NVP and NVP-CDs-10 during the initial cycle.

Meanwhile, diffraction peaks originating from NVP appear and increase in intensity. Once the V^{3+}/V^{4+} redox reaction is complete, the initial diffraction peaks disappear, and the new peaks remain unchanged, indicating a two-phase reaction in NVP. During discharging, the diffraction peaks of NVP fade, whereas those of NVP reappear, confirming the high structural reversibility of the cathode material. Further structural analysis shows that the lattice parameters *a/b* and *c* of NVP/CDs-10 are

decreased by 0.52% and 0.62%, respectively, compared with those of NVP, accompanied by a 0.95% reduction in unit-cell volume (Fig. 6(d)). These results confirm the suppressed lattice deformation of NVP due to CDs incorporation. Such reduced structural variation is favorable for mitigating repeated CEI rupture and reconstruction during cycling.

To investigate the practical feasibility of the CDs-mediated regulation strategy, NVP/CDs-10 was paired with a hard carbon (HC) anode to assemble an NVP/CDs-10||HC full cell (Fig. 7(a)). The full cell exhibits a charge/discharge voltage plateau of approximately 3.3 V (Fig. 7(b) and 7(c)), and delivers a highly reversible capacities of 124.6, 108.9, 99.1, 85.5, 69.9, and 55.2 mAh g⁻¹ at rates of 0.1, 1, 2, 3, 4, and 5 A g⁻¹, respectively (Fig. 7(d) and Fig. S15 in the ESM). According to the rate capabilities, a high energy density of 382.6 Wh kg⁻¹ can be attained at a power density of 324.3 W kg⁻¹, based on the mass of the cathode. Notably, even at an ultrahigh power density of 7965 W kg⁻¹, the full cells still deliver 226.2 Wh kg⁻¹ within only approximately 102.2 s per charge, demonstrating its promising fast-charging capability (Fig. 7(e)). Furthermore, the full cell retains 93.4 mAh g⁻¹ after 100 cycles at 0.5 A g⁻¹ with 89.4% capacity retention (Fig. 7(f)). Additionally, 96.1% capacity retention after 1500 cycles under 1 A g⁻¹ is delivered in Fig. 7(g) and 7(h) and Fig. S16 in the ESM, demonstrating the durable cycling stability of the full cell.

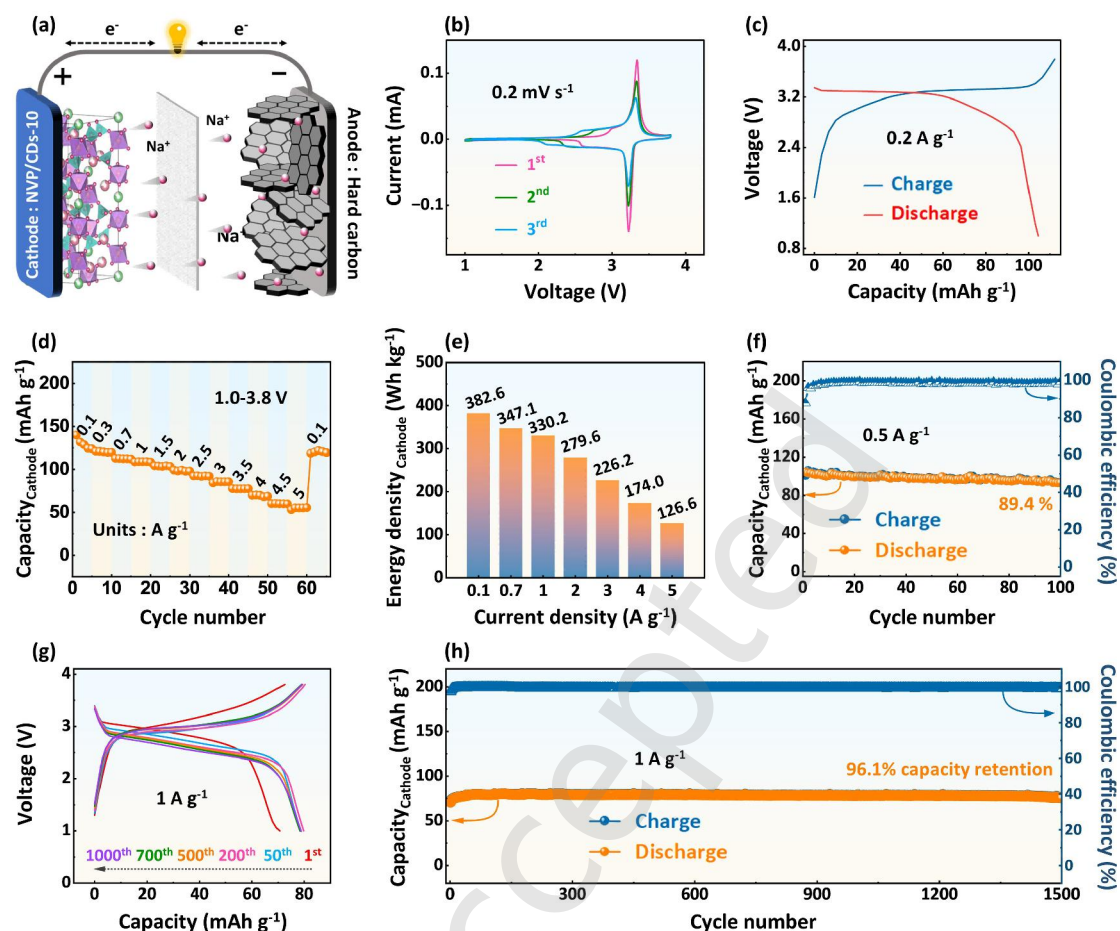


Figure 7 Electrochemical performance of NVP/CDs-10||HC full cell. (a) Schematic diagram of the full cell. (b) CV curve of the full cell. (c) Charge/discharge curve for the first cycle at 0.2 A g⁻¹. (d) Rate, and (e) energy densities of the full cell. (f) Cycling capability of the full cell at 0.5 and ((g) and (h)) 1 A g⁻¹ (based on mass of cathode).

3 Conclusions

In summary, a hydroxyl-functionalized CDs-mediated dual-regulation strategy was developed to couple hierarchical architecture construction with interfacial chemistry regulation in NVP cathodes. The hydroxyl-rich CDs acted as multifunctional regulators rather than passive conductive additives, promoting the assembly of NVP nanosheets into hierarchical nanoflower-like microspheres. Such a nanosheet-assembled porous architecture shortens Na⁺ diffusion pathways, while the CDs-derived thin carbon layer facilitates electron transport. Meanwhile,

CDs-regulated surface chemistry enabled the formation of a thin, uniform, and NaF-rich CEI film, which suppresses resistive byproduct accumulation and lowers interfacial resistance. Consequently, the optimized NVP/CDs-10 cathode delivered 49.5 mAh g⁻¹ at 300 C and retained 95.5% of its capacity after 50000 cycles. Moreover, the NVP/CDs-10||HC full cell exhibits high energy density (382.6 Wh kg⁻¹) and fast-charging capability (226.2 Wh kg⁻¹ within only ~102.2 s per charge). More broadly, this work offers a transferable design strategy in which a single nano-additive jointly tailors the bulk structure and interfacial chemistry of polyanionic cathodes for fast-charging and durable electrochemical energy storage.

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Electronic Supplementary Material

Architecting $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ microflower cathodes with NaF-rich interfaces for ultrafast and ultrastable sodium-ion storage

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1 Material Preparation

(1) Carbon dots: Carbon dots (CDs) were synthesized through a hydrothermal method using sucrose as the carbon source. Briefly, sucrose (1 mmol) was dissolved in 30 mL of deionized water and stirred at room temperature for 15 min. The solution was subsequently transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 3 h. After the autoclave was naturally cooled to room temperature, the obtained solution was transferred into a centrifuge tube and allowed to stand for 1 h. A pale-yellow transparent CDs solution was finally obtained.

(2) Synthesis of NVP/CDs: All reagents, including V_2O_5 ($\geq 99\%$), $H_2C_2O_4 \cdot 2H_2O$ ($\geq 99.5\%$), NaH_2PO_4 ($\geq 99\%$), and n-propanol, were of analytical grade and used without further purification. NVP/CDs samples were synthesized by a co-precipitation method followed by calcination under an argon atmosphere. Briefly, V_2O_5 (2 mmol) and $H_2C_2O_4 \cdot 2H_2O$ (6 mmol) were dissolved in 20 mL of deionized water at 70 °C for 30 min. NaH_2PO_4 (6 mmol) dissolved in 5 mL of deionized water was then slowly added to the above solution and stirred for 0.5 h. Subsequently, CDs solution with different volumes, 5, 10, and 15 mL, was introduced, followed by the addition of 50 mL of n-propanol. The resulting precursor was dried at 80 °C for 24 h and then annealed at 750 °C for 6 h under an argon atmosphere to obtain the final electrode materials.

2 Material Characterization

The crystal structural analysis of all the samples was tested by X-ray diffraction (XRD, Bruker D8 Advance). The morphological structure was investigated using

scanning electron microscopy (SEM, JEOL JSM-7610F Plus) and high-resolution transmission electron microscopy (HRTEM, JEOL JSM-F200) with energy-dispersive spectroscopy (EDS). The carbon content was measured by TG. The specific surface area was compared by BET. Graphitic and amorphous carbon identification via Raman spectrum. The chemical bonds and functional groups in the samples were analyzed by FT-IR, and the chemical state of the elements on the surface of the samples was investigated by XPS (Thermo Scientific K-Alpha).

3 Electrochemical Measurements

Electrochemical measurements were carried out using CR2032 coin cells assembled in an argon-filled glove box with ultra-high-purity Ar atmosphere. The working electrodes were prepared by mixing the active material, Ketjen black (KB), and polyvinylidene fluoride (PVDF) binder at a mass ratio of 8:1:1, with N-methyl-2-pyrrolidone (NMP) used as the solvent to form a homogeneous slurry. The slurry was coated onto aluminum foil and dried in a vacuum oven at 100 °C for 12 h. The mass loading of the active material was approximately 1 mg cm⁻². For the full cell, NVP/CDs-10 was used as the cathode material, and hard carbon was used as the anode. Before full-cell assembly, the hard carbon electrode was pre-sodiated with sodium metal. A 1 M NaPF₆ solution in dimethoxyethane (DME) was used as the electrolyte, and a glass fiber membrane (GF/A) was used as the separator. Galvanostatic charge and discharge tests at different current densities were performed using a LAND battery testing system with LANDdt-V7.4 software. Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation

(CHI1030C). Electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (CHI660E, Shanghai Chenhua) over a frequency range from 100 kHz to 0.01 Hz. Electrochemical measurements were conducted at 25 °C and 60 °C.

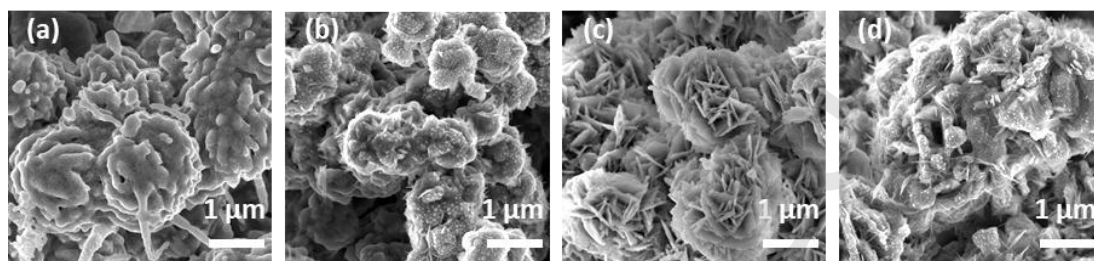


Figure S1 SEM images of (a) NVP, (b) NVP/CDs-5, (c) NVP/CDs-10, and (d) NVP/CDs-15.

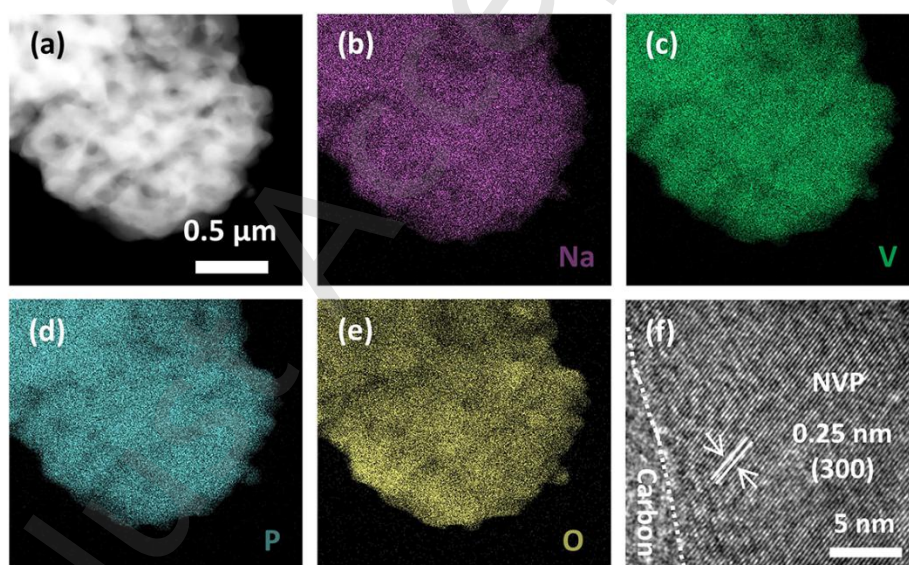


Figure S2 (a) STEM, (b-e) element mapping, and (f) HRTEM images of NVP.

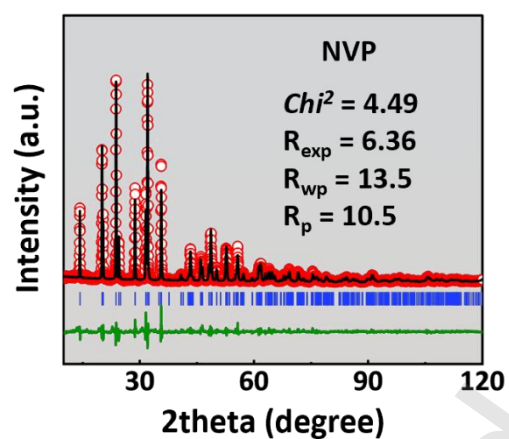


Figure S3 Refined XRD patterns of NVP.

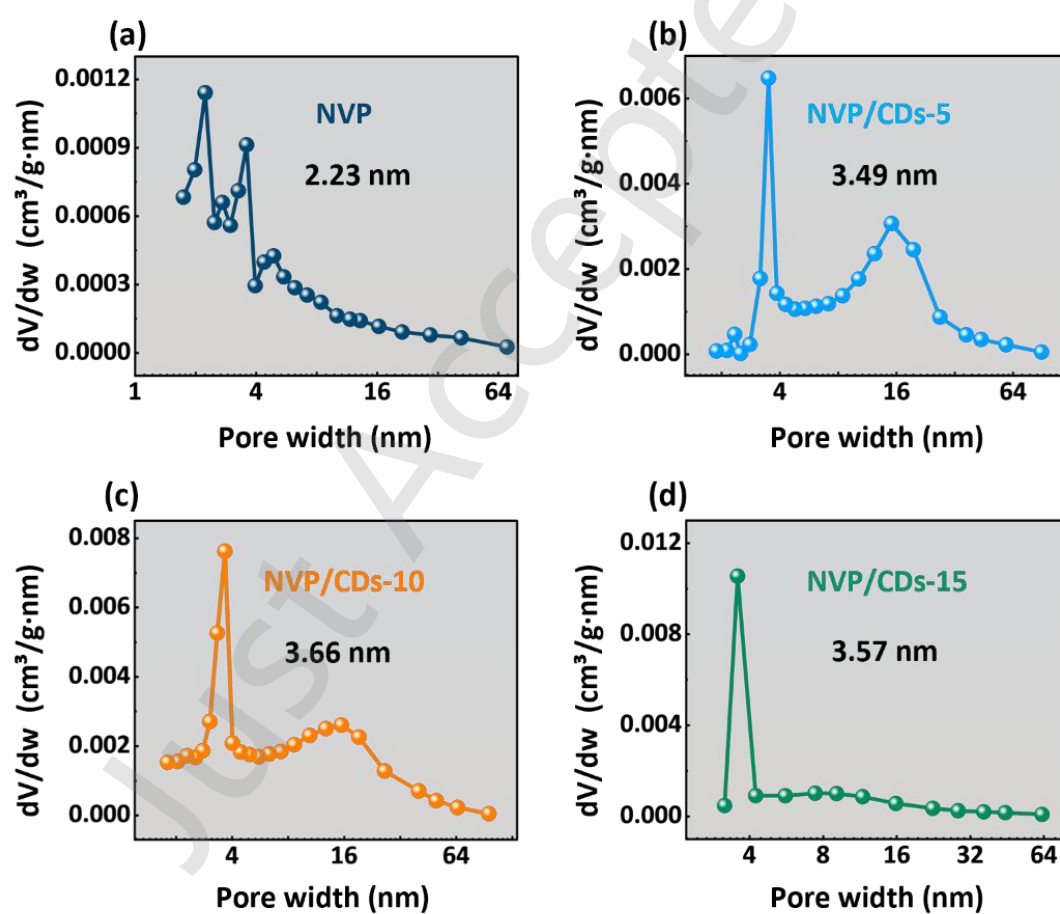


Figure S4 Pore size distributions of all samples.

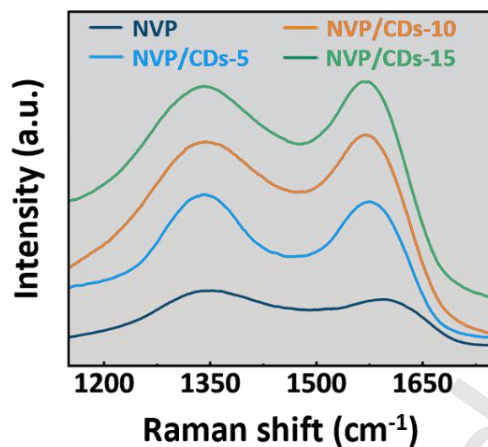


Figure S5 Raman spectra of all samples.

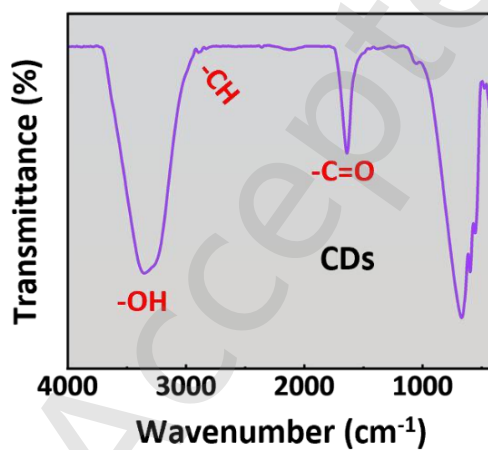


Figure S6 FTIR spectra of CDs.

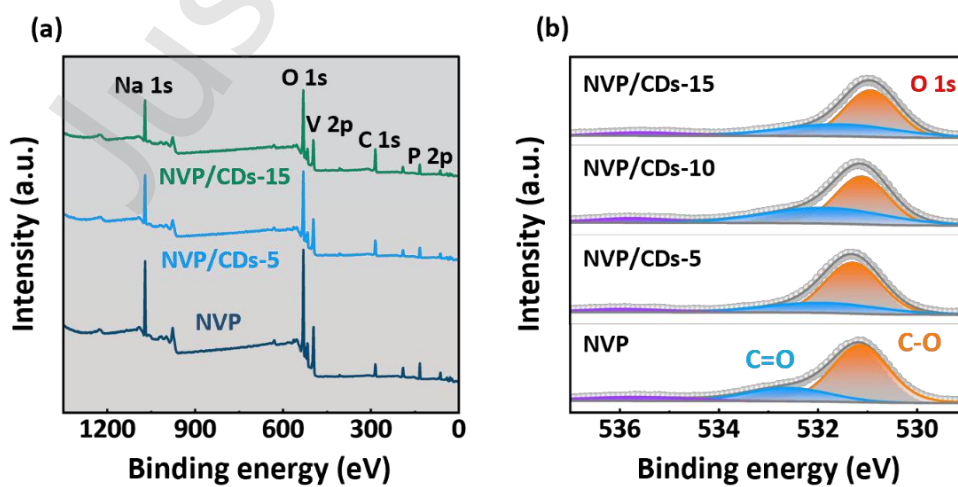


Figure S7 (a) XPS survey of NVP, NVP/CDs-5, and NVP-CDs-15. (b) O 1s XPS

spectra of all samples.

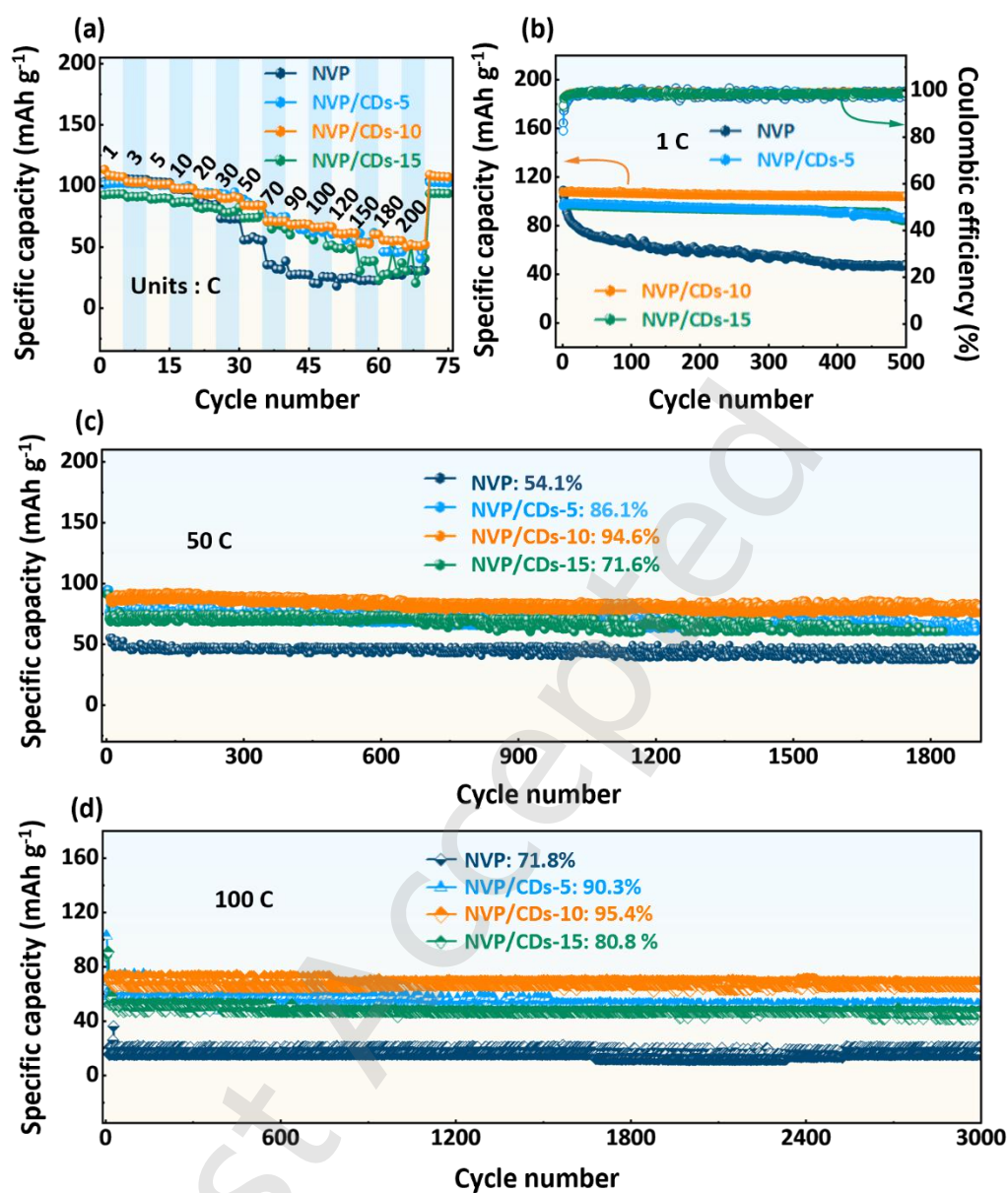


Figure S8 (a) Rate and cycling performances of all samples under (b) 1 C, (c) 50 C, and (d) 100 C.

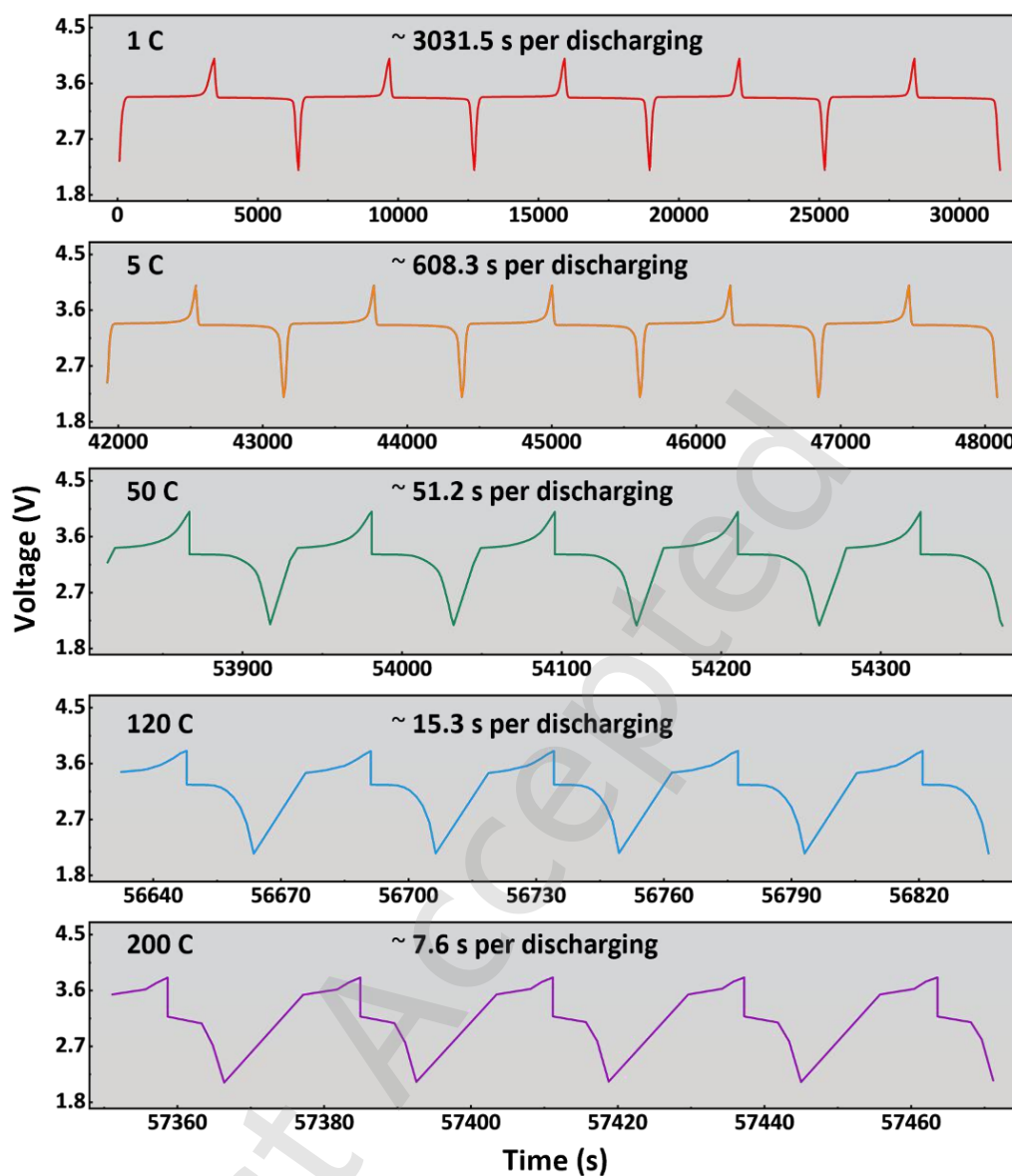


Figure S9 Time-voltage profiles of half cell under different current densities according to the rate test.

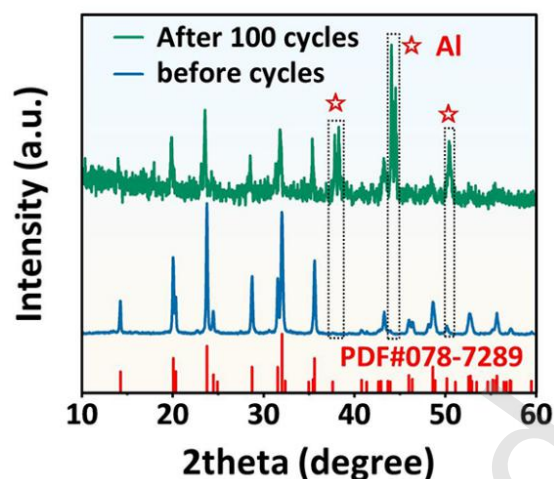


Figure S10 XRD patterns of NVP/CDs-10 before and after 100 cycles at 1 C.

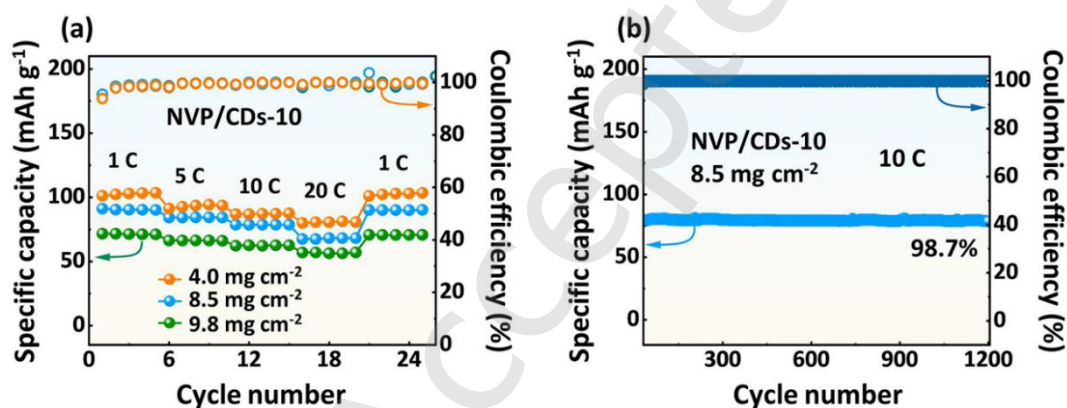


Figure S11 (a) Rate performance of NVP/CDs-10 at loads of 4.0, 8.5, and 9.8 mg cm⁻² and (b) 10 C at 8.5 mg cm⁻².

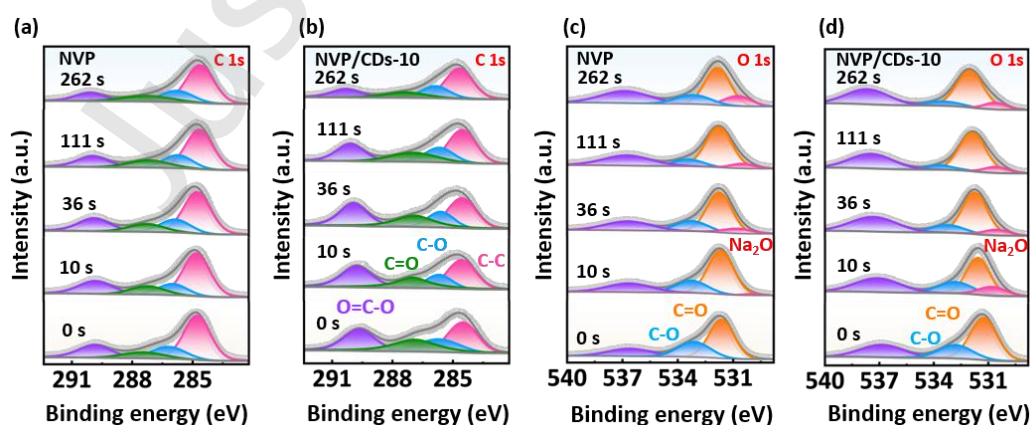


Figure S12 (a, b) C 1s, and (c, d) O 1s XPS spectra of NVP and NVP/CDs-10 after 1000 cycles.

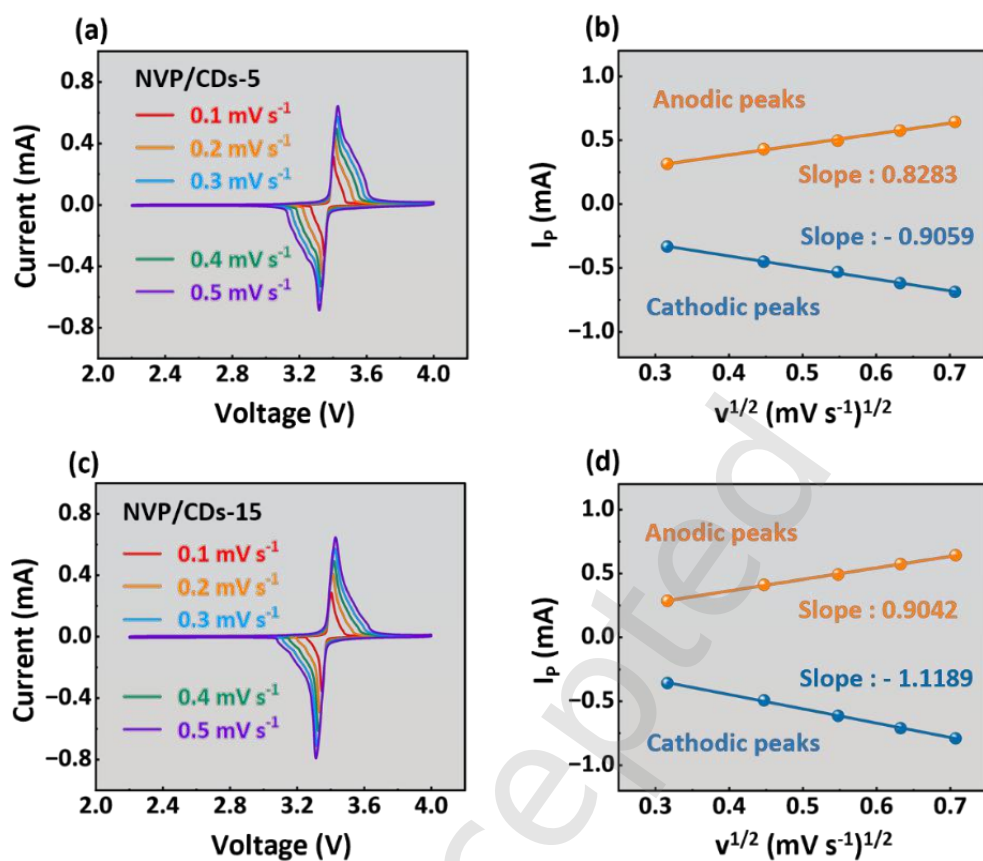


Figure S13 (a, b) CV curves and I_p - $v^{1/2}$ linear fitting of NVP/CDs-5 and (c, d) NVP/CDs-15 at different scan rates.

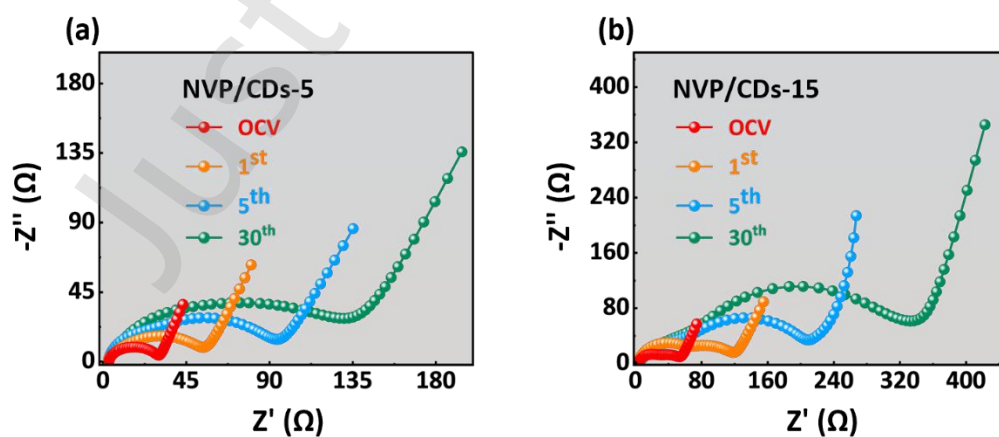


Figure S14 Nyquist plots of (a) NVP/CDs-5 and (b) NVP/CDs-15 at different cycles.

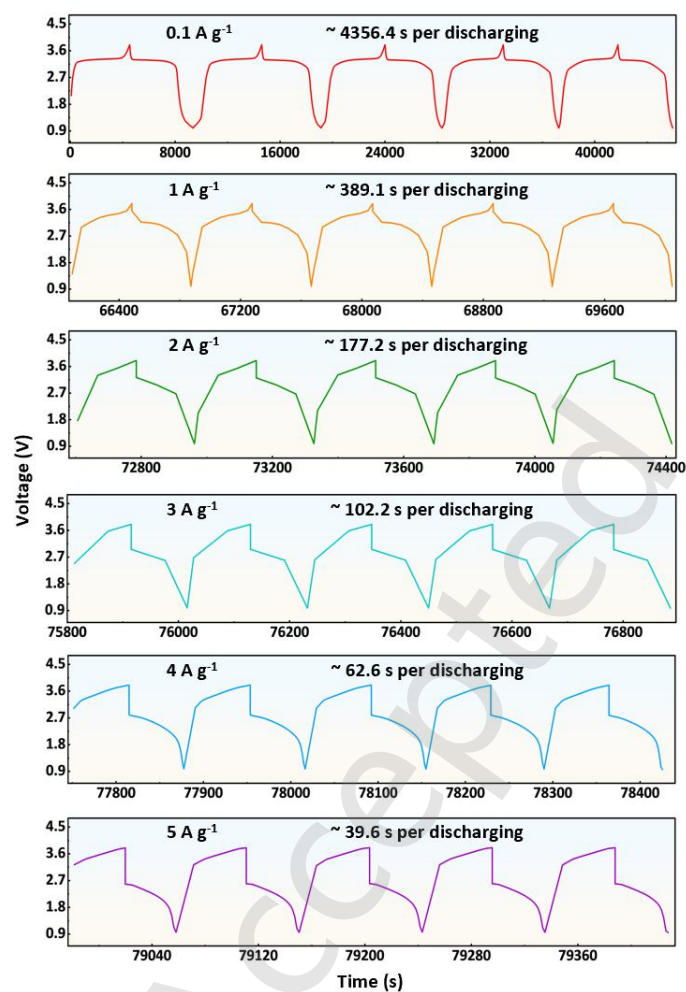


Figure S15 Time-voltage curves of the full cell at different current densities according to the rate test (based on the mass of the cathode).

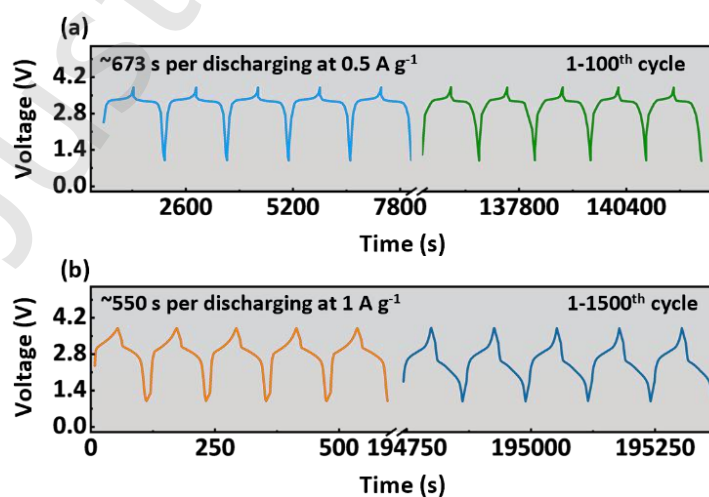


Figure S16 Time-voltage curves of the full cell at (a) 0.5 A g⁻¹ and (b) 1 A g⁻¹ (based on the mass of the cathode).

Table S1 Lattice parameters and evaluation parameters of NVP and NVP/CDs-10.

Samples	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	γ (deg)	<i>V</i> (Å ³)	<i>R</i> _{wp}	<i>R</i> _p	<i>Chi</i> ²
VP	8.72616	8.72517	21.80922	90.00000	120.00000	13.5	10.5	4.49
NVP/CDs-10	8.72616	8.72371	21.81395	90.00000	120.00000	12.0	9.30	3.50

Table S2 Lattice parameters and evaluation parameters of NVP.

Name	x	y	z	B	occ.	Mult.
V1	0.3333	0.6667	0.01911	-0.432	0.291	12
Na1	0.3333	0.6667	0.1667	11.413	0.142	6
Na2	0.6667	0.97082	0.0833	3.755	0.352	18
P1	-0.04411	0.3333	0.0833	-0.083	0.437	18
O1	0.14193	0.49765	0.07762	1.297	1.000	36
O2	0.54047	0.8448	-0.02643	2.045	1.000	36

Table S3 Lattice parameters and evaluation parameters of NVP/NCDs-10.

Name	x	y	z	B	occ.	Mult.
V1	0.3333	0.6667	0.01914	0.422	0.308	12
Na1	0.3333	0.6667	0.1667	10.609	0.136	6
Na2	0.6667	0.97045	0.0833	4.234	0.354	18
P1	-0.04376	0.3333	0.0833	0.845	0.468	18
O1	0.14193	0.49765	0.07762	1.297	1.000	36
O2	0.54047	0.8448	-0.02643	2.045	1.000	36

Table S4 Comparison of the electrochemical performances among the as-developed

NVP/CDs-10 and other reported high-rate NVP materials in NIBs.

Sample	Rate capability (mAh g ⁻¹ /Rate)		Capacity retention
NVP/CDs-10	108.8/1.0 C 66.1/100 C	83.8/50.0 C 51.1/200 C	95.5 % /50000 cycles /300 C
NVP/NSC [1]	116.7/0.5 C 108.6/5.0 C 91.0/50.0 C	114.4/1.0 C 102.9/10.0 C 83.2/100.0 C	72.2 %/10000 cycles/100 C
NVP-Cr [2]	106.1/1 C	99.8/200 C	82.2 %/7300 cycles/50 C
NVP60 [3]	117.3/1 C 107.0/5 C 97.8/9 C	111.7/3 C 101.9/7 C	79.5 %/1000 cycles/10 C
NVP/C [4]	115.0/0.3 C 103.0/30.0 C	110.0/10.0 C	84 %/3000 cycles/30 C
NVP/ME [5]	129.5/0.3 C 117.2/3.0 C 95.8/20.0 C	124.0/0.7 C 111.0/7.0 C	78.5 %/3000 cycles/5 C
HP-NVP [6]	98.0/0.5 C 90.0/10.0 C 61.0/100.0 C	94.0/2.0 C 78.0/50.0 C	100 %/10000 cycles/20 C
NVP@C [7]	113.8/1.0 C 100.6/20.0 C 80.5/100.0 C	109.3/5.0 C 90.4/50.0 C	89.7 %/1000 cycles/1 C
NVP-180 [8]	101.3/1.0 C 99.8/7.0 C 99.3/10.0 C	100.2/5.0 C 99.5/9.0 C	88.7 %/1200 cycles/10 C
NVP/NSFC [9]	117.8/0.5 C 115.8/2.0 C 100.5/10.0 C 98.1/100.0 C	111.1/1.0 C 103.2/5.0 C 98.2/50.0 C	90.2 %/5000 cycles/100 C

Table S5 Sodium diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) of all electrodes.

Process	NVP	NVP/CDs-5	NVP/CDs-10	NVP/CDs-15
Charge	6.45×10^{-11}	8.73×10^{-10}	1.51×10^{-9}	8.72×10^{-10}
Discharge	3.84×10^{-11}	1.01×10^{-9}	1.82×10^{-9}	1.31×10^{-9}

Table S6 The R_{ct} value of all electrodes at various cycles.

Samples		OCV	1 st	5 th	30 th
NVP	$R_{\text{CEI}} (\Omega)$	12.9	19.8	28.3	30.1
	$R_{\text{ct}} (\Omega)$	50.9	94.2	100.3	277.6
NVP/CDs-5	$R_{\text{CEI}} (\Omega)$	9.4	13.6	15.5	16.9
	$R_{\text{ct}} (\Omega)$	18.1	40.7	77.8	116.2
NVP/CDs-10	$R_{\text{CEI}} (\Omega)$	5.7	7.9	17.6	17.7
	$R_{\text{ct}} (\Omega)$	5.8	11.4	21.6	28.2
NVP/CDs-15	$R_{\text{CEI}} (\Omega)$	23.3	56.5	88.4	98.3
	$R_{\text{ct}} (\Omega)$	30.5	62.5	85.1	192.3

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