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Novel co-precipitation method for one-pot fabrication of Co-Ni multiphase composite electrode and its application to high energy-density pseudocapacitor

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Methods

Electrode fabrication with active material. A Co-Ni multiphase composite thin film was prepared by a new process (Fig *S*1). The cobalt precursor, cobalt nitrate hydrate ($Co(NO_3)_2{\cdot}6H_2O$) and the nickel precursor ($Ni(NO_3)_2{\cdot}6H_2O$) were added. The molar ratios of the $Co(NO_3)_2{\cdot}6H_2O$: $Ni(NO_3)_2{\cdot}6H_2O$ was 4 : 6. The composite preparation process was started after the addition of 100ml of 1M LiOH solution as the precipitant and 10ml of 2 M hydroxylamine NH_2OH solution as the chelating agent by applying 0.9 V between the electrodes overnight at room temperature (25°C). The titanium (Ti) substrate used was pre-coated with a commercial activated carbon to form the anode and pre-coated with acetylene black to form the cathode, respectively. The obtained electrode surfaces were rinsed with deionized water and finally dried overnight at 60°C in air. The final loading amount was 15mg.

FTIR studies. Fig *S*2 shows the FTIR spectrum of the Co-Ni multiphase composite thin films. From the spectrum, it can be seen that the broad band centred around 3400 cm^{-1} and 1500 cm^{-1} is assigned to the stretching vibration mode of -OH group and the strong band around 520 cm^{-1} is associated with the Co-O vibrations. The strong band observed around at 660 cm^{-1} corresponds to the Ni-O-H vibrations and the one around at 1380 cm^{-1} corresponds to the NiO_3^- vibrations.[1] In summary, the spectrum indicates the presence of Co-O, Ni-O-H and -OH groups. It also confirms that the composite material is in the α- phase. Thus the formation of the α- phase Co-Ni multiphase composite thin films is supported by the FTIR studies.[2, 3] The results also support the presence of $Co(OH)_2$, CoOOH, and $Ni(OH)_2$ found by the XPS analysis as discussed in our manuscript.

Cyclic voltammetry study. The capacitance performance was primarily determined due to these Faradic reactions.[4, 5]

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^- \quad (1)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (2)$$

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (3)$$

The specific capacitance C_{sp}, of the electrode can be calculated according to the following relation:

$$C = \frac{I \cdot t}{\Delta V} \quad (4)$$

where I is the discharge current [A], Δt is the discharge time [s] and ΔV is the potential window [V] of the discharge process, and m is the mass of the active materials [g].[6, 7]

Galvanostatic charge-discharge analysis. Fig *S*3 shows the galvanostatic charge-discharge curves at various current densities. The shape of the discharge curves shows pseudocapacitance similar to the result of the CV curves. The specific capacitances of the sample at the current density of 5 mA cm^{-2} was 840 F g^{-1}.

Energy density and power density analysis. Energy density of the electrode can be derivered from the CV curves using the following equation :

$$\mathrm{ED} = \frac{1}{2} \cdot C_{SP} \cdot \Delta V^2 \qquad (5)$$

where C_{sp} is specific capacitance (F) and ΔV is the potential window (V).[8, 9] The power density of the electrode can be calculated from the following equation:

$$\mathrm{PD} = \frac{\mathrm{ED}}{\Delta t} \qquad (6)$$

where ED is the energy density, and Δt is the discharge time (s).[9] The energy density of the composite film was about 38.9 Wh $\mathrm{kg^{-1}}$ at the scan rate of 1 mV $\mathrm{s^{-1}}$, whereas its power density was approximately 21 kW $\mathrm{kg^{-1}}$ at 1000 mV $\mathrm{s^{-1}}$. We also calculated the energy and power densities of other materials to compare with those of our material.[5, 10, 11, 12] The result is shown in Fig. *S*5. In fact, in previous studies, the electrochemical properties were already saturated. However, in our study on composite material electrodes made by the co-precipitation method, the electrochemical properties were similar or better.

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Table S1 The variation of pH with the amount of 1 M LiOH used as the precipitant in the Co-Ni solution. The fabrication method of the Co-Ni multiphase composite thin films mostly depends on pH control. The Co-Ni solution remains neutral after the reaction.

Molar ratio (Co:Ni)	1M LiOH Solution (ml)					
	0	30	60	90	100	100 (12h)
4:6	3.3	6.4	6.6	6.8	6.9	6.8

Table S2 EDX analysis of Co and Ni in the thin films fabricated with a given molar ratio of cobalt nitrate and nickel nitrate.

Molar ratio (Co:Ni)	Co(atomic %)	Ni(atomic %)	O(atomic %)
4:6	12.56	18.73	68.71

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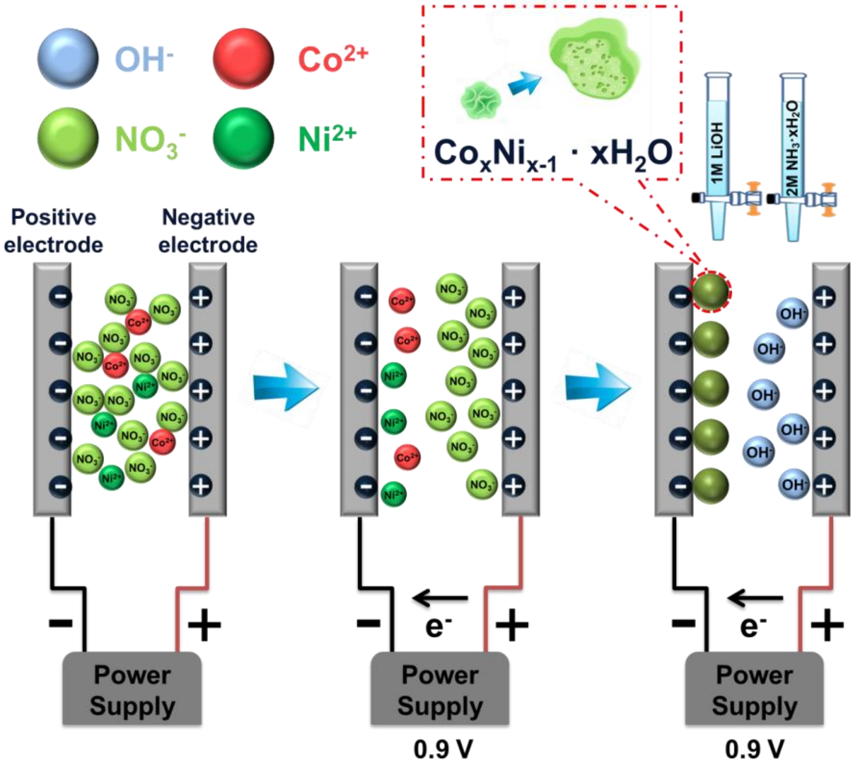

Fig. S1. Schematic drawing of the Co-Ni multiphase composite film and its synthetic process based on the novel co-precipitation method.

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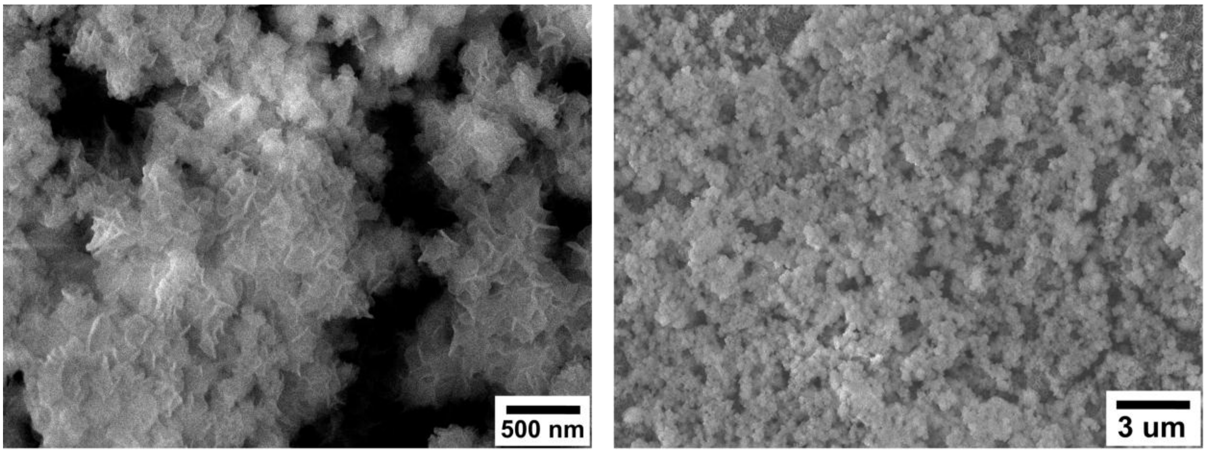

Fig *S*2. SEM images of the Co-Ni multiphase composite film showing its a corrugated morphology.

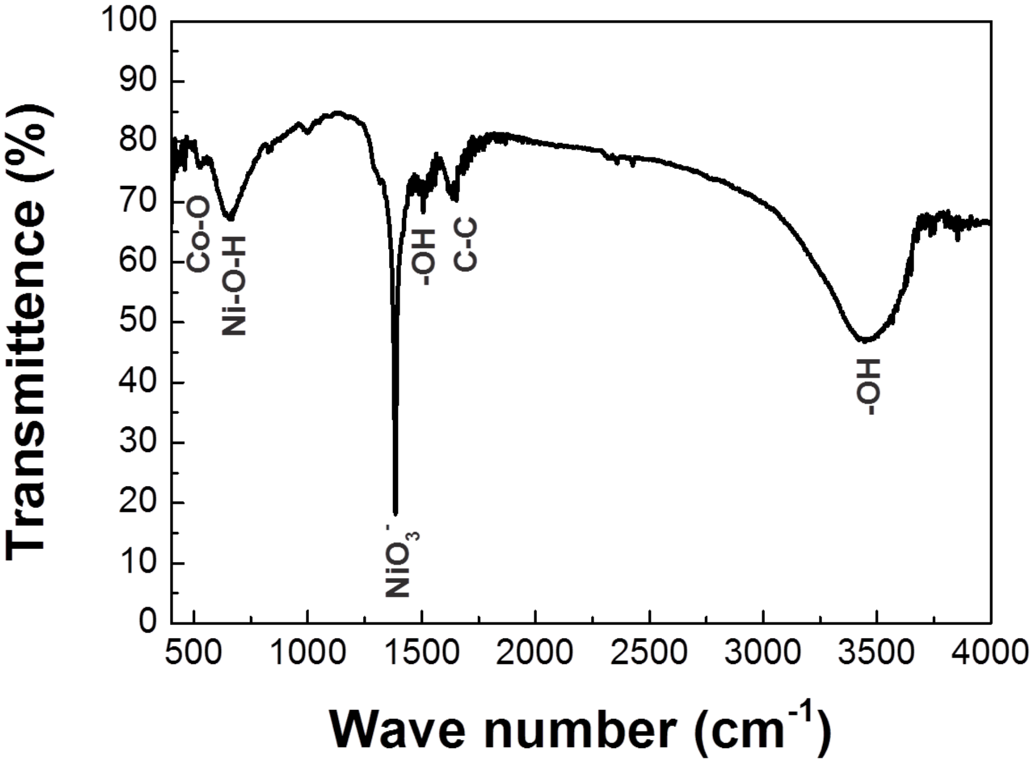

Fig *S*3. FTIR spectra of the Co-Ni multiphase composite film. Co-O, Ni-O-H, NiO_3^- and -OH groups appear around at 520 cm^{-1}, 660 cm^{-1}, 1380 cm^{-1}, 3400 cm^{-1} and 1500 cm^{-1}, respectively.

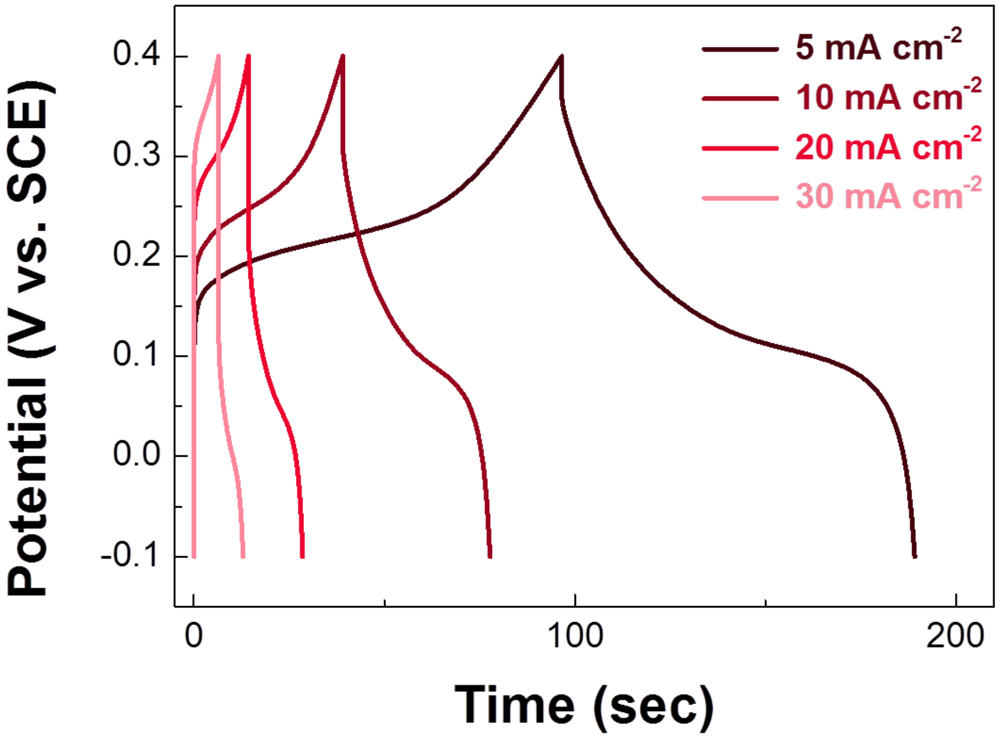

Fig. *S*4. The galvanostatic charge-discharge curves of the Co-Ni multiphase composite film at various current densities.

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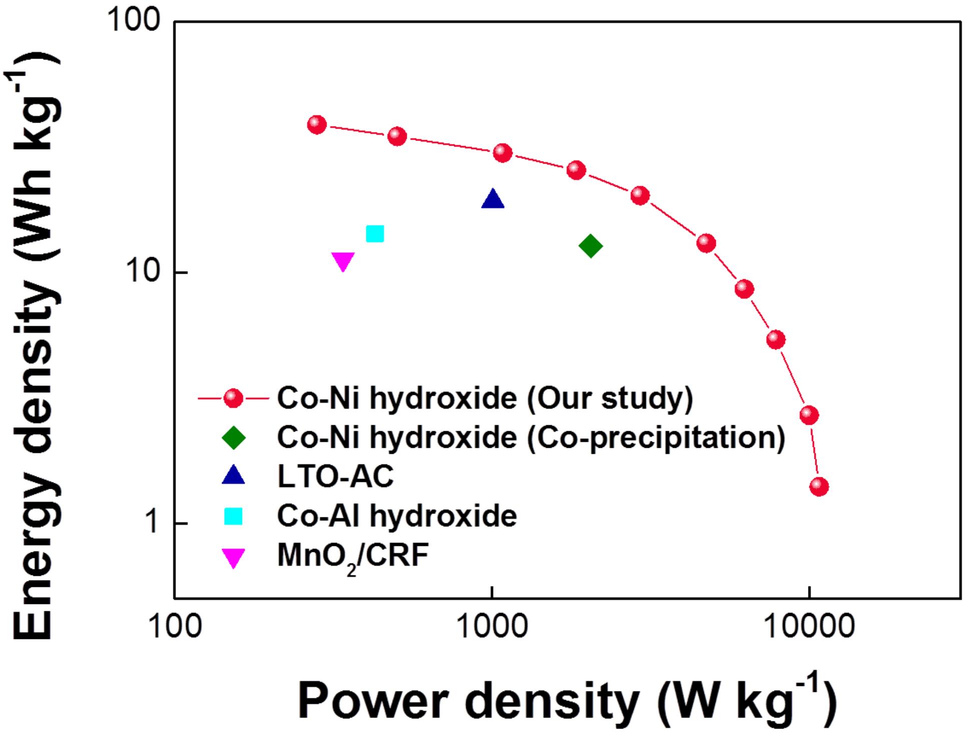

Fig. *S*5. Ragone plot representing the energy and power density in a supercapacitor of the Co-Ni multiphase composite film compared with those of other composite materials fabricated by various methods for supercapacitor