Electronic Supplemental information

Self-templated flower-like NiCoZn-carbonate hydroxides hollow nanospheres for asymmetric supercapacitors with high performance

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Evaluation of electrochemical measurements

The gravimetric specific capacitance of a single electrode in a three-electrode system was calculated from the GCD curve according to the following equation:

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

Where C is the specific capacitance (F g⁻¹), I is the discharge current (A), Δt is the discharge time (s), m is the mass of active material (g).

The specific capacitance of the asymmetric capacitor in a two-electrode system was obtained by the following equation:

$$C = \frac{I \times \Delta t}{M \times \Delta V}$$
(2)

Where C is the specific capacitance (F g⁻¹), M is the total mass of the positive and negative electrodes (g).

According to the charge matching principle, the optimal mass ratio of $Ni_1Co_1Zn_{0.25}$ -CH to AC is 1:3.57 to assemble asymmetric supercapacitors.

$$q_{+} = q_{-} \tag{3}$$

$$q = mCV \tag{4}$$

 $\frac{m_{+}}{m_{-}} = \frac{C_{-} \times V_{-}}{C_{+} \times V_{+}}$ (5)

Where *q* is the electrode charge, m_{+}/m_{-} is the mass of the positive/negative active material (g), C_{+}/C_{-} is the specific capacitance of the positive/negative material, V_{+}/V_{-} is the voltage window of the positive/negative electrode.

The power density (P) and the energy density (E) are calculated as follows:

$$E = \frac{C \times V^2}{2 \times 3.6}$$
(6)
$$P = \frac{3600 \times E}{\Delta t}$$
(7)



Fig. S1. SEM images of $Ni_1Co_1Zn_{0.25}$ -G prepared without the addition of PVP (K30) at different magnifications. **a**, low magnification. **b**, high magnification.

Fig. S1 shows SEM images of Ni₁Co₁Zn_{0.25}-G prepared without the addition of PVP (K30) at different magnifications. It can be seen that Ni₁Co₁Zn_{0.25}-G prepared without the addition of PVP (K30) is a ball-shape with a diameter of about 1.3 μ m, which are not completely uniform and some balls connect together.



Fig. S2. SEM images of NiCoZn-G prepared with different additions of Zn^{2+} . **a**, Ni₁Co₁Zn₀-G. **b**, Ni₁Co₁Zn_{0.25}-G. **c**, Ni₁Co₁Zn_{0.5}-G. **d**, Ni₁Co₁Zn₁-G.

SEM images of NiCoZn-G prepared with different additions of Zn^{2+} are shown in Fig. S2. The results indicate that NiCoZn-G prepared by the solvothermal reaction with different additions of Zn^{2+} is uniform and well dispersed with a diameter of about 400 nm, indicating that PVP (K30) plays the role of a stabilizer and size control agent.



Fig. S3. SEM images of NiCoZn-CH prepared with different additions of Zn^{2+} at different magnifications. **a-b**, Ni₁Co₁Zn₀-CH. **c-d**, Ni₁Co₁Zn_{0.25}-CH. **e-f**, Ni₁Co₁Zn_{0.5}-CH. **g-h**, Ni₁Co₁Zn₁-CH.

As shown in Fig. S3, the diameter of $Ni_1Co_1Zn_0$ -CH is about 500 nm, $Ni_1Co_1Zn_{0.25}$ -CH and $Ni_1Co_1Zn_{0.5}$ -CH are about 800 nm, and $Ni_1Co_1Zn_1$ -CH is about 3 μ m. Flower-like nanospheres with interconnected two-dimensional nanosheets can provide a large specific surface area and abundant active sites for redox reactions, and facilitate the rapid diffusion of electrolyte ions. With the increase in Zn²⁺ additions from 0 to 1 mmol, a clear change in nanosheets from small and thick to thin and large, and a gradual increase in the size of the nanospheres can be seen. However, excessive addition of Zn²⁺ can destroy the flower-like structure and reduce the structural stability.



Fig. S4. SEM images of $Ni_1Co_1Zn_{0.25}$ -CH prepared with different additions of urea at different magnifications. **a-b**, 0 mmol. **c-d**, 3 mmol. **e-f**, 9 mmol.

Fig. S4 displays SEM images of Ni₁Co₁Zn_{0.25}-CH prepared with different additions of urea at different magnifications. The results show that the nanosheets on the surface of nanospheres can be formed without the addiction of urea due to the hydrolysis reaction of NiCoZn-G nanospheres to produce hydroxide nanosheets (Fig. S4a-b). Fig. S4c-d shows the stacking and interweaving of the nanosheets into a flower-like structure and the nanosheets are uniform. As shown in Fig. S4e-f, spherical structures of NiCoZn-CH are destroyed and decomposed into stacked nanosheets. The reason is that more carbonate ions and hydroxide ions are released at high urea concentrations, and NiCoZn-G solid spheres are greater etched, destroying the spherical structure.



Fig. S5. EDS spectra of Ni1Co1Zn0.25-CH.

Fig. S5 shows the EDS spectra also indicate the presence of Ni, Co, Zn, C and O elements and the weight percentages of O, Ni, Co, C and Zn elements are 32.5%, 24.6%, 24.5%, 12% and 6.3%.



Fig. S6. The enlarged XRD patterns of $Ni_1Co_1Zn_{0.25}$ -G, $Ni_1Co_1Zn_0$ -CH and $Ni_1Co_1Zn_{0.25}$ -CH.



Fig. S7. CV and GCD curves of other NiCoZn-CHs. **a-c**, CV curves at various scan rates from 10 to 100 mV s⁻¹. **d-f**, GCD curves at various current densities from 1 to 10 A g⁻¹.

Fig. S7 shows the CV and GCD curves of the other NiCoZn-CHs. Fig. S6a-c show the CV curves of the other NiCoZn-CHs at different additions of Zn²⁺ at scan rates from 10 to 100 mV s⁻¹. There is no obvious change in the CV curve shape as the scan rate increases from 10 to 100 mV s⁻¹ due to the reversible redox reaction. Fig. S7e-f demonstrate the GCD curves of other NiCoZn-CHs at different current densities from 1 to 10 A g⁻¹. Ni₁Co₁Zn₀-CH, Ni₁Co₁Zn_{0.5}-CH, and Ni₁Co₁Zn₁-CH exhibit poor electrochemical properties.



Fig. S8. Comparative electrochemical performance of Ni₁Co₁Zn_{0.25}-CH-X prepared with different additions of urea (X=0, 3, 6, 9 mmol). **a**, CV curves of Ni₁Co₁Zn_{0.25}-CH-X at 60 mV s⁻¹. **b**, GCD curves of Ni₁Co₁Zn_{0.25}-CH-X at 1 A g⁻¹. **c**, Variations of specific capacitance of Ni₁Co₁Zn_{0.25}-CH-X with different current densities. **d**, EIS curves of Ni₁Co₁Zn_{0.25}-CH-X. The inset is an enlarged diagram of the high-frequency range.

Fig. S8 shows the three-electrode electrochemical performance of $Ni_1Co_1Zn_{0.25}$ -CH-X at different additions of urea (X=0, 3, 6, 9 mmol). All CV curves of these electrodes show clear redox peaks at 0-0.6 V at a scan rate of 60 mV s⁻¹(Fig. S8a). The GCD curves of these electrodes are plotted (Fig. S8b). The discharging time first increases and then decreases when the addition of urea increases, where $Ni_1Co_1Zn_{0.25}$ - CH-6 shows the longest discharge time. Furthermore, Ni₁Co₁Zn_{0.25}-CH-X (X=0, 3, 6, 9 mmol) show approximately 54.3%, 66.9%, 72.3%, and 71.5% specific capacitance retention at current densities from 1 to 10 A g⁻¹ (Fig. S8c). Fig. S8d shows the Nyquist plots of these electrodes. the R_{ct} and R_s values of Ni₁Co₁Zn_{0.25}-CH-6 is lower than the other electrodes. The above comparison shows that the electrochemical performance of NiCoZn-CH can be optimized by adjusting the parameters of urea addition.



Fig. S9. CV and GCD curves of Ni₁Co₁Zn_{0.25}-CH-X prepared with different additions of urea (X=0, 3, 9 mmol). a-c, CV curves at various scan rates from 10 to 100 mV s⁻¹.
d-f, GCD curves at various current densities from 1 to 10 A g⁻¹.

Fig S9 shows the CV and GCD curves for the other $Ni_1Co_1Zn_{0.25}$ -CH-X prepared with different additions of urea (X=0, 3, 9 mmol). Fig. S9a-c show the CV curves of other $Ni_1Co_1Zn_{0.25}$ -CH-X with different additions of urea at scan rates from 10 to 100 mV s⁻¹. As the scan rate increases from 10 to 100 mV s⁻¹, there is no significant change in the shape of the CV curves. Fig S9e-f indicate the GCD curves of the other $Ni_1Co_1Zn_{0.25}$ -CH-X at different current densities from 1 to 10 A g⁻¹. $Ni_1Co_1Zn_{0.25}$ -CH-0, $Ni_1Co_1Zn_{0.25}$ -CH-3, and $Ni_1Co_1Zn_{0.25}$ -CH-9 exhibit poor electrochemical properties.



Fig. S10. Comparative electrochemical performance of NiCoZn-Gs. **a**, CV curves of NiCoZn-Gs at 60 mV s⁻¹. **b**, GCD curves of NiCoZn-Gs at 1 A g⁻¹. **c**, Variation of capacitances of NiCoZn-Gs at different current densities. **d**, EIS plots of NiCoZn-Gs, the inset is an enlarged plot of the high-frequency range.

Fig. S10 shows the three-electrode electrochemical performance of NiCoZn-Gs. All CV curves of these electrodes show clear redox peaks in the potential window of 0-0.6 V at 60 mV s⁻¹, with the integral area increasing and then decreasing when the Zn²⁺ addition is increased (Fig. S10a). The GCD curves of these electrodes are plotted (Fig. S10b). When the Zn²⁺ addition increases, the discharge time first increases and then decreases. In addition, Ni₁Co₁Zn_{0.25}-G shows the longest discharge time. The specific capacitance retentions of Ni₁Co₁Zn₀-G, Ni₁Co₁Zn_{0.25}-G, Ni₁Co₁Zn_{0.5}-G, and $Ni_1Co_1Zn_1$ -G are about 72.9%, 65.3%, 54.1% and 58.5% at 1 to 10 A g⁻¹ (Fig. S10c). Fig. S10d shows the Nyquist plots of these electrodes. The R_{ct} of $Ni_1Co_1Zn_{0.25}$ -G is lower than the other electrodes.



Fig. S11. CV and GCD curves of the NiCoZn-Gs. **a-c**, CV curves of NiCoZn-Gs at various scan rates from 10 to 100 mV s⁻¹. **d-f**, GCD curves of NiCoZn-Gs at various current densities from 1 to 10 A g⁻¹.

Fig. S11 shows the CV and GCD curves of NiCoZn-Gs. Fig. S11a-d show the CV curves for NiCoZn-G at different Zn^{2+} additions at scan rates from 10 to 100 mV s⁻¹. Compared to Ni₁Co₁Zn₀-G, Ni₁Co₁Zn_{0.5}-G and Ni₁Co₁Zn₁-G, Ni₁Co₁Zn_{0.25}-G has the largest CV integral area. Due to the reversible redox reaction, there is no obvious change in the CV curve shape as the scan rates increase from 10 to 100 mV s⁻¹. Fig. S11e-h display the GCD curves of NiCoZn-Gs at 1 to 10 A g⁻¹, Ni₁Co₁Zn₀-G, Ni₁Co₁Zn_{0.5}-G, and Ni₁Co₁Zn₁-G exhibit shorter discharge time than Ni₁Co₁Zn_{0.25}-G. As shown in Fig. S9f, the specific capacitances of Ni₁Co₁Zn_{0.25}-G are 647.2 F g⁻¹, 603 F g⁻¹, 532.6 F g⁻¹, 486 F g⁻¹, 450.8 F g⁻¹ and 422.8 F g⁻¹ at 1-10 A g⁻¹, respectively. The above performance comparison shows that the electrochemical performance of the precursors can be optimized by adjusting the process parameters with the addition of Zn²⁺.



Fig. S12. EIS plots of $Ni_1Co_1Zn_{0.25}$ -CH and $Ni_1Co_1Zn_{0.25}$ -CH (after 10000 cycles), the inset is an enlarged plot of the high-frequency range.

Fig. S12 shows the Nyquist plots of $Ni_1Co_1Zn_{0.25}$ -CH and $Ni_1Co_1Zn_{0.25}$ -CH (after 10000 cycles). The R_s and R_{ct} of $Ni_1Co_1Zn_{0.25}$ -OH are lower than $Ni_1Co_1Zn_{0.25}$ -CH (after 10000 cycles).



Fig. S13. Equivalent fitting circuit diagram

- Rs: the equivalent series resistance
- Rct: the charge transfer resistance
- Rw: the diffusion resistance
- Cdl: Double layered capacitance



Fig. S14. CV and GCD curves of AC. **a**, CV curves at various scan rates from 10 to 100 mV s^{-1} . **b**, GCD curves at various current densities from 1 to 10 A g^{-1} .

The electrochemical properties of the AC electrode are also investigated in a three-electrode configuration, as shown in Fig. S14. The rectangular CV curves at different scan rates and triangular GCD curves at different current densities can be seen, which are consistent with the capacitive characteristics of the electric double-layer energy storage mechanism. Based on the discharge curves of the GCD, the specific capacitances are calculated to be 109.95, 105.72, 100.76, 98.34, 95.76, and 93.3 F g⁻¹ for different current densities from 1 to 10 A g⁻¹.

Electrode	Impedance value (ohm)			
	R _s	R _{ct}	R _s +R _{ct}	
Ni ₁ Co ₁ Zn ₀ -CH	0.76	0.79	1.55	
Ni ₁ Co ₁ Zn _{0.25} -CH-6	0.52	0.57	1.09	
Ni ₁ Co ₁ Zn _{0.25} -CH (After 10000 cycles)	0.67	1.36	2.03	
Ni ₁ Co ₁ Zn _{0.5} -CH	1.05	0.82	1.87	
Ni ₁ Co ₁ Zn ₁ -CH	2.11	1.4	3.51	
Ni ₁ Co ₁ Zn _{0.25} -CH-0	0.64	0.9	1.54	
Ni ₁ Co ₁ Zn _{0.25} -CH-3	0.9	1.08	1.98	
Ni ₁ Co ₁ Zn _{0.25} -CH-9	0.61	1.55	2.16	

 Table S1 The result of EIS data of different electrodes.

Nano-structure	Electrolyte	Specific capacitance	Rate performance	Cycling stability	Ref.
Cu _x Co _{2-x} (CO ₃)(OH) ₂ nanoplates	6 M KOH	789 F·g ⁻¹ at 1 A·g ⁻¹	49.6% (from 1 to 10 A g-1)	77.5% over 3000 cycles at 5 $A \cdot g^{-1}$	[S1]
MnNiCoCH/CF nanoneedles	6 M KOH	1440.52 F·g ⁻¹ at 1 A·g ⁻¹	70.76% (from 1 to 10 A $g^{\text{-1}}$)	90.78% over 8000 cycles at 5 $A \cdot g^{-1}$	[S2]
FeCoP nanosheets@Ni-Co carbonate hydroxide nanoneedles	2 M KOH	795.5 $C \cdot g^{-1}$ at 1 $A \cdot g^{-1}$	85.5% (from 1 to 20 A g ⁻¹)	89.7% over 5000 cycles at 5 $A \cdot g^{-1}$	[S3]
Dandelion-like (Ni _{0.89} Cu _{0.11}) ₂ (OH) ₂ CO ₃	2 M KOH	1017.3 F·g ⁻¹ at 1 A·g ⁻¹	61.4% (from 1 to 10 A g $^{-1})$	68.5% over 4000 cycles at 5 $A \cdot g^{-1}$	[S4]
Mesoporous NiCuFeCoMn multistructure carbonate	1 M KOH	1241 F·g ⁻¹ at 1 A·g ⁻¹	26% (from 3 to 15 A g ⁻¹)	84.7% over 5000 cycles at 10 $A \cdot g^{-1}$	[S5]
Co(CO ₃) _{0.5} (OH)/Ni ₂ (CO ₃)(OH ₎₂ nanobelts	2 M KOH	987 F·g ⁻¹ at 1 A·g ⁻¹	72.9% (from 1 to 30 A g^{-1})	82.9% over 2000 cycles at 10 $A \cdot g^{-1}$	[S6]
Hybrid NiCo(CO ₃)(OH) ₂ nanowire/ NiMn(CO ₃)(OH) ₂ nanosheet	1 M KOH	$1673.3 \text{ F} \cdot \text{g}^{-1}$ at $1 \text{ A} \cdot \text{g}^{-1}$	27.1% (from 3 to 15 A g^{-1})	82.1% over 5000 cycles at 5 $A \cdot g^{-1}$	[S7]
MoS ₂ /NiCoHC	2 M KOH	1296 F·g ⁻¹ at 1 A·g ⁻¹	79.2% (from 1 to 10 A $g^{\text{-1}}$)	81.5% over 5000 cycles at 5 $A \cdot g^{-1}$	[S8]
Sunflower-like nickel– copper carbonate hydroxide	2 M KOH	1185.9 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$	60.8% (from 1 to 10 A g ⁻¹)	93.1% over 5000 cycles at 2 $A \cdot g^{-1}$	[S9]
Nickel carbonate hydroxide/nitrogen doped carbon quantum dots nanosheets	3 M KOH	727 C·g ⁻¹ at 1 A·g ⁻¹	66.4% (from 1 to 15 A g ⁻¹)	82.4% over 5000 cycles at 10 $A \cdot g^{-1}$	[S10]
GCNF/PANI/Ni ₂ (CO ₃)(OH) ₂	3 M KOH	1565 F·g ⁻¹ at 1 A·g ⁻¹	46.5% (from 1 to 20 A $g^{\text{-1}}$)	80.8% over 4000 cycles at 5 $A \cdot g^{-1}$	[S11]
Flower-like Ni ₁ Co ₁ Zn _{0.25} -CH hollow nanospheres	6 M KOH	1585.2 F g ⁻¹ at 1 A g ⁻¹	72.3% (from 1 to 10 A g ⁻¹)	87.9% over 10, 000 cycles at 10 A·g ⁻¹	This work

Table S2 The comparison of the electrochemical performance of various transition metal-based CHs.

Supercapacitor device	Voltage (V)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Cycling stability	Ref.
Cobalt hydroxide carbonate/GF//C-FP	1.5	28	554	99.84% over 6000 cycles at 10 $A \cdot g^{-1}$	[S12]
NF@Co-CH@NiCoMn-CH//AC	1.5	20.31	748.46	90.4% over 6000 cycles at 5 $A \cdot g^{-1}$	[S13]
Nickel-Copper carbonate hydroxide//AC	1.6	32.7	359.9	88.8% over 5000 cycles at 2 $A \cdot g^{-1}$	[S9]
NiCo(CO ₃)(OH) ₂ /NiMn(CO ₃)(OH) ₂ //Graphene	1.6	27.2	702.7	89.4% over 5000 cycles at 5 $A \cdot g^{-1}$	[S7]
MoS ₂ /NiCoHC//AC	1.5	16.4	375	65% over 5000 cycles at 5 $A \cdot g^{-1}$	[S8]
MnNiCo-CH/CF//AC	1.5	30.04	749.97	83.86% over 8000 cycles at 5 $\rm A{\cdot}g^{-1}$	[S2]
NiZnCoCH//AC	1.5	29.6	375	80.2% over 5000 cycles at 4 $\rm A{\cdot}g^{-1}$	[S14]
Ni ₁ Co ₁ Zn _{0.25} -CH//AC	1.6	333.7	400	99.9% over 15000 cycles at 10 A·g ⁻¹	This work

Table S3 The comparison of the electrochemical performance of supercapacitors based on various CHs-based active materials.

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