

Supporting Information

Tailoring the capacitive performance of ZnCo_2O_4 by doping of Ni^{2+} and fabrication of asymmetric supercapacitor

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Materials

Graphite flakes powder ($\leq 20\mu\text{m}$, 99%), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Cobalt nitrate tetra hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$), Citric acid monohydrate and Graphite flakes powder ($\leq 20\ \mu\text{m}$, 99%) are purchased from Sigma-Aldrich, India. Sodium Nitrate (NaNO_3 , 99 wt%), hydrazine hydrate ($\text{H}_6\text{N}_2\text{O}$, 99 wt%) potassium permanganate (KMnO_4 , 99.5 wt%), hydrogen peroxide (H_2O_2 , 30 wt%), 1-methyl 2-pyrrolidone (NMP) ($\text{CH}_3\text{NC}_4\text{H}_6\text{O}$) are obtained using E-Merck, India. Sulfuric acid (H_2SO_4 , 98 wt %) is acquired via Ranbaxy laboratories, Ltd. Poly (vinylidene fluoride) (PVDF) ($-\text{CH}_2-\text{CF}_2-$)_n purchased from Alfa Aesar, India. All the chemicals and reagents are used as received without any further purification. Deionized (DI) water is obtained from MILLIPORE water system.

Preparation of Graphene oxide (GO)

GO has been synthesized by graphite flakes using modified Hammer's method. In typical synthesis, 1 g of graphite flakes and 1 g of Na_2NO_3 are mixed with 50 ml H_2SO_4 in 1000 ml round bottom flask and stirred for $\frac{1}{2}$ h. Afterwards, 6 g of KMnO_4 is added pinch by pinch under constant stirring and the temperature is maintained below $5\ ^\circ\text{C}$ using ice bath. 80 ml of DI water was slowly added with vigorous stirring. The solution is further diluted by the addition of 200 ml of water followed by 6 ml of H_2O_2 . The resultant mixture was stirred for 1 h. Then the filtered solution is filtered and washed with hot DI water several time until the pH of the solution become ~ 6 . The product was dried under vacuum at $90\ ^\circ\text{C}$. The powder is re-dispersed with the known amount of DI water to make a GO solution.

Preparation of reduced graphene oxide (rGO):

20 ml of GO solution has been taken in beaker and stirred for 1 h. Subsequently, add few drops of hydrazine hydrate and kept at 80 C under stirring. The resultant product was washed several times with water followed by ethanol.

Material characterization:

Phase identification and crystalline nature of the synthesized materials was analyzed using Powder X-ray diffraction (XRD) measurements with Rigaku smart lab X-ray diffractometer using *Cu K α* radiation ($\lambda = 1.5418 \text{ \AA}$) as a X- ray source and the 2θ values ranges from 10 to 80 ° with the step degree of 6 °/min. Lab Ram Evolution Spectrometer (Horiba) recorded Raman spectrum with argon-ion continuous wave laser (532 nm) as the excitation source. The width of the slit used for recording the Raman spectrum is 400 nm with the integration time of 5 s. The power at sample while recording the Raman spectrum of all samples is 10 kW. Elemental composition and oxidation states of $\text{Ni}_{0.75}\text{Zn}_{0.25}\text{Co}_2\text{O}_4$ sample were analyzed by X-ray photoelectron spectroscopy (XPS) with thermo scientific, MULTILAB 2000 using *Mg K α* (1253.6 eV) as a radiation source. Surface morphology of the material were analyzed by Field emission scanning electron microscopy (FE-SEM) with EDAX, Carl Zeiss SUPRA 55VP microscope.

Electrochemical characterization:

Doping of Ni with ZnCo_2O_4 and their influences on electrochemical properties were measured by various electrochemical techniques such as cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) using BioLogic SP-300 Modular Research Grade Potentiostat/Galvanostat/FRA electrochemical workstation. The fabrication of working electrodes is by mixing the active material, super P carbon, and poly vinylidene fluoride (PVDF) with ratio of 75:20:5 and make slurry using N-methyl pyrrolidone as a solvent. The

slurry is coated on the nickel foam as a substrate and it was kept in an oven 6 h for drying and the resulted working electrode contains ~ 3 mg of active material. A typical three-electrode setup equipped with above working electrode, a slice of Pt as a counter electrode and Hg/HgO as a reference electrode dipped in 3.5 M KOH as an electrolyte was used for the electrochemical characterization. Asymmetric supercapacitor device has been fabricated using Ni-doped ZnCo₂O₄ and rGO as a working electrodes in aqueous electrolyte.

The specific capacity values of all the electrode materials are evaluated from the CD profile using following equation.

$$C_g = \frac{I \times \Delta t}{m} \quad (1)$$

Where, C_g is the specific capacity of the electrode (C/g), I is the applied current for the charge-discharge cycles (A), Δt is the discharge time (s), m is the active mass of the working electrode (g) and ΔV is the operating potential window of the working electrode vs. Hg/HgO. The total capacity (C_t), coulombic efficiency (η) energy density (E) and power density (P) could be calculated by the following equations.

$$C_t = \frac{I \times \Delta t}{M} \quad (2)$$

$$C_g = 2 \times C_t \quad (3)$$

$$\eta = \frac{\Delta t_{discharge}}{\Delta t_{charging}} \times 100\% \quad (4)$$

$$E = \frac{C_t V}{2} \times \frac{1000}{3600} \quad (5)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (6)$$

Where, C_t is the total capacity (C/g), M is the total active mass of both the electrodes, C_g is the specific capacity (C/g), η is the coulombic efficiency (%), E is the energy density

(Wh/kg), V is the operating voltage (V), P is the power density (W/kg) of the fabricated symmetric supercapacitor.

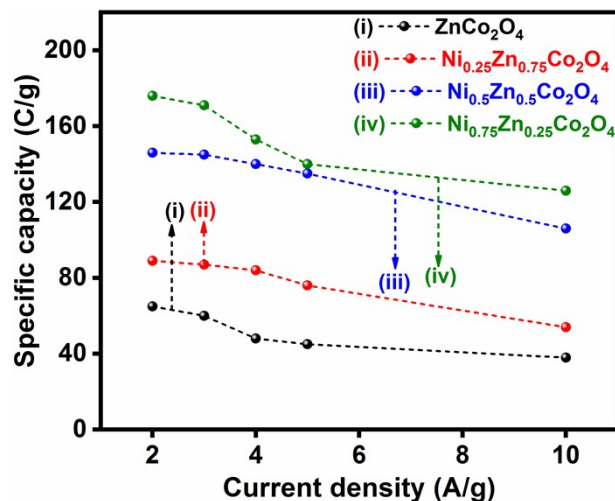


Figure S1. Plot of specific capacity (C/g) vs. current density (A/g) of (i) ZnCo₂O₄, (ii) Ni_{0.25}Zn_{0.75}Co₂O₄, (iii) Ni_{0.5}Zn_{0.5}Co₂O₄, and (iv) Ni_{0.75}Zn_{0.25}Co₂O₄.

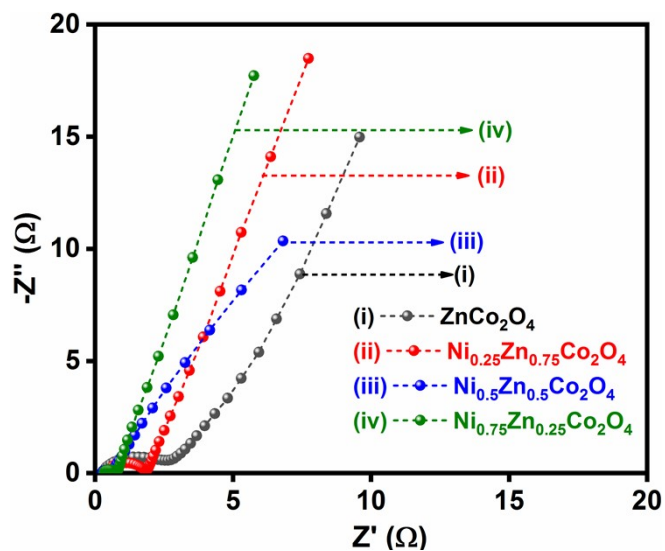


Figure S2. EIS of (i) ZnCo₂O₄, (ii) Ni_{0.25}Zn_{0.75}Co₂O₄, (iii) Ni_{0.5}Zn_{0.5}Co₂O₄, and (iv) Ni_{0.75}Zn_{0.25}Co₂O₄.

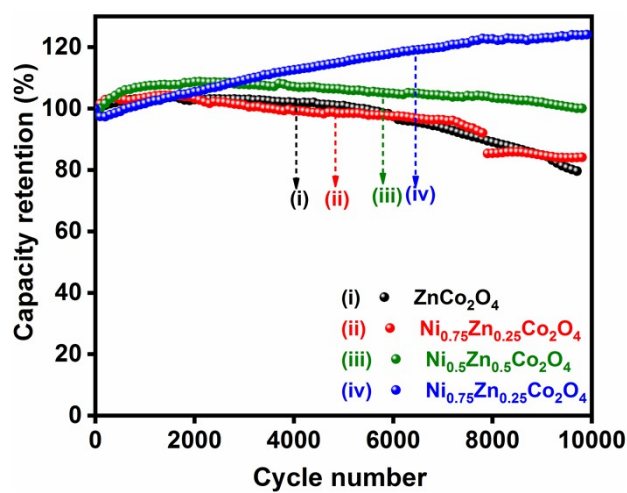


Figure S3. Long cycle plot of (a) ZnCo₂O₄, (ii) Ni_{0.25}Zn_{0.75}Co₂O₄, (iii) Ni_{0.5}Zn_{0.5}Co₂O₄, and (iv) Ni_{0.75}Zn_{0.25}Co₂O₄.

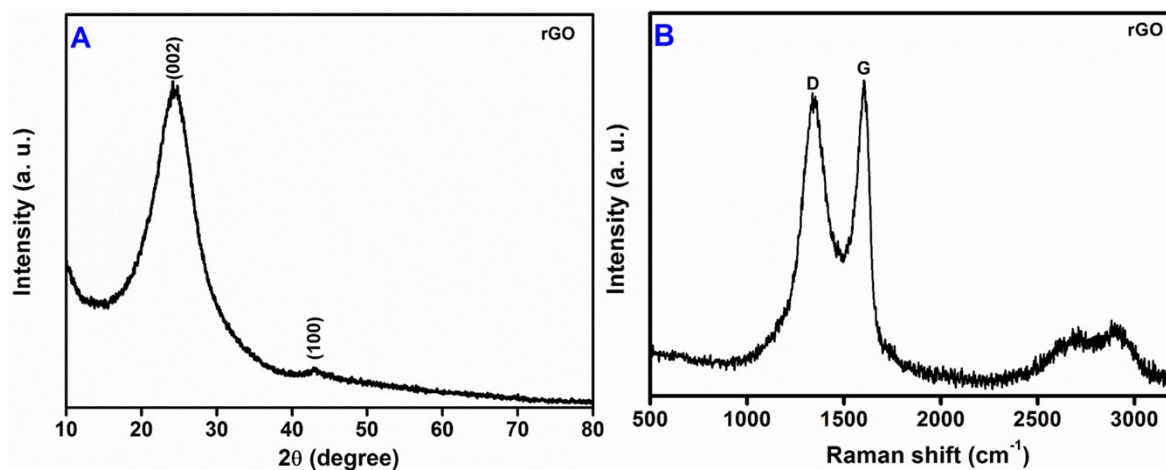


Figure S4. (A) XRD, and (B) Raman spectra of Rgo.

Table S1. Specific capacity of ZnCo_2O_4 , $\text{Ni}_{0.25}\text{Zn}_{0.75}\text{Co}_2\text{O}_4$, $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Co}_2\text{O}_4$, and $\text{Ni}_{0.75}\text{Zn}_{0.25}\text{Co}_2\text{O}_4$ at various current densities.

Material	specific capacity (C/g) at different current densities (A/g)				
	2	3	4	5	10
ZnCo_2O_4	65	60	48	45	38
$\text{Ni}_{0.25}\text{Zn}_{0.75}\text{Co}_2\text{O}_4$	89	87	84	76	54
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Co}_2\text{O}_4$	146	145	140	139	106
$\text{Ni}_{0.75}\text{Zn}_{0.25}\text{Co}_2\text{O}_4$	176	171	152	140	126