Supporting information

Unveiling the effect of growth time on the bifunctional layered hydroxide electrodes for high-performance energy storage and green energy conversion

Jyoti Prakash Das¹, Swapnil Shital Nardekar¹, Dhanasekar Kesavan¹, Kousik Bhunia¹
Ravichandran Vishwanathan¹, Sang-Jae Kim¹,²,³*

¹Nanomaterials & System Lab, Major of Mechatronics Engineering, Faculty of Applied Energy System, Jeju National University, Jeju- 63243, Republic of Korea.
²Nanomaterials & System Lab, Major of Mechanical System Engineering, College of Engineering, Jeju National University, Jeju- 63243, Republic of Korea.
³Research Institute of New Energy Industry (RINEI), Jeju National University, Jeju- 63243, Republic of Korea.

*Corresponding Email id.: kimsangi@jejunu.ac.kr
Materials and methods

S1. Materials

The precursor materials such as Nickel Nitrate hexahydrate (Ni(NO₃)₂·6H₂O), Cobalt nitrate hexahydrate(Co(NO₃)₂·6H₂O), HMTA, and Potassium hydroxide were procured from Daejung Chemicals & metals co.Ltd., S. Korea. The materials were used for application without any post-treatment in analytical grade without any prior treatment.

S2. Instrumentation

The crystal structure and phases of the NiCo LDH electrode were analyzed using an Empyrean X-ray diffractometer (XRD) (Malvern Pan analytical, UK). The source of the XRD was Cu-Kα under a current of 40mA and a voltage of 40kV. The Laser Raman for the NiCo LDH was carried out using LabRAm HR Evolution Raman Spectroscopy (Horiba Jobin-Yvon, France) with Ar⁺ ion laser functioning at 10mW power with the excitation wavelength of 514nm. The morphology of the NiCo LDH was analyzed using a Field emission scanning electron microscope (TESCAN, MIRA3) coupled with an energy-dispersive X-ray spectroscopy (EDS) analyzer for the quantitative analysis of the samples. The electrochemical performance of the active electrode or ASC device was analyzed using an AUTOLAB PGSTAT302N electrochemical workstation. The Brunauer-Emmett-Teller (BET) surface area of composites analyzed based on the des-adsorption isotherms of inert nitrogen was performed using BELSORP MINI X, Microtrac MRB Chem BET analyzer. All samples were degassed under vacuum conditions at 250 ºC for 4 h. The apparent surface area was computed from the nitrogen adsorption data in the relative pressure range between 0.05 and 0.3.

S3. Synthesis of NiCo LDH

NiCo LDH were directly grown over Ni-foam via the one-step hydrothermal process. At first, the precursor solution was prepared by homogeneous mixing of Ni (NO₃)₂· 6H₂O and Co (NO₃)₂· 6H₂O with C₆H₁₂N₄ in the ratio of 2:1:3 in 40 ml DI water to allow for constant stirring until the formation of a light pink colour solution. Prior to the hydrothermal deposition, we have followed the standard protocol for the mass calculation after the hydrothermal growth of the Ni-Co LDH over the nickel foam. Step 1: The NF substrate is cleaned thoroughly with dilute HCl and ethanol to remove the oxide layer and the volatile substances respectively and kept for drying at 80° C for 4 h. After drying the weight of the NF was measured and noted as W1. Step 2: Then the cleaned NF was kept for the hydrothermal reaction for the designated
period and cleaned thoroughly with absolute ethanol and DI water to remove the excess deposits and kept for drying for 6 hours to remove all the moisture contents. After drying the weight of the hydrothermally treated NF with grown NiCo LDH for 3 different time intervals [6h,8h,10h] is measured and the weight is recorded as W2. The difference between W2 and W1 is obtained as the effective mass of the grown NiCo LDH over the NF. After that, as grown Ni-foam was taken out and rinsed several times with ethanol and DI water. At last, Nico LDH@Ni electrode was dried in a hot air oven (70°C) for overnight and used for further study. The NiCo LDH samples obtained at various reaction time intervals (from 6 to 10 h) were named as NiCo LDH-6, NiCo LDH-8, and NiCo LDH-10, respectively.

S4. Preparation of graphene oxide (GO) and reduced graphene oxide (rGO) nanosheets

The graphene oxide (GO) sheets were prepared using the modified Hummers' method, whereas the reduced graphene oxide (rGO) sheets were prepared via a thermal reduction method, as reported in the literature$^{1,2}$.

S4. Electrochemical analysis of active electrodes via three-electrode configuration

The electrochemical characterizations of as properad electrodes were carried out in three-electrode (3E) configuration method by employing NiCo LDH or graphene as the working electrode, platinum sheet as the counter electrode, and Ag/AgCl as the reference electrode with 3M KOH solution as the electrolyte at room temperature. Here, the active mass loading of the electrode was measured using the Dual range Semi-micro-Balance (AUW-220D, Shimadzu) from the difference between mass before and after hydrothermal treatment/ slurry coating. The performance evaluation of electrode or ASC device were analysed through the best practice methods such as cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS), respectively.

S4. Electrochemical studies of NiCo LDH//Graphene ASC device via two-electrode configuration

The asymmetric supercapacitor was fabricated by sandwiching positrode (NiCo LDH) and negatrode (rGO) having cross-sections (1*1) cm$^2$ separated by a whatmann paper as a separator and tied together with Teflon tape. The as-prepared device was dipped in a cylindrical beaker in a 3M KOH electrolyte solution. The charge balancing of both (positrode and negatrode) electrodes was done by using following equation as suggested in the previous literature$^{34}$. 
\[ \frac{m^-}{m^+} = \frac{[C^- \times \Delta V^-]}{[C^+ \times \Delta V^+]} \]................. (1)

where \( m^- \) and \( m^+ \) represent the mass of the negative and positive electrodes, \( C^- \) and \( C^+ \) denote the specific capacitance of the negative and positive electrodes, and, \( \Delta V^- \) and \( \Delta V^+ \) are the potential window of the negatrode and positrode obtained using the three-electrode system, respectively. The active mass of the positive and negative electrodes are 0.95 mg and 2.33 mg. The mass of the device is 3.28 mg. The specific capacitance \( C_{sp} \), specific capacity \( Q \), energy density \( E \), and power density \( P \) of the fabricated asymmetric supercapacitor were calculated using the following equations \(^5\text{-}^7\).

\[ C_{sp} = \int I \, dV / \Delta V \times M \times S \]------------------------------------(1)

\[ C_{sp} = I \times \Delta t / \Delta V \times M \]-------------------------------------(2)

\[ Q = [I \times \Delta T] / [m\times3.6] \]-----------------------------------(3)

\[ E = (C_{sp} \times \Delta V^2)/2 \]---------------------------------------------(4)

\[ P = E / \Delta t \]----------------------------------------------(5)

Here “\( C_{sp} \)” and “\( Q \)” are the specific capacitance \( (\text{Fg}^{-1}) \) and capacity \( (\text{mAh g}^{-1}) \); “\( I \)” is the current “\( \Delta t \)” is the discharge current(s), “\( \Delta V \)” is the operating potential window \( (\text{V}) \); “\( M \)” is the mass of the electrode \( (\text{g}) \), “\( E \)” is the energy density and “\( P \)” is the power density respectively \(^8\text{-}^{12}\).
Figure S1. Growth of NiCo LDH over Ni-foam after hydrothermal reaction (10 h).
Figure S2. X-ray diffraction pattern of NiCo LDH grown on Ni-foam
Figure S3. FE-SEM micrograph of bare Ni-foam
Figure S4. The EDAX mapping depicted the homogeneous growth of Ni, CO, and O homogeneously distributed throughout the Ni-foam (A-E).
Figure S5 The EDAX mapping confirms the homogeneous distribution of Ni, Co, and O
Figure S6. BET surface area analysis (A) NiCo LDH-8 (B) NiCo LDH-6
Figure S7. Survey spectrum of NiCo LDH-10
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Figure S9. Electrochemical characterization of NiCo LDH-8 (A) Cyclic voltammetry (CV) profiles of NiCo LDH-6 (B) Charge-discharge profile of NiCo LDH electrode measured at various current densities (C) Specific capacitance (D) Specific capacity of the NiCo LDH electrode at various current densities
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<table>
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<th>Materials</th>
<th>Electrolyte</th>
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<th>Cycles</th>
<th>Capacitance retention (%)</th>
<th>Ref.</th>
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Table S1. Comparison of specific capacitance of other binder-free NiCo LDH work
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<th>Power density (W kg⁻¹)</th>
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<td>Co-Fe LDH@NiO-Ni//AC</td>
<td>22</td>
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<td>NiFe-LDH@MnO₂//NiFe-LDH@FeOOH</td>
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<td>NiCoFe-LDH//AC</td>
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<td>NiCo₂S₄/CFP//AC</td>
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<td>180</td>
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<td>NiCo₂S₄/GA//AC</td>
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Table S2. Energy density vs Power density of various binder-free NiCo LDH works.
References:


