

Mechanistic Insights into the Structural, Electrochemical, and Charge-Storage Behavior of CNT@NiO Electrodes for High-Capacitance and Durable Supercapacitors

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Background

- There is a growing demand for renewable energy storage.
- Li-ion batteries are limited by cost, safety concerns, and environmental pollution.
- Supercapacitors offer high power density, quick charge/discharge, and outstanding stability¹.
- Besides the choice of materials, the synthesis method is crucial as it determines the material's structure, interface, and properties³.
- Transition metal oxides (e.g., RuO₂, MnO₂, and NiO) and carbon materials (e.g., carbon nanotubes and graphene) are excellent choices for supercapacitor electrode materials due to their exceptional electrochemical properties².

Objectives

- Fabrication** Spray pyrolysis of pure NiO and CNT@NiO at 350 °C.
- Characterization** XRD, SEM/EDX, FTIR, BET analysis.
- Electrochemistry** CV, GCD, EIS in 2M KOH (0–0.7 V).
- Charge storage** Dunn's model quantification of Faradaic vs. capacitive contributions.

Method

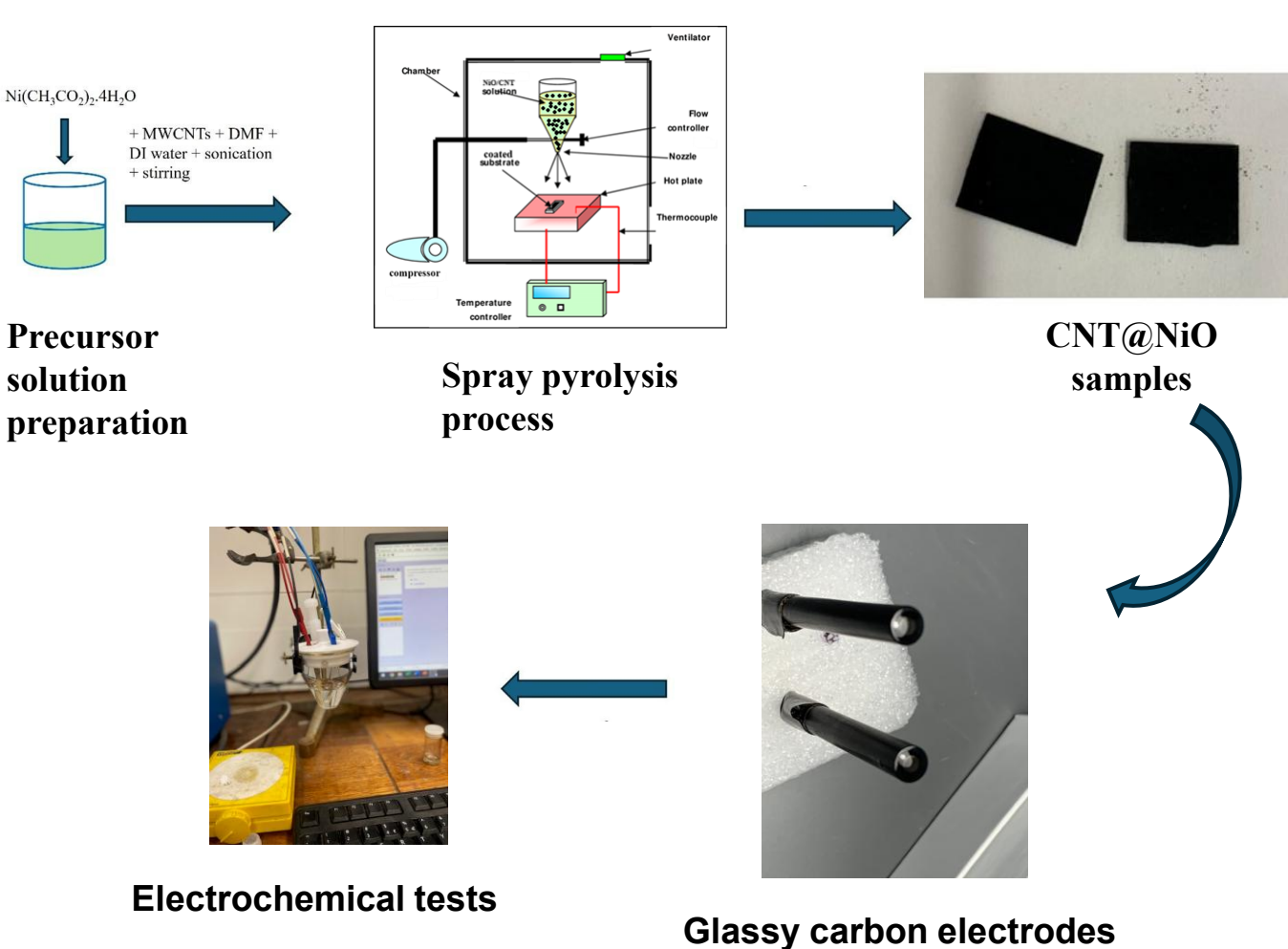


Fig. 1. Schematic illustration of the material preparation procedure.

Table 1. Spray pyrolysis process parameters.

Parameters	Deposition temperature (°C)	Solution flow rate (mL/min)	Carrier gas type	Carrier gas pressure (bar)	Carrier gas flow rate (L/min)	Nozzle diameter (mm)	Nozzle to substrate distance (cm)	Total deposition time (min)
Values	350	5.9	air	3–4	20–23	0.8	30	30

Results

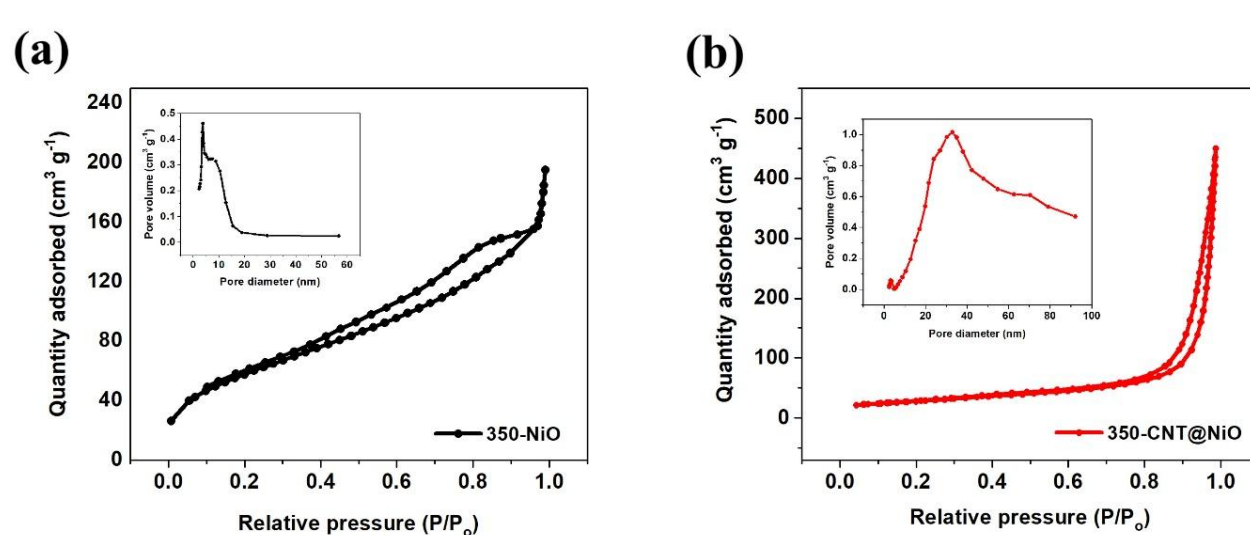


Figure 2. N₂ adsorption/desorption isotherm of (a) 350-NiO and (b) 350-CNT@NiO. Insets provide BJH pore size distributions.

Table 2. BET Surface & Pore Analysis

Parameter	350-NiO	350-CNT@NiO	Significance
Isotherm type	Type IV (H3 hysteresis)	Type IV (H3 hysteresis)	Both mesoporous
Specific surface area	29.55 m ² g ⁻¹	46.51 m ² g ⁻¹	+57% more active sites
Pore volume	0.30 cm ³ g ⁻¹	0.69 cm ³ g ⁻¹	+130% — buffers volume expansion
Mean pore diameter	6.10 nm	27.37 nm	Deeper ion penetration
BJH peak pore size	3.77 nm	32.55 nm	Enhanced ion diffusion

Table 3. Specific capacitance of pristine NiO vs. CNT@NiO

Current Density (A g ⁻¹)	NiO (F g ⁻¹)	CNT@NiO (F g ⁻¹)
2	18.92	472.4
3	9.72	330.7
4	4.15	327.5
5	2.57	325.0

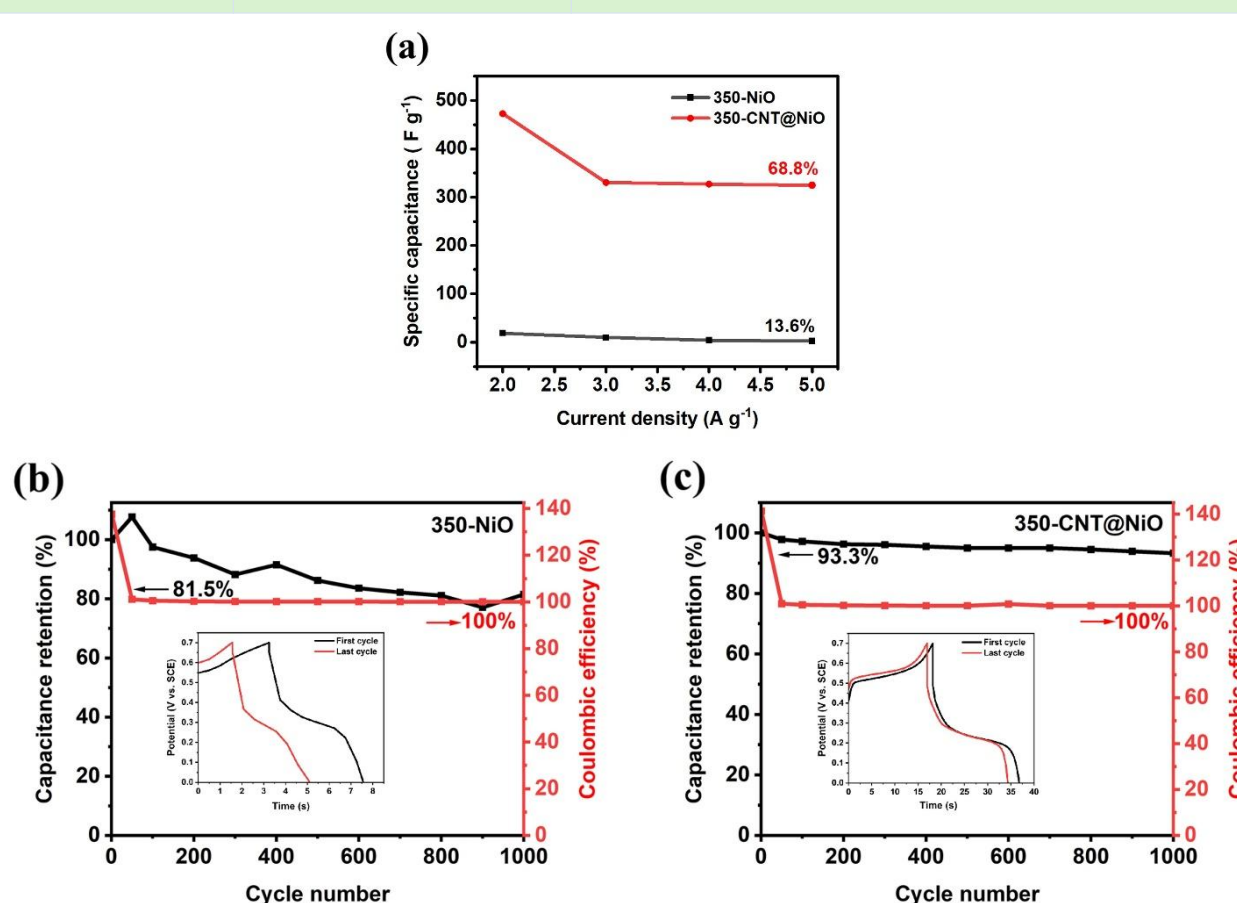


Fig. 3. (a) Rate capability of the electrodes. Cycle life and coulombic efficiency of (b) 350 NiO and (c) 350-CNT@NiO at 2 A g⁻¹ after 1,000 cycles (insets show first and last GCD curves during cycling).

Table 4. EIS Fitting Parameters

Parameter	350-NiO	350-CNT@NiO
Rs (Series resistance)	18.68 Ω	7.74 Ω
Rct (Charge transfer)	6.40 μΩ	1.52 μΩ
Cdl (Double-layer cap.)	2.98 μF	6.95 μF
Warburg impedance	22.94 kΩ s ^{-1/2}	0.195 kΩ s ^{-1/2}
Relaxation time (τ ₀)	0.00147 s	1.47 s

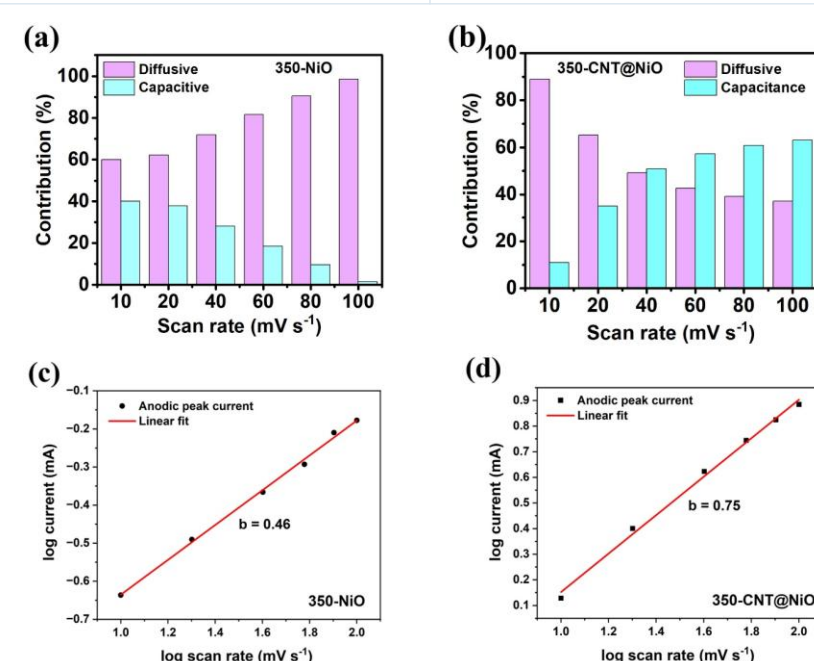


Fig. 4. Contribution of capacitive vs diffusive currents using Dunn's model in (a) 350-NiO and (b) 350-CNT@NiO. Charge storage nature using power law in (c) 350-NiO and (d) 350-CNT@NiO.

Conclusion

- CNT@NiO via spray pyrolysis achieved an exceptional specific capacitance of 472.4 F g⁻¹ at 2 A g⁻¹ — 25× improvement over pristine NiO.
- Rate capability: 68.8% (CNT@NiO) vs. 13.6% (NiO) — CNTs open conductive pathways across the nanostructure.
- Cyclic stability: 93.3% retention after 1,000 cycles for CNT@NiO vs. 81.5% for NiO — structural integrity maintained by CNT framework.
- Spray pyrolysis confirmed as a low-cost, scalable, effective fabrication route for high-performance supercapacitor electrodes.
- Dunn's analysis: CNT@NiO shows mixed charge storage (b = 0.75); NiO is diffusion-controlled (b = 0.46).

Future Work

- Detailed interfacial analysis via TEM and XPS.
- Long-term cycling (>5,000 cycles) in full-cell configurations.
- Optimize CNT: NiO ratio and spray parameters for maximum performance.

References

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