

Venus flytrap-inspired $\text{MnP}_4/\text{CoP}_2$ heterojunction with morphology-interface synergistic integration for high-energy-density supercapacitors

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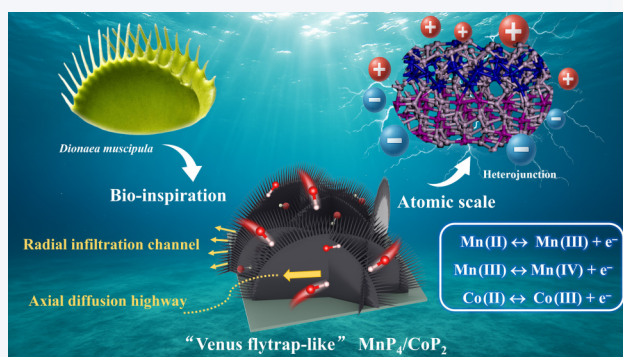
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ABSTRACT: Nature-derived distinctive architectures hold great promise for boosting supercapacitor performance through their multi-scale ion transport pathways and robust frameworks. However, simultaneously achieving interfacial charge modulation to break high energy-density limitations remains a fundamental challenge. Drawing inspiration from the hierarchical porosity and stimulus-responsive behavior of *Dionaea muscipula* (Venus flytrap) leaves, we engineer a biomimetic $\text{MnP}_4/\text{CoP}_2$ heterostructure through NH_4F -mediated hydrothermal synthesis and gas-phase phosphidation. The Venus flytrap-like nanosheet-nanowire network establishes dual-scale ion transport pathways: Primary nanosheets (7–10 μm) enable axial electrolyte diffusion highway, while vertically aligned secondary nanowires (~ 700 nm) enhance radial penetration via nanoconfined capillary effects. Concurrently, the $\text{MnP}_4/\text{CoP}_2$ heterointerface generates a built-in electric field (work function difference: 0.219 eV), driving interfacial electron transfer and modulating Mn/Co valence states to optimize OH^- adsorption energy (-3.51 eV) as confirmed by density functional theory (DFT) calculations. This synergistic integration of morphology and interfacial engineering yields exceptional electrochemical performance: a high areal capacity of $3014 \text{ mC}\cdot\text{cm}^{-2}$ at $1 \text{ mA}\cdot\text{cm}^{-2}$, and 70.58% capacity retention after 8000 cycles. When paired with YP-50 in an asymmetric supercapacitor (ASC), the $\text{MnP}_4/\text{CoP}_2/\text{YP-50}$ device delivers a high energy density of $88.5 \text{ Wh}\cdot\text{kg}^{-1}$ at $798.8 \text{ W}\cdot\text{kg}^{-1}$, outperforming state-of-the-art Mn/Co-based systems. In addition, the ASC exhibits exceptional cycling stability (68.29% capacity retention after 10,000 cycles at $5 \text{ A}\cdot\text{g}^{-1}$) and practical viability, powering 12 light-emitting diodes (LEDs) for over 10 min. Our work proposes a design principle that integrates the wisdom of natural structures with rational heterostructure configuration, providing a scalable paradigm for developing advanced energy storage materials.



KEYWORDS: bio-inspiration, Venus flytrap, heterojunction, built-in electric field, supercapacitor

1 Introduction

The rapid depletion of global fossil fuels and the comprehensive implementation of carbon neutrality strategies have made the

development of efficient and sustainable energy storage technologies a critical priority for addressing energy crises and environmental pollution [1, 2]. Among the currently available energy storage devices, lithium-ion batteries (LIBs) and lithium-metal batteries (LMBs) dominate due to their high energy density (E ($\text{Wh}\cdot\text{kg}^{-1}$)) and commercial maturity. However, both systems are hindered by limitations, such as safety concerns, high cost, limited rate capability, and relatively short cycle life under extreme conditions [3–5]. In this context, supercapacitors have emerged as a complementary and indispensable energy storage technology. Supercapacitors, distinguished by their ultrafast charge/discharge

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rates (second-level response), high power density (P ($\text{W}\cdot\text{kg}^{-1}$), $> 10 \text{ kW}\cdot\text{kg}^{-1}$), and exceptional cycle life ($> 10^5$ cycles), have emerged as indispensable components in smart grid frequency regulation and regenerative energy systems for new energy vehicles [6, 7]. However, conventional supercapacitors suffer from limited energy density ($< 10 \text{ Wh}\cdot\text{kg}^{-1}$), significantly lower than that of lithium-ion batteries, primarily due to the low specific capacity of electrode materials and insufficient utilization of redox-active sites [8, 9]. In recent years, transition metal-based materials, including layered double hydroxides (LDHs) [10], metal oxides (TMOs) [11], metal sulfides (TMSs) [12], and metal phosphides (TMPs) [13], have attracted considerable attention owing to their multivalent redox characteristics and high theoretical specific capacitance. Nevertheless, single-component systems face inherent challenges, such as poor intrinsic conductivity, structural collapse during cycling, and sluggish ion diffusion kinetics, resulting in practical performance far below theoretical expectations.

Heterojunction interface engineering, achieved by constructing interfaces between dissimilar materials (e.g., $\text{NiSe}_2/\text{CoSe}_2$ [14], $\text{Co}_{0.85}\text{Se}/\text{Ni}_3\text{S}_2$ [15], $\text{CuCo}_2\text{S}_4/\text{MoS}_2$ [16], $\text{Ni}_3\text{S}_2/\text{Ni}_2\text{O}_3$ [17], and $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ [18]), has been recognized as a pivotal strategy to enhance electrochemical performance. This approach not only introduces additional electroactive components but also leverages work function differences between materials to generate built-in electric fields, thereby optimizing charge transfer pathways and reaction kinetics. For instance, Jiang et al. [19] demonstrated that the $\text{CoMoO}_4/\text{CoP}$ heterojunction reduces charge transfer resistance (R_{ct}) to 0.88Ω and elevates specific capacitance to $3056.4 \text{ F}\cdot\text{g}^{-1}$ through electronic coupling and interfacial synergy. Shen et al. [20] further revealed via theoretical calculations that heterointerfaces can modulate electronic structures to optimize OH^- adsorption behavior, as evidenced by the reduction in adsorption energy from -2.2 eV for NiCo_2O_4 to -2.5 eV for $\text{NiCo}_2\text{O}_4/\text{Nb}_2\text{CT}_x$.

Meanwhile, bio-inspired hierarchical architectures—mimicking natural structures, such as honeycomb networks [21], diatomaceous porous frameworks [22], micro-nanochannels in lotus leaves [23], and bristle-like configurations of foxtail grass [24]—have been designed to construct three-dimensional (3D) interconnected nano-networks. These architectures synergistically enhance ion transport efficiency and structural stability. Compared to conventional nanostructures (e.g., nanoflowers, nanosheets, and nanorods), bioinspired hierarchical morphologies enable rapid directional electrolyte infiltration through hierarchically designed micropores–mesopores–macropores, while vertical nanowires or nanopillars provide mechanical anchoring to suppress volume expansion during cycling [25–27]. Furthermore, open-surface structures increase the electrochemically active area [28], significantly improving the exposure and utilization efficiency of active sites. However, challenges remain in the precise control of complex morphologies for scalable synthesis, and reports on the synergistic effects between bio-inspired architectures and heterojunctions are still limited.

Inspired by the efficient prey-capture mechanism of *Dionaea muscipula* (Venus flytrap) leaves—which integrate hierarchical porosity with rapid stimulus-responsive material [29, 30]—herein we propose a “morphology–interface” synergistic integration strategy and successfully construct a Venus flytrap-like $\text{MnP}_4/\text{CoP}_2$ heterostructured biomimetic electrode. Specifically, ammonium fluoride (NH_4F)-mediated hydrothermal synthesis is first employed

to grow a nanosheet–nanowire hierarchical MnCo-LDH network on nickel foam (NF). This structure mimics the multiscale penetration channels and mechanical framework of a flytrap leaf to facilitate electrolyte infiltration and alleviate volume expansion. Subsequent gas-phase phosphidation transforms the precursor into a $\text{MnP}_4/\text{CoP}_2$ heterojunction, where a built-in electric field (work function difference: 0.219 eV) triggered strong electronic coupling and accelerated reaction kinetics. Density functional theory (DFT) calculations further reveal that interfacial charge redistribution in $\text{MnP}_4/\text{CoP}_2$ significantly enhances OH^- adsorption, with the adsorption energy of -3.51 eV . Consequently, the $\text{MnP}_4/\text{CoP}_2$ electrode delivered a high areal capacity (Q ($\text{mC}\cdot\text{cm}^{-2}$)) of $3014 \text{ mC}\cdot\text{cm}^{-2}$ in 6 M potassium hydroxide (KOH), while the assembled asymmetric supercapacitor (ASC) achieved an energy density of $88.5 \text{ Wh}\cdot\text{kg}^{-1}$ and powered 12 light-emitting diodes (LEDs) for 10 min. This work not only provides a biomimetic design paradigm for high-performance supercapacitor electrodes but also elucidates the intrinsic mechanisms underlying the synergy between heterojunctions and morphological optimization, laying a scientific foundation for next-generation energy storage devices.

2 Experimental

2.1 Materials

Manganese(II) sulfate monohydrate ($\text{MnSO}_4\cdot\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$), NH_4F , urea ($\text{CO}(\text{NH}_2)_2$), hydrochloric acid (HCl), KOH, anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$), anhydrous methanol (CH_3OH), acetone ($(\text{CH}_3)_2\text{CO}$), and sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and used as received without further purification. NF ($5 \text{ cm} \times 3 \text{ cm}$) was successively ultrasonicated in acetone and ethanol for 15 min each, followed by drying under vacuum at 60°C for subsequent use.

2.2 Synthesis of Venus flytrap-like MnCo-LDH , MnCoO_3 , and $\text{MnP}_4/\text{CoP}_2$ hierarchical architectures

The Venus flytrap-like MnCo-LDH was synthesized via a one-step hydrothermal method. Specifically, 2 mmol of $\text{MnSO}_4\cdot\text{H}_2\text{O}$, 1 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 9 mmol of $\text{CO}(\text{NH}_2)_2$, and 10 mmol of NH_4F were dissolved in sequence into 60 mL of deionized water (DIW) under magnetic stirring to form a homogeneous precursor solution. A pre-treated NF substrate was immersed in the solution and subjected to magnetic stirring for 20 min to achieve homogeneous surface wetting. The mixture was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and hydrothermally treated at 120°C for 8 h in a convection oven. After natural cooling to room temperature, the NF substrate was retrieved, uniformly coated with a purple-colored MnCo-LDH layer. To remove loosely adhered particles, the coated NF was ultrasonically washed three times with DIW and absolute ethanol. Finally, the product was vacuum-dried at 60°C for 12 h , yielding a freestanding $\text{MnCo-LDH}/\text{NF}$ electrode exhibiting a Venus flytrap-like hierarchical architecture.

The as-prepared MnCo-LDH was calcined in a muffle furnace at 350°C for 2 h (heating rate: $2^\circ\text{C}\cdot\text{min}^{-1}$, air atmosphere) to obtain MnCoO_3 . Subsequently, $\text{MnP}_4/\text{CoP}_2$ heterostructures were synthesized via gas-phase phosphidation. Specifically, 2.0 g of $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ and 0.5 g of MnCoO_3 were placed in the upstream

and downstream zones of a tube furnace, respectively. High-purity N_2 was introduced at 60 sccm for 15 min to purge residual oxygen. The furnace was then heated to 400 °C, maintaining the reaction for 2 h to facilitate PH_3 generation and phosphidation. The final product (MnP_4/CoP_2) was collected after natural cooling. By comparing the weight of NF before and after the phosphorization process, the mass loading of MnP_4/CoP_2 was calculated to be $4.7\text{ mg}\cdot\text{cm}^{-2}$ (Fig. S1 in the Electronic Supplementary Material (ESM)). For comparison, $MnSO_4\cdot H_2O$ or $Co(NO_3)_2\cdot 6H_2O$ were excluded from the hydrothermal precursor synthesis, followed by phosphidation under identical conditions, yielded phase-pure CoP_2 and MnP_4 , respectively.

2.3 Electrochemical measurements

Electrochemical evaluations were conducted in a three-electrode configuration using a 6 M KOH aqueous electrolyte. The as-prepared samples served as the working electrode, with Hg/HgO and Pt electrodes functioning as the reference and counter electrodes, respectively. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS, 0.01–10⁵ Hz) were performed on a CHI 760E workstation (Chenhua, China) under ambient conditions. Long-term cycling stability was assessed using a CT2001A battery tester. Q was calculated via $Q = \frac{2I \int V dt}{\Delta V}$ [31, 32], where I (mA) denotes the discharge current, t (s) represents the discharge time, $\int V dt$ represents the integrated area under the discharge curve, and ΔV (V) is the operating voltage window, and S (cm²) represents the electrode area.

For the all-solid-state ASC assembly, MnP_4/CoP_2 and activated carbon (AC; YP-50) served as the positive and negative electrodes, respectively, separated by a poly(vinyl alcohol) (PVA)-KOH gel electrolyte. The YP-50 negative electrode was prepared by homogenizing YP-50, acetylene black, and polytetrafluoroethylene (PTFE) binder in an 8:1:1 mass ratio in acetone, followed by compression onto nickel foam at 15 kPa. The gel electrolyte was synthesized by dissolving 3 g of PVA in 30 mL DIW at 95 °C, after which 10 mL of a 3 M concentrated KOH solution was incorporated. To ensure charge balance, the mass ratio of the positive and negative electrodes was tuned according to the equation: $\frac{m^+}{m^-} = \frac{C^+ \Delta V^-}{C^- \Delta V^+}$, where m (g) and C (F·g⁻¹) represent the mass and specific capacitance of electrode, respectively. E and P were derived from $E = \frac{C_{cell} V^2}{7.2}$ and $P = \frac{3600E}{\Delta t}$, where C_{cell} (F·g⁻¹) and Δt (s) represent the specific capacitance of ASC and discharge time, respectively.

Other experimental details, including material characterization and DFT calculations, can be found in the ESM.

3 Results and discussion

3.1 Synthesis of Venus flytrap-like MnCo-LDH, MnCoO₃, and MnP_4/CoP_2 hierarchical architectures

As schematically illustrated in Fig. 1(a), we successfully constructed a biomimetic MnP_4/CoP_2 heterostructure through a three-step synthetic strategy. The hierarchical architecture was initiated by the directional growth of Venus flytrap-like MnCo-LDH precursors on NF substrates via a hydrothermal method (Fig. 1(b)). Scanning electron microscopy (SEM) characterization reveals a well-defined

architecture comprising primary nanosheets (7–10 μm in length and ~ 100 nm in width) with uniformly distributed secondary nanowires (~ 700 nm in length) along their edges. This “nanosheet–nanowire” hierarchy exhibits striking morphological similarity to the predatory organs of *Dionaea muscipula* leaves (the inset of Fig. 1(b)), arising from the synergistic regulation of NH_4F . Specifically, F^- ions orchestrate anisotropic growth through metal ion coordination and selective adsorption on specific facets, while NH_4^+ modulates solution pH dynamically to suppress nanosheet agglomeration [33, 34]. Control experiments with varying NH_4F concentrations (8–12 mmol, Fig. S2 in the ESM) identified 10 mmol as the optimal condition, achieving a balance between structural integrity and suppression of particle overgrowth. Subsequent calcination at 350 °C transformed MnCo-LDH into $MnCoO_3$ (Fig. 1(c)), reducing nanosheet thickness slightly while preserving the original hierarchical framework—a testament to its exceptional thermal stability. Gas-phase phosphidation further converted $MnCoO_3$ into the MnP_4/CoP_2 heterostructure (Fig. 1(d)). Notably, this process introduces abundant mesopores (average diameter of 20.0 nm, Fig. S3 in the ESM) within the nanosheets while maintaining the continuity of the ordered nanosheet–nanowire network. Such a hierarchical porous architecture establishes three-dimensionally interconnected channels for efficient electrolyte infiltration. Transmission electron microscopy (TEM) analysis (Fig. 1(e)) shows the formation of phosphide crystallites (~ 20 nm in diameter) on nanosheet surfaces, accompanied by distinct lattice fringes corresponding to the (222) plane of MnP_4 (2.26 Å spacing) and the ($\bar{1}02$) plane of CoP_2 (2.79 Å spacing) (Fig. 1(f)). A discernible lattice mismatch region at the heterointerface suggests the presence of interfacial strain. Selected-area electron diffraction (SAED) pattern (Fig. 1(g)) displays polycrystalline diffraction rings indexed to the (110) and (112) planes of MnP_4 and the ($\bar{1}02$) plane of CoP_2 , unambiguously confirming heterojunction formation. This interfacial configuration is anticipated to enhance electrochemical performance through dual synergistic mechanisms: (i) The built-in electric field at the heterointerface facilitates accelerated charge transfer kinetics during redox reactions [35], and (ii) interfacial electron redistribution optimizes adsorption energetics at active sites for improved reaction dynamics [36]. In addition, as illustrated in Fig. S4 in the ESM, SEM-energy dispersive X-ray spectroscopy (EDS) elemental mapping analysis indicates that Mn, Co, and P exhibit a highly uniform distribution across the sample surface. For comparison, Fig. S5 in the ESM depicts the phase-pure CoP_2 and MnP_4 reference samples obtained under identical phosphidation conditions. CoP_2 is composed of radially assembled, plate-like crystallites a few hundred nanometres thick that aggregate into tightly packed flower-shaped microspheres (2–4 μm in diameter), producing a mechanically robust yet relatively non-porous framework. By contrast, MnP_4 forms a “grass-carpet” array of needle-like nanocrystals (1–2 μm in length) that emanate vertically or obliquely from the substrate, giving rise to an open three-dimensional network with abundant accessible surface area. The Venus flytrap-like MnP_4/CoP_2 heterostructure thus integrates the structural rigidity of plate-like CoP_2 crystallites with the high porosity of MnP_4 nanoneedles, furnishing a hierarchical architecture that simultaneously offers large electrolyte-accessible area and superior mechanical stability—attributes expected to translate into enhanced electrochemical performance.

X-ray diffraction (XRD) analysis elucidates the crystallographic

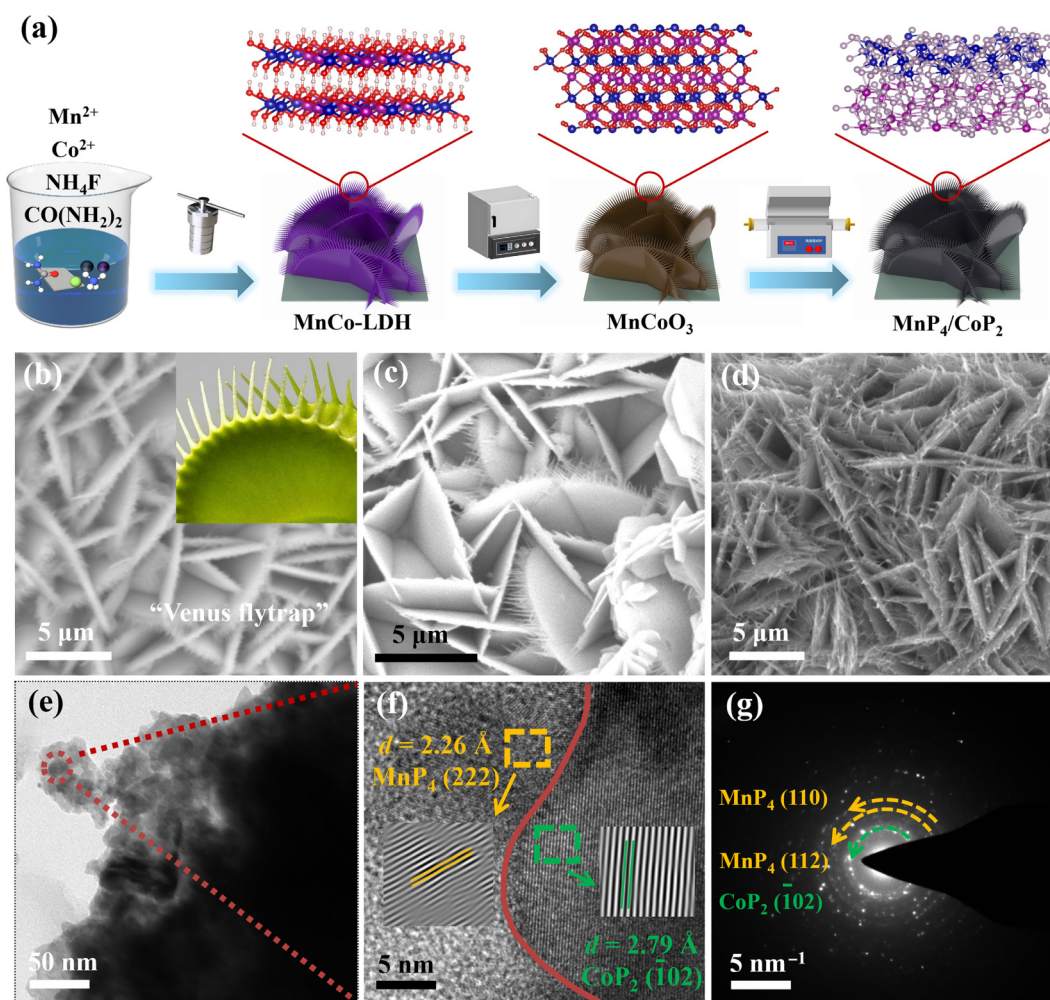


Figure 1 (a) Graphical illustration of the MnP₄/CoP₂ fabrication process. (b)–(d) SEM images of (b) MnCo-LDH, (c) MnCoO₃, (d) MnP₄/CoP₂. (e) TEM, (f) high-resolution TEM (HRTEM) images, and (g) SAED pattern of MnP₄/CoP₂.

evolution during the synthetic process (Fig. 2(a)). The pristine MnCo-LDH exhibits diffraction peaks in excellent agreement with the standard LDH phase (JCPDS Nos. 10-144 and 30-0443) [37], confirming the successful construction of a hydrotalcite-like structure. Following oxidation at 350 °C, emerging peaks at $2\theta = 24.5^\circ, 33.5^\circ, 36.4^\circ, 44.6^\circ, 54.8^\circ, 57.9^\circ,$ and 65.4° are indexed to the (012), (104), (110), (202), (116), (018), and (300) planes of MnCoO₃ (PDF#00-012-0476), signifying complete transformation into a spinel-type oxide. Subsequent gas-phase phosphidation yields distinct diffraction peaks at $2\theta = 18.2^\circ, 31.0^\circ, 32.9^\circ, 47.7^\circ, 58.7^\circ, 60.9^\circ,$ and 63.9° , corresponding to the ($\bar{2}02$), ($\bar{3}11$), (008), ($\bar{5}13$), ($\bar{1}35$), ($\bar{3}31$), and (1114) plane of MnP₄ (PDF#04-007-1451) and the distinct diffraction peaks at $2\theta = 23.6^\circ, 24.8^\circ, 36.8^\circ,$ and 81.2° corresponding to the (011), ($\bar{1}11$), (021), and ($\bar{4}32$) plane of CoP₂ (PDF#04-003-4573), unambiguously verifying the formation of a CoP₂/MnP₄ heterostructure. X-ray photoelectron spectroscopy (XPS) provides deeper insights into the electronic configurations across the synthesis stages. The high-resolution Co 2p spectra (Fig. 2(b)) feature two predominant peaks at 781.7 and 796.7 eV, corresponding to the 2p_{3/2} and 2p_{1/2} orbitals of Co²⁺, respectively, whereas the peaks at 780.95 and 795.05 eV are associated with Co³⁺ [38]; the remaining signals arise from satellite features. Notably, a positive binding energy shift is observed for Co in MnP₄/CoP₂ compared to MnCoO₃, indicative of an electron-

deficient state induced by phosphidation. In the Mn 2p spectra (Fig. 2(c)), the peaks at 643.03 and 655.2 eV are ascribed to Mn⁴⁺ (2p_{3/2} and 2p_{1/2}), while those at 641.23 and 654.22 eV are assigned to Mn³⁺; additional signals at 637.43 and 653.31 eV stem from Mn²⁺ [39, 40]. Conversely, the Mn 2p spectra reveal a negative shift for Mn species, suggesting electron enrichment at Mn sites. This antagonistic binding energy shift underscores a pronounced interfacial electron transfer from Co to Mn at the MnP₄/CoP₂ heterojunction, generating a localized built-in electric field that synergistically enhances charge transfer kinetics. As summarized in Table S1 in the ESM, the increased fraction of Mn²⁺ furnishes abundant redox-active sites for multi-electron reactions [41], while the presence of Co³⁺ enhances bulk conductivity and structural robustness [42]. Deconvolution of the P 2p spectrum (Fig. 2(d)) reveals a dominant peak at 129.53 eV, attributed to metal–phosphorus (M–P) bonding, and a secondary peak at 134.2 eV corresponding to oxidized phosphorus species (P–O) [43]. The appearance of the relatively strong P–O signal is primarily attributed to surface oxidation upon brief exposure of the phosphide material to air, a common phenomenon observed in transition metal phosphides [43–45]. Notably, the resulting thin P–O layer serves as a self-passivating interphase that enhances surface wettability [46], promotes electrolyte infiltration and improves interface stability. This protective layer effectively

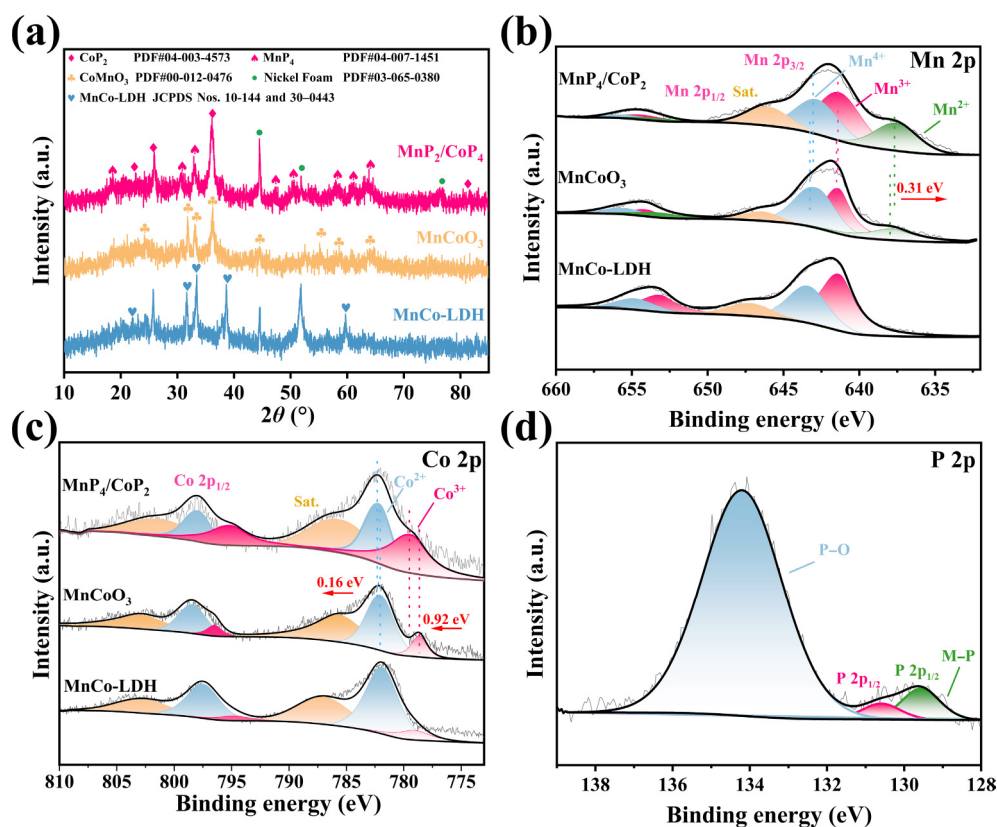


Figure 2 (a) XRD patterns of MnCo-LDH, MnCoO₃, and MnP₄/CoP₂. ((b)–(d)) XPS spectra of (b) Co, (c) Mn, and (d) P.

mitigates active material dissolution during cycling, thereby contributing to enhanced electrochemical durability without compromising the intrinsic conductivity or structural integrity of the phosphide material [47].

3.2 Electrochemical performance of Venus flytrap-like Mn₄P₂/CoP₂

To comprehensively evaluate the energy storage performance of MnCo-LDH, MnCoO₃, CoP₂, MnP₄ and MnP₄/CoP₂, a series of multiscale electrochemical characterizations were conducted in 6 M KOH electrolyte (Fig. 3). As shown in the CV curves (Fig. 3(a)), all five materials exhibit well-defined and separated redox peak pairs within the 0–0.6 V voltage window, indicating a predominant pseudocapacitive behavior governed by surface redox reactions [48]. Notably, MnP₄/CoP₂ demonstrates a significantly higher anodic peak current density (95 mA·cm⁻²) than that of MnCoO₃ (28 mA·cm⁻²), MnCo-LDH (24 mA·cm⁻²), CoP₂ (73 mA·cm⁻²), and MnP₄ (68 mA·cm⁻²), attributable to the synergistic effect of the phosphidation-induced heterointerface and the hierarchical nanosheet-nanowire architecture. GCD profiles (Fig. 3(b)) quantitatively demonstrate the enhanced storage capacity. At 1 mA·cm⁻², MnP₄/CoP₂ delivers an areal capacity of 3014 mC·cm⁻², outperforming MnCoO₃ (762 mC·cm⁻²), MnCo-LDH (429 mC·cm⁻²), CoP₂ (2208 mC·cm⁻²), and MnP₄ (1838 mC·cm⁻²). The asymmetry plateaus observed in the GCD curves align with the CV profiles, reflecting the multivalent redox transitions involved in the charge storage process, including the following reversible reactions [49–51]



Scan rate-dependent CV analysis (Fig. 3(c)) reveals that the redox peak positions of MnP₄/CoP₂ exhibit slight shifts ($\Delta V < 10\%$) across 5–50 mV·s⁻¹, indicating exceptional redox reversibility [52]. This superior rate response is primarily due to its hierarchically porous structure, which provides three-dimensional ion diffusion pathways, alleviating mass transport limitations under fast scan conditions. Figure 3(d) displays the GCD curves of MnP₄/CoP₂ at various current densities, with the corresponding areal capacities summarized in Fig. 3(e). The MnP₄/CoP₂ electrode delivers areal capacities of 3014, 2722, 2501, 2239, 1811, and 1597 mC·cm⁻² at current densities of 1, 2, 3, 5, 10, and 20 mA·cm⁻², respectively. Based on the measured mass loading, the corresponding specific capacitances are calculated to be 1425, 1287, 1183, 1059, 856, and 755 F·g⁻¹ at estimated current densities of approximately 0.21, 0.43, 0.64, 1.06, 2.13, and 4.26 A·g⁻¹. As the current density increases to 20 mA·cm⁻², MnP₄/CoP₂ still retains 52.9% of its initial capacity. This capacity decay is primarily attributed to the intrinsic kinetic limitations of pseudocapacitive materials under high-rate conditions, where shortened charge/discharge durations restrict electrolyte ion diffusion and hinder access to deeper redox-active sites [53]. EIS analysis (Fig. 3(f)) highlights charge transport advantages. The equivalent series resistance (R_s) and R_{ct} , extracted from the fitted equivalent circuit (inset of Fig. S8 in the ESM), are summarized in Table S2 in the ESM. Notably, MnP₄/CoP₂ exhibits the lowest R_{ct} value (1.20 Ω), in comparison with MnCoO₃ (7.14 Ω), MnCo-LDH (25.30 Ω), CoP₂ (20.21 Ω), and MnP₄ (2.65 Ω), evidencing accelerated reaction kinetics via interfacial

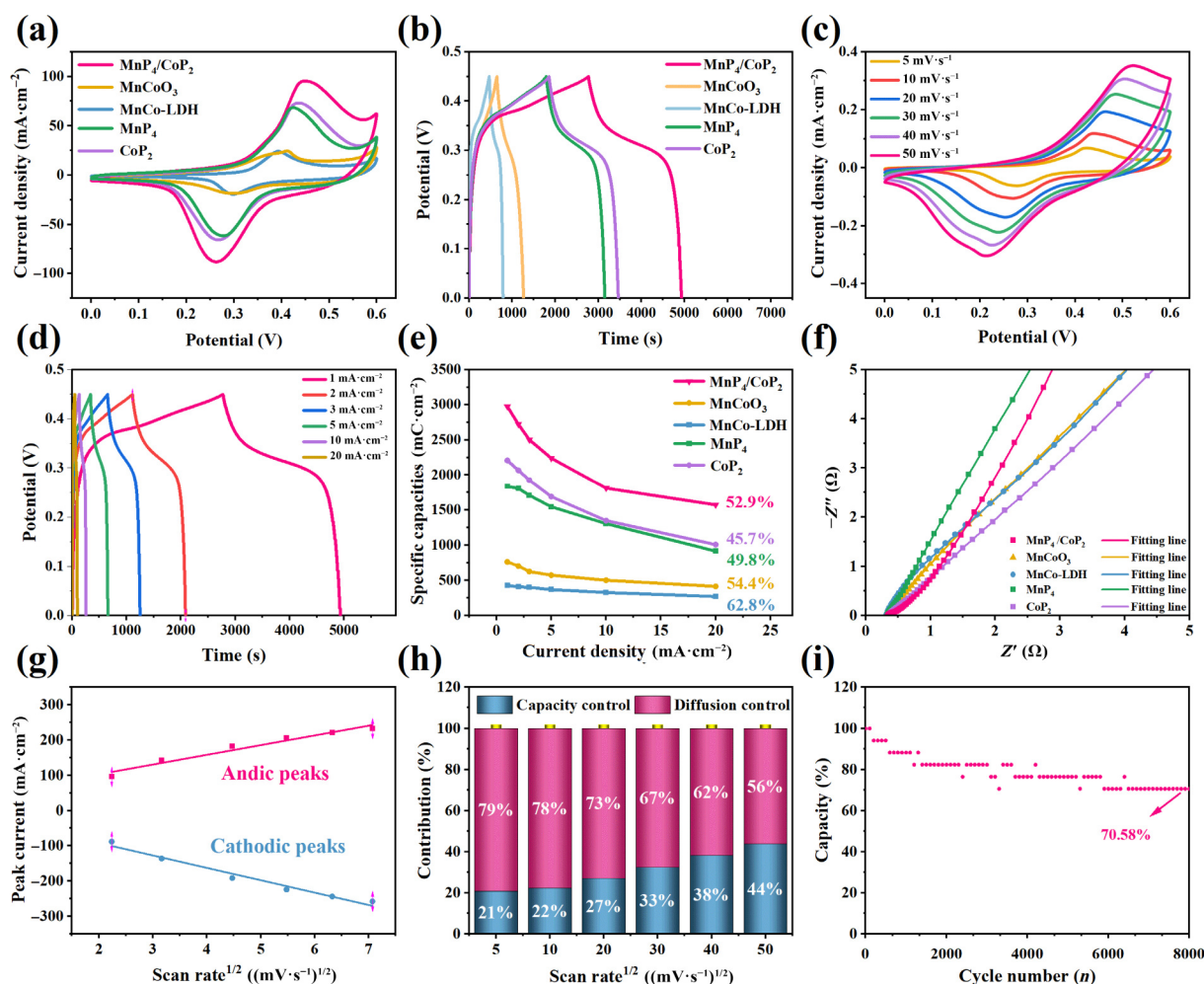


Figure 3 ((a) and (b)) Comparison of electrochemical performance of MnCo-LDH, MnCoO₃, MnP₄, CoP₂ and MnP₄/CoP₂: (a) CV curves at 5 mV·s⁻¹ and (b) GCD curves at 1 mA·cm⁻². ((c) and (d)) Capacity performance of MnP₄/CoP₂: (c) CV curves at different scan rates and (d) GCD curves at various current densities. (e) Specific capacitance plot and (f) Nyquist plots of MnCo-LDH, MnCoO₃, MnP₄, CoP₂ and MnP₄/CoP₂. (g) Peak current density versus scan rate plot and (h) capacitive-controlled contribution ratio of MnP₄/CoP₂. (i) Cyclic performance plot of MnP₄/CoP₂ at 50 mA·cm⁻².

electron pathways. Remarkably, the steeper Warburg slope in the low-frequency region further indicates enhanced ion diffusion enabled by the nanosheet-nanowire network. Power-law analysis of peak currents and capacitive/diffusion-separation models decouples the charge storage mechanisms [54, 55]

$$i_p = av^b \quad (4)$$

$$i = k_1v + k_2v^{1/2} \quad (5)$$

Here, i_p represents the peak current density, i represents the current density, v represents the scan rate, and a and b are the coefficients. A b value of 1 or 0.5 indicates a capacitive or diffusion-controlled process, respectively. The constants k_1 and k_2 denote the contributions from capacitive and diffusion-controlled mechanisms. As shown in Fig. 3(g), a linear relationship between peak current and the square root of scan rate is observed for both cathodic and anodic processes, indicating diffusion-controlled dominance. Figure 3(h) further quantifies the contribution of capacitive and diffusion-controlled processes at different scan rates. Even at a high scan rate of 50 mV·s⁻¹, diffusion processes still account for 53% of the total current, consistent with the rapid ion-access pathways provided by the hierarchical porous structure.

Long-term cycling tests (Fig. 3(i)) demonstrate robust stability: MnP₄/CoP₂ retains 70.58% of its initial capacity after 8000 cycles at 50 mA·cm⁻². To further investigate the morphology and structure on performance post-cycling, additional structural and surface analyses—including XRD, SEM, XPS, and EDS mapping are conducted. As shown in Fig. S9(a) in the ESM, the characteristic Venus flytrap-like architecture composed of interconnected nanosheets and nanowires undergoes partial structural collapse and aggregation after 8000 cycles, which reduces surface area and limits electrolyte accessibility. XRD patterns reveal the appearance of new diffraction peaks corresponding to MnP₄O₁₁ and Co₃(PO₄)₂ (Fig. S9(b) in the ESM), indicating phase transitions likely induced by prolonged redox interactions with OH⁻ ions during cycling. XPS analysis further confirms chemical evolution: Compared with the pristine electrode, post-cycling Co 2p spectra exhibit an increased Co³⁺/Co²⁺ ratio, and Mn 2p spectra reveal a relative enrichment of Mn³⁺ species (Figs. S9(c) and S9(d) in the ESM). These results suggest that continuous redox cycling promotes surface oxidation and compositional rearrangement, which may impact redox activity and structural integrity. Moreover, SEM-EDS mapping (Fig. S10 in the ESM) demonstrates a uniform elemental distribution of Mn, Co, P, O, and K across the cycled electrode surface, with K

originating from the KOH electrolyte. Nevertheless, comparative analysis with state-of-the-art Mn/Co-based composites (Table S3 in the ESM) underscores the competitive performance of $\text{MnP}_4/\text{CoP}_2$ in both capacity density and cyclability.

To further validate the practical potential of $\text{MnP}_4/\text{CoP}_2$, an ASC was assembled using $\text{MnP}_4/\text{CoP}_2$ as the positive electrode, commercial YP-50 as the negative electrode, and KOH-PVA gel as the electrolyte (device configuration and digital photograph illustrated in Fig. 4(a) and Fig. S11 in the ESM, respectively). The YP-50 electrode exhibits typical electric double-layer capacitive behavior in a three-electrode system, characterized by rectangular CV profiles (-1.0 – 0 V), quasi-triangular GCD curves, and excellent rate capability (Fig. S12 in the ESM), meeting the requirements for high-performance negative electrode materials [56]. CV and GCD tests are conducted to determine the optimal working voltage window of the ASC device. As shown in Fig. 4(b), the CV curve area increases steadily as the voltage window expands from 1.2 to 1.6 V, indicating enhanced charge storage capacity. However, at 1.7 V, pronounced polarization emerges, which can be attributed to the onset of water decomposition in the electrolyte. The corresponding GCD curves (Fig. 4(c)) also exhibit abnormal voltage drops at this voltage. Accordingly, a voltage window of 0 – 1.6 V is selected for subsequent evaluations. The ASC demonstrates exceptional rate capability, as evidenced by well-retained CV profiles across 5 – 50 $\text{mV}\cdot\text{s}^{-1}$ (Fig. 4(d)). GCD curves collected at various current densities (Figs. 4(e) and 4(f)) further confirm the superior performance. The device exhibits specific capacitances of

$249, 191.3, 159.9, 130.3, 92.1$, and 54.4 $\text{F}\cdot\text{g}^{-1}$ at current densities of $1, 2, 3, 5, 10$, and 20 $\text{A}\cdot\text{g}^{-1}$, respectively. At a low current density of 1 $\text{A}\cdot\text{g}^{-1}$, a slight tailing is observed in the discharge profile, which is commonly attributed to the intrinsic ion transport limitations of the PVA-KOH gel electrolyte and the delayed desorption of pseudocapacitive materials [57]. The Ragone plot (Fig. 4(g)) illustrates a favorable trade-off between energy and power densities: The ASC delivers a high energy density of 88.5 $\text{Wh}\cdot\text{kg}^{-1}$ at a power density of $13,977.6$ $\text{W}\cdot\text{kg}^{-1}$. Impressively, even at a high power density of 19.4 $\text{Wh}\cdot\text{kg}^{-1}$, outperforming many previously reported MnCo-based ASC systems (Table S4 in the ESM). Moreover, the $\text{MnP}_4/\text{CoP}_2$ //YP-50 device demonstrates remarkable cycling stability. As shown in Fig. 4(h), the ASC exhibits a typical activation behavior during cycling, with an initial decline followed by a gradual increase in capacitance, which is commonly observed in solid-state gel electrolyte systems due to the progressive wetting and interfacial stabilization process [58]. After $10,000$ cycles at a current density of 5 $\text{A}\cdot\text{g}^{-1}$, the device retains 68.3% of its initial capacitance, demonstrating satisfactory long-term cycling stability and structural robustness under high-rate operation. Notably, as depicted in Fig. S13 in the ESM, two such ASC units connected in series successfully powered 12 LEDs for over 10 min, showcasing their real-world applicability. Collectively, these electrochemical evaluations firmly establish the exceptional performance of the Venus flytrap-inspired $\text{MnP}_4/\text{CoP}_2$ architecture for high-efficiency energy storage applications.

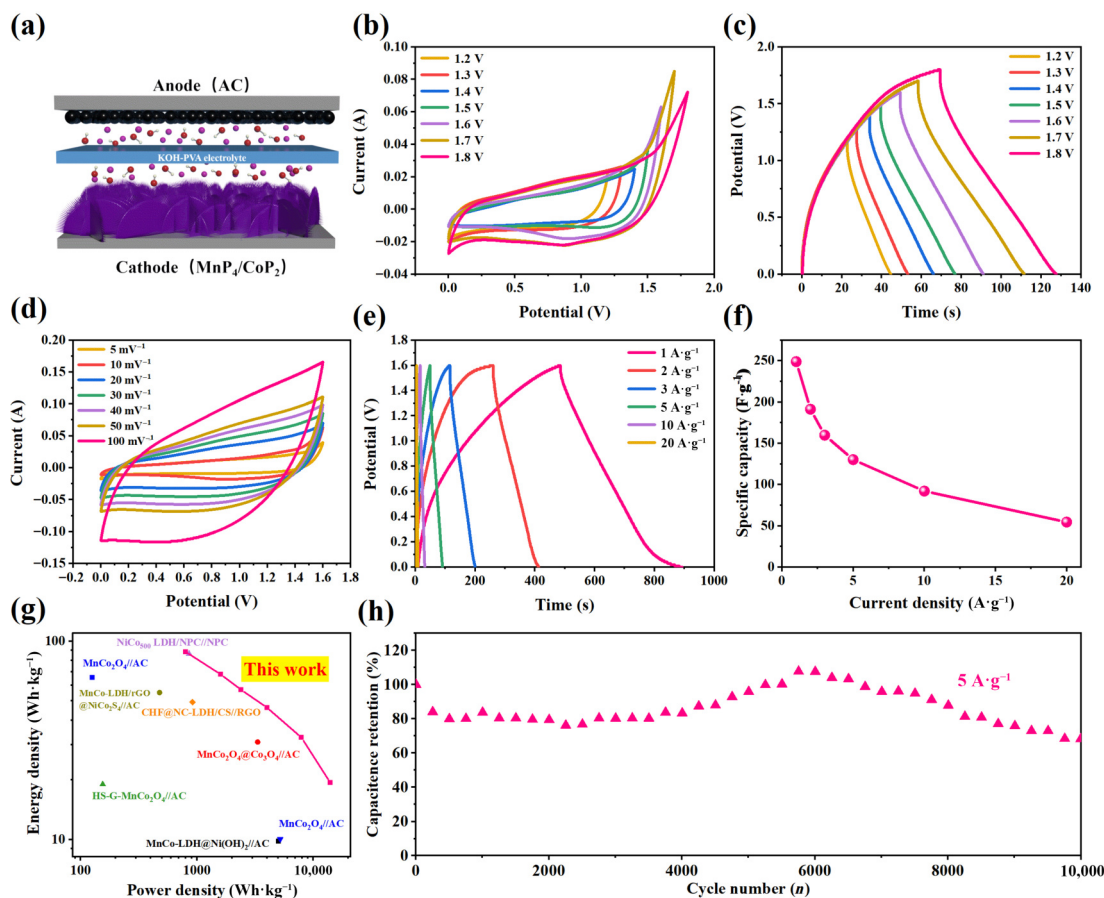


Figure 4 (a) Schematic illustration of the $\text{MnP}_4/\text{CoP}_2$ //AC ASC. (b) CV curves at 5 $\text{mV}\cdot\text{s}^{-1}$ under different working voltages, (c) GCD plots at 5 $\text{A}\cdot\text{g}^{-1}$ under different working voltages, (d) CV curves at different scan rates, (e) GCD curves at different current densities, and (f) specific capacity plot of $\text{MnP}_4/\text{CoP}_2$ //AC. (g) Ragone plot of the ASC compared to previous reports and (h) cycling stability test of $\text{MnP}_4/\text{CoP}_2$ //AC.

3.3 Theoretical perspective into the electrochemical performance

To unravel the intrinsic advantages of the $\text{MnP}_4/\text{CoP}_2$ heterostructure for energy storage, DFT calculations were conducted to systematically investigate its electronic structure and interfacial properties. Structural optimization results (Fig. 5(a)) demonstrate a stable and tightly bonded heterointerface between MnP_4 and CoP_2 . The total density of states (TDOS, Fig. 5(b)) reveals pronounced electronic states near the Fermi level for $\text{MnP}_4/\text{CoP}_2$, indicative of enhanced electronic conductivity [59] compared to MnCo-LDH and MnCoO_3 , which facilitates rapid charge transfer. Further projected density of states (PDOS) analysis (Fig. 5(c)) highlights significant orbital hybridization between Mn 3d, Co 3d, and P 2p states near the Fermi level, suggesting strong electronic coupling at the interface. As depicted in Fig. 5(d), the calculated work functions of MnP_4 , CoP_2 , and $\text{MnP}_4/\text{CoP}_2$ are 4.925, 4.706, and 4.862 eV, respectively. The 0.219 eV difference between MnP_4 and CoP_2 induces a built-in electric field at the heterointerface [60], driving directional electron transfer from CoP_2 to MnP_4 (Fig. 5(e)). This internal electric field not only accelerates interfacial charge separation but also promotes the kinetics of redox reactions. The charge density difference map (Fig. 5(f)) corroborates this behavior, showing clear electron accumulation on the MnP_4 side and depletion on the CoP_2 side, thereby confirming the presence of pronounced charge redistribution and strong interfacial coupling within the heterostructure. In addition, the adsorption configuration of OH^- on the $\text{MnP}_4/\text{CoP}_2$ surface is illustrated in Fig. 5(g). OH^- adsorption energy calculations

(Fig. 5(h)) reveal that the $\text{MnP}_4/\text{CoP}_2$ heterostructure exhibits a significantly stronger affinity (−3.51 eV) compared to its individual components (MnP_4 : −1.52 eV and CoP_2 : −1.84 eV) and precursor materials (MnCoO_3 : −2.26 eV and MnCo-LDH : −2.52 eV). This indicates a stronger affinity for OH^- species, suggesting that the heterostructure provides more abundant and highly active adsorption sites [12]. Therefore, these DFT results demonstrate that the $\text{MnP}_4/\text{CoP}_2$ heterostructure possesses favorable characteristics in terms of electronic modulation, interfacial charge engineering, and adsorption energy kinetics.

By integrating experimental characterization with DFT analyses, we elucidate the fundamental mechanism underpinning the remarkable electrochemical performance of the Venus flytrap-inspired $\text{MnP}_4/\text{CoP}_2$ heterostructure. As illustrated in Fig. 6, this exceptional behavior arises from the synergistic interplay between the biomimetic hierarchical architecture and heterointerface engineering. Specifically, the orderly arranged nanosheet–nanowire network in $\text{MnP}_4/\text{CoP}_2$ emulates the multiscale porous configuration of Venus flytrap leaves, thereby constructing a dual-mode ion-transport system: Primary nanosheets establish an unobstructed axial highway for rapid electrolyte diffusion, while secondary nanowires furnish a robust radial infiltration channel through nano-confined capillary effects. Concurrently, the formation of the $\text{MnP}_4/\text{CoP}_2$ heterojunction induces a built-in electric field at the interface, expediting charge transfer and enhancing electrochemical reaction kinetics. Furthermore, the concomitant charge redistribution modulates the valence states of Mn and Co, simultaneously creating plentiful redox-active sites

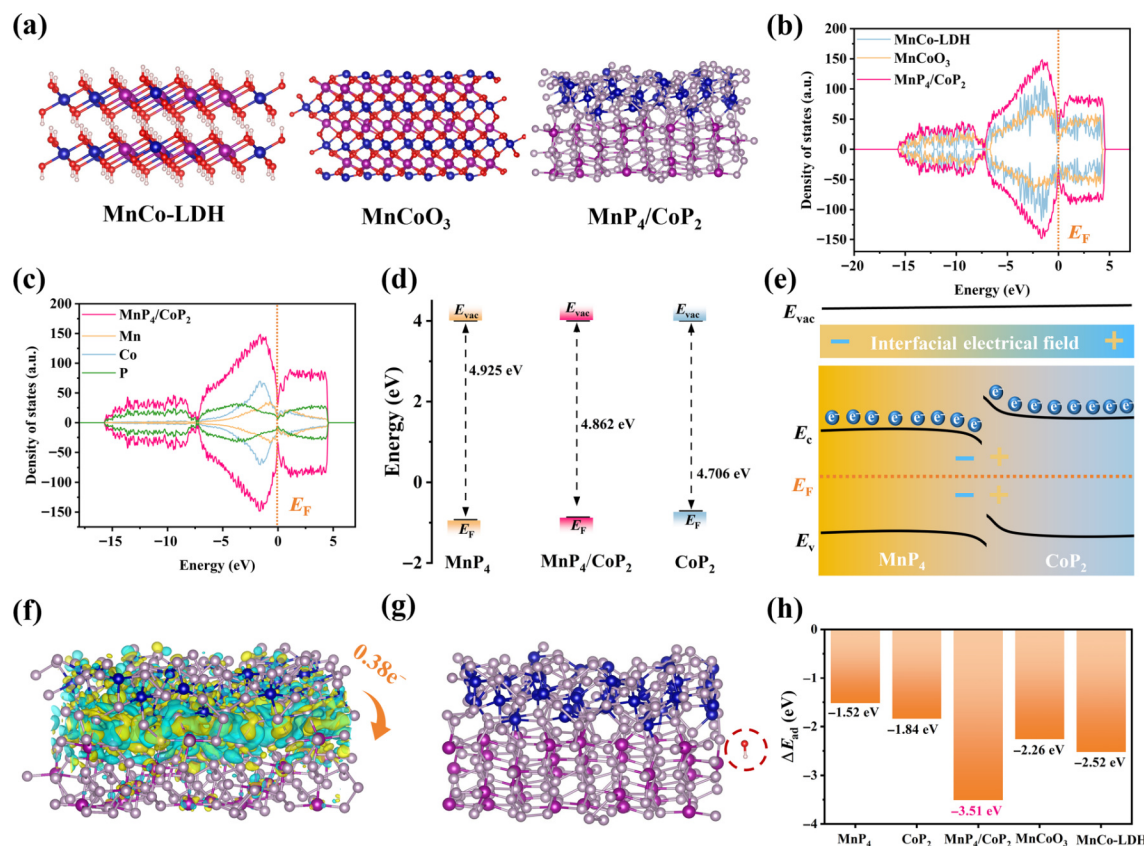


Figure 5 (a) Optimized structural models and (b) TDOS plots of MnCo-LDH , MnCoO_3 , and $\text{MnP}_4/\text{CoP}_2$. (c) PDOS plot of $\text{MnP}_4/\text{CoP}_2$. (d) Work function values of MnP_4 , CoP_2 , and $\text{MnP}_4/\text{CoP}_2$. (e) Charge redistribution illustration at the heterointerface and (f) charge density difference plot of $\text{MnP}_4/\text{CoP}_2$. (g) Structural model of $\text{MnP}_4/\text{CoP}_2$ adsorbing OH^- . (h) The adsorption energy of OH^- on MnP_4 , CoP_2 , $\text{MnP}_4/\text{CoP}_2$, MnCoO_3 , and MnCo-LDH .

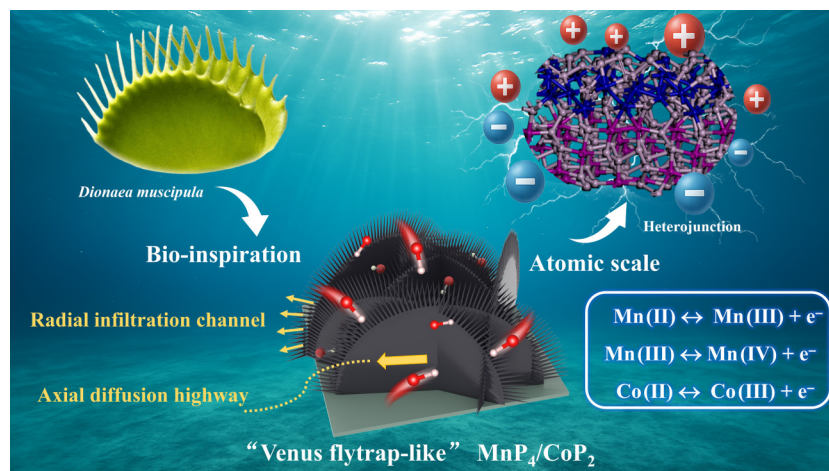


Figure 6 The energy storage mechanism of Venus flytrap-like $\text{MnP}_4/\text{CoP}_2$.

conductive to multi-electron reactions and bolstering OH^- adsorption capability. This combined strategy of hierarchical structural engineering and interfacial electronic modulation enables $\text{MnP}_4/\text{CoP}_2$ to exhibit a highly sensitive and rapid electrochemical response toward OH^- ions, functionally mirroring the Venus flytrap's swift closure behavior upon external stimulus. Such a design vividly demonstrates the successful translation of biomimetic principles into structural construction and responsive functionality within the electrode system.

4 Conclusions

In summary, inspired by Venus flytrap leaves, we successfully designed a biomimetic $\text{MnP}_4/\text{CoP}_2$ heterostructure via hydrothermal synthesis and gas-phase phosphidation. The Venus flytrap-like nanosheet-nanowire network establishes a hierarchical framework, enabling dual-scale ion transport pathways for rapid electrolyte infiltration and structural resilience. Meanwhile, the difference in work functions between MnP_4 and CoP_2 (0.219 eV) induces a built-in electric field at the heterointerface, driving a directional electron flow from CoP_2 to MnP_4 . This charge redistribution enriches the Mn^{2+} and Co^{3+} species, creating abundant active sites for pseudocapacitive reactions. DFT calculations substantiate this phenomenon and further reveal that the optimized $\text{MnP}_4/\text{CoP}_2$ configuration exhibits the most favorable OH^- adsorption energy (−3.51 eV). Consequently, the $\text{MnP}_4/\text{CoP}_2$ electrode delivers outstanding electrochemical performance, including a high areal capacity of $3014 \text{ mC}\cdot\text{cm}^{-2}$ at $1 \text{ mA}\cdot\text{cm}^{-2}$, excellent rate capability (52.9% capacity retention at $20 \text{ mA}\cdot\text{cm}^{-2}$), and robust cycling stability (70.58% capacity retention after 8000 cycles). When assembled into an ASC device ($\text{MnP}_4/\text{CoP}_2/\text{YP-50}$), the device achieves a remarkable energy density of $88.5 \text{ Wh}\cdot\text{kg}^{-1}$ at a power density of $798.8 \text{ W}\cdot\text{kg}^{-1}$, surpassing most reported Mn/Co-based systems, while maintaining 68.29% capacity retention after 10,000 cycles. Notably, two serially connected ASC devices successfully powered 12 LEDs for over 10 min, further demonstrating their practical viability. This work highlights the synergistic effect of biomimetic hierarchical architecture and interfacial charge regulation, offering a versatile strategy for the development of next-generation electrode materials endowed with high energy density and long-term durability.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. H. S.: Data curation, investigation, formal analysis, writing – original draft. Y. C. L.: Investigation, methodology, writing – review & editing, formal analysis. C. P.: Visualization, data cuation. M. Z. G.: Investiagtion, conceptualization. L. L. C.: Funding acquisition, project administration, writing – review & editing. X. C. Y.: Funding acquisition. Z. L.: Project administration, funding acquisition. Z. J.: Funding acquisition, project administration. All the authors have approved the final manuscript.

Use of AI statement

None.

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