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PAPER

Enhancement of electrochemical energy storage performance of MOF-5 and Eucalyptus plant bark derived rGO composite

Robin Saini¹, Priyanka Wadhwa², Karuna Jain³, Mayank Pathak⁴, Pratap Singh¹, Rahul Kumar Dhaka³, Sandeep Kumar⁵  and Manoj Kumar Singh⁶ ¹ Department of Physics and Astrophysics, School of Basic Sciences, Central University of Haryana, Mahendergarh, 123031, India² Department of Bio-nanotechnology, Guru Jambheshwar University of Science and Technology, Hisar, 125001, India³ Department of Chemistry, Chaudhary Charan Singh Haryana Agriculture University, Hisar, 125001, India⁴ Centre for Advanced Materials Research, The University of Texas at El Paso, TX, 79968, United States of America⁵ Department of Physics, Punjab Engineering College (Deemed to be University), Chandigarh, 160012, India⁶ Department of Applied Sciences and Humanities, School of Engineering & Technology, Central University of Haryana, Mahendergarh, Haryana, 123031, IndiaE-mail: manojksingh@cuh.ac.in**Keywords:** metal-organic frameworks (MOFs), energy storage, supercapacitors, specific capacitance, energy density, power densitySupplementary material for this article is available [online](#)**Abstract**

Metal Organic Frameworks (MOFs) and carbon derivatives based composites are an interesting class of materials having complementary properties, with the high surface area and tunable porosity of MOFs together with excellent electrical conductivity of carbon based materials. Here in, we report a facile one step solvothermal synthesis of composite made of MOF-5 and Eucalyptus bark derived rGO. MOF-5/rGO composite (MRG) has a high specific surface area ($1150 \text{ m}^2 \text{ g}^{-1}$). MRG was studied for electrochemical energy storage application using Cycle Voltammetry (CV), Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS). The MRG has high specific capacitance of 1366.6 F g^{-1} as calculated by GCD at 1 A g^{-1} current density, Energy density of $150.7 \text{ W h kg}^{-1}$ and Power density of 450.3 W kg^{-1} at a current density of 1 A g^{-1} as calculated by GCD with $1 \text{ M H}_2\text{SO}_4$. The coulombic efficiency for the MRG composite was found to be 89.3% at higher current density. The cyclic stability data shown that composite material is retaining $\sim 80.9\%$ capacitance even after 10000 cycles. Moreover, symmetrical two electrode device of MRG shown a specific capacitance of 262.4 F g^{-1} at a current density of 1 A g^{-1} , while the device retained 83.7% capacitance after 10000 charging discharging cycles. The energy density and power density of device were found to be 36.4 W h kg^{-1} and 498.6 W kg^{-1} at a current of 1 A g^{-1} . The enhanced electrochemical performance of MRG is attributed to the synergistic effect between MOF-5 and rGO leading to the enhanced conductivity and provides larger surface area for charge storage.

1. Introduction

The global energy demand is escalating with increasing population. The current dependence on fossil fuels is contributing primarily to the carbon emissions [1–3]. Renewable energy sources are playing the key role to achieve the energy demand coupled with environmental challenges imposed by fossil fuels [3, 4]. However, challenges such as location specificity, over reliance on natural resources (wind, sunlight, water and geothermal) weather, season and time make renewable energy alternatives relatively less feasible to be adopted on ground [5, 6]. These challenges have motivated the scientists to achieve progress in energy storage field using devices like batteries, capacitors, fuel cells including supercapacitors. Lithium ion batteries uses Li^+ to move between anode and cathode for charging and discharging, are among the most common alternatives used during past few decades [7, 8]. Their high energy density along with impressive cyclic stability and their employability in the portable devices make them a promising candidate in energy storage field. However, safety concerns, low power density and use of flammable electrolytes are issues that have forced the researchers to explore better alternatives

for energy storage devices [9]. Because of their extended life cycle and higher power density, supercapacitors have emerged as a viable alternative for energy storage devices in recent times [10]. However, their moderate energy density necessitate the research to improve the supercapacitor. Therefore, it is essential to design cutting-edge electrode materials that can concurrently supply high power density and high energy density. Such advanced electrode materials can make significant contribution in making supercapacitor devices which can be suitable for their use in portable devices (smartphones, backup power systems, camera flashlights etc), electric vehicle industry, electronic industries and in large number of other applications.

Several materials such as metal oxides [11, 12], mxenes [11], conducting polymers [13–15] and carbon based materials [16] have been employed for making electrode materials for supercapacitor application. Saha *et al* developed $\text{Ti}_3\text{C}_2\text{T}_z/\text{rGO}$ based porous material for supercapacitor electrodes and found electrodes showing enhanced potential window of 1.5 V with a large specific capacitance of 920 F g^{-1} , while the symmetric two electrode device formed with $\text{Ti}_3\text{C}_2\text{T}_z/\text{rGO}$ shown an areal capacitance of 158 mF cm^{-2} and capacitance retention of 93% after 10000 cycles. [17] Gao *et al* synthesized rGO/PPy composite with which delivered a specific capacitance of 389.3 F g^{-1} at 1 A g^{-1} current density in three electrode system while a specific capacitance of 266.8 F g^{-1} for symmetrical supercapacitor device at a current density of 0.25 A g^{-1} . [18] Chetri *et al* developed a $\text{Co}_3\text{O}_4\text{-PANI@ZIF-8}$ (positive electrode) and ZIF-8NPC (negative electrode) based asymmetric supercapacitor device which shown a energy density of 52.81 Wh kg^{-1} with a power density of 751.51 W kg^{-1} and 18.75 Wh kg^{-1} energy density with a power density of 7500 W kg^{-1} while the device retained 88.43% capacitance even after 10000 charging and discharging cycles. [19] However the research challenge is to develop sustainable materials with enhanced efficiency for energy storage application [20]. Metal–Organic Frameworks (MOFs) [21–23] are an exceptionally intriguing group of porous materials suitable to be used in electrode preparation due to their robust framework [23], high porosity [24], large surface area [25] and adjustable pore size. MOFs have been used in gas separation [26], photocatalysis [27], drug delivery [28], sensing [29] and energy storage [12, 13]. However, low conductivity of MOFs and inefficient transfer of ions to the current collector, limit their use for electrochemical energy storage. [30] Thus, development of MOFs composites using conducting material like graphene [31], reduced graphene oxide (rGO) [32], metal derivatives and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [33], conducting polymer etc can be used to improve the conductivity along with capacitive properties of MOFs. These composites synergistically give improved results in comparison to pristine materials (graphene, conducting polymers and other carbon based materials) due to elevated surface area of MOFs along with superior conductivity of conducting materials.

MOF-5, a Zinc metal ion and Terephthalic acid (H_2BDC) based Metal–Organic Framework having high surface area was used in various works for electrodes preparation for supercapacitor application. Apart from its surface area its low conductivity is one of major issue which limits its use as an electrode material as low conductivity reduces overall capacitive properties. A number of researchers reported works based on composites including MOF-5 have been developed to use them for making electrodes. Kishore Babu *et al* [34] synthesized a MOF-5 and NiCo_2O_4 based electrode material having specific capacitance of 357.9 F g^{-1} at 1 A g^{-1} . Raul Diaz *et al* [35] tuned the electrical properties of MOF-5 with Co_8 to improve the supercapacitive behavior of electrode in an electrolyte (0.1 M) tetrabutylammonium hexafluorophosphate. Ping Wen *et al* [36] synthesized a composite of carbonized MOF-5 and rGO and used it for electrochemical energy storage application. The composite showed high specific capacitance (312 F g^{-1} @ 0.5 A g^{-1} current density) in KOH electrolyte and capacitance retention of 86% after 5000 cycles.

The available literature indicates that there is still scope of development of MOF-5 with improved capacitance for supercapacitor application. The composites of Reduced Graphene Oxide (rGO) with Metal–Organic Frameworks (MOFs) are strategically engineered to leverage the complementary properties of both materials. rGO, derived from the reduction of graphene oxide, offers exceptional electrical conductivity owing to its sp^2 hybridized carbon structure. This conductivity facilitates efficient charge transfer within the composite, crucial for enhancing energy storage device performance. Moreover recently scientific community is focussing on deriving the carbon based materials like Graphene, rGO, CNTs, Quantum dots among the others using waste materials or plant biomass. This approach has advantages like cost-effectiveness, biocompatibility, versatility and sustainability. Eucalyptus plant bark has amount of carbon content and its natural porosity makes it a potential candidate for preparing carbon based materials [37]. Further its inherent structure provides alternative pathways for ion transport and electrical conductivity for enhanced overall energy storage capacity. Moreover it is a fast growing renewable source and its eco-friendly and cost-effective nature makes it a suitable candidate for deriving carbon based materials. So in this research work, keeping in mind the versatile properties of graphene based materials including their electrical conductivity and high surface area of MOF-5, a composite of MOF-5 with rGO was synthesized via solvothermal method. As far as we aware the synthesis of pristine MOF-5 and rGO derived from Eucalyptus plant bark biomass composite hasn't been reported yet for supercapacitor application. Moreover, composite material was used for the development of symmetrical supercapacitor device which is rarely done with MOF based materials. Not only this composite demonstrated a broader potential range in the

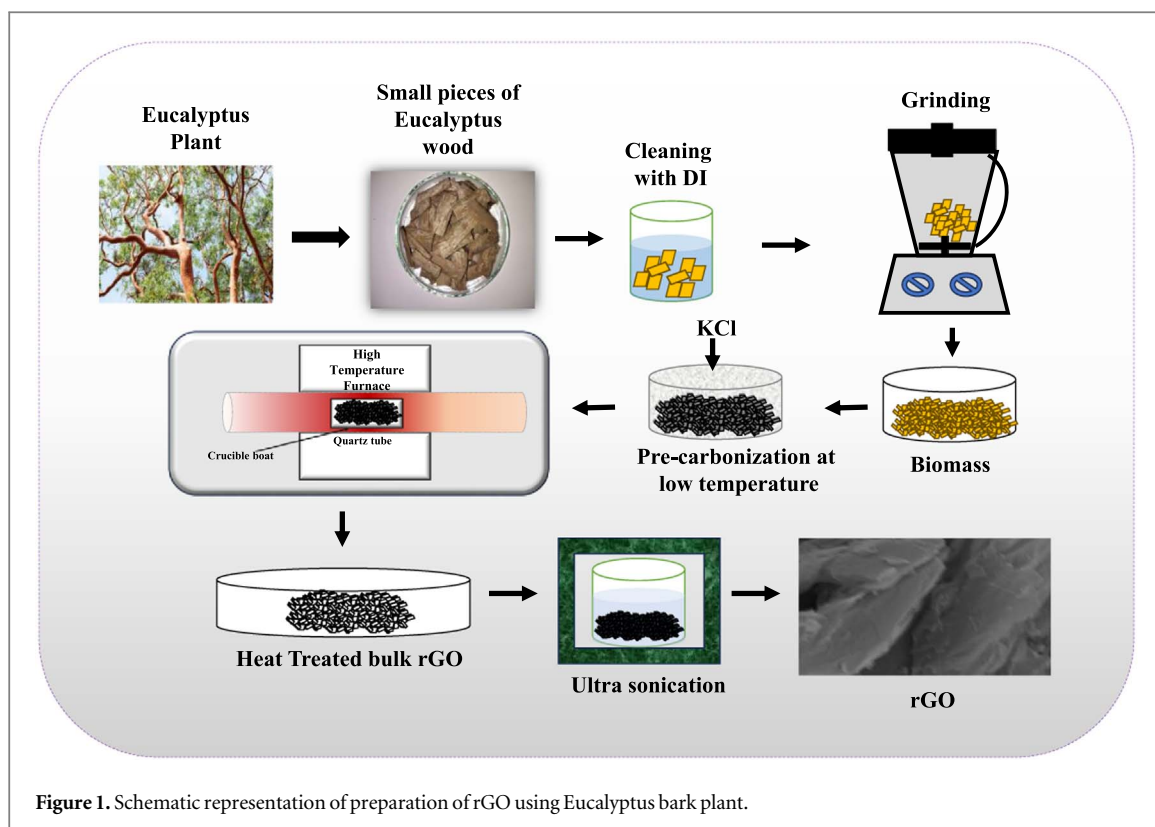


Figure 1. Schematic representation of preparation of rGO using Eucalyptus bark plant.

case of symmetrical supercapacitor device owing to practical applicability of the material towards energy storage application. The reduced graphene oxide was prepared using Eucalyptus bark keeping in mind its high carbon content, cost effectiveness and ecofriendly nature [37].

2. Experimental

2.1. Materials and methods

The Eucalyptus bark (EB), was collected from agriculture farm of CCS Haryana Agricultural University, Hisar. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99.99%), Terephthalic acid (H_2BDC) (99.99%), Dimethylformamide (DMF) (99.5%) were procured from Sigma Aldrich (AR grade). Sulphuric acid (H_2SO_4), Polyvinyl di- fluoride (PVDF), N-Methyl pyrrolidone (NMP), Ethanol, and Isopropyl alcohol (IPA) of analytical grade (AR) from Central drug House (CDH) a commercial source and was used without any additional purification. Origin lab 8.0 software 2018 was used for graphical work. The Electrochemical investigations including CV, GCD and EIS were performed using Electrochemical analyzer Metrohm Autolab PGSTAT 302 N.

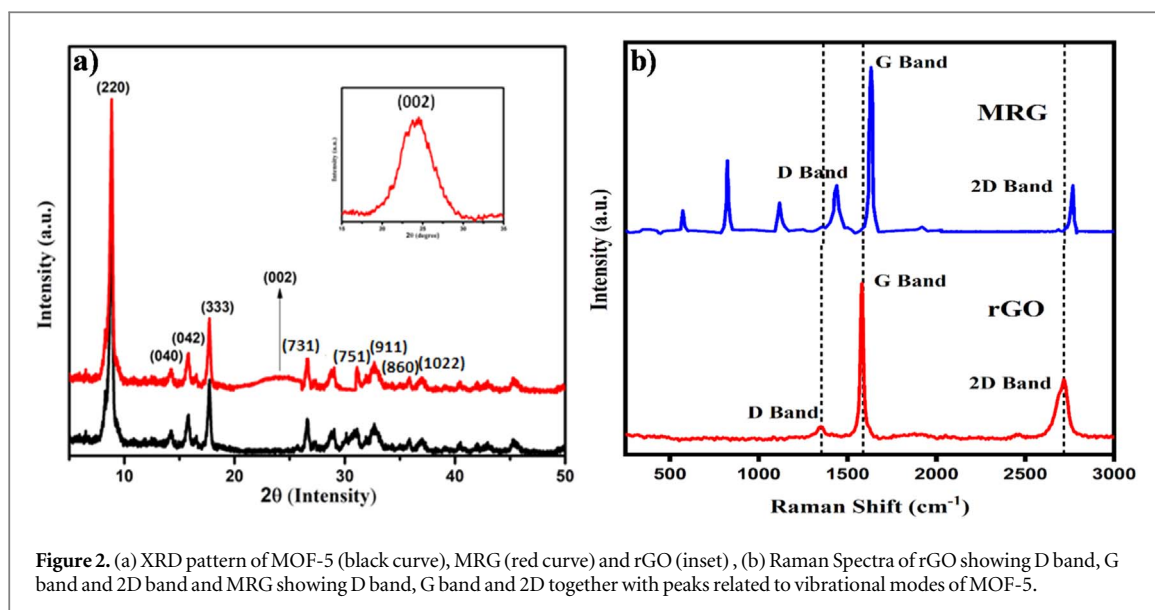
2.2. Synthesis of materials

2.2.1. Synthesis of MOF-5

MOF-5 was produced via solvothermal synthesis method. In brief; $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 g) in Dimethylformamide (DMF) (50 ml) (solution A) and terephthalic acid (H_2BDC) (1.275 g) in DMF (50 ml) (solution B). This solution was added drop wise to solution (A) followed by transfer of in a Teflon lined steel autoclave (12 h, 140 °C). Solution was then centrifuged and white coloured precipitates were gathered which were rinsed multiple times with ethanol and deionized water and vacuum dried (120 °C) to get MOF-5 crystals.

2.2.2. Synthesis of reduced graphene oxide (rGO) using Eucalyptus bark

The rGO was prepared from Eucalyptus bark (EB) via two steps process involving precarbonization followed by ultrasonication (figure 1). EB was rinsed with double distilled water (3–4 times) to eliminate dust and impurities, subsequently dried in sunlight for 2 days and then in an oven (90 °C, 4 h). Thereafter, the dried EB was finely pulverized and pyrolyzed (pyrolysis temperature: 650 °C, heating time: 1 h, heating rate: 5 °C min⁻¹) in nitrogen (N_2) gas inert atmosphere in a tube furnace. The carbonized material was finely grounded. This pre-carbonization step lays the groundwork for nucleating graphene like material. Further, the carbonaceous Eucalyptus biochar (EB) powder was thoroughly mixed with activating agent (KCl) in 1:2 ratio and subjected to secondary heating (940 °C) and at elevated heating rate (10 °C min⁻¹) in N_2 gas atmosphere (10 ml min⁻¹) [38].



The activated char was washed with double distilled water and then with isopropyl alcohol (IPA) to discard organic impurities followed by ultrasonication. The ultrasonicated sample was dried, filtered and named as rGO for further studied on structural and electrochemical evaluations.

2.2.3. Synthesis of MRG composite

The MRG composite was synthesized using a one-step solvothermal method. Initially, 1.6 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.48 g of terephthalic acid were dissolved in DMF (14 mL) with continuous stirring until appearance of a clear solution was obtained followed by addition of rGO (5 wt%) and continuous stirring upto 1 h [39]. The resulting mixture was then conveyed to a Teflon-lined steel autoclave and heated (140°C , 12 h). The product was then collected, rinsed with ethanol and dried (at 55°C) under vacuum.

2.3. Characterizations

The synthesis of MOF-5, rGO and MRG was confirmed via powder x-ray diffraction (p-XRD, Rigaku Smart Lab 3Kw) over a range (2θ) of 5° – 80° at a scan speed of 2° min^{-1} and scanning step of 0.02° with radiation energy source Cu-K α ($\lambda = 1.540 \text{ \AA}$). To study the chemical bond and oxidation states present within the material MRG was characterize using x-Ray Photoelectron Spectroscopy (XPS) using PHI 5000 VersaProbe III setup. The molecular interactions and surface chemistry of materials were analyzed using Fourier transform Infrared spectroscopy (FTIR) using Perkin Elmer Spectrum, BX II setup in the spectral range of 400 – 4000 cm^{-1} through 8 scans at 4 cm^{-1} resolution using KBr pelletization method. Size, shape and morphology of materials were studied using Field Emission Scanning Electron Microscopy (FESEM) on 7610 F Plus/JEOL setup and Transmission Electron Microscopy (TEM) using Tecnai G2 20 TWIN was used to analyzed high magnified image of samples. For chemical analysis synthesized samples were studied using Raman spectrophotometer (WITec Alpha300 model). N_2 adsorption–desorption analysis was done on Quantachrome Autosorb iQ Station 2 to determine porosity and specific surface area of the synthesized samples using Brunner Emmett Teller (BET) model.

3. Results and discussion

3.1. X-ray diffraction

The x-ray diffraction pattern of MOF-5 (figure 2) was found to be in the good agreement with JCPDS card number 96-432-6738. Although one intense peak at 6.8° is missing in the XRD pattern which is probably due to altered atomic orientations in the crystal planes due to solvent and other adsorbate molecules that fill the pores of MOF-5 which was also noticed by saha *et al* in their study [40]. The XRD pattern of rGO showed only a single diffraction broad peak at $2\theta \sim 24.3^\circ$ (002) plane indicates amorphous nature and confirms the formation of rGO [41]. The key peaks of MRG composite and MOF-5 were mainly showed at $2\theta \sim 9.52^\circ$ (220), 13.82° (040), 15.4° (042) and 17.985° (333). Broad diffraction peak of rGO at $2\theta \sim 24.3^\circ$ corresponding to (002) plane, hence confirms the synthesis of MRG composite (figure 2). The crystal planes with either even hkl values ((220), (040), (042)) or odd hkl values (333) confirms the Face Centred Cubic (FCC) structure of MOF-5 crystals and MRG

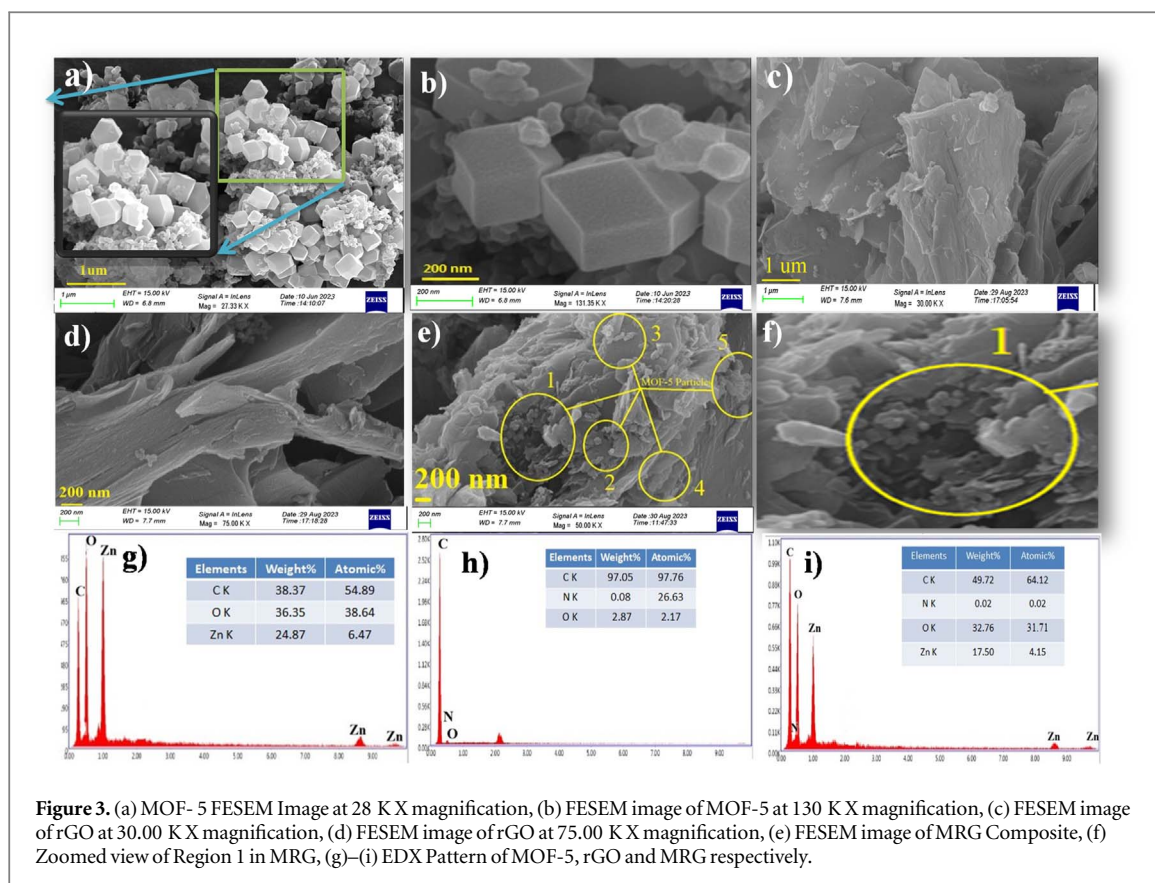


Figure 3. (a) MOF-5 FESEM Image at 28 K X magnification, (b) FESEM image of MOF-5 at 130 K X magnification, (c) FESEM image of rGO at 30.00 K X magnification, (d) FESEM image of rGO at 75.00 K X magnification, (e) FESEM image of MRG Composite, (f) Zoomed view of Region 1 in MRG, (g)–(i) EDX Pattern of MOF-5, rGO and MRG respectively.

having Fm-3m space group. The only peak in rGO sample is also reflects in MRG material at same point as in rGO confirming the successful formation of MRG.

3.2. Raman spectroscopy studies

Raman spectrum of as prepared rGO shown D (Disorder band), G (Graphitic band) and 2D (second order overtone of D band) at 1349 cm^{-1} , 1575 cm^{-1} and 2720 cm^{-1} respectively (figure 2(b)). The low intensity D band is indicating the presence of certain defects in the rGO sheets. The sharp G band signifies the high degree of crystallinity, presence of sp^2 hybridized carbon atoms and in-plane vibrations of carbon atoms in rGO sheets. The 2D band indicates the layered structure of rGO. The intensity ratio I_{2D}/I_G is coming out to be 0.81 for rGO which is nearly approaching 1 and indicating presence of a very few layers in the material. Further a low value of I_D/I_G (0.02) ratio is indicating the high quality of synthesis and graphitization of the material. Further, the composite material shows the peaks of rGO together with other peaks at 568 cm^{-1} , 812 cm^{-1} and 1115 cm^{-1} [42] which are due to the presence of MOF-5 particles and corresponds to the presence of vibrational mode of $-\text{COO}^-$ groups. Further a relatively high intensity of D band in the composite may be attributed to a larger number of defects in the final composite. The little shift of bands (D, G and 2D) towards the right for MRG is because of the stress or strain produced in rGO layers due composite formation.

3.3. Morphological (SEM and TEM) and elemental composition studies

The morphology of MOF-5, rGO and MRG including shape and size were studied using FESEM. The shape of MOF-5 was found to be cubical (figures 3(a) and (b)) with 146.7 nm of average particle size. For rGO (figures 3(c) and (d)) clear sheet like structure can be seen with some of them wrinkled witnessing the successful preparation. In the MRG composite sample it can be concluded that rGO sheet is acting like a robust matrix for the MOF-5 particles [43] and providing its surface to the MOF-5 particle or it can be said that the MOF-5 particles are gently resting on the surface of rGO [44]. The hybrid structure of the composite may provide its structural stability. For determining the elemental composition, the prepared materials were characterized using EDS (figures 5(g)–(i)). The EDS spectra of MOF-5 depicts the presence of expected elements Carbon (due to organic linker and rGO), Oxygen (due to organic linker) and Zinc (due to metal salt) in the material with weight percent 38.37%, 36.35% and 24.87% respectively and atomic percentage 54.89%, 38.64% and 6.47% respectively (figure 3(g)). EDX spectra of rGO is showing the presence of high amount of carbon content with 97.05% weight percent and 97.76% of atomic percentage, also a little amount of oxygen and nitrogen were present. In MRG (figure 3(i)) the amount of carbon is higher i.e. 49.72% as compared to MOF-5 due to the presence of rGO matrix together with

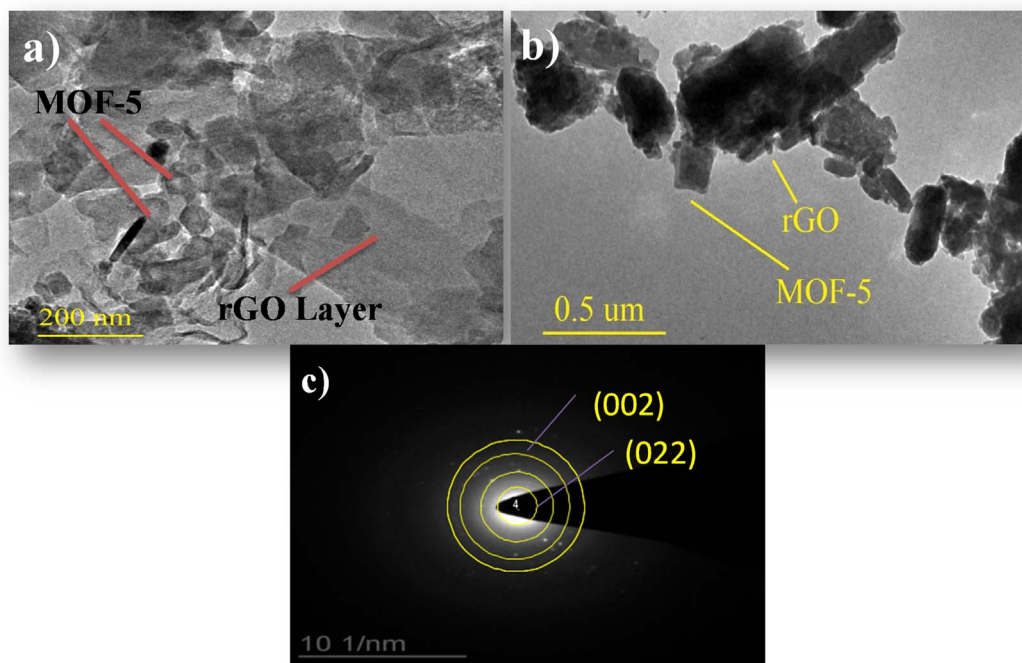


Figure 4. (a)–(b) TEM images of MRG composite, (c) selected area diffraction pattern of MRG.

organic linker, while presence of nitrogen (0.02%), oxygen (32.76%) and Zinc (17.5%) were also confirmed using EDX spectroscopy. For further confirming the dispersion of MOF-5 particles within the rGO matrix and to confirm the structural information drawn from XRD pattern the composite material was characterized using Transmission Electron Microscopy (TEM) (figures 4(a)–(b)) and the structural information drawn from p-XRD pattern of MRG was verified using selected area Electron Diffraction (SAED) pattern (figure 4(c)). TEM image of the composite material reveals the presence of MOF-5 particles on the rGO surface [45]. The faded and randomly dotted rings in the SAED pattern of composite material is confirming the polycrystalline nature of the composite which is found in good agreement with the observed XRD pattern of the composite. The d spacing as calculated from SAED pattern corresponding to (022) plane was found to be $9.03 \text{ \AA}$ while for (002) plane it came out to be $3.4 \text{ \AA}$ where (022) corresponds to MOF-5 and (002) corresponds to rGO.

3.4. Fourier transform infrared spectroscopic (FTIR) studies

The surface chemistry and molecular interactions of prepared MOF-5, rGO and MRG samples were characterized using FTIR (figure 5). Both samples exhibited peaks around 700 cm^{-1} , is due to Zn-O bending vibrations. In the MRG composite, a low-intensity, broad peak around 1241 cm^{-1} was attributed to C–O stretching from reduced Graphene Oxide (rGO), while a peak at 2012 cm^{-1} suggested the presence of C≡C stretching or metal-carbon bonds. Additionally, a peak around 2163 cm^{-1} indicated the presence of nitrile groups (C≡N). Both samples showed peaks around 1360 cm^{-1} due to C–H bending vibrations [46], inherent to the aromatic rings in MOF-5. A slight shift in this peak for the MRG composite suggested bond formation between rGO and MOF-5. Peaks in the range of $1400\text{--}1500 \text{ cm}^{-1}$ were ascribed to C–O stretching vibrations. [47] An absorption peak at 1497 cm^{-1} in MOF-5 was attributed to C=C stretching within the aromatic ring of terephthalic acid. Peaks at 3414 cm^{-1} and 3128 cm^{-1} in MOF-5 indicated the presence of adsorbed O–H groups, likely due to moisture. Additionally, several peaks in the range of $1000\text{--}1150 \text{ cm}^{-1}$ corresponded to the in-plane bending of C–H bonds in the aromatic rings of the organic linker. In the MRG sample, a peak at 3604 cm^{-1} pointed to the presence of O–H stretching vibrations. These findings confirm the successful incorporation and interaction of rGO within the MOF-5 framework, providing valuable insights into the structural characteristics of the composite material.

3.5. Surface area and pore distribution studies (BET)

The surface area and pore size distribution of the prepared materials were determined using N_2 adsorption analysis (BET) (figures 6(a)–(f)). The surface area of MOF-5 was approximately $860 \text{ m}^2 \text{ g}^{-1}$ while pore radius of 1.9 nm was determined using Barrett–Joyner–Halenda (BJH) theory indicate microporous nature of MOF-5 [48]. Type-IV adsorption isotherm observed for rGO is the characteristic of mesoporous materials ($S_{\text{BET}} 118 \text{ m}^2 \text{ g}^{-1}$, pore size

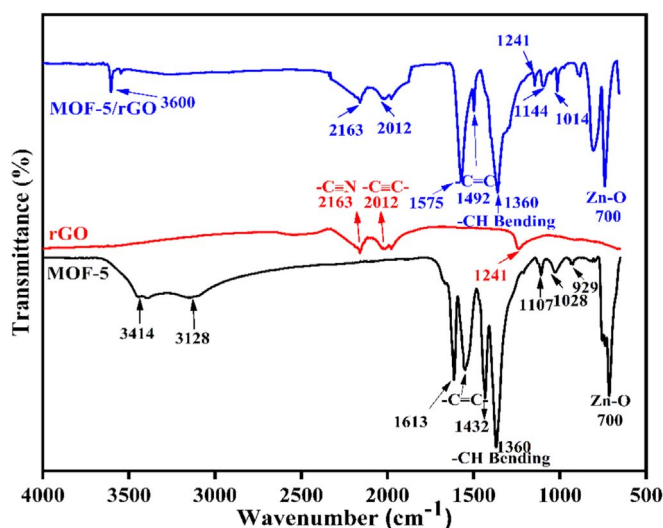


Figure 5. FTIR spectra of MOF-5, rGO and MRG.

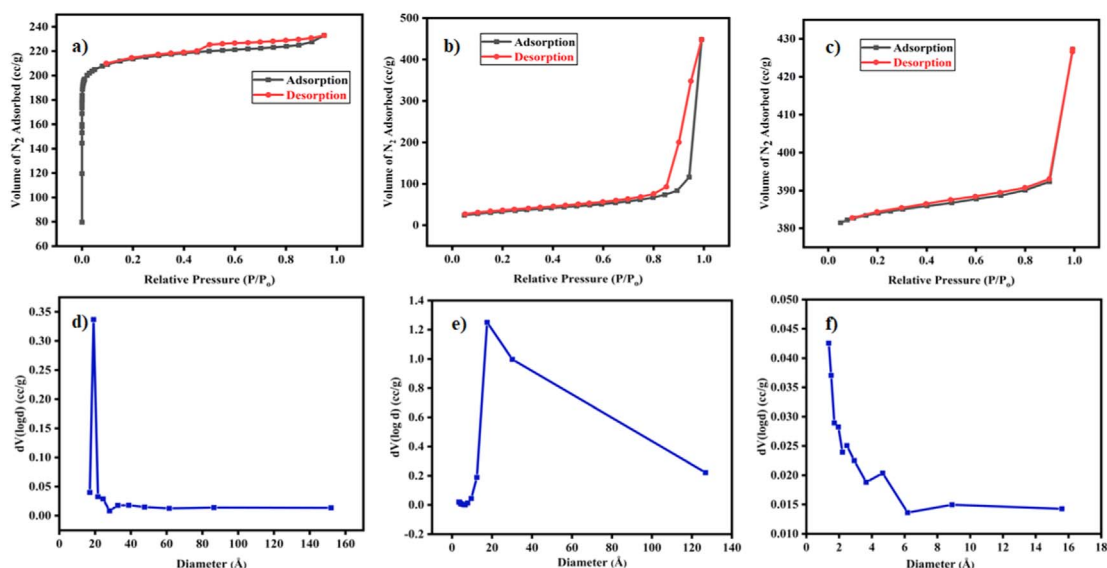


Figure 6. (a)–(c) N_2 adsorption/desorption Plot of MOF-5, rGO and MRG, (d)–(f) Pore distribution curves of MOF-5, rGO and MRG.

17.53 nm) [49]. The surface area of MRG ($1150 \text{ m}^2 \text{ g}^{-1}$) was considerably higher than that of the pristine MOF-5 ($860 \text{ m}^2 \text{ g}^{-1}$). Although the nature of curve for MRG has changed but pore size of the composite material being below 2 nm indicates retained microporosity. The increased surface area can be depicted by the increased number of adsorption sites as the adsorption in the case of composite is not only taking place on the external surface of the MOF-5 but rGO surface is also available for the adsorption. Hence synergistically the large surface area of the composite material was depicted.

3.6. X-ray photoelectron spectroscopy (XPS)

XPS studies and their outcomes are important to understand bonding configuration and chemical environment. The survey spectra (figure 7(a)) mainly shows elements and bonding present in MRG sample. C1s XPS spectrum (figure 7(b)) of MRG having peak at 288.5 eV, assigned to O-C=O bonds signifies the presence of residual oxygen-comprising functional groups, such as -COOH or C=O moieties. The presence of a peak at 284.6 eV, corresponding to C-C or C=C bonds, reflects the restoration of sp^2 carbon network characteristic of graphene in the reduced material and successful formation of rGO due to the removal of oxygen-consisting groups and the presence of the graphitic structure [50]. Overall, the deconvoluted C1s XPS spectrum provides convincing

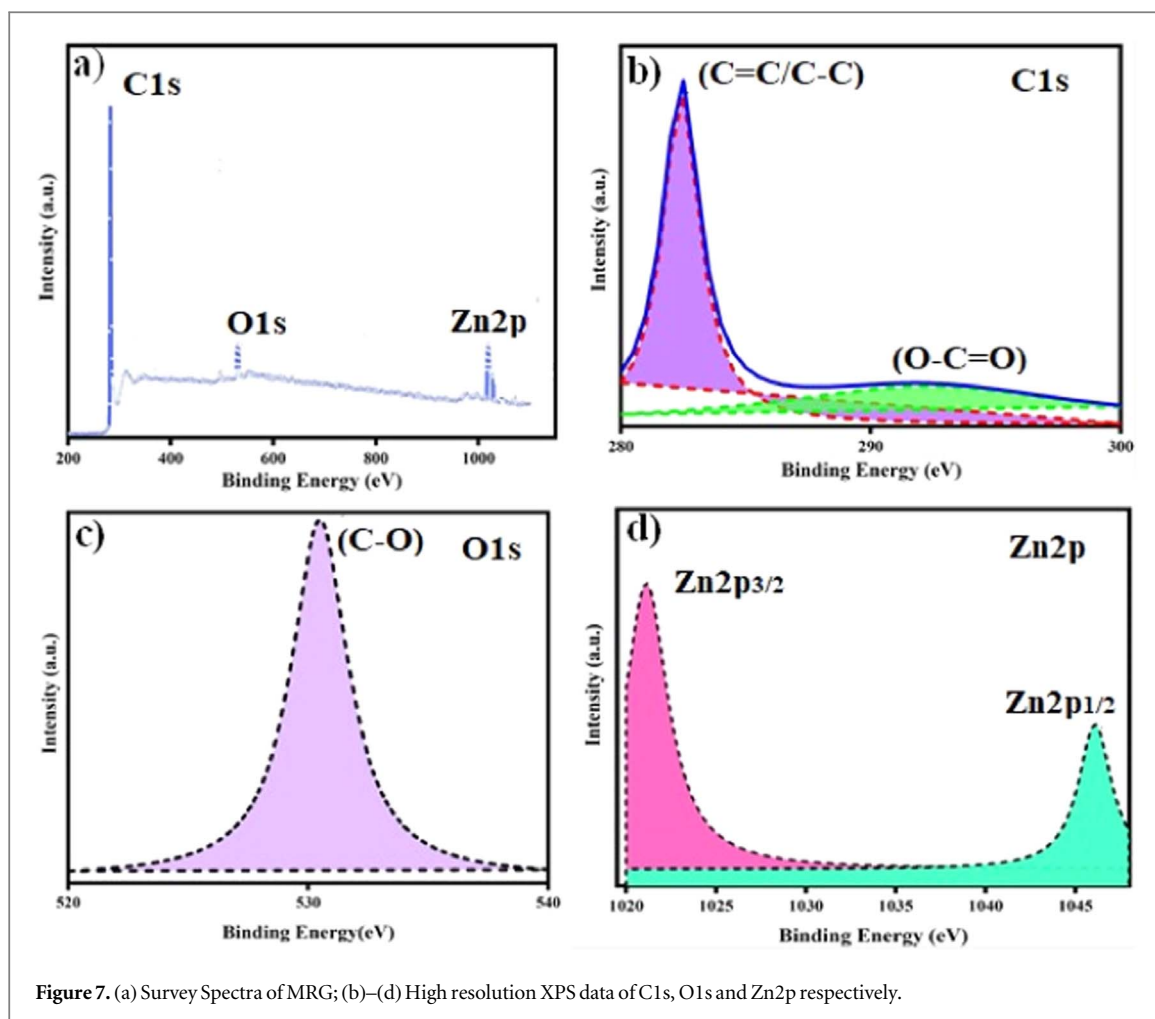


Figure 7. (a) Survey Spectra of MRG; (b)–(d) High resolution XPS data of C1s, O1s and Zn2p respectively.

evidence of the reduction process, i.e. transformation of Eucalyptus biomass to rGO in MRG composite material. The O1s spectrum (figure 6(c)) having peak at 534.5 eV is attributed to lattice oxygen participating in C–O bonds within the material's structure. Lattice oxygen refers to oxygen atoms integrated into the crystal lattice, forming bonds with adjacent atoms. The presence of this peak suggests the existence of oxygen atoms bonded to carbon atoms within the lattice framework or surface of the material. Zn2p peak (figure 7(d)) typically splits into two peaks: Zn2p_{3/2} and Zn2p_{1/2}. This splitting arises due to spin–orbit coupling, a relativistic effect where the interaction between an electron's spin and its orbital motion leads to a splitting of energy levels. The Zn2p_{3/2} peak at 1022.1 eV represents the higher binding energy state of the Zn2p orbital, while the Zn2p_{1/2} peak at 1046.3 eV represents the lower binding energy state [50]. The energy difference between these two peaks is characteristic of the chemical environment of the zinc atom in the compound being analysed. The prepared composite (MRG) was having functional groups moieties carboxylic and carbonyl, unsaturated and saturated, bonding between carbon and carbon (C–C, C=C) and bonding between carbon and oxygen (C–O). A sp² carbon network may be attributed to graphene formation including chemical environment of Zn.

4. Preparation of working electrodes and electrochemical measurements

The working electrodes for electrochemical studies were made by using 80% active materials (MOF-5, rGO, and MRG), PVDF(10%) and carbon black (10%) (figure 8). NMP was used as a solvent followed by stirring for 12 h. The resulting slurry was drop-casted on a graphite sheet, covering a 1 cm × 1 cm area. The electrodes were dried at 80 °C in vacuum oven at for a duration of 12 h, yielding a deposited sample mass (1 mg). The working electrode, facilitated the electrochemical reactions. A reference electrode, calomel (Ag/AgCl), provided a stable reference potential for accurate measurements. A platinum counter electrode (Pt) served to complete the circuit and facilitate the exchange of electrons during electrochemical processes. Electrochemical measurements was conducted using a 1 M H₂SO₄ solution.

CV was conducted to examine the charge storage capacity of MOF-5, rGO and MRG at various scan rates including (2, 5, 10, 20, 50 and 100) mV s^{−1}. GCD was performed to examine the charge/discharge kinetics,

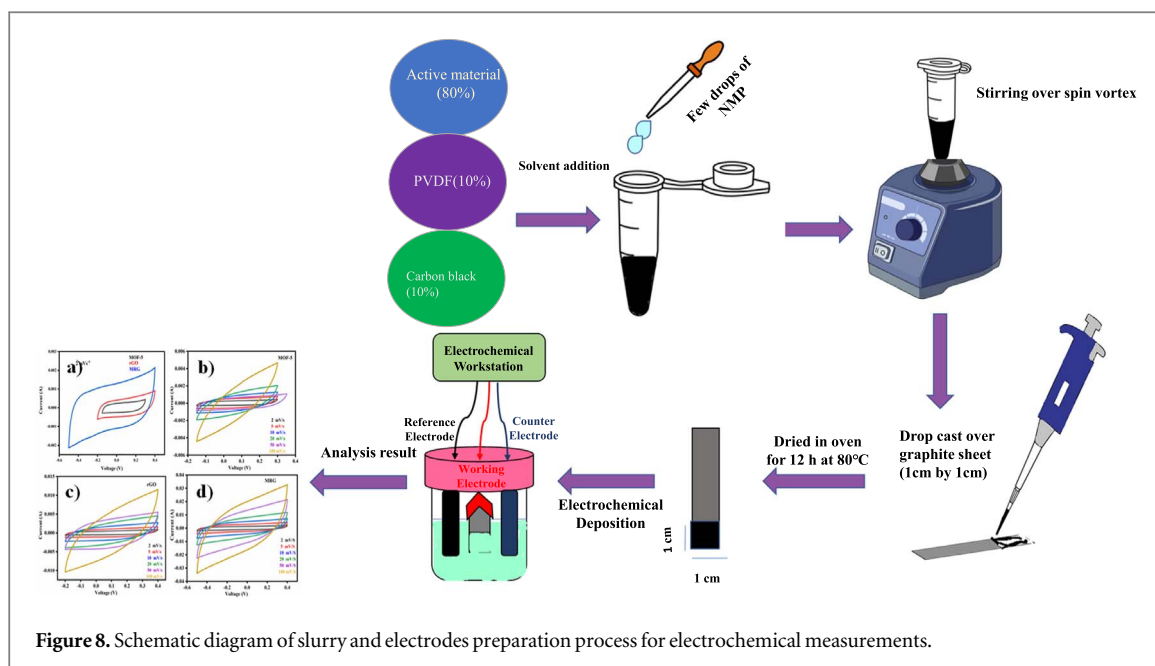


Figure 8. Schematic diagram of slurry and electrodes preparation process for electrochemical measurements.

energy density and power density of prepared materials at numerous current density (1, 2, 3 and 4) A g^{-1} . Moreover, EIS was employed to get solution resistance of electrolyte and charge transfer resistance at the electrode surface.

4.1. Cyclic voltammetry (CV) analysis and cyclic stability study

To study the electrochemical performance, working electrodes were tested using Cyclic Voltammetry (CV) and SCs involves measuring the current response while varying the voltage applied to the electrode in a cycling manner (figures 9(a)–(e)). After getting the I-V plot at different scan rates were drawn and equation (1) was applied [51] to evaluate specific capacitance from CV data,

$$C = \frac{\int Idv}{m \times s \times \Delta t} \quad (1)$$

Here, C, I, s, ΔV and m represents the specific capacitance (F g^{-1}), electrode current (A), scan rate (mV s^{-1}), potential window (Volts) and mass deposited on electrode respectively. The specific capacitance of MOF-5, rGO and MRG comes is 218.33, 415.77 and 1122.22 F g^{-1} respectively at 2 mV s^{-1} scan rate (figure 9(a)). The improved specific capacitance in case of MRG is due to synergistic effect of MOF-5 and rGO due to increased surface area and it will enhanced the number of active sites for ion adsorption. Moreover, electrically conducting nature of rGO also provides better pathways for ion transportation and fast charging/discharging kinetics. The deviations from the ideal rectangular shapes in the CV curves of MOF-5, rGO and MRG is suggesting the EDLC behaviour of the materials and charge storage is taking place through the adsorption of electrolyte ions (H^+ and SO_4^{2-}) at the electrode/electrolyte interface. The enhanced surface area of MRG ($1150 \text{ m}^2 \text{ g}^{-1}$) versus MOF-5 ($860 \text{ m}^2 \text{ g}^{-1}$) and rGO ($118 \text{ m}^2 \text{ g}^{-1}$) is responsible for more number of available sites for better charge storage capacity. The deviation of CV curve from ideal rectangular shape at higher scan rate may be attributed to heightened electrolyte and film resistance. This change indicates of limitations in charge transfer kinetics. At higher scan rates, the capacitance tends to decrease due to the constrained interaction duration between the electrode and electrolyte. This limited interaction time restricts the contribution of deeper electrode sites, compromising the overall charge storage capacity. Further, the high scan rate hampers the ion diffusion process, leading to reduced effective capacitance of the electrode material [52]. In case of MOF-5, rGO and MRG Potential window comes out to be 0.45, 0.6 and 0.9 V respectively. The high potential window for a supercapacitor refers to the upper limit of operating voltages where the device can withstand charging and discharging without experiencing significant degradation or damage. Increasing this window can improve the energy density and overall performance of supercapacitors, making them more suitable for energy storage applications. Table 1 is indicating the capacitance values for MOF-5, rGO and MRG at different scan rates.

Furthermore, The enduring stability of the MRG electrode is striking, manifesting nearly 80.9 capacity retention even after undergoing 10000 continuous charge–discharge cycles (figure 10(e)). This long-term stability signifies the exceptional performance of MRG composite electrode. The charge storage mechanism in MRG composite is mainly dominated by EDLC nature of rGO due to its large surface area and high conductivity.

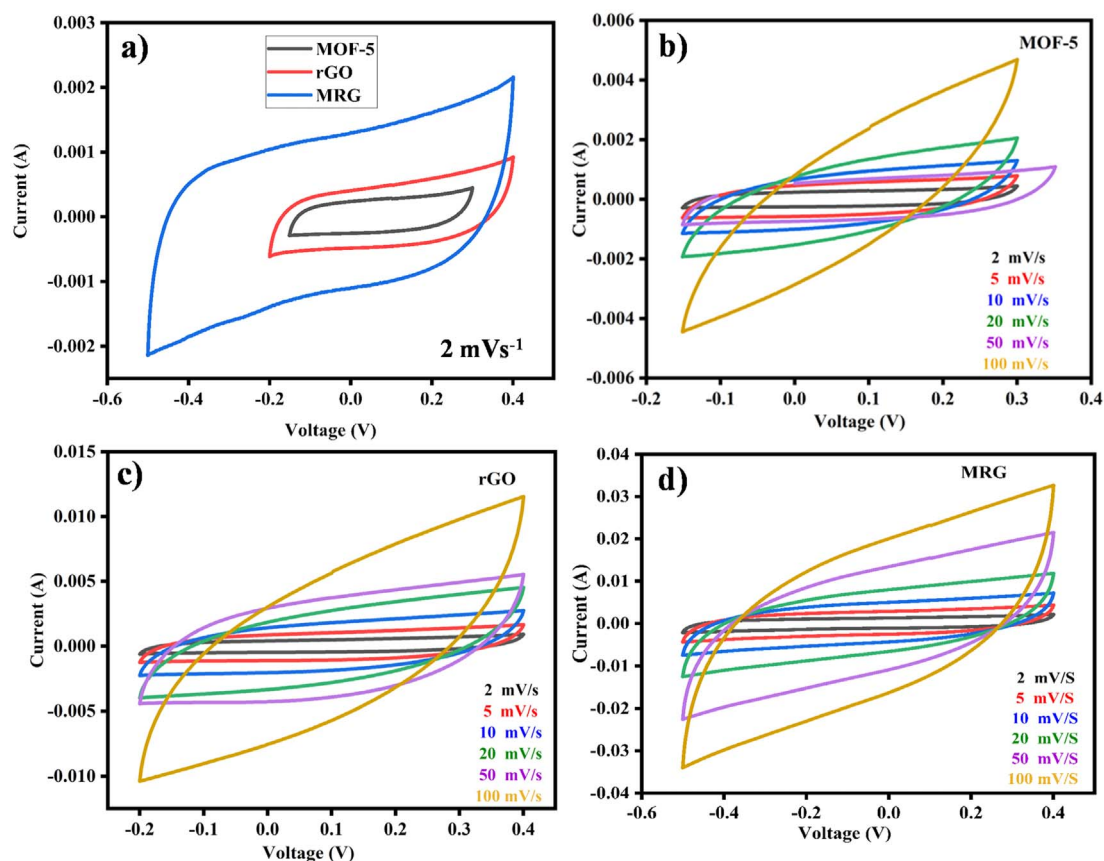


Figure 9. (a) CV curves for MOF-5, rGO and MRG at 2 mV s⁻¹ (b)–(d) CV curves of MOF-5, rGO and MRG at different scan rates and.

Table 1. Electrochemical performance of the MOF-5, rGO, MRG on a three electrode system in 1 M H₂SO₄ representing CV curves at different scan rates.

Scan rate (mV s ⁻¹)	Specific capacitance (F g ⁻¹)		
	MOF-5	rGO	MRG
2	218.33	415.77	1122.22
5	176.13	352.21	950.33
10	136.88	293.22	793.33
20	92.31	217.12	611.34
50	25.21	122.56	410.66
100	30.22	90.55	303.55

Layered structure of rGO provides surface for electrolyte ion adsorption and forming EDLC which supports non faradic charge storage. The presence of MOF-5 particles over rGO layers enhances the charge storage performance by facilitating the ion migration. The high surface area and porous structure of MOFs is supporting the migration of greater number of ions to the rGO layers hence enhancing the overall accessibility of ions to the rGO surface. During charging ions from electrolyte diffuse through MOF-5 channels and accumulates on rGO layers while during discharging they goes back to the electrolyte. The solvothermal synthesis method has ensured the dispersion of MOF-5 particles over rGO layers and providing pathways for better ion transport during charging and discharging while lowering the charge transfer resistance. This composite exhibits superior performance across all crucial metrics including specific capacitance, energy density, and power density positioning it as a standout candidate in advanced energy storage applications.

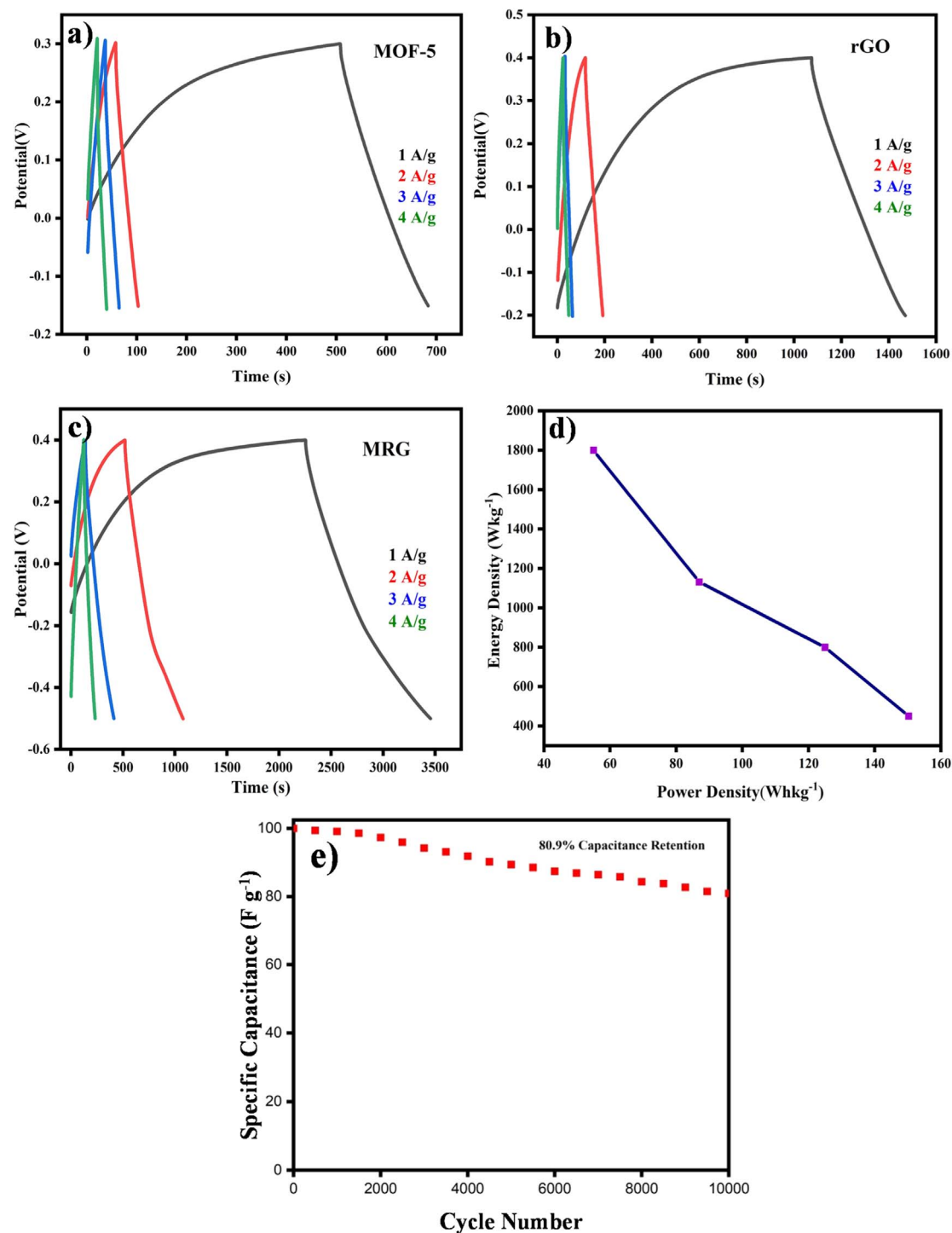


Figure 10. (a)–(c) GCD curve of MOF-5, rGO, MRG, (d) ragone plot for MRG and (e) cyclic stability curve of MRG.

4.2. Galvanostatic charge–discharge analysis (GCD)

GCD is a technique used in electrochemistry to measure the charge and discharge characteristics of energy storage devices, such as batteries and supercapacitors. This method involves applying a constant current to the system to measure the charge and discharge behaviour, enabling the determination of important parameters like specific capacitance, energy density, and power density. Figures 10(a)–(c) illustrates Galvanostatic charge–discharge (GCD) curves of MOF-5, rGO and MRG electrodes utilizing the optimized (Reference Ag/AgCl Electrode) under a constant current density of 1 A g^{-1} , 2 A g^{-1} , 3 A g^{-1} and 4 A g^{-1} . These results reaffirm the superior performance of the MRG composite electrode in contrast to the pristine MOF-5 electrode, validating its enhanced electrochemical behaviour and superior ionic transport capabilities. These findings further underscore the potential of the MRG composite as a promising candidate for advanced energy storage

Table 2. The variations in capacitance performance of MOF-5, rGO and MRG under different operating conditions (1 Ag^{-1} , 2 Ag^{-1} , 3 Ag^{-1} and 4 Ag^{-1}) from GCD values.

Current density (A g^{-1})	Specific capacitance (F g^{-1})		
	MOF-5	rGO	MRG
1.0	437.62	716.67	1366.66
2.0	253.33	266.79	1111.12
3.0	206.67	211.12	773.33
4.0	172.33	188.21	488.88

applications. Specific capacitance from GCD plots, Energy density and power density of electrode material are calculated using equations (2)–(4) respectively [53].

$$\text{Specific Capacitance, } C = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

$$\text{Energy density, } E = \frac{C \times \Delta V^2}{2 \times 3.6} \quad (3)$$

$$\text{Power density, } P = \frac{3600 \times \Delta E}{\Delta t} \quad (4)$$

Where $C (\text{F g}^{-1})$ = Specific capacitance, $\Delta t (\text{sec})$ = discharge time, $m (\text{mg})$ = mass deposited on electrode, $\Delta V (\text{Volts})$ = potential window, $E (\text{W h Kg}^{-1})$ = Energy density, $P (\text{W kg}^{-1})$ = Power density.

The distinctive nonlinearities observed in the GCD patterns is due to the presence of quasi reversible Faradaic reactions within the system. These Faradaic processes cause variations in the charge/voltage ratio, resulting into dynamic fluctuations during discharge. Consequently, determination of specific capacitances in such cases requires an integration approach, involving varying charge-voltage relationship resulting from these Faradaic reactions. At a current density of 1 A g^{-1} , (for comparison). The specific capacitance values are determined as 437.77 F g^{-1} for MOF-5, 716.67 F g^{-1} for rGO, and notably higher for MRG 1366.66 F g^{-1} . These findings clearly highlights the remarkable capacitance enhancement particularly for composite (MRG) for MRG, at higher current densities, highlighting its potential for improved energy storage applications across a range of operational conditions. Materials (MOF-5, rGO and MRG) were studied at different current density, notably found that increasing current density restricts ion diffusion and accessibility to the electrode surface, limiting effective charge storage. Elevated currents induce polarization, uneven ion distribution, and heightened resistance, impeding efficient ion movement and reducing capacitance [52]. Additionally, higher currents may trigger unwanted Faradaic reactions, altering electrode materials and diminishing their capacitive behaviour, contributing to decreased overall capacitance. This is reason that on increasing current densities specific capacitance decreased (shown in above table). Energy density and power comes out to be $150.7 \text{ W h Kg}^{-1}$ and 450.3 W Kg^{-1} respectively for MRG at 1.0 A g^{-1} current density (from equations (3) and (4)). The Coulombic efficiency (η), which is a crucial parameter for evaluating the efficiency and reversibility of the charge storage process in electrochemical systems. It measures the ease with which ions are inserted and removed during the charging and discharging processes. The Coulombic efficiency (%) of the synthesized material was calculated using the following formula [54]:

$$\eta = \frac{t_1}{t_2} \times 100 \quad (5)$$

where t_1 and t_2 represents the discharging and charging times, respectively. In this study, the calculated Coulombic efficiency for the MRG composite was found to be 89.3% at higher current density of 4 A g^{-1} . This value indicates that the MRG composite exhibits a high degree of Coulombic efficiency, suggesting effective charge–discharge cycles with minimal losses. The high Coulombic efficiency of the MRG composite with the $1 \text{ M H}_2\text{SO}_4$ electrolyte, demonstrates its potential for high-performance energy storage applications. The variation of power density and energy density for MRG at different current densities is shown by Ragone plot (figure 10(d)). Table 2 is indicating the capacitance values using GCD at different current densities.

4.3. Impedance measurements (EIS)

EIS was employed to analyse the electrochemical dynamics of prepared electrodes. EIS captured the electrical response to an applied alternating current (AC) signal across a frequency ranging from 0.01 Hz to 10^6 Hz . Analysis of the impedance spectrum provided critical electrochemical parameters such as solution resistance R_s and R_{ct} [55]. Additionally, EIS offered a comprehensive understanding of processes occurring at the electrode/

electrolyte interface, including charge transport and diffusion impedance. EIS was conducted to investigate the kinetics of charges and mainly to calculate the values of solution resistance of electrolyte and charge transfer resistance in the MRG composite material. EIS was observed in the frequency range 0.1 Hz to 10^6 Hz and the observed data was used to fit the equivalent circuit using NOVA software and to calculate the required parameters. The Nyquist plot illustrate the imaginary (Z'') and real (Z') impedances (figure 11(a)). Nyquist plots typically begin at high frequencies because the sample diffusion is restricted, impacting the impedance behavior observed in the system. In the fitted circuit (figure 11(b)) there are several components including R_s , R_p , CPE and W. R_s (solution resistance) was coming out to be 1.54Ω indicating the low value of resistance proposed by the electrolyte solution to the stream of current. R_p , charge transfer resistance which indicates the resistance at electrode/electrolyte interface and also the kinetics of charge transfer at the interface was found to be $810 \text{ m}\Omega$. Its low value is indicating that charges transfer quickly at the interface. The non-ideal capacitive behaviour was signified due to the existence of CPE (constant phase element) which depends on the frequency of the applied AC voltage signal and representing the presence of surface roughness, porosity of active material and heterogeneity of coated material over the electrode. Warburg element (W) in the circuit signifies ion diffusion kinetics within the electrochemical system and varies directly as $\sqrt{w}$, where w is frequency of applied AC voltage. The nyquist plot (figure 11(a)) which is plot between real impedance (Z') and imaginary impedance (Z'') provided overall behaviour of the electrochemical system and used to find R_s and R_{ct} .

4.4. Two electrode device electrochemical measurement

Active material (MRG composite), Carbon black and polyvinylidene fluoride (PVDF) in an 8:1:1 ratio were mixed into adequate amount of N-methyl-2-pyrrolidone (NMP) to make prepare slurries. Graphitic sheet was treated in nitric acid for 24 h and washed with D. I. water and ethanol. The dried pieces were coated with the slurry and dried overnight in an oven at 60°C . The cell was assembled in Teflon Swagelok assembly (figure 12(a)). Assembly contained two symmetric slurry-coated pieces of graphitic sheet separated by a piece of Whatman paper soaked in $1 \text{ M H}_2\text{SO}_4$. The electrochemical performance of the MRG based symmetrical supercapacitor device was investigated using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and Electrochemical Impedance measurements (EIS) measurements. Figure 12(b) represents the CV curves of symmetrical device at different scan rates corresponding to potential window ranging from 0.0 to 1.0 V. The specific capacitance was found to be 223.25 F g^{-1} at a scan rate of 2 mV s^{-1} . However, as the scan rate heightens, the specific capacitance of the device drops down to 21.73 F g^{-1} at 100 mV s^{-1} . This decrease in specific capacitance is attributed to the increased ion transport resistance encountered at higher scan rates. At higher scan rates, ions persist less time to penetrate into the bulk of the electrode material, which leads to a decline in capacitance. Specifically, the restricted transport of electrolyte ions to the inner regions of the electrode at higher scan rates contributes to this decrease. Conversely, at lower scan rates, ions have sufficient time to diffuse deeper into the electrode, effectively increasing the interaction area between the ions and the electrode surface. Moreover, this decrease in capacitance may also be linked to the decreased active area of the electrodes due to the presence of unreacted zinc atoms, which could inhibit ion transport into the electrode bulk. Figure 12(c) displays the galvanostatic charging–discharging curves for the composite-based electrodes at different current densities. The linearity depicted in these charge–discharge curves reflects the electrochemical double-layer capacitor (EDLC) behavior of the electrode material. At higher current densities, the faster charge–discharge cycles restrict the movement of electrolytic ions, inhibiting them from effectively reach the electrode's porous structure. This restricted ion diffusion reduces the effective utilization of the active material, resulting in a lower specific capacitance. Moreover, at lower current densities, ions have more time to migrate into the deeper regions of the electrode, leading to greater interaction with the electrode surface and higher capacitance. Specific capacitance of MRG composite at different scan rates (1,2,3 and 4) A g^{-1} comes out to be (262.41, 178.31, 107.04 and 45.2) F g^{-1} respectively. In figure 12(d) Cyclic stability data shown that the device has retained 83.71% specific capacitance which make this material as a potential material for supercapacitor device. Comparison of the specific capacitance after 10000 cycles and before stability test is also shown in figure 12(e). Figure 12(f) displays the specific capacitance (C_s) and current density relationship of supercapacitor device which is showing that as the current density increases specific capacitance decreases. The energy density and power density at 1 A g^{-1} comes out to be 36.4 W h kg^{-1} and 498.6 W kg^{-1} respectively. Solution resistance (R_s) and charge transfer resistance as calculated from the fitted circuit of EIS were came out to be 1.7Ω and 3.72Ω respectively as shown in figure 12(g), while the equivalent circuit is as shown in the figure 12(i). Ragone plot depicted in figure 12(j) showing the relationship between energy density (ED) and power density (PD), as ED decreased the PD increased Tables 3 and 4.

Table 3. Comparison of previously reported works related to rGO and MOF-5 with the present work.

Electrode material	Substrate	Electrolyte	Scan rate/current density	Specific capacitance	References
CMOF-5-GO	Graphite sheet	1 M H ₂ SO ₄	1 A g ⁻¹	195.4 F g ⁻¹	[56]
PEDOT/rGO	Graphite sheet	6.0 M KOH	10 mVs ⁻¹	102.8 F g ⁻¹	[57]
NiCo ₂ Se ₄ /rGO	Ni Foam	6.0 MKOH	2 A g ⁻¹	139 F g ⁻¹	[58]
MoS ₂ @CNT/rGO	—	H ₂ SO ₄ /PVA	0.1 mA cm ⁻²	129 mF cm ⁻²	[59]
MOF-5/AC-C nsp 850	Ni Foam	6.0 M KOH	2 mVs ⁻¹	193 F g ⁻¹	[60]
rGO/MWCNT	Ni Foam	2 M KOH	0.25 A g ⁻¹	200 F g ⁻¹	[61]
CMOF-5-80	Graphite sheet	1 M H ₂ SO ₄	1 A g ⁻¹	218 F g ⁻¹	[62]
rGO ₁₀₀ -CNT ₅₀ -Co ₃ S ₄ //N doped graphene	Ni Foam	6.0 M KOH	0.5 A g ⁻¹	127 F g ⁻¹	[63]
MOF-5/V ₂ CT _x	Ni Foam	3.0 M KOH	2 A g ⁻¹	235 F g ⁻¹	[64]
MRG	Graphite sheet	1 M H ₂ SO ₄	1 A g ⁻¹	262.4 F g ⁻¹	This work

Table 4. Comparison of biomass derived carbon materials for electrochemical performance with current work.

Material	Substrate	Electrolyte	Scan Rate (mV s^{-1}) / current density (A g^{-1})	Specific capacitance (F g^{-1})	References
Coffee Ground/rGO	Carbon paper	5 M KOH	0.5 A g^{-1}	440	[65]
Rice Husk, GO	Glassy Carbon Electrode	1 M Na_2SO_4	1.0 A g^{-1}	158.6	[66]
Hazelnut, Graphene Like Carbon	Pallets	1 M Na_2SO_4	0.2 A g^{-1}	320.9	[67]
Chestnut, Activated Carbon	Stainless steel mesh	6 M KOH	1.0 A g^{-1}	160	[68]
Willow Wood, activated carbon	Nickel Foam	1 M Na_2SO_4	5.0 A g^{-1}	2800	[69]
Tobacco Rods	Nickel Foam	6 M KOH	0.5 A g^{-1}	263	[70]
MRG	Graphite sheet	1 M H_2SO_4	1.0 A g^{-1}	262.4	This Work

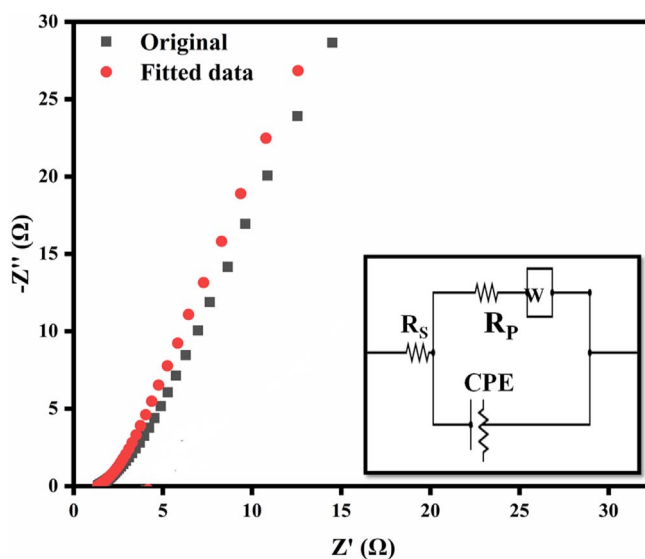


Figure 11. Nyquist plot for MRG composite and, fitted circuit for MRG (Inset).

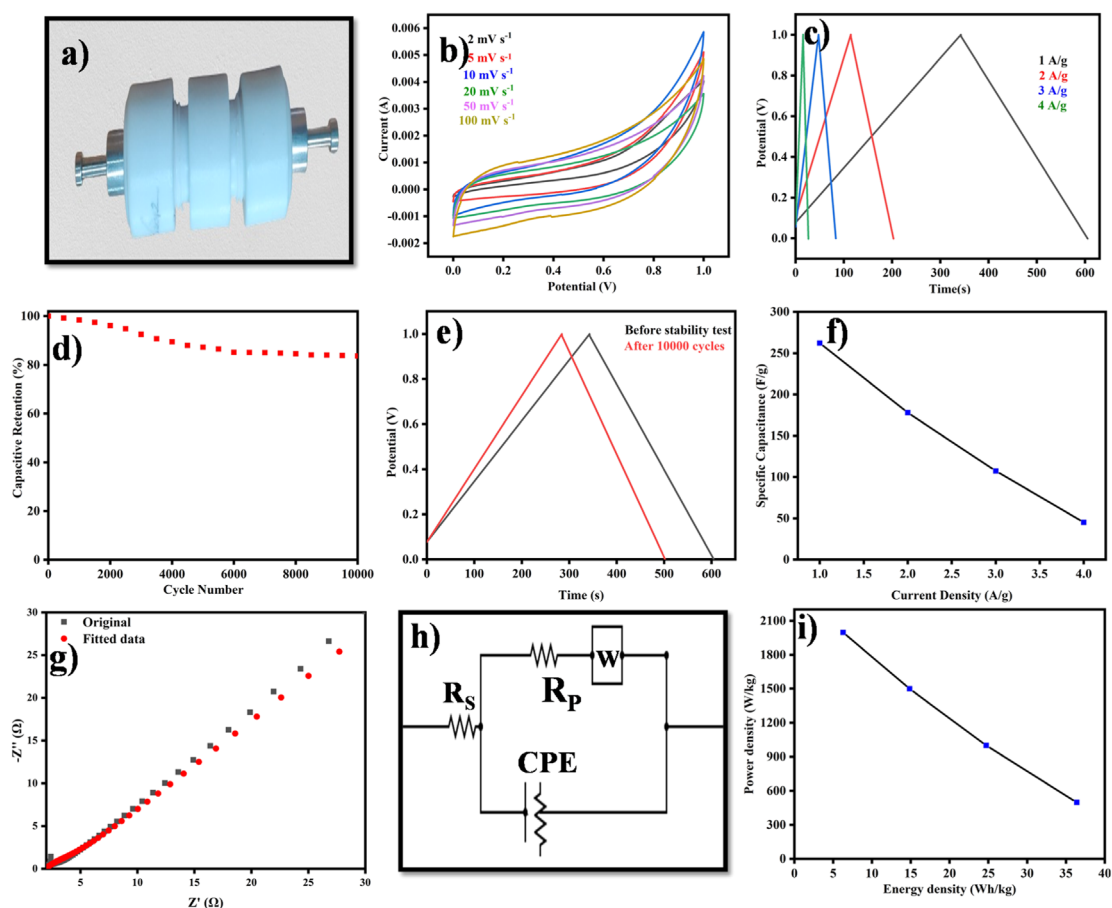


Figure 12. (a) Swagelok type two electrode symmetric device (b) CV curves of device at different scan rates (c) GCD curves of device at different current densities (d) Cyclic Stability data of device (e) GCD curve before and after cyclic stability test (f) Variation of specific capacitance with current density (g) EIS curves for device (h) Fitted circuit for symmetrical device (i) Ragone plot for device showing variation of Energy density with power density.

5. Conclusion

In this work, MRG composite was being synthesized using one step solvothermal method and used as an electrode material for supercapacitor application with a superior energy and power density on a three electrode system. For reducing the cost of synthesis, rGO was synthesized using Eucalyptus derived carbonaceous material as a precursor. The XRD, XPS, FTIR, Raman spectroscopy and morphological studies (SEM and TEM) concluded successful integration of MOF-5 particles on the rGO surface. The composite shown a unique morphology in which rGO surface was decorated by MOF-5 particles. Further N_2 sorption studies showed that MRG has higher surface area ($1150 \text{ m}^2 \text{ g}^{-1}$) in comparison to the pristine MOF-5 ($860 \text{ m}^2 \text{ g}^{-1}$). The layered structure of rGO integrated with the high surface area of MOF-5 synergistically shown enhanced surface area. The synthesized materials underwent electrochemical analysis through CV, GCD, and EIS to determine specific capacitance, energy density, power density, solution resistance, and charge transfer resistance in 1 M H_2SO_4 electrolyte while graphite sheet was used as current collector. The MRG has high specific capacitance (1366.6 F g^{-1}) as calculated by GCD at 1 A g^{-1} current density, Energy density of $150.7 \text{ W h kg}^{-1}$ and Power density of 450.3 W kg^{-1} at a current density of 1 A g^{-1} as calculated by GCD in H_2SO_4 (1 M). The coulombic efficiency for the MRG composite was found to be 89.3% at higher current density. The cyclic stability data shown that composite material is retaining $\sim 80.9\%$ capacitance even after 10000 cycles. The results for the MRG are significantly better as compared to the pure MOF-5. The presence of rGO layers in the MRG provides porous and conducting support to the MOF-5 particles combined with the high porosity coupled with high specific surface area of MOF-5. Moreover, rGO provides π -conjugated system in which π electrons are delocalized providing charge transfer paths within the material and increased the overall conductivity of the material significantly. The solution resistance R_s and charge transfer resistance R_{ct} using EIS data was coming out to be 1.54Ω and $810 \text{ m}\Omega$. The symmetrical supercapacitor device of MRG shown a specific capacitance of 262.4 F g^{-1} with an energy density 36.4 W h kg^{-1} and power density of 498.6 W kg^{-1} , while the device retained 83.7% of specific capacitance after going through 10000 charging discharging cycles. The low resistance value is also attributed to the high conductivity value of the MRG. In the future studies the results can be optimized by varying the amount of rGO in the composite material while with these results the composite is capable of showing good results with a fabricated device.

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Data availability statement

The data cannot be made publicly available upon publication because they contain sensitive personal information. The data that support the findings of this study are available upon reasonable request from the authors.

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Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Author contributions

Robin Saini: Conceived and designed the study, performed experiments, Methodology conceptualization, visualization, data analysis, writing original draft. **Priyanka Wadhwa:** Methodology, conceptualization, data analysis, writing original draft. **Karuna Jain:** Methodology, data analysis, review & editing. **Mayank Pathak:**

Conceptualization, data analysis, writing—review & editing. **Pratap Singh**: writing—Review & Editing. **Rahul Kumar Dhaka**: Resources, supervision, writing-review and editing. **Sandeep Kumar**: Supervision, review & editing. **Manoj Kumar Singh**: Resource, Supervision, conceptualization, methodology, writing—review & editing. All authors read and approved the final manuscript.

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