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Positive Carbon Dots Induced Electrodeposition of NiCo-LDH Nanosheets for High-Performance Supercapacitors

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ABSTRACT: The electrodeposition process is a low-cost, highefficiency, and binder-free route to synthesize layered double hydroxides (LDHs) for high-performance supercapacitors. However, the disordered growth of LDH nanosheets in direct electrodeposition would limit exposure of active sites and easily cause collapse during cycling. Here, we report a kind of positively charged carbon dots (p-CDs) that induce the ordered growth of ultrathin LDH hierarchical nanostructures in a one-step electrodeposition process. The precise regulation of the NiCo-LDH surface morphology was achieved by changing the concentration of p-CDs, which could adsorb NO₃⁻ in the electrolyte and induce



electrodeposition. The as-prepared electrode delivers an enhanced specific capacitance of 1896 F g^{-1} at 1 A g^{-1} and an excellent rate performance (87.6% capacitance retention at 20 A g^{-1}). A supercapacitor based on the composite LDH/CDs and active carbon exhibits a high energy density of 46.06 Wh kg⁻¹ with a power density of 750 W kg⁻¹ and a remarkable cycle stability (78.3% after 30,000 cycles at 5 A g^{-1}). This research presents a successful example of CD application in electrochemical energy storage.

KEYWORDS: nickel cobalt layered double hydroxides, carbon dots, supercapacitors, electrodeposition, surface engineering

1. INTRODUCTION

In comparison with conventional batteries, hybrid supercapacitors (HSCs) have the advantages of fast charging and discharging, good cycling stability, and long service life by combining the principles of traditional batteries and symmetric supercapacitors (SSCs).^{1,2} In general, SSCs have positive and negative electrodes made of the same material, while in HSCs, the positive and negative electrodes belong to different types of materials (battery type and capacitor type, respectively). As a result, HSCs can utilize different potential windows of two electrodes to maximize the working voltage and achieve higher capacities over SSCs ultimately.^{3,4} Layered double hydroxides (LDHs) are typical HSC positive-electrode materials possessing unique two-dimensional layered structures and high theoretical capacities,^{5,6} which can be prepared by templateassisted,⁷ hydrothermal,⁸ and sol-gel methods.⁹ These popular methods are actually complex and inefficient because the powder products need to be combined with binders and conducting additives before assembling into HSCs, resulting in the inactive mass of the electrode and the agglomeration of the active materials.^{10–12}

Electrodeposition, a synthetic method that enables the direct growth of active materials on substrates through in situ chemical reactions, has received intensive attention in the preparation of LDH electrodes due to its advantages of being low-cost, highly efficient, and binder-free. Besides, electrodeposition can precisely regulate the nanostructure of the deposition layer by controlling voltage, deposition time, and the composition of electrolytes.^{13,14} Roy et al. synthesized CoMn-LDH on the surface of graphite using the electrodeposition method, which delivered a specific capacitance of 191 mF cm⁻² and 83.2% capacitance retention over 10,000 cycles.¹⁵ Lee et al. grew NiCoFe-LDH on the nickel foam, which exhibited a specific capacitance of 1321 F g⁻¹ and a capacitance retention of 88.6% over 10,000 cycles.¹⁶ However, direct electrodeposition on substrates often leads to the disordered growth of LDH nanosheets that limit exposure of active sites, resulting in diminished capacitance. Additionally, the structural integrity of the nanosheets is compromised, which suffers from deformation and collapse during cycles.^{17,18}

Carbon dots (CDs), as a new kind of zero-dimensional carbon nanomaterials, have attracted emerging attention in energy storage applications,^{19–21} as well as the wide research in fluorescence analyses and biotechniques.^{22–24} Due to the adjustable composition and the rich functional groups on their surfaces, CDs exhibit unique properties such as good solubility in solvents and homogeneous dispersibility in host materials, as

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Scheme 1. Preparation Process of p-CDs and LDH/CD@CC



well as the ability to participate in material self-assembly.^{25,26} In our previous work, we found that different amounts of CDs added to NiCo₂O₄ in the hydrothermal reaction could change its morphology. The flower-like NiCo₂O₄/CDs composite electrode had an excellent capacity of 2168 F g⁻¹ at 1 A g⁻¹ while keeping good cycling stability (99.9% after 5000 cycles).²⁷ Therefore, it is possible to control the growth process and the product structures of LDHs with the addition of CDs in electrodeposition, thus enhancing the electrochemical performance of electrodes through surface engineering. Moreover, polar functional groups of CDs can improve the wettability of the electrode that would better interact with the electrolyte and accelerate the ion-/electron-transfer process at the surface of electrodes.²⁸

Although most CDs have negative charges on their surfaces, we synthesized a kind of positively charged CDs (p-CDs) in the present work, for it has a strong interaction with anions in the electrolyte, thus inducing the electrodeposition of metal ions to obtain some ordered nanostructures.²⁹ By just altering the concentration of p-CDs in electrolytes for electrodeposition, we controlled the nanostructure of NiCo-LDH and optimized its electrochemical performance facilely. Meanwhile, p-CDs in the composite electrode increase the specific capacity and the cycle stability of electrodes by assisting in the formation of efficient electrode-electrolyte interfaces. The well-designed LDH/CD4@CC shows a high specific capacitance of 1896 F g^{-1} at 1 Å g^{-1} and a good rate capability of 87.5% retention at 20 Å g^{-1} . An HSC based on LDH/CD4@ CC and active carbon delivers high energy densities of 46.06 Wh kg⁻¹ at 750 W kg⁻¹ and 36.25 Wh kg⁻¹ at 7500 W kg⁻¹, with a capacitance retention of 78.3% at 5 A g⁻¹ after 30,000 cycles. These results confirm that the optimal surface engineering of NiCo-LDH can be realized by adding multifunctional p-CDs in a one-step electrodeposition process.

2. EXPERIMENTAL SECTION

2.1. Synthesis of p-CDs. 0.548 g of cetylpyridinium chloride monohydrate (CPC) and 0.72 g of NaOH were first added to 100 mL of deionized water and then stirred for uniform mixing. After ultrasonication with a power of 1500 W for 30 min (Sonics VCX-1500), the resulting mixture was neutralized with diluted hydrochloric acid until pH = 7. The as-prepared solution was dialyzed in water for 3 days, while the cutoff molecular weight of the dialysis bag was 3500. The dialyzed solution was freeze-dried to obtain the final p-CDs powder.

2.2. Synthesis of LDH/CD@CC. Before electrodeposition, the carbon cloth (CC) was cut into rectangle pieces $(1 \times 1.5 \text{ cm}^2)$ and then ultrasonically cleaned with acetone, ethanol, and deionized water successively. In order to improve its hydrophilicity, CC was treated with diluted nitric acid at 140 °C for 200 min hydrothermally, washed with deionized water, and then dried at 60 °C. The as-treated CC was used as the working electrode (WE), with a platinum film as the counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode (RE). LDH/CDx@CC was prepared in 30 mL of aqueous electrolyte containing 40 mM Ni(NO₃)₂, 40 mM Co(NO₃)₂, and x mg of p-CDs with a voltage of -1.0 V for 800 s, where x refers to 1, 2, 4, 6, and 8. The as-obtained film was rinsed with deionized water several times and dried in a vacuum oven at 60 °C. For comparison, LDH@CC was prepared under the same conditions without adding p-CDs.

2.3. Characterization. The morphological and elemental analyses of p-CDs, LDH@CC, and LDH/CDx@CC were characterized by using a field emission scanning electronic microscope (SEM, Zeiss Gemini SEM 300) and a high-resolution field emission transmission electron microscope (HRTEM, JEOL JEM-2100F), respectively. The Fourier transform infrared (FTIR) spectra were collected from 4000 to 400 cm⁻¹ by using a Thermo Fisher Nicolet iS10 spectrometer. The X-ray diffraction (XRD) patterns were obtained using a Bruker D2 Endeavor X-ray diffractometer to explore the crystal phase of all materials. The fluorescence spectra were acquired by a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. The analysis of elements was conducted through high-resolution X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha instrument.

2.4. Electrochemical Measurements. The electrochemical performances of all of the samples were tested in 6 M KOH aqueous electrolytes at room temperature. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were tested by a three-electrode system on a CHI660D (Shanghai Chenhua Instrument Corp.) electrochemical workstation. The cycling GCD test was performed on a LAND battery tester. All samples were used as the working electrodes, employing Hg/HgO and Pt as the reference and counter electrodes, respectively. The gravimetric specific capacitance (C, F g⁻¹) was calculated by following equation³⁰

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where *I*, Δt , *m*, and ΔV represent the current density (A), discharge time (s), mass loading of LDH/CD on CC (g), and potential window (V), respectively.

In addition, HSC was assembled by an LDH/CD4@CC cathode, an active carbon (AC) anode, and a 6 M KOH electrolyte. To fabricate the AC anode, activated carbon, acetylene black, and poly(vinylidene difluoride) were mixed with a mass ratio of 80:10:10



Figure 1. (a) HRTEM images of p-CDs. (b) Photos of CPC solutions and p-CD solutions under room light and UV light. (c) PL emission spectra of p-CDs and CPC. (d) XRD patterns and (e) FTIR spectra of p-CDs and CPC. (f) ζ -Potential distribution of the p-CDs.

and then cast onto a piece of nickel foal. The loading mass of AC was evaluated by eq 2 to get the charge balance between the positive and negative electrodes for HSC $\,$

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

where m_+/m_- , C_+/C_- , and $\Delta V_+/\Delta V_-$ are the mass of active materials (g), specific capacitance (F g⁻¹), and potential window (*V*) of the cathode and anode electrodes, respectively. The energy density (*E*, Wh kg⁻¹) and power density (*P*, W kg⁻¹) of the HSC were calculated based on eqs 3 and 4³¹

$$E = \frac{C \times \Delta V^2}{7.2} \tag{3}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{4}$$

where C, ΔV , and Δt represent the specific capacitance (F g⁻¹), potential window (V), and discharge time (s) of HSC, respectively.

3. RESULTS AND DISCUSSION

The preparation process of p-CDs and LDH/CDx@CC is illustrated in Scheme 1. In the presence of NaOH, deprotonation of CPC first takes place on the α -carbon of the alkyl chain.³² Prompted by strong ultrasonication, hydrophobic groups of surfactants spontaneously converge, followed by polymerization and carbonization, forming carbonized cores of carbon dots. Owing to the hydrophilic effect of the pyridine groups, most of such groups will remain on the surface of carbon dots so as to form positively charged p-CDs. The electrodeposition process of LDH/CDx@CC was conducted using a potentiostatic method at a constant voltage of - 1.0 V (vs SCE) in a three-electrode cell, where CC, Pt plate, and SCE work as WE, CE, and RE, respectively. As

shown in Figure S1, the electrolyte used for electrodeposition did not show any agglomeration after the addition of p-CDs, indicating that p-CDs can be stably dispersed in the nitrate solution. The NiCo-LDH/CD nanosheets were successfully anchored on the surface of CC after 800 s electrodeposition in an aqueous solution containing cobalt nitrate, nickel nitrate, and p-CDs. Benefitting from the electrostatic interaction with positively charged function groups, NO_3^- would be adsorbed on the surface of p-CDs, thus releasing more free metal ions to precipitate with OH⁻ on the surface of CC and inducing the electrodeposition process. The average mass loadings of LDH@CC, LDH/CD1@CC, LDH/CD2@CC, LDH/CD4@CC, LDH/CD4@CC, LDH/CD6@CC, and LDH/CD8@CC are about 2.9, 2.7, 2.2, 1.5, 1.5, and 1.4 mg cm⁻², respectively.

As shown in Figure 1a, p-CDs are well-dispersed nanoparticles with uniform diameters of about 4 nm, and an inplane lattice spacing of 0.21 nm was observed, corresponding to the (100) plane of graphite.³³ Many cationic surfactants are regarded as fluorescence quenchers,³⁴ and CPC shows no fluorescence under UV light. In contrast, p-CDs synthesized from CPC exhibit yellow-green fluorescence under UV light, as shown in Figure 1b. The PL spectra of CPC reveal a broad emission at around 536 nm, which is typical for carbon dots (Figure 1c).³⁵ The XRD patterns and FTIR spectra of CPC and p-CDs are compared in Figure 1d,e. XRD patterns of p-CDs have a weak peak centered around 21°, indicating a nearly amorphous structure of p-CDs. According to FTIR spectra results, the intensive band at 3424 cm⁻¹ indicates the presence of N-H bonds, while spectral bands at 1630 and 1384 cm⁻¹ are probably due to C=N and C-N bonds, respectively, which suggests that the nitrogen-containing functional groups in CPC are well preserved in p-CDs. In the wide-range survey of XPS in Figure S2a, carbon, oxygen, and nitrogen elements

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Figure 2. SEM images of (a, b) LDH@CC, (c, d) LDH/CD1@CC, (e, f) LDH/CD2@CC, (g, h) LDH/CD4@CC, (i, j) LDH/CD6@CC, and (k, l) LDH/CD8@CC.



Figure 3. TEM and HRTEM images of (a, b) LDH@CC and (c, d) LDH/CD4@CC, respectively.

are present in p-CDs. In the high-resolution spectra (Figure S2b), N 1s can be deconvoluted into three peaks, assigned to pyridinic N (29.0%), pyrrolic N (36.2%), and graphitic N (34.8%).³⁶ Owing to the presence of positively charged nitrogen-rich functional groups, p-CDs show a high ζ -potential of +62.0 mV in Figure 1f, so they have the ability to strongly couple with negative NO₃⁻ ions in the electrolyte during the electrodeposition process.

 ζ -Potentials of the electrolyte with p-CDs in electrodeposition were measured to confirm the interaction between p-CDs and nitrates. Cobalt nitrate and nickel nitrate aqueous solution is electrically neutral but shows an average ζ -potential of + 27.5 mV after the introduction of p-CDs (Figure S3), which means that although NO₃⁻ ions are adsorbed on p-CDs, they still have strong positive charges to participate in electrodeposition to precipitate with OH⁻. The effects of p-CDs on the surface engineering of NiCo-LDH are investigated

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Figure 4. High-resolution XPS spectra of (a-c) LDH@CC and (d-f) LDH/CD4@CC.

in detail by SEM. After electrodeposition, NiCo-LDH nanosheets exist on the surface of the carbon cloth, as proved by EDS mapping (Figure S4). The signals of nickel, cobalt, carbon, and oxygen are distributed homogeneously on the electrodes, where the carbon signal is strong because the nanosheets are very thin compared to the substrate. When p-CDs are absent, the growth of pristine LDH on carbon cloth is disordered, and a large amount of nanosheets is densely stacked together (Figure 2a,b), which is an unstable structure and will get crushed and detached during cycles. In contrast, when more and more p-CDs are incorporated, the thickness of LDH nanosheets becomes thinner and thinner, and the hierarchical structures are observed in Figure 2c-j. In general, the appropriate nanosheet distance ensures structural stability and provides a large specific surface area simultaneously, which renders better contact with the electrolyte and high electrochemical performance.³⁷ However, when too many p-CDs are added, the nanosheets will collapse and densely stack again, as shown in Figure 2k,l, because they are too thin to support themself on the CC. These phenomena indicate that the positively charged CDs have strong interactions with NO₃⁻ ions and influence the number of free metal ions, which restrict the growth of nanosheets and optimize the surface engineering of the electrode.

The TEM images of LDH@CC and LDH/CD4@CC are compared in Figure 3a,c. The latter has more folds and exhibits a more complex structure, which may provide more surface area in contact with the electrolyte and facilitate ion storage. In the HRTEM images, both LDH@CC and LDH/CD4@CC (Figure 3b,d) have lattice spacings of 0.26 and 0.23 nm, which can be attributed to the (012) crystal planes of Ni(OH)₂. 0.75H₂O (PDF#38–0715) and the (015) crystal planes of NiCo-LDH,³⁸ respectively. It is difficult to ensure that the products of electrodeposition are LDHs or a mixture of different metal hydroxides, but the lattice spacing of 0.16 nm owing to the (110) crystal planes of Co(OH)₂ (PDF#45-0031) could only be found in LDH@CC in contrast to LDH/ CD4@CC, indicating that p-CDs lead to a more homogeneous binding of Ni²⁺ and Co²⁺ with OH⁻ caused by more free metal ions. Moreover, p-CDs with a characteristic lattice spacing of 0.21 nm can be clearly observed in LDH/CD4@CC. Figure S5 compares the XRD patterns of the CC and the as-prepared electrodes. After electrodeposition, a typical peak at 10.8° can be recognized in LDH@CC and LDH/CD1@CC, which is indexed to (003) plane of hydrotalcite-like structure nitrateintercalated cobalt hydroxides (PDF#50-1891). This peak is no longer obvious when the amount of p-CDs further increases, which corroborates the HRTEM results. In the FTIR spectra of the as-prepared electrodes (Figure S6), the spectral bands at 3452, 1636, 1382, and 629 cm⁻¹ are assigned to O-H bonds, C=O bonds, interlayer NO₃⁻ anions, and Ni/ Co-O bonds, respectively.^{39,40}

The XPS full-range scan spectra in Figure S7 demonstrate that both LDH@CC and LDH/CD4@CC are mainly composed of C, O, Ni, and Co, while the additional N signals at around 405 eV are attributed to p-CDs and the interlayer NO_3^- anions in NiCo-LDH. Figure 4 compares the high-resolution spectra of Co 2p, Ni 2p, and O 1s. In Figure 4a, the peaks at 781.3 and 797.1 eV are ascribed to Co^{3+} , while the peaks at 784.4 and 802.1 eV are ascribed to Co^{2+} . In addition, two satellite peaks at around 787.6 (Co $2p_{3/2}$) and 805.4 eV (Co $2p_{1/2}$) can be assigned to the binding energies of $2p_{3/2}$ and $2p_{1/2}$, respectively. Similarly, high-resolution spectra of Ni 2p (Figure 4b) can be deconvoluted into three groups of Ni²⁺ (855.9 and 873.7 eV), Ni³⁺ (858.7 and 878.9 eV), and satellite peaks (862.3 and 882.3 eV).^{41,42} The spectra of O 1s in Figure 4c include two peaks at 530.8 and 531.9 eV, corresponding to OH⁻ and metal-O, respectively.⁴³ The element composition

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Figure 5. (a) CV curves at 5 mV s⁻¹ and (b) GCD curves at 1 A g⁻¹ of the as-prepared electrodes. (c) GCD curves under various current densities and (d) capacitive contribution at various scanning rates of LDH/CD4@CC. (e) Rate capabilities and (f) Nyquist plots of the as-prepared electrodes.

of LDH/CD4@CC is the same as that of LDH@CC, and the contents of each component can be found in Table S1.

In order to evaluate the electrochemical performance of LDH@CC and LDH/CDx@CC (x = 1, 2, 4, 6, 8) as electrode materials for SCs, electrochemical tests including CV and GCD were carried out in a standard three-electrode system using 6 M KOH as the electrolyte. Well-defined redox pairs and two recognizable potential plateaus are found in Figure 5a,b, which are features of pseudocapacitance. The redox processes can be judged as the reversible faradic reactions of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺/Co⁴⁺, and the corresponding reaction formulas are shown as follows.⁴⁴

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-$$
(5)

$$Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e^-$$
(6)

$$CoOOH + OH^{-} \rightleftharpoons CoO_{2} + H_{2}O + e^{-}$$
(7)

The positions of the redox peaks change as the content of p-CDs varies, indicating that p-CDs are able to control the surface states of NiCo-LDH. As a result, LDH@CC and LDH/ CDx@CC (x = 1, 2, 4, 6, 8) deliver specific capacitances of 1422, 1478, 1616, 1896, 1774, and 1672 F g⁻¹ at 1 A g⁻¹, respectively. Among them, LDH/CD4@CC has the largest capacitance and the longest discharge time. This sample also has the best performance at high current densities, exhibiting capacities of 1738, 1692, and 1660 F g⁻¹ at 10, 15, and 20 A g⁻¹, respectively (Figure 5c). Moreover, its GCD curves remain symmetrical and undistorted as the current density increases, which indicates the superior reversibility and electronic conductivity of LDH/CD4@CC. Figure S8 shows the CV curves of LDH/CD4@CC under 2, 5, 10, and 20 mV s⁻¹. The redox pair peaks have similar shapes and shift to positive and negative potentials with the increased scanning rate, which can be explained by the polarization of the electroactive materials.⁴⁵ The respective specific contributions from capacitive-controlled (k_1v) and diffusion-controlled $(k_2v^{1/2})$ behavior can be quantified based on the following formula.⁴⁶

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$$i = i_{\rm cap} + i_{\rm diff} = av^b \tag{8}$$

$$i = k_1 v + k_2 v^{1/2} \tag{9}$$

$$i/\nu^{1/2} = k_1 \nu^{1/2} + k_2 \tag{10}$$

The capacitive contribution is calculated for different scanning rates, as shown in Figure 5d. When the scanning rate is gradually increased, the capacitive contribution in the whole capacitance enlarges together, which means that the charge storage mechanism is dominated by the diffusion-controlled redox reaction. As a result, LDH/CD4@CC shows excellent rate performance with a capacitance retention of up to 87.5% at 20 A g⁻¹, superior to that of LDH@CC (81.5%), as shown in Figure 5e and Table S2. In addition, LDH/CD4@CC exhibits the best cycling stability with a capacitance retention of 79.7% after 2000 cycles, better than the other as-prepared electrodes (Figure S9). The EIS test was carried out to measure the electronic transport capacity of the electrode, as shown in Figure 5f. The equivalent series resistance (R_s) refers to a combination of intrinsic resistance, solution resistance, and interface resistance, while the charge transfer resistance (R_{ct}) relates to the Faradaic reaction. Warburg resistance (W) is



Figure 6. (a) CV curves of the HSC at different current potentials under 10 mV s⁻¹. (b) CV curves of the HSC at different scan rates. (c) GCD curves of the HSC at different current densities. (d) Rate capabilities, (e) Ragone plot, and (f) cycling performance of the HSC.

caused by the diffusion process of electrolyte ions.⁴⁷ No obvious semicircle could be observed in the high-frequency region of all curves, indicating the low $R_{\rm ct}$ of all as-prepared electrodes.⁴⁸ However, when excessive p-CDs are added, diffusion resistance becomes worse and influences the electrochemical performance of electrolyte ions restricted by dense stacking of very thin nanosheets.

The LDH/CD4@CC cathode and the AC anode are assembled into an HSC for further investigation. According to eq 2, the average mass loading of LDH/CD4 on the CC is about 1.5 mg cm⁻², and the mass loading of AC is about 5.4 mg cm⁻². The CV test is used to determine the optimized potential window for the HSC, as shown in Figure 6a. As the working potential window rises from 1.1 to 1.5 V, the shape of the CV curve remains similar while no evident oxygen evolution is observed. On the basis of this result, CV and GCD tests were measured at various scan rates of 5-50 mV s^{-1} , and the current densities increased from 1 to 10 A g^{-1} in the working potential range of 0-1.5 V (Figure 6b,c). The CV curve maintains a quasirectangular shape at any scan rate, which is one of the characteristics of HSCs. As the current density increases, GCD curves are still symmetrical and undistorted, revealing excellent reversibility, rate capability, and Coulombic efficiency. In Figure 6d, such HSC delivers specific capacitances of 147.4, 138.4, 137.4, 131.0, 122.1, and 116.0 F g^{-1} at 1, 2, 3, 5, 8, and 10 A g^{-1} , respectively. Even at a high current density of 10 A g^{-1} , it retains 78.7% of its specific capacitance. Figure 6e reveals the Ragone plots of the HSC with energy and power densities, compared with those of the related NiCo-LDH materials using electrodeposition in the last three years. A maximum energy density of 46.06 Wh kg^{-1} is realized at a power density of 750 W kg⁻¹, and it remains 36.25 Wh kg⁻¹ when the power density increases to 7500 W kg⁻¹.

The specific energy of our HSC is higher than those of reported HSC devices such as NiCoZn-LDH@PANI//AC,⁴⁹ NiCoFe-LDH//AC,⁵⁰ TU-NiCo-LDH//AC,⁵¹ and NiCo-LDH@PANI//AC⁴⁸ (Table S3). In addition, the HSC device exhibits extreme cycling stability with a capacitance retention of 78.3% after 30000 cycles at a current density of 5 A g⁻¹, and the corresponding GCD curves are undistorted during the cycling test (Figures 6f and S10). These electrochemical performances of the LDH/CD4@CC//AC are mainly ascribed to the hierarchical structure of LDH nanosheets with an enlarged specific surface area and enhanced stability, which are based on surface engineering by p-CDs.

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4. CONCLUSIONS

In this work, we synthesized a kind of positively charged carbon dots by strong sonication on surfactant molecules facilely. After addition to the electrolyte, such p-CDs can control the electrodeposition process of NiCo-LDH to form hierarchical nanosheets on the carbon cloth. The concentration of p-CDs has significant influences on the surface morphology of NiCo-LDH. As an electrode of a symmetric supercapacitor, the optimal LDH/CD4@CC sample possesses a stable hierarchical nanostructure and exhibits a high specific capacitance of 1896 F g⁻¹ at 1 A g⁻¹ and good rate capability with 87.6% capacitance retention from 1 to 20 A g^{-1} . Moreover, the HSC device based on LDH/CD4@CC and active carbon delivers high energy densities of 46.06 and 36.25 Wh kg⁻¹ at power densities of 750 and 7500 W kg⁻¹, respectively. Such an HSC still retains 78.3% of capacitance after 30,000 cycles at 5 A g^{-1} , indicating an excellent energy storage performance of LDH/CD4@CC//AC. Our present work provides a simple and efficient method for preparing

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NiCo-LDH-based HSCs with both high capacitances and long life spans.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.4c00952.

Details of material characterization methods and additional characterization results of EDS, XRD, FTIR, XPS, CV, and cycle stability (PDF)

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Notes

The authors declare no competing financial interest.

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