Ni-Co layered double hydroxide coated on microsphere nanocomposite of graphene oxide and single-walled carbon nanohorns as supercapacitor electrode material

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Summary
Ni-Co layered double hydroxides (LDH) have received considerable attention as excellent pseudocapacitor electrode materials. In this paper, a novel utilization of the composite of graphene oxide (GO) and single-walled carbon nanohorns (SWCNHs) is reported as an effective substrate for LDH coatings. We successfully synthesized hierarchical nanostructures composed of Ni-Co LDH as well as microsphere composites of GO and oxidized SWCNHs (o-NH). A dense microsphere composite of GO and o-NH was synthesized using the spray-drying method (s-(GO/o-NH)). Subsequently, the prepared Ni-Co LDH nanosheets were directly coated on the s-(GO/o-NH) microspheres using the hydrothermal method (LDH@s-(GO/o-NH)). Moreover, the electrochemical characteristics of the LDH@s-(GO/o-NH) supercapacitor electrodes were evaluated in a 6 M KOH electrolyte. In the three-electrode system, the LDH@s-(GO/o-NH) composite electrode exhibited a significantly high gravimetric specific capacitance (1046 F g⁻¹ at 1 mV s⁻¹) and excellent specific capacitance retention (84% retention after 10 000 cycles at 100 mV s⁻¹) compared with 211 F g⁻¹ and 79% for the LDH@s-GO composite electrode, respectively. The supercapacitive behavior of the LDH@s-GO and LDH@s-(GO/o-NH) electrodes in the two-electrode system exhibited a trend similar to that of the three-electrode system. The superior electrochemical performance of the LDH@s-(GO/o-NH) composite electrode can be ascribed to its high electrical conductivity and pseudocapacitance, indicating that the s-(GO/o-NH) microsphere composite with an interconnected pore network structure can be utilized as a support for effectively coating Ni-Co LDH components. The LDH@s-(GO/o-NH) composite electrode is a promising candidate for pseudocapacitor applications because of its excellent electrochemical characteristics and facile synthesis, making it suitable for industrial and consumer applications.
1 | INTRODUCTION

Currently, clean and renewable energy applications are being investigated to solve the increasingly serious energy and environmental issues. The demand for more efficient energy storage devices, such as supercapacitors and rechargeable batteries, has significantly increased. In particular, supercapacitors have received considerable attention because of their high power density, fast charge/discharge rate, and long cycle stability. Supercapacitors are classified as electric double-layer capacitors (EDLCs) or pseudocapacitors, depending on their energy storage mechanism.\(^1\)–\(^3\) The charge storage in an EDLC is associated with a non-Faradaic process through physical adsorption and desorption of electrolyte ions at the interfaces between the electrode materials and electrolytes. Charge storage in pseudocapacitors is primarily based on reversible Faradaic reactions between the surface functional groups on the electrode materials and the electrolyte ions.

Porous carbon materials with various pore structures, such as activated carbons,\(^4\)–\(^5\) activated carbon fibers,\(^6\) carbon nanofibers,\(^7\)–\(^9\) carbon nanotubes (CNTs),\(^10\),\(^11\) graphene,\(^12\)–\(^15\) and single-walled carbon nanohorns (SWCNHs),\(^15\)–\(^20\) have been investigated as electrode materials for EDLC systems by non-Faradaic processes. For supercapacitor electrode applications, graphene oxide (GO) has attractive advantages, such as abundant functional groups and multidimensional electron transport pathways, but it also has serious disadvantages, including restacking of graphene sheets during the reduction process, nearly insulating characteristics, and low bulk density. SWCNHs have also been studied as supercapacitor electrode materials because of their large specific surface area (SSA), controllable pore structure, and high electrical conductivity.\(^15\)–\(^20\) Conical tubular-structured SWCNHs with diameters of 2 to 3 nm and lengths of 30 to 50 nm form stable spherical agglomerates with diameters of 80 to 100 nm and have closed graphitic single-wall structures similar to those of single-walled CNTs (SWCNTs) (Figure S1). However, unlike SWCNTs with high crystallinity, SWCNHs have many structural defects (e.g., pentagons and heptagons) such that nanoscale holes are easily formed on the surface of SWCNHs in oxidizing atmospheres, resulting in a high SSA.\(^16\),\(^18\),\(^20\),\(^21\) Our previous study reported that a graphene/SWCNH composite supercapacitor electrode with a high electrode bulk density (1.23 g cm\(^{-3}\)), bulk density of commercial activated carbon electrode: 0.65 g cm\(^{-3}\)) and a large SSA (786 m\(^2\) g\(^{-1}\)) was prepared using spray-drying followed by thermal reduction, resulting in excellent electrochemical performance with a lower sheet resistance (0.005 \(\Omega\) sq\(^{-1}\)) and higher specific volumetric capacitance (80 F cm\(^{-3}\) at 1 A g\(^{-1}\)) in an organic electrolyte system compared with commercial activated carbon electrodes (0.293 \(\Omega\) sq\(^{-1}\) and 57 F cm\(^{-3}\) at 1 A g\(^{-1}\), respectively).\(^15\) However, because the high-density graphene/SWCNH composite was an EDLC-type supercapacitor electrode, it showed relatively low specific capacitance values compared with previously reported pseudocapacitor-type electrodes.\(^22\)

Supercapacitor electrodes using metal hydroxides,\(^23\)–\(^27\) metal oxides,\(^28\)–\(^35\) and conducting polymers\(^36\)–\(^38\) are considered highly suitable candidates for pseudocapacitive energy storage systems because of the reversible Faradaic reactions at the interfaces between the electrode materials and electrolytes. In particular, Ni(OH)\(_2\) and Co(OH)\(_2\) nanostructures with controllable architectures are promising electrode materials for supercapacitor applications because of their low cost, abundance, environmental friendliness, and excellent electrochemical performance.\(^23\)–\(^27\) Ni(OH)\(_2\) and Co(OH)\(_2\) nanostructures have been synthesized primarily by hydrothermal and electrochemical deposition methods.\(^23\)–\(^27\) The electrochemical performances of Ni(OH)\(_2\) and Co(OH)\(_2\) electrodes are greatly affected by their structures and morphologies. To improve the supercapacitive performance of Ni(OH)\(_2\) and Co(OH)\(_2\) electrodes, composite materials of Ni(OH)\(_2\) and Co(OH)\(_2\) nanostructures and carbon materials (graphene, CNT, etc.) with porous structures and high electrical conductivities have been investigated.\(^23\)–\(^27\) Su et al synthesized hollow-structured Ni(OH)\(_2\)/Co(OH)\(_2\)/rGO composite exhibited an extremely high specific capacitance (1292.8 F g\(^{-1}\) at 1 A g\(^{-1}\)) and stable cycle retention (85.9% after 2500 cycles). Ghosh et al reported hierarchical Co(OH)\(_2\)CO\(_3\) and Ni(OH)\(_2\) porous architecture supported by carbon fibers, with a maximum specific capacitance of 789 F g\(^{-1}\) at 2 A g\(^{-1}\) using a hydrothermal method.\(^25\) Bao et al synthesized metal-organic framework-derived α-Co/Ni(OH)\(_2\)/Co\(_3\)O\(_4\) hollow nanocages with superior specific capacitance (1000 F g\(^{-1}\) at 1 A g\(^{-1}\)) using...
a neoteric top-down etching and in situ oxidizing strategy processes.\textsuperscript{26} Zhou et al reported heterojunction $\alpha$-Co(OH)$_2$/\textit{a}-Ni(OH)$_2$ nanorods using a hydrothermal method.\textsuperscript{27} The Ni(OH)$_2$/rGO/Ni(OH)$_2$/rGO composite electrode with layer-by-layer construction showed a high specific capacitance (981.5 F g$^{-1}$ at 0.1 A g$^{-1}$) and excellent cycle retention (123.6% at 5 A g$^{-1}$ after 10,000 cycles). Previous studies have indicated that the supercapacitive behavior of Ni(OH)$_2$/Co(OH)$_2$/carbon composite electrodes strongly depends on the structure, morphology, and intrinsic properties of carbonaceous substrates. Moreover, the electrochemical performance of Ni-Co layered double hydroxide (LDH) electrodes is much superior to that of Ni or Co hydroxide, as supported by various previous studies.\textsuperscript{39,40} Song et al reported that exfoliated LDH materials in solution have superior surface activity compared to that of bulk or layered hydroxides.\textsuperscript{39} Chen et al reported that the electrochemical performance of Ni-Co LDH electrodes is superior to that of Ni or Co hydroxide, which is associated with the easy access and deep diffusion of electrolytes, improved electron transportation from the active material to the current collector, and enhanced pseudocapacitance contribution of Ni-Co LDH.\textsuperscript{40}

In this study, we propose an efficient two-step strategy to synthesize composite materials of Ni-Co LDH with superior surface activity, GO, and oxidized SWCNH (o-NH). In the first step, a mixture of GO and o-NH was spray-dried to prepare spherical nanocomposite particles, which were suitable for mass production because of the facile and cost-effective process (s-(GO/o-NH)). In the second step, ultrathin Ni-Co LDH nanosheets were coated on the spherical particles of s-(GO/o-NH) using hydrothermal treatment (LDH@s-(GO/o-NH)). The effects of the carbonaceous substrate structure on the morphology and electrochemical performance of Ni-Co LDH were investigated by comparing s-(GO/o-NH) and spray-dried GO (s-GO) as carbonaceous substrates. Finally, the pseudocapacitive behavior of the composite electrodes was investigated in terms of their specific capacitance and cycle performance for potential application as supercapacitor electrodes.

2 \ | \ EXPERIMENTAL

2.1 \ | \ Materials

The GO nanoparticles were purchased from Standard Graphene (GO-V50, Korea). Pristine SWCNHs (p-NH), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), hexamethylenetetramine (C$_6$H$_{12}$N$_4$), and trisodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O) were purchased from Sigma-Aldrich (USA). Subsequently, other materials were synthesized as follows: (a) To fabricate o-NH, p-NH powder (50 mg) was added to HNO$_3$ (500 mL, 70%) and stirred for 48 hours at 25°C. The HNO$_3$-treated p-NH was then filtered using a polystyrene membrane filter and washed several times with deionized (DI) water and ethanol. Finally, the resulting black powder was freeze-dried (o-NH). (b) To fabricate s-GO, the GO powder (1.0 g) was dispersed in DI water (100 mL) for 0.5 hours using a horn-type ultrasonicator (300 W, 1-s pulse on and 1-s pulse off). The GO suspension was then spray-dried using hot air flow at 200°C (s-GO). (c) To fabricate s-(GO/o-NH), a mixed suspension of GO and o-NH with a weight ratio of 1:1 (total sample weight of 1 g) was spray-dried under the same conditions as s-GO (s-(GO/o-NH)). In addition, Ni-Co LDH-coated carbonaceous nanocomposites were fabricated. (d) To fabricate LDH@s-GO, the s-GO powder (100 mg) was dispersed in DI water (400 mL) containing Ni(NO$_3$)$_2$·6H$_2$O (2 mmol), Co(NO$_3$)$_2$·6H$_2$O (4 mmol), C$_6$H$_{12}$N$_4$ (5 mmol), and Na$_3$C$_6$H$_5$O$_7$·2H$_2$O (0.5 mmol); this mixture was then refluxed at 90°C for 6 hours. The Ni-Co LDH-coated s-GO was collected by centrifugation (5000 rpm for 0.5 hours), washed with DI water and ethanol several times, and then freeze-dried (LDH@s-GO). (e) LDH@s-(GO/o-NH) was also fabricated under the same conditions as LDH@s-GO (LDH@s-(GO/o-NH)). The preparation processes for LDH@s-GO and LDH@s-(GO/o-NH) are schematically represented in Figure 1.

2.2 \ | \ Characterization

The morphologies of the composite materials were characterized using field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450, FEI, USA), energy-dispersive X-ray spectroscopy (EDX, Verios 460, FEI, USA), and high-resolution transmission electron microscopy (HR-TEM, Tecnai G2 F20, FEI, USA). The surface chemical structures of the composite materials were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha instrument, USA) using incident monochromatic Al-K$_\alpha$ radiation (1486.6 eV) under vacuum (<10$^{-8}$ Pa) at room temperature. All the XPS spectra were calibrated using the C 1s peak at 284.4 eV. Raman spectroscopy was performed using an excitation laser with a wavelength of 514 nm (inVia Reflex Raman microscope, Renishaw, UK). X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku SmartLab, Japan) with Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm) to confirm the crystalline structure of the
composite materials. Thermogravimetric analysis (TGA, TA Q50, TA Instruments, USA) was carried out in an air atmosphere with a heating rate of 10°C min⁻¹ in the temperature range of 40°C to 1000°C. The pore structures of composite materials were determined using N₂ adsorption isotherms at −196°C (BELSORP-max, Microtrac-BEL, Japan) after pre-evacuation for 2 hours at 150°C. The SSAs and micropore volumes were determined using α₃ plots. The total pore volumes were calculated from the N₂ adsorption amount at a relative pressure (P/P₀) of 0.99. The pore size distributions were determined using the Barrett-Joyner-Halenda (BJH) method.

2.3 Cell fabrication and electrochemical measurements

The electrochemical properties were measured using an electrochemical analyzer (ZIVE-SP2, WonA Tech, Korea) with conventional two- and three-electrode cell configurations in 6 M KOH electrolyte at 25°C. To evaluate the two-electrode electrochemical performance, supercapacitor electrodes with diameters of 15 mm were fabricated by mixing the active material (LDH@s-GO or LDH@s-(GO/α-NH) at 80 wt%), conducting material (carbon black [Super P] at 10 wt%), and binder (polytetrafluoroethylene at 10 wt%). These cells were fabricated by inserting a glass fiber separator (thickness of 240 μm, Whatman Inc.) between both electrodes. Moreover, a Ni foil was used as the current collector. Galvanostatic charge/discharge (GCD) measurements were performed using an automatic battery cycler system (WBCS3000, WonA Tech, Korea) at a potential of 0 to 1 V at a current density of 0.1 to 10 A g⁻¹. Specific capacitance values (Cₛ) were calculated from the GCD curves.

Working electrodes were fabricated to evaluate the three-electrode electrochemical performance of the synthesized samples. The working electrodes were prepared as follows: 5 wt% Nafion solution (100 μL) was added as a binder to 1 mL of a 4:1 volume ratio of DI water/ethanol. Subsequently, the samples weighing 4 mg were dispersed in a bath-type ultrasonicator for 0.5 hours to obtain homogeneous ink solutions. Finally, 1 μL of ink solution was loaded onto a working electrode with a diameter of 3 mm. The working, reference, and counter electrodes were fabricated using active material-coated glass carbon, Ag/AgCl, and Pt wire, respectively. Cyclic voltammetry (CV) measurements were performed between −0.2 and 0.4 V at scan rates ranging from 1 to 100 mV s⁻¹. The gravimetric capacitances of the three-electrode system were calculated from the CV plots using Equation (1):

\[ C_g = \frac{1}{ms(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV, \]  

where \( C_g \) is the gravimetric capacitance (F g⁻¹), \( s \) is the potential scan rate, \( m \) is the total weight of the active material (g), \( V \) is the potential window, and the integration of \( I(V)dV \) is the discharging part of the CV. The contribution of the Ni-Co LDH component to the gravimetric capacitance was calculated using Equation (2):

\[ C_{sp}^{LDH} = \frac{C_{sp}^{LDH}}{m_{LDH}} = \frac{m_{carbon}}{m_{LDH}} \left\{ C_{sp}^{total} \left( 1 + \frac{m_{LDH}}{m_{carbon}} \right) - C_{sp}^{carbon} \right\}, \]

where \( C_{sp}^{LDH} \) is the specific capacitance of the Ni-Co LDH component (F g⁻¹); \( C_{sp}^{total} \) is the total capacitance (F); \( m_{LDH} \) and \( m_{carbon} \) are the weights of the Ni-Co LDH and carbon components, respectively (g); \( C_{sp}^{carbon} \) is the specific capacitance of the carbon component (F g⁻¹). Finally, electrochemical impedance spectroscopy (EIS) measurements were performed.
in the frequency range of 100 mHz to 1 MHz at 1.0 V (ZIVESP2, WonA Tech, Korea).

3 | RESULTS AND DISCUSSION

After spray-drying the GO solution, s-GO showed a crumpled paper-like morphology because of rapid solvent evaporation during the spray-drying process (Figure 2A). In our previous study, we reported that the weight ratio of GO to o-NH was a key factor in the formation of a stable spherical structure. The GO/o-NH mixture weight ratio of 1:1 was the most stable condition for the formation of a dense spherical structure because the GO nanosheets could fully envelop the o-NH nanoparticles during the spray-drying process (Figure 2C). This morphological distinction between s-GO and s-(GO/o-NH) can be explained by the filling of o-NH nanoparticles into the interstitial spaces between the GO nanosheets during the spray-drying process. The diameters of the s-GO and s-(GO/o-NH) microspheres averaged approximately 4 to 5 μm. Previous studies have reported that the nucleation, growth, and morphology of LDHs on carbonaceous substrates can be controlled by adding Na3C6H5O7·C12H2O. In the absence of Na3C6H5O7·C12H2O, thin LDH coating layers with a distorted hierarchical structure were formed on the external surface of the carbonaceous substrates. The LDH@s-GO and LDH@s-(GO/o-NH) samples exhibited a three-dimensional hierarchical structure of thin Ni-Co LDH nanosheet-coated microflower-like structures (Figure 2B,D). The lateral size and thickness of the Ni-Co LDH nanosheets on s-GO were several hundred nanometers and 200 to 300 nm, respectively. For comparison, LDH@s-(GO/o-NH) was composed of thin Ni-Co LDH nanosheets with a thickness of approximately 10 to 50 nm (Figure S2). LDH@s-GO exhibited an irregular crumpled paper-like structure, whereas LDH@s-(GO/o-NH) still maintained a dense spherical structure, depending on the structure of the carbonaceous substrates. Additionally, EDX mapping analysis of the LDH@s-(GO/o-NH) microsphere surface was performed to confirm the Ni-Co LDH coating states. Figure 3 shows the FE-SEM and EDX mapping images of the LDH@s-(GO/o-NH) microspheres with diameters of 5 to 10 μm. The uniform distribution of C, O, Ni, and Co on the LDH@s-(GO/o-NH) surface was confirmed by the EDX mapping analysis, indicating the successful coating of Ni-Co LDH on the surface of s-(GO/o-NH) (Figure 3C-F).

HR-TEM observations were performed to better understand the morphological structure of the microspheres (Figure 4). The s-GO appeared as semi-transparent images (Figure 4A), whereas the s-(GO/o-NH) appeared as black spherical images (Figure 4C). These results can be explained by the filling effect of o-NH nanoparticles with respect to the GO structure during the spray-drying process, depending on the presence of o-NH nanoparticles. As shown in the HR-TEM image of LDH@s-GO with a diameter of approximately 6 μm, Ni-Co LDH nanosheets with a thickness of approximately 200 to 300 nm were coated on the s-GO surface (Figure 4B). In contrast, LDH@s-(GO/o-NH) was coated with Ni-Co LDH nanosheets with a thickness of only a few nanometers, while maintaining the spherical morphology (Figure 4D). The morphological differences between LDH@s-GO and LDH@s-(GO/o-NH) can be attributed to the different growth structures of the Ni-Co LDH layers because of the distinct porosity of the carbonaceous substrates. The pore structures of the samples are discussed in detail later in this paper. According to the HR-TEM images of LDH@s-GO and LDH@s-(GO/o-
NH), the LDH@s-(GO/o-NH) structure may provide a stronger interfacial bonding strength between the Ni-Co LDH nanostructure and carbonaceous substrate, compared with that for the LDH@s-GO structure (schematic illustrations in Figure 4B,D).

XPS measurements were performed to confirm the surface chemical species of LDH@s-(GO/o-NH) (Figure 5). The survey XPS spectrum of LDH@s-(GO/o-NH) showed the presence of C, O, Ni, and Co (Figure 5A). Moreover, Figure 5A shows the atomic percentages of C, O, Ni, and Co in LDH@s-(GO/o-NH). The atomic percentage ratio of Ni to Co was similar to the atomic ratio of 1:2 when they were used as precursors in the synthesis, showing a trend similar to that of LDH@s-GO (Figure S3A). The obtained XPS results were in good agreement with previously reported results for Ni-Co LDHs. The deconvoluted C 1s XPS spectrum of LDH@s-(GO/o-NH) consisted of three carbonaceous components, corresponding to C−C/C=C, C−OH, and C=O groups near 284.8, 286.4, and 288.2 eV, respectively (Figure 5B). The deconvoluted O 1s XPS spectrum of LDH@s-(GO/o-NH) showed component peaks near 530.6, 531.6, and 532.5 eV, assigned to Ni/Co-OH, O−C=O, and C−OH functional groups on the sample surface, respectively (Figure 5C). As shown in the comparison of C 1s and O 1s XPS spectra of the two samples (Figure S3B,C), LDH@s-GO contained a much larger amount of C−OH functional groups than that for LDH@s-(GO/o-NH), which primarily originated from the surface chemical structure of the s-GO substrate. The
narrow-scan XPS spectra of Ni 2p and Co 2p of LDH@s-(GO/o-NH) exhibited main peaks at approximately 854 and 779 eV, respectively (Figure 5D,E). The Ni 2p_{3/2} and Ni 2p_{1/2} peaks were deconvoluted into satellites and two spin-orbit doublets were assigned to two oxidation states (Ni^{2+} and Ni^{3+}) (Figure 5D). In the Co 2p XPS spectrum, the Co 2p_{3/2} and Co 2p_{1/2} peaks were deconvoluted into satellites and two spin-orbit doublets were assigned to two oxidation states (Co^{2+} and Co^{3+}) (Figure 5E). Based on these calculations, LDH@s-(GO/o-NH) contained higher amounts of Ni^{3+} and Co^{3+} ions than Ni^{2+} and Co^{2+} ions (Figure 5D,E). The large amounts of Ni and Co oxidation states are expected to enable fast charge transport across the interface between the electrode and electrolyte. Overall, similar tendencies were observed in the Ni 2p and Co 2p XPS spectra of LDH@s-GO (Figure S3D,E).

The crystalline structures of s-GO, s-(GO/o-NH), LDH@s-GO, and LDH@s-(GO/o-NH) were observed using XRD (Figure 6A). Predominant carbon peaks at a 2θ value of approximately 10° assigned to the (001) plane were observed in the XRD patterns of s-GO and s-(GO/o-NH) (Figure S4). The carbon peak of s-(GO/o-NH) at approximately 25°, assigned to the (002) plane, can be attributed to the graphene-like structure of o-NH (Figure S4). After the Ni-Co LDH coating process, LDH@s-GO and LDH@s-(GO/o-NH) showed peaks at 9, 34, and 60°, assigned to the (003), (012), and (110) planes, respectively, which can be attributed to Ni(OH)_{2} and Co(OH)_{2}. LDH@s-GO and LDH@s-(GO/o-NH) also exhibited a strong diffraction peak for metal glycolate at 9°, assigned to the (003) plane associated with Ni-Co LDH coating layer. After the Ni-Co LDH coating process, the carbon peaks at the (001) and (002) planes nearly disappeared, indicating the successful coating of Ni-Co LDH nanosheets on the spherical composite structures of s-GO and s-(GO/o-NH).

Raman spectroscopy was used to identify the graphitic structure of the carbon materials. The Raman
spectra of all samples exhibited strong peaks for the G-band ($I_G$, graphitic structure) at 1585 to 1604 cm$^{-1}$ and the D-band ($I_D$, disordered structure) at 1338 to 1364 cm$^{-1}$ (Figure 6B). The $R$ values ($I_D/I_G$) were calculated from the integrated intensity ratio of the D-band to the G-band to quantitatively determine the defects in the carbon materials. Therefore, the relative defectiveness of the carbon samples was confirmed using the $R$ values. As shown in Figure 6B, the $s$-(GO/o-NH) (1.08) exhibited a higher $R$ value compared with that of s-GO (0.82) because of the increased defect concentration induced by the oxygen functional groups of o-NH. After Ni-Co LDH coating on s-GO and s-(GO/o-NH), the $R$ values of LDH@s-GO and LDH@s-(GO/o-NH) slightly increased, from 0.82 and 1.08 to 0.88 and 1.19, respectively, indicating that the Ni-Co LDH coating process did not significantly change the graphitic structure of carbonaceous substrates. The metal hydroxide peaks of LDH@s-GO and LDH@s-(GO/o-NH) were observed at approximately 500 cm$^{-1}$, which are associated with the overlapping peaks of Ni-O and Co-O vibration modes.

Figure S5 shows the TGA curves for s-GO, o-NH, s-(GO/o-NH), LDH@s-GO, and LDH@s-(GO/o-NH). The TGA curve of s-GO exhibited two main weight loss peaks. The first and second drastic weight losses at 200°C and 500°C were attributed to the decomposition of the O-based functional groups and thermal-oxidative decomposition of the graphene structure, respectively. Meanwhile, the TGA curve of o-NH exhibited one major weight loss peak, at 600°C, resulting from the thermal-oxidative decomposition of the NH structure. The TGA curve of s-(GO/o-NH) exhibited a thermal-oxidative decomposition behavior similar to that of s-GO. However, the weight loss at 500°C was considerably higher than that of s-GO, which may be associated with a lower combustion temperature for o-NH nanoparticles because of the accelerated decomposition by the neighboring GO nanosheets. The thermal-oxidative decomposition temperatures of LDH@s-GO and LDH@s-(GO/o-NH) decreased considerably to approximately 300°C. This result indicates that the transition metals and their oxides introduced during the Ni-Co LDH coating process played a catalytic role in the decomposition reactions of s-GO and o-NH with oxidative gases. From the TGA curves of LDH@s-GO and LDH@s-(GO/o-NH), the residual components after thermal oxidation at 1000°C were expected to be Ni and Co oxides. The contents of residual components were approximately 32.9 and 52.8 wt%, respectively.

The pore structures of s-GO, o-NH, s-(GO/o-NH), LDH@s-GO, and LDH@s-(GO/o-NH) were determined using $N_2$ adsorption isotherms at $-196°C$ (Figure 7A). The $N_2$ adsorption isotherm of the o-NH was type II, which is in good agreement with the previously reported result. The steep $N_2$ adsorption amount at low P/P$_0$ is related to both the interstitial pores between the adjacent SWCNHs and the internal pores formed by oxidation on the tips or sidewalls of the SWCNHs. The $N_2$ adsorption isotherm shape of s-GO exhibited a typical type-IV with a distinct hysteresis loop of intermediate shape between H3 and H4 types, indicating the presence of a mesopore structure. Likewise, the s-(GO/o-NH) showed a type-IV $N_2$ adsorption isotherm, with an H2-type hysteresis loop, which has a triangular shape with broad adsorption and steep desorption branches, indicating a mesoporous structure with an interconnected pore network resulting from hybrid spherical clusters containing GO nanosheets and o-NH nanoparticles. After the Ni-Co LDH coating process, the $N_2$ adsorption isotherms of LDH@s-GO and LDH@s-(GO/o-NH) also exhibited a type-II shape with relatively low adsorption capacities. The pore size distributions of s-GO, o-NH, s-(GO/o-NH), LDH@s-GO, and LDH@s-(GO/o-NH) are shown in Figure 7B and Figure S6. The average pore sizes of all the samples were found to be in the mesoporous region (Figure S6). In particular, s-GO exhibited a broad pore size distribution in the range of 1 to 100 nm, whereas s-(GO/o-NH) exhibited a pore size distribution of less than 20 nm, indicating the presence of narrow mesopores (Figure 7B). As shown in Table 1, s-GO exhibited relatively low total and micropore SSAs (158 and 28 m$^2$ g$^{-1}$, respectively), mostly composed of external SSAs (meso/...
macropore SSAs), whereas o-NH exhibited high total and micropore SSAs (953 and 606 m² g⁻¹, respectively). The total SSA of s-(GO/o-NH) (254 m² g⁻¹) was between those of s-GO and o-NH, indicating the mixing effect of s-GO and o-NH. After the Ni-Co LDH coating process, the drastic decreases in the total SSAs of LDH@s-GO (8 m² g⁻¹) and LDH@s-(GO/o-NH) (30 m² g⁻¹) were primarily a result of pore blocking by the large metal hydroxide particles. As a result, s-(GO/o-NH) mostly contained pores in the micropores and narrow mesopore (<20 nm) ranges, as well as abundant oxygen functionalities, resulting in the formation of thinner LDH layers with stronger bonding strength between the LDH nanosheets and carbonaceous substrate compared with that for s-GO.

CV, cycle retention, and EIS measurements were performed using two- and three-electrode systems in 6 M KOH aqueous electrolyte to evaluate the electrochemical properties of the supercapacitor electrodes fabricated with s-GO, s-(GO/o-NH), LDH@s-GO, and LDH@s-(GO/o-NH) as the active materials. In the three-electrode systems, the CV curves of the electrodes at scan rates ranging from 1 to 100 mV s⁻¹ and voltages ranging between −0.2 and 0.4 V are shown in Figure 8 and Figure S7. The s-GO and s-(GO/o-NH) electrodes exhibited rectangular CV curves, indicating a typical EDLC behavior (Figure S7). The CV curve area increased as the scan rate increased from 1 to 100 mV s⁻¹ while maintaining its shape. However, the LDH@s-GO and LDH@s-(GO/o-NH) electrodes exhibited a pair of redox reaction peaks in the potential range of −0.2 to 0.4 V, indicating pseudocapacitive characteristics (Figure 8A,B). Two pairs of broad redox peaks, attributed to the Ni-Co LDH layers, were observed because of the polarization of the Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ couples as well as the Ohmic resistance during the Faradaic reactions. The redox peak current increased almost linearly as the scan rate increased from 1 to 100 mV s⁻¹. In addition, the oxidation and reduction peaks shifted to higher and lower potentials, respectively.

Reversible redox reactions can be described using Equations (3) to (5).

\[
\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \tag{3}
\]

\[
\text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \tag{4}
\]

\[
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{Co}_2\text{O}_3 + \text{H}_2\text{O} + e^- \tag{5}
\]

Figure 8C shows the CV curves of LDH@s-GO and LDH@s-(GO/o-NH) supercapacitor electrodes at a scan
rate of 1 mV s\(^{-1}\). The CV curve of the LDH@s-(GO/o-NH) electrode exhibited two pairs of strong redox peaks. The CV curve of the LDH@s-(GO/o-NH) electrode exhibited a significantly larger integrated area and higher current response than those for the LDH@s-GO electrode, indicating superior pseudocapacitive performance resulting from the coating of Ni-Co LDH nanosheets with more electrochemically active sites.

As shown in Figure 8D and Figure S8, the gravimetric specific capacitances calculated from the CV curves at a scan rate of 1 mV s\(^{-1}\) were in the following order of magnitude: LDH@s-(GO/o-NH) (1046 F g\(^{-1}\)) > LDH@s-GO (211 F g\(^{-1}\)) > s-(GO/o-NH) (15 F g\(^{-1}\)) > s-GO (12 F g\(^{-1}\)). The gravimetric specific capacitances of all electrodes decreased as the scan rate increased from 1 to 100 mV s\(^{-1}\), originating from a sufficient immersion of the electrolyte into the active materials at a low scan rate. The gravimetric specific capacitance of the LDH@s-(GO/o-NH) electrode (1046 F g\(^{-1}\)) was approximately five times higher than that of the LDH@s-GO electrode (211 F g\(^{-1}\)) at a scan rate of 1 mV s\(^{-1}\). In general, the double-layer capacitance of the electrode materials is directly proportional to their SSA, as shown by the specific capacitance results of s-GO and s-(GO/o-NH) electrodes at scan rates of 1 to 100 mV s\(^{-1}\) (Figure S8). However, the pseudocapacitance behavior exhibited a completely different trend from that of the double-layer capacitance (Figure 8D). The pseudocapacitive contribution of the LDH@s-(GO/o-NH) electrode should be promoted by relatively stronger chemical interactions between the Ni-Co LDH nanosheets and s-(GO/o-NH) substrate surface, which has abundant oxygen functionalities compared with that of s-GO. This LDH@s-(GO/o-NH) structure as a supercapacitor electrode could accelerate the diffusion of electrolyte ions and enhance the mechanical stability of the electrode, which is due to the directly interconnected LDH nanosheets on the s-(GO/o-NH) substrate with a high electrical conductivity and the porous structure of the interconnected pore network. The s-(GO/o-NH) electrode (10.2 S m\(^{-1}\)) incorporated with o-NH nanoparticles could provide a higher electrical conductivity compared to that of the s-GO electrode (8.9 S m\(^{-1}\)). These results suggested that the o-NH nanoparticles were effectively inserted into the junctions.
between the GO nanosheets, resulting in the formation of more electrically conductive channels in the s-(GO/o-NH) composite via the electrical bridging effect. The LDH@s-(GO/o-NH) electrode exhibited a significantly high specific capacitance retention of 84% at a scan rate of 100 mV s\(^{-1}\) after 10 000 cycles (Figure 8E). In contrast, the LDH@s-GO electrode exhibited comparatively low capacitance retention of 79% at a scan rate of 100 mV s\(^{-1}\) after 10 000 cycles. Figure 8F shows the gravimetric specific capacitances calculated using only the LDH component of the LDH@s-GO and LDH@s-(GO/o-NH) electrodes in the three-electrode system. The LDH contents in LDH@s-GO and LDH@s-(GO/o-NH) were determined from the residual amounts of the TGA curves at 600°C. The gravimetric specific capacitance of the LDH@s-(GO/o-NH) electrode (1462 F g\(^{-1}\)) was also significantly higher than that of the LDH@s-GO electrode (328 F g\(^{-1}\)) at a scan rate of 1 mV s\(^{-1}\), indicating that the s-(GO/o-NH) structure provided a more effective substrate for supporting the Ni-Co LDH components with more electrochemically active sites than those for the s-GO substrate.

The electrochemical behaviors of LDH@s-GO and LDH@s-(GO/o-NH) were investigated in a two-electrode system. Figure 9A shows the GCD curves of LDH@s-(GO/o-NH) from 0.1 to 10 A g\(^{-1}\). Specific capacitances were calculated from the GCD curves. Figure 9B shows the specific capacitance retention of the LDH@s-GO and LDH@s-(GO/o-NH) electrodes as a function of the discharge current density from 0.1 to 10 A g\(^{-1}\). The LDH@s-GO and LDH@s-(GO/o-NH) electrodes had specific capacitance values of 687 and 1165 F g\(^{-1}\), respectively, at a discharge current density of 0.1 A g\(^{-1}\). The specific capacitances of both electrodes decreased with increasing discharge current density. The LDH@s-GO and LDH@s-(GO/o-NH) electrodes exhibited capacitance retentions of 87% and 82%, respectively, at a current density of 3 A g\(^{-1}\) after 10 000 cycles (Figure 9C). Figure 9D shows the gravimetric specific capacitances calculated using only the LDH components of the LDH@s-GO and LDH@s-(GO/o-NH) electrodes. The gravimetric specific capacitance of the LDH@s-(GO/o-NH) electrode (1629 F g\(^{-1}\)) was also much higher than that of the LDH@s-GO electrode (1065 F g\(^{-1}\)) at a scan rate of 0.1 A g\(^{-1}\). The supercapacitive behavior of the LDH@s-GO and LDH@s-(GO/o-NH) electrodes in the two-electrode system exhibited a trend similar to that of the three-electrode system, demonstrating that the structures and properties of the substrates for the LDH coating are crucial for maximizing the capacitive performance of the supercapacitor electrodes.

The EIS measurement results of the supercapacitor electrodes are shown as Nyquist plots in the frequency range of 100 mHz to 1 MHz in Figure 10. Both the LDH@s-GO and LDH@s-(GO/o-NH) electrodes exhibited a single semicircle in the high-frequency range. The resistance (R) of the LDH@s-(GO/o-NH) electrode in the electrolyte was significantly lower (1.31 Ω) than that of the LDH@s-GO electrode (2.57 Ω). The charge-transfer resistance (R\(_{CT}\)) values were calculated from the diameters of
the semicircles. The $R_{CT}$ is closely related to the electrical conductivity of electrodes at the interface of the electrodes and aqueous electrolytes.\textsuperscript{45,56} The $R_{CT}$ of the LDH@s-(GO/o-NH) electrode in the electrolyte had a lower value (3.47 $\Omega$) than that of the LDH@s-GO electrode (4.16 $\Omega$). The straight line in the low-frequency region, known as the Warburg impedance (diffusion impedance), of the LDH@s-(GO/o-NH) electrode showed a much steeper slope than that of the LDH@s-GO electrode, indicating the enhanced diffusion behavior of electrolyte ions at the electrode surface.\textsuperscript{45,56}

These resistance results obtained from EIS measurements showed a trend similar to the measured electrical conductivity values of the LDH@s-GO (4.3 S m$^{-1}$) and LDH@s-(GO/o-NH) (7.1 S m$^{-1}$) electrodes. Therefore, the LDH@s-(GO/o-NH) supercapacitor electrode exhibited a superior electrochemical performance (high gravimetric specific capacitance, strong redox reaction, low charge transfer resistance, and stable cycle performance) compared to that of the LDH@s-GO electrode.

Figure 11 shows the Ragone plot for comparing the power and energy densities of the LDH@s-(GO/o-NH) electrode, which was derived from the GCD curves, with the previously reported LDH-based supercapacitor electrodes. The LDH@s-(GO/o-NH) electrode exhibited a high energy density of 25.9 Wh kg$^{-1}$ at a power density of 100 W kg$^{-1}$, maintaining 16.7 Wh kg$^{-1}$ at a high power density of 7500 W kg$^{-1}$. Moreover, the Ragone plot clearly demonstrated the superior performance of the LDH@s-(GO/o-NH) supercapacitor electrode compared to those of various recently reported LDH-based supercapacitor electrodes.\textsuperscript{57-63}

4 | CONCLUSIONS

In this study, Ni-Co LDH nanosheets were directly coated onto s-(GO/o-NH) microspheres to develop a nanostructured electrode material for pseudocapacitive energy storage applications. The s-(GO/o-NH) composites exhibited a relatively high SSA and electrical conductivity, providing a large effective surface area for contact and reactions between the active materials and electrolyte ions during the electrochemical process. The s-(GO/o-NH) microsphere composite with an interconnected pore network structure was successfully utilized as an effective support for coating Ni-Co LDH components. In a three-electrode system, the LDH@s-(GO/o-NH) composite electrode exhibited a significantly high gravimetric specific capacitance (1046 F g$^{-1}$ at 1 mV s$^{-1}$) and excellent specific capacitance retention (84% retention after 10 000 cycles at 100 mV s$^{-1}$) in an aqueous electrolyte system compared with 211 F g$^{-1}$ and 79%, respectively, for the LDH@s-GO composite electrode. These results could be ascribed to the high electrical conductivity and pseudocapacitance due to the nanohybrid composite structure of s-(GO/o-NH) and coated Ni-Co LDH components, respectively. The LDH@s-(GO/o-NH) composite electrode is a promising candidate for pseudocapacitor applications because of its excellent electrochemical characteristics and facile synthesis, making it suitable for industrial and consumer applications.

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SUPPORTING INFORMATION
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