Flexible All-Solid-State Supercapacitor Based on Carbon-Supported Ni-Embedded Boron Nitride

Shrabani De[a], Binod Raj KC[a], Gayani Pathiraja[b], Bishnu Prasad Bastakoti[a*]

[a]Department of Chemistry, North Carolina A&T State University, 1601 E. Market St. Greensboro, NC 27411 (USA)

[b]Department of Nanoscience, Joint School of Nanoscience and Nanoengineering, University of North Carolina at Greensboro, 2907 East Gate City Blvd, Greensboro, NC 27401 (USA)

*Email: bpbastakoti@ncat.edu

S1. Experimental Section

Preparation of gel electrolyte (PVA-KOH)

The PVA-KOH gel electrolyte was prepared following the previously reported method[1]. Typically, 10 ml 9 wt% PVA solution was first prepared at 90 °C. Then, 5 ml KOH solution (10 wt%) was added dropwise into the PVA solution. The obtained semi-transparent liquid was used as gel electrolyte for the fabrication of flexible device.

Electrochemical measurements for supercapacitor

The electrochemical performance in three-electrode configuration was analyzed in 1 M KOH electrolyte. Electroactive material coated carbon cloth was used as working electrode with Ag/AgCl electrode and Pt wire, serving as reference and counter electrodes, respectively. The working electrode was prepared by painting a slurry of electroactive materials (by mixing the prepared samples (80 wt%), carbon black (10 wt%), and PVDF (10 wt%) with few drops of NMP) on a 1 cm × 1 cm carbon cloth. Cyclic voltammetry (CV) was carried out within a potential range of -0.2 to 0.5 V and the galvanostatic charging discharging (GCD) study was performed within 0.0 to 0.45 V to evaluate the electroactivity of the prepared samples. The mass loading of active material was 0.5 mg. The electrochemical impedance spectroscopy (EIS) analysis was conducted from a frequency of 1 MHz to 1 Hz at 10 mV amplitude at room temperature. The specific capacitance (C in F g^{-1}) was evaluated using GCD plots by using the Eq. S1[2]:

$$C = \frac{i \times \Delta t}{m \times \Delta V} \quad \text{(S1)}$$

Where, i is the charging–discharging current, Δt is the time required in seconds for the discharge cycle, m is the mass loaded, and ΔV is the voltage range.

The asymmetric supercapacitor device (ASC) was fabricated by painting the slurry of electroactive materials (using the above-mentioned ratios) on a piece of carbon cloth with dimension of 2 cm × 2 cm and analysed in two electrode electrochemical setup. The ASC device was assembled using the synthesized material as positive electrode and cigarette filter-derived carbon as negative electrode. The electrochemical analysis was performed within the voltage range of 0.0 to 1.1 V using PVA/KOH gel electrolyte. The active mass loading was 5 mg for both cathode and anode. The specific capacitance (C in F g^{-1}) of the device study was calculated using the following equation[3]:

$$C = \frac{4 \times i \times \Delta t}{m \times \Delta V} \quad \text{(S2)}$$

The specific energy density (E in W h kg^{-1}) and power density (P in W kg^{-1}) of the device were evaluated using Eq. S3, and Eq. S4, respectively[2]:

$$E = \frac{C\Delta V^2}{7.2} \quad \text{(S3)}$$

$$P = \frac{E \times 3600}{\Delta t} \quad \text{(S4)}$$

The stored charge (Q) is dependent on specific capacitance (C), voltage window (ΔV), and mass of the active material (m) of the corresponding electrode[4].

$$Q = C \times \Delta V \times m \quad \text{(S5)}$$

When the charge equivalence ($Q_+ = Q_-$) is applied, the mass ratio (m_+/m_-) of the positive and negative electrode can be calculated using the following equation[4]:

$$\frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+} \quad \text{(S6)}$$

The calculated mass ratio of positive and negative electrode using Eq. S6 is 0.1.

The volumetric energy density of the all-solid-state asymmetric supercapacitor (ASSASC) device was also evaluated using the following method. The specific energy density (E) was calculated from the discharge time obtained from the GCD analysis using Eq. S3. The dimension of the current collector (carbon cloth) was 2 cm × 2 cm × 0.04 cm.

The volumetric energy density (E_v) could be estimated by Eq. S7[5]:

$$E_v = \frac{E \times m}{2 \times 2\ cm \times 2\ cm \times 0.04\ cm} \quad \text{(S7)}$$

Where, 'm' is the sum of the active masses (in kg) of the positive electrode (Ni-BN/C) and negative electrode (C). The active masses of positive and negative electrode for the ASSASC device were 5 mg and 5 mg, respectively. The volume of two pieces of current collectors as negative electrode and positive electrode is $2 \times 2\ cm \times 2\ cm \times 0.04\ cm$.

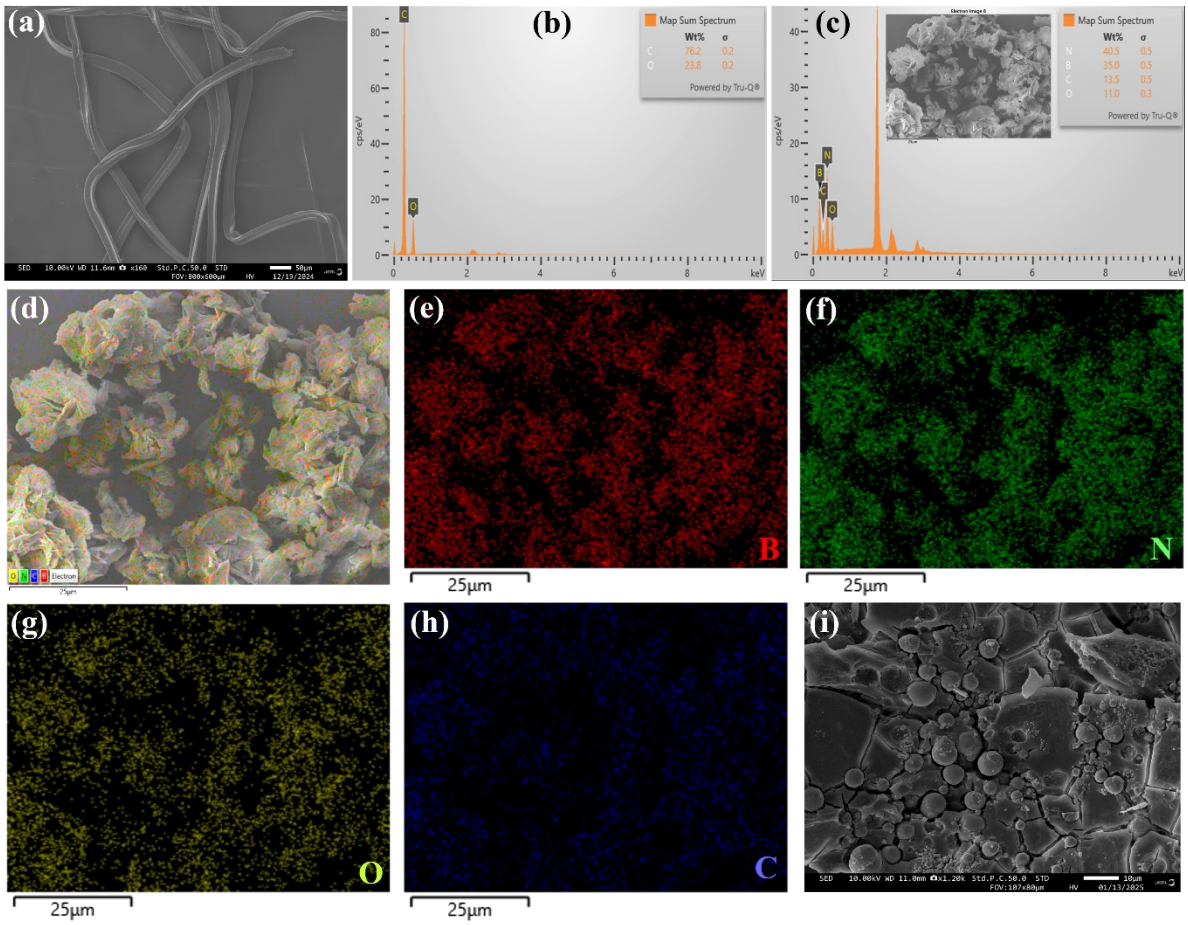

Fig. S1. (a) FESEM image of cigarette filter, EDS analysis of (b) cigarette filter, and (c) BN with percentages of elements present, (d) FESEM overlay map, and (e-h) elemental mapping of B, N, O, and C of BN, respectively, (i) FESEM image of Ni-BN-1:5.

S2. Trasatti method analysis

To find out the capacitive contribution of the synthesized materials (C, BN, BN/C, and Ni-BN/C) from their respective electron double layer and pseudocapacitance, the Trasatti method was used. The following steps are obeyed for this theoretical analysis. The corresponding areal capacitance of the final composites was calculated by using the following equation:

$$C = \frac{S}{2.\Delta V.v}$$ (Equation S8)

Where, C is the areal capacitance in mF/cm^2, ΔV is the voltage window in V, v is the scan rate in V/s and S is the area enclosed by the corresponding cyclic voltammograms in mA V/cm^2. Reciprocal of the calculated areal capacitances (C^{-1}) and the square root of the scan rates ($v^{-1/2}$) should be in linear co-relationship assuming ion diffusion follows a semi-infinite diffusion pattern [Figure S5(a-c)][6].

$C^{-1} = \text{Constant}.\ v^{1/2} + C_T^{-1}$ (Equation S9)

Where is C_T the maximum capacitance, which can be considered as the sum of electron double-layer capacitance and pseudocapacitance and can be calculated from intercept in the Y-axis of C^{-1} and $v^{-1/2}$plot[7]. Again, calculated areal capacitances show the linear relationship with the reciprocal of the square root of the scan rates assuming a semi-infinite diffusion pattern [Figure S5(d-f)][8].

$C = \text{Constant}.\ v^{-1/2} + C_{EDL}$ (Equation S10)

Here, C_{EDL} is the maximum electron double layer capacitance and it can be found from the extrapolate intercept in Y-axis[7]. Subtraction value of maximum electron double layer capacitance (C_{EDL}) from maximum capacitance (C_T) gives the maximum pseudocapacitance (C_{PS}). So, the capacitance contribution can be calculated by using the following equation:

$$C_{EDL}\ \% = \frac{C_{EDL}}{C_T} \times 100$$ (Equation S11)

$$C_{PS}\ \% = \frac{C_{PS}}{C_T} \times 100$$ (Equation S12)

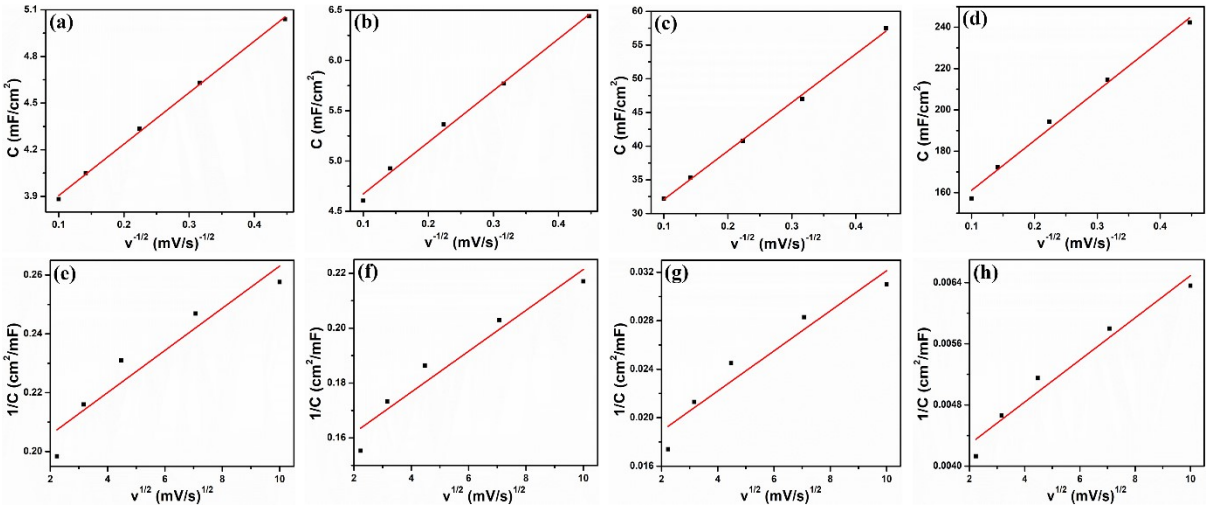

Fig. S2. Plots of areal capacitance (C) vs. reciprocal of square root of scan rate ($v^{-1/2}$) of (a) C, (b) BN, (c) BN/C, and (d) Ni-BN/C; Plots of reciprocal of areal capacitance (C^{-1}) vs. square root of scan rate ($v^{1/2}$) of (e) C, (f) BN, (g) BN/C, and (h) Ni-BN/C.

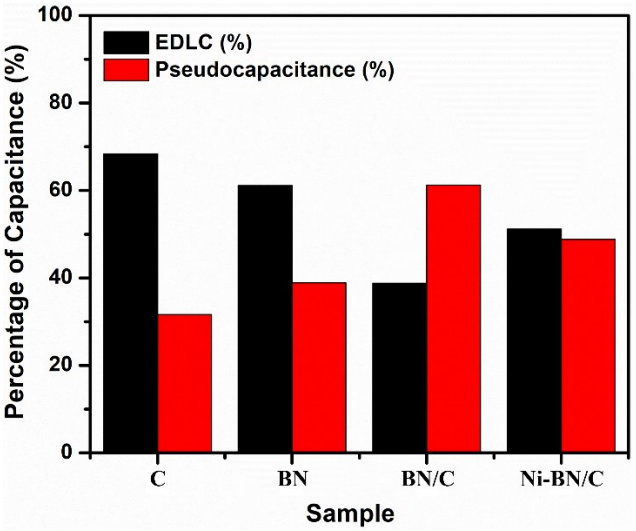

Fig. S3. Bar plot of percentage of capacitance contribution evaluated for C, BN, BN/C, and Ni-BN/C.

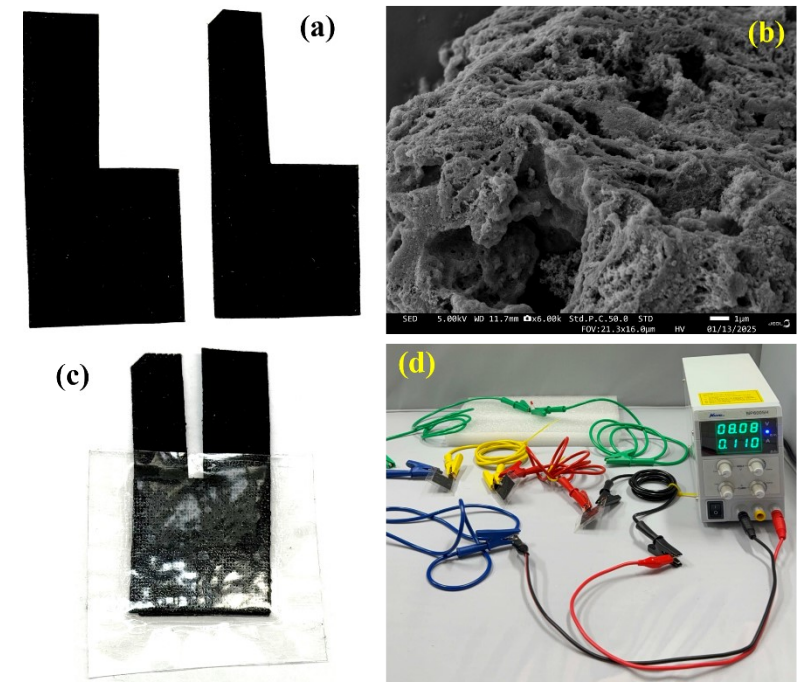

Fig. S4. (a) Digital photographs of carbon cloths used as current collectors, (c) FESEM image of Ni-BN/C after the cycling performance, (c) photograph of the assembled ASSASC device, and (d) charging setup for four ASSASC devices connected in series.

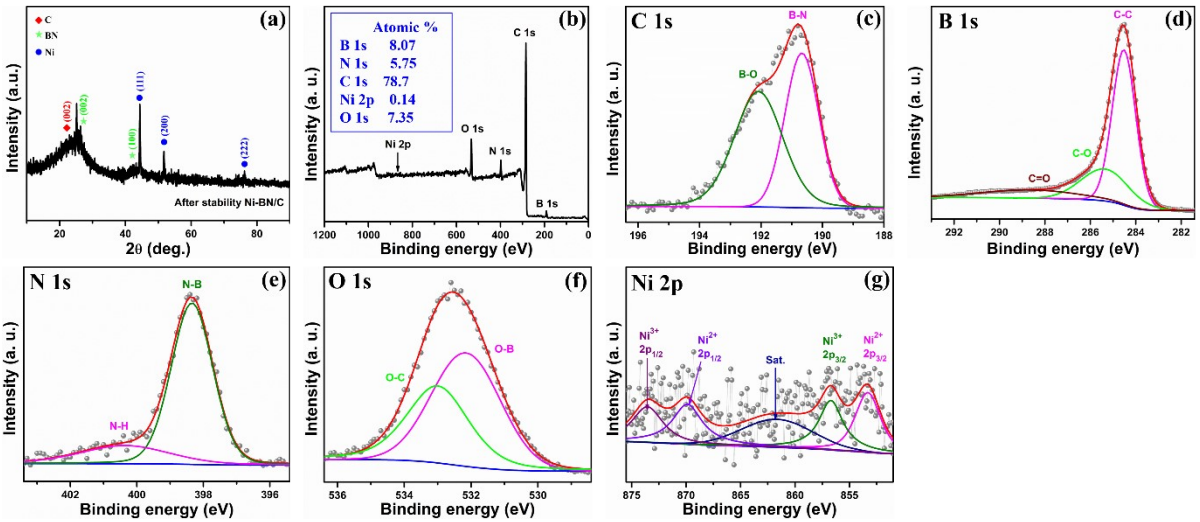

Fig. S5. (a) XRD of Ni-BN/C after cyclic stability study; XPS spectra of Ni-BN/C after cyclic stability study (b) survey scan, deconvoluted spectra of (c) C 1s, (d) B 1s, (e) N 1s, (f) O 1s, and (g) Ni 2p.

References

1. Z. Ping, L. XiaoJing, R. Anye and G. Peng, *Journal of Electroanalytical Chemistry*, 2016, **782**, 154-160.
2. S. De, C. K. Maity, S. Sahoo and G. C. Nayak, *ACS Applied Energy Materials*, 2021, **4**, 3712-3723.
3. M. D. Stoller and R. S. Ruoff, *Energy Environmental Science*, 2010, **3**, 1294-1301.
4. E. Redondo, L. W. Le Fevre, R. Fields, R. Todd, A. J. Forsyth and R. A. Dryfe, *Electrochimica Acta*, 2020, **360**, 136957.
5. S. De, C. K. Maity, M. J. Kim and G. C. Nayak, *Electrochimica Acta*, 2023, **463**, 142811.
6. S. Ardizzone, G. Fregonara and S. Trasatti, *Electrochimica Acta*, 1990, **35**, 263-267.
7. Y.-H. Lee, K.-H. Chang and C.-C. Hu, *Journal of Power Sources*, 2013, **227**, 300-308.
8. J. Duay, S. A. Sherrill, Z. Gui, E. Gillette and S. B. Lee, *ACS nano*, 2013, **7**, 1200-1214.