

## Supporting Information

### Candle soot derived Carbon nanodot/Polyaniline Hybrid Materials through Controlled Grafting of Polyaniline Chains for Supercapacitors

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## **Experimental Section**

### **Detailed method of preparation**

#### **Preparation of Carbon nanodot (CND)**

The candle soot is collected by placing a knife just over the candle flame and then it is oxidized by refluxing for 12 hours in 9(M) HNO<sub>3</sub> solution. The black residue with brown colored supernatant is then centrifuged for 30 minutes at 13000 rpm and the black color residue separated to get a perfectly transparent, homogeneous brown colored solution. This solution is then neutralized with Na<sub>2</sub>CO<sub>3</sub> followed by extensive dialysis with a dialysis bag having MWCO 12000. The solution found after dialysis is freeze dried to get the oxidized CNDs. The yield of CNDs finally obtained after dialysis is ~ 350 mg from 1 gm of carbon soot taken (about 35% conversion).

#### **Preparation of *N,N'*-bis(4'-aminophenyl)-1,4-quinonediimine (APQD): a trimer of aniline in emeraldine state**

Synthesis of APQD is carried out following a literature reported procedure by Wei et. al.<sup>1</sup> In a typical procedure, 0.86 gm (8 mmol) of p-phenylenediamine is dissolved in a solution of 100 ml aqueous 1 (M) HCl and 40 ml ethanol. Solution is then cooled to about -5°C in a NaCl and crushed ice bath. In the next step 1.8 gm (8mmol) of APS is added in this solution with stirring under air atmosphere. After 5 minutes, the reaction solution becomes dark brown and then 1.5 ml (16 mmol) of aniline, freshly purified through vacuum distillation, is added quickly. After several minutes, a blue particle suspension is formed and reaction mixture is stirred vigorously for additional 30 minutes. Solid product is then collected by filtration through a Buchner funnel and is washed repeatedly with 30 ml of 1 (M) HCl followed by 80 ml double distilled water. The product obtained is then treated with 40 ml 1(M) aqueous solution of ammonia for 2 hours. The

mixture is finally filtered and remaining solid is washed with double distilled water until filtrate becomes neutral which is followed by drying. The weight of the final product is 0.85 gm that is a 30% of yield is produced. The compound shows melting point at 172°C; FT-IR: 3419 cm<sup>-1</sup>, 1594 cm<sup>-1</sup>, 1496 cm<sup>-1</sup>, 1284 cm<sup>-1</sup>, 1221 cm<sup>-1</sup>, 1159 cm<sup>-1</sup> and 821 cm<sup>-1</sup>.

#### **Preparation of CND capped *N,N'*-(4'-aminophenyl)-1,4-quinonediimine derivative (CNDT)**

In a round bottom flask, 80 mg CND is mixed with 8 ml of oxaloyl chloride followed by addition of 1 ml dried DMF and then the mixture is stirred at room temperature under argon atmosphere for 4 hours in a magnetic stirrer. After that, oxaloyl chloride is removed under reduced pressure. The residue is then dissolved in 12 ml purified and dried DMF and kept under argon atmosphere (solution-I). In another round bottom flask, 250 mg APQD (which is pre-treated with 100 ml 0.01 (M) HCl solution in water followed by washing with acetone and drying) is dissolved in 9 ml dried DMF and thoroughly sonicated (solution-II). Then in an ice cold condition, solution-I is slowly added in drop wise fashion into solution-II over a long time period (~ 4 hours) which is followed by addition of 3 ml triethylamine and then the mixture is stirred in a magnetic stirrer overnight at 5°C. Finally the product is dialyzed in water to remove DMF and other water soluble components and freeze dried to get the final product weighing 185 mg.

#### **Grafting of Polyaniline from Carbon nanodot surface**

A stock solution of about 0.4 (M) aniline is prepared by adding 10 ml aniline in 250 ml of 0.6(M) HCl (Stock 'A'), having 0.2 ml (204 mg) purified aniline equivalent in 5 ml of it. Aniline polymerizations are carried out in presence of different amounts of CNDT or CND. In a typical polymerization procedure, 50 mg of CNDT is mixed with 40 ml water and stirred overnight in a magnetic stirrer. In next step, 5 ml stock 'A' is added to it and sonicated for an hour. Then the mixture is stirred at 4°C for 3 hours followed by addition of 0.613 gm of ammonium perdisulfate

(APS) ([Aniline]:[APS] = 1:1.25), dissolved in 5 ml water, quickly into it. An instant development of blue color is observed which becomes more intense with time due to the pernigraniline salt formation and after 55 minutes the colour changes to green indicating emeraldine salt formation and hence the polymerization is completed. The entire polymerization is monitored through UV/VIS spectrophotometric method by withdrawing 100 micro liters of aliquot from the polymerization mixture time to time. After completion of polymerization, the green precipitate is centrifuged and washed thoroughly with 0.2 (M) HCl solution followed by water in multiple times and then dried in a vacuum oven for 48 hours. The aniline conversion noted is 47% through gravimetry. The sample is named CNDTP50(1) and when the above polymerization is carried out in presence of [Aniline]:[APS] = 1:1.75, the aniline conversion is found to be 71% and the sample is named CNDTP50(2). Similarly other polymerization reactions using 10 mg, 20 mg, 30 mg of CNDT or 15 mg CND as additives are named CNDTP10, CNDTP20, CNDTP30 or CNDP15 respectively.

#### **Reduction followed by re-oxidation of CND/PANI hybrid material**

Reduction of the oxygenated functionalities present on the CND surface of CND/PANI (CNDTP) hybrid materials is carried out following a literature reported method<sup>2</sup> which is followed by reoxidation of the PANI chains to the emeraldine state. In a typical experiment, 60 mg CNDTP50(1) is dispersed in 50 ml deionized water, then 0.2 ml hydrazine monohydrate is added and the mixture is heated at 95°C for 1 hour. In subsequent stage, the product mixture is cooled, sonicated, washed several times with deionized water to remove excess hydrazine and finally the product is collected by filtration. The resulting material is dispersed further in 10 ml 2 (M) HCl followed by addition of 40 mg APS. The mixture is sonicated well and stirred at room

temperature for overnight. Final product is collected through centrifugation, washed several times with deionized water and dried in vacuum oven for 48 hours.

### **Characterization**

UV-VIS spectroscopy of CND and CNDTP/CNDP systems are carried out in Hitachi U-3210 UV-vis spectrophotometer. Photoluminescence (PL) studies of CNDs are conducted in Horiva Jovin Yvon Fluoromax-3 instrument. Analysis of surface morphology of the samples are done in FESEM (JEOL, JSM 6700F) instrument operating at 5 kV after coating with platinum for 90 s. Samples are prepared for FESEM analysis either through casting from dilute aqueous dispersion or powder samples pasted on carbon tape. Surface topology of the samples casted from dilute aqueous dispersion on freshly cleaved mica surface is observed through atomic force microscopy (AFM) (Veeco, model AP0100) in noncontact mode at a tip resonance frequency of 300 kHz. TEM imaging of the samples are carried out by HRTEM (JEOL, 2010EX) instrument operating at an acceleration voltage of 200 kV. In this purpose, a very much dilute aqueous dispersion of the sample is drop casted onto a 300 mesh carbon coated copper grid and after drying it is used for TEM analysis directly. The FTIR spectroscopy is carried out in FTIR-8400S instrument (Shimadzu) using KBr pellets. XPS analysis of the samples is performed by using a focused monochromatized Al K $\alpha$  X-ray source (1486.8 eV) in Omicron Nano-Technology 0571 XPS instrument. Raman spectroscopic studies are performed using a Raman triple spectrometer (model T-64000, Horiba-Jobin Yvon) fitted with a synapse detector. The samples were excited with a 514.5 nm laser (Spectra Physics, model Stabilite 2017). The WAXS analysis of the powder samples are performed by using a Bruker AXS diffractometer (D8 advance) using CuK $\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ), a generator voltage of 40 kV and a current of 40 mA. The specific surface area of the samples were calculated from the N<sub>2</sub> adsorption and desorption isotherms measured

using Autosorb 1C instrument (Quantachrome, USA) at 77 K .Electrochemical experiments like cyclic voltgram (CV) and galvanostatic charge/discharge (GCD) is done by a CHI6087E electrochemical workstation (CHI, USA) by a conventional three electrode system. A modified glassy carbon electrode (GCE) is used as working electrode along with a saturated calomel electrode (SCE) as the reference electrode. Pt wire electrode is used as auxiliary electrode and 1(M) H<sub>2</sub>SO<sub>4</sub> as electrolyte.

**Electrode fabrication and electrochemical measurements**

Glassy carbon electrodes (GCE) (3 mm in diameter, surface area of 0.07 cm<sup>2</sup>) are carefully polished with 1, 0.3, and 0.05 μm alumina powder and sequentially washed through water and ethanol with sonication at room temperature until a mirror finish was obtained before use. The preparation of supercapacitor electrode is done by casting a slurry, containing 80% of the active material with 10% Carbon Black and 10% PVDF in (1:1) 1-methyl-2-pyrrolidone (NMP)/cresol medium, onto GCE. The coating is then dried in a vacuum oven at 60<sup>0</sup>C for about 24 hours and subsequently electrochemical measurements are carried out in 1(M) H<sub>2</sub>SO<sub>4</sub> medium. The specific capacitance (C<sub>s</sub>), energy density (E) and power density (P) are calculated from the following equations

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \text{ (F/g) .....(i)}$$

$$E = \frac{C_s \times \Delta V^2}{7.2} \text{ (W h/kg).....(ii)}$$

$$P = \frac{E \times 3600}{\Delta t} \text{ (W/kg).....(iii)}$$

Here I = current (A), Δt = discharge time (s), ΔV = voltage window (V) after deduction of the IR drop and m = mass of the active material.

Further, the charge storage performances of hybrid materials are compared by operating CV and GCD tests in two electrode cell configurations containing two symmetrical electrodes. In order to fabricate the symmetrical cell, a pair of GCE electrode are loaded with equal amount of the above mentioned slurry containing 80% of the active material with 10% Carbon Black and 10% PVDF in (1:1) 1-methyl-2-pyrrolidone (NMP)/cresol medium and then dried as stated above. The electrodes are separated by Whatman filter paper in 1(M) aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte. The material based specific capacitance (C<sub>E</sub>) of individual electrodes; energy density (E<sub>S</sub>) and power density (P) of symmetrical supercapacitors are calculated from GCE tests according to the following relations:

$$C_E = 4 \times \frac{i \times \Delta t}{m \times \Delta V} \dots\dots\dots (iv)$$

$$E_S = \frac{C_E \times \Delta V^2}{28.8} \dots\dots\dots (v)$$

$$P = 3600 \times \frac{E_S}{\Delta t} \dots\dots\dots (vi)$$

Where ‘i’ is the applied current in ampere (A), ‘m’ is the total mass of the active material used in cell, ΔV is the potential window in volt (V) excluding the IR drop and Δt is the total discharge time in second (s).

UV/VIS study of CND:

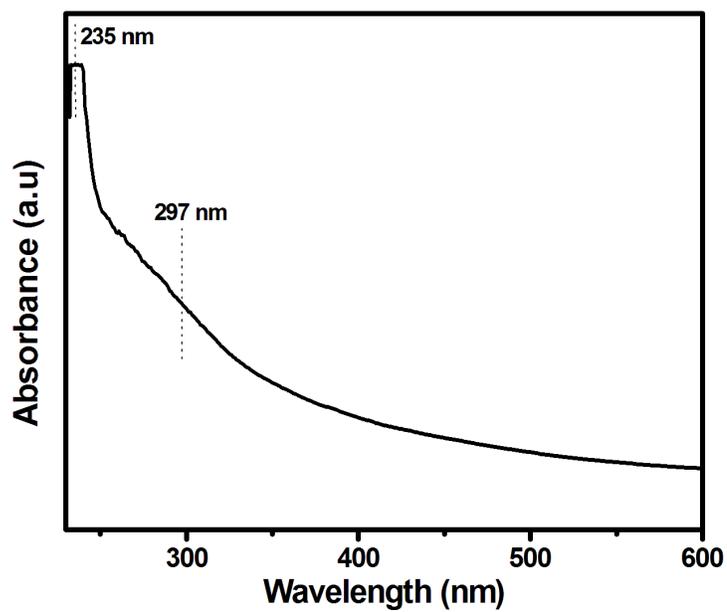
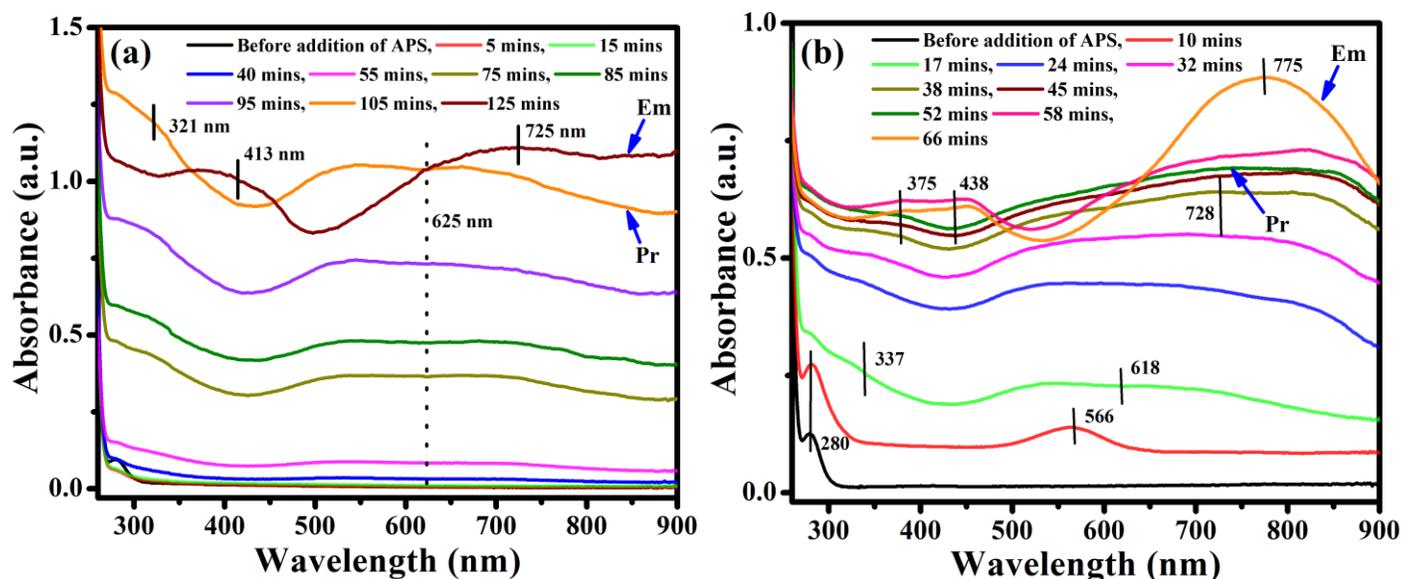


Figure S1: UV/VIS spectrum of CND in aqueous medium

## UV/VIS study of CNDP composite during aniline polymerization with time:

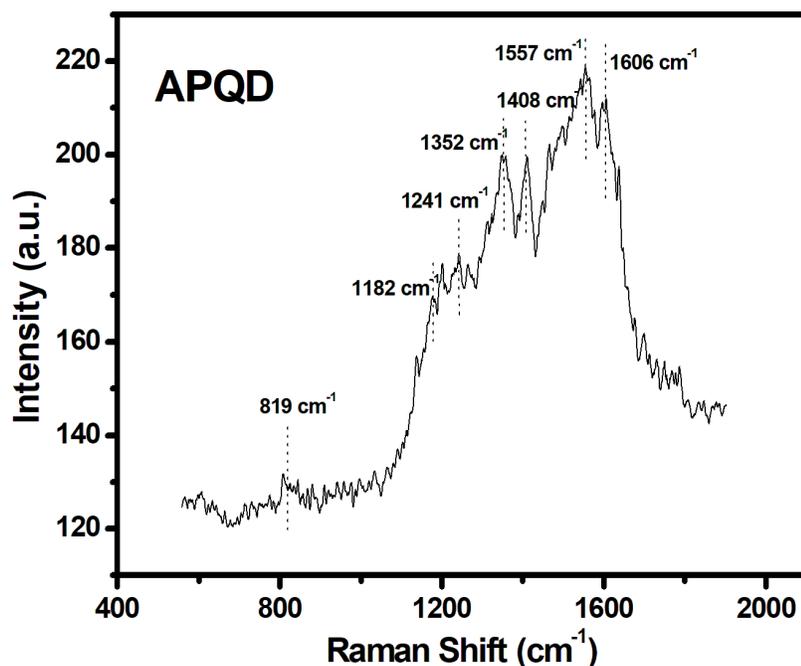


**Figure S2:** Evolution of UV/VIS spectra during aniline polymerization with time: a) for CNDP15 system and b) CNDTP50(1) system

In Figure S2(a) absorption centered at 321 nm and 625 nm corresponding to the high and low energy band absorptions of pernigraniline salt form<sup>3-5</sup> respectively. The beginning of polymerization is observed visually through development of blue coloration after a long induction period of about 65 minutes. After 125 minutes the signal positions are changed to 413 nm and 725 nm corresponding to amalgamated ( $\pi$ - $\pi^*$ ) band of benzenoid ring with ( $\pi$ -polaron) transition for the former and (polaron- $\pi^*$ ) for the latter respectively for emeraldine salt form.<sup>3-6</sup> The transition from pernigraniline to emeraldine salt form also becomes apparent visually through a color change from blue to green of the polymerization mixture. This indicates stock of APS is exhausted and the aniline polymerization is terminated.<sup>3</sup> In Figure S2(b) the signal at 280 nm corresponds to ( $n$ - $\pi^*$ ) transition originating from CNDT surface functionalities before addition of APS and at the initial stage of polymerization after 10 mins. A relatively sharp signal

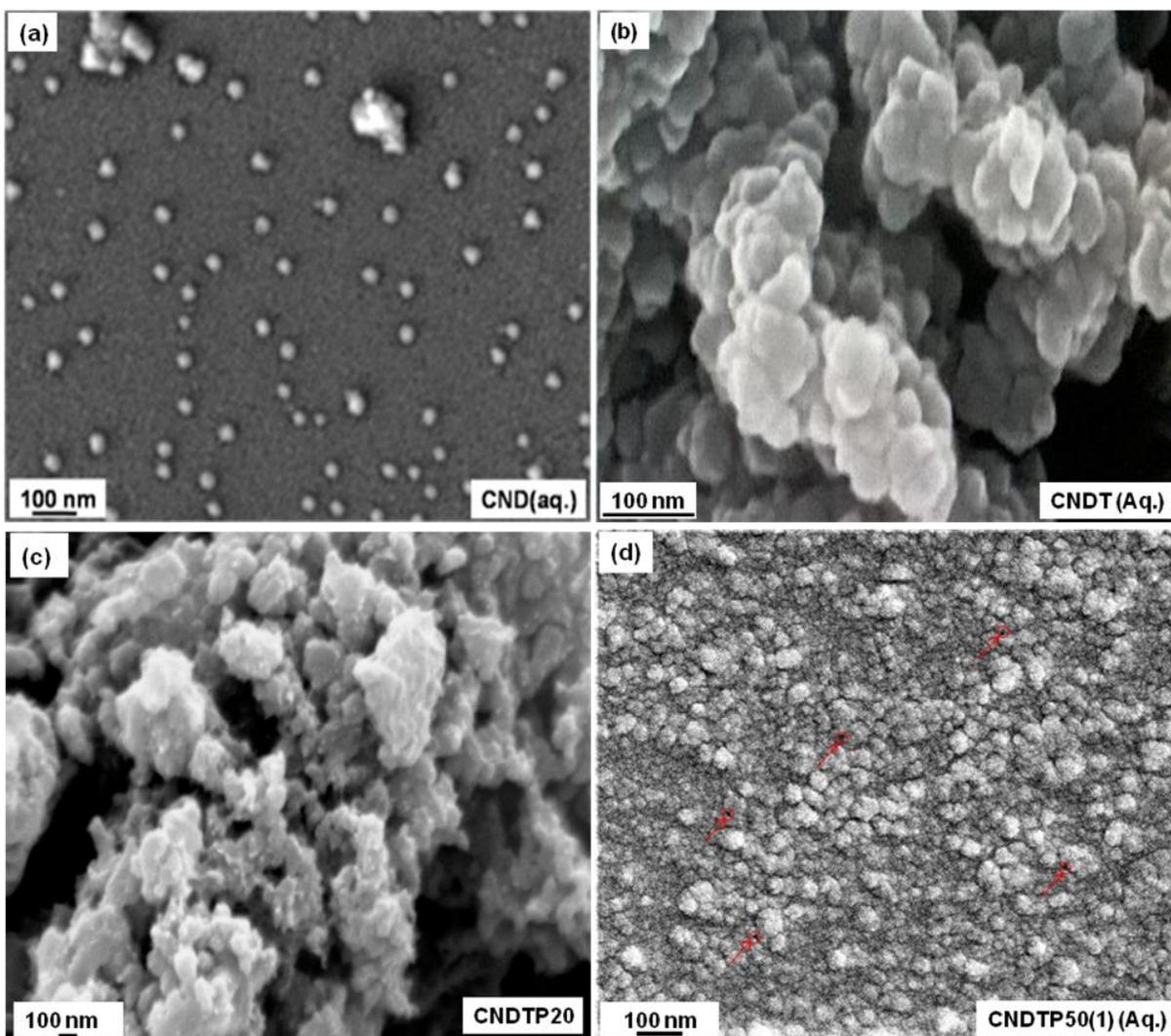
at 566 nm probably signifying the pernigraniline salt form of oligomeric aniline (generated through oxidation of APQD moieties) is observed after 10 mins of reaction. However, with increasing degree of polymerization, these signals disappear and absorptions at ~337 nm and a broad signal at ~618 nm appear due to pernigraniline salt formation of PANI.<sup>6</sup> Signals at 337 nm and 618 nm show a continuous red shift up to 375 and 728 nm (after 52 mins) until the stock of APS is exhausted probably signifying increase in length of  $\pi$ -conjugation due to the growth of PANI chains. At 58 mins of polymerization, the absorption signal is completely shifted to produce a pair of signals at 438 nm and 775 nm corresponding to the high and low energy polaron band of emeraldine salt form respectively and no further shift in signal intensity or absorption position is observed signifying termination of polymerization.

### Raman spectrum of APQD:



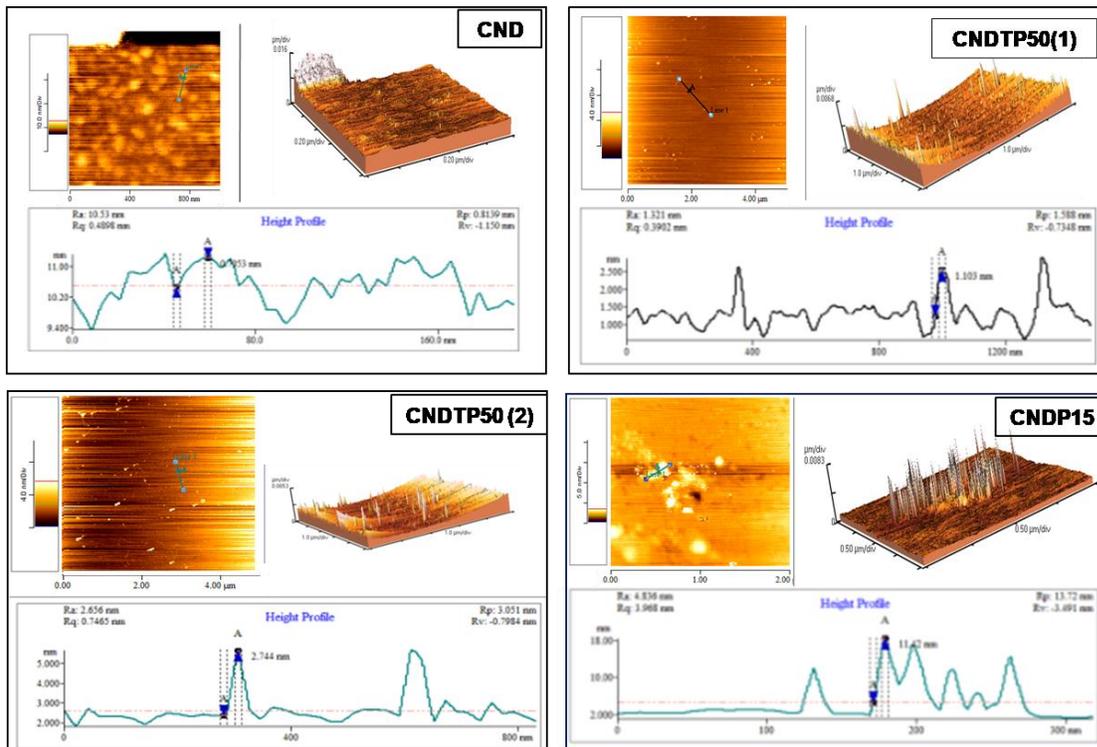
**Figure S3:** Raman spectrum of N,N'-(4'-aminophenyl)-1,4-quinonediimine (APQD) obtained after exciting at 514.5 nm. Signals at 819 cm<sup>-1</sup>, 1182 cm<sup>-1</sup>, 1241 cm<sup>-1</sup>, 1352 cm<sup>-1</sup>, 1408 cm<sup>-1</sup>, 1557 cm<sup>-1</sup> along with a shoulder at 1606 cm<sup>-1</sup> are attributed to ring deformation of benzene/quinonoid rings, (C-H) bending of the benzene ring, C-N stretching vibration of the benzenoid ring, protonated C-N stretching, (C=N) stretching of quinonoid ring and (C-C) stretching of the benzene/quinonoid ring respectively

**FESEM images of CND, CNDT, CNDTP20, CNDTP50(1):**

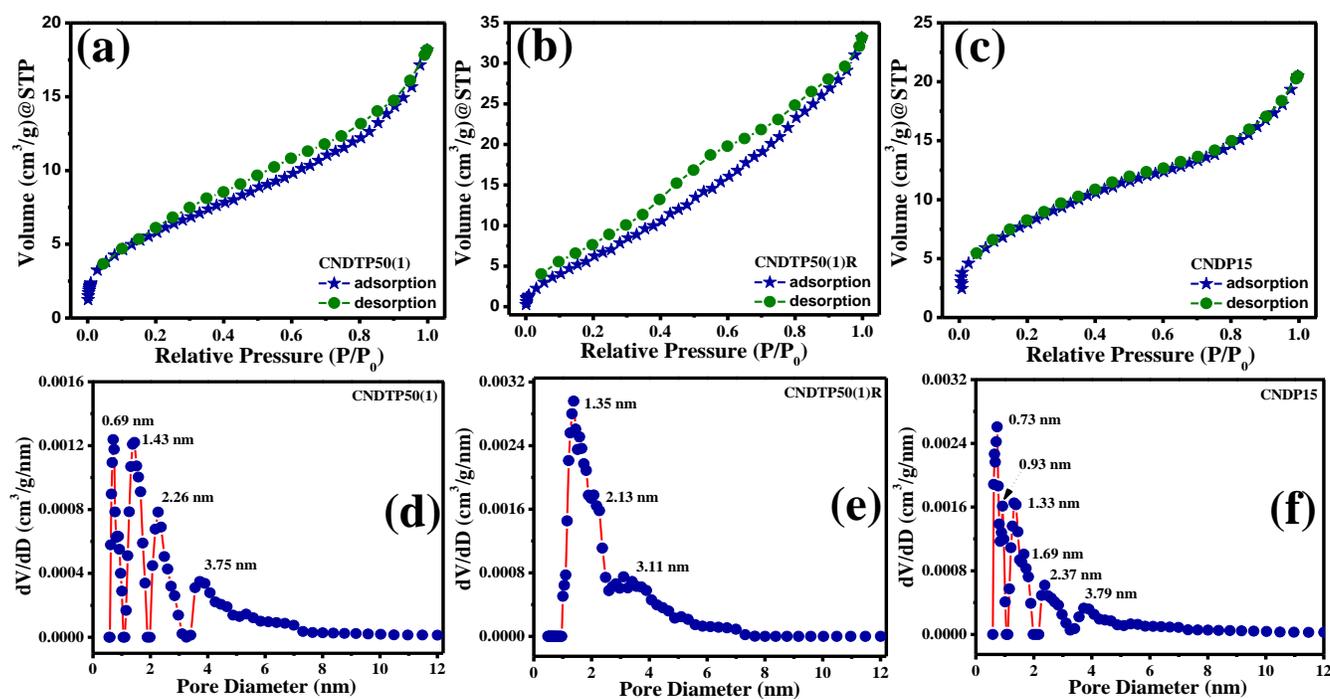


**Figure S4:** FESEM images of a) CND casted from a dilute aqueous solution, b) CNDT casted from dilute aqueous dispersion, c) CNDTP20 powder sample pasted on carbon tape, d) CNDTP50(1) casted from dilute aqueous dispersion, encircled are pores having sizes in the range of 5 to 15 nm.

**AFM analysis for CND, CNDTP50 (1), CNDTP50 (2) and CNDP15 samples:**



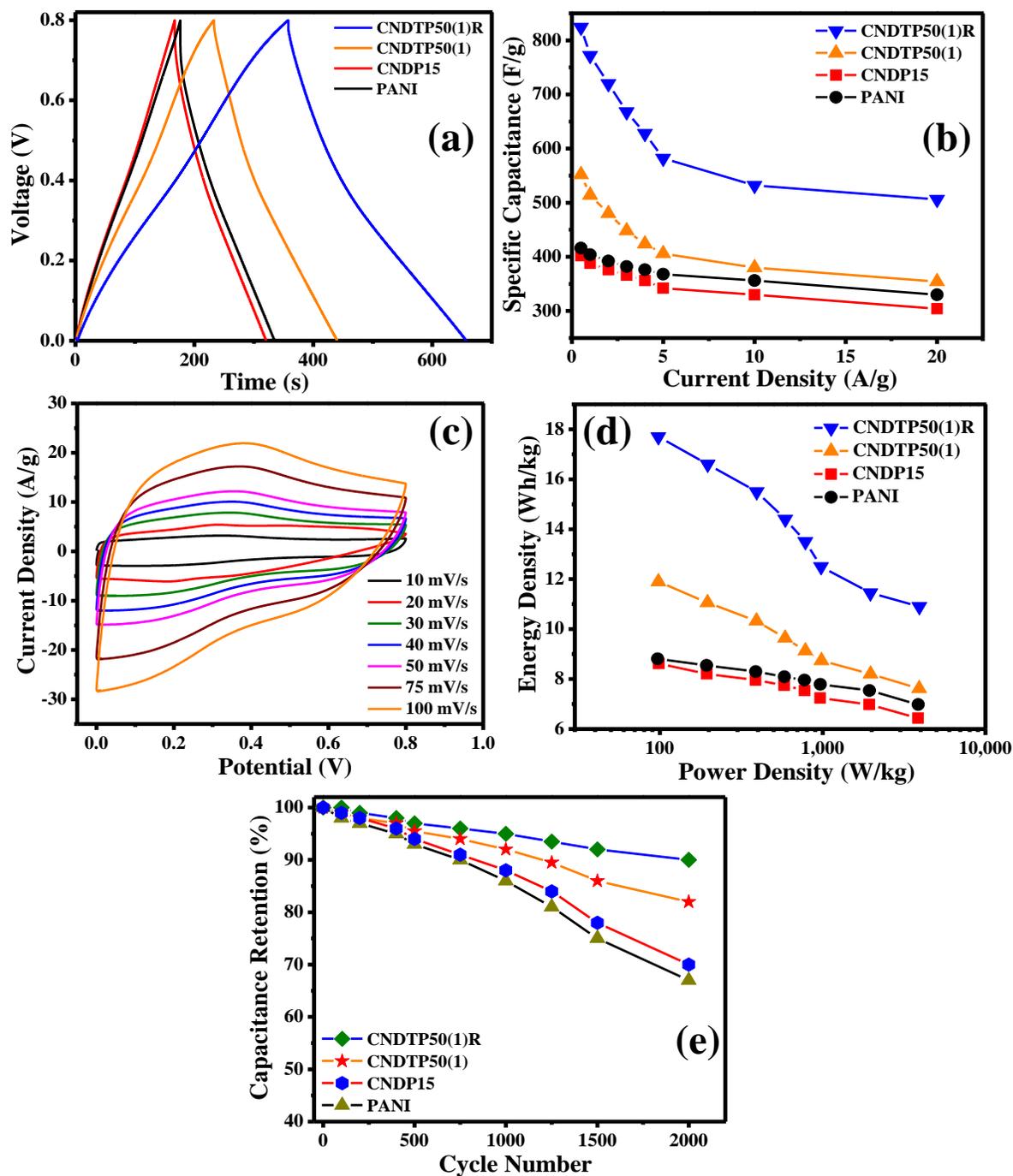
**Figure S5:** AFM analysis on mica surface for CND, CNDTP50(1), CNDTP50(2) and CNDP15 samples after casting from their dilute aqueous dispersion.



**Figure S6:** (a)-(c) represents N<sub>2</sub> adsorption/desorption isotherm and (d)-(f) pore size distribution (slit pore, NLDFT equilibrium model) of CNDTP50(1), CNDTP50(1)R, and CNDP15 respectively.

**Table S1:** Summary of BET surface area, pore volume and pore diameter

Sample	BET surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Pore diameter range (nm)
CND	13.38	0.051	(1.58-6.9)
CNDTP50(1)	22.58	0.028	(0.69-6.99)
CNDTP50(1)R	33.29	0.049	(1.35 - 6.68)
CNDP15	28.29	0.032	(0.73-4.46)



**Figure S7:** Electrochemical analysis of the samples carried out in a two electrode cell. (a), (b), (d) and (e) represents galvanostatic charge/discharge curves, plot of specific capacitance vs. current density, Ragone plot [values for max. energy density and power density: 17.7 Wh/kg & 3924 W/kg for CNDTP50(1)R; 11.9 Wh/kg & 3918 W/kg for CNDTP50(1); 8.81Wh/kg & 3865 W/kg for PANI; 8.62 Wh/kg & 3858 W/kg for CNDP15] and cyclic stability respectively corresponding to CNDTP50(1)R, CNDTP50(1), CNDP15, PANI samples and (c) scan rate variation plots for CNDTP50(1)R sample.

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