Supporting Information for

Post-Synthesis Isomorphous Substitution of Layered Co-Mn Hydroxide Nanocones with Graphene Oxide as High-Performance Supercapacitor Electrodes

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EXPERIMENTAL SECTION

All chemicals of analytical grade were purchased from Wako chemical Reagents Company (Japan). They were used without further purification. Milli-Q water was used throughout the experiments.

Materials Synthesis. Layered $Co(OH)_2$ NCs were prepared via an oil bath synthesis. In a typical synthesis, $CoCl_2 \cdot 6H_2O$ (99.5%, 2.5 mmol), urea (99.0%, 17.5 mmol) and SDS (98.0%, 6.24 mmol) were charged into a three-neck flask and dissolved in 250 mL Milli-Q water under stirring at room temperature. The flask was then placed in an oil bath and heated at 110 °C for 8 h under continuous magnetic stirring and nitrogen as gas protection. The resulting product was

centrifuged, washed with Milli-Q water and absolute ethanol for 5 times, and finally dried in air at 60 °C for 8 h.

Layered Co-Mn hydroxide NCs were prepared by a two-step oil bath synthesis. In a typical synthesis, $CoCl_2 \cdot 6H_2O$ (99.5%, 1.67 mmol), urea (99.0%, 17.5 mmol) and SDS (98.0%, 4.16 mmol) were charged into a three-neck flask and dissolved in 250 mL Milli-Q water under stirring at room temperature. The flask was then placed in an oil bath and heated at 110 °C for 6 h under continuous magnetic stirring and a nitrogen gas protection. The resulting product was centrifuged, washed with Milli-Q water and absolute ethanol for 1 time. And then, the product, 8.33 mmol $MnCl_2 \cdot 4H_2O$, 2.08 mmol SDS were charged into the three-neck flask, dissolved in 250 mL Milli-Q water again and the flask was then placed in the oil bath. The reaction was carried out under the same conditions for 2 h. The resulting product was centrifuged, washed with Milli-Q water and absolute ethanol for 5 times, and finally dried in air at 60 °C for 8 h.

Graphene oxide was synthesized through a modified Hummers method. The purified graphite was stirred in a mixed solution of H_2SO_4 (50 mL) and KNO_3 (1.2 g) to obtain a suspension, and then 6 g of $KMnO_4$ was slowly added. After 6 hours, 30 mL of Milli-Q water was added to the suspension and it was kept below 80 ^oC in a cooling bath. Afterwards, 200 mL Milli-Q water was further added, and then 6 mL H_2O_2 (30 wt %) was slowly added dropwise. Thereafter, the suspension was stirred for 1 hour and finally diluted with water to 1000 mL. After that, the suspension was stirred for 1 hour and finally diluted with water to 1000 mL. Finally, the suspension was repeatedly decanted for several times until the pH reached 5. In order to exfoliate the graphene slurry in water, ultrasonic treatment was performed for 2 hours to synthesize a brown graphene oxide nanosheet colloidal suspension.

GO/Co-Mn NCs was prepared by a facile physical mixing method. The layered Co-Mn hydroxide nanocones (0.02 g) and 3 mL graphene oxide (1 g L^{-1}) were charged into a PETE bottle and dissolved in 7 mL absolute ethanol. And then, the PETE bottle was put onto the magnetic stirrer for 24 h. Finally, removed the absolute ethanol by centrifugation and dried in air at 60 °C for 8 h.

Materials Characterization. The crystallographic structures of the materials were determined by a RIGAKU Miniflex 600 X-ray diffractometer equipped with Cu-Ka radiation (λ= 1.54184 Å). The microstructure and morphology of the as-prepared products were examined by scanning electron microscopy (FEI, Helios Nanolab 600i). And transmission electron microscopy, selected area electron diffraction and high-resolution transmission electron microscopy (TEM, SAED, HRTEM) were obtained with a Tecnai G2 F20 field emission transmission electron microscope operated at 200 kV. Atomic force microscope (AFM) images were acquired in tapping mode using a Si tip cantilever with a force constant of about 20 N/m. The X-ray photoelectron spectroscopy spectra were recorded with a Thermo Fisher ESCALAB 250Xi spectrophotometer.

Electrochemical Measurement. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were tested with a Gamry Interface 1000 electrochemical workstation, using a three electrode cell with 1 M KOH as the electrolyte, a Hg/HgO electrode as reference electrode, and platinum plate as counter electrode, respectively. For electrochemical measurements, layered $Co(OH)_2$ NCs, layered Co-Mn hydroxide NCs and GO/Co-Mn NCs were used as working electrodes. The working electrodes were prepared as follows: 80 wt. % of as-prepared products were mixed with 10 wt. % of acetylene black (>99.9%) and 10 wt. % Polyvinylidene Fluoride (PVDF, >99.9%) in an agate mortar until a homogeneous black powder was obtained. Then 300 μL of N-methyl-2-pyrrolidone (NMP) was added to obtain a homogeneous slurry. After stirring

with a magnetic stirrer for 24 h, the suspension was dropped on cleaned nickel foams. And the working electrodes were dried at 60 °C for 12 h in air and then were pressed under 40 MPa.

The specific capacity could be calculated based on the discharge curves using the equation:

$$C = \frac{I\,\Delta t}{m}$$

Where I is current discharge current, Δt is the time for a full discharge, and m indicates the mass of the active material. The electrochemical measurements of the asymmetric supercapacitor were carried out in a two-electrode cell in 1M KOH aqueous electrolyte solution. It was assembled using layered GO/Co-Mn hydroxide NCs as the positive electrode and active carbon (AC) as the negative electrode. The electrodes were separated by the diaphragm. In order to get the best performance, the conservation of charge between the two electrodes should follow $q^+ = q^-$ and the mass of the material of the positive and negative should be calculated by the next equations:

$$q = C * \Delta V * m$$

$$m^+/m^- = (C^- * \Delta V^-)/(C^+ * \Delta V^+)$$

Where C ($F \cdot g^{-1}$) is the specific capacitance of electrode, m (g) is the active materials mass on the electrode, and ΔV (V) is the potential window.

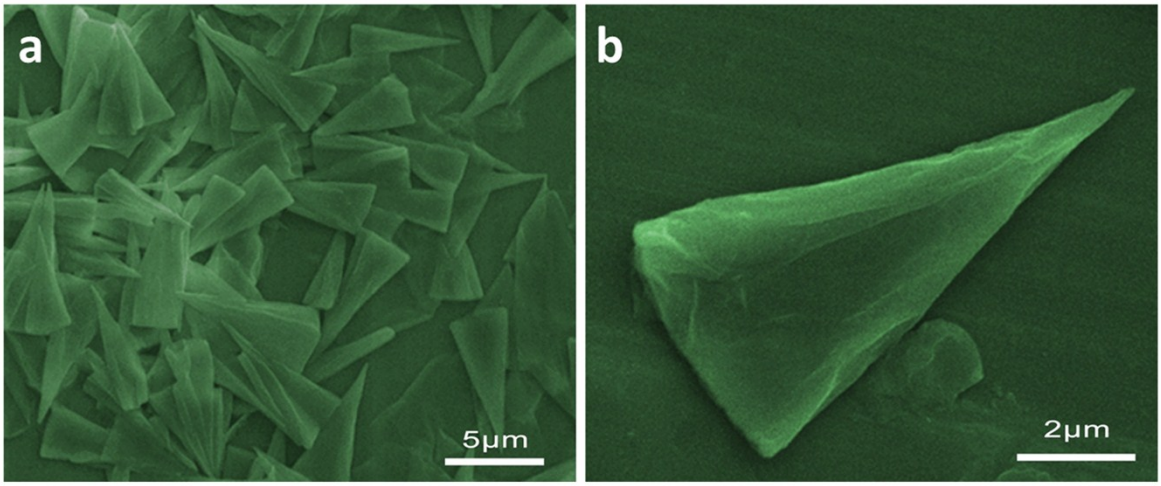

Figure S1. (a) Low-magnification and (b) High-magnification SEM images of layered $Co(OH)_2$ NCs.

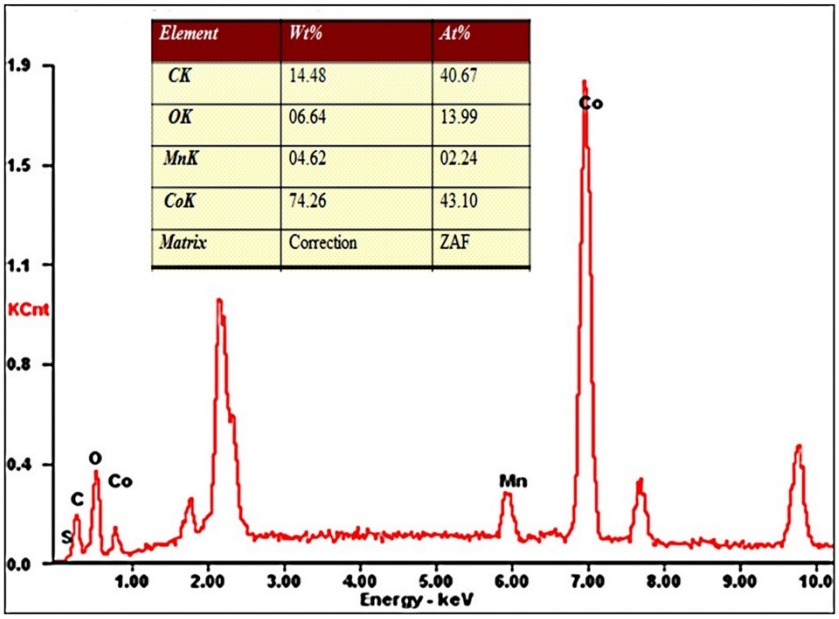

Figure S2. The EDS of layered Co-Mn hydroxide NCs.

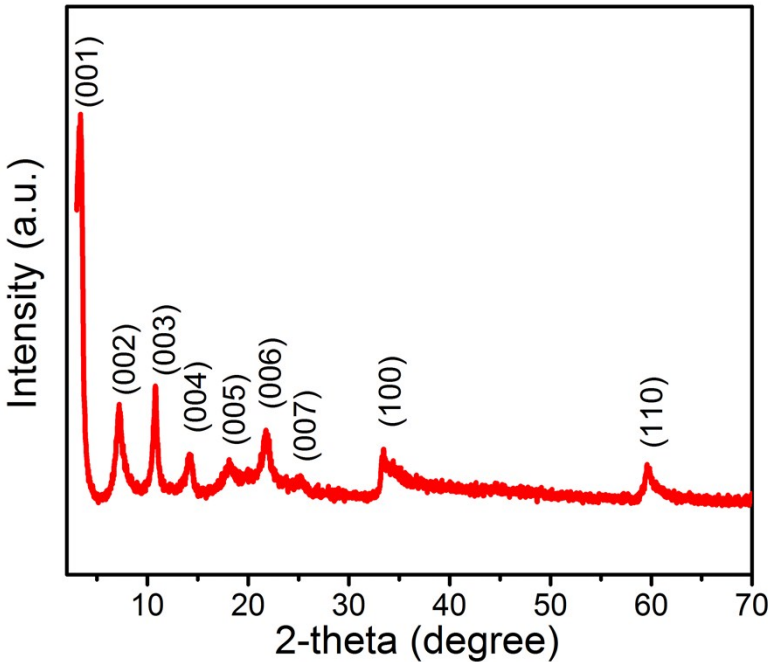

Figure S3. XRD pattern of the as-prepared GO/Co-Mn NCs.

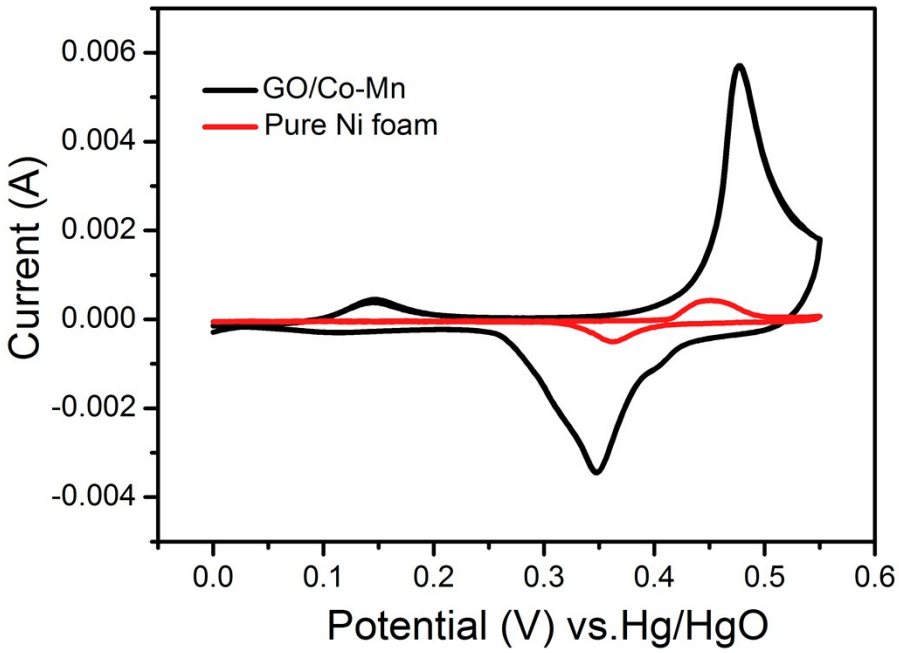

Figure S4. CV curves of the pure Ni foam and GO/Co-Mn NCs at the scan rate of 5 mV s^{-1}.

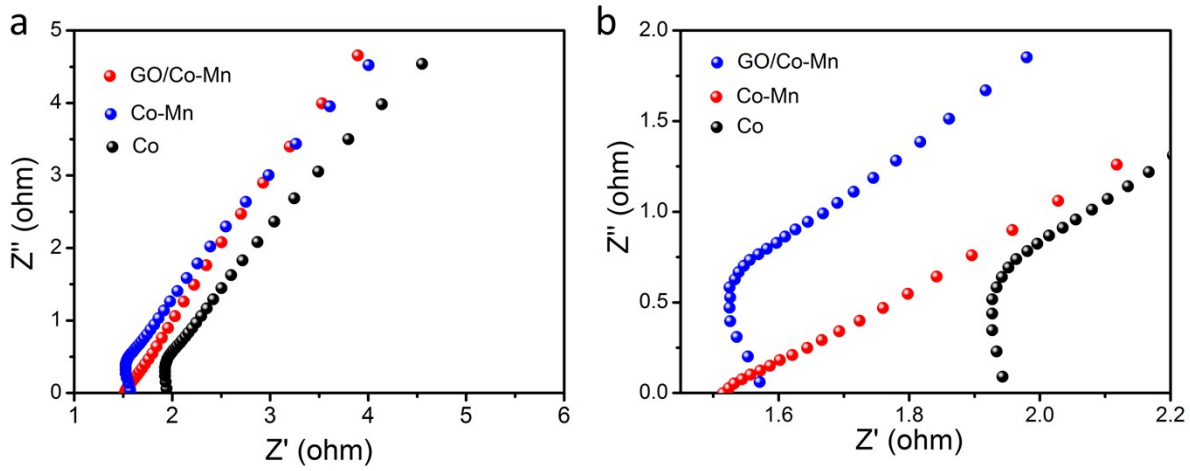

Figure S5. (a) Electrochemical impedance spectroscopy (EIS) of layered $Co(OH)_2$ NCs, layered Co-Mn hydroxide NCs, and GO/Co-Mn NCs electrodes, respectively; (b) The detail view of the EIS at high frequency region.

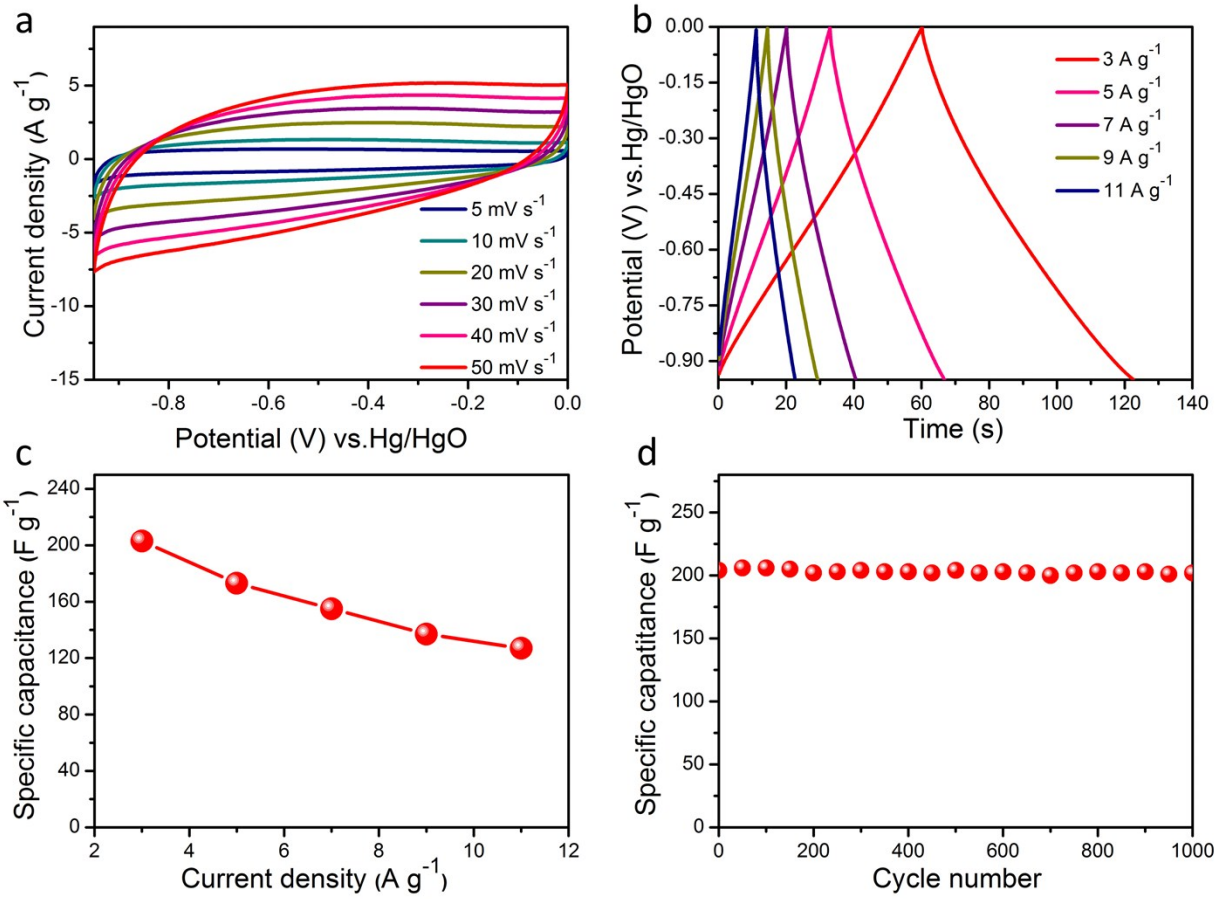

Figure S6. Electrochemical characterizations of the AC. (a) CV curves at various scan rates; (b) Galvanostatic charge/discharge curves at various current densities; (c) The corresponding specific capacitances at various densities; (d) The cycling performance at the current density of 3 A g^{-1}.

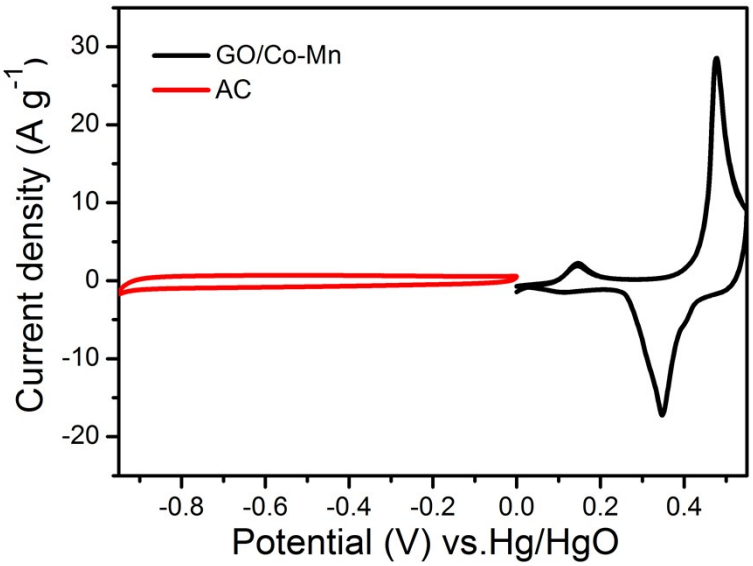

Figure S7: CV curve of the positive electrode GO/Co-Mn NCs and the negative electrode AC tested at 5 mV s^{-1}

Table S1. Comparison of the specific capacitance about some previous reported $Co(OH)_2$ based composite as the electrode materials of SCs.

Materials for electrodes of SCs	Current density ($A\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$)	Specific capacity ($C\ g^{-1}$)	Ref.
CoMn- LDH/CF	2	1079	863	12
Ni-Co hydroxide nanorod	3	1030	412	14
Mn-Co LDH hollow cages	2	511	223	15
Co-Al LDH@PEDOT core/shell NPA	1	672	437	16
Co-Al LDH NS	1	1031	515	17
$Co(OH)_2$/graphene/Ni foam	2	693.8	381.6	20
GO/Co-Mn composite	3	1231	1231	This work

Table S2. Comparation of the maximum energy density and power density of some previous reported $Co(OH)_2$ based composites as the electrode materials of ASCs.

Positive Materials	Negative Materials	Energy density ($Wh\ kg^{-1}$)	Power density ($W\ kg^{-1}$)	Ref.
Ni-Co hydroxide nanorod	CG	26.3	320	14
$Co(OH)_2$-nanowires	NTAC	13.1	1880	32
Ni-Co hydroxide nanoneedles embedded in GH	GH	32.74	320	33
NiCo double hydroxide	AC	25.3	2250	34
Co/Al-13 LDHs	rGO	34.7	390	35
CoMn-LDH	AC	4.4	2500	36
NiCo-T6	AC	40.1	801.2	37
PPy/rG-O//$Co(OH)_2$/NEMG	PPy/rG-O	24.9	224	38
GO/Co-Mn composite	AC	25.6	6734	This work