Supporting Information

Preparation of $MnFe_2O_4$ Decorated Flexible Graphene Wrapped with PANI and its Electrochemical Performances for Hybrid Supercapacitors

Kalimuthu Vijaya Sankar, Ramakrishnan Kalai Selvan*

Solid State Ionics and Energy Devices Laboratory, Department of Physics, Bharathiar University, Coimbatore – 641 046, Tamil Nadu, India.

Corresponding Authors Information:

*E-mail address: **selvankram@buc.edu.in** **(R.K.Selvan)**

Charge Balancing between (AC) positive and (CMGP) negative electrodes:

The charge balancing between the electrodes are important for hybrid supercapacitor. It can be expressed as [1, 2]

$$q^{+} = q^{-} \tag{1}$$

Further, the charge stored in the positive and negative electrodes can be expressed as

$$q^{+} = C_{+} \times \Delta V_{+} \times m_{+} \tag{2}$$

$$q^{-} = C_{-} \times \Delta V_{-} \times m_{-} \tag{3}$$

For Positive electrode

$$q^{+} = 236.5 \times 0.4 \times 1 \times 10^{-3} \tag{4}$$

$$q^{+} = 151 \times 10^{-3}\, C \tag{5}$$

For negative electrode

$$q^{-} = 188 \times 0.8 \times 1 \times 10^{-3} \tag{6}$$

$$q^{-} = 150.4 \times 10^{-3}\, C \tag{7}$$

It reveals that the charge stored in the positive electrode is almost same as negative electrode ($q^{+} \approx q^{-}$).

In addition, the mass balancing between positive and negative electrodes can be expressed as

$$\frac{m_{+}}{m_{-}} = \frac{C_{-} \times \Delta V_{-}}{C_{+} \times \Delta V_{+}} \tag{8}$$

$$m_{+} = \frac{188 \times 0.8}{236.5 \times 0.4} \times 1 \times 10^{-3} \tag{9}$$

$$m_{+} = \frac{150.4}{94.6} \times 1 \times 10^{-3} \tag{10}$$

$$m_{+} = 1.58 \times 10^{-3} \tag{11}$$

Hence, the optimized mass ratio between AC and CMGP is approximately 1.6.

Equations

(i). The specific capacitance of the electrode is calculated using the following equation as

$$C_p = \frac{\int i(V)dV}{m \times \Delta V \times s}$$

Where, C_p is specific capacitance F g^{-1}, i(V) is CV current (mA), m is mass of active material, ΔV is potential window (V), and s is scan rate.

(ii). Area occupied hydrated (S) ions in the electrode can be calculated using

$$S = \frac{C_p \times N \times \Delta V \times \sigma}{F}$$

Where, N is Avogadro's number, σ is cross-sectional area of hydrated ions, and F is Faraday constant.

(iii). The specific capacitance is calculated from charge-discharge analysis is

$$C_s = \frac{i \times \Delta t}{m \times \Delta V}$$

Where, C_s is specific capacitance (F g^{-1}), i is current density (mA cm^{-2}), Δt is the discharge time (sec), m is mass of active material (mg), and ΔV is potential window (V).

(iv). The active site in the electrode material can be calculated using the following equation as

$$z = \frac{C_s \times n \times \Delta V \times M}{F}$$

Where, C_s is specific capacitance F g^{-1}, n is number of transfer of electrons, ΔV is potential window (V), M is molecular weight, and F is Faraday constant.

(v). The energy density and power density of the hybrid supercapacitor is calculated using the following equation

$$E_{cell} = \frac{1}{2} C_{cell} \Delta V^2$$

$$p_{cell} = \frac{E_{cell}}{\Delta t}$$

Where, E_{cell} is energy density of the cell (Wh kg^{-1}), C_{cell} is specific capacitance (F g^{-1}), P_{cell} is power density (W kg^{-1}).

Calculation of theoretical specific capacitance

$MnFe_2O_4$:

Let's consider a single electron is transfer in the $MnFe_2O_4$ during electrochemical reaction means the theoretical specific capacitance can be found using following manner

$$C_t = \frac{n \times F}{\Delta V \times m}$$

= (1*96487)/(0.8*230.6262)

=5 22 F g^{-1}

Hence, the theoretical specific capacitance for $MnFe_2O_4$ is 522 F g^{-1}. The reported graphene theoretical specific capacitance is **550** F g^{-1} [1]. Hence, the theoretical specific capacitance for MG-20 as

For $MnFe_2O_4$ (80%)

100 % of Mn = 522

80% of Mn = (522*80)/100 = 418 F/g

For graphene (20%)

100 % of graphene = 550

20% of graphene = (550*20)/100 = 110 F/g

Hence, MG-20 has theoretical specific capacitance is 528 F/g

Further, the theoretical specific capacitance for **PANI is 2000** F/g [2].

Hence, the theoretical specific capacitance for MGP-5 as

For MG-20 (95%)

100 % of MG-20 = 528

95% of MG-20 = (528*95)/100 = 418 F/g

For PANI (5%)

100 % of PANI = 2000

5% of PANI = (2000*5)/100 = 100 F/g

Hence, MGP-5 has theoretical specific capacitance is 601 F/g

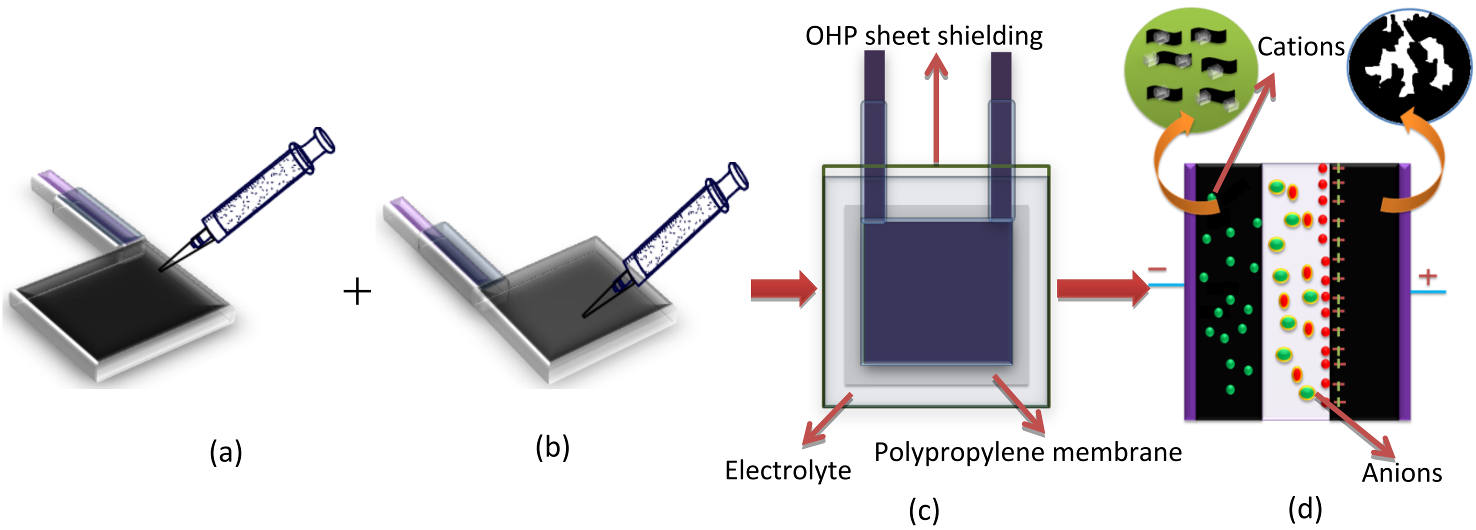


Fig. S1 Schematic representation for the (a, b) preparation of MGP (Negative) and activated carbon (Positive) electrodes, (c) is the fabricated hybrid supercapacitor and (d) the charge storage mechanism in hybrid supercapacitor.

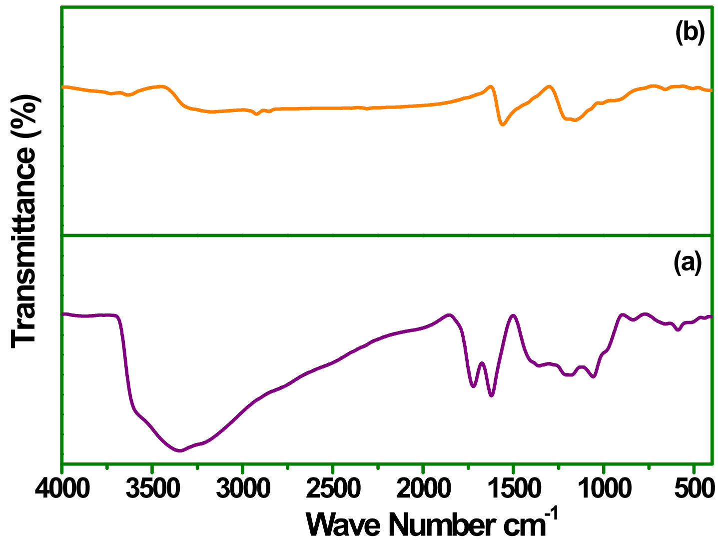


Fig. S2 FT-IR spectra of (a) graphene oxide and (b) graphene.

The FT-IR (Figure S2(a)) spectrum of graphene oxide reveals that the presence of functional groups like carbonyl group (1058 cm^{-1}), epoxyl (1203 cm^{-1}), hydroxyl (1358 cm^{-1}), and carboxyl (1722 cm^{-1}). Subsequently, the C-C band of graphitic carbon and adsorbed water peaks are observed at 1622 and 3346 cm^{-1}. On the other hand, the disappearance and reduction of intensity of the peaks of above mentioned wave number is represents (Figure S2(b)) the deoxygenation or reduction of graphene oxide to graphene. Hence, the NaOH is playing as a reducing agent for producing graphene via green route method.

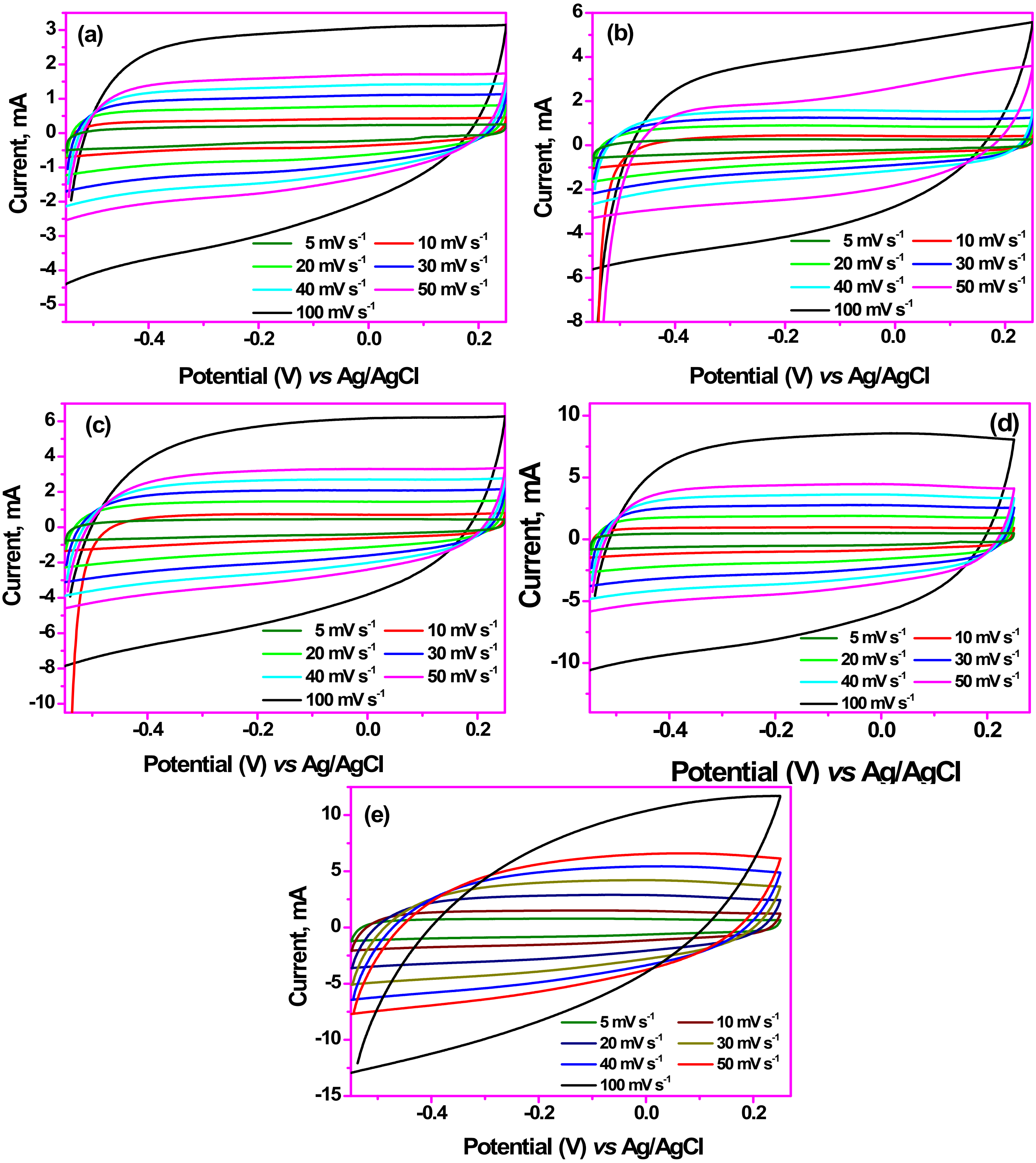


Fig. S3 CV curves of M-3, MG-5, MG-10, MG-20, and MG-30 at different scan rates such as 5-100 mV s^{-1}.

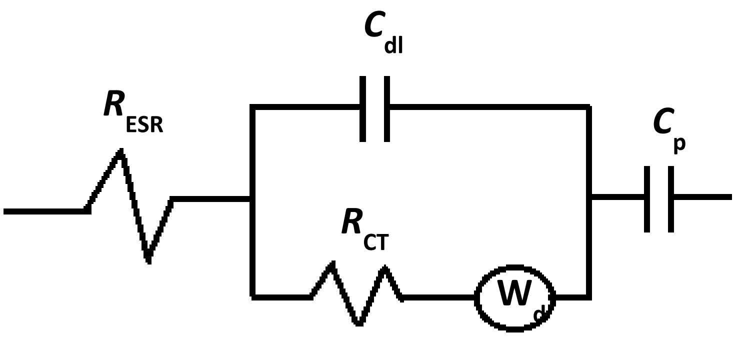


Fig. S4 Equivalent circuit for fitting impedance plot.

In this equivalent circuit, R_{ESR}, R_{ct}, C_{dl}, W_d and C_p are represents the equivalent serious resistance, charge transfer resistance, double layer capacitance, Warburg factor and pseudocapacitance.

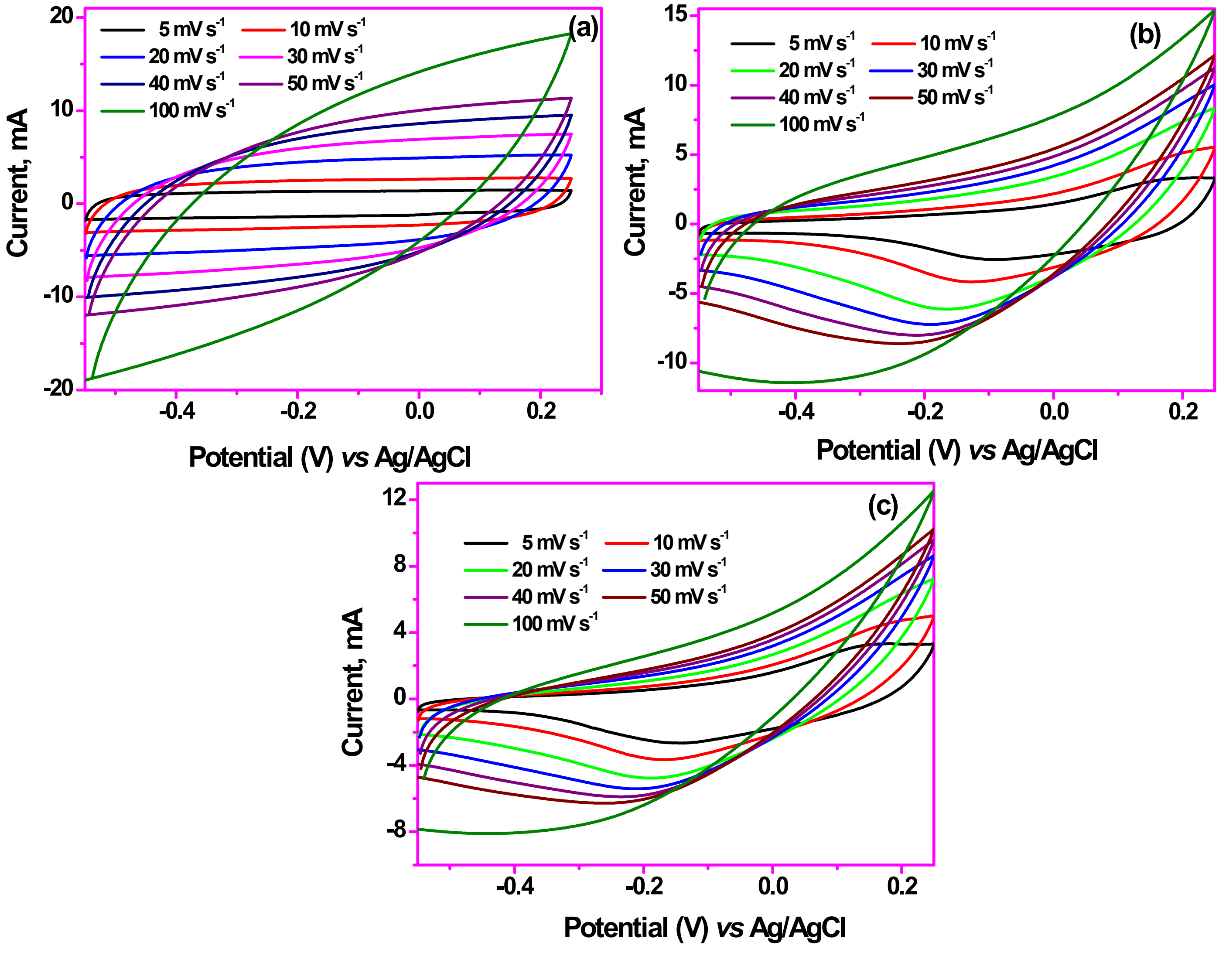
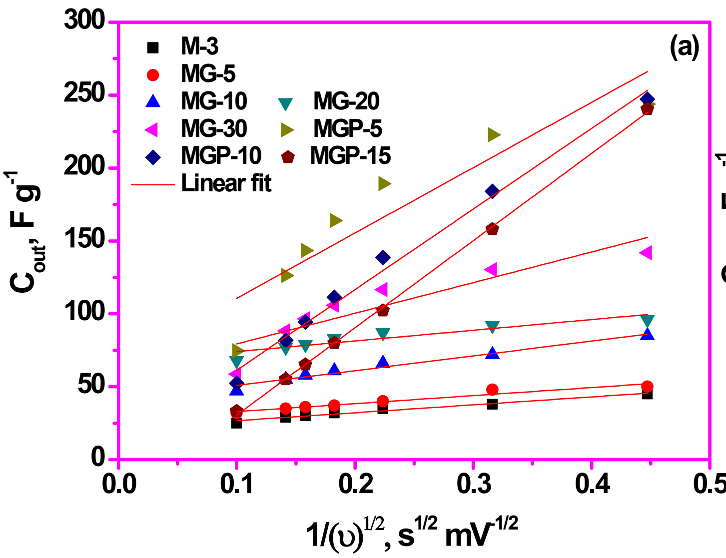


Fig. S5 CV curves of (a) MGP-5, (b) MGP-10 and (c) MGP-15 at different scan rates.



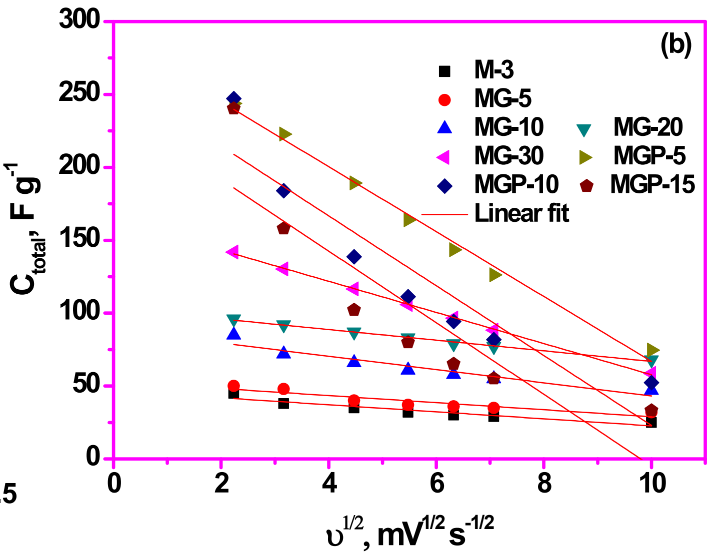


Fig. S6 Trasatti plot of (a) C_{out} *versus* $1/(u)^{1/2}$ and (b) C_{total} *versus* $(u)^{1/2}$ for M-3, MG-5, MG-10, MG-20, MG-30, MGP-5, MGP-10 and MGP-15.

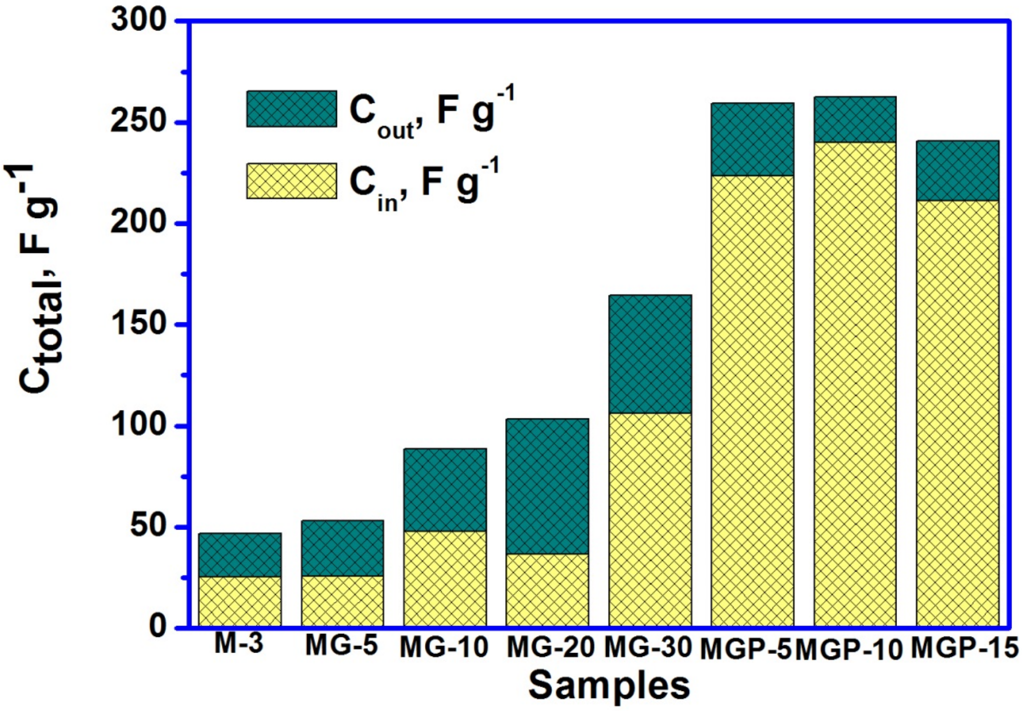


Fig. S7 Comparison of the total specific capacitance exhibited by inner and outer surface of the electrodes of M-3, MG-5, MG-10, MG-20, MG-30, MGP-5, MGP-10 and MGP-15.

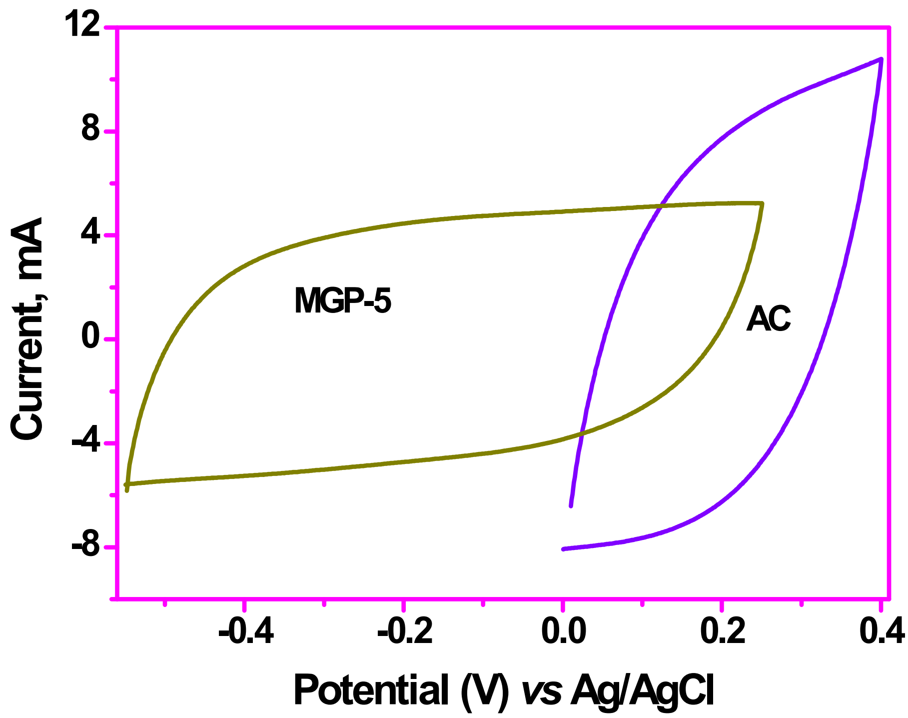


Fig. S8 CV curve of positive and negative electrodes at 20 mV s^{-1} in 1M NaCl electrolyte.

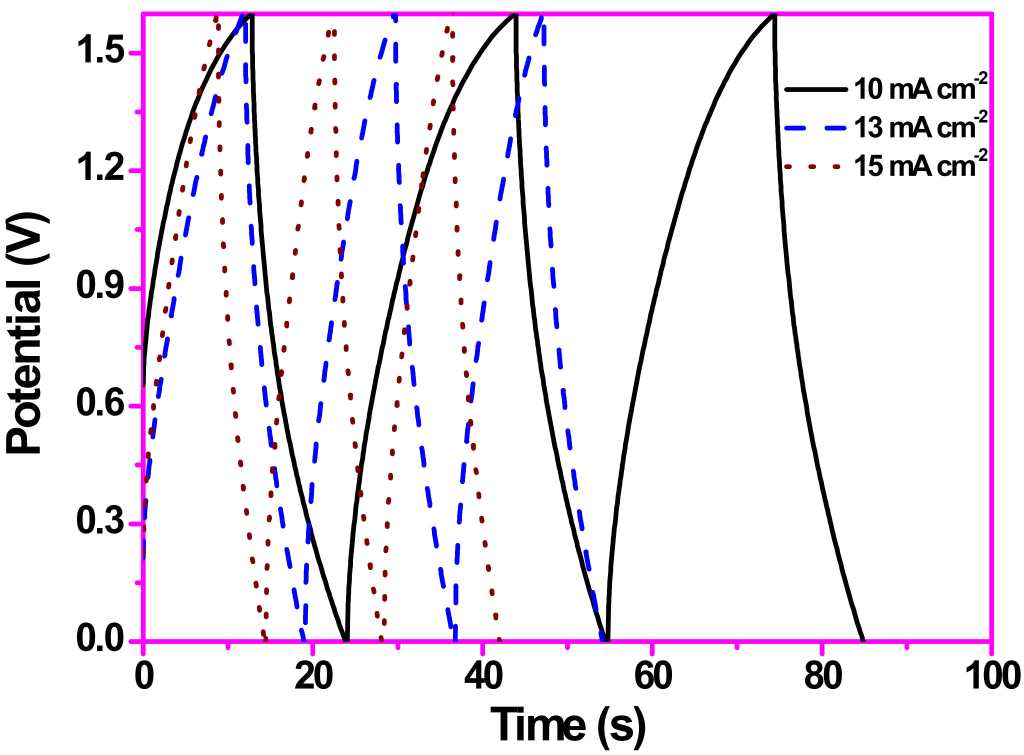


Fig. S9 GCDs curves of hybrid supercapacitor at different current densities.

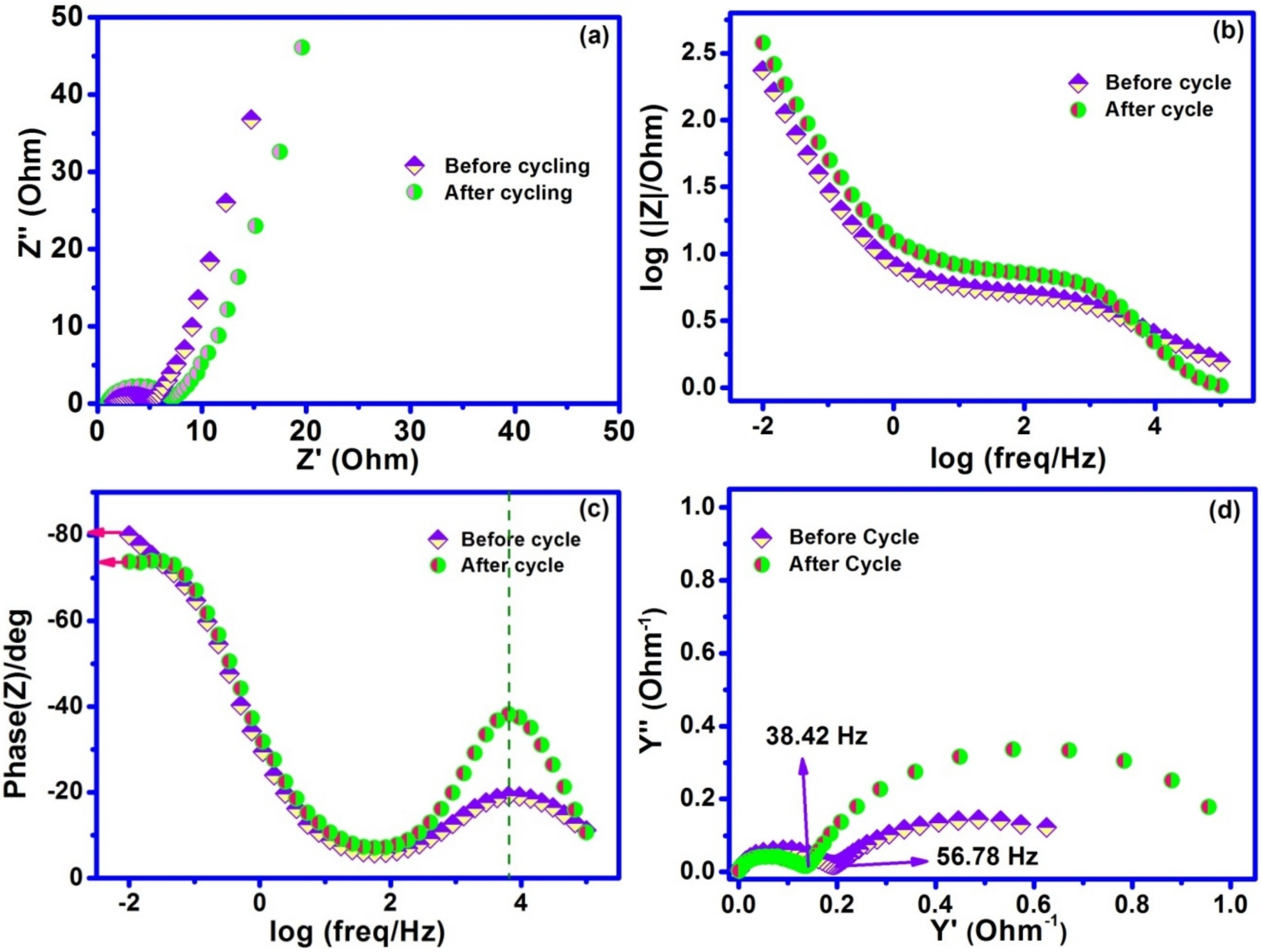


Fig. S10 (a) Nyquist plot, (b, c) bode plot and (d) admittance plot of hybrid supercapacitor before and after cycling.

Table 1. Electrochemical impedance spectra fitted parameters

Sample	C_{dl} (F) x 10^{-6}	W_d (Ohm $S^{-1/2}$)	C_p (F)	Error (χ/√N)
M-3	23.84	36.91	0.022 87	0.05260
MG-5	27.17	15.10	0.056 12	0.05912
MG-10	12.83	10.63	0.041 84	0.05942
MG-20	15.42	7.108	0.028 07	0.06139
MG-30	36.41	16.84	0.107 30	0.05302
MGP-5	28.00	5.063	0.180 50	0.06552
MGP-10	26.20	25.78	0.086 59	0.08763
MGP-15	25.20	27.82	0.086 59	0.07356
Cell before cycling	11.08	11.64	0.050 11	0.07615
Cell after cycling	9.236	14.80	0.044 92	0.09200

References

1. X. Li, H. Song, Y. Zhang, H. Wang, K. Du, H. Li, Y. Yuan and J. Huang, *Int. J. Electrochem. Sci.,* 2012, **7,** 5163 – 5171.
2. H. Li, J. Wang, Q. Chu, Z. Wang, F. Zhang and S. Wang, *J. Power Sources,* 2009, **190**, 578–586.