Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Facile Functionalization of Boron Nitride (BN) for the Development of High-Performance Asymmetric Supercapacitors

Chandan Kumar Maity[a], Sumanta Sahoo[a], Kartikey Verma[b], Ajaya Kumar Behera[c], and Ganesh Chandra Nayak[a*]

[a]Department of Chemistry, IIT (ISM) Dhanbad, 826004, Dhanbad, India
[b] Department of Chemical Engineering, IIT Kanpur, 208016, Kanpur, India
[c]Department of Chemistry, Utkal University, Bhubaneswar, 751004, India

S1. Synthesis of binary composites m_K-BN/CNT and m_H-BN/CNT

To synthesize m_K-BN/CNT binary composite, initially 0.05 g m_K-BN and 0.05 g CNT were added with 50 ml deionized water in a 100 ml beaker. Then it was sonicated for 30 minutes to disperse properly. After that the resulting dispersed mixture was filtered and dried in an electric oven. For m_H-BN/CNT binary composite, same procedure was followed. Here m_H-BN was used in place of m_K-BN.

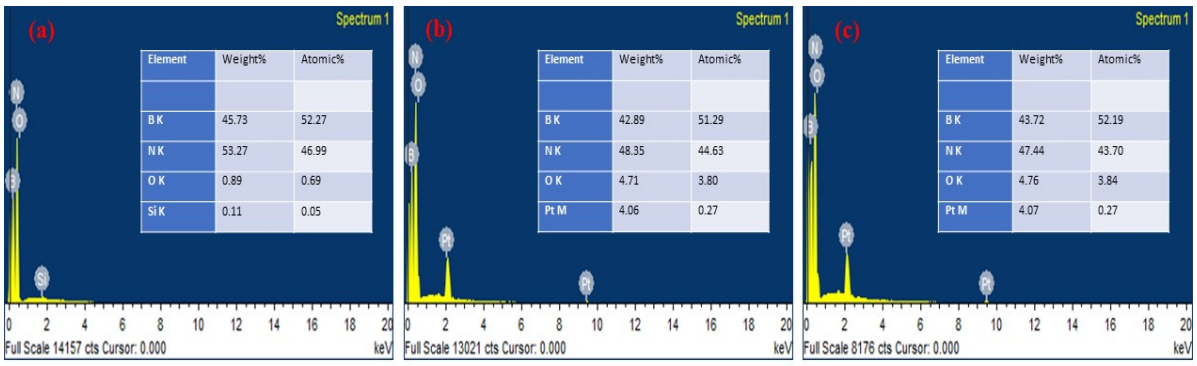

Figure S1. EDS analysis of (a) BN (b) m_H-BN, and (c) m_K-BN.

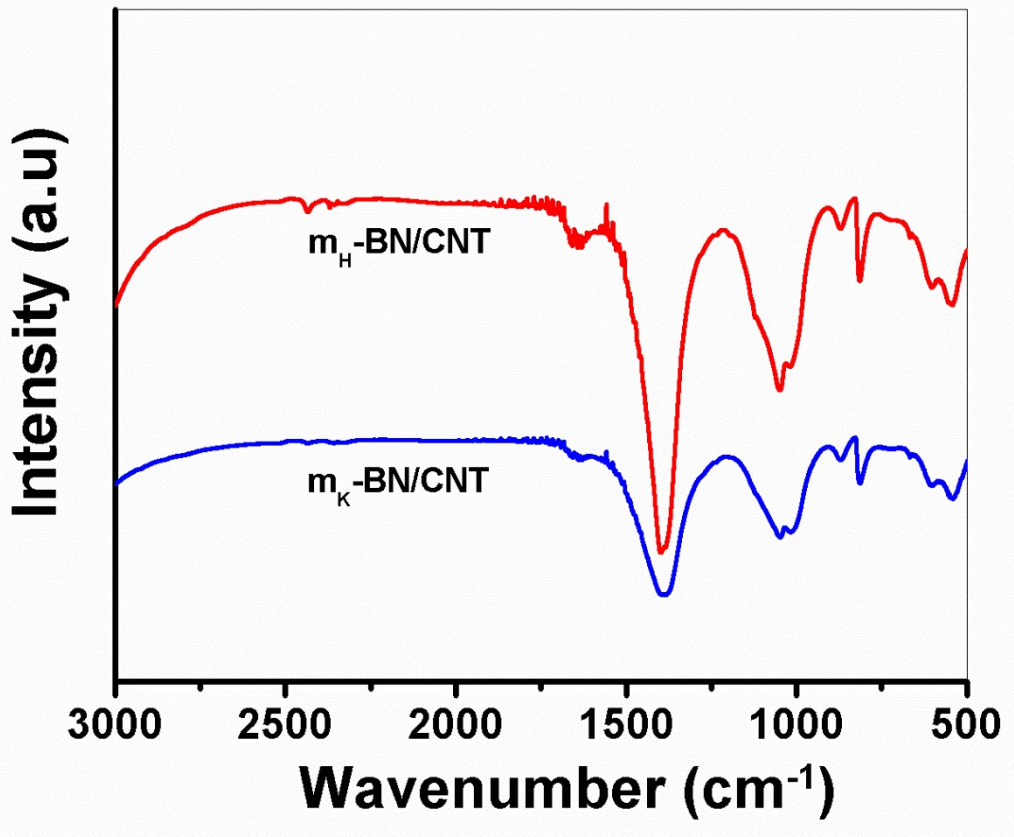

Figure S2. FTIR spectra of m_H-BN/CNT, and m_K-BN/CNT.

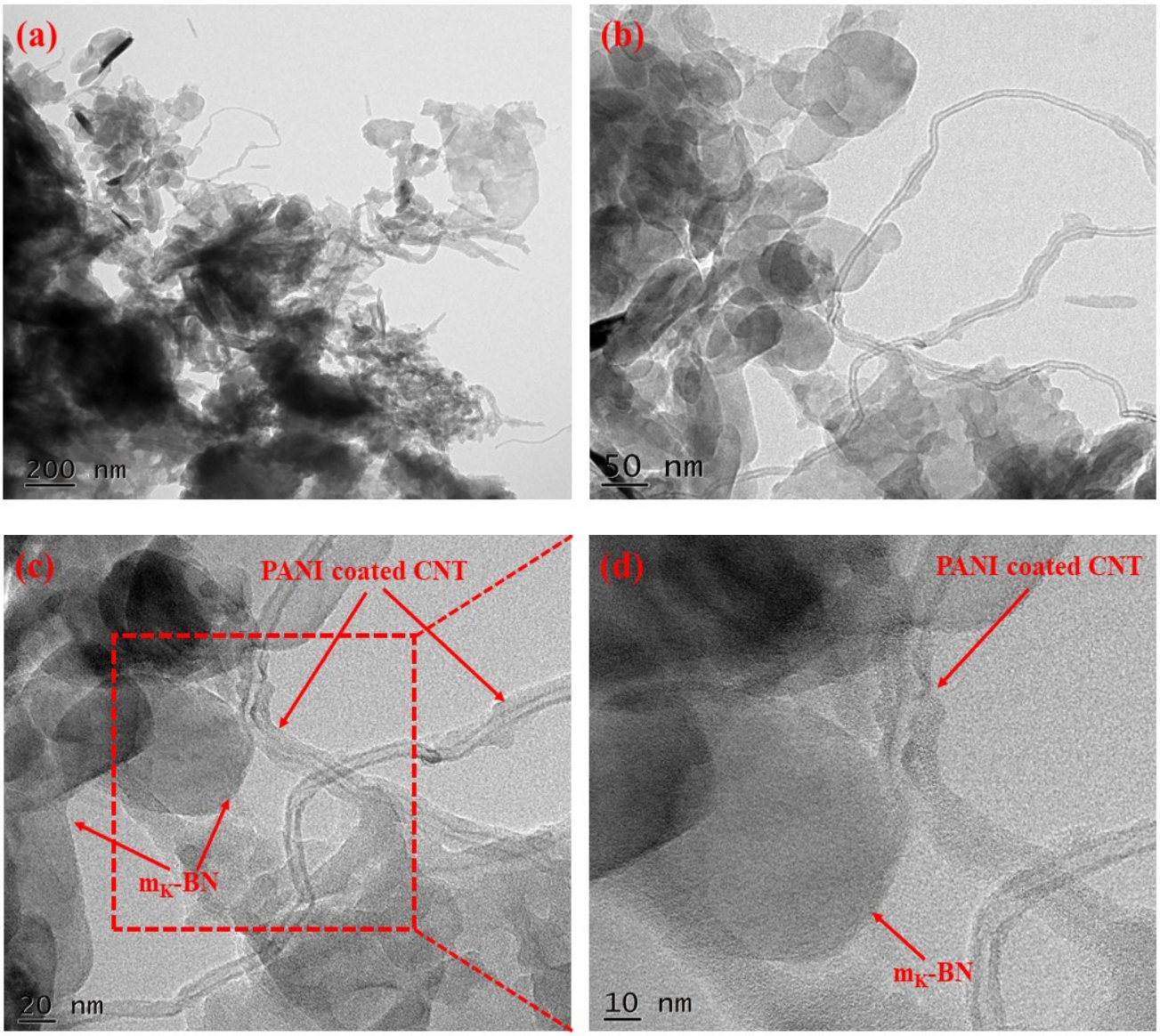

Figure S3.TEM images of m_K-BN/CNT/PANI in lower (a, b) and higher magnification (c, d).

Table S1. Calculated specific surface area, total pore volume and pore diameter of modified boron nitride and ternary composites:

Sample	**Specific surface area (m^2/g)**	**Total pore volume (cc/g)**	**Average pore diameter (nm)**
m_K-BN	50.49	0.094	3.301
m_H-BN	42.14	0.079	3.92
m_K-BN/CNT/PANI	93.35	0.130	3.130
m_H-BN/CNT/PANI	89.77	0.119	5.404

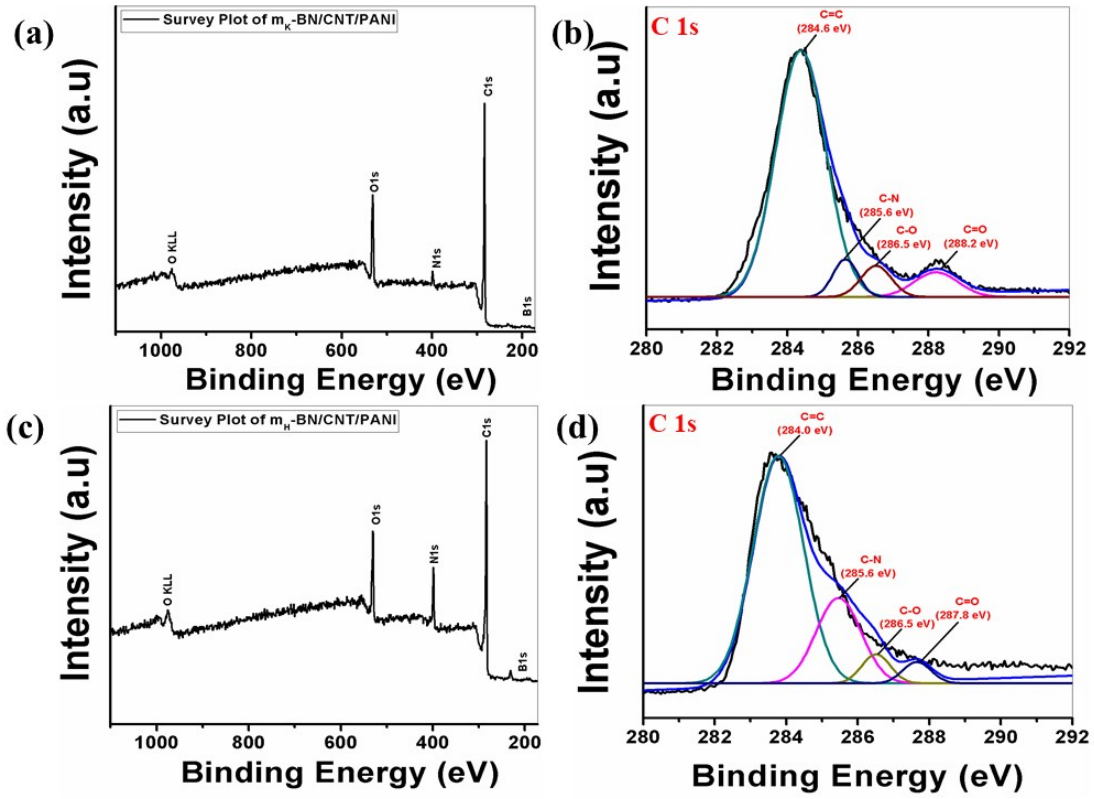

Figure S4. XPS (a) Survey plot, and (b) C 1s spectra of m_K-BN/CNT/PANI; (c) Survey plot, and (d) C 1s spectra of m_H-BN/CNT/PANI.

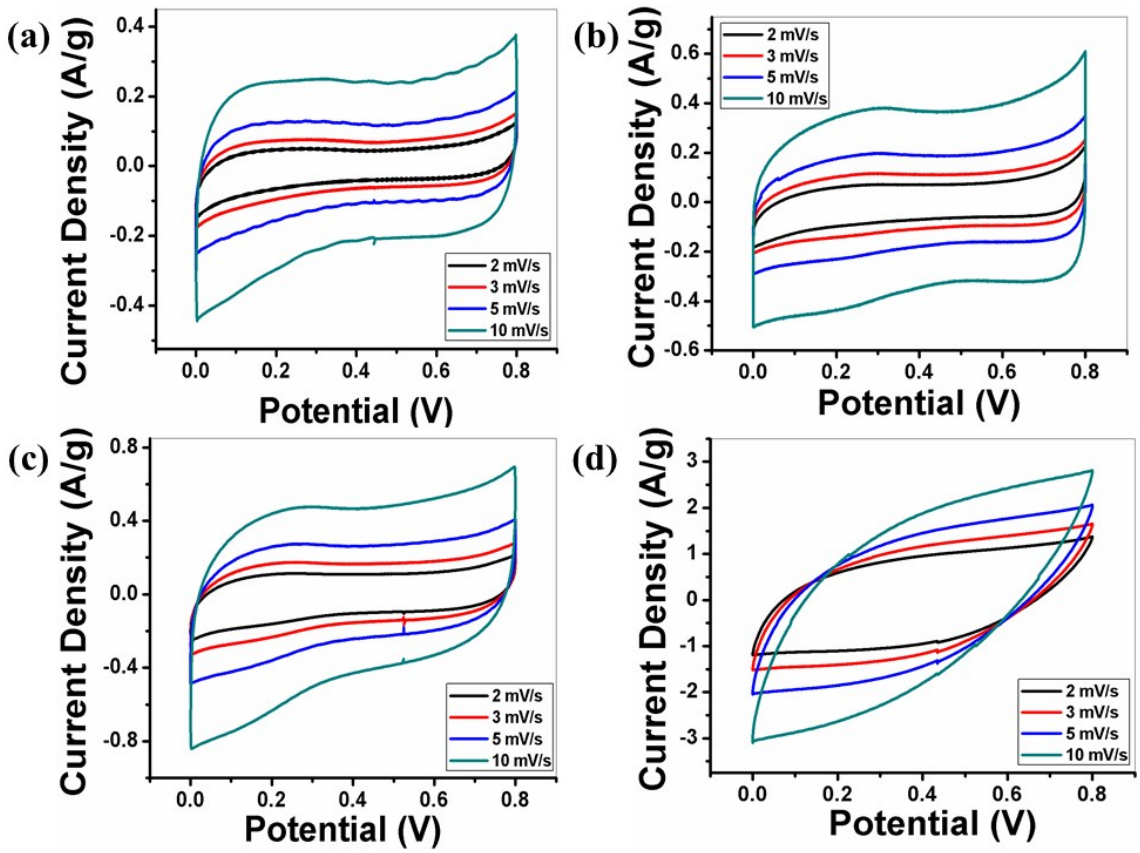

Figure S5. CV plots of (a) BN (b) m_H-BN (c) m_K-BN, and (d) m_H-BN/CNT/PANI at different scan rates (2-10 mV/s) in 1M aqueous KCl solution as electrolyte in three electrode system.

S2. Trasatti Method Analysis

To calculate the electron double layer and pseudocapacitive contribution to the overall capacitance of the electrodes, Trasatti method is applied. This theoretical analysis was carried out by using the following steps.

The areal capacitances of the ternary composites were calculated by using the following equation:

$$C = \frac{S}{2.\,\Delta V.v} \qquad \text{(Equation S1)}$$

Here *C* corresponds to the areal capacitance (in mF/cm^2), ΔV is the potential range (in V), S denotes the area enclosed by corresponding cyclic voltammograms (in $mA \cdot V/cm^2$) and v corresponds to the scan rate (in V/s). It is assumed that the ion diffusion follows a semi-infinite diffusion pattern, which means the 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.[1] (Figure S6. For BN, m_H-BN, m_K-BN, m_H-BN/CNT/PANI, and m_K-BN/CNT/PANI)

$$C^{-1} = Constant.\ V^{1/2} + C_T^{-1} \quad \text{(Equation S2)}$$

Here C_T denotes the maximum capacitance, which can be the sum of electron double layer capacitance and pseudocapacitance and calculated from the intercept in the Y-axis of C^{-1} Vs. $v^{1/2}$ plot.[2] For this case, also the calculated areal capacitances show the linear relationship with the reciprocal of the square root of the scan rates presuming a semi-infinite diffusion pattern.[3] (Figure S7. For BN, m_H-BN, m_K-BN, m_H-BN/CNT/PANI, and m_K-BN/CNT/PANI)

$$C = Constant.\ V^{-1/2} + C_{EDL} \quad \text{(Equation S3)}$$

Here, C_{EDL} is the utmost electron double layer capacitance and it can be calculated from the extrapolated intercept in Y-axis.[3] the Subtraction value of maximum electron double layer capacitance (C_{EDL}) from maximum capacitance (C_T) gives the maximum pseudo-capacitance (C_{ps}). So, the capacitance contribution can be calculated by using following equation:

$$C_{EDL}\% = \frac{C_{EDL}}{C_T} \times 100 \quad \text{(Equation S4)}$$

$$C_{PS}\% = \frac{C_{PS}}{C_T} \times 100$$

(Equation S5)

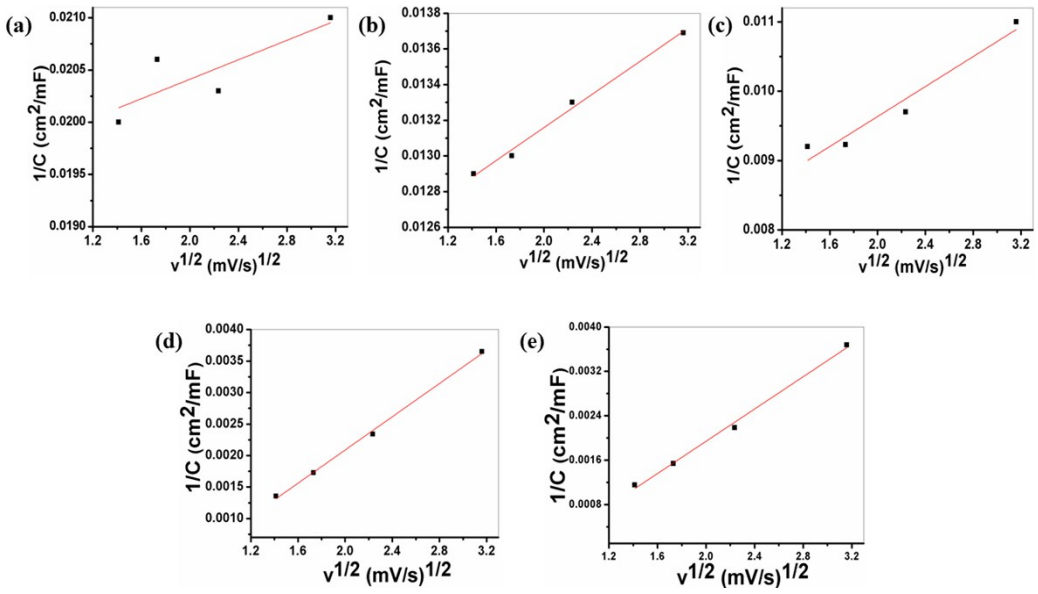

Figure S6. Plots of reciprocal of areal capacitance (C^{-1}) *vs.* square root of scan rate ($v^{1/2}$) of (a) BN, (b) m_H-BN (c) m_K-BN, (d) m_H-BN/CNT/PANI, and (e) m_K-BN/CNT/PANI.

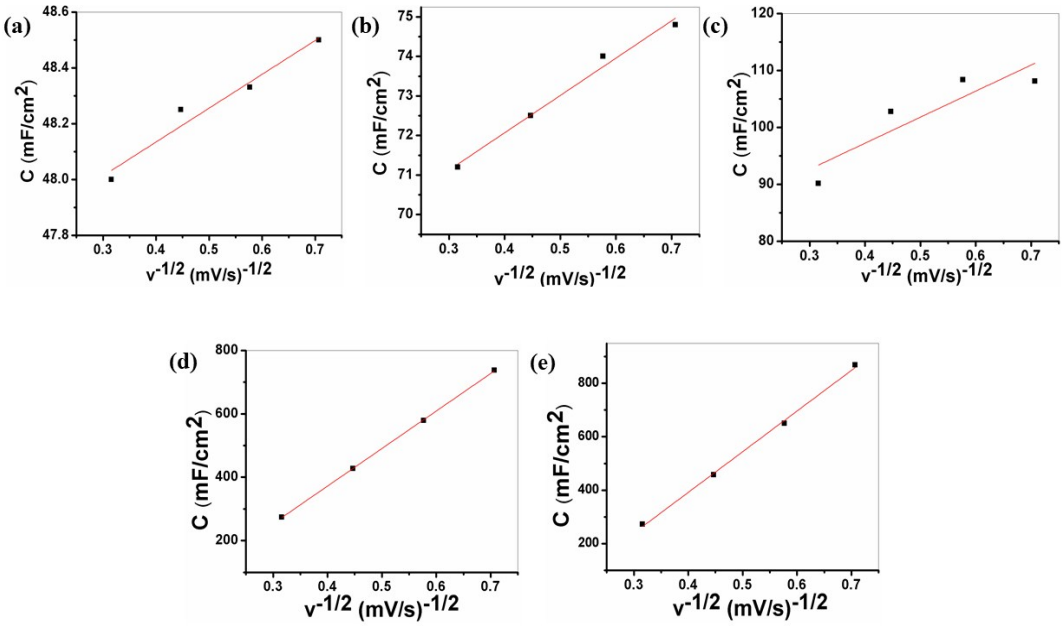

Figure S7. Plots of areal capacitance (*C*) *vs.* reciprocal of square root of scan rate ($v^{-1/2}$) of (a) BN, (b) m_H-BN (c) m_K-BN, (d) m_H-BN/CNT/PANI, and (e) m_K-BN/CNT/PANI.

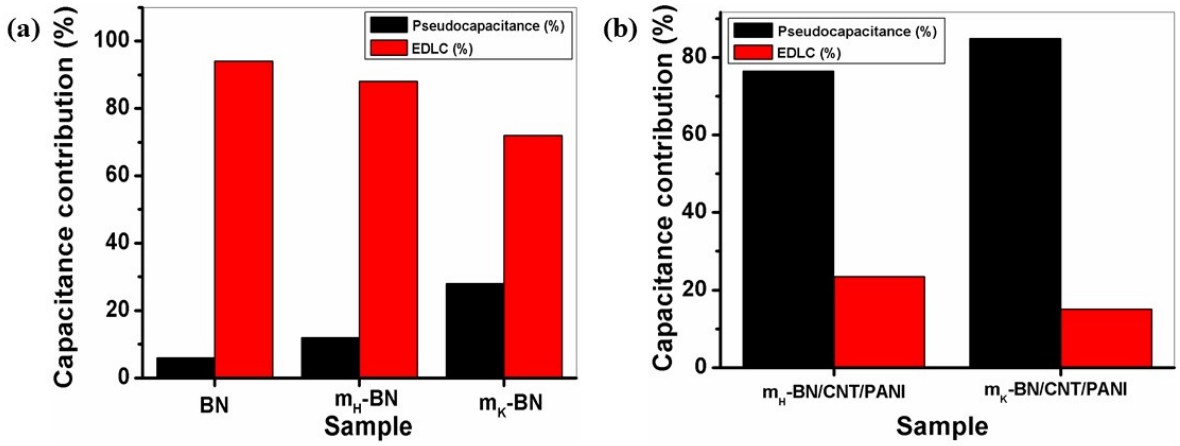

Figure S8. Bar plot of percentage of capacitance contribution evaluated for (a) BN & m_K/m_H-BN, and (b) m_H-BN/CNT/PANI & m_K-BN/CNT/PANI.

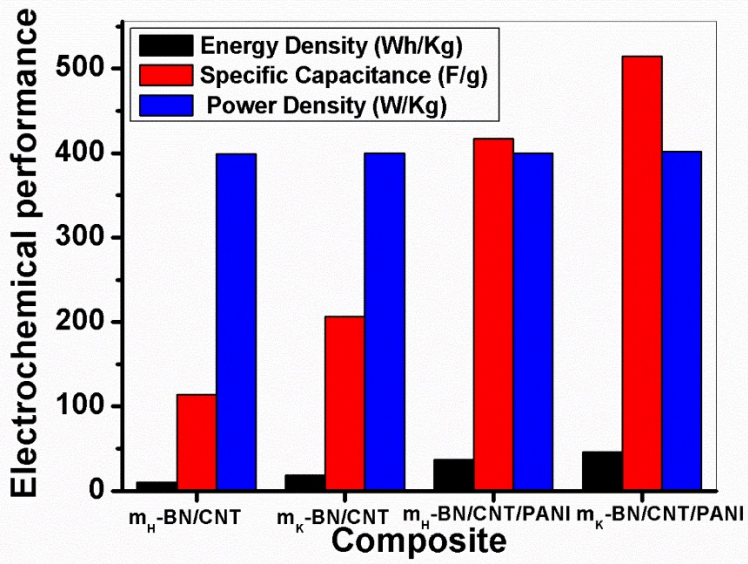

Figure S9. Bar plot of specific capacitance, energy density and power density of m_H-BN/CNT, m_K-BN/CNT, m_H-BN/CNT/PANI, and m_K-BN/CNT/PANI in 1M aqueous KCl solution as electrolyte in three electrode system.

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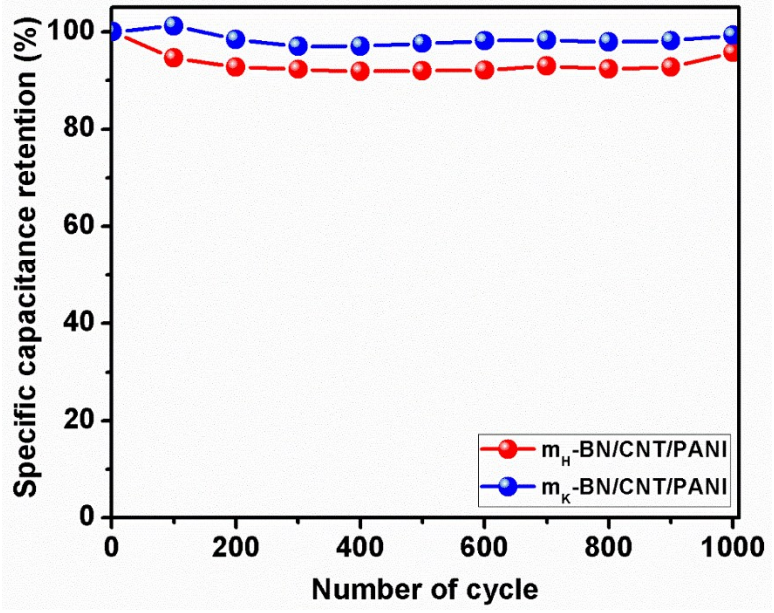


Figure S10. Cyclic stability curves of m_H-BN/CNT/PANI and m_K-BN/CNT/PANI composites up to 1000 cycles in 1M aqueous KCl solution as electrolyte in three electrode system.

S3. Device fabrication

Preparation of Cathode: m_H-BN/CNT/PANI along with carbon black (CB) and binder PVDF in the weight ratio (80:15:5) was thoroughly grinded with NMP solvent. The obtained paste was coated over 2x4 cm carbon fiber (current collector) and dried overnight, which acted as the cathode for the supercapacitor device.

Preparation of Anode: CB and PVDF in the ratio 90:10 were thoroughly mixed with NMP solvent. The paste was coated over 2x4 cm carbon fiber (current collector) and dried overnight, which acted as the anode for the supercapacitor device.

Device set-up: The cathode and the anode were assembled together with tissue paper as the separator which was then pressed using G-Clamp and 1M $TEABF_4$ in DMSO as well as 1M $TEABF_4$ in acetonitrile (ACN) were used as the electrolyte. All electrochemical analysis was performed in Biologic SP 300 instrument.

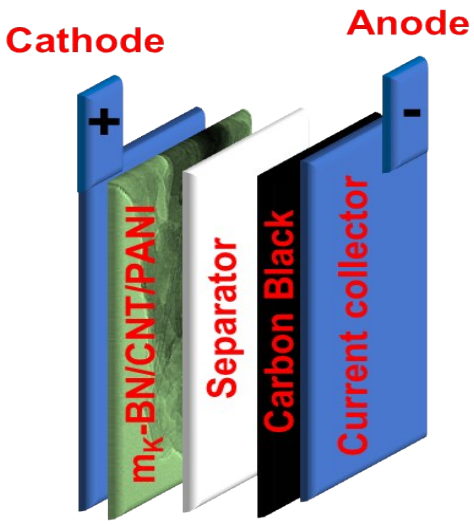


Figure S11. Schematic representation of ASC device.

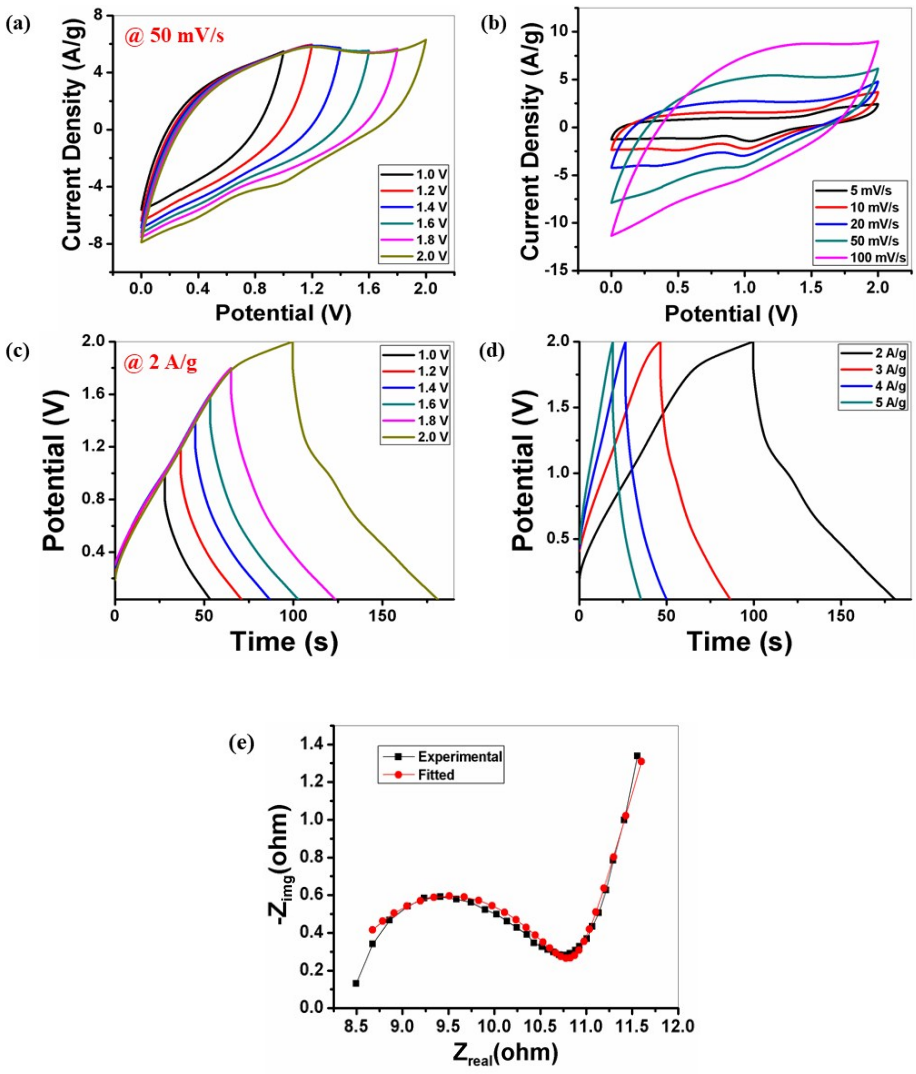
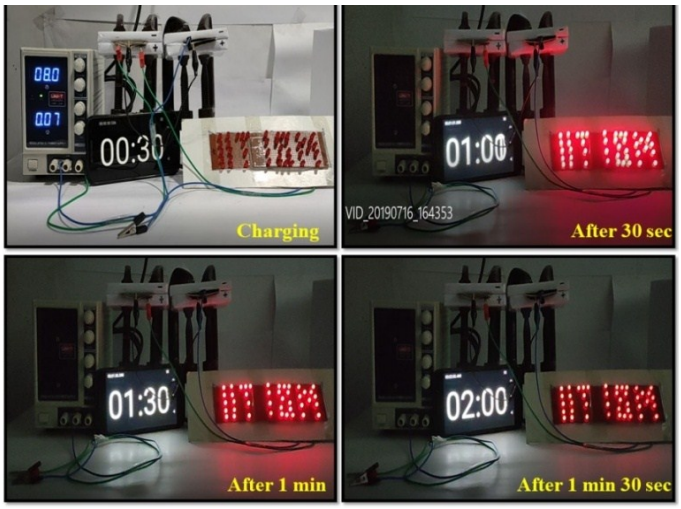


Figure S12. Electrochemical performance of the ASC in 1M $TEABF_4$/Acetonitrile: (a) CV plots at different potential windows at a constant scan rate of 50 mV/s, (b) CV plots at different scan rates within the potential window of 0 to 2.0 V, (c) GCD plots at different potential windows at a constant current density of 2 A/g, (d) the GCD plots at different current densities within the potential window of 0-2.0 V, and (e) fitted Nyquist plot .

(a)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Charging
01:00
VID_20190716_164353
After 30 sec
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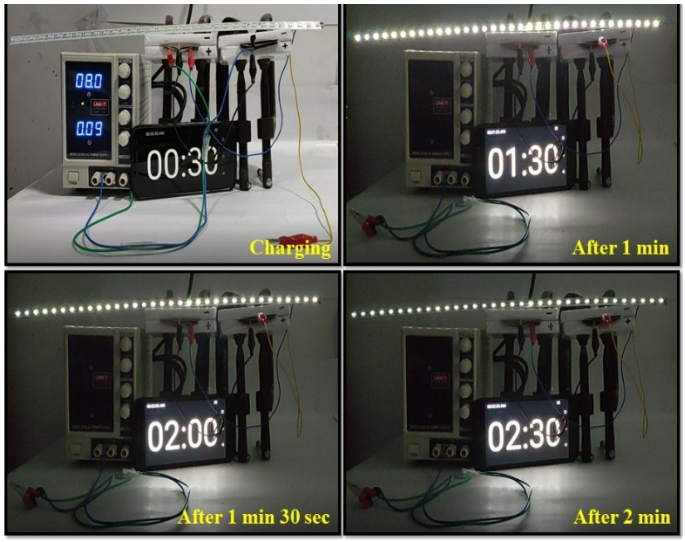
After 1 min
02:00
After 1 min 30 sec

(b)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Charging
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After 1 min
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After 1 min 30 sec
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After 2 min

(c)

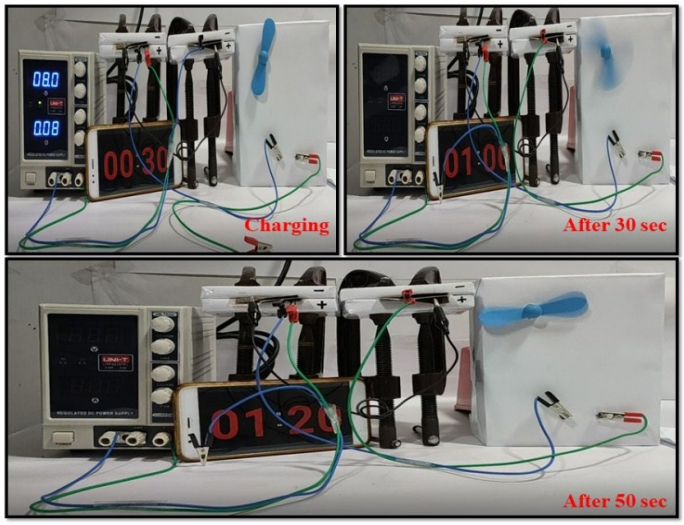
Charging
After 30 sec
After 50 sec

Figure S13. Demonstrations of the practical application of the devices with respect to time during discharging (two ASC devices were connected in series): (a) charging set up of the devices and glowing of 43 red LEDs with the logo of IIT-ISM, (b) charging set up of the devices and lighting of 4 V LED strip, and (c) charging set up of the devices and running of 2V fan.

References:

1. S. Ardizzone, G. Fregonara and S. Trasatti, *Electrochim. Acta.,* 1990, **35,** 263-267.

2. Y. H. Lee, K. H. Chang and C. C. Hu, *J. Power Sources.,* 2013, **227,** 300-308.

3. J. Duay, S. A. Sherrill, Z. Gui, E. Gillette and S. B. Lee, *Acs Nano.,* 2013, **7,** 1200-1214.