

Design and plasma-assisted *in situ* construction of layered MXene/CNTs/NiCo-LDH heterostructures for enhanced electrochemical performance

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ABSTRACT: MXene is a promising electrode material for supercapacitors due to its excellent conductivity, but its self-stacking impedes ion and electron transport. To address this issue, carbon nanotubes (CNTs) were introduced as conductive spacers, and NiCo-layered double hydroxides (LDH) was rapidly deposited via an assisted liquid-phase plasma electrolysis method to construct a stable heterostructure. This design effectively alleviates ion/electron transport resistance, improves charge transfer efficiency, and mitigates the volume expansion of NiCo-LDH during cycling. Density functional theory analysis reveals enhanced electronic conductivity and ion migration at the MXene/CNT/NiCo-LDH heterointerface. Benefiting from the synergistic structure, the electrode achieves a high specific capacitance of 2145 F·g⁻¹ and maintains 95.2% of its initial capacitance after 5000 cycles. The assembled asymmetric supercapacitor delivers an energy density of 41.9 Wh·kg⁻¹ at 425.1 W·kg⁻¹ and retains 91% of capacitance after 5000 cycles. Moreover, the flexible device exhibits remarkable stability under multiple bending angles without distortion of cyclic voltammetry (CV) curves.

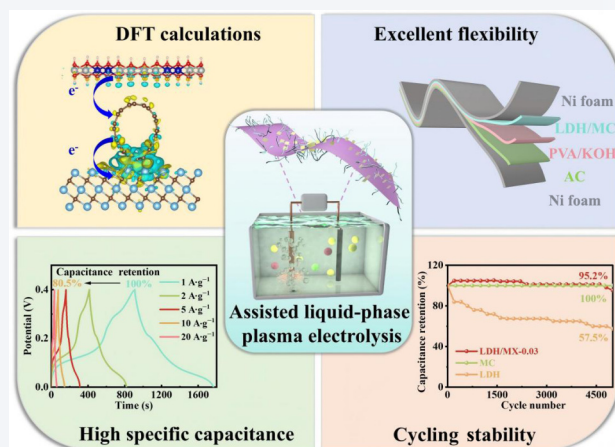
KEYWORDS: assisted liquid-phase plasma electrolysis, density functional theory (DFT) calculation, flexible, heterointerface, deposition dynamics

1 Introduction

Green technologies are widely regarded as the key enablers in the transformation of the global socio-economic landscape. With the continuous advancements, the clean energy is being increasingly supplied, and the harmful carbon emissions are being significantly

reduced. Among these technologies, supercapacitors have been recognized as a safe, reliable, durable, and environmentally friendly energy storage devices. The rapid charge/discharge capability, extended cycle life, and high power density are provided in comparison with the conventional storage systems [1, 2]. The electrochemical performance of supercapacitors is primarily determined by the characteristics of the electrode materials, in which both the composition and microstructure are considered as the critical factors affecting the charge storage behavior and electrical conductivity [3].

MXene is classified as a typical two-dimensional (2D) transition metal carbide or carbonitride, and is known for its high electronic



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conductivity and high specific surface area. Its typical chemical formula is expressed as $M_{n+1}X_nT_x$ ($n = 1, 2, 3$, or 4), where M denotes a transition metal, X represents C or N, and T_x indicates the surface termination groups. MXene is generally synthesized by selectively etching the A element from the MAX-phase precursor ($M_{n+1}AX_n$) using HF or a LiF/HCl solution [4, 5]. Due to its tunable chemical composition and unique layered structure, MXene has been widely applied in the various fields, including the energy storage [6], catalysis [7], sensing [8], and electromagnetic interference shielding [9]. Among the various MXene types, $Ti_3C_2T_x$ has been extensively investigated owing to its rich surface chemistry, excellent metallic conductivity, superior flexibility, and favorable hydrophilicity. Therefore, it is considered a highly promising candidate for the electrode applications in the energy storage devices [10–12]. However, similar to other 2D materials, MXene nanosheets are prone to the self-stacking and aggregation due to the strong van der Waals interactions between the adjacent layers. This stacking tendency results in a considerable reduction in the exposure of active sites, thereby limiting the electrochemical performance of MXene-based materials [13, 14]. To address this issue, the various strategies have been proposed, among which the introduction of an intermediate layer has been demonstrated to be particularly effective in suppressing the self-restacking and enhancing the electrochemical properties of MXene-based composites. Typically, zero-, one-, or two-dimensional (0D/1D/2D) nanostructures, such as the nanoparticles, nanotubes, nanowires, or other nanosheets, have been incorporated between MXene layers to mitigate the aggregation and facilitate the ion transport [15–17].

For example, aniline-pyrrole (ANPY) random copolymer particles were introduced into the MXene interlayers by Zhou et al. [18], serving as the spacer bands that mitigated the stacking tendency and generated the additional ion migration channels. Composite scaffold electrodes were fabricated by Chen et al. [19] through embedding MXene with highly nitrogen-doped carbon nanosheets (CN), which acted as spacers and facilitated the formation of a hierarchical porous structure. In another study, $M-Ti_3C_2T_x@MS$ aerogel was prepared by Cai et al. [20] by integrating MXene with melamine sponge (MS), in which MXene was uniformly distributed throughout the MS framework. This unique architecture enhanced the ion accessibility, suppressed the nanosheet restacking, and exposed a large number of active sites.

In the supercapacitor applications, layered double hydroxides (LDHs) composed of bimetallic elements have been widely investigated as the promising electrode materials. The superior performance results from a high surface area, plentiful active sites, and minimized ion diffusion lengths, all of which promote the effective ion exchange with the electrolyte [21]. Among the various pseudocapacitive materials, NiFe-LDH, CoAl-LDH, and NiCo-LDH ($NiCo_2(OH)_6$) have attracted the most attention owing to their high redox activity and tunable chemical composition. In particular, NiCo-LDH has been regarded as a highly effective electrode material, and high specific capacitance (C_s) has been achieved as a result of its interconnected layered structure and favorable redox kinetics [22–25]. However, the practical application of NiCo-LDH has been limited by several intrinsic drawbacks, including the low electrical conductivity, weak structural stability, and poor cycling durability [26–28]. Therefore, the considerable efforts have been devoted to developing strategies to overcome these limitations and improve the overall electrochemical performance.

At present, the synthesis of NiCo-LDH materials mainly relies on methods such as hydrothermal, co-precipitation, electrodeposition, and sol-gel techniques. However, these routes are often constrained by complex procedures, long processing times, and poor scalability. For example, hydrothermal and solvothermal methods require high temperature and pressure, resulting in high energy consumption and time inefficiency. Co-precipitation generally suffers from poor control over nucleation and growth, leading to non-uniform particle size distribution. Electrodeposition, despite being relatively simple, often causes uneven coverage and weak adhesion on substrates. The sol-gel process, on the other hand, usually involves a lengthy synthesis cycle. Moreover, NiCo-LDH structures obtained from these strategies frequently exhibit intrinsic drawbacks, including irregular morphology, low crystallinity, limited electrical conductivity, and poor structural stability during cycling, which collectively hinder their electrochemical performance in supercapacitors [29–33]. To overcome these limitations, assisted liquid-phase plasma electrolysis was adopted as an alternative, following a comparison with the conventional nanomaterial synthesis techniques. The process has been demonstrated to operate effectively under the ambient temperature and pressure conditions, without the need for vacuum systems or high-temperature treatment, thereby increasing its adaptability to the various environments. Compared with the traditional heat treatment processes, this method allows surface modification of materials to be completed within a significantly shorter duration, which greatly enhances the processing efficiency and enables the one-step synthesis of target products [34, 35].

The integration of conductive carbon frameworks and LDH active materials have demonstrated the enhanced electrochemical performance. For example, Li et al. [36] constructed the integrated carbon materials and layered double metal hydroxides composites that exhibited the improved capacitive behavior due to increased conductivity and accessible active sites. Similarly, Zhou et al. [37] reported the sandwich-like NiFe-LDH/ $MnCO_3$ /MXene ternary nanocomposites that serve as the battery-type electrodes for asymmetric supercapacitors with high energy density and relatively stable cycling. In another study, Yang et al. [38] achieved the *in situ* anchored NiMn-LDH nanosheets on Ti_3C_2 MXene via the chemical bonds, leading to the superior supercapacitor performance ascribed to the enhanced interfacial contact. While these studies illustrate the effectiveness of combining MXene with carbon components and LDH nanosheets for high-performance electrodes, they primarily rely on the physical blending or conventional *in situ* growth methods, and do not systematically address the interfacial electronic interaction and charge-adsorption behavior underpinning the synergistic effects. In contrast, the present work utilizes a plasma-assisted liquid-phase electrolysis strategy to construct a tightly integrated MXene/CNT/NiCo-LDH heterojunction, enabling the enhanced interfacial coupling and optimized OH^- adsorption capability, as supported by the theoretical and experimental analyses. This rational interfacial engineering provides the deeper insight into the structure-property relationship governing the charge-storage kinetics and distinguishes the current study from previously reported hybrid systems.

In our previous work, the MXene/NiCo-LDH heterostructure was systematically studied, revealing that direct LDH growth on MXene is still constrained by the severe MXene restacking and limited ion diffusion. Based on these findings, carbon nanotubes (CNTs) are introduced in this work as the conductive spacers to

further mitigate the self-stacking issue, optimize the electrode architecture, and enhance the electrochemical performance. MC (formed by inserting CNTs into the layers of MXene) was employed as the conductive substrate. The uniform growth of NiCo-LDH nanosheets on the surface of MC was achieved via an assisted liquid-phase plasma electrolysis technique. This hierarchical architecture synthesized was found to improve the internal structural organization, enhance the electrical conductivity, and minimize the volumetric fluctuation of NiCo-LDH during the charge-discharge processes. The fabricated LDH/MC-0.03 electrode exhibited a high C_s of 2145 F·g⁻¹ and excellent cycling stability, with 95.2% capacitance retention after 5000 cycles. Furthermore, the assembled LDH/MC-0.03//AC asymmetric device delivered an energy density of 41.9 Wh·kg⁻¹ at 425.1 W·kg⁻¹. Density functional theory (DFT) calculations further confirmed that the unique structure enhanced the electronic conductivity and increased the adsorption energy of OH⁻ ions. The flexible device also demonstrated the remarkable mechanical stability, maintaining 93.12% of its capacitance under a 150° bending condition. Upon returning to its original state (0°), the device exhibited the rapid recovery of energy storage performance, with a recovery rate of 97.6%. These findings offer a novel approach for designing high-performance electrode materials.

2 Experimental section

2.1 Synthesis of MXene

Twenty milliliters of 40% HF solution was first added into a polytetrafluoroethylene (PTFE) beaker, followed by the addition of 1 g of Ti₃AlC₂ powder. The mixture was stirred at a constant temperature of 40 °C for 48 h to selectively etch the aluminum layer. After the reaction, the product was centrifuged and repeatedly rinsed with the deionized water (DI) until the pH stabilized 6–7. The obtained precipitate underwent the ultrasonication using a cell disruptor for 5 min to facilitate the exfoliation. A second centrifugation was performed at 3000 rpm to remove the unexfoliated particles, followed by the lyophilization to obtain the few-layered Ti₃C₂T_x nanosheets.

2.2 Preparation of MC

0.5 g of CNTs was added into 40 mL of DI, and was crushed with a cell crusher for 30 min to prevent CNTs from entangling. Then, 0.5 g of MXene was introduced and stirred continuously for 6 h. After the stirring was completed, the lyophilization by filtration was performed to obtain MC.

2.3 Preparation of LDH/MC

1 g of NaNO₃ and 0.25 g of NaOH were dissolved in DI to form 50 mL of A solution; 2.4 g of Co(NO₃)₂·6H₂O and 1.2 g of Ni(NO₃)₂·6H₂O were mixed in 250 mL DI to form the B solution with stirring. Under the magnetic stirring, the A solution was dropped into the B solution, and then 0.01, 0.02, 0.03, and 0.04 g of MC were added the above mixed solution and ultrasonicated to obtain the precursor solution of LDH/MC composites.

The electrolyzer consisted of an alternating direct-current power supply, the graphite and U-shaped copper electrodes were used for the anode and cathode, and the precursor solution functioned as both the reaction medium and the electrolyte. After applying a potential of 240 V for 180 s, the cathode rapidly excited a strong

plasma arc at the electrode-electrolyte interface. The transient high temperature and localized pressure generated by the arc not only accelerated ionization and electron transfer in the solution, but also induced vigorous thermal effects and interfacial physicochemical reactions. These synergistic processes facilitated the nucleation and growth of nanosheets, thereby enabling the rapid formation of LDH/MC composites with a three-dimensional conductive framework. After the completion of reaction, the products were collected via the precipitation and centrifugation, and subsequently freeze-dried to yield the LDH/MC composite powder. To examine the effect of MC content on the electrochemical behavior of composites, a series of composites were systematically synthesized according to the MC content, and the corresponding samples were successively named as LDH/MC-0.01, LDH/MC-0.02, LDH/MC-0.03, and LDH/MC-0.04 respectively. The specific preparation process of LDH/MC composites is shown in Fig. 1.

2.4 Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were employed to comprehensively assess the electrochemical properties of samples. The C_s is calculated as follows [39]

$$C_s = \frac{I \cdot \Delta t}{\Delta V \cdot m} \quad (1)$$

where I , m , Δt , and ΔV represent the current (A), active material mass (g), discharge time (s), and applied voltage range (V), respectively. In assembled asymmetric supercapacitor (ASC), the mass of active materials on the positive and negative electrodes should be adjusted to satisfy the charge balance condition ($q^+ = q^-$). The mass proportion is calculated as follow [40]

$$\frac{m_+}{m_-} = \frac{C_- \cdot \Delta V_-}{C_+ \cdot \Delta V_+} \quad (2)$$

where m_+ (g) and m_- (g) refers to the mass of the positive and negative electrode material. C_+ and C_- (F·g⁻¹) represent the C_s of the positive and negative electrode material. ΔV (V) is voltage window of the positive and negative electrode material. Energy density E (Wh·kg⁻¹) and power density P (W·kg⁻¹) of ASC devices were calculated as follows [41]

$$E = \frac{C_s \cdot \Delta V^2}{2 \times 3.6} \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

2.5 DFT calculation

All calculations (including geometric, energetic, and electronic property) were performed by Vienna *ab initio* simulation package (VASP) [42]. Here, the H 1s¹, C 2s²2p², O 2s²2p⁴, Ni 3d⁸4s², and Co 3d⁷4s² states were considered as the valence electrons. The exchange-correlation functional was described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [43, 44]. Electron-ion interactions were treated using the projector-augmented wave (PAW) potential [45]. A 500 eV kinetic energy cutoff was set for the plane waves, while the Brillouin zone sampling utilized a 2 × 2 × 1 Monkhorst-Pack k -point mesh [46]. Energy and force convergence criteria were defined as 10⁻⁴ eV·atom⁻¹ and 0.01 eV·Å⁻¹, respectively. In this study, Ti₃C₂T_x

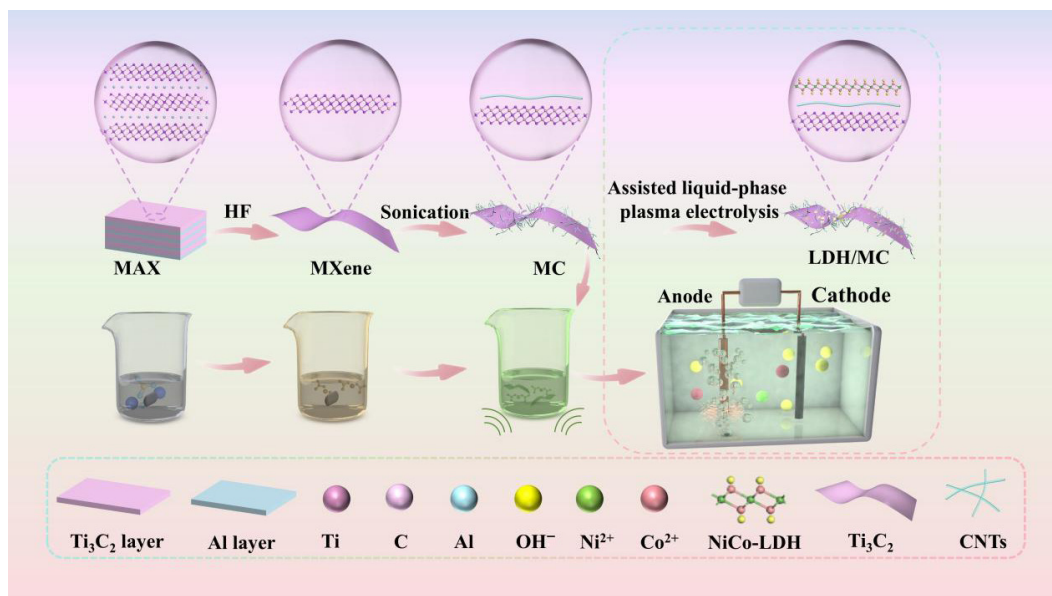


Figure 1 Synthesis process of LDH/MC samples.

MXene, metallic CNTs, and $\text{NiCo}_2(\text{OH})_6$ (NiCo-LDH) were selected as the research subjects. The (001) surface of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is modeled with lattice parameters $a = 12.27 \text{ \AA}$ and $b = 21.24 \text{ \AA}$. Metallic (3,3) CNTs with lattice parameters $a = 12.30 \text{ \AA}$ and $b = 20.54 \text{ \AA}$ were employed, along with NiCo-LDH(001) with lattice parameters $a = 11.20 \text{ \AA}$ and $b = 19.19 \text{ \AA}$. The (001) surface of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was adopted, as it represented the most exposed basal plane and played a dominant role in the interfacial charge transfer and ion adsorption during the electrochemical processes. Metallic (3,3) CNTs were employed due to their high electrical conductivity and structural simplicity, which enabled the efficient electron transport and effective coupling with MXene and LDH phases. Meanwhile, the (001) surface of NiCo-LDH was selected because it was the thermodynamically stable basal plane and was commonly regarded as the primary surface participating in OH^- adsorption and surface redox reactions. These components were used to construe the heterojunction structure of MXene-CNT-NiCo-LDH and MXene-CNT, and their lattice mismatch rates were 6.4% and 2.4%, respectively. A $20 \text{ \AA}$ vacuum spacing was introduced along the Z-axis to avoid the spurious interactions between the periodic replicas. The van der Waals (vdW) interactions were described with Grimme's DFT-D3 approach [47]. The OH^- adsorption energy is calculated using the following formula

$$E_{\text{ads}} = E_{\text{slab}} + E_{\text{OH}^-} - E_{\text{total}} \quad (5)$$

where E_{slab} is the base energy, E_{OH^-} is the isolated OH^- energy, and E_{total} is the total energy of the system after adsorption.

2.6 Characterization of morphology and structure

The physical phases of the samples were analyzed via X-ray diffraction (XRD, Bruker D8 Advance, Germany). The topography was examined using the transmission electron microscopy (TEM, JEOL JEM-2100F, Japan), and the scanning electron microscopy (SEM, JEOL JSM-7610F, Japan). To study the vibrational modes, Fourier-transform infrared spectroscopy (FT-IR, Shimadzu IRTracer-100, Japan) and Raman spectroscopy (HORIBA France S.A.S, France) were performed. X-ray photoelectron spectroscopy

(XPS, Thermo Scientific ESCALAB Xi+, USA) was employed to characterize the chemical bonding states. Thermogravimetric (TG) analysis (Hitachi STA200, Japan) was carried out to identify the weight ratios of components for the LDH/MX-0.03 composite. Nitrogen adsorption-desorption isotherms were obtained using a physical adsorption instrument (ASAP 2460, Micromeritics, USA). The Brunauer-Emmett-Teller (BET) theory was employed to determine the specific surface area of LDH/MX-0.03 composites.

3 Results and discussion

3.1 Structure and morphology

The morphology of all samples was analyzed via SEM and TEM (Fig. 2). The SEM image of Ti_3AlC_2 (Fig. S1(a) in the Electronic Supplementary Material (ESM)) reveals a compact layered structure. After etching with HF, the few-layer MXene nanosheets with the smooth surfaces were obtained (Fig. 2(a)). When MXene was mixed with CNTs at a 1:1 ratio (Fig. 2(b)), CNTs were uniformly distributed on both the surface and interlayer regions of MXene. These CNTs served as the structural supports and conductive bridges, resulting in a more open architecture. This configuration shortened the ion diffusion pathways, and enhanced the accessibility to active sites, thereby improving the rate capability and facilitating the electrochemical reactions. As shown in Figs. 2(c)–2(f), with the increase of MC content, the distribution pattern of NiCo-LDH evolved from the aggregated clusters to more uniform coverage, until the excessive MC content hindered the formation of a continuous LDH coating. At high MC loading, the competitive surface coverage and spatial confinement hinder the homogeneous growth of LDH nanosheets, leading to the discontinuous or aggregated morphologies. Among all tested composites, LDH/MC-0.03 exhibited a clearly uniform coating of NiCo-LDH on the MC framework. Consequently, the LDH/MC-0.03 sample exhibits the most uniform and continuous LDH distribution, representing an optimal morphological integrity. Further microstructural analysis of LDH/MC-0.03 was conducted by TEM (Fig. 2(g)), in which MXene and CNTs were observed to

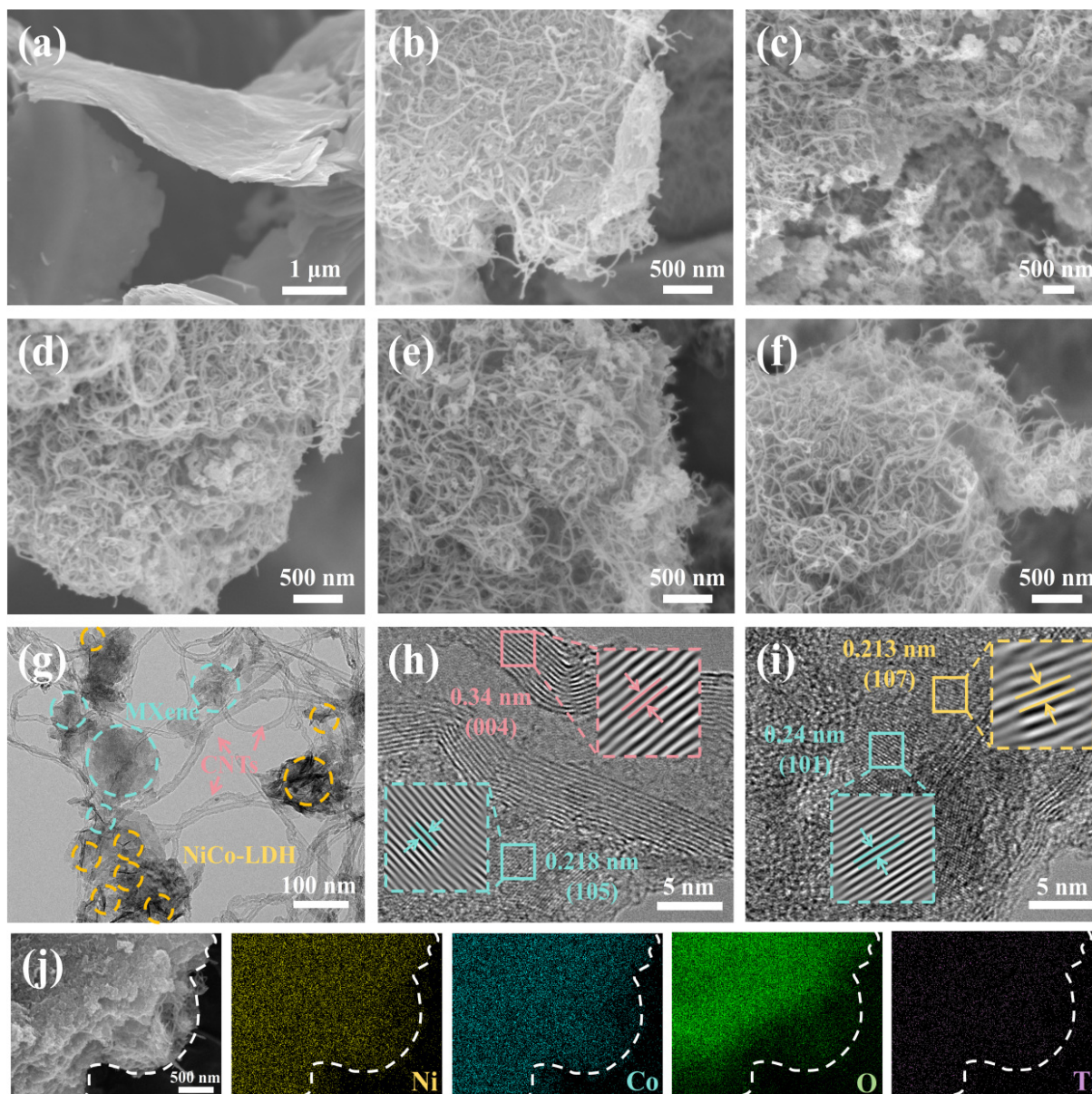


Figure 2 SEM morphologies of (a) MXene, (b) MC, (c)–(f) LDH/MC-0.01, LDH/MC-0.02, LDH/MC-0.03, and LDH/MC-0.04, (g) TEM, ((h) and (i)) HRTEM, and (j) mapping pattern of LDH/MC-0.03 composite.

be closely intertwined, forming an integrated MC framework, while NiCo-LDH nanosheets were evenly grown on their surface, yielding a stable 3D network. High-resolution TEM (HRTEM) images of LDH/MC-0.03 (Figs. 2(h) and 2(i)) displayed the lattice spacings of 0.218 and 0.240 nm, matching the (105) and (101) crystal planes of MXene, respectively. The presence of lattice fringes with spacings of 0.340 and 0.213 nm corresponded to the (004) crystal plane of CNTs and the (107) plane of NiCo-LDH. Elemental mapping (Fig. 2(j)) confirmed the homogeneous distribution of Ni, Co, O, and Ti elements, further verifying the uniform growth of NiCo-LDH on the MC substrate.

The crystal structures of MC substrate and all composites were analyzed by XRD (Fig. 3(a)). By comparison with the pattern of Ti_3AlC_2 (Fig. S1(b) in the ESM), the (002) diffraction peak was observed to shift from 9.3° to 8.5° . Moreover, the characteristic (004) and (008) peaks of Ti_3AlC_2 disappeared, indicating that the Al layers between the Ti_3AlC_2 planes had been successfully removed.

This result confirms the successful formation of Ti_3C_2 [48, 49]. The shift of the (002) peak toward a lower angle reflects an increase in the interlayer spacing [50]. This expanded interlayer distance is expected to provide more accessible channels for the transportation of electrolyte ion, thereby enhancing the electrochemical performance. The XRD pattern shows a carbon (002) peak at 25.6° , confirming the presence of CNTs in the MC substrate (Fig. 3(a)). According to the standard JCPDS card (No. 40-0216), the diffraction peaks located at 2θ values of 12.4° , 34.6° , and 60.8° were assigned to the (003), (012), and (110) crystal planes of NiCo-LDH, respectively. It was further observed that the intensity of these diffraction peaks increased with the mass ratio of MC, where the intensified and sharpened diffraction peaks indicate the improved long-range structural ordering and phase stability. This effect can be attributed to the role of MC as a conductive and structurally robust substrate, which facilitates the nucleation and crystallization of LDH domains [51]. In addition, the reduced lattice distortion and

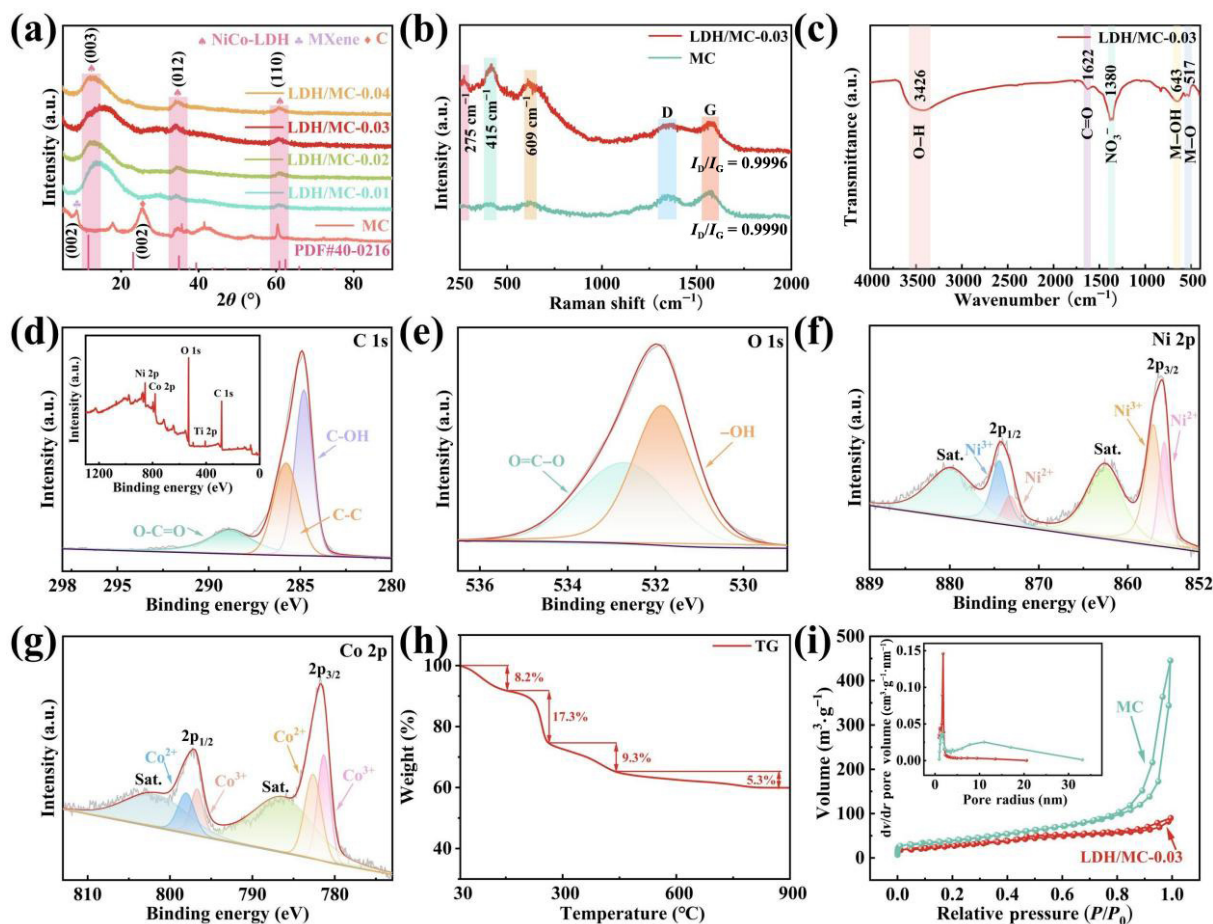


Figure 3 (a) XRD of LDH/MC and MC. (b) Raman of MC and LDH/MC-0.03. (c) FT-IR, (d)–(g) XPS, (h) TG of LDH/MC-0.03 composite. (i) BET analysis of MC and LDH/MC-0.03 composite.

enhanced crystallinity of NiCo-LDH implied the presence of fewer structural defects, which were beneficial for improving the charge transport and the ion diffusion throughout the electrode material [52].

Raman spectroscopy was employed to investigate the chemical characteristics of the electrode materials. Similar Raman features were observed for both MC and LDH/MC-0.03 composites, as shown in Fig. 3(b). The vibrational band at 609 cm^{-1} was attributed to the in-plane vibrations of functional groups in the MXene structure [53, 54]. The peaks at 275 and 415 cm^{-1} corresponded to the stretching vibrations of M–O and M–OH bonds (M = Ni, Co) [55–57], confirming the incorporation of NiCo-LDH. The D band at 1347 cm^{-1} originated from the structural defects or disordered carbon regions, whereas the G band at 1573 cm^{-1} was associated with the E_{2g} vibrational mode of sp^2 -hybridized carbon, serving as an indicator of graphitization [58]. To evaluate the degree of disorder in the carbon phase, the intensity ratio of the D and G bands (I_D/I_G) was calculated. The I_D/I_G values were determined to be 0.9990 for MC and 0.9996 for LDH/MC-0.03, indicating a slight increase in defect density after the incorporation of NiCo-LDH. These structural defects can serve as the additional electrochemically active sites for the electron and ion transport, effectively increasing the electrode–electrolyte contact area and contributing to the enhanced charge storage. Moreover, the presence of such active sites may also facilitate the oxygen reduction reactions, thereby improving the overall energy storage capacity.

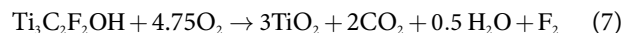
FT-IR spectroscopy was conducted to identify the functional groups in the samples (Fig. 3(c)). The broad absorption band at 3426 cm^{-1} was attributed to the stretching vibrations of O–H groups [59]. The band at 1622 cm^{-1} corresponded to the stretching vibration of C=O bonds [60, 61]. A distinct absorption peak at 1380 cm^{-1} was assigned to the stretching vibration of residual NO_3^- ions located within the NiCo-LDH interlayers [59]. Additionally, the peaks at 643 and 517 cm^{-1} were attributed to the stretching vibrations of M–OH and M–O bonds (M = Ni, Co), respectively [59, 62], confirming the successful incorporation of NiCo-LDH into the MC composite framework. The appearance of –OH and oxygen-containing groups in the FT-IR spectra indicates the enhanced interfacial interactions within the composites. Such interfacial optimization not only improves the structural stability but also facilitates the efficient electron and ion transport, thereby contributing to superior electrochemical performance [63].

The chemical bonding states of composite were further examined using XPS. Based on the survey spectrum, as shown in Fig. 3(d), the LDH/MC composite was found to consist of C, O, Ni, Co, and Ti elements. The presence of these elements confirms the successful incorporation of all constituent components and the preservation of their characteristic chemical states. In the C 1s spectrum (Fig. 3(d)), three distinct peaks were observed at binding energies of 284.8, 285.7, and 288.8 eV, which were assigned to C–OH [62], C–C [64], and O–C=O [65] bonds, respectively. These signals suggest the coexistence of surface functional groups derived

from both MXene and carbon nanotubes. The O 1s spectrum (Fig. 3(e)) displayed two major peaks at 531.7 and 532.7 eV, corresponding to –OH [64] and O=C–O [66] groups, respectively. The presence of –OH groups is particularly significant, as these sites can participate in Faradaic redox reactions, thereby enhancing the pseudocapacitive performance. In the Ni 2p spectrum (Fig. 3(f)), two well-defined peaks were detected at 855.9 eV (Ni 2p_{3/2}) and 873.2 eV (Ni 2p_{1/2}). Peak deconvolution revealed the presence of both Ni²⁺ (855.9, 873.2 eV) and Ni³⁺ (857.1, 874.4 eV), indicating that Ni existed in the mixed oxidation states. These Ni²⁺/Ni³⁺ redox pairs are known to contribute significantly to the pseudocapacitance via the reversible Faradaic reactions [67]. In addition, the satellite peaks located at 862.6 and 879.9 eV further confirmed the presence of Ni species [68]. The Co 2p spectrum (Fig. 3(g)) exhibited the peaks at 782.6 eV (2p_{3/2}) and 798.0 eV (2p_{1/2}), which were assigned to Co²⁺ species from Co(OH)₂. Additional peaks observed at 781.3 and 796.7 eV were attributed to Co³⁺, likely arising from the interfacial interactions with the MXene matrix. Satellite peaks at 786.9 and 802.4 eV provided the further evidence for the coexistence of Co²⁺ and Co³⁺ species [69, 70]. The Ti 2p spectrum (Fig. S2 in the ESM) displayed the four peaks at 455.2, 457.1, 461.3, and 463.2 eV, corresponding to Ti²⁺ (2p_{3/2}), Ti³⁺ (2p_{3/2}), Ti²⁺ (2p_{1/2}), and Ti³⁺ (2p_{1/2}), respectively [68, 71], confirming the presence of partially oxidized titanium species derived from MXene.

To quantitatively analyze the composition of composite, TG analysis was conducted. TG curve of MC sample (Fig. S3 in the ESM) revealed a multi-step thermal decomposition process. The initial weight loss observed between 30–179 °C was attributed to the evaporation of physically adsorbed water. Upon further heating, the oxidation of MXene phase occurred, leading to the formation of a TiO₂ layer and resulting in a slight mass gain of ~ 1.39%. At the elevated temperatures, the decomposition of surface functional groups and the release of CO₂ led to an additional mass loss of 1.24%, indicating the complete transformation of MXene into TiO₂. At ~ 452 °C, the CNTs began to undergo the oxidation, a process that continued until the complete combustion was at 900 °C, resulting in a substantial weight loss of 54.87%. Based on the overall mass changes, the MC sample was estimated to contain the adsorbed and crystallized water of 1.82%, CNTs of 54.87%, and MXene of 43.31%, yielding an approximate mass ratio of MXene to CNTs of 0.789.

TG curve of LDH/MC-0.03 composite (Fig. 3(h)) displayed the four decomposition stages. The first stage was at 30–154 °C: A mass loss of 8.2% was recorded, and primarily attributed to the removal of surface-adsorbed and interlayer water. The second stage was at 154–265 °C: A further mass loss of 17.3% was observed, which was ascribed to the initial oxidation of MXene and the dehydroxylation of NiCo-LDH component. The third stage was at 265–441 °C: An additional weight reduction of 9.3% was detected, corresponding to the complete phase transformation of NiCo-LDH into the spinel NiCo₂O₄ and the continued oxidation of MXene. The fourth stage was at 441–871 °C: CNTs were fully oxidized, resulting in a mass loss of 5.3%. Based on the mentioned above MXene-to-CNT mass ratio of 0.789, the composition of LDH/MC-0.03 sample was estimated as follows: the adsorbed and crystallized water of 8.2%, NiCo-LDH of 82.32%, CNTs of 5.3%, and MXene of 4.18%. These results demonstrated that NiCo-LDH constituted the dominant component in the composite. The thermal decomposition and phase transformation processes involved could be described by the following reaction equations



Moreover, the pore structure and surface area are considered as the critical factors to influence the electrochemical behavior of electrode materials. To investigate these characteristics, the pore size distributions and N₂ adsorption–desorption isotherms of MC and LDH/MC-0.03 were analyzed, as shown in Fig. 3(i). Both samples showed the type-IV isotherms accompanied by the clear H3 hysteresis behavior, reflecting the formation of mesoporous networks favorable for the efficient ion movement and the charge retention. The BET surface area of MC was measured to be 144.53 m²·g^{−1}, which exceeded that of LDH/MC-0.03 (107.24 m²·g^{−1}). The pore size distribution of MC was primarily concentrated in the mesoporous range of 2–10 nm, accompanied by a portion of larger mesopores in the 10–30 nm range. In contrast, LDH/MC-0.03 exhibited a narrower average pore radius of 2.53 nm, suggesting that the incorporation of NiCo-LDH partially blocked or filled the larger pores originally presented in the MC framework. As a result, a narrowed pore size distribution was observed, which may reduce the accessible surface area for the electrolyte ions. The composite retained the outstanding electrochemical performance, even with a decrease in the specific surface area. This could be attributed to the introduction of NiCo-LDH, which contributed to the abundant Faradaic redox-active sites. These pseudocapacitive contributions were found to effectively compensate for the reduced electric double-layer capacitance associated with the lower surface area. Therefore, the synergy between the hierarchically porous MC substrate and the redox-active NiCo-LDH was shown to enhance the charge transport and ultimately improved the overall capacitance of composites.

3.2 Surface wettability

In the wettability analysis, the static contact angle method was employed to evaluate the interaction between the 6 M KOH electrolyte and the surface of the electrode samples. All synthesized materials were observed to exhibit the contact angles in the range of 16° to 30°, with LDH/MC-0.03 displaying the smallest value of 16.45°, as shown in Figs. S4(a)–S4(d) in the ESM, indicating a strong hydrophilic character. This high level of wettability was primarily attributed to the presence of abundant hydrophilic surface functional groups, such as –OH and –O. The excellent surface wettability plays a crucial role in enhancing electrochemical performance. A lower contact angle enables more rapid electrolyte infiltrate and facilitates the diffusion of ion throughout the porous electrode framework. As a result, the ionic active sites become more accessible, and the charge storage can occur more efficiently. The strong hydrophilicity of LDH/MC-0.03 composite improved the ion transport kinetics and more effective utilization of electrochemical active regions, ultimately contributing to the enhancement of capacitive performance.

3.3 Electrochemical performance

CV profiles of all samples exhibited the similar shapes, with the distinct redox peaks observed in each curve, as displayed in Fig. 4(a). This characteristic feature confirmed that composites

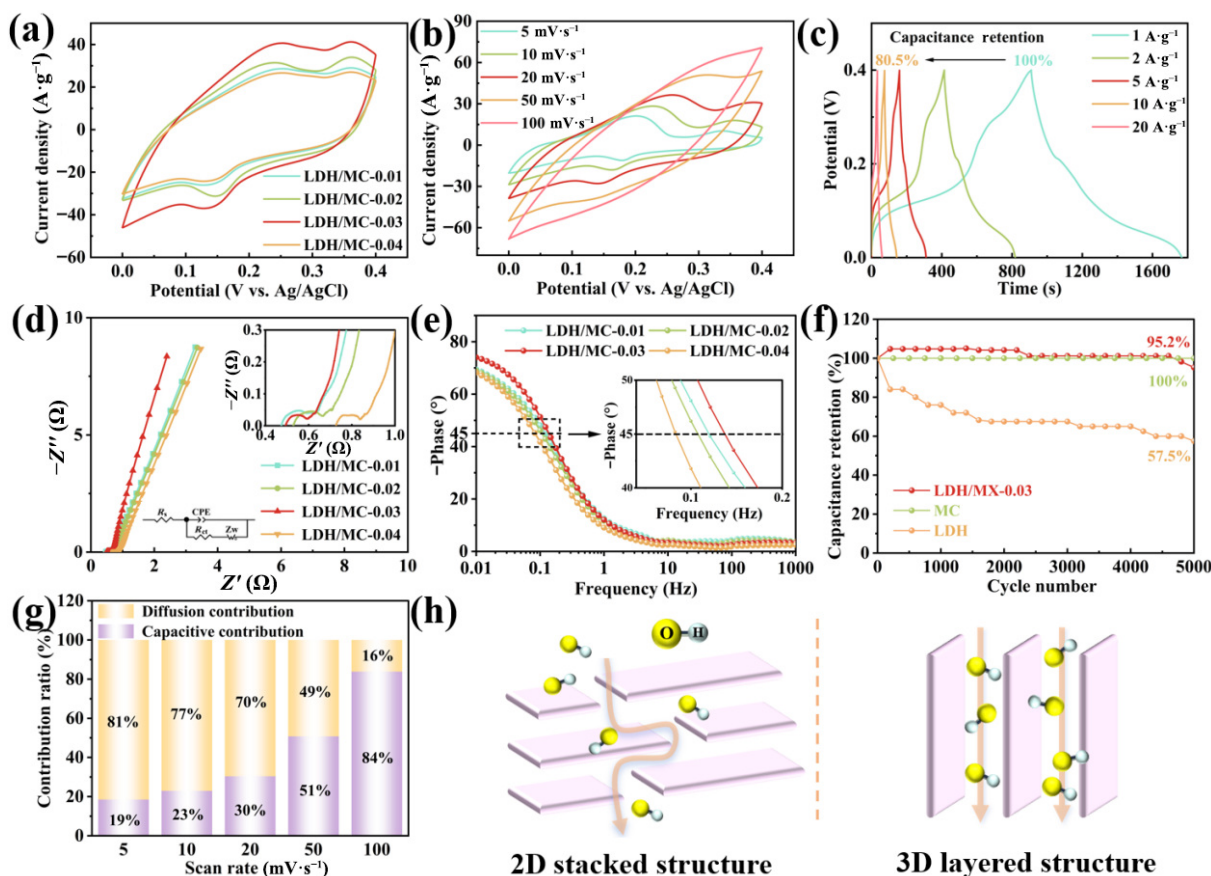
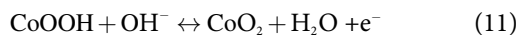
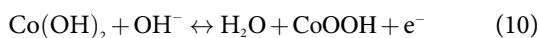
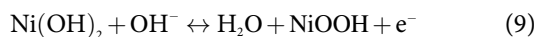


Figure 4 (a) CV of all composites. (b) CV, (c) GCD of LDH/MC-0.03. (d) EIS. (e) The relationship between phase angle and frequency for all composites. (f) Cyclic performance. (g) Capacitive and diffusion-controlled capacitance contribution ratio. (h) Schematic comparison of OH⁻ diffusion pathways in 2D stacked and 3D layered structures.

possessed the typical Faradaic capacitive behavior [72]. The redox peaks are attributed to the reversible redox transitions of Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ ions in the presence of OH⁻ during the electrochemical process [68]. As the electrochemical reaction proceeds, OH⁻ is gradually transported from the surface toward the interior of the active material through the internal diffusion channels. This ion migration facilitates the redistribution of internal charges and promotes the transformation of the chemical states within the active phase [73]. The electrochemical redox reactions underlying this process can be described as follows [74]



As shown in Fig. 4(a), the LDH/MC-0.03 electrode exhibited the most pronounced redox peaks and the largest enclosed area in the CV curves, predicating the highest C_s among all samples. The result was further corroborated by the data presented in Fig. S5(a) in the ESM, where the LDH/MC-0.03 electrode displayed the longest discharge time, indicating the superior charge storage capability. Based on the results calculated using Eq. (1), the C_s values of LDH/MC-0.01, LDH/MC-0.02, LDH/MC-0.03, and LDH/MC-0.04 were determined to be 1959, 2025, 2145, and 1846 F·g⁻¹ at 1 A·g⁻¹, respectively. It should be noted that the C_s in this work was

normalized by the total mass of active materials, which was a commonly adopted and practically relevant approach for evaluating the composite supercapacitor electrodes. This normalization reflects the overall charge storage capability of the integrated MXene/CNT/NiCo-LDH electrode rather than that of a single component. Although TG analysis indicates a relatively high NiCo-LDH content, the excellent electrochemical performance of MXene/CNT/NiCo-LDH composite cannot be solely attributed to the LDH phase. In our previous report (Applied Surface Science 723 (2026) 165628), it could be found that the contribution of a single NiCo-LDH to the capacitance was limited. The MXene and CNT components play the essential roles in constructing a highly conductive network, facilitating the fast electron transport, improving the electrolyte accessibility, and enabling more efficient utilization of LDH redox-active sites. The measured capacitance arises from the synergistic effect of the three components rather than from LDH alone. These results revealed that with the increase of MC content, the C_s initially increased and then decreased. The initial enhancement in the capacitance was attributed to the uniform distribution of NiCo-LDH nanostructures on the conductive framework, which provided more electroactive sites and facilitated the ion transport. However, when the MC content exceeded the optimal level, the relative proportion of NiCo-LDH was reduced, leading to a decline in the pseudocapacitive contribution and thus a decrease in C_s . Figure 4(b) shows the CV curves of LDH/MC-0.03 at different scan rates. With the increase of scan rate, an enlarged enclosed area was observed, reflecting a higher current response. The consistent CV profile shape

highlighted the superior electrochemical reversibility and stable redox behavior of electrode material. Furthermore, the GCD curves (Fig. 4(c)) exhibited the distinct voltage plateaus and nearly symmetrical charge–discharge profiles, which was consistent with the Faradaic redox reactions. Even at 10 A·g⁻¹, the LDH/MC-0.03 electrode still retained a C_s value of 1727.5 F·g⁻¹, corresponding to 80.5% of its initial capacitance, demonstrating the excellent rate capability and structural stability during the rapid charge–discharge cycles. Compared to the capacitance of 23.2 F·g⁻¹ for the MC sample, as shown in Fig. S5(b) in the ESM, the LDH/MC-0.03 composite exhibited a significant increase in capacitance. The significant enhancement in C_s compared to the capacitance of 23.2 F·g⁻¹ for the MC sample (Fig. S5(b) in the ESM) is primarily attributed to the strong pseudocapacitive contribution of NiCo-LDH, which provides the abundant redox-active sites. However, the high capacitance of MXene/CNT/NiCo-LDH electrode cannot be solely explained by the presence of NiCo-LDH. The MXene/CNT framework plays a crucial role in activating and fully utilizing the intrinsic pseudocapacitance of NiCo-LDH by suppressing the agglomeration, increasing the exposure of electrochemically active sites, and enabling the rapid ion transport and efficient electron transfer. Consequently, the heterojunction architecture allows the pseudocapacitive behavior of NiCo-LDH to be more effectively expressed, resulting in a substantially higher overall capacitance. Therefore, the enhanced capacitance arises from the synergistic effect between the intrinsically pseudocapacitive NiCo-LDH and the conductive MXene/CNT scaffold. In addition, compared to the similar composites, the superior electrochemical characteristics of LDH/MC-0.03 outperformed the similar systems previously reported in the Refs. [18, 75–81], as shown in Table 1. Specifically, compared with previously reported MXene- or LDH-based electrodes, the MXene-CNT-NiCo-LDH heterostructured electrode in this study exhibits a simultaneously enhanced C_s and cycling stability, rather than improving only a single performance metric. The achieved high capacitance at a relatively high current density demonstrates the efficient charge storage kinetics, while the capacity retention after the long-term cycling indicates an excellent structural robustness. These advantages are attributed to the synergistic integration of highly conductive MXene/CNT networks with the pseudocapacitive NiCo-LDH component, as well as the intimate interfacial coupling constructed via the plasma-assisted liquid-phase electrolysis. This combination effectively overcomes the common trade-off between high capacitance and cycling durability reported in previous studies.

The reaction kinetics of composites were further investigated by EIS (Fig. 4(d)). Typically, a Nyquist plot comprises a semicircle in the high-frequency region and a straight line in the low-frequency

region, representing the distinct electrochemical processes. The series resistance (R_s) was determined from the intercept of the curve on the real axis. Among all tested samples, the LDH/MC-0.03 electrode exhibited the lowest R_s value (0.7 Ω). In the high-frequency region, the semicircle corresponds to the charge transfer resistance (R_{ct}), with a smaller diameter indicating a lower interfacial resistance. The LDH/MC-0.03 sample exhibited the smallest R_{ct} value (0.09 Ω), reflecting the faster electron exchange at the electrode–electrolyte interface. Additionally, the nearly vertical line observed in the low-frequency region confirmed the rapid ion transport and excellent diffusion capability. As shown in Fig. S5(c) in the ESM, the R_s and R_{ct} of MC are 0.91 and 0.66 Ω , respectively. These results collectively demonstrate that the unique layered architecture of LDH/MC-0.03 effectively reduced the ion diffusion resistance and significantly improved the reaction kinetics, thereby contributing to its superior electrochemical performance. The accelerated charge-transfer kinetics and enhanced rate performance can be well rationalized by the DFT results, which demonstrate interfacial charge redistribution, increased electronic states near the Fermi level, and optimized OH⁻ adsorption behavior induced by the MXene/CNTs/NiCo-LDH heterointerface. The Bode plots shown in Fig. 4(e) illustrate the relationship between phase angle and frequency for all composites. Among the samples, LDH/MC-0.03 exhibited the highest phase angle of $\sim 74^\circ$, while other composites showed the values of $\sim 70^\circ$. The phase angle of LDH/MC-0.03 electrode is closer to 90° , indicating more ideal capacitive behavior and reduced resistive contribution. This feature reflects the improved charge storage dynamics and faster ion transport at the electrode–electrolyte interface, which supports its superior electrochemical response [39, 82]. The relaxation time (τ), representing the minimum time required for the system to release the stored energy, was calculated using the frequency corresponding to a phase angle of 45° , based on the equation $\tau = 1/f$. As shown in the inset of Fig. 4(e), LDH/MC-0.03 exhibited the shortest τ value among the tested samples, indicating a faster charge–discharge response and more efficient transition between the energy storage and release.

The cycling stability of NiCo-LDH, MC, and LDH/MC-0.03 was evaluated at 10 A·g⁻¹, as shown in Fig. 4(f). Notably, the C_s of LDH/MC-0.03 increased during the initial stage of the cycling test, particularly within the first 200 cycles, which was attributed to the processes such as the ion intercalation between the NiCo-LDH layers and the activation of redox pairs. From 200 to 2400 cycles, a slight decline in capacitance was observed, possibly resulting from the structural adjustments, including the motion of dislocation, slippage of grain boundary, and atomic diffusion [62]. Despite this,

Table 1 Comparison of LDH/MC-0.03 with previously reported in the three-electrode system

NO.	Materials	Electrolyte	C_s	Rate capability	Capacitance retention	Ref.
1	ANPY/MXene	1 M H ₂ SO ₄	451.75 F·g ⁻¹ (1 A·g ⁻¹)	86.3% (8 A·g ⁻¹)	91.8% (5000)	[18]
2	Mn/NiCo-LDH	6 M KOH	518 C·g ⁻¹ (1 A·g ⁻¹)	78 % (100 A·g ⁻¹)	100.7% (10,000)	[75]
3	NiCo-LDH/rGO	2 M KOH	1675 F·g ⁻¹ (1 A·g ⁻¹)	83.8% (10 A·g ⁻¹)	81.2% (10,000)	[76]
4	NiCo-LDH	6 M KOH	1962 F·g ⁻¹ (1 A·g ⁻¹)	66.4% (30 A·g ⁻¹)	73.3% (3000)	[77]
5	NiCo-LDH/ HKUST-1	2 M KOH	1674 F·g ⁻¹ (1 A·g ⁻¹)	73.4% (10 A·g ⁻¹)	80% (2000)	[78]
6	NiCo-LDH@Co-NC-2	6 M KOH	1909 F·g ⁻¹ (1 A·g ⁻¹)	67.6% (10 A·g ⁻¹)	69.5% (10,000)	[79]
7	Ni-S/1d-Ti ₃ C ₂	6 M KOH	840.4 C·g ⁻¹ (1 A·g ⁻¹)	64.3% (30 A·g ⁻¹)	66.5% (5000)	[80]
8	NiCo-LDH/ MXene	1 M KOH	136.9 F·cm ⁻² (0.5 mA·cm ⁻²)	65% (1 mA·cm ⁻²)	74.2% (7000)	[81]
9	LDH/MC	6 M KOH	2145 F·g ⁻¹ (1 A·g ⁻¹)	80.5% (10 A·g ⁻¹)	95.2% (5000)	This work

the LDH/MC-0.03 electrode still maintained 95.2% of its initial capacitance after 5000 cycles, indicating the excellent structural integrity and long-term cycling stability. In contrast, the NiCo-LDH sample retained only 57.5% of its original capacitance, while the MC sample showed the negligible capacity decay. The SEM images (Fig. S6 in the ESM) further confirm the retention of morphology for the LDH/MC-0.03 composite. After the extended cycling, the interconnected MC network remains continuous, and the ultrathin LDH nanosheets are still uniformly distributed across the conductive scaffold. Although the slight edge rounding and local agglomeration can be observed, the overall hierarchical architecture is preserved. This observation confirms that the plasma-assisted heterojunction architecture effectively buffers the volume variation associated with the repeated redox reactions and maintains the robust interfacial contact during the long-term cycling. These findings suggest that the superior cycling performance of LDH/MC-0.03 can be attributed to the synergistic interaction among its components. In the 3D layered structure, MC provides mechanical support and an interconnected conductive framework, confining NiCo-LDH nanosheets within its layers/pores to suppress aggregation. This structural design effectively mitigated the volume expansion of NiCo-LDH during the repeated redox cycling, thereby maintaining the structural coherence and enhancing the cycling durability.

A detailed analysis of electrochemical behavior and the energy storage mechanism of LDH/MC-0.03 sample was conducted to gain the deeper insight into its performance characteristics. During the charge storage process at the electrode-electrolyte interface, three primary mechanisms were identified as contributing to the overall capacitance: (1) Non-Faradaic electrostatic adsorption, in which electrolyte ions are physically adsorbed onto the electrode surface without undergoing the charge transfer reactions [62]; (2) Faradaic surface redox reactions, involving the fast and reversible electron exchange between the surface atoms and electrolyte ions, resulting in the oxidation state transitions and charge storage [83]; (3) Faradaic intercalation processes, whereby the electrolyte ions are inserted into the bulk structure of electrode, enabling the deeper charge storage beyond the surface [84].

In this study, CV curves were systematically recorded at the scan rates ranging from 5 to 100 mV·s⁻¹ to elucidate the charge storage mechanism. The relationship between the redox peak current i (mA) and scan rate v (mV·s⁻¹) can be quantitatively described by a power-law dependence (Eqs. (12) and (13)), where a and b are fitting parameters. The exponent b provides the insight into the underlying charge-storage kinetics, with values approaching 0.5 indicating the diffusion-governed behavior and those nearing unity suggesting a surface-controlled capacitive response [85]

$$i(v) = av^b \quad (12)$$

$$\log(i) = \log a + b \log(v) \quad (13)$$

As presented in Fig. S7 in the ESM, the calculated b values are 0.38 for the anodic peak and 0.52 for the cathodic peak. These values reveal that the electrochemical process is governed by the mixed kinetics, involving both diffusion-limited ion transport and surface redox reactions. Such behavior indicates a synergistic charge-storage mechanism arising from the coupling of bulk diffusion and interfacial capacitive processes, rather than a single dominant pathway. To quantitatively distinguish between the capacitive and

diffusion-controlled contributions to the total current, a series of kinetic analyses were performed using the following equations [14]

$$i = k_1 v + k_2 v^{\frac{1}{2}} \quad (14)$$

In the equation, the term $k_1 v$ represents the capacitive contribution, while $k_2 v^{\frac{1}{2}}$ reflects the diffusion contribution. The proportion of capacitive contribution was found to increase with the increase of scan rate, while the diffusion-controlled contribution gradually decreased, as shown in Fig. 4(g) and Fig. S8 in the ESM. This phenomenon results from the reduced ion diffusion time at the higher scan rates, which limits the electrolyte ion infiltration into the electrode. At 100 mV·s⁻¹, the capacitive-controlled process contributed ~ 84% to the overall charge storage. This high percentage confirmed that the LDH/MC-0.03 electrode exhibited the rapid charge storage kinetics.

This performance mainly resulted from the unique 3D layered structure of LDH/MC composite. Compared with the conventional stacked structure, where OH⁻ ions were required to traverse the tortuous diffusion pathways, the ordered 3D layered structure provides more direct and shorter ion transport channels (Fig. 4(h)). The ion diffusion and electron transfer were both facilitated by this structure, enabling the reversible adsorption and desorption of OH⁻ ions. These structural advantages significantly enhanced the electrochemical performance, demonstrating that the LDH/MC-0.03 electrode was well-suited for the next-generation energy storage applications.

To gain deeper insight into the practical utility of the 3D layered structure LDH/MC-0.03 electrode, an ASC device (labeled LDH/MC-0.03//AC) was fabricated (Fig. 5(a)). The CV curves of the AC and LDH/MC-0.03 electrodes are presented in Fig. 5(b). The two electrodes were observed to exhibit the distinct potential windows and different energy storage mechanisms, with AC displaying the typical electric double-layer capacitance and LDH/MC-0.03 exhibiting the pseudocapacitive behavior. Based on the charge balance principle (Eq. (2)), the optimal mass ratio between LDH/MC-0.03 and AC was calculated to be approximately 1:5.85, according to the GCD result of AC (Fig. S9 in the ESM). To identify the operating voltage window of ASC, CV measurements were conducted at the various voltage ranges of 20 mV·s⁻¹. The current response was observed to increase gradually with the voltage up to 1.7 V, beyond which a sharp rise in current occurred due to the onset of the oxygen evolution reaction (Fig. 5(c)). According to these findings, 0–1.7 V was chosen as the optimal operating voltage window. Figure 5(d) displays the CV curves of the ASC recorded at scan rates from 5 to 100 mV·s⁻¹. The curves exhibited a quasi-rectangular shape in the range of 0–0.8 V and distinct redox peaks from 0.8–1.7 V, indicating that the electric double-layer capacitance from AC and pseudocapacitance from LDH/MC-0.03 were successfully integrated. Notably, even at 100 mV·s⁻¹, the curve shape remained stable without the significant distortion, confirming the good electrochemical reversibility and favorable rate capability of LDH/MC-0.03//AC device.

The GCD curves (Fig. 5(e)) were observed to exhibit a relatively symmetric and nonlinear profile, indicating a good electrochemical reversibility. According to Eq. (1), C_s values at 0.5, 1, 2, 5, and 10 A·g⁻¹ were calculated to be 104.4, 95.0, 84.5, 65.9, and 42.2 F·g⁻¹, respectively. To assess the real-life performance potential of ASC, E and P were further evaluated using Eqs. (3) and (4). The corresponding results are presented in the Ragone plot, as shown in Fig. 5(f). $E = 41.9$ Wh·kg⁻¹ was obtained at $P = 425.1$ W·kg⁻¹. Even at

$P = 8469.3 \text{ W}\cdot\text{kg}^{-1}$, the device still delivered $E = 16.9 \text{ Wh}\cdot\text{kg}^{-1}$, highlighting its remarkable rate capability. These values exceed those reported in many previous studies, as summarized in Table 2 [79, 86–92].

In addition, the electrochemical durability of LDH/MC-0.03//AC device was evaluated. 91% of initial capacitance was retained after 5000 cycles, and the Coulombic efficiency remained close to 100%, as shown in Fig. 5(g), indicating an excellent durability. During the initial stage of cycling, the activation of electrode and the opening of the mesoporous structure created the favorable conditions for the ion intercalation. These changes facilitated the smoother ion transport into the electrode, resulting in a gradual increase in C_s .

However, with the prolonged cycling, a slight decrease in capacitance was observed, which may be attributed to the structural deformation on the electrode surface caused by the repeated insertion and extraction of ion. The Nyquist plots before and after the cycling test are presented in Fig. 5(h). The R_s was slightly reduced from 1.309 to 1.266 Ω , whereas the R_{ct} was significantly increased from 0.981 to 3.415 Ω after the cycle. This increase could be related to the loss of active materials and phase transitions that occurred during the extended cycling. For instance, the partial collapse of the layered structure may reduce the accessible surface area and active sites. Nevertheless, the slope of the line, which represented the ion diffusion resistance, remained nearly

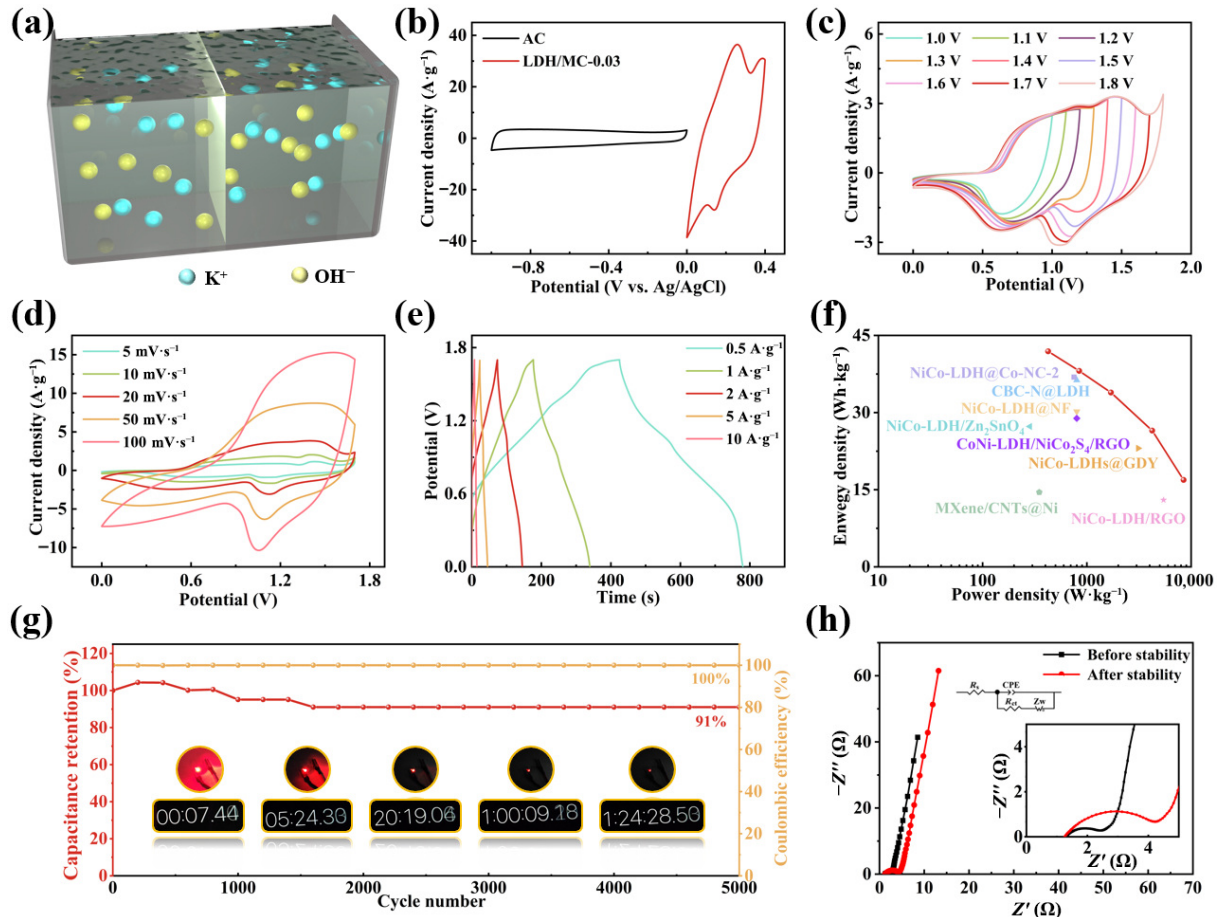


Figure 5 (a) Schematic diagram of LDH/MC-0.03//AC. (b) CV of AC and LDH/MC-0.03 composites. (c) and (d) CV curves at different voltage windows and different scanning rate, respectively. (e) GCD curve. (f) Ragone chart. (g) Cycling stability at 10 $\text{A}\cdot\text{g}^{-1}$ and real pictures of a LED bulb at different luminous stages of LDH/MC-0.03//AC device and (h) EIS curves before and after the cycle test.

Table 2 Comparison with previously reported ASC devices

NO.	Materials	Electrolyte	$P \text{ (W}\cdot\text{kg}^{-1})$	$E \text{ (Wh}\cdot\text{kg}^{-1})$	Ref.
1	NiCo-LDH@Co-NC-2	6 M KOH	752.6	36.9	[79]
2	NiCo-LDH/rGO	3 M KOH	5442	13	[86]
3	NiCo-LDH/ Zn_2SnO_4	2 M KOH	284.2	27.3	[87]
4	CBC-N@LDH	6 M KOH	800.2	36.3	[88]
5	NiCo-LDH@NF	6 M KOH	800	30.2	[89]
6	MXene/CNTs@Ni	1 M H_2SO_4	350	14.5	[90]
7	NiCo-LDHs@GDY	6 M KOH	3108.91	23.06	[91]
8	CoNi-LDH/ NiCo_2S_4 /rGO	2 M KOH	800	28.88	[92]
9	LDH/MC-0.03	6 M KOH	425.1	41.9	This work

unchanged after 5000 cycles, suggesting that the ion transport within the electrode remained efficient. These results confirmed that the LDH/MC-0.03//AC device maintained the high conductivity and demonstrated the strong potential for the long-term stable operation. Furthermore, two ASC devices connected in series were capable of powering a light-emitting device (LED) light for 84 min, demonstrating the practical feasibility of the fabricated system. LDH/MC-0.03 exhibits the excellent electrochemical performance, primarily due to the following factors: (1) The unique 3D layered structure architecture facilitates the formation of numerous active edge sites and abundant heterogeneous interfaces, significantly increasing the density of electrochemically active centers. (2) The exposed interfaces effectively lower the diffusion barrier of ion, thereby accelerating the adsorption and transport of OH^- ions. (3) The ultrathin NiCo-LDH nanosheets offer the plentiful ion diffusion pathways, enhancing both the synergistic interactions and chemical coupling within the system, which improves the migration efficiency of ion. (4) MC serves as a conductive framework, provides not only the continuous electron transport pathways but also the structural reinforcement, effectively preventing the mechanical collapse during the charge-discharge processes.

To systematically evaluate the electrochemical response under the various mechanical deformation conditions, the performance tests were conducted at the different bending angles. A flexible ASC was fabricated using PVA/KOH gel as the electrolyte, LDH/MC-0.03 as the positive electrode, and AC as the negative electrode. The layered configuration of the device is illustrated in Fig. 6(a). CV and GCD curves were recorded under the multiple bending angles of 0° , 30° , 60° , 90° , 120° , 150° , and returned 0° , as shown in Figs. 6(b) and 6(c). The corresponding operating scenarios are presented in Fig. S10 in the ESM. The shapes of CV and GCD curves remained highly consistent across all bending states, indicating the stable electrochemical performance under the mechanical deformation. This result confirms the synergistic effect between the mechanical flexibility and energy storage capability. As depicted in Fig. 6(d), when the device was bent to 150° , 93.2% of its original capacitance

was retained. Upon returning to the initial flat state, the capacitance rapidly recovered, reaching 97.6% of the original capacitance. Furthermore, a 1000-cycle charge-discharge test was conducted at a 90° bending angle (Figs. 6(e) and 6(f)), and the capacitance retention and Coulombic efficiency still remained at 96.15% and 100%, respectively. The above results confirm the outstanding mechanical durability and long-term electrochemical reliability of device under the repeated deformation.

3.4 DFT

To comprehensively investigate the effect of the 3D layered heterointerfaces on the electrochemical performance, DFT calculations were carried out on three systems: NiCo-LDH, MXene/CNTs, and MXene/CNTs/NiCo-LDH. The atomic configurations of the three models are shown in Figs. 7(a)–7(c). The constructed heterostructure enables the intimate interfacial contact between MXene/CNTs and NiCo-LDH, which is essential for the interfacial electronic interaction. The corresponding charge density difference maps are presented in Figs. 7(d) and 7(e), where the yellow and blue regions indicate the charge accumulation and depletion, respectively. In the MXene/CNTs system, the free electrons generated during the redox reactions are transferred from CNTs to MXene. In contrast, in the MXene/CNTs/NiCo-LDH system, electrons are first transferred from NiCo-LDH to CNTs through the interface and subsequently to MXene. The charge density difference plots provide the direct evidence of interfacial charge redistribution in the MXene/CNT and MXene/CNT/NiCo-LDH heterostructures. The pronounced electron accumulation and depletion regions are observed at the interfaces, indicating the strong electronic coupling and charge transfer between MXene, CNTs, and NiCo-LDH. This interfacial charge redistribution promotes the electron delocalization across the heterojunction and effectively reduces the energy barrier for electron transport, thereby enhancing the overall electrical conductivity of the composite electrode. Such theoretical predictions are in good agreement with the experimentally observed reduced charge transfer resistance and improved rate capability [93].

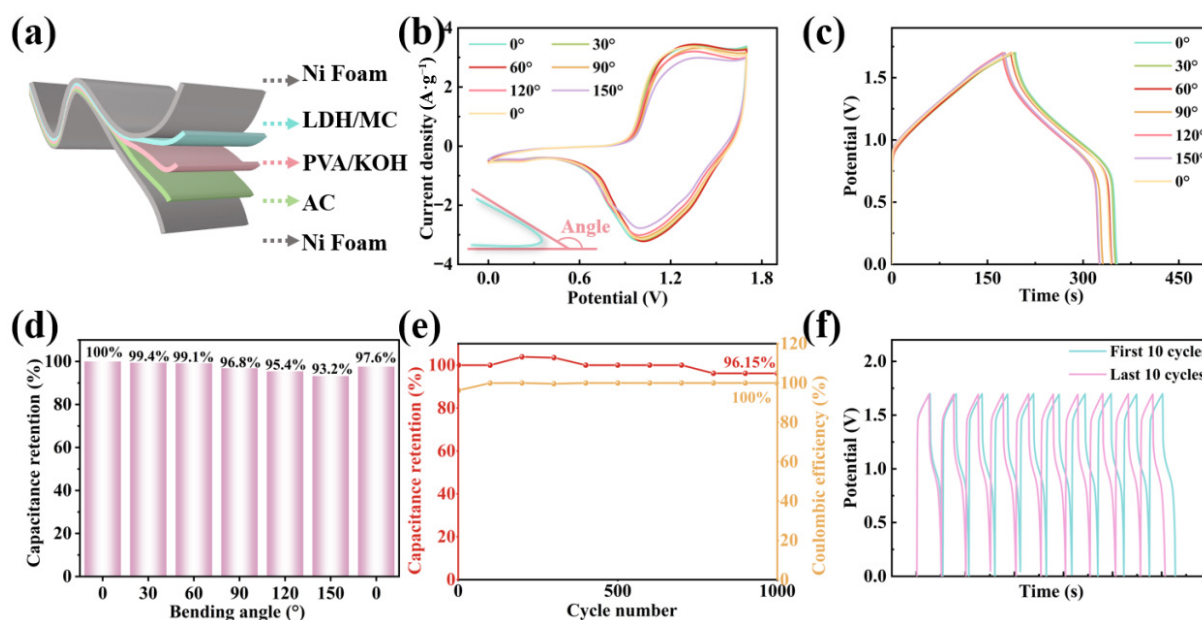


Figure 6 (a) Schematic diagram of the flexible device. (b)–(d) CV, GCD and capacitance retention at the different angles. (e) Cycling stability at $5 \text{ A}\cdot\text{g}^{-1}$. (f) GCD curve in the first ten and the last ten cycles.

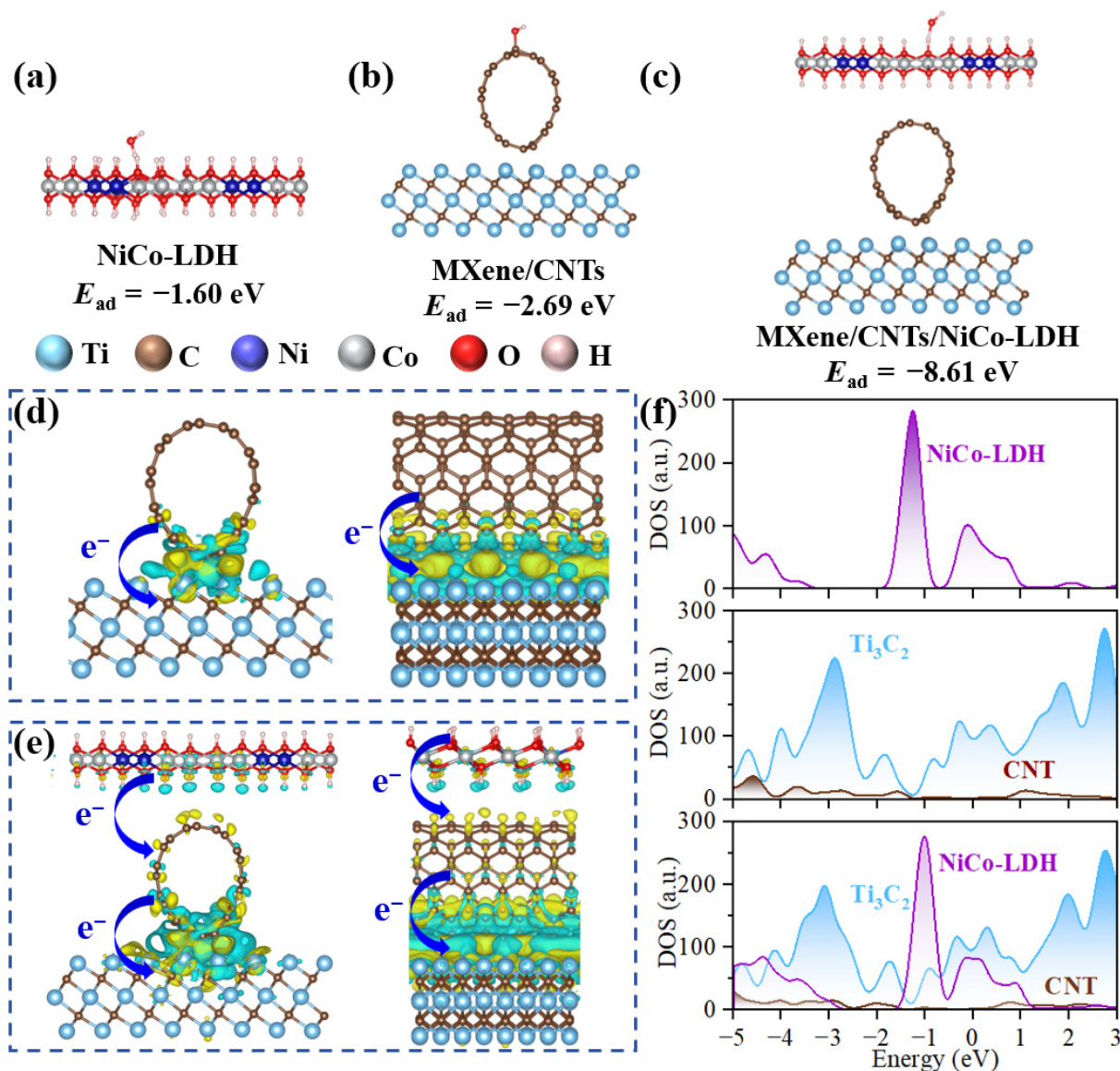


Figure 7 (a)–(c) Crystal structures of MXene/CNTs, NiCo-LDH, and MXene/CNTs/NiCo-LDH. (d) Charge density difference of MXene/CNTs. (e) Charge density difference of MXene/CNTs/NiCo-LDH. (f) DOS of MXene/CNTs, NiCo-LDH, and MXene/CNTs/NiCo-LDH.

The electronic properties of the three systems were further evaluated through the density of states (DOS) analysis (Fig. 7(f)). All systems exhibit the zero bandgap, confirming their metallic characteristics. Notably, the MXene/CNTs/NiCo-LDH composite shows a higher DOS near the Fermi level compared to either MXene/CNTs or NiCo-LDH alone, indicating the enhanced metallic behavior and the superior electronic conductivity. This improved conductivity contributes to the better cycling stability and rate performance of electrode. The results indicate that the 3D layered heterointerface not only provides abundant electron-active sites but also promotes the involvement of paired electrons in conduction, thereby significantly enhancing charge transport efficiency.

In addition, the adsorption behavior of OH^- ions on the electrode surface, an essential factor influencing the supercapacitor performance, was investigated. To gain the deeper insight into the interfacial redox processes occurring in a KOH electrolyte, the OH^- adsorption energies were calculated for all three systems. Among

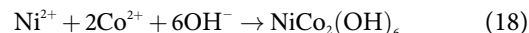
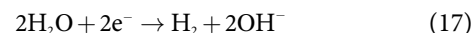
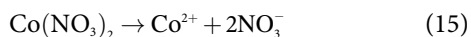
them, the MXene/CNTs/NiCo-LDH composite exhibits the lowest adsorption energy (-8.61 eV), which is significantly lower than that of MXene/CNTs (-2.69 eV) and NiCo-LDH (-1.60 eV). This result indicates a much stronger affinity for OH^- ions in the alkaline environments [94]. This strong adsorption capacity facilitates the effective OH^- accumulation on the electrode surface, creating the favorable conditions for the subsequent charge-transfer processes. Acting as a precursor to the redox reactions, this adsorption step enhances the reaction kinetics and significantly improves the C_s of the electrode material. Consistent with DFT, the MXene/CNTs/NiCo-LDH electrode exhibits a reduced R_a and the enhanced rate capability in electrochemical measurements. These results demonstrate that the optimized OH^- adsorption behavior revealed by DFT provides a direct mechanistic explanation for the experimentally observed performance enhancement. The role of CNTs as conductive spacers can be further understood by combining the electronic-structure analysis with the experimental electrochemical results. Owing to their metallic nature, CNTs

introduce the abundant electronic states near the Fermi level and provide the continuous electron transport pathways between MXene and NiCo-LDH. Meanwhile, the pronounced charge redistribution at the MXene-CNT and CNT-NiCo-LDH interfaces indicates the strong interfacial electronic coupling, enabling an efficient electron transfer across the heterostructure. In addition to enhancing the intrinsic conductivity, CNTs effectively separate the adjacent MXene layers and NiCo-LDH nanosheets, alleviating the restacking and preserving accessible active surfaces.

3.5 Deposition dynamics

A series of effects induced by the assisted liquid-phase plasma electrolysis, along with the associated physicochemical reactions, is a critical factor in shaping the microstructure of composite, and plays a key role in determining their final properties. Hence, the detailed exploration of the deposition mechanism is key to the rational development of the advanced energy storage materials.

The deposition mechanism of LDH/MC composites involves the several key steps (Fig. 8). Under the applied electric field, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ undergo the electrolytic dissociation, releasing the abundant Ni^{2+} and Co^{2+} ions, as described by Eqs. (15) and (16). Simultaneously, a cathodic reduction reaction occurs in which H^+ ions accept the electrons at the cathode surface, generating H_2 gas bubbles. These bubbles are ionized under the electric field, initiating the plasma arc discharge and altering the local reaction environment. As shown in Eq. (17), the evolution of H_2 is accompanied by a continuous accumulation of OH^- ions produced through the water ionization, leading to a local increase of OH^- concentration near the cathode



Driven by both the concentration gradients and the applied electric field, Co^{2+} and Ni^{2+} ions migrate toward the OH^- -enriched region. When these metal ions sufficiently interact with OH^- ions, a precipitation reaction occurs, leading to the formation of NiCo-LDH, as represented in Eq. (18). This process, comprising the ion dissociation, gas evolution and ionization, ion migration, and subsequent chemical reactions, operates synergistically to facilitate the formation of NiCo-LDH composites. As shown in Fig. S11 in the ESM, the photographic images of plasma discharge captured during operation confirm the formation of a stable, localized micro-plasma region at the electrode-electrolyte interface. This high-energy micro-discharge zone accelerates the generation of reactive species ($-\text{OH}$, electrons, and local heating), which collectively promote the rapid nucleation and growth of NiCo-LDH nanosheets on the MC framework. In the plasma-activated region, energetic electrons and micro-heating effects facilitate the partial ion dissociation and enhance the hydroxide formation, enabling the prompt precipitation of LDH nanosheets without the need for prolonged reaction times. This rapid, non-equilibrium environment is consistent with the ultrathin LDH morphology observed in SEM images. These reactions provide a solid foundation for the further investigation into the structural features and functional applications of composites.

4 Conclusions

A 3D layered heterointerfaces LDH/MC composite was successfully synthesized via an assisted liquid-phase plasma electrolysis technique. This method is both straightforward and time-efficient, enabling the rapid fabrication of the desired material. The synthesized NiCo-LDH forms ultrathin nanosheets, providing

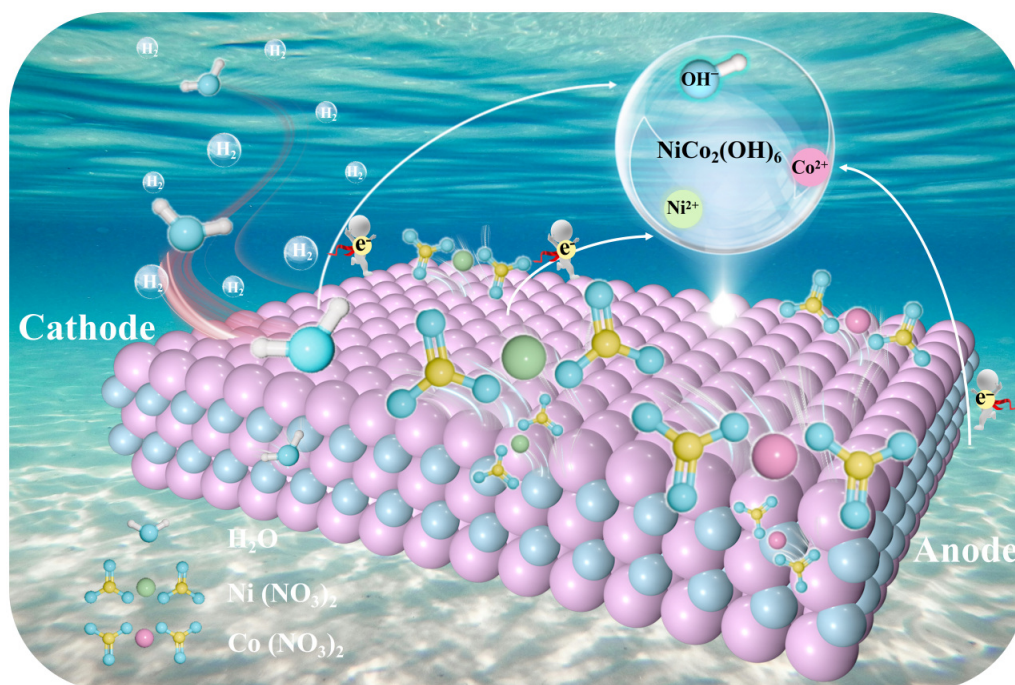


Figure 8 Deposition mechanism of LDH/MC composites via the assisted liquid-phase plasma electrolysis.

extensive exposure of active sites for electrochemical reactions. Structural and compositional characterizations, including XRD, XPS, Raman spectroscopy, TG analysis, and DFT calculations, confirm the successful formation of the target composite. The optimized LDH/MC-0.03 sample demonstrates the outstanding electrochemical performance, delivering a high C_s of 2145 F·g⁻¹, an excellent cycling stability with the retention of 95.2%, and the strong rate capability maintaining 80.5% of its capacitance at 10 A·g⁻¹ in the three electrode system. These enhancements are primarily attributed to the high density of redox-active sites, the improved OH⁻ adsorption/desorption kinetics, and the efficient electron/ion transport pathways. The assembled ASC device achieves a C_s of 104.4 F·g⁻¹ at 0.5 A·g⁻¹ and delivers a maximum $E = 41.9$ Wh·kg⁻¹ at $P = 425.1$ W·kg⁻¹. Even after 5000 cycles at 10 A·g⁻¹, 91% of the initial capacitance is still retained. Furthermore, the flexible ASC exhibits the stable electrochemical performance under the various mechanical deformations. This work exhibits the potential of LDH/MC composites in high-performance supercapacitors.

Electronic Supplementary Material: Supplementary material (materials and reagents, preparation of electrode materials, SEM and XRD of Ti₃AlC₂, XPS spectrum of Ti 2p, TG curve of MC, contact angles of all composites with 6 M KOH electrolyte, GCD curves of LDH/MC and MC, EIS of MC, SEM morphology of LDH/MC-0.03 before and after 5000 cycles, linear plot of $\log i$ vs. $\log v$ during anode and cathode, capacitive and diffusion-controlled capacitance contribution ratio of LDH/MC-0.03 composite, GCD curve of AC; practical operating scenarios for flexibility tests, photographs of the plasma discharge generated during the assisted liquid-phase plasma electrolysis process) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908685>.

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

N. J. Z.: Writing – original draft, data curation. L. H. M.: Data curation. Y. F. Z.: Writing – review & editing. Y. H. S.:

Investigation. W. Z.: Data curation. M. Y. L.: Supervision. W. W. C.: Investigation. X. B. X.: Data curation. C. X. H.: Data curation. X. Y. Y.: Data curation. W. D.: Writing – review & editing. X. Q. S.: Writing – review & editing. Y. P. Z.: Writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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