Supporting Information

Polyaniline-MnO_2 nanotubes hybrid nanocomposite as supercapacitor electrode material in acidic electrolyte

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1. Experimental

1.1 Material characterization

Powder X-ray diffraction (XRD) measurements were performed using PANalytical X'PERT Pro X-ray diffractometer with nickel-filtered Cu Kα radiation at a step size of 0.016°. Fourier transform infrared (FTIR) spectra were recorded using Perkin-Elmer 580B infrared spectrophotometer using KBr pellet technique. The morphology of samples were characterized using a field-emission scanning electron microscope (FESEM;FEI Quanta) and a high resolution transmission electron microscope (HRTEM; Technai-G20, 200 kV).

1.2 Preparation of supercapacitor electrodes and electrochemical measurements

The electrodes, used for the electrochemical measurements were prepared by mixing the as-prepared PANI/MNTs and 5 wt% Nafion (binder) with a mass ratio of 95:5 in Isopropanol and then resulting gel solution was spray coated on conducting carbon fabric (SGL, Germany). These

prepared electrodes were vacuum dried overnight at 120°C. The weight of the electrode was measured by a METTLER TOLEDO XS105 analytical balance with an accuracy of 0.01 mg. Aluminum plates were used as current collector, polypropylene as a separator and 1M H_2SO_4 as electrolyte in the supercapacitor electrode assembly. A symmetric model capacitor was constructed using two PANI/MNTs films as electrodes. The capacitive properties of the cells were investigated by cyclic voltammetry (CV), chronopotentiometry (CP) and impedance spectroscopy (EIS). All electrochemical measurements were carried out with a CHI608C electrochemical workstation.

2. Result and discussion

2.1 X-ray diffraction

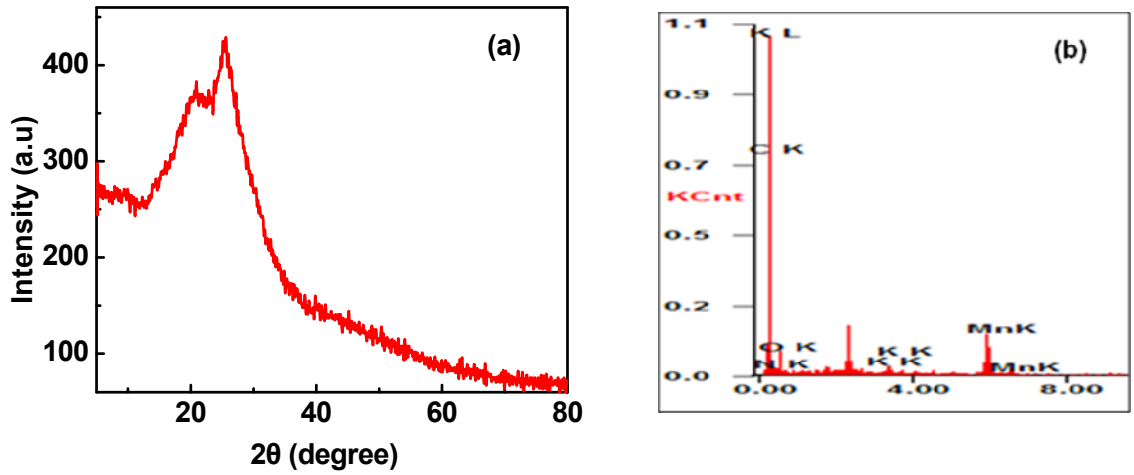

Fig. S1 X-ray diffraction pattern (a), EDS spectra (b) of PANI/MNTs hybrid nanocomposite

Fig. S1(a) shows the XRD pattern of PANI/MNTs hybrid nanocomposite. The XRD pattern of PANI/MNTs composite is mainly dominated by the PANI. The peak around 2θ ~ 20° and 25° has a similar profile as that of free PANI in literature.[1-2] Although, the broadening at 2θ ~ 25°

suggests the presence of MnO_2 that is inactive in XRD. Fig. S1 (b) shows EDS spectrum of PANI/MNTs hybrid nanocomposite also proving the existence of manganese element.

2.2 Conductivity measurement

Electrical conductivity of the samples at room temperature were measured using the four-probe arrangement connected to a Keithley 2400 source meter. The powder samples were pressed into pellets of 13 mm diameter using hydraulic press. The measured conductivity of MNTs and PANI/MNTs are 5 x 10^{-4} S/cm and 5 x 10^{-2} S/cm respectively.

2.3 Electrochemical analysis

Chronopotentiometry test gives the direct information about the electrochemical capacitance. The value of the specific capacitance (C_S) was obtained from the charge–discharge cycling measurements according to the following equation

$$C_s = \frac{2 \times I \times \Delta t}{m \Delta V} \qquad (1)$$

where I is the discharge current, m is the mass of material at each electrode and Δt_d is the time required for discharging the capacitor during the voltage drop of ΔV(after correcting for iR drop). A factor of 2 is incorporated due to the series capacitance formed in a two-electrode system.

The energy density E, power density P and coulombic efficiency η were calculated using following equations

$$E = \frac{1}{2} C_{cell} V^2 \qquad \mathbf{(2)}$$

$$P = \frac{E}{\Delta t_d} \quad \textbf{(3)}$$

$$\eta = \frac{\Delta t_d}{\Delta t_c} \quad \textbf{(4)}$$

Where $C_{cell} = ½\ C_S$ is the specific capacitance of the cell, V is the cell voltage after correcting for iR drop and Δt_c and Δt_d are charging and discharging time respectively.

Fig. S2 represents the variation of specific capacitance and magnitude of iR drop with specific current density. The iR drop is attributed to the equivalent series resistance (ESR) of PANI/MNTs hybrid system which arises due to the resistance of both the electrolyte and the PANI/MNTs film. The increase in iR drop at fixed potential with increasing the specific current density is mainly attributed to the resistance of the electrolyte. The increase in iR with increasing potential is generally attributed to increase in film resistance. A maximum capacitance of 626 F/g was calculated for the specific current density of 2 A/g. When specific current density increased from 2 A/g to 20 A/g a drop of about 23% was observed in the specific capacitance i.e 77% capacitance was still retained. The good retention of capacitance values at higher current densities manifests the high rate capability of the electrode material.

The power density is determined by the rates at which discharging of an electrical energy storage device is conducted by the storage device. Fig. S3 shows the variation of power density and coulombic/discharge efficiency with specific current densities. A maximum power density of 5 kW/kg and 98.5% coulombic efficiency was measured at a specific current density of 20 A/g.

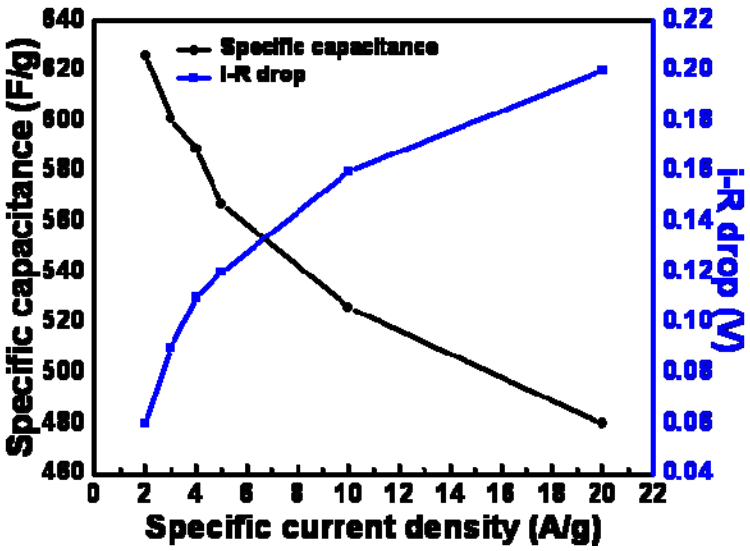

Fig. S2 Variation of specific capacitance and iR drop with specific current density

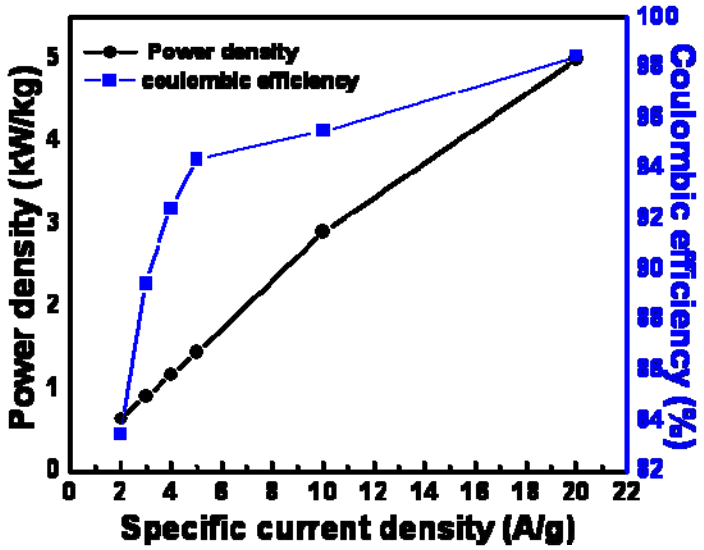

Fig. S3 Variation of power density and coulombic efficiency with specific current density

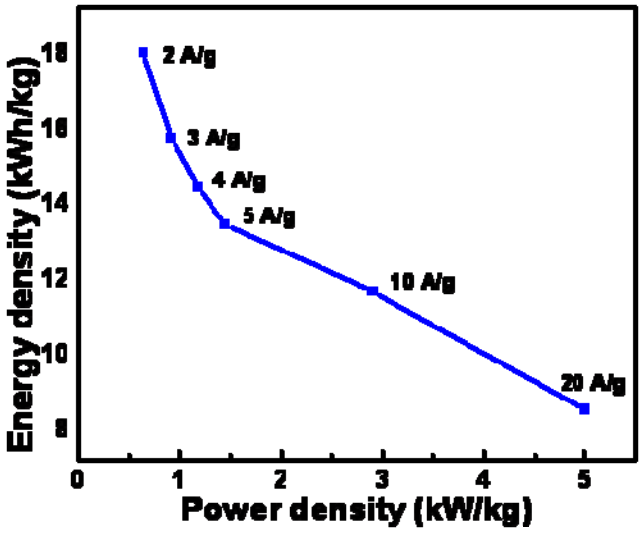

Fig. S4 Ragone plot

The Ragone plot, the relationship between energy density and current density, is shown in the Fig.S4. At present, the commercial supercapacitor based on activated carbons typically show energy density 4-5 Wh/kg with power density of 1-2 kW/kg.[3] The present study have shown that the PANI/MNTs based symmetric supercapacitor could store higher energy density compare to commercial supercapacitor based on activated carbons, without compromising in energy density.

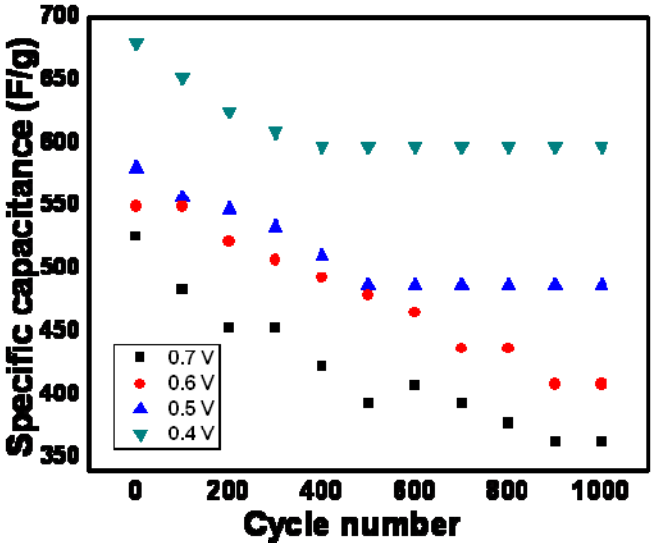

Fig. S5 Variation of specific capacitance with respect to cycle number at a 20 specific current density of 10 A/g

Table.1 Literature data on PANI/MnO_2 based electrodes for supercapacitor applications

Material	Specific capacitance (F/g)	Remark	Ref.
PANI/MnO2	601.48	Capacitance from charge-discharge measurement in three electrode configuration, 0.1 mA cm^{-2}	4
PANI/MnO2	500	Capacitance from CV, 50 mVs^{-1}	5
PANI/MnO_2/AC	408	Capacitance from charge-discharge measurement, 4 mA cm^{-2}, organic electrolyte	6
PANI/MnO2/MWCNTs	384	Capacitance from charge-discharge measurement, 2.5 mA cm^{-2}, organic electrolyte	7
PANI/MnO2	532	Capacitance from charge-discharge measurement, 2.4 mA cm^{-2},	8
PANI/MnO2	588	Capacitance from charge-discharge measurement, 1 mA cm^{-2},	9
PANI/MnO2	510	Capacitance from charge-discharge measurement in three electrode configuration, 1 A/g	10

Reference

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