Electronic Supplementary Information

Enhanced supercapacitor performance of 3D architecture tailored using atomically thin rGO-MoS_2 2D sheets

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I. Experimental Section

Synthesis of GO

Materials

$K_2S_2O_8$, Conc. H_2SO_4, P_4O_{10}, Powdered graphite, $KMnO_4$, 30% H_2O_2, 2.5% H_2SO_4, 11% HCl. All the chemicals were of analytical grade and purchased from Sigma Aldrich, USA. All the reagents were used without any purification and deionized water was used in all the experiments.

Methodology

GO was synthesized from graphite powder by a modified Hummers method. 12 g of graphite powder is pre-oxidized in a solution of 50 mL of concentrated H_2SO_4, 10 g of P_2O_5 and $K_2S_2O_8$. The resultant solution is then diluted with DI and filtered. The filtrate is washed with DI water and then dried it in air. For further oxidation, concentrated H_2SO_4 (460 mL) is added while maintaining the temperature at 0° C using an ice bath to prevent overheating and explosion. 60 g of $KMnO_4$ is gradually added keeping the low temperature (<10° C) and the mixture is stirred for 2 h at 35° C. Then, keeping the temperature at 60°C, 920 mL is added slowly maintaining the temperature under 60° C. Again 2.8 L DI water and 50 mL of 30% H_2O_2 are added and allowed to settle for a day. The mixture is further centrifuged, and washed with 10 % HCl solution. It is then washed with DI water and dried in air. As a next step, it is diluted to make a 2% w/w dispersion and filled in dialysis tubes. The brown dispersion was extensively dialyzed to remove residual metal ions and acids for 2 weeks followed by filtration and drying graphene oxide sheets

Preparation of PPy-rGO, PPy-MoS_2 and PPy electrodes

The PPy-rGO was synthesized by electrodeposition method. In a typical procedure, 1 mg mL^{-1} of GO in aqueous dispersion was mixed with 0.1 M of pyrrole (Sigma-Aldrich), purified by distillation and 0.1 M of sodium para-toluenesulfonate (NaPTS, Sigma-Aldrich), in 50 mL of water and was stirred for half an hour at room temperature. NaPTS is a supporting electrolyte cum doping agent for the electrochemical polymerization of pyrrole. Then this solution that acts as the electrolyte was kept in a cyclic voltammetry pot. The electrodeposition was performed at constant potential of 0.6 V by employing a piece of carbon felt with an effective area of ~ 2.5 cm^2 as working electrode immersed in the electrolyte under mild stirring. A calomel electrode (SCE) and a platinum wire were used as reference electrode and counter electrode, respectively. The electrodepositions were performed for different durations from 30 min to 2 h, for different deposition potentials from 0.4 to 0.8 V and by varying the area of deposition.

Similarly, PPy-MoS_2 was synthesized by electrodeposition method. In this procedure, 7 mM of ammonium tetrathiomolybdate (ATTM, Sigma-Aldrich) was mixed with 0.1 M of pyrrole (Sigma-Aldrich) purified by distillation, and 0.1 M of sodium para-toluenesulfonate (NaPTS, Sigma-Aldrich), in 50 mL of water and was stirred for half an hour at room temperature. The electrodeposition was performed in a cyclic voltammetry pot by the same method described in PPy-rGO synthesis.

PPy electrode was also prepared by the same method by electrochemical polymerization of pyrrole monomer. 0.1 M of pyrrole monomer (Sigma-Aldrich) purified by distillation was mixed with 0.1 M of sodium para-toluenesulfonate (NaPTS, Sigma-Aldrich), in 50 mL of water and was stirred for half an hour at room temperature and electrodeposition was performed.

The SEM images of PGMo for different MoS$_2$ concentrations

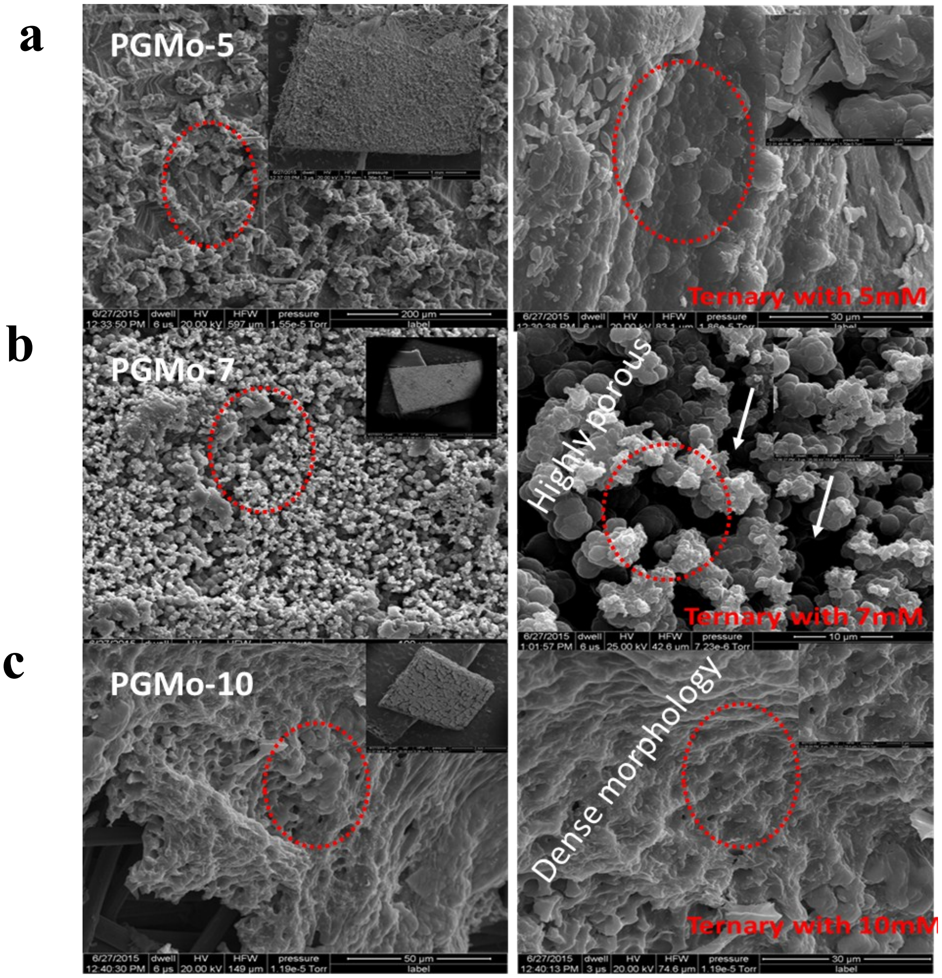

Fig. S1 FESEM images of (a) PGMo-5 (b) PGMo-7 and (c) PGMo-10**.**

The content of MoS$_2$ in the prepared 3D ternary architecture can be optimized for extraction of tunable properties by changing the concentration of ATTM. PGMo-5 portrays a surface morphology of fibrous dense or stacked GO sheets, since the amount of MoS$_2$ is too less to be dispersed to prevent stacking of rGO. For PGMo-10, MoS$_2$ petals are restacked during the fabrication process with a close robust physical contact to form a less porous dense framework. As a consequence, the optimum concentration of MoS$_2$ (PGMo-7) in the prepared 3D ternary architecture allows us to exploit the synergistic effects of the integrated components to the maximum and tap the best in achieving the superior properties.

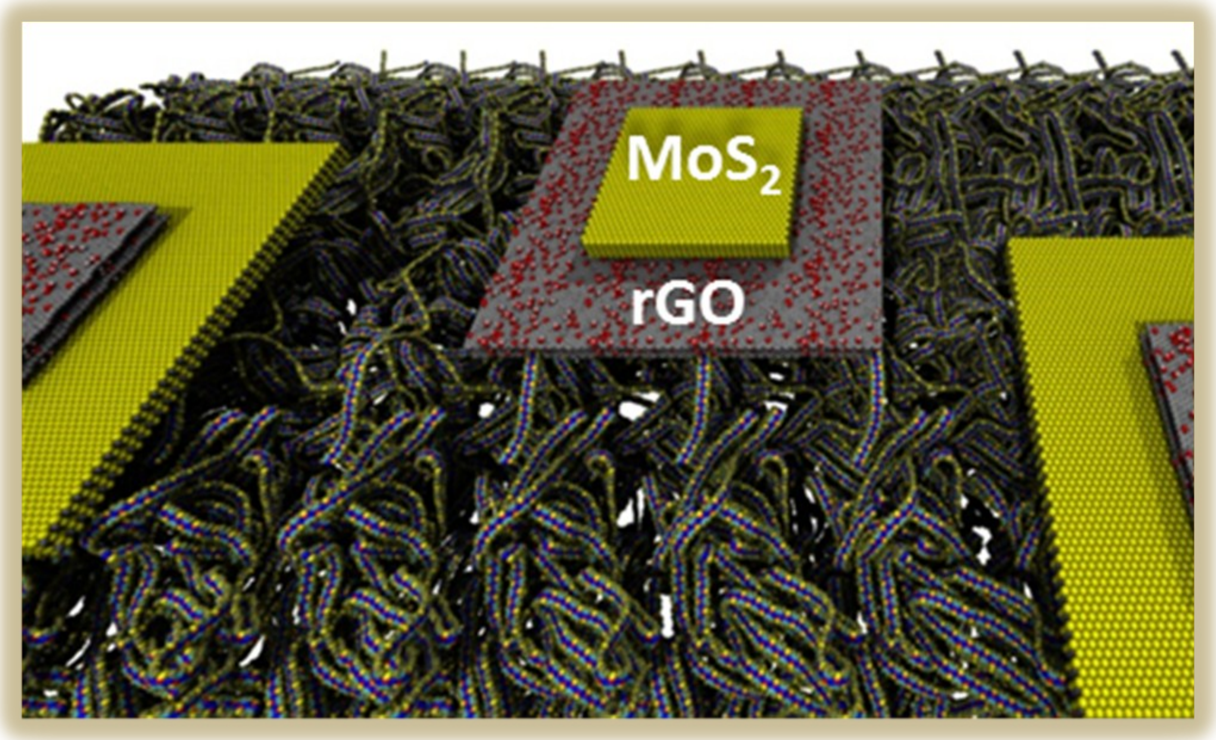

Fig. S2 Schematic of the proposed 3D ternary architecture PGMo.

Simulations suggest the improved stability of the ternary system during cycling and it is due to MoS$_2$ which acts a framework to prevent PPy from cracking (SEM images of Fig. 4) while rGO flakes protect MoS$_2$ fragments, by preventing large deflexions in the latter, thereby reducing their average stress. The simulations were carried within the LAMMPS MD package using a hybrid methodology.

FTIR spectra of PGMo, PPy-rGO, PPy-MoS$_2$ and PPy

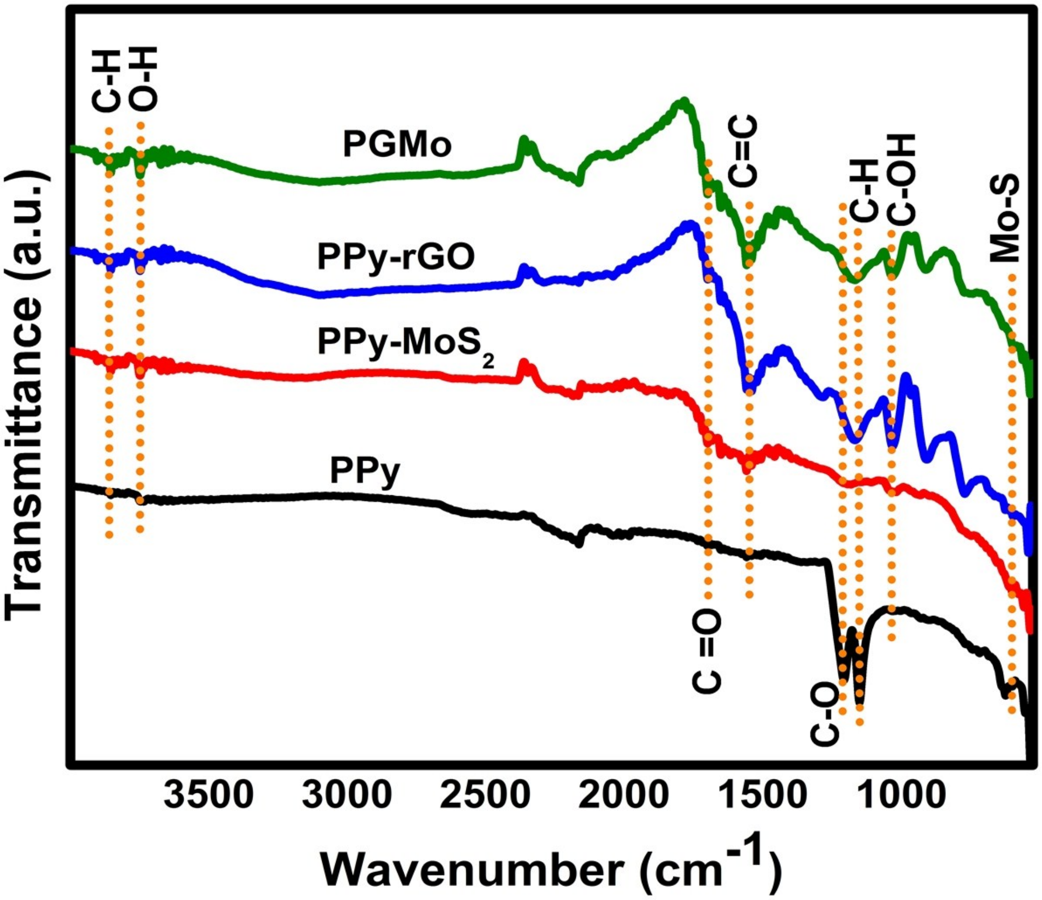

Fig. S3 FTIR spectra of PGMo, PPy-rGO, PPy-MoS$_2$ and PPy.

EDX spectrum of PGMo

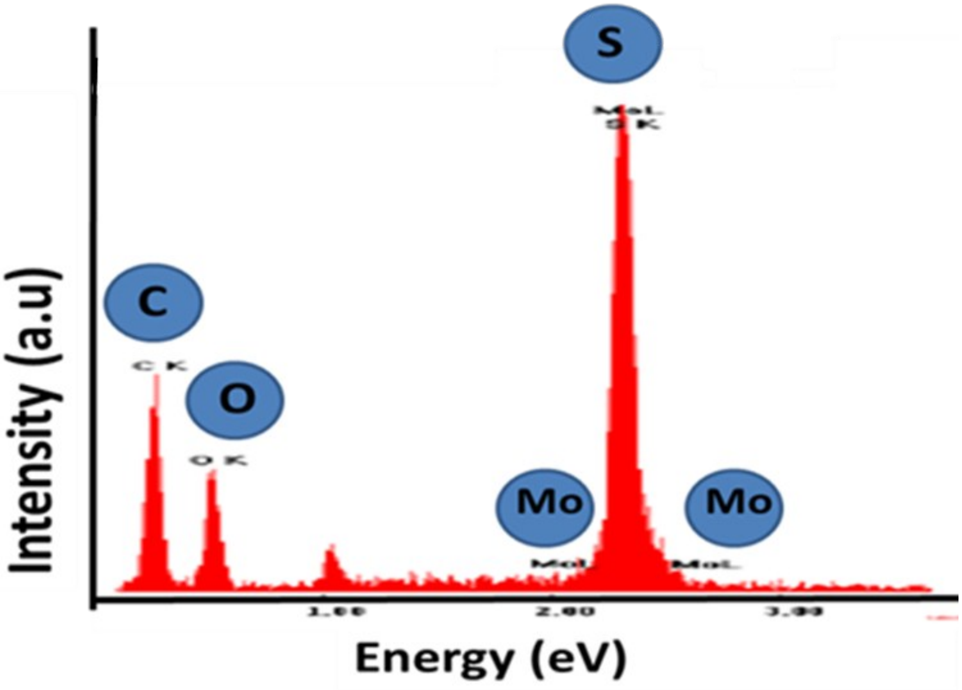

Fig. S4 EDX spectrum of the 3D ternary architecture, PGMo.

Elemental identification of PGMo is achieved using energy-dispersive X-ray spectrometry (EDX). The spectrum shown in Fig. S4 revealed the presence of Mo, S, C and O in the prepared ternary nanostructure.

Sl. No.	Element	Wt %	At %
1.	C	55.01	75.05
2.	O	14.57	14.92
3.	Mo	16.22	2.77
4.	S	14.21	7.26
	Total	100.00	100.00

Table S1. Percentage of elemental composition of Mo, S, C and O in the prepared ternary nanoarchitecture, PGMo.

XPS spectrum of PGMo

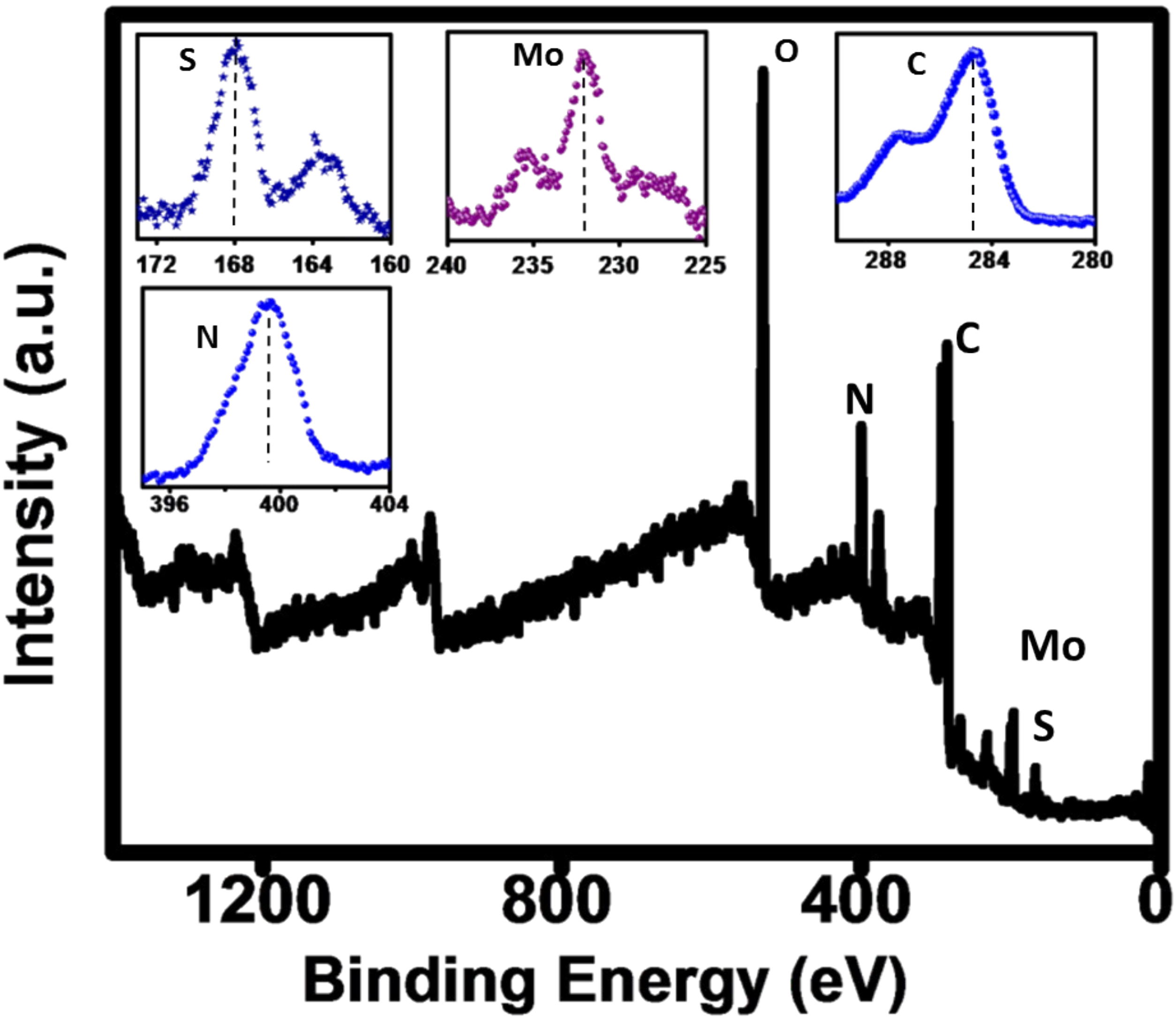

Fig. S5 XPS spectrum of the 3D ternary architecture, PGMo.

The insets show high-resolution XPS spectra of the Mo 3d, S 2p, N 1s, and C 1s regions. The Mo peaks are observed as a Mo 3d-core level at 232 eV and the S 2p peak is located at 168.2 eV (marked in the inset) which match the previous reports of MoS_2 phase. Along with Mo and S, the presence of carbon, nitrogen and oxygen are confirmed in PGMo.

TGA curves of PGMo, PPy-rGO, PPy-MoS_2 and PPy

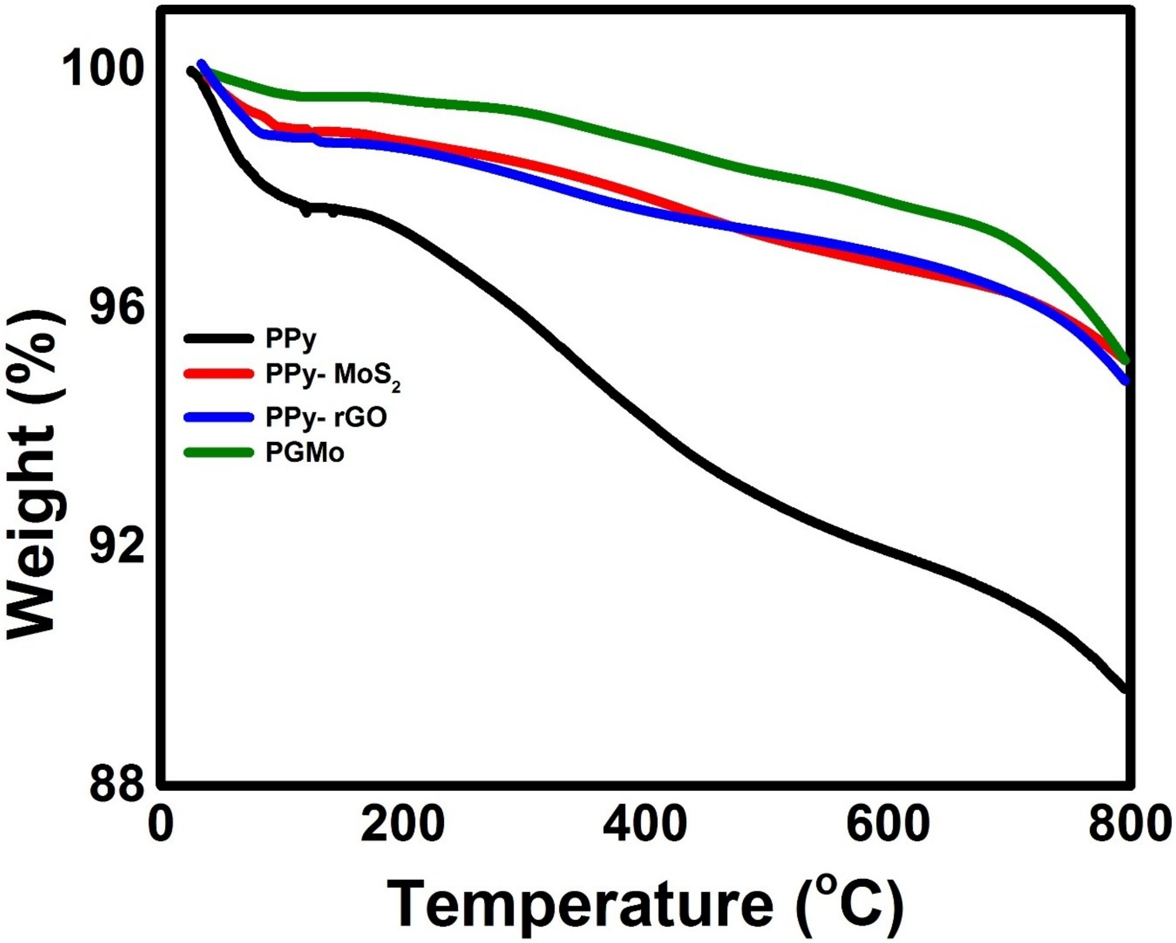

Fig. S6 TGA curves of PGMo, PPy-rGO, PPy-MoS_2 and PPy electrodes.

TGA curves exhibit two weight losses. The loss of mass around 80 ^{0}C to 120 ^{0}C is ascribed to the desorption of physically adsorbed water molecules. PGMo, PPy-rGO, PPy-MoS_2 show a steady and gradual weight loss of 3 % appearing upto 700 ^{0}C. The weight loss appears between 230 ^{0}C - 250 ^{0}C, which can probably be attributed to the removal of oxygen-containing groups. The thermal behavior obtained in the range of 300 ^{0}C - 450 ^{0}C might be caused by the decomposition of the amorphous carbon and graphite, and by the oxidation of MoS_2 in the composites.

BET studies of PGMo, PPy-rGO, PPy-MoS$_2$

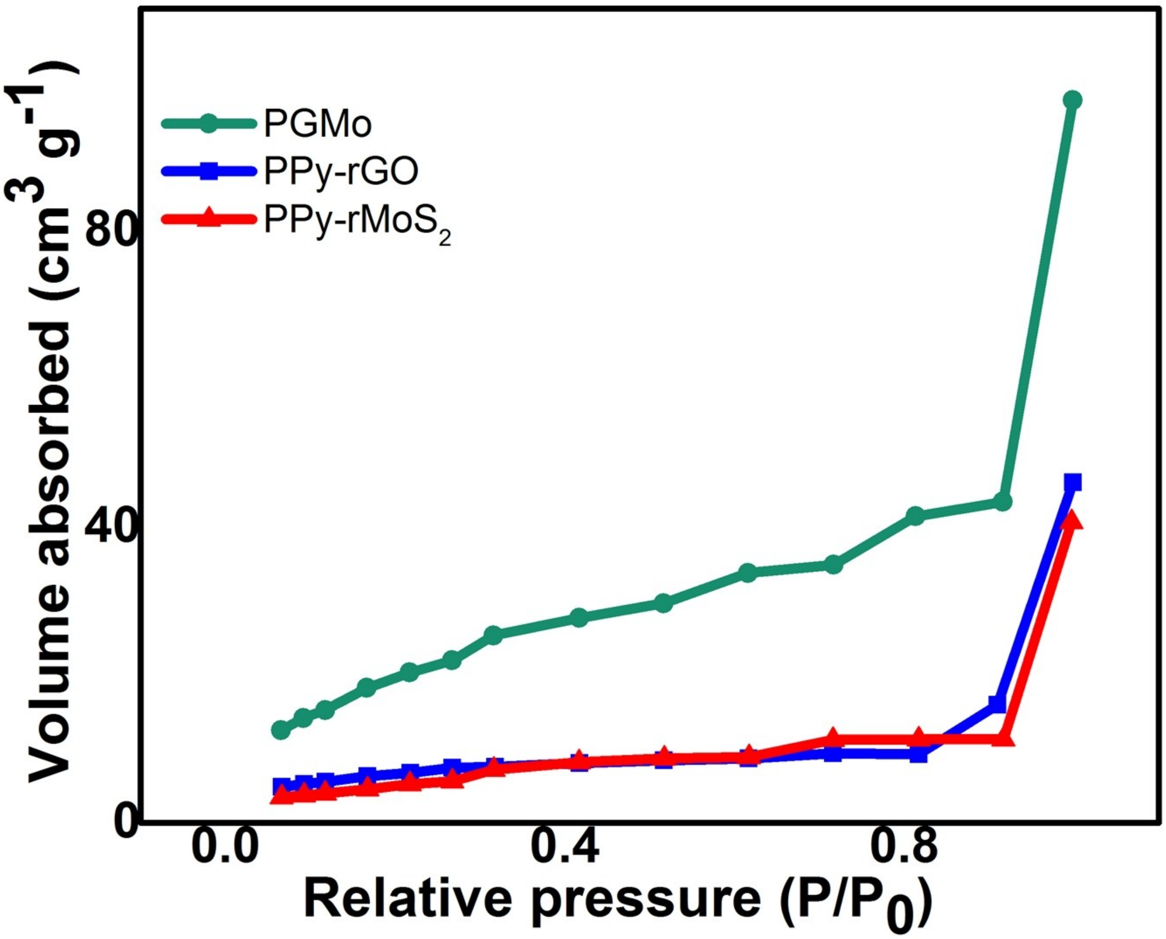

Fig. S7 (a) Nitrogen adsorption–desorption isotherms of PGMo, PPy-rGO, PPy-MoS$_2$

N$_2$ adsorption–desorption isotherm dusk speck measurements are conducted to investigate the Brunauer–Emmett–Teller (BET) specific surface area of PPy-MoS$_2$, PPy-rGO and PGMo. The specific surface area is maximum in the case of PGMo (147.5 m^2 g^{-1}), followed by PPy-rGO (42.43 m^2 g^{-1}) and is less for PPy-MoS$_2$ (39.79 m^2 g^{-1}).

Electrochemical studies of PGMo

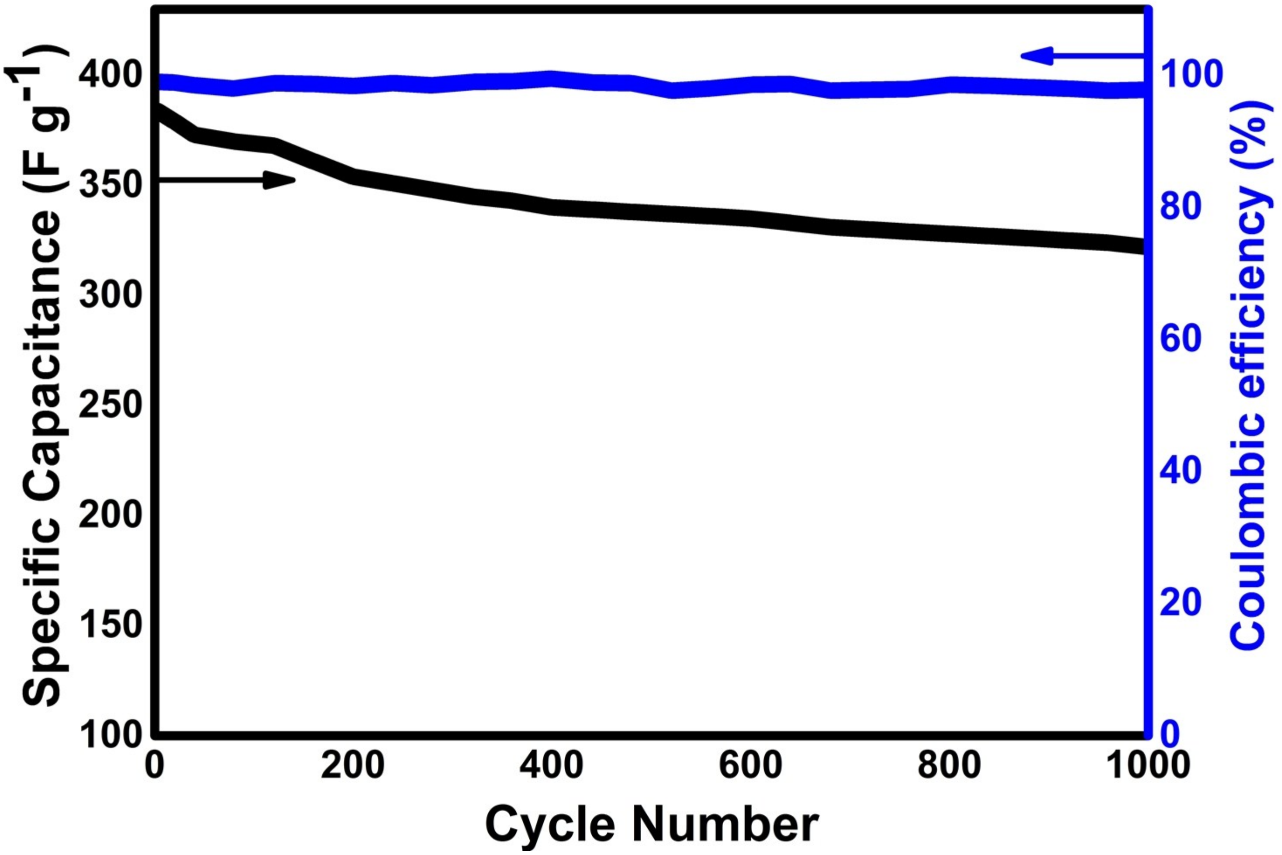

Fig. S8 The Cycling stability and Coulombic efficiency of PGMo

The cycling stability of PGMo at a constant current density of 1 A g^{-1} as a function of cycle number along with the coulombic efficiency of the tested electrode for 1000 charge-discharge cycles. The structural integrity offered by the synergistic effect of PPy, rGO and MoS$_2$ is the reason for the high cycling performance of PGMo. PGMo electrode exhibits a superior coulombic efficiency of 97 % after 1000 charge-discharge cycles. This stability reveals good reversibility of the redox reaction in the system.

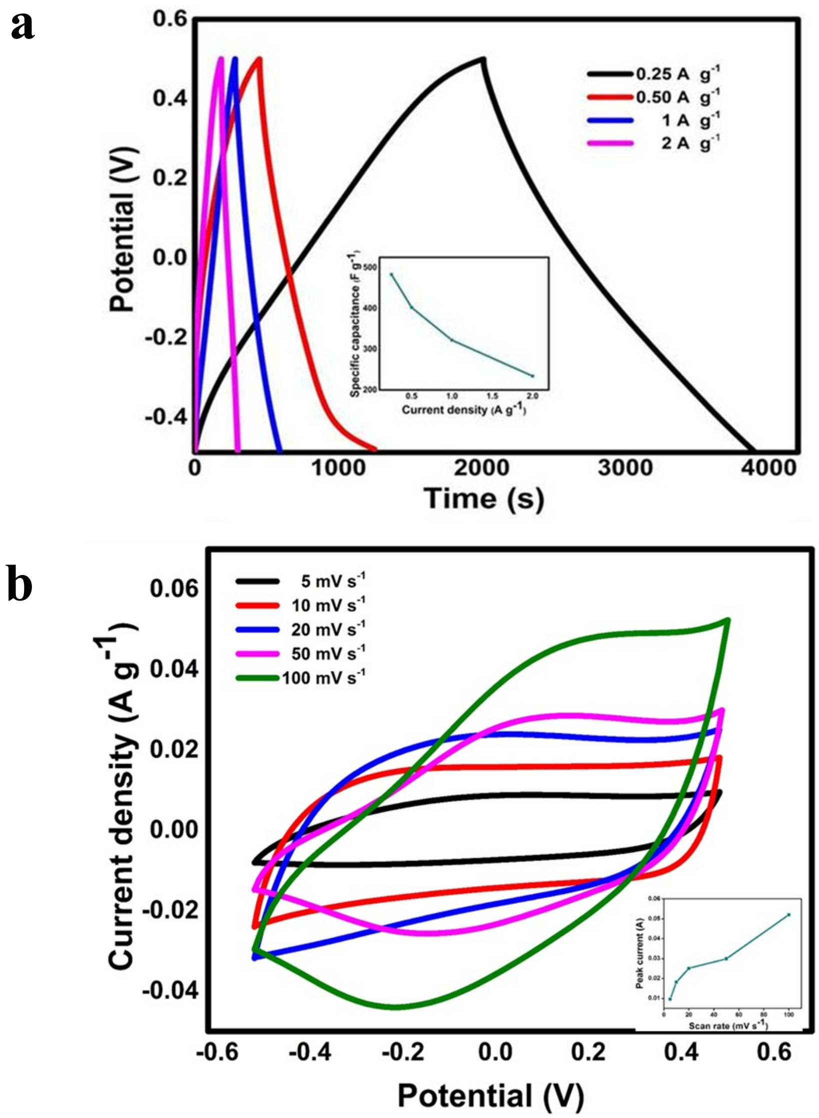

Fig. S9 The GCD and CV profiles of PGMo electrode (a) Galvanostatic charge/discharge curves of PGMo for the first ten cycles at different current densities 0.25, 0.5, 1 and 2 A g^{-1} in the voltage range of -0.5 to 0.5 V at room temperature in 1 M KCl electrolyte. The specific capacitance depends on current density, that is the capacitance retention is shown in Fig. (a) inset. The capacitance decreases as the current density increases and a good retention is maintained. (b) Cyclic Voltammograms of PGMo for different scan rates of 5, 10, 20, 50 and 100 mV s^{-1} for the first 10 cycles of the electrode between -0.5 to 0.5 V versus SCE in 1 M KCl. The relationship between the CV peak current with scan rate is shown in Fig. (b) inset.

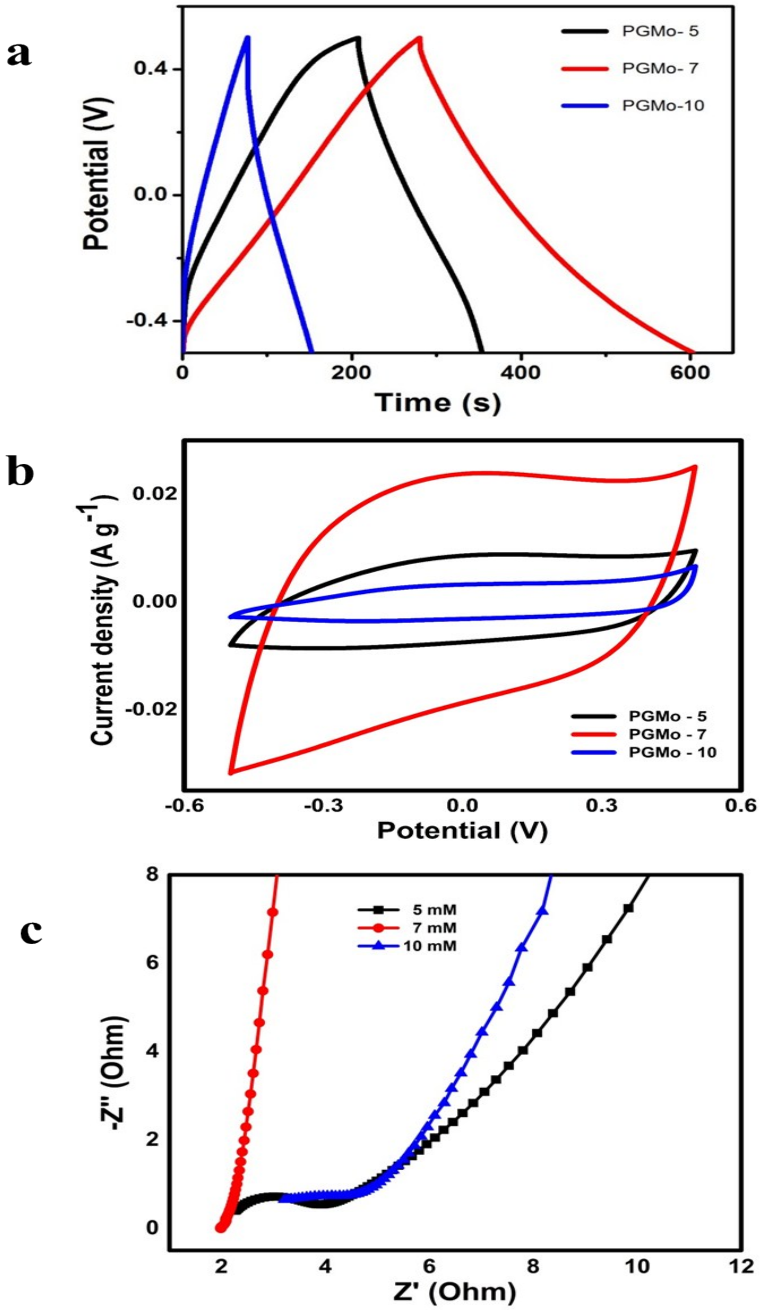

Fig. S10 (a-c) Electrochemical profiles of PGMo at different loadings of MoS_2, PGMo-5, PGMo-7 and PGMo-10. (a) Galvanostatic charge/discharge curves for the first ten cycles at a current density of 1 A g^{-1} in the voltage range of -0.5 to 0.5 V at room temperature. (b) Representative CVs for the first 10 cycles of the electrodes between -0.5 to 0.5 V versus SCE in 1 M KCl at a scan rate of 10 mV s^{-1}. (c) Nyquist plots of the electrodes obtained with an amplitude of 5 mV over the frequency range of 100 k Hz and 0.01 Hz.

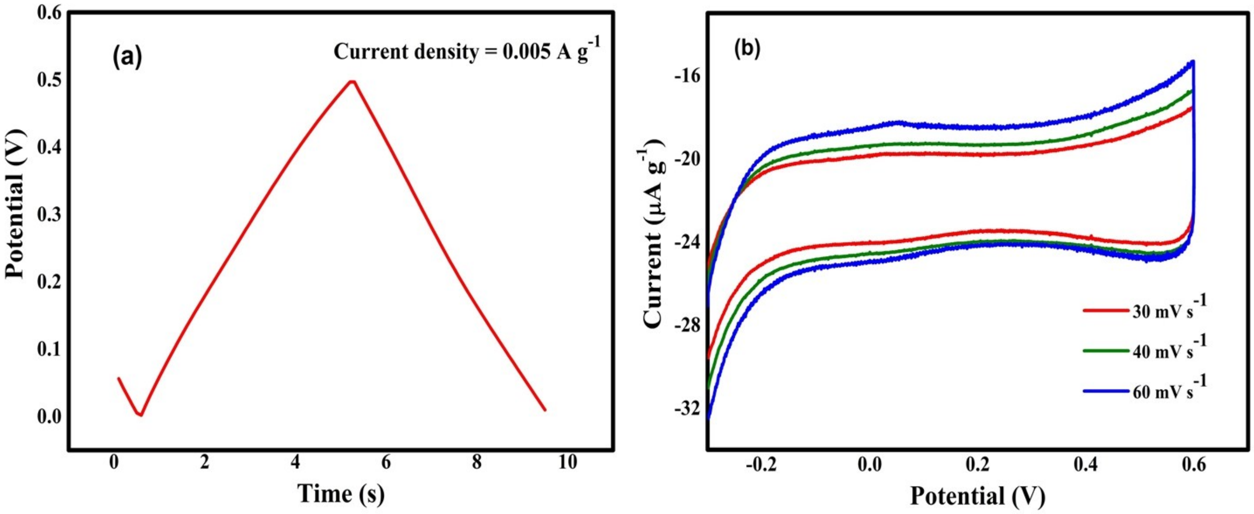

Fig. S11 Electrochemical profile of bare carbon felt substrate (a) Galvanostatic charge/discharge curves of CF at a current density of 0.005 A g^{-1} in the voltage range of 0 to 0.5 V at room temperature in 1 M KCl electrolyte shows symmetric linear curve with the specific capacitance 4 mF g^{-1} at a current density of 0.005 A g^{-1}. (b) CV curves of CF between -0.2 to 0.6 V in 1 M KCl shows the electric double layer capacitor (EDLC) behavior and the current difference between the reversible CV curves at a scan rate of 60 mV s ^{1} is negligible and of the order of 5.8 μA. Thus the specific capacitance (values) of the PGMo on CF substrate has no contribution from CF.