

Synthesis and characterization of synergetic Pd/MoO₃-rGO hybrid material as efficient electrode for supercapacitor application

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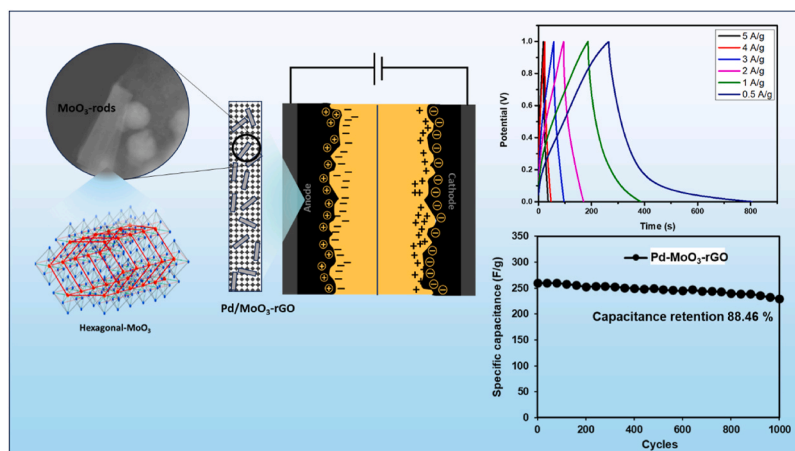
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HIGHLIGHTS

- Synthesized and characterized Pd/MoO₃-rGO nanocomposites to evaluate the effects of Pd doping on supercapacitor performance.
- The integration of Pd with MoO₃-rGO forms a distinctive nanocomposite structure that enhances pseudocapacitance and ion diffusion capabilities.
- Pd doping in MoO₃-rGO improves supercapacitor performance by increasing conductivity and stability.
- MoO₃ contributes to enhanced charge transfer, ion diffusion, and Faradaic storage within the nanocomposite.
- Pd/MoO₃-rGO exhibited a 2.7-fold increase in specific capacitance compared to Pd-rGO.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, study synthesized Pd-rGO and Pd/MoO₃-rGO nanocomposites via a one-pot hydrothermal method, serving as efficient electrodes for supercapacitor applications. Various analytical techniques, including XRD, XPS, HRTEM, BET, and Raman spectroscopy, were employed to characterize the structural, morphological, and physiochemical properties to assess the electrochemical supercapacitor performance of nanocomposite materials. The analyses confirmed that the charge transfer mechanism between the MoO₃-NR with Pd-rGO in Pd/MoO₃-rGO samples has significantly improved the electrochemical performance of Pd/MoO₃-rGO by 2.7 times compared to Pd-rGO sample (105.00 F/g at 0.5 A/g). Remarkably, the Pd/MoO₃-rGO hybrid material exhibited excellent electrochemical activity, boosting a specific capacitance of 291.50 F/g at a current density of 0.5 A/g, accompanied by energy density and power density values of 18.06 Wh/kg and 250.00 W/kg, respectively.

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Furthermore, it demonstrated noteworthy stability over prolonged usage, retaining 88.46 % of its capacity after 1000 cycles at a constant current density of 1.0 A/g. These findings underscore the promising potential of the Pd/MoO₃-rGO nanocomposite as a highly effective electrode material for supercapacitors.

1. Introduction

A quest for developing sustainable energy storage solutions is becoming a global trend to decrease the consumption of fossil fuels and greenhouse gas emissions that cause severe environmental impacts. Renewable energy sources like solar, hydropower, and wind power are the best solutions for addressing these concerns [1]. However, the electrical energy produced from these sources must be stored efficiently and used immediately on demand. In leading energy storage technologies, a supercapacitor (SCs) is an electrochemical energy storage device that delivers power in various applications, such as hybrid electric vehicles, portable electronic devices, and alternative energy systems [2,3], such as fuel cell/supercapacitor hybridization [4]. Its unique combination of high-power density and the ability to charge/discharge rapidly without significant degradation makes it suitable for long-term use [5, 6].

The performance of SCs is primarily dependent on the characteristics of electrode materials and their configuration. Researchers have explored various transition metal oxide nanostructures for SCs application, including MnO₂ [7–9], Co₃O₄ [10], NiO [11], and CeO₂ [12]. Among these, MoO_x emerged as a significant material interest due to its layered structure and highly stable thermal and chemical properties, enabling excellent electrochemical activity for potential application in SCs. Since MoO_x undergoes multiple oxidation states, it forms various polymorphic phases [13,14]. The primary polymorphic forms are α -MoO₃ and β -MoO₃, which exhibit very high stability at room temperature and possess orthorhombic and monoclinic crystal structures, respectively [15,16]. In addition, the metastable hexagonal phase of MoO₃ (h -MoO₃) emerges from MoO₆ octahedra arranged in a zigzag chain, resulting in a hexagonal rod-like structure [17–21]. The ability to form nanostructures like nanorods and nanoplates boasts high electrical conductivity, further improving its electrochemical performance by providing high surface area and short diffusion paths [19]. The one-dimensional h -MoO₃ rods demonstrate conductivity levels approximately 550 times higher than those of α -MoO₃. Their incorporation of channels, voids, and crystallite boundaries enhances ion migration, producing superior conductivity [22–25]. To further improve the electrochemical supercapacitance, MoO₃ nanostructures are often incorporated with carbon nanomaterials or second transition metals to provide additional pseudocapacitance through redox reactions [26,27].

Previous reports elucidated the key reason for improving the electrochemical performance of MoO₃-based nanocomposite for SCs performance [28,29]. An increase in the surface hydroxyl group density and improved ionic and electronic conductivity of MoO₃ nanowires significantly improve the specific capacitance of MoO₃-based electrode nanocomposite materials [29]. Incorporating layered graphene sheets in MoO₃-rGO nanostructure supplies abundant surface-active sites for MoO₃ nanosheet, increasing the active surface area for ions interaction. Graphene layers improve electrical conductivity and stabilize the volume and crystal structure changes during repeated charging and discharging operations [30]. The synergic effects between abundant oxygen vacancies in MoO_{3-x} and the conductive network of rGO, along with the expansion of 2-D diffusion channels, further enhance SCs performance [31,32]. The electron conduction promoting effect of electrical conducting polymer and their synergistic interaction with MoO₃ nanorods and conductive rGO matrix contribute to superior electrochemical performance compared to stand-alone MoO₃ and MoO₃-rGO composite [33,34]. The coexistence of various intercalation sites and the strong interaction with the graphene matrix result in enhanced electrochemical performance [34]. The layered structure between ultrathin

MoO₃ nanocrystals and graphene nanosheets facilitates charge transport, while the 3D porous graphene frameworks enable rapid ion diffusion and electron transport [35,36]. The MoO₃ nanoparticles support the short diffusion path length for electrolytes in the vertical direction, provide the transport pathway for electrons in a parallel direction, and potentially tailor the graphene layer to allow electrolytes to migrate into the composite materials [37,38]. The coated carbon layer on the MoO₃ surface accommodates volume changes and improves conductivity and active sites, leading to remarkable performance as electrode materials for supercapacitors [38–41]. The morphology and crystal phases of MoO₃ are even responsible for SCs performance while exposing the (110) and ($\bar{1}$ 10) planes with pyramidal morphology to provide active sites for the intercalation of electrolytes and ions [18,27, 36,38]. Researchers observed that incorporating palladium (Pd) into the MoO₃ host lattice provides good electrical conductivity and structural stability [22]. In recent studies, Pd stands out among the noble metals widely applied in various fields, including energy storage, gas sensors, photocatalysts, and more [42]. Pd has unique properties in combination with MoO₃ structure due to its ionic radius (0.755 Å) being closer to Mo (0.730 Å). Hence, Pd emerges as the metal best suited for doping in the MoO₃ structure with rGO [27].

Previous research has extensively explored MoO₃-based nanostructures and their composites, particularly with carbon nanomaterials like graphene. However, there is a significant gap in studies specifically focusing on noble metal-doped MoO₃ nanocomposites for supercapacitor (SC) applications. While the synergistic effects of MoO₃ with transition metals and carbon nanomaterials have been investigated, the interaction of noble metals, such as palladium (Pd), with MoO₃ in the context of SCs remains insufficiently studied. Although Pd has been suggested to enhance the electrical conductivity and structural stability of MoO₃, research on the specific electrochemical performance of Pd-doped MoO₃-rGO nanocomposites is lacking. The impact of Pd incorporation into MoO₃ structures, particularly in combination with reduced graphene oxide (rGO), on supercapacitor performance has not yet been thoroughly examined.

This study introduces a novel approach to synthesizing and characterizing Pd/MoO₃-rGO nanocomposites, with a focus on the effects of Pd doping on the electrochemical performance of MoO₃-based SCs. The research posits that Pd, with its ionic radius comparable to that of Mo, can be effectively doped into MoO₃ structures, potentially enhancing supercapacitor performance by improving conductivity and stability. The aim of this work is to bridge the research gap by investigating the effects of Pd incorporation on charge transfer characteristics, which could result in superior electrochemical performance compared to existing MoO₃ or MoO₃-rGO composites. Additionally, the novelty of this work lies in exploring the combination of Pd with MoO₃ and rGO, creating a unique nanocomposite structure that could offer enhanced pseudocapacitance and ion diffusion capabilities. Ultimately, this research holds significant potential for advancing the development of sophisticated supercapacitors, contributing to the creation of more efficient and reliable integrated alternative energy systems.

2. Materials and methodologies

In this work, all chemicals were used without further purification: Graphite powder (with a particle size <20 μ m, Asbury carbon, New Jersey, USA) served as the precursor for synthesizing graphene. Sodium nitrate (NaNO₃, ACL Labscan, Thailand) facilitated the additional oxidation of graphite layers. Potassium permanganate (KMnO₄, Samchun, Korea, 99.30 wt%) and sulphuric acid (H₂SO₄, Samchun, Korea,

98.00 vol%) acted as the oxidizing agent during GO synthesis. Hydrogen peroxide (H_2O_2 , QREc, Thailand, 35.00 vol%) and hydrochloric acid (HCl, ACL Labscan, 37.00 vol%) were used to refine and eliminate impurities from GO nanosheets. Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Loba Chemie, 99.30 wt%) was the precursor for MoO_3 synthesis. Palladium chloride (PdCl_2 , Sigma Aldrich, 99.00 wt%) and carbon black served as electrodes for the supercapacitor. Ammonia solution (NH_4OH , Loba Chemie, 30.00 vol%) and sodium dodecyl sulfate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, Fisher Scientific) were employed as surfactants.

2.1. GO synthesis

This work synthesized graphene oxide (GO) by a modified Hummer's method, as described in previous literature [12]. In a typical method, 5.00 g of graphite powder and 2.50 g of NaNO_3 were mixed in a 200.0 ml beaker containing 150.0 ml of conc. H_2SO_4 . The mixture was stirred in an ice bath for 1 h to form a homogenous solution, maintaining the temperature below 5 °C. Nearly 15.00 g of KMnO_4 was gradually added to the above reaction mixture and continuously stirred for the next 7 h at 40 °C, until the solution turned dark grey. In the next step, the solution was added with 450 ml of DI water while constantly stirring for 3 h at 98 °C, and then the GO slurry was cooled at temperature. Subsequently, 700.0 ml of DI water and 135.00 ml of 15.00 % H_2O_2 were added to obtain the GO suspension. In the end, 100.00 ml of 5.00 % HCl solution was added to remove the excess salt from GO. The retrieved GO suspension was washed multiple times with DI water until the pH of the suspension reached 6–7. Finally, the collected GO slurry was filtered and dried at 80 °C for 24 h to collect GO powder.

2.2. MoO_3 -rods synthesis

MoO_3 -NRs were synthesized via a one-step hydrothermal method [43]. In a typical procedure, 1.50 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were dissolved in 60.0 ml of DI water and stirred for 30 min. About 0.17 g of sodium 0.01 M dodecyl sulfate solution was added to the previous reaction mixture and stirred for 60 min to obtain a homogenous solution. The pH of the solution was adjusted to 2–3 by gradually adding 37 % HCl solution while stirring vigorously. The transparent molybdate solution was transferred into a 100 ml Teflon-lined stainless-steel autoclave with heat at 24 h at 180 °C. After the hydrothermal treatment, the transparent solution turned dark blue, indicating the formation of MoO_3 nanorods. Finally, the product was collected by washing multiple times with ethanol and DI water and then dried at 150 °C for 6 h. In the synthesis process, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 7\text{H}_2\text{O}$ was mixed with a surfactant in a sealed vessel and then heated at high temperature and pressure.

The precursor decomposes into MoO_6 octahedra, which form the MoO_3 -Rods [21]. The sodium dodecyl sulfate (SDS) used as a capping agent for the synthesis of MoO_3 nanorods [44], essentially protecting the growing nanoparticle surface to control its shape and size, preventing an uncontrolled aggregation and promoting the formation of elongated, rod-like structures by selectively binding to specific crystal facets during the nucleation and growth process. The Ostwald ripening mechanism is often involved, where smaller crystallites dissolve and redeposit onto larger ones, forming well-defined nanorods. The surfactant or capping agent affects the shape and size of MoO_3 -Rods, and a layered structure of MoO_6 octahedra forms the MoO_3 structure. The alternating layers of MoO_6 octahedra give rise to the packed hexagonal pattern in MoO_3 -Rods [21]. These unique features of MoO_3 nanorods can contribute to better electrochemical performance, including higher energy/power density, improved cycling stability, and faster charging/discharging rates, making them promising candidates for advanced energy storage applications.

2.3. Pd-rGO and $\text{Pd/MoO}_3\text{-rGO}$ composites synthesis

For $\text{MoO}_3\text{-rGO}$ synthesis, 75.00 mg of MoO_3 -Rods, 75.00 mg of PdCl_2 , and 480.00 mg of GO were added to the DI water. To synthesize Pd-rGO , 480.00 mg of graphene oxide (GO) and 150.00 mg of palladium chloride (PdCl_2) were dissolved in 60.0 ml of deionized water (DI water). The above mixture solution was sonicated for 1.5 h to prepare the homogenous solution. The solution was transferred to a Teflon-lined stainless-steel autoclave and subjected to a heat treatment at 140 °C for 24 h. The solid deposit of Pd/rGO and $\text{Pd/MoO}_3\text{-rGO}$ nanocomposite was washed several times with ethanol and DI water and dried at 80 °C for 12 h. Finally, the powdered $\text{Pd/MoO}_3\text{-rGO}$ and Pd/rGO samples were sent for characterization.

2.4. Electrode preparation for electrochemical characterizations

All the electrochemical experiments were conducted using a two-electrode configuration from three electrochemical workstations. The reference and the counter electrode were combined to make a single electrode for the two electrode systems. The electrochemical station is set up by connecting the working electrode to the working terminal and the combined reference/counter electrode to the opposite electrode terminal, sandwiching the separator immersed in the electrolytic solution. The reference electrode was calibrated before the electrochemical experiments. In a typical procedure, the working electrodes were prepared by blending the electroactive materials (Pd-rGO and $\text{Pd/MoO}_3\text{-rGO}$), carbon black, and PVDF in a mass ratio of 80:0:10 in 2.00–3.00 ml of N-methyl-2-pyrrolidone (NMP) as a solvent. The mixture was sonicated for 1 h to obtain a homogenous slurry. Subsequently, the slurry was dropped casted onto a nickel foam substrate, size dimension of $2 \times 1 \text{ cm}^2$ with an active area of $1 \times 1 \text{ cm}^2$, and then dried at 80 °C for 12 h to remove excess solvent. The average mass loading was about 2.00 mg/ cm^2 for both electrodes. A Whatman filter paper was soaked in a 6.0 M KOH electrolyte solution to apply as an electrode separator to avoid electrical short-circuiting. The filter paper was sandwiched between two electrodes to assemble the symmetric supercapacitor.

Electrochemical techniques, including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS), are conducted to assess the electrochemical properties of the prepared electrode material. Cyclic voltammetry was carried out in the potential range of 0.0–1.0 V at varying scan rates (10–250 mV/s) to explore the redox behaviour and capacitance of electrodes. The specific capacitance (C_{sp}) was calculated from CV results using well-defined relations.

$$C_{\text{sp}}(\text{F/g}) = \frac{\int i \, dv}{m \Delta V} \quad (1)$$

Where i stands for the integrated area of the CV curve (V), m in mass loading of active material in g, S denotes the scan rate ($S = \text{V/s}$), and ΔV represents the potential range (V). The galvanostatic charge/discharge (GCD) test evaluated the energy storage and charge/discharge. The data from the GCD curve was used to calculate the specific capacitance, following the equations:

$$\text{Specific capacitance } (C_s) = \frac{i \Delta t}{m \Delta V} \quad (2)$$

Where i is for the applied current (A), Δt represents the discharge time, m is the mass loading of active material in g, and ΔV denotes the potential range (V). In addition, the relation between energy density and power density in terms of the Ragone plot was calculated based on references [28].

2.5. Characterizations

Powder X-ray diffraction (PXRD) patterns of Pd-rGO and $\text{Pd/MoO}_3\text{-rGO}$

rGO were characterized by the Rigaku, SmartLab X-ray diffractometer with monochromatic Cu K α radiation 1.5406 Å wavelength. A Renishaw spectrometer with a 532 nm laser source wavelength was used to record the Raman spectra of the sample, respectively. The Pd-rGO and Pd/MoO₃-rGO nanocomposite were imaged using the High-Resolution Transmission Electron Microscope attached to a scanning transmission electron microscope (STEM, HRTEM, JEOL JEM-2100F, Japan). HRTEM imaging of the samples was characterized by depositing a few drops of the colloidal solution of the binary/ternary nanocomposites onto a carbon-coated copper wire grid and allowing it to dry at room temperature before analysis. The chemical compositions of the samples were analyzed using X-ray Photoelectron Spectroscopy (XPS) with an Al K α X-ray source (1487 eV) on a ULVAC-PHI, Inc. instrument. The surface pore structure of samples was studied using Brunauer-Emmett-Teller (BET) analysis performed using the Nova Touch LX2 model by Quantachrome Instruments, USA. The electrochemical performance of Pd-rGO and Pd/MoO₃-rGO was evaluated using a three-electrode system and 6 M KOH electrolyte at room temperature (Princeton Applied Research, Versa-STAT 3, AMETEK). In this work, all the data were fitted using the Gaussian function after the Shirley background correction using the Origin 2019b software.

3. Results and discussion

3.1. Structural characterizations

Schematic illustration of GO reduced to rGO in Pd-rGO and Pd-rGO-MoO₃ composites is presents in Fig. 1(a). During the hydrothermal process, GO converts to reduced rGO without using a separate reducing agent. The high temperature and pressure conditions drive the reduction process. During this process, the oxygen-containing functional groups on GO are broken down and release oxygen, converting GO to reduced graphene oxide (rGO). Formation of Pd-rGO-MoO₃ Composite, The GO is reduced to rGO, palladium nanoparticles, and MoO₃ nanostructures become well-dispersed and intimately mixed within the rGO matrix. This results in a stable composite with enhanced conductivity and structural integrity [45,46]. X-ray diffraction (XRD) spectra were obtained to analyze the crystal structure of MoO₃-NR, Pd-rGO, and Pd/MoO₃-rGO samples. This analysis provides invaluable insights into the structural characteristics of the inspected samples. Such insights are pivotal for comprehending the properties and performance of supercapacitors. The XRD patterns of MoO₃-NR, depicted in Fig. 1(b), reveal diffraction signals at $2\theta = 9.6^\circ, 16.7^\circ, 19.3^\circ, 29.2^\circ$ and 35.2° (JCPDS card No. 21–0569). This alignment suggests successfully synthesizing pure hexagonal MoO₃ nanorods [47,48]. These peaks can be assigned to the (100), (110), (200), (210), (300), and (310) crystal planes of typical MoO₃. Notably, the prominent peak occurring below $2\theta = 10^\circ$ serves as a distinctive feature, differentiating the h-MoO₃ crystal structure from other polymorphic phases of MoO₃ [49,50,51]. For this reason, the hexagonal arrangement of atoms facilitates the movement of electrons within the material (Fig. 1(c)), contributing to enhanced electrical conductivity. The intensity of these peaks indicates the quality of the sample and the degree of crystallinity in the MoO₃-NR.

The XRD pattern of Pd-rGO and Pd/MoO₃-rGO samples are shown in Fig. 1(d). The XRD peaks of both Pd-rGO and Pd/MoO₃-rGO exhibit similar peaks positions at around $2\theta = 40.0^\circ, 46.4^\circ, 67.8^\circ, 82.5^\circ$, and 87.0° correspond to the (111), (200), (220), (311), and (222) of fcc-type crystal structure of Pd nanoparticles (JCPDS card No. 05–0681). In addition, a broad peak centered around $2\theta = 20.0$ – 28.0° , reflecting the (002) crystal plane of the rGO graphitic carbon lattice, is observed in both samples. These peak positions remain unchanged for Pd-rGO and Pd/MoO₃-rGO nanocomposite samples. However, the introduction of MoO₃-NRs in Pd-rGO leads to the occurrence of a small peak at a slightly lower diffraction angle in the vicinity of the Pd diffraction peak in Pd/MoO₃-rGO nanocomposite compared to Pd-rGO. This feature can arise from forming a new phase or strain within the Pd crystal lattice by

incorporating MoO₃ into the Pd/rGO matrix. The interaction between Mo and Pd can lead to lattice distortions or interfacial phase formation, manifesting as additional peaks in the XRD pattern.

Moreover, previous researchers observed that the alloying of Mo in Pd can cause a shift in the diffraction peaks at lower angles due to differences in the atomic radii of Mo and Pd, resulting in new diffraction peaks at lower angles. However, the present work shows the occurrence of a new diffraction peak at the lower 2θ , suggesting a new phase of Pd crystal phases with expanded interatomic distance due to the incorporation of MoO₃ lattice (as shown in Fig. 1(c)). This expansion in the Pd lattice system facilitates a better charge transfer process by creating an active site center due to the improved electronic coupling of Pd and MoO₃. This charge transfer mechanism, caused by altering the crystal structure of Pd, may play a crucial role in the enhanced electrochemical performance of the Pd/MoO₃-rGO nanocomposite sample. In the previous reports, the researcher claims the introduction of Pd nanoparticles with various transition elements results in a negative shift diffraction peak of the Pd crystal system, including Mo [52,53], Cu [54], Sn [49], and Ni [55]. Notably, the absence of Mo diffraction peaks and its oxide or hydroxide in the Pd/MoO₃-rGO nanocomposite sample indicates that a substantial amount of Pd is present in crystallized phases [50,54]. The crucial issue identified in this part is the significant impact of incorporating MoO₃ into the Pd lattice, which leads to the formation of a new Pd crystal phase with expanded interatomic distances. This structural alteration enhances the charge transfer process, likely contributing to the superior electrochemical performance of the Pd/MoO₃-rGO nanocomposite. Understanding this mechanism is essential for further optimizing and developing advanced nanocomposite materials for electrochemical applications.

3.2. Raman analysis

Raman spectroscopy is a versatile and non-destructive technique for studying structural and electronic properties and nanomaterials [47,56,57]. Herein, a typical Raman spectrum of GO, MoO₃, Pd-rGO, and Pd/MoO₃-rGO samples are presented in Fig. 2. Within the 100–1200 cm^{−1} frequency range, Raman spectra of MoO₃ nanostructure show nine Raman active modes, as shown in Fig. 2(a). Pure-MoO₃ Raman spectra peaks are displayed at 192 cm^{−1} (O = M = O twisting), 276 cm^{−1} (O = M = O wagging), 332 cm^{−1} (O–M–O bending), 370 cm^{−1} (O–M–O scissoring), 660 cm^{−1} (O–M–O stretching), 818 cm^{−1} (M = O sym-stretching), and 990 cm^{−1} (M = O asym-stretching), which confirms the MoO₃-NRs formation [56–59]. Other peaks at 140 and 119 cm^{−1} are due to the translation of a rigid chain (T_b mode) [60]. These modes reported in the literature verify the formation of MoO₃ nanostructure [61]. The Raman spectra of GO, Pd-rGO, and Pd/MoO₃-rGO were also recorded to investigate the synergic effect between Pd and Pd/MoO₃-Rods with graphitic carbon support material. The recorded Raman spectra of Pd-rGO and Pd/MoO₃-rGO samples reveal the four other Raman bands at 538, 747, 893, and 1065 cm^{−1}, indicating vibrational modes and structural characteristics, as shown in the inset of Fig. 2(b). The peaks at 538 and 747 cm^{−1} associated with out-of-plane vibrations of carbon atoms, reflecting defects and disorder in the rGO, whereas the peak at 893 cm^{−1} is linked to the C–C bond stretching modes, which are sensitive to the degree of reduction and functional groups on the rGO surface. The peak at 1065 cm^{−1} is typically attributed to the D band, which is related to disorder in the carbon lattice [62,63].

However, the D and G bands in Raman spectroscopy are the most important characteristic peaks for rGO-based nanocomposite structures. The D-band (~1350 cm^{−1}) is associated with the presence of defects or disorder in the carbon lattice. It typically arises due to the breathing modes of sp² atoms in rings. A high intensity of the D-band relative to the G-band indicates a higher defect density. The G-band (~1580 cm^{−1}) represents the graphitic nature of the material. It is associated with the stretching of the C–C bonds in the plane of sp² hybridized carbon atoms. A prominent G-band suggests a well-ordered, graphitic structure. For

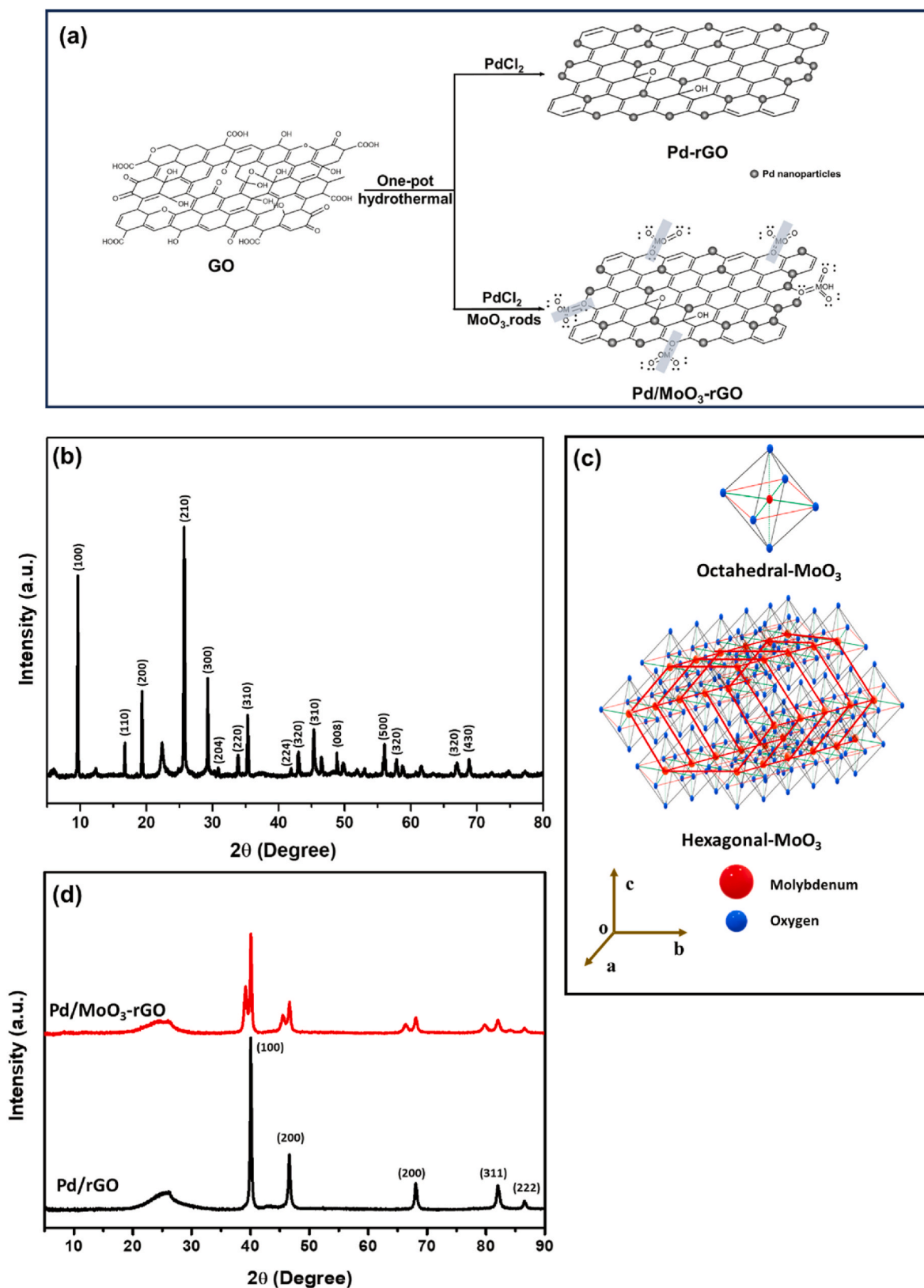


Fig. 1. Proposed mechanism of (a) GO reduced to rGO in Pd-rGO and Pd-rGO-MoO₃ composites, XRD spectra of (b) MoO₃-Rods (c) schematic structure of hexagonal-MoO₃ (d) XRD spectra of Pd-rGO and Pd/MoO₃-rGO samples.

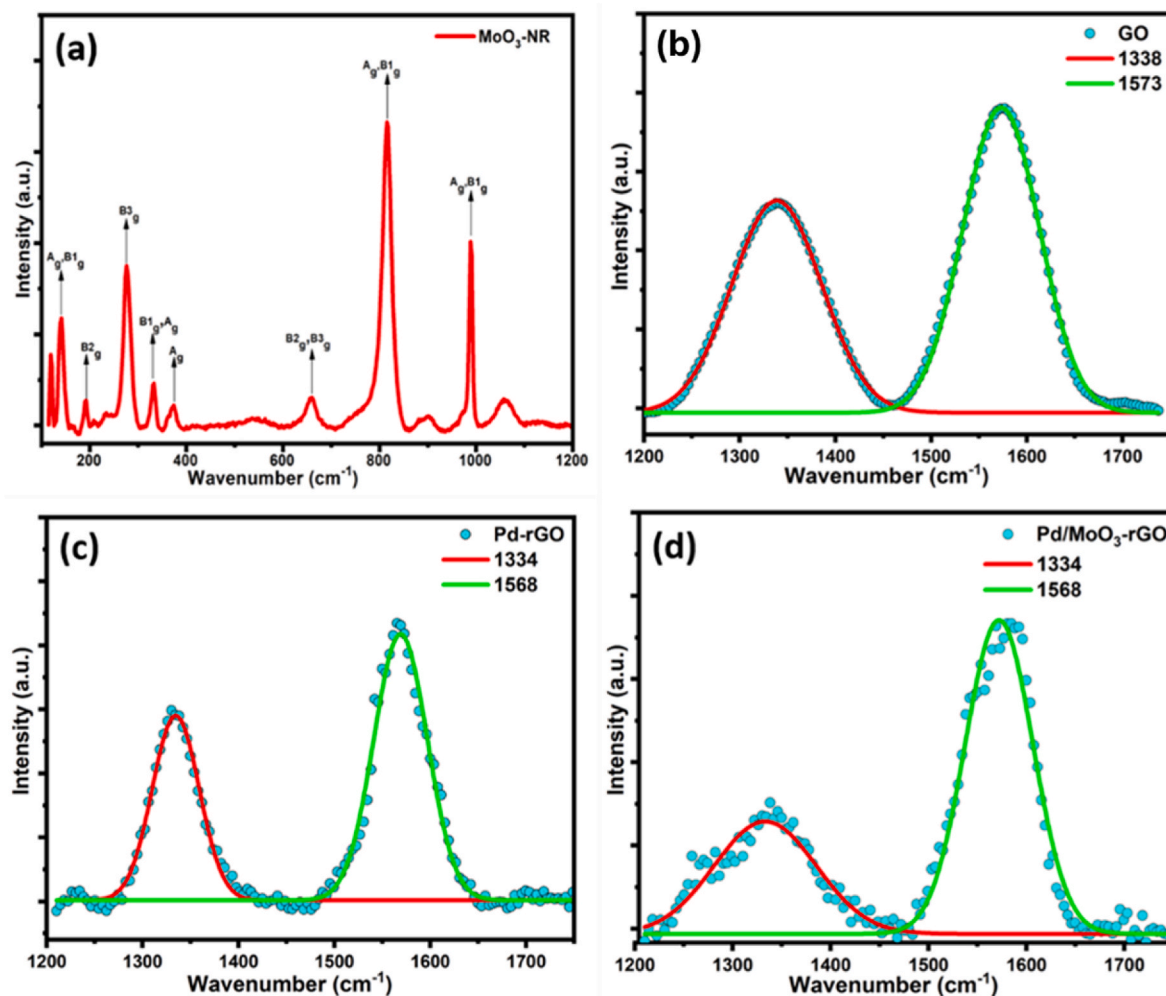


Fig. 2. Laser Raman spectra of (a) MoO_3 -nanorods, comparative D-band and G-band of (b) GO, (c) Pd-rGO, and (d) Pd/ MoO_3 -rGO samples.

supercapacitor electrodes, MoO_3 and Pd play significant roles in affecting the D and G band intensities. MoO_3 Enhances the structural integrity and contributes to the overall stability of the composite. The interaction of MoO_3 with rGO affects the defect density and the graphitic nature of the material, influencing the D/G band ratio. Pd improves electrical conductivity and facilitates charge transfer. The presence of Pd can reduce the number of defects in the rGO structure, potentially lowering the D-band intensity and increasing the G-band intensity. Concentrating on these bands allows for a consistent and straightforward comparison between different samples, especially when assessing the degree of reduction and quality of rGO. While it's true that other Raman peaks can be observed, these may arise from various sources and complicate the analysis. The D and G bands offer a more direct and reliable means to evaluate the structural and electronic properties of rGO, which is critical for understanding the role and performance of Pd-rGO and Pd/ MoO_3 -rGO samples. In this context, focusing on the D and G bands is a deliberate choice to ensure clarity and relevance in interpreting the Raman spectra.

Comparing this with X-ray Diffraction (XRD) spectra, the XRD spectra will provide complementary information about the crystalline structure and phase purity of the samples. For instance, peaks corresponding to Pd, MoO_3 , and rGO in the XRD pattern will confirm the successful incorporation of these materials into the composite. The intensity and position of the XRD peaks can also give insights into the degree of crystallinity and the interaction between different components.

Fig. 2(b) shows laser Raman spectra of GO samples with two peaks

around 1338 and 1572 cm^{-1} . The peak at 1338 cm^{-1} results from the out-of-plane breathing mode of sp^2 carbon, which is related to defects in the graphite skeleton. The G-band around 1572 cm^{-1} is associated with the first-order E2g phonon and in-plane stretching vibration of C=C bonds [48,62]. The Raman spectrum of Pd-rGO and Pd/ MoO_3 -rGO primarily shows rGO signals even after adding Pd and MoO_3 nanomaterials, which can be attributed to the dominant Raman scattering characteristics of rGO. Graphene-based materials, including rGO, have strong Raman-active modes, particularly the D and G bands, which can overshadow the signals from other components like Pd and MoO_3 [63, 64]. The significantly lower Pd-rGO and Pd/ MoO_3 -rGO nanocomposite intensity than pure rGO can arise from interaction effects [63]. Incorporating Pd and MoO_3 may have changed the electronic environment of rGO, affecting its Raman scattering efficiency.

Furthermore, the comparison between the peak position and intensity of the D and G-bands of Pd-rGO and Pd/ MoO_3 -rGO is presented in Table 1. A notable peak shift was observed in the D and G-band of Pd/

Table 1

Fitting parameter for Raman spectra of GO, Pd-rGO, and Pd/ MoO_3 -rGO nanocomposites.

Samples	Position		Intensity		I_D/I_G ratio
	D-band	G-band	D-band	G-band	
GO	1338	1573	780	1140	0.68
Pd-rGO	1334	1568	150	210	0.71
Pd/ MoO_3 -rGO	1334	1568	45	110	0.40

MoO₃-rGO for the corresponding GO peaks by 4 cm^{-1} . This charge transfer between Pd/MoO₃ and rGO can be understood using Raman spectroscopy, a powerful tool for examining charge transfer in carbon-metal nanocomposites. The relative Raman peak shift is directly proportional to the carrier injected upon adsorption or contact with electron-donating and electron-accepting molecules, clusters, or NPs.

The charge transfer occurs due to matching the Fermi level of the C-structure to the adsorbate [65]. A red or blue shift signifies the softening or stiffening of Raman bands arising due to the charge transfer of electrons from the adsorbate to C-structures and vice versa. A blue shift in the present work suggests the occurrence of charge transfer from Pd/MoO₃ to rGO structure, which validates the existence of the charge

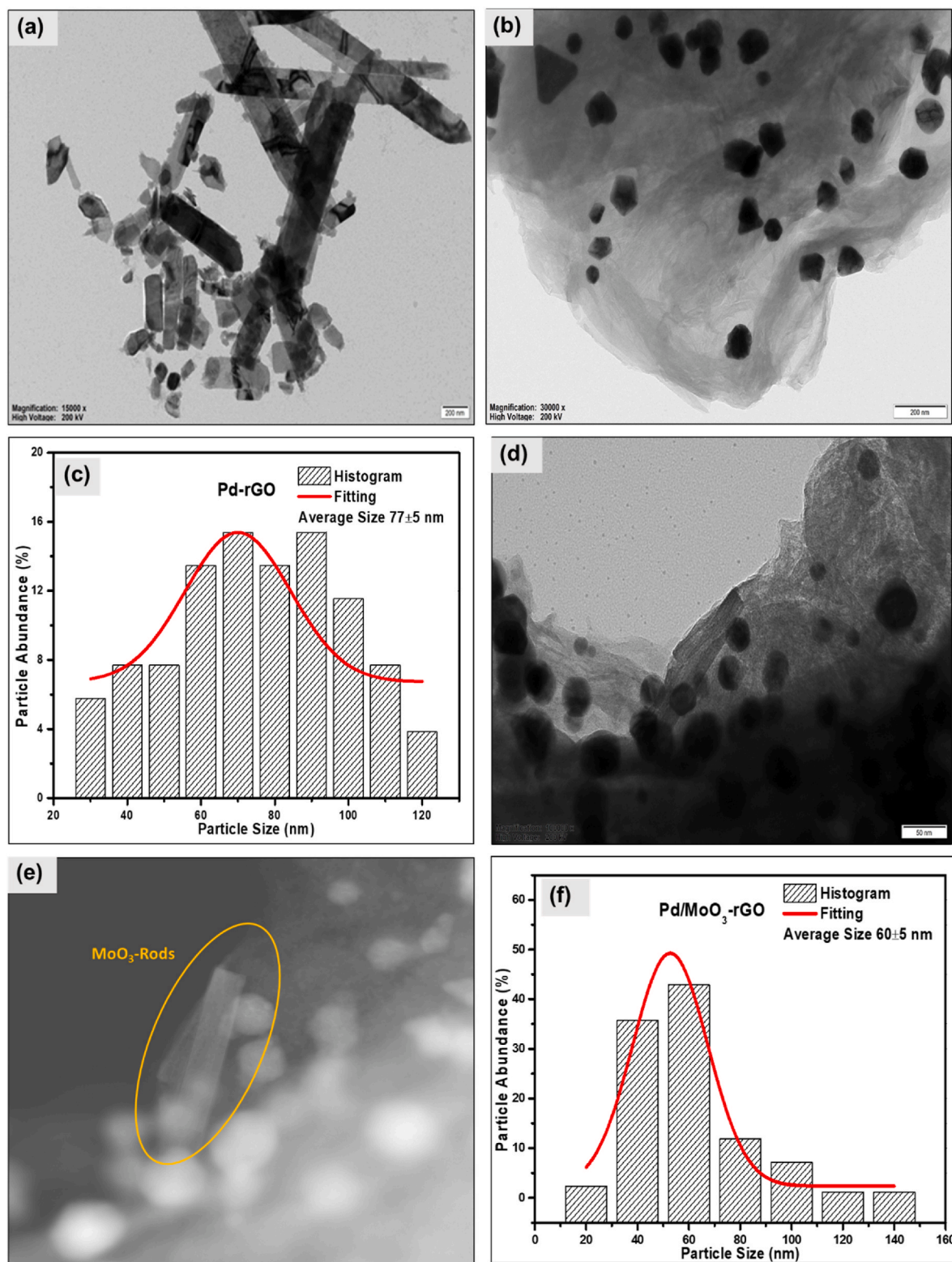


Fig. 3. HRTEM images, (a) MoO₃-Rods, (b) Pd-rGO, (c) histogram plots of Pd-rGO, (d) Pd/MoO₃-rGO image, (e) STEM image, and (f) Histogram plot for Pd/MoO₃-rGO samples.

transfer effect between Pd/MoO₃ and rGO sheet [66–68].

The successful formation of MoO₃ nanostructures, as confirmed by Raman peaks, is crucial for understanding their role in nanocomposites. Additionally, the observed blue shift in Raman peaks for Pd/MoO₃-rGO indicates a significant charge transfer from Pd/MoO₃ to rGO, which is essential for enhancing the electrochemical performance of the nanocomposite. The study further demonstrates a synergistic effect among Pd, MoO₃, and rGO, where the incorporation of Pd and MoO₃ alters the electronic environment of rGO, affecting its Raman scattering efficiency and potentially improving the overall performance of the material.

3.3. Morphological characterizations

HRTEM image analysis was performed to record the samples' microstructure (size and shape), as illustrated in Fig. 3(a–e). Fig. 3(a) presented the HRTEM micrograph of MoO₃-NR displaying the rod lengths extending from several hundred nanometers to a few micrometers, with fragmented parts of MoO₃-NR. Fig. 3(b) demonstrates the successful Pd nanoparticles (Pd NPs) anchoring onto the rGO sheet in the Pd-rGO sample. In addition, the HRTEM images reveal the diverse shapes of Pd NPs, including spherical, triangular, cubic, pentagonal, hexagonal, and rod-like. The regular polygonal shapes, such as triangles and cubes, result from the face-centered cubic (fcc) crystal structure of the Pd NPs. The regular polygonal structure formation is associated with surface energy minimization of certain crystal facets of Pd NPs, such as {111} and {100} [69]. As a result, Pd NPs tend to form shapes that expose low-energy facets, leading to regular polygonal structures [70].

In contrast, Fig. 3(d and e) displays the presence of both Pd and MoO₃-NR in a Pd/MoO₃-rGO nanocomposite sample, further confirmed using a STEM image. Fig. 3(e) presents the STEM image depicting MoO₃-NR in the yellow encircle region of the Pd/MoO₃-rGO sample, confirming that MoO₃-NRs structure remains intact under the hydrothermal process. Fig. 3(c–f) represents the histogram plot showing the statistical evaluation of Pd NPs in Pd-rGO and Pd/MoO₃-rGO samples, which revealed a broad particle size distribution ranging from 20 to 100 nm, with an average Pd size of around 77 and 60 nm, respectively. These observations provide valuable insights into the morphology and distribution of Pd nanoparticles in the rGO matrix and their interaction with MoO₃ nanorods in the composite structure.

3.4. Pore structure

The specific surface area and porous structure of GO, Pd-rGO, and Pd/MoO₃-rGO samples were investigated by the N₂ adsorption-desorption technique. Fig. 4(a) presents N₂ adsorption-desorption isotherms of electrode samples. Both curves show type IV, which gradually

increases at low relative pressure and sharply increases above 0.45–0.95 relative pressure (P/P_0), with both curves showing a perfect hysteresis loop. The surface areas of GO, Pd-rGO, and Pd/MoO₃-rGO nanocomposites are 64.16, 41.70, and 34.70 m²/g, respectively (Table 2). It can be observed that the surface area of Pd/MoO₃-rGO decreases due to the blocking of pores by MoO₃. The pore size distribution was estimated using the Barrett-Joyner-Halenda (BJH) approach. The pore size distribution curve shows the sample is mesoporous, and the pore diameter was around 2.0 nm (Fig. 4(b)). Additionally, the pore diameter of Pd/MoO₃-rGO is 1.9 nm, smaller than that of GO and Pd-rGO (2.2 nm). From these results, it can be concluded that both samples exhibit a mesoporous structure, serving as reservoirs where a significant amount of electrolyte ions can accumulate. These mesopores facilitate ion diffusion by providing channels for transport and predominantly facilitate ion storage, effectively increasing the sample's specific capacitance. Generally, the mesoporous configuration exhibited by Pd-rGO and Pd/MoO₃-rGO samples renders them promising candidates for energy storage applications, as they offer an increased surface area for ion adsorption and efficient ion diffusion pathways, ultimately improving their electrochemical performance. Incorporating MoO₃ into rGO composites improves pore structure and surface area, which enhances ion diffusion and storage. This mesoporous structure is crucial for developing high-performance energy storage materials.

3.5. Surface chemistry analysis

XPS surface analysis was recorded to corroborate the elemental composition in GO, Pd-rGO, and Pd/MoO₃-rGO samples. The prominent peaks of XPS results were deconvoluted to determine the chemical structure by fitting the data with Shirley background subtraction. The width, position, and relative intensity of each peak were established by adjusting the fitting parameters summarized in Table 3. In Fig. 5(a), the high-resolution XPS scan of MoO₃-Rods reveals two prominent peaks at 232 eV and 530 eV, representing the Mo 3d and O 1s orbitals, respectively. The exact binding energy of these peaks may vary depending on the oxidation state of Mo and the degree of crystallinity of the sample. The Mo 3d peak was deconvoluted into two peaks at 232.8 and 236.1 eV,

Table 2
BET surface area, pore radius, pore diameter, and pore volume of samples.

Samples	S _{BET} (m ² /g)	Pore Radius (Å)	Pore diameter (nm)	Pore Volume (cm ³ /g)
GO	64.16	11.10	2.20	0.066
Pd-rGO	41.78	11.10	2.20	0.072
Pd-MoO ₃ -rGO	34.76	9.70	1.90	0.066

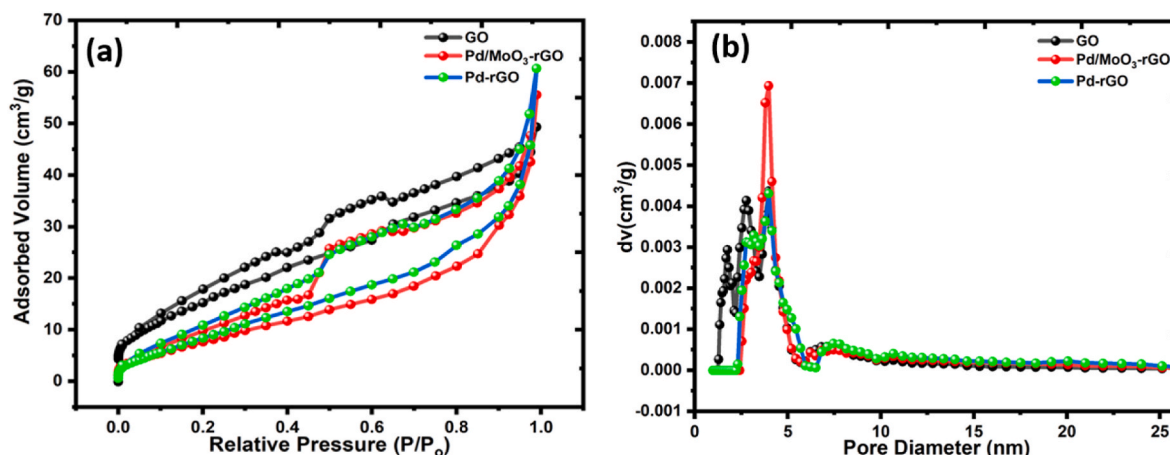


Fig. 4. (a) Nitrogen adsorption-desorption isotherm curves and (b) pore size distribution plots of GO, Pd-rGO, and Pd/MoO₃-rGO nanocomposites.

Table 3Fitting parameter of XPS spectra of MoO₃, Pd-rGO, and Pd/MoO₃-rGO.

Sample	Peak	Position (eV)	Intensity (Counts)	Remark	
MoO ₃	Mo 3d _{5/2}	232.8	8474.0	$\Delta BE_{Mo^{6+}3d} = 1.1 \text{ eV}$	
	Mo 3d _{3/2}	236.0	5438.0		
Pd/MoO ₃ -rGO	Pd ⁰ 3d _{5/2}	334.6	564.8	$\Delta BE_{Pd^{0+}3d} = 0.9 \text{ eV}$	
	Pd ⁰ 3d _{3/2}	339.9	342.8		
	Pd ²⁺	336.3	99.8		
	3d _{5/2}	341.9	98.3	$\Delta BE_{C\ 1s} = 0.3 \text{ eV}$	
	Pd ²⁺				
	3d _{3/2}	231.7	510.7		
	Mo 3d _{5/2}				
	Mo 3d _{3/2}	234.8	426.0	$\frac{Pd^{2+}}{Pd^0} = 17\%$	
C 1s	284.7	5080.5			
Pd-rGO	Pd ⁰ 3d _{5/2}	335.5	1378.0		
	Pd ⁰ 3d _{3/2}	340.8	826.0		
	C 1s	284.4	5675.0		

corresponding to the Mo 3d_{5/2} and Mo 3d_{3/2} for the Mo⁶⁺ oxidation state, which confirms the presence of MoO₃ (Fig. 5(b)) [57,64]. The O 1s peak is usually observed near 531.0 eV and can be used to identify the chemical environment of the oxygen atoms in MoO₃ by deconvoluting the O 1s peak in XPS spectra of MoO₃-Rods. Fig. 5(c) shows the deconvoluted O 1s peak, which is resolved into two peaks, with the first at around 530.4 eV associated with oxygen atoms in the MoO₃ lattice and the second, at higher binding energy (531.0 eV), linked to oxygen atoms on the surface or near-surface of MoO₃-Rods.

Table 4 provides the relative elemental composition of C, O, and Pd

in the Pd-rGO and Pd/MoO₃-rGO samples, estimated using the XPS analysis. The relative atomic percentage of C (81.60 at. %), O (16.45 at. %), Pd (0.82 at. %), and Mo (1.13 at. %) in Pd/MoO₃-rGO, significantly comparable with C (81.32 at. %), O (16.25 at. %), Pd (1.39 at. %) in Pd-rGO sample. The relative atomic percentages at. % of carbon (81–82 %) and oxygen (10–16 %) in the Pd/rGO and Pd/MoO₃-rGO samples confirm the effective reduction of GO to rGO. In the final composite, the ratio of rGO is substantial, as indicated by the high carbon content. This ratio ensures the composite's structural integrity and enhanced properties, contributing to its overall application performance. The weight of precursor PdCl₂ (177.33 g/mol, 75 mg) and as-synthesized MoO₃ nanorods (143.94 g/mol, 75 mg) are in 1:1 in 480 mg of GO for Pd/MoO₃-rGO samples. The relative atomic percentage (at. %) of Pd estimated manually in the Pd/Mo ratio for Pd/MoO₃-rGO samples was around 42 and 44 %, which is in good agreement with XPS, respectively.

We expect that increasing the ratio of Pd in the Pd-rGO-MoO₃

Table 4Elemental analysis of Pd-rGO and Pd/MoO₃-rGO nanocomposites.

Samples	Elements Atomic % (Using XPS)					Pd/(Mo + Pd) at. %	
	C %	O % (belong to MoO ₃)	O % (belong to rGO)	Mo %	Pd %	XPS	Manual
Pd/MoO ₃ -rGO	81.60	6.45	10.00	1.13	0.82	42	44
Pd-rGO	82.36	–	16.25	–	1.39	–	–

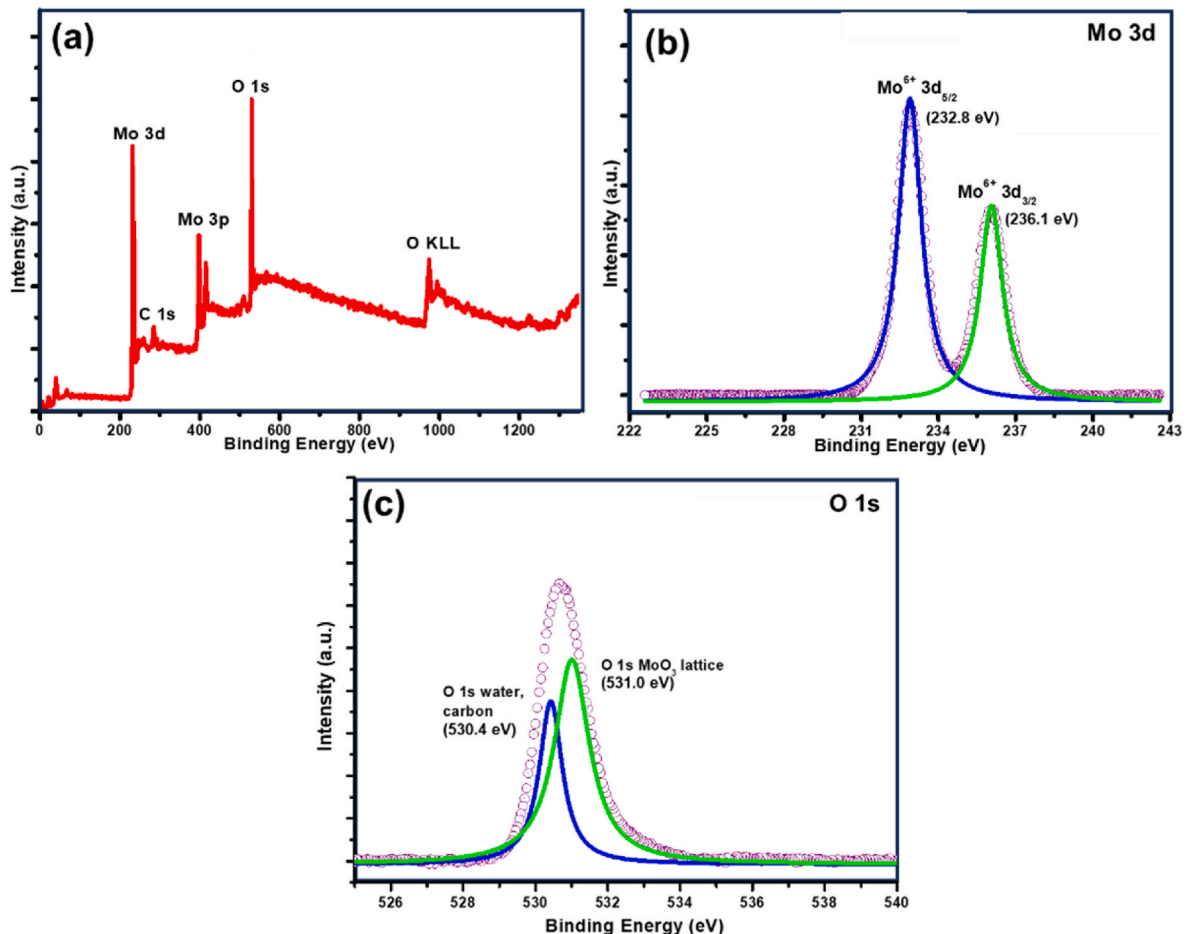


Fig. 5. XPS spectra of MoO₃-Rods (a) high-resolution scan, (b) Mo 3d peak, and (c) O1s peak.

composite will enhance the electrical conductivity, thereby enabling faster charge and discharge cycles in supercapacitors. Palladium nanoparticles significantly influence electrical conductivity, as conductivity generally decreases with smaller particle sizes due to increased electron surface scattering [71]. This scattering can hinder electron flow, increasing electrical resistance and reducing conductivity [72]. In this study, the prepared sample showed a favorable outcome since the particle size was suitable for use as a supercapacitor electrode, where electron scattering is minimized. However, excessive Pd may lead to nanoparticle aggregation, causing them to lose their unique properties and behave more like bulk materials. This reduces the effective surface area and, consequently, limits performance in supercapacitors [72].

The high-resolution XPS scan of Pd-rGO (Fig. 6(a)) displays three major peaks at 284.0 eV, 335.0 eV, and 531.0 eV, which belong to C 1s, Pd 3d, and O 1s orbitals, respectively. The C 1s and O 1s peaks (Fig. 6(b and c)) were deconvoluted into two peaks each. The C 1s peaks centered at 284.4 eV and 285.0 eV, related to the sp^2 -carbon skeleton and hydroxyl functional ($>C-OH$) groups surrounding the graphitic structure (Fig. 6(b)). Fig. 6(c) shows O 1s peaks resolved into two peaks, centered at 531.4 eV and 533.0 eV, corresponding to carboxyl or hydroxyl functional groups on the surface of the rGO sheet. The spin-orbit splitting distinguishes the XPS spectrum of the Pd 3d orbital into Pd 3d_{3/2} and Pd 3d_{5/2} doublet peaks in Fig. 6(d). The Pd 3d peak of the Pd-rGO sample was deconvoluted into 335.5 eV and 340 eV, corresponding to Pd⁰ 3d_{5/2} and Pd⁰ 3d_{3/2} doublet.

Fig. 7(a) presents the high-resolution XPS scan of the Pd/MoO₃-rGO, showing four peaks at 232.0 eV, 284.0 eV, 400.0 eV, 335.0 eV, and 531.0 eV, corresponding to Mo 3d, C 1s, N 1s, Pd 3d, and O 1s orbitals respectively [28]. The C 1s, N 1s, and O 1s peaks, as shown in Fig. 7

(b–d), have been deconvoluted into two peaks each, reflecting the typical graphitic carbon skeleton $C=C/C-O$ (284.7/285.0 eV) surrounded by different oxygen- and nitrogen-containing species like, hydroxyl $C-O$ (530.4/532.0 eV), and pyridinic nitrogen $C=N$ (397.7/398.8 eV). The existence of N 1s peak in the XPS spectrum of the Pd/MoO₃/rGO sample may be either inadvertently introduced from the laboratory atmosphere or the molybdenum precursor (NH₄)₆Mo₇O₂₄·4H₂O. Fig. 7(c) shows the O 1s peak in Pd/MoO₃-rGO, resolved into two peaks at around 530.1 and 532.0 eV. The first peak is associated with the Mo–O bond in MoO₆ octahedra, and the second with oxygenous species ($C=O$) near the surface of the rGO structure [73].

The Pd 3d band of Pd/MoO₃-rGO in Fig. 7(e) reveals four peaks related to two peaks for neutral Pd⁰ (334.6 and 339.9 eV) and two peaks for divalent Pd²⁺ (336.3 and 341.8 eV) [28,45,46,74]. The binding energy of the neutral Pd⁰ 3d band shows a slight decrease by 0.9 eV and 0.5 eV compared to Pd-rGO, indicating a change in the electronic structure of Pd caused by the Mo introduction [74]. This decrement in the binding energy of Pd can signify the charge transfer from Pd to MoO₃ [74]. Incorporated Mo in the Pd-rGO nanocomposite interacts with the electronic structure of Pd, decreasing the electron density around Pd and causing a shift in the Pd binding energy to the lower value. However, the Mo 3d doublet peak in Pd/MoO₃-rGO sample was shifted to lower binding energy in comparison to pristine MoO₃ nanorods, centered at 231.7 and 234.8 eV assigned to the Mo 3d_{5/2} and Mo 3d_{3/2} orbital electrons of Mo⁵⁺ in Pd/MoO₃-rGO sample in comparison to 232.8 and 236.0 eV assigned to the Mo 3d_{5/2} and Mo 3d_{3/2} orbital electrons of Mo⁶⁺ in MoO₃ nanorods, respectively. Similarly, Fig. 7(f) shows the Mo 3d peak was decomposed into two peaks at 231.7 and 234.8 eV, significantly lower binding energy than pure MoO₃ by $\Delta BE = 1.1$ eV,

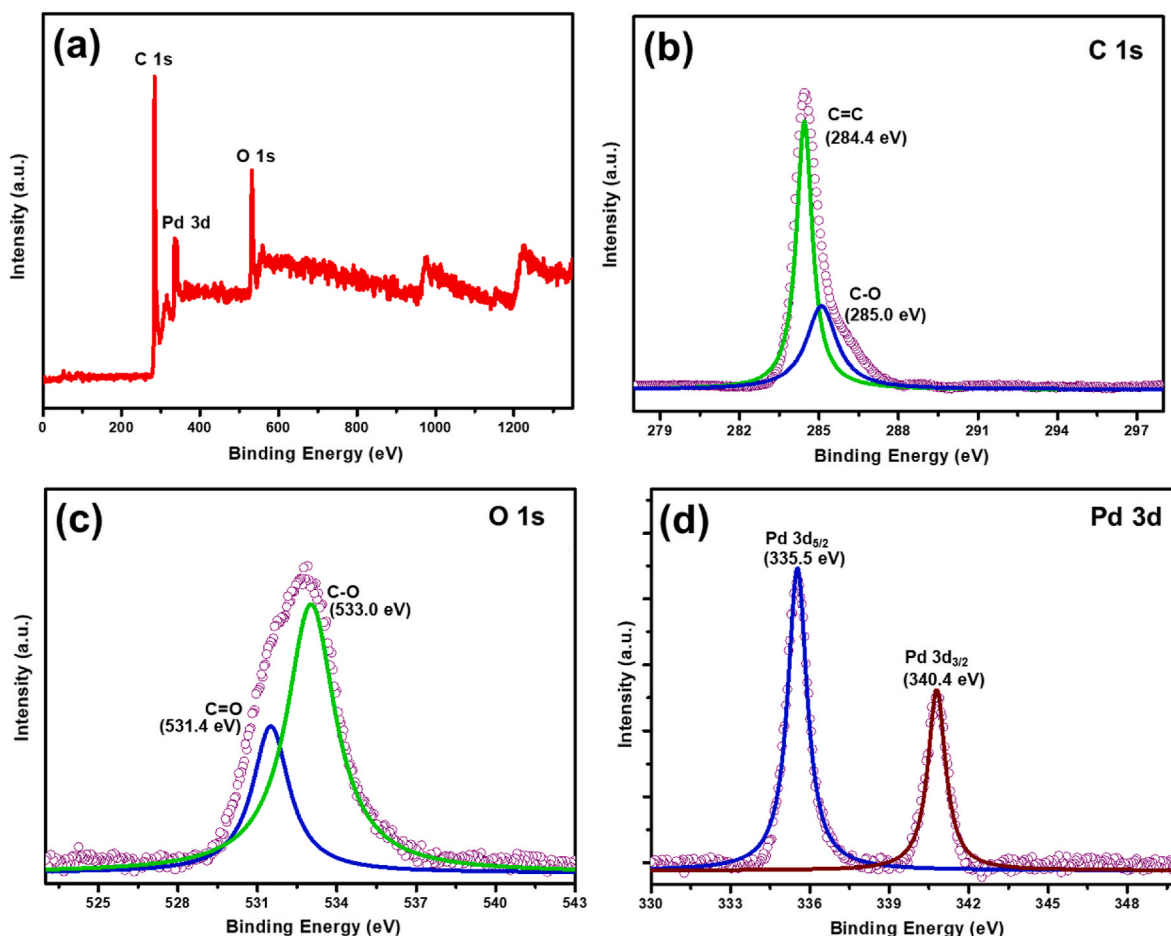


Fig. 6. XPS spectra of Pd-rGO (a) high-resolution scan, (b) O 1s peak, (c) C 1s, and (d) Pd 3d peak of Pd-rGO sample.

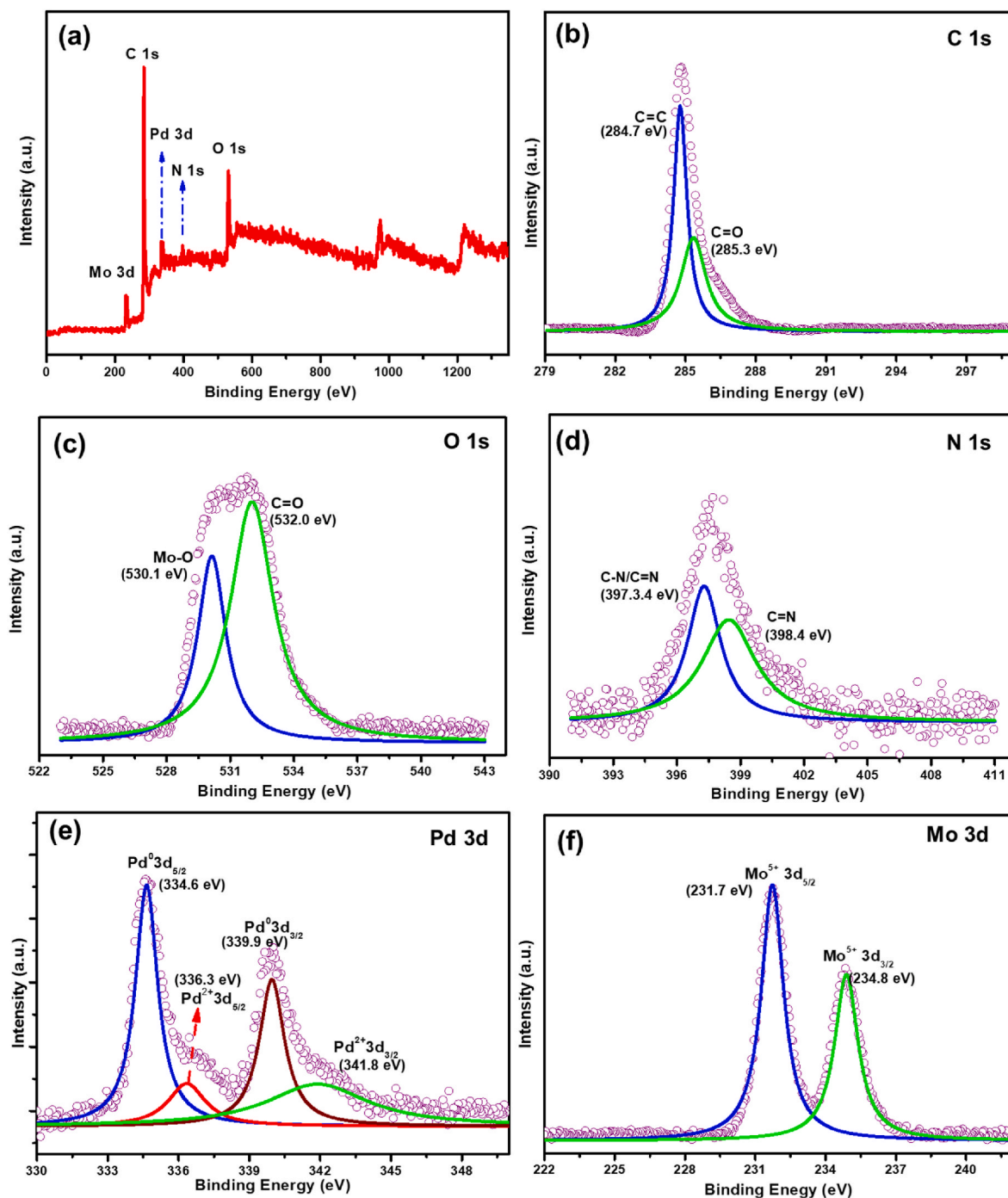


Fig. 7. XPS spectra of Pd/rGO-MoO₃ (a) high-resolution scan, (b) C 1s, (c) O 1s, (d) N 1s, (e) Pd 3d, and (f) Mo 3d peaks of Pd/MoO₃-rGO sample.

which signifies the change in oxidation state of Mo 3d ($\text{Mo}^{\delta+}$ $5 < \delta < 6$), via electron transfer mechanism. Which is in good agreement with the O-vacancy in Pd/MoO₃-rGO sample caused by the hydrothermal method's annealing of Pd/MoO₃-rGO. Previously, several researchers observed that the O-vacancy concentration has been significantly increased after annealing under high temperature [75]. When the O²⁻ ion is partly removed from MoO₃, the Mo⁶⁺ could be reduced to Mo⁵⁺ to maintain the charge neutrality of the material. Consequently, the oxidation of Pd⁰ to Pd²⁺ electrons signify that electron released from Pd to Mo helps attain charge neutrality in MoO₃ nanorods. Thus, the O-vacancy in MoO₃ can greatly improve the electrical conductivity for enhanced supercapacitive performance. The intensity ratio Pd²⁺/Pd⁰ was around 0.17, which means about 17 % of Pd atoms may undergo

oxidation by the neighboring MoO₃ structure via electron transfer. The concurrent higher BE shift of C 1s peak (ΔBE 0.3 eV) and lower binding energy shifts of Pd 3d and Mo 3d peaks suggest a charge transfer from Pd-rGO to MoO₃ [66]. The intensity ratio Pd²⁺/Pd⁰ was around 0.17, which means about 17 % of Pd atoms may undergo oxidation by the neighboring oxygenous species. The presence of Pd⁰ and Pd²⁺ oxidation states can be important for electrochemical and electrocatalytic applications. Furthermore, introducing MoO₃ in Pd-rGO results in synergic charge transfer from the Pd and rGO structures to MoO₃, which may help improve the electrochemical performance of Pd/MoO₃-rGO.

In summary, the XPS analysis confirms the successful incorporation of MoO₃ into the Pd-rGO matrix, with significant changes in the electronic structures of Pd and MoO₃. The observed charge transfer between

Pd-rGO and MoO_3 could enhance the electrochemical performance of the Pd/ MoO_3 -rGO composite, making it promising for supercapacitor applications.

4. Electrochemical studies

The electrochemical performance of Pd-rGO and Pd/ MoO_3 -rGO was evaluated using CV, GCD, and EIS measurements in the 6 M KOH electrolytic solution. Fig. 8(a and b) presents the CV curves of Pd-rGO and Pd/ MoO_3 -rGO at different scan rates ranging from 5 mV/s to 250 mV/s, respectively. The nearly rectangular-shaped CV curve of Pd/rGO and

Pd/ MoO_3 -rGO displays electrical double-layer capacitance behaviour [76,77]. However, the appearance of a redox peak at 0.4 V in Pd/ MoO_3 -rGO suggests the pseudocapacitance behaviour in the working electrode. In addition, the specific capacitance of both samples increases with decreasing scan rate (as shown in Fig. 8(e)). The selection of scan rate or current density significantly impacts the specific capacitance of electrode material. The highest value of specific capacitance of Pd-rGO and Pd/ MoO_3 -rGO nanocomposites were observed at a slow scan rate of 5 mV/s, which was 109.00 and 292.00 F/g. The ions have sufficient time to diffuse into the graphene layers at the slow scan rate, leading to higher specific capacitance. Inevitably, the fast

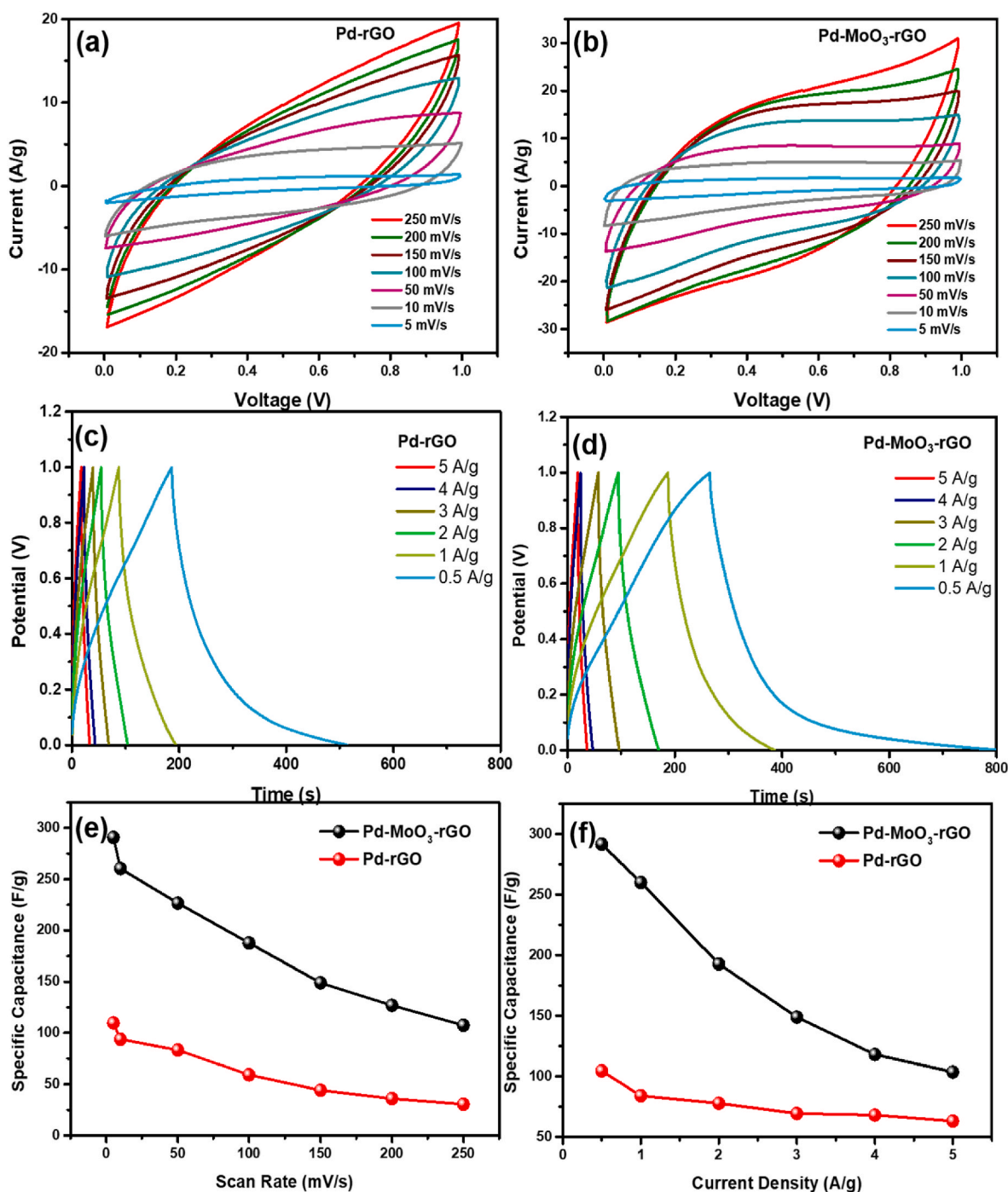


Fig. 8. Electrochemical performances of the supercapacitor electrodes, CV curves were determined with different scan rates (a) Pd-rGO (b) Pd- MoO_3 -rGO, (c) specific capacitance vs. scan rates plots, GCD curves at different scan rates (d) Pd-rGO (e) Pd/ MoO_3 -rGO and (f) specific capacitance vs. current density plots in 6 M KOH electrolytic solution.

charge/discharge process at higher scan rates does not provide enough time for ion diffusion, resulting in lower specific capacitance [77]. Notably, Pd/MoO₃-rGO demonstrated 2.72 times higher specific capacitance than the Pd-rGO sample. This significant increase in specific capacitance of the Pd/MoO₃-rGO nanocomposite, despite its lower surface area compared to Pd-rGO and GO, can be attributed to the two major synergic processes. Firstly, the incorporation of MoO₃ into the Pd/rGO matrix enhances the overall electrochemical performance due to the pseudocapacitive behaviour of MoO₃, which provides additional charge storage mechanisms beyond the electric double-layer capacitance of rGO [75]. Secondly, the charge transfer from the Pd/rGO matrix to MoO₃-NR improves the electrical conductivity and facilitates faster charge transfer migration. The interaction between Pd, MoO₃, and rGO also creates a more efficient ion diffusion and electron transport network, leading to better utilization of the active material [33]. These combined effects result in a higher specific capacitance for the Pd/MoO₃-rGO nanocomposite, even with a lower surface area. Furthermore, we have accessed the GCD electrochemical performance of Pd-rGO and Pd/MoO₃-rGO nanocomposites, as depicted in Fig. 8(c and d). The GCD curves were recorded at different current densities of 0.5 A/g to 5.0 A/g within the potential window of 0.0 V–1.0 V. Both electrode materials have demonstrated nearly symmetrical charge/discharge times and a low potential drop, indicating small internal resistance offered by electrodes. The discharge curve of both samples deviates from the typical triangular shape due to pseudocapacitive behaviour. Fig. 8(e and f) presents the plot of specific capacitance versus varying scan rate and current density. It is evident from the GCD curve that as the current density increases, the discharge period decreases, suggesting that the rapid diffusion of ions impacts the charge storage capability. This behaviour is confirmed by the electrode results, showing a slight shift from 50.00 F/g to 104.00 F/g for Pd-rGO and a significant shift from 104.00 F/g to 291.50 F/g for Pd/MoO₃-rGO, within the range of 0.5–5.0 A/g. (Fig. 8(f)). In summary, the results show that incorporating MoO₃ into Pd-rGO significantly enhances the specific capacitance of the electrode material. Pd/MoO₃-rGO demonstrated up to higher capacitance compared to Pd-rGO, benefiting from both pseudocapacitive behavior and improved charge transfer properties. This results in more efficient energy storage and faster charge/discharge processes, making Pd/MoO₃-rGO a superior choice for high-performance supercapacitor applications.

Fig. 9(a and b) presents the Ragone plot and cyclic stability curves of Pd-rGO and Pd/MoO₃-rGO electrode-based supercapacitors using anhydrous electrolytes under different current densities. The energy density and power density for both electrode materials were calculated using the following relations:

$$E_D = \frac{1}{2} \frac{C_{sp} \Delta V^2}{3.6} \quad (3)$$

$$P_D = \frac{E_D}{t_{dis}} \times 3600 \quad (4)$$

Where C_{sp} , ΔV , t_{dis} , E_D , and P_D represents the specific capacitance, potential window, discharge time, energy, and power density of electrode material. Energy density and power density serve as crucial indicators for evaluating supercapacitor performance. Fig. 9(a) shows the Ragone plot related to the energy density and power density of the Pd-rGO and Pd/MoO₃-rGO electrodes. Additionally, the cyclic stability of the composite is assessed using the chronopotentiometry technique at a current density of 1 A/g (Fig. 9(b)). The maximum power and energy density of Pd/MoO₃-rGO is 250.00 W/kg and 18.06 Wh/kg at a current density of 0.5 A/g, respectively. Compared to Pd-rGO (250 W/kg and 14.51 Wh/kg at a current density of 0.5 A/g), the Pd/MoO₃-rGO electrode exhibits superior supercapacitor performance. The significant improvement in the energy density of Pd/MoO₃-rGO compared to Pd-rGO can be explained based on synergic charge transfer between the Pd-rGO matrix and MoO₃, which enhances the overall electrochemical performance. The presence of MoO₃ likely provides an efficient electron transport network for ion diffusion and electron-accepting ability via the charge transfer process, resulting in higher capacitance in Pd/MoO₃-rGO than Pd-rGO. The Pd/MoO₃-rGO composite has demonstrated excellent cyclic stability over 1000 cycles, retaining 88.46 % of its specific capacitance, while Pd-rGO exhibits 82.14 % retention of specific capacitance. Moreover, retaining 88.46 % of its capacity after 1000 cycles, although not the highest reported in recent literature, still reflects a reasonable level of stability. Based on the previous reports, as summarized in Table 5. It is worth noting that the as-prepared electrode materials possess significantly higher specific capacitance compared to the previously reported work. However, several researchers have demonstrated high cyclic stability at the cost of lower specific capacitance. Hence, this work shows that the Pd/MoO₃-rGO nanocomposite surpasses the criteria of efficient electrode material over most of the carbon-supported MoO₃-rGO electrode material for supercapacitor application. The Pd/MoO₃-rGO composite significantly enhances supercapacitor performance compared to Pd-rGO. It improves energy density while maintaining the same power density, showing better energy storage capability. The synergistic effect of Pd-rGO and MoO₃ enhances charge transfer and electron transport, with MoO₃ facilitating efficient ion diffusion. Additionally, Pd/MoO₃-rGO exhibits superior cyclic stability, while not the highest stability reported, it offers a balanced performance with high capacitance and durability, making it a strong candidate for

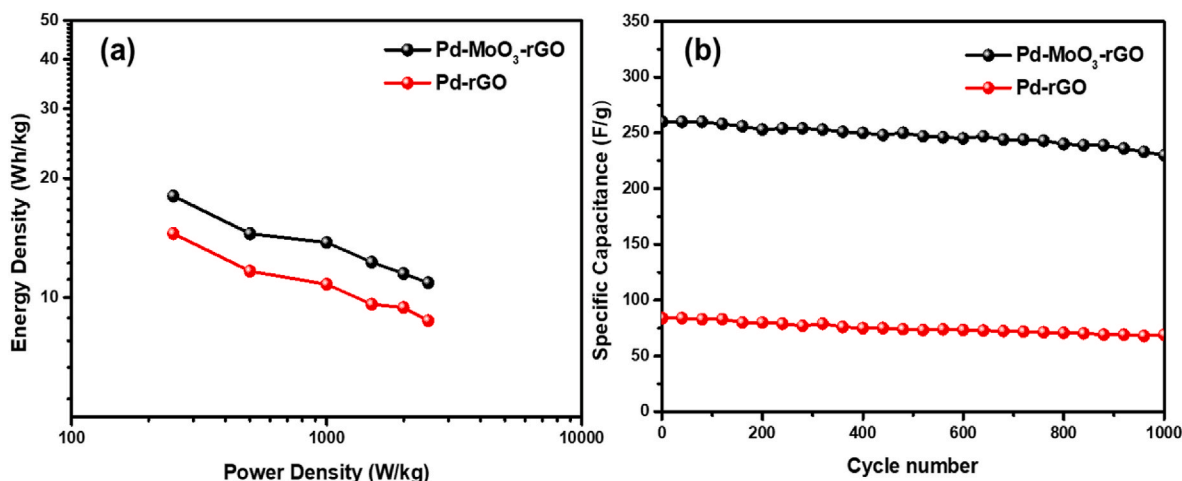


Fig. 9. Supercapacitor performance (a) Ragone plot (b) cycling stability of Pd-rGO and Pd/MoO₃-rGO.

Table 5Comparison of various carbon-supported MoO₃ electrode materials for supercapacitor application.

Electrode samples	Electrolytes	Potential Window (V)	Current density (A/g) or Scan rate (mV/s)	Specific capacitance (F/g)	Cyclic Stability (Numbers)	Ref.
H ₃ MoO ₃ -NWs	1 M H ₂ SO ₄	0.00–1.00	0.50	168.00	97 % at 3000	[29]
MoO ₃ -VG	1 M N ₂ SO ₄	–1.00–0.00	1.00	275.00	72 % at 1000	[30]
h-MoO ₃ -Pyr	1 M H ₂ SO ₄	0.05–0.65	0.25	230.00	74 % at 3000	[18]
h-MoO ₃ Pris	1 M H ₂ SO ₄	0.05–0.65	0.25	160.00	65 % at 3000	[18]
h-MoO ₃ -Hex	1 M H ₂ SO ₄	0.05–0.65	0.25	130.00	62 % 3000	[18]
MoO ₃ /G/Aerosol	6 M KOH	0.00–1.00	1.00	148.00	82 % at 5000	[78]
MoO ₃ -MWCNT	1 M N ₂ SO ₄	–1.00–1.00	0.50	210.00	98 % at 2000	[79]
PPy/MoO ₃ -rGO	0.5 M K ₂ SO ₄	–0.60–0.40	0.10	175.00	88 % at 600	[40]
β-MoO ₃ @C	1 M KOH	–0.90–0.20	0.20	81.00	94 % at 500000	[41]
MoO ₃ -rGO	1 M H ₂ SO ₄	0.00–1.00	5.00	255.00	90 % at 3000	[28]
MoO ₃ -Graphene	1 M N ₂ SO ₄	0.00–1.00	5.00	148.00	81 % at 1600	[80]
MoO ₃ /PdO	3 M KOH	0.0–0.6 V	2.00	127.00	–	[27]
Pd/MoO₃-rGO	6 M KOH	0.00–1.00	0.50	292.00	88.46 % at 1000	This Work

advanced supercapacitor applications. Most studies commonly benchmark supercapacitor materials for stability at 3000 cycles or more, while our current results for the Pd/MoO₃-rGO hybrid material cover only 1000 cycles due to initial testing constraints. This shorter testing period provides early insights into the material's stability and performance trends, essential for determining feasibility before proceeding with long-term testing. The decision to focus on 1000 cycles was influenced by resource limitations, as longer testing requires a charge-discharge battery tester, and we prioritized evaluating short-term capacitance retention and conductivity. The material is still in the optimization phase, and further adjustments may be needed before extending testing. Nonetheless, the initial 1000-cycle results offer promising stability, providing a solid foundation for future testing to meet or exceed the standard 3000-cycle benchmark.

Moreover, we have fitted the CV curve using the power law to evaluate the charge storage mechanism in Pd-rGO and Pd/MoO₃-rGO nanocomposite materials. In particular, we investigate the relation between the logarithms of the scanning rate (log(v)) and peak current (log(i)), as shown in Fig. 10. The power law equation is expressed as eq. (5)

$$I = aS^b \quad (5)$$

In the fitted power law, *i* denotes peak current, *S* denotes scanning rate, and *b* denotes a dynamic variable [81]. A value near 1 denotes a capacitive storage mechanism, whereas a value near 0.5 suggests the dominance of a diffusion-driven behavior. The estimated 'b' values in our Pd-rGO and Pd/MoO₃-rGO analyses are 0.58 and 0.64, respectively [78]. The Pd/MoO₃-rGO electrodes have *b* values higher than 0.50 (*b* =

0.64), indicating that the electrode has both diffusive and capacitive (or Faradaic) controlled capacitance, resembling hybrid-type supercapacitor behaviour [81,82]. Compared to Pd/MoO₃-rGO, the Pd-rGO electrodes have a lower *b* value (*b* = 0.58), suggesting a more prominent role in the diffusion-controlled process. Consequently, Pd-rGO and Pd/MoO₃-rGO verify that diffusive and diffusive-capacitive controlled behaviors predominate.

To evaluate the quantitative assessment of diffusive and capacitive behavior in Pd-rGO and Pd/MoO₃-rGO nanocomposite materials. The following power-fitting relation is utilized [81–83].

$$I(v) = k_1 v + k_2 v^{1/2} \quad (6)$$

where $k_1 v$ and $k_2 v^{1/2}$ represent the contribution of the current resulting from the diffusion and capacitive mechanism, respectively. The value of k_1 and k_2 are determined by the linear fitting of the plot of $\frac{I(v)}{v^{1/2}}$ vs. $v^{1/2}$. The CV curve for the active electrode materials, obtained at a scan rate of 50 mV/s, is illustrated in Fig. 11(a and b). The cyan shading in the CV curves indicates the charge storage through diffusion behavior, while the green area represents the current contribution resulting from capacitive behavior. The bar graphs in Fig. 11(c and d) show the corresponding non-Faradaic (capacitive) and Faradaic (diffusion) percentage contributions. These results show that at lower scan rates, the diffusion contribution predominates, while at higher scan rates, the capacitive contribution becomes more significant [77]. This finding implies that electrolyte ions have enough time to engage in Faradaic interactions with the electrode materials at lower scan rates. While at higher scan rates, ions do not have enough time, which leads to non-Faradaic charge storage. Furthermore, compared to the Pd-rGO sample, the introduction of active sites, charge transfer process, and creation of an efficient electric conductive network by MoO₃ addition accounts for the notable increase in the Faradaic charge storage ability of the Pd/MoO₃-rGO sample. The MoO₃-NR facilitates ion migration via a metallic conductive pathway; these sites work in concert with the Pd-rGO matrix to enhance the performance of the electrochemical supercapacitor. It is observed that the Faradaic capacitive behaviour for Pd/MoO₃-rGO increases to 36 %, compared to 17 % in Pd-rGO at the scan rate of 50 mV/s. However, with a further increase in the scan rate from 50 mV/s to 250 mV/s, the capacitive behaviour only increased by 19 %, which shows that Pd/MoO₃-rGO sample retains the electrical double layer characteristics even at the higher scan rate. This finding highlights the potential of Pd/MoO₃-rGO nanocomposite sample as an excellent performing supercapacitor electrode material for practical applications where high performance and cyclic stability are crucial requirements.

In conclusion, the data suggest that the Pd/MoO₃-rGO nanocomposite is highly effective for supercapacitor applications, combining high Faradaic charge storage with good capacitive performance. The significant enhancement in Faradaic charge storage with MoO₃ addition is attributed to the improved charge transfer processes and the creation

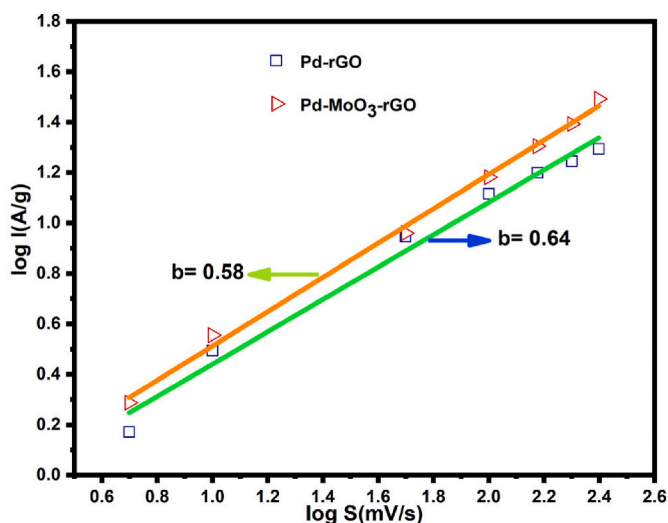


Fig. 10. log (*S*) vs. log (*I*) plot for *b* parameter estimation for Pd-rGO and Pd/MoO₃-rGO samples.

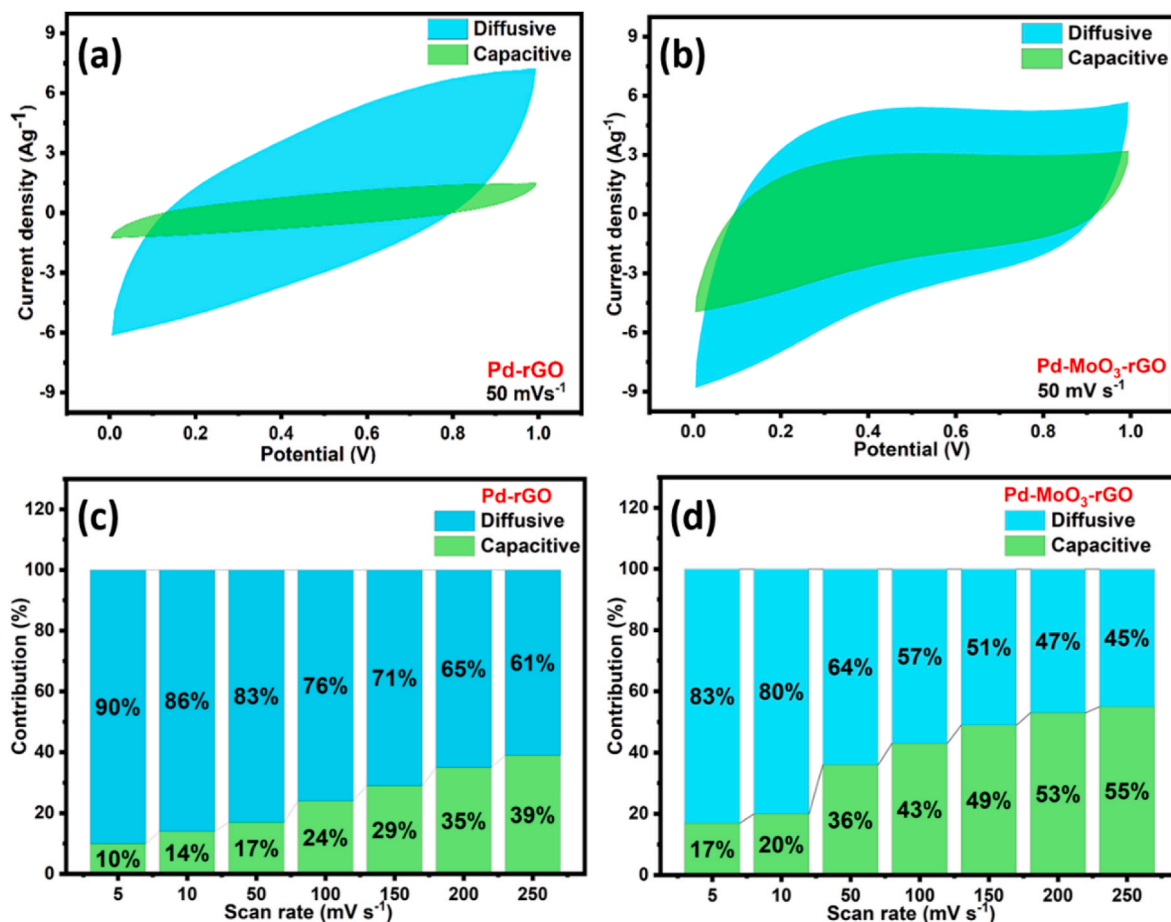


Fig. 11. (a–b) Capacitive and diffusion contributions of supercapacitor device at 50 mV/s of Pd/rGO and Pd/MoO₃-rGO, and (c–d) Percentage contribution separation of intercalation and capacitive current to the scan rates of Pd/rGO and Pd/MoO₃-rGO.

of a more efficient conductive network. This improvement allows for better performance in practical applications where high power and stability are essential. The observation that the Pd/MoO₃-rGO sample retains its capacitive behavior even at higher scan rates underscores its potential for applications requiring rapid charge-discharge cycles and consistent performance. The results validate the efficacy of the Pd/MoO₃-rGO nanocomposite as a promising material for advanced supercapacitors, suggesting its suitability for high-performance and durable energy storage solutions.

The electrochemical impedance spectroscopy (EIS) was measured over the range of 10 mHz–100 kHz, and the resultant Nyquist plots are displayed in Fig. 12. All the samples show the Nyquist plot with two common components including a semicircle at a high-frequency region and a straight line at a low-frequency region. The Nyquist plot for samples Pd-rGO and Pd/MoO₃-rGO was obtained using electrochemical impedance spectroscopy (EIS) data and fitted using the Z-view software and Randle circuit diagram (Fig. 12(a and b)). The high-frequency region of the Nyquist plot shows a minimal semicircle arc, representing

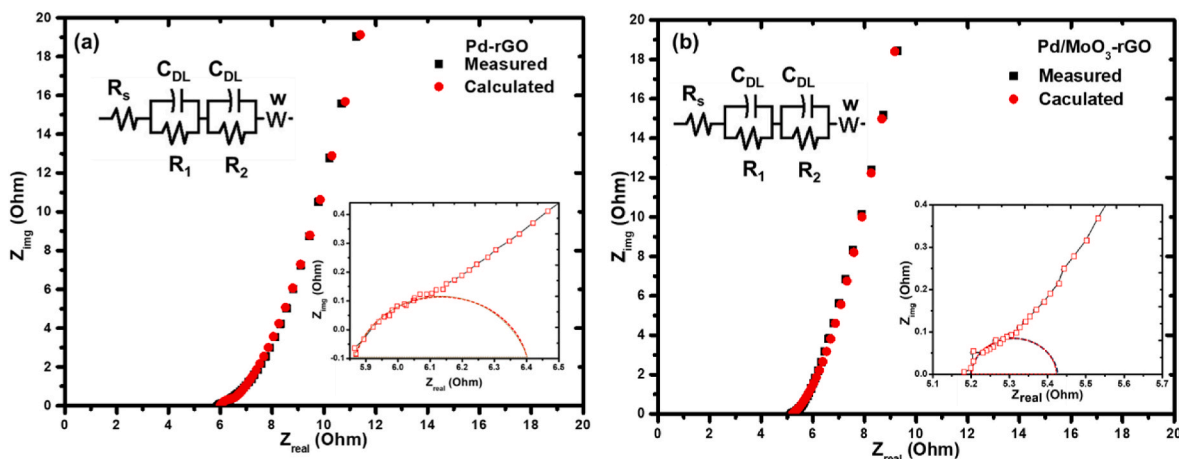


Fig. 12. Nyquist plots of (a) Pd-rGO and (b) Pd-MoO₃-rGO.

supercapacitor behaviour. The diameter of the semicircle corresponds to capacitance, while its position on the complex plane relates to the resistance of the sample. The Warburg impedance in the low-frequency to real axis region is depicted as a straight line and is associated with diffusion-controlled charge transport kinetics (Fig. 12(a and b)) [22]. EIS data were then analyzed to determine charge transfer resistance and low-frequency capacitance in various frequency bands. Table 6 provides a summary of the fitting parameters for components R_s , R_1 , R_2 , C_{DL} , and W . The analysis of Nyquist plots indicates that the Pd/MoO₃-rGO electrode displays a smaller diameter in the semicircle observed at the high-frequency zone compared to the pure Pd-rGO electrode. The resistance associated with electrolyte conduction is denoted by solution resistance (R_s). The composite electrodes of Pd/MoO₃-rGO demonstrate enhanced conductivity, with a lower resistance value (5.198 Ω) compared to Pd-rGO (5.978 Ω). The interconnected nanocrystalline structure between Pd and MoO₃-rGO potentially facilitates electrolyte infiltration due to the improved interactive interface between the electrolyte and the dynamic material. In summary, the low-frequency EIS spectra show an ideal supercapacitive behaviour with a sloping line indicating diffusion-controlled ions into the electrode surface and resistance associated with electrodes, electrolytes, and other system components [18,56]. Both electrodes display comparable Randle circuit components, except for a marked difference in charge transfer resistance (R_1 and R_2).

5. Conclusion

Materials for Pd-rGO and Pd/MoO₃-rGO nanocomposite electrodes were synthesized using the hydrothermal method to explore the effectiveness of a synergistic hybrid material for supercapacitor applications. The results presented that Pd/MoO₃-rGO exhibits superior supercapacitor performance (291.50 F/g at a current density of 0.5 A/g) compared to Pd-rGO (104.00 F/g at 0.5 A/g). Additionally, the prepared Pd/MoO₃-rGO supercapacitor demonstrates a higher energy density of 18.06 Wh/kg compared to Pd-rGO (14.51 Wh/kg). The Pd-rGO and Pd/MoO₃-rGO nanocomposite electrodes maintain high cyclic stability, retaining 88.46 % and 82.14 % of their initial capacity after 1000 charge/discharge cycles, respectively. The performance enhancement of the prepared supercapacitor can be concluded as follows.

- (1) Incorporating Pd nanoparticles into the system enhances the charge transfer by leveraging their remarkable electrical conductivity and catalytic activity. This augmentation significantly improves the kinetics of charge/discharge reactions.
- (2) Integration of MoO₃ into the Pd-rGO system assists in establishing an interconnected conductive network within the composite material. This network ensures efficient electron transport throughout the electrode, reducing internal resistance and facilitating rapid charge/discharge processes.
- (3) MoO₃ introduces additional active sites for Faradaic reactions, while rGO acts as a conductive support, facilitating electron transfer. This synergy results in enhanced capacitance and energy storage capabilities compared to individual components.
- (4) The presence of MoO₃ in the composite creates pathways for ion diffusion owing to its porous structure. This enhances electrolyte penetration into the electrode material, increasing the active surface area available for charge storage and improving capacitance.
- (5) The study demonstrates that the Pd/MoO₃-rGO nanocomposite outperforms the Pd-rGO sample in supercapacitor applications. The addition of MoO₃ enhances Faradaic charge storage due to improved charge transfer and conductivity, achieving a 36 % Faradaic contribution at 50 mV/s, compared to 17 % for Pd-rGO. At higher scan rates, the Pd/MoO₃-rGO maintains good capacitive behavior, indicating its suitability for applications requiring both high performance and cyclic stability.

Table 6

Equivalent circuit diagram parameters for Pd-rGO and MoO₃-rGO.

Samples/Parameters	R_s	C_{DL}	R_1	C_{DL}	R_2	W
Pd-rGO	5.978	0.0012	0.275	0.022	19.320	0.078
Pd/MoO ₃ -rGO	5.198	0.0006	28.72	0.013	5550.0	0.075

Hybrid materials such as Pd-MoO₃-rGO show significant potential for advancing supercapacitor technology. Their synergistic effects improve electrochemical performance, rendering them valuable contenders for energy storage applications. In addition, Future work should focus on exploring the detailed charge transfer mechanisms, optimizing the nanocomposite's performance by varying component ratios and surface modifications, and expanding its applications to catalysis and energy storage devices.

CRediT authorship contribution statement

Waritnan Wanchan: Writing – original draft, Software, Data curation. **Gaurav Kumar Yogesh:** Writing – original draft, Software, Data curation. **Rungsima Yeetsorn:** Writing – review & editing, Supervision, Methodology. **Yaowaret Maiket:** Methodology, Investigation. **Pankaj Koinkar:** Supervision, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2024.130134>.

Data availability

No data was used for the research described in the article.

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