



Electrical conductivity and electrochemical studies of Cr-doped MoO₃ nanoflakes for energy storage applications

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Abstract

The growing demand for electricity has increased the interest of the researchers towards exploration of energy storing devices (ESDs). With the motif for developing electrochemical energy storage devices, this research work is focussed on the study of MoO₃ nanoparticles and its doping with chromium as an efficient electrode material for energy storage applications. The nanoparticles were synthesized by hydrothermal method and were examined by powder X-ray diffraction, which determined the thermodynamically stable orthorhombic phase of MoO₃, and their morphologies were examined using scanning electron microscopy displaying flake-like structures. The typical vibrational bands of Mo–O were identified from Infra-red and Raman spectral analysis. The ultra violet diffuse reflectance spectra revealed the decrease in optical band gap after doping with chromium. The temperature dependent AC and DC conductivities were enhanced on doping. Electrochemical behaviour of the nanoparticles was probed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) measurements and galvanostatic charge–discharge (GCD) analysis for which specific capacitance (C_{sp}) value of 334 Fg⁻¹ was achieved for Cr-doped MoO₃ nanoparticles. The electrochemical performance of the sample was found to be increased after doping with Cr.

Keywords MoO₃ · Cr doping · Electrical conductivity · Specific capacitance · GCD

Introduction

The energy demand of the world is exponentially increasing with population rise. If surplus power is produced, the storage is always hasslesome. According to international energy agency (IEA), the COVID-19 pandemic is found to impact on global energy demand due to lockdowns, but it may increase due to massive vaccination and rescind of shutdown throughout the world citing the decrease in infection rate. In post pandemic period, it is envisaged that energy demand may increase by more than 4% in successive years [1]. The electricity demand is predicted to grow in a fast pace than in a decade over 1000 TWH [2]. In that context, energy storing devices (ESDs) are proved to be a bounty for the researchers,

industrialists and the governments [3]. The ESDs are broadly classified into batteries and supercapacitors. Both the types have similar configurations that of electrochemical devices [4]. Among various renewable energy resources and storage systems, the research is burgeoning on these ESDs [5]. Notably, the uninterrupted energy supply being demanded by the consumers has its own impact on sustainability of environment to a greater extent [6].

Metal oxide nanoparticles are found to have versatile applications in electronics, spintronics, electronics, photo electronics, optoelectronics, laser technology, photocatalysis, sensors etc. [7]. Thus, the metal oxide nanoparticles are found as suitable candidates to be used in ESDs [8]. The electrically insulating pseudocapacitive properties of transition metal oxides in batteries and capacitors are found to be enhanced as the size of the material is reduced [9]. As the dimensions of energy storage materials were reduced in size, the diffusion path lengths of ions were decreased, thereby enhancing the non-insertion charge storage dramatically [10]. Metal oxides are being explored widely as anode materials for their striking electrochemical features. They are found to possess intercalation mechanism similar to that of graphite [11]. The performance of metal oxide is

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based on its morphology, size which in turn determines the diffusion kinetics and cyclability [12]. The wide band gap energy (presage as semiconductors) has not denied its role as electrodes or electrochemical sensors in energy devices.

Among different metal oxides with layered structures, α - MoO_3 have gained distinct attention due to their unique properties such as high-specific surface area, chemical and photochemical stability, optical transparency and their ease of fabrication [13]. MoO_3 nanoparticles are broadly classified as three types, thermodynamically stable α - MoO_3 , metastable β - MoO_3 which can be reconverted to ' α ' form by heating it above 400 °C and third form h- MoO_3 is a *n*-type semiconductor with band gap energy of 3.2 eV, with extraordinary photochromic and electrochromic properties [14]. α - MoO_3 is considered to be one of the most promising low-cost material having high electrochemical activity and eco-friendly nature when compared with other transition metal oxides [15]. There are certain reports that emphasise the better electrochemical behaviour of MoO_3 nanoparticles [16–18], and also the enhancement in electrochemical behaviour of certain metal oxides when doped with chromium [19, 20]. Cr as Cr(III)/Cr(II) is used as an anode in redox energy storage system with Fe(III)/Fe(II) as counter electrode. This triggered us to carry out the electrochemical studies for MoO_3 on doping with Cr since it has been not reported yet and is considered to be the novelty of the present work.

In the present work, chromium is used as dopant for enhancing the energy storage properties of the MoO_3 nanoparticles. Doping of chromium has proved to exhibit a synergic effect on electrochemical properties which is greatly attributed to bulk doping, surface coating and reduction in size [21]. It is also corroborated that dopant chromium improves discharge capacity and columbic efficiency of electrode materials, and hence it is considered as a suitable candidate for doping in our study.

Methods and materials

Preparation of undoped and chromium-doped MoO_3 NPs

To synthesise MoO_3 nanoparticles, accurately weighed 0.1 M ammonium heptamolybdate tetrahydrate (AHM) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved in 50 mL of deionised water and stirred constantly for 20 min at room temperature. To this solution, hydrochloric acid (1 M) was added dropwise to form molybdic acid at pH ~ 1 and stirring was continued for 4 h to obtain white precipitate. This precipitate was then washed recurrently with deionised water and ethanol until free from impurities, filtered using whatman filter paper and then dried in hot air oven for 6 h at 60 °C.

The product was finally annealed at 400 °C for 2 h in a muffle furnace to get MoO_3 nanoparticles. Similar procedure was implemented for the synthesis of Cr-doped MoO_3 . During the reaction course, chromium (III) nitrate nonahydrate (0.1215 g, 0.5 mmol) was added along with AHM.

Instrumentation techniques

The powder XRD of all the samples were analysed on X'pert PRO model powder X-ray diffractometer in 2θ range of 20°–60° obtained at a scan rate of 2° min^{-1} involving the source of Cu- K_α X-ray radiation. The morphologies of the sample surface were imaged using JSM-6700 model field emission scanning electron microscope (JEOL, Japan) for which the elemental compositions were achieved on Quan-Tax 200 Energy Dispersive X-ray spectrometer (RONTEC's EDX system, Germany). The HRTEM images were scanned using JEM-2100 Plus model high-resolution transmission electron microscope of JEOL, Japan. The FTIR spectra were recorded on SHIMADZU spectrometer by pelletizing the samples with KBr in the range of 4000–400 cm^{-1} . FT Raman spectra of the samples were recorded by exciting the samples at a wavelength of 1064 nm using the source Nd:YAG laser on EZ Raman IFS 66 V spectrometer of Enwave optronics, made in the USA. DRS coupled JASCO V-530 dual beam spectrophotometer was equipped for recording the absorption spectra. The frequency-dependent conductivity measurements of all the samples were performed by Precision LCR Meter (Agilent 4284A) covering the frequency range from 100 Hz to 1 MHz, within a temperature range of 303 to 383 K. Each of the samples was positioned between a pair of blocking electrodes having a diameter of 2.5 cm under spring pressure. Electrochemical investigations of the samples were performed on a three-electrode system, taking the synthesized nanoparticles working electrodes, Ag/AgCl as reference electrode and platinum wire as the counter electrode.

Electrode fabrication

The slurry of electrode material was prepared from 85 wt% of synthesized nanoparticles, 10 wt% of activated carbon (Sigma-Aldrich) and 5 wt% of polytetrafluoroethylene (Sigma-Aldrich) using ethanol. The working electrode was prepared by a thin coating of this slurry onto a nickel foil (1 cm^2) and drying at 80 °C for 8 h. All the electrochemical analyses were performed at room temperature taking 2 M KOH as electrolytic solution. The specific capacitance (C_{sp}), energy density (E), and power density (P) values were calculated from the obtained GCD curves using the following relations [22]:

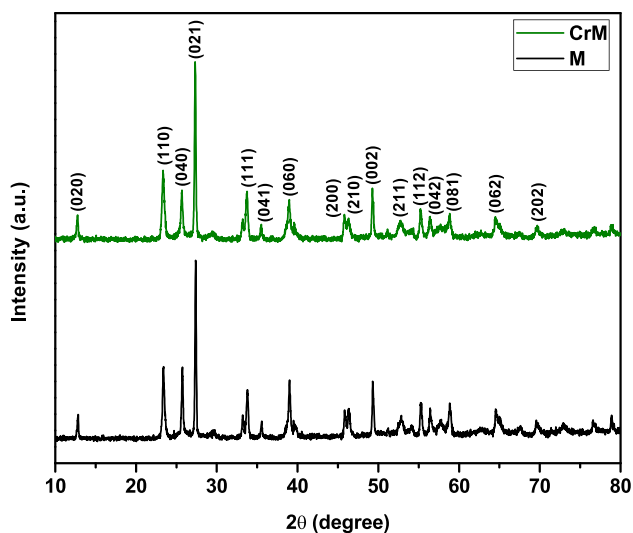


Fig. 1 XRD patterns of MoO₃ and Cr-doped MoO₃ NPs

$$C_{sp} = \frac{I_d \times T_d}{\Delta V \times m}$$

$$E = \frac{1}{2} C_{sp} (\Delta V)^2$$

$$P = \frac{E \times 3600}{T_d}$$

where I_d and T_d = discharge-current and discharge time, m = loaded mass of electrode, ΔV = potential window.

Results and discussion

The structure and phase purity of the synthesized MoO₃ and Cr-doped MoO₃ NPs were analysed by X-ray diffraction analysis. The peaks (Fig. 1) could be well indexed to the orthorhombic phase of MoO₃ in accordance to the reported literature values (JCPDS card No. 05–0508) [23]. The space group and the lattice parameters were found to be *Pbnm* and $a = 3.962$ Å, $b = 13.858$ Å and $c = 3.697$ Å respectively [24]. The lattice parameter values of doped sample were found to be $a = 3.973$ Å, $b = 13.749$ Å and $c = 3.583$ Å. The high intense peaks at 23.35°, 25.67° and 27.33° corresponds to (1 1 0), (0 4 0) and (0 2 1) planes showing the better crystalline nature of the NPs.

Due to low Cr concentration and also the radius of Mo⁶⁺ (0.59 Å) nearly same as that of Cr³⁺ (0.62 Å), no change in XRD peaks were observed after doping. But the change in lattice parameter values confirms the effective doping of Cr³⁺ into the lattices of MoO₃.

The morphologies of the NPs were observed from scanning electron microscopic images at various magnifications (Fig. 2(a–h)) which were found to exist as flakes. The incorporation of Cr ions in MoO₃ did not affect the morphology for doped sample. The energy dispersive X-ray spectroscopy analysis also confirmed that no other impurities were detected from the elemental composition of MoO₃ and Cr-doped MoO₃. The high intensity peaks arising at 2.3 keV and 0.5 keV corresponds to Mo and O atoms respectively present in the MoO₃ nanoparticles. Elemental mappings (Fig. 3) of the prepared samples revealed

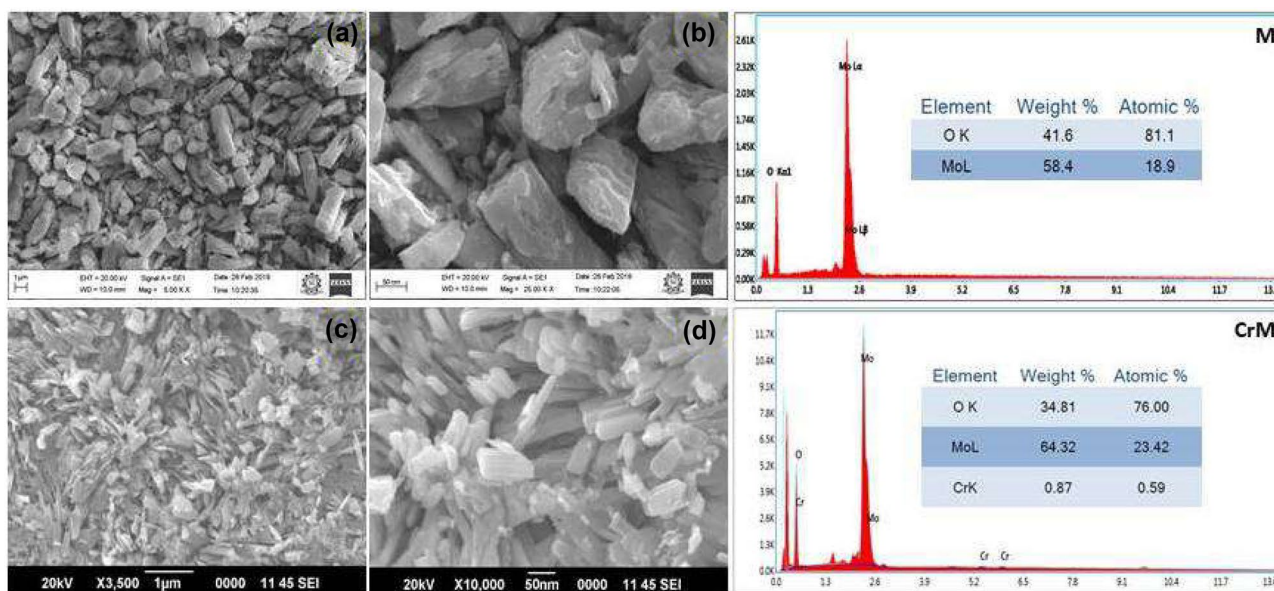
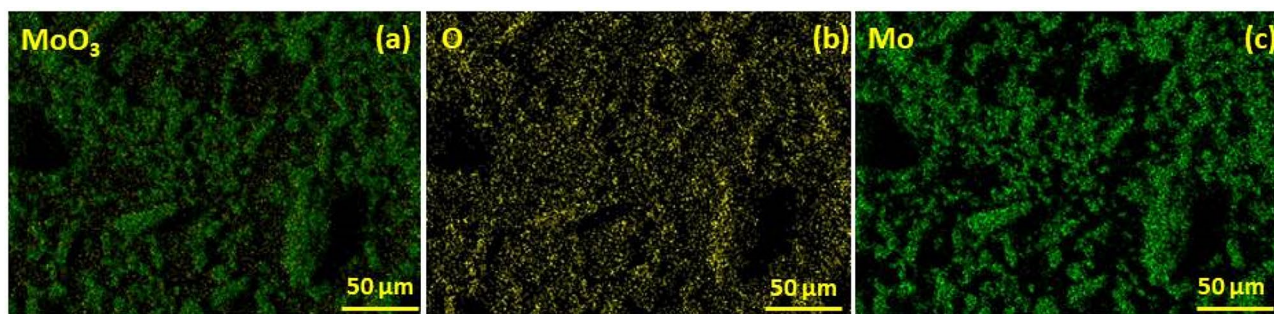
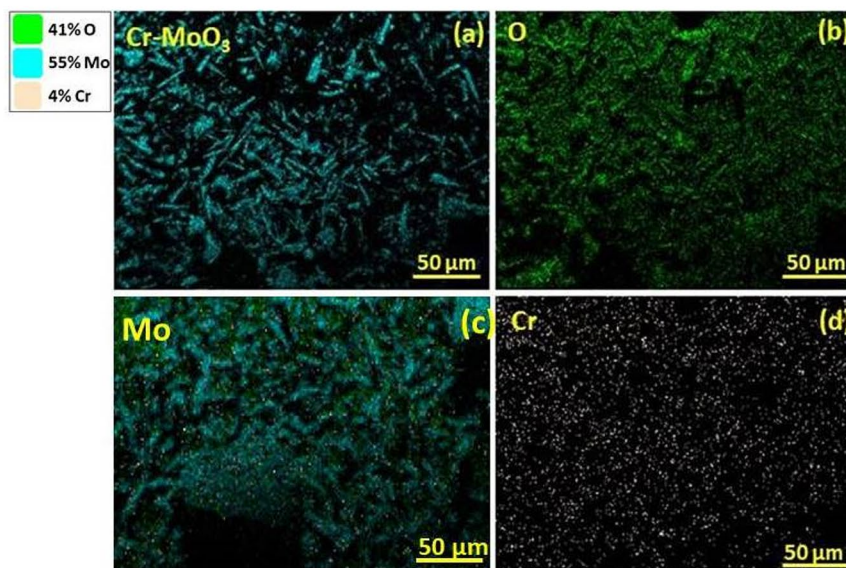


Fig. 2 SEM images and EDX spectra of MoO₃ (a, c) and Cr-doped MoO₃ (b, d) NPs



a Elemental mapping of MoO₃ NPs



b Elemental mapping of Cr doped MoO₃ NPs

Fig. 3 (a) Elemental mapping of MoO₃ NPs. (b) Elemental mapping of Cr-doped MoO₃ NPs

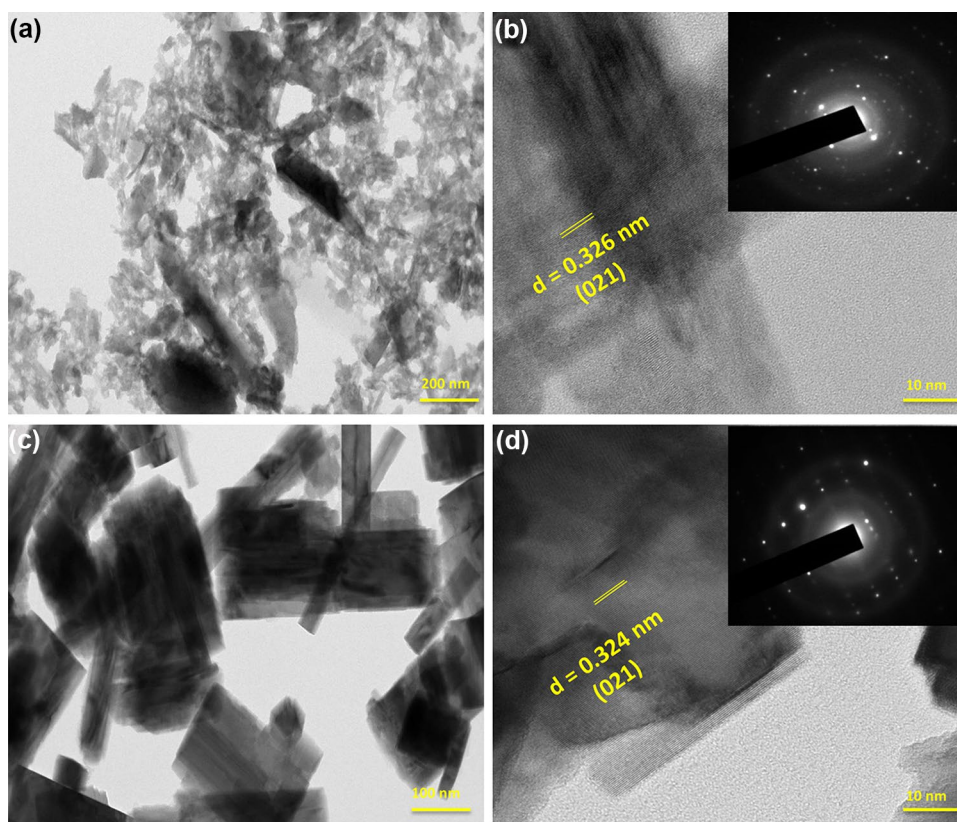
the presence of Cr, Mo and O atoms. Moreover, the mapping of elements exposed that both the undoped and doped nanoparticles were homogeneously distributed. The TEM and HRTEM images of MoO₃ and Cr-doped MoO₃ nanoparticles (Fig. 4a–d) exhibits observable lattice fringes of crystallographic planes whose *d* spacing were found to be 0.326 nm and 0.324 nm for MoO₃ and Cr-doped MoO₃ respectively corresponding to (021) plane.

Figure 5 shows the vibrational spectra of the NPs in which the bands observed at 2335, 2976 and 3222 cm⁻¹ seem to arise from the H–O–H bending mode and symmetric and asymmetric O–H modes for the water of representation [25]. The strong vibration bands observed at 972 cm⁻¹, 868 cm⁻¹ corresponds to the stretching vibrations of Mo=O [26]. The less intense peak at 635 cm⁻¹ and sharp peak at 506 cm⁻¹ indicate the stretching vibrations of oxygen atoms in Mo–O–Mo units and vibrations of oxygen atoms linked to three molybdenum atoms, respectively [27].

The Raman spectra (Fig. 6) shows a well-defined sharp peak at 1004 cm⁻¹ representing the asymmetric stretching vibrations of the terminal Mo⁶⁺=O bonds [28]. The high intensity peak observed at 823 cm⁻¹ could be ascribed to the symmetric stretching of Mo–O–Mo bonds [29]. The broad band observed at 663 cm⁻¹ corresponds to the asymmetric stretching and the weak band at 460 cm⁻¹ is attributed to bending vibrations of triply coordinated oxygen Mo–O–Mo bonds. Moreover, the band seen at 364 cm⁻¹ can be assigned to the scissoring mode of O–Mo–O bonds [30]. The band centred at 326 cm⁻¹ originates from the bending vibrations of O–Mo–O bonds. The characteristic band at 272 cm⁻¹ is ascribed to the Mo=O wagging modes of the terminal oxygen atom [31]. The samples doped with Cr showed the same Raman peaks as the pure α-MoO₃ sample (Fig. 4a), indicating that the crystalline structure was preserved during the doping process [32].

The UV–Vis absorption spectra of the samples are shown in Fig. 7, α-MoO₃ exhibit an absorption onset at

Fig. 4 TEM images (a, b) and HRTEM images (c, d) (inset: SAED pattern) of MoO₃ and Cr-doped MoO₃ NPs



432 nm and 465 nm for Cr-doped nanoparticles. The direct band gap energies of both undoped and doped nanoparticles are calculated using Kubelka–Munk (K–M) function as follows [33]:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K(\lambda)}{S(\lambda)} \propto \alpha = \frac{(h\nu - E_g)^n}{h\nu}$$

where R denotes the diffuse reflectance of the samples. Here, the direct band gap can be obtained by drawing a tangent on the curve obtained on plotting $(F(R)h\nu)^2$ vs. photon energy ($h\nu$). The band gap energies of M and CrM were calculated to be 2.83 eV and 2.64 eV respectively.

Electrical conductivity of a semiconductor is a temperature dependent process that occurs due to orderly motion of weakly held charged particles under the effect of an applied

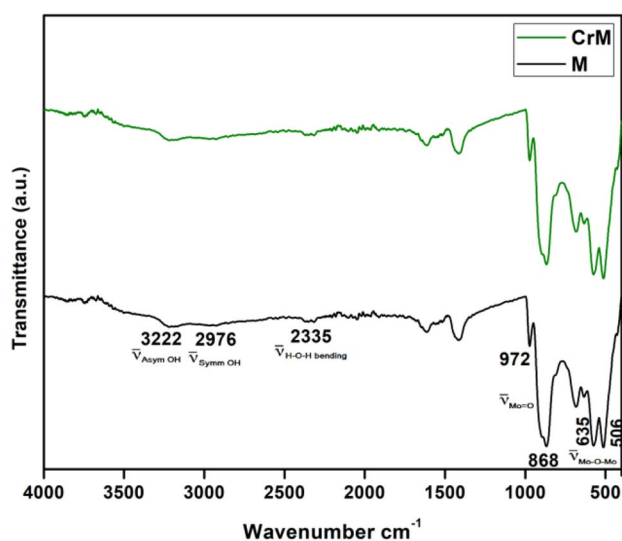


Fig. 5 FTIR spectra of MoO₃ and Cr-doped MoO₃ NPs

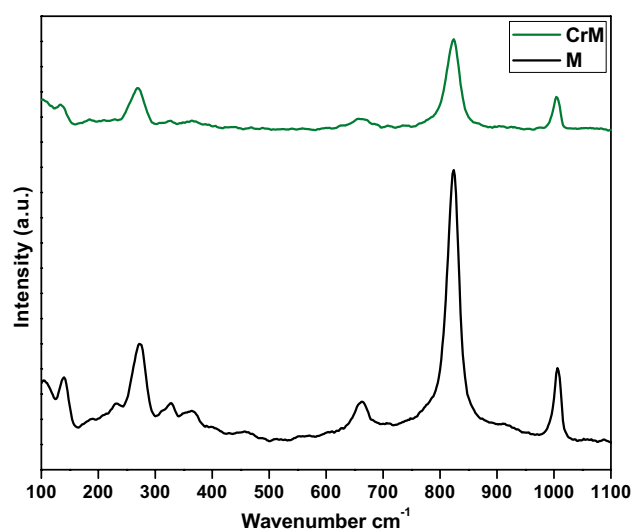


Fig. 6 Raman spectra of MoO₃ and Cr-doped MoO₃ NPs

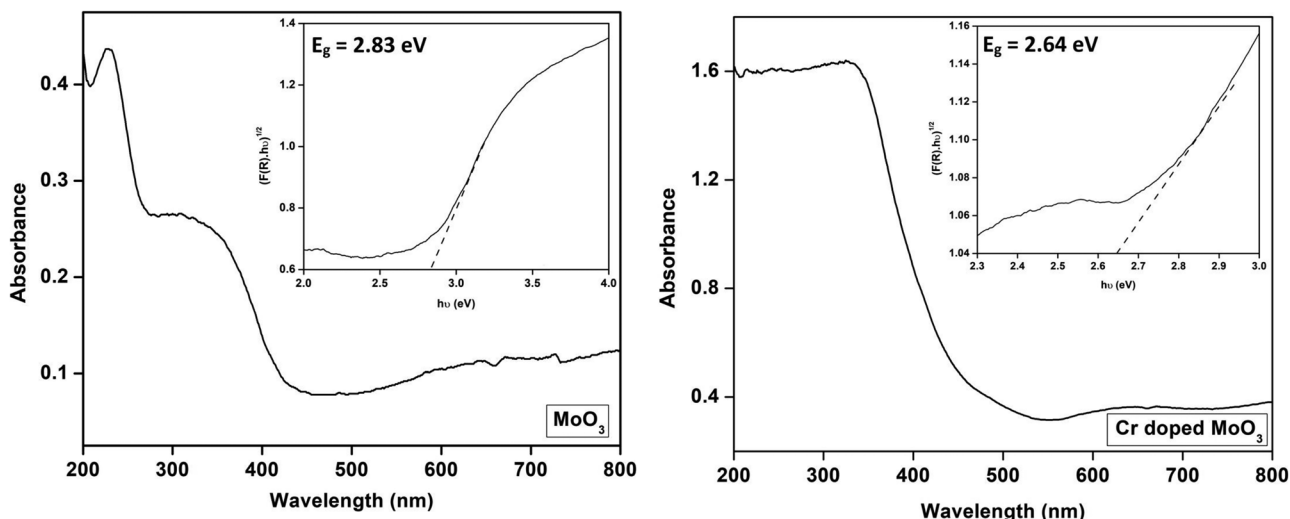


Fig. 7 Absorbance spectra of MoO₃ and Cr-doped MoO₃ NPs (inset: band gap calculation using Kubelka–Munk (K–M) function for MoO₃ and Cr-doped MoO₃ nanoparticles)

electric field. The frequency-dependent ac conductivity (σ_{ac}) was calculated using the following formula [34]:

$$\sigma_{ac}(\omega) = G_p(\omega) \cdot \frac{t}{A}$$

where G_p is the measured conductance of the sample, t and A are the thickness of the sample and contact area between the electrode and electrolytic surface respectively. The AC conductivity of the undoped and Cr-doped MoO₃ samples at varying temperatures are shown in Fig. 8. From the figure, two points are considered: (i) a plateau at low frequency

region which is related to DC conductivity (σ_{dc}), (ii) the high frequency corresponds to a bulk relaxation phenomenon, which arises on account of migration of trapped ions related to ac conductivity [35]. It is observed that the σ_{ac} values for all the samples increases on raising the frequency and also temperature, showing that the most probable mechanism for conductivity of MoO₃ and Cr-doped MoO₃ nanoparticles is ion hopping mechanism [36]. It is also observed from the figure that AC conductivity increases on Cr-doping due to the induced charge carrier density by the addition of dopant [37].

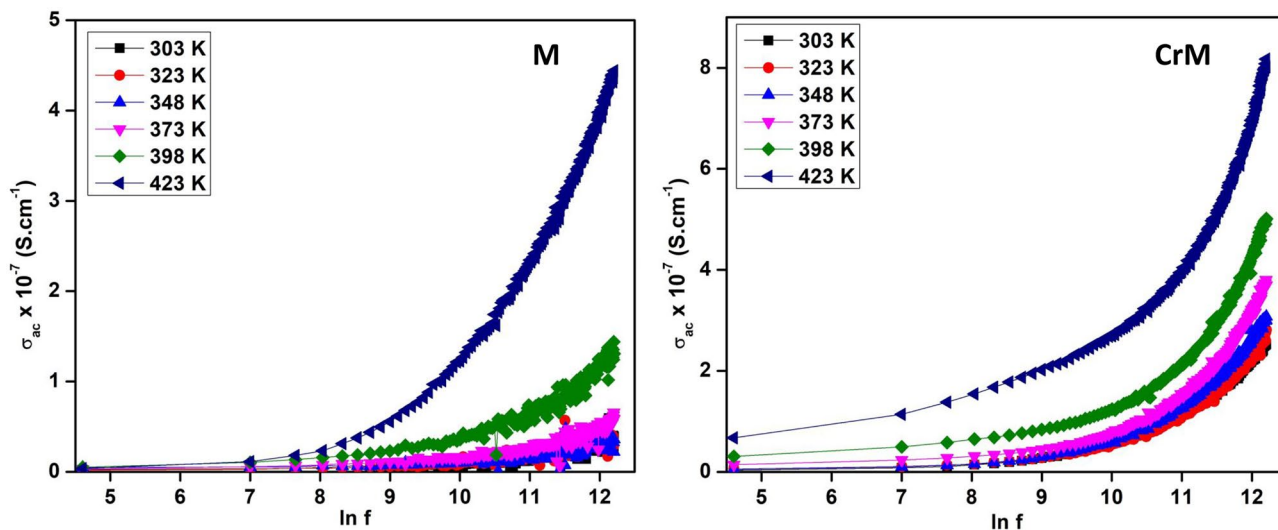


Fig. 8 Frequency-dependent σ_{ac} of MoO₃ and Cr-doped MoO₃ NPs at varying temperatures

Table 1 The values of σ_{dc} , S and E_a for MoO_3 and Cr-doped MoO_3 NPs

Compound	T (K)	$\sigma_{dc} \times 10^{-9}$ ($\text{S}\cdot\text{cm}^{-1}$)
MoO_3	303	4.09
	323	4.78
	348	5.18
	373	6.82
	398	8.03
	423	8.33
Cr-doped MoO_3	303	5.62
	323	6.64
	348	7.31
	373	11.94
	398	15.53
	423	19.32

The DC conductivity (σ_{dc}) arises due to hopping of metal ions in a random manner between the defects states [38]. The σ_{dc} values (Table 1) are obtained by extrapolating the plateau of the σ_{ac} spectra in Fig. 7. The temperature dependent σ_{dc} increases after doping due to the availability of Cr ions for migration.

The electrochemical performance of M and CrM were studied by cyclic voltammetry (CV). The redox peaks observed in both the samples (Fig. 9) indicate the charges which could be associated to faradic redox reactions [39].

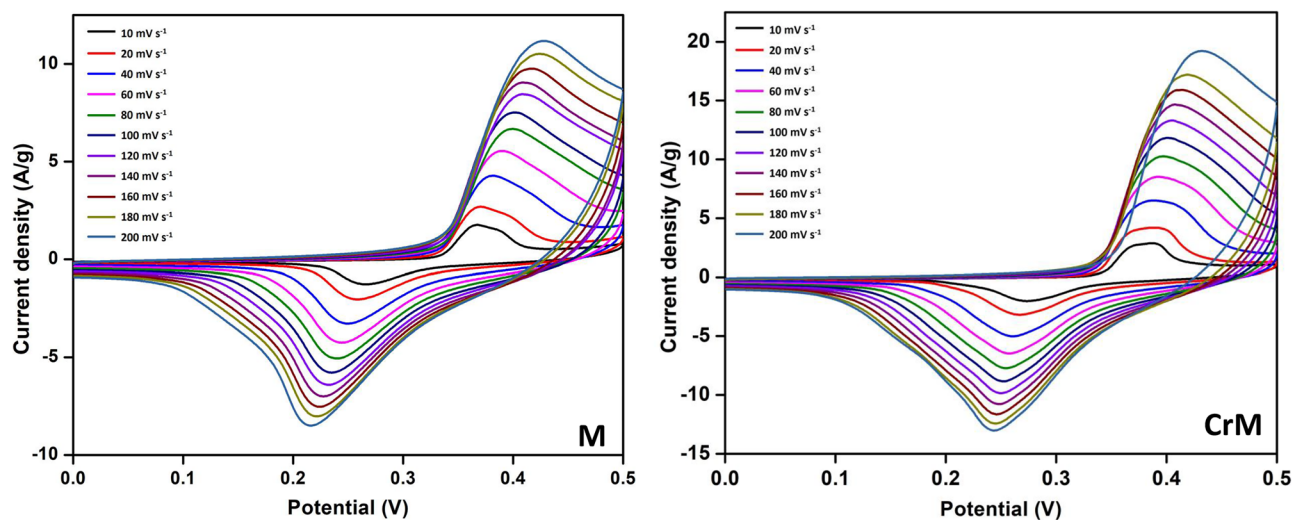
The doped sample showed greater current response when compared to that of undoped electrode. For undoped sample, the oxidation peak was observed at 0.4 V (11 A/g) and

reduction peak at 0.2 V (-8 A/g) was obtained for undoped sample while for doped sample, the oxidation peak was found at 0.4 V (19 A/g) and reduction peak at 0.2 V (-12 A/g). This confirms that the doped sample having interconnected network possess good porosity, thereby leading to better mobilization of electrons from electrolyte to the electrode surface [40].

The GCD analysis is considered as the more sensible approach to better understand the supercapacitive features present in a material [41]. The GCD profiles are recorded in the potential range of 0–0.5 V at different current densities from 1 to 10 A/g and are presented in Fig. 10.

The specific capacitance values along with energy and power density values for MoO_3 and Cr-doped MoO_3 nanoparticles are provided in Table 2.

The electrodes M and CrM have specific capacitance values of 230 and 344 F g^{-1} at the current density of 1 A g^{-1} . The specific capacitance values decreases at higher scan rates due to the existence of inner active sites which is unable to withstand the redox transition. The small convexer appearing in GCD curves is attributed to the doping of Cr ions and its participation in redox reactions. The minor voltage drop observed during discharging is an indicative of the conducting nature of the electrodes. Furthermore, the discharge time was decreased as current densities increased from 1 to 10 A g^{-1} which was also the same trend for specific capacitance values. It could be attributed to less ion diffusion in electrolyte and charge transfer in the electrode material resulting in less active material's participation in redox reactions and thus increase in the polarization value at higher current densities [42].

**Fig. 9** CV curves of MoO_3 and Cr-doped MoO_3 NPs at various scan rates

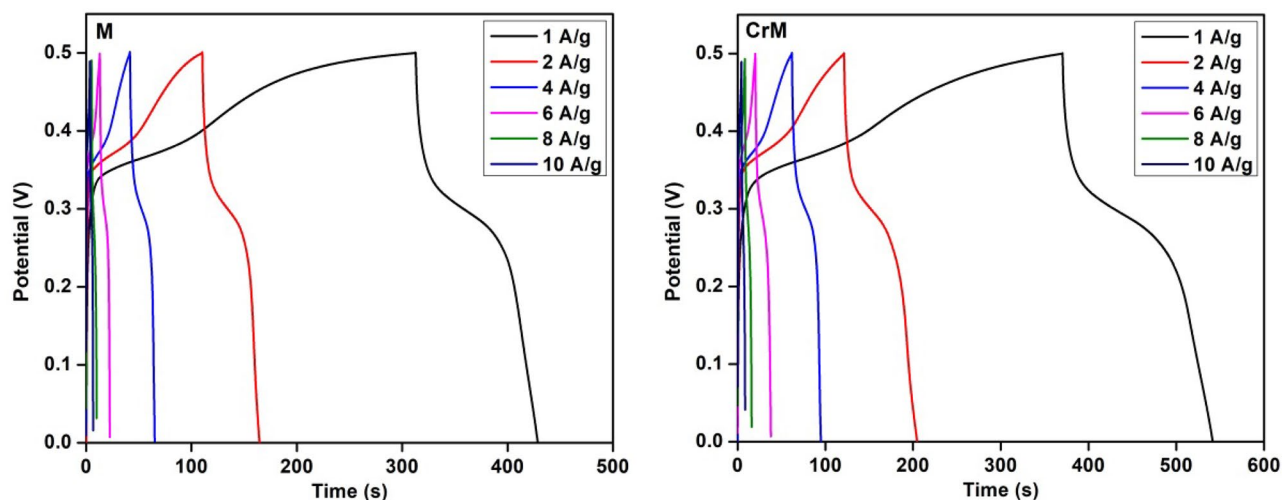


Fig. 10 GCD curves of MoO₃ and Cr-doped MoO₃ NPs with various applied current

Table 2 Specific capacitance (C_{sp}) values of synthesized NPs

	Current density (A/g)	Specific capacitance (F/g)		Energy density (W h Kg ⁻¹)		Power density (W Kg ⁻¹)	
		M	CrM	M	CrM	M	CrM
1		230	344	28	43	900	900
2		216	336	27	42	1800	1800
4		192	264	24	33	3600	3600
6		108	216	13	27	5400	5400
8		80	128	10	16	7200	7200
10		60	80	7	10	9000	9000

Conclusion

The MoO₃ and Cr-doped MoO₃ nanomaterials were prepared via hydrothermal route. The powder XRD analyses could be indexed to thermodynamically stable orthorhombic phase with space group *Pbnm*. The SEM and HRTEM revealed the flake-like morphologies. The direct band gap energies obtained using Kubelka–Munk relation shows a decrease in band gap value after doping. The AC conductivity revealed that the mechanism behind conduction process is ion hopping. The DC conductivity increases after doping due to the migration of Cr ions. From CV studies, the doped sample shows better redox behaviour due to the interconnected network leading to ion mobilization. The specific capacitance of MoO₃ was increased after doping with chromium at the current density of 1 Ag⁻¹ making it a promising material for energy storage applications.

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Author contribution R. Biju Bennie. A: conceptualization, methodology, formal analysis, investigation, writing—original draft, writing review and editing. A. Nirmal Paul Raj: validation, formal analysis, resources, writing review and editing, visualisation. A. Jerold Antony: methodology, resources, data curation, writing—original draft, writing review and editing. S. Iyyam Pillai: methodology, formal analysis, investigation, resources. C. Joel: conceptualization, supervision, project administration.

Data availability All data generated or analysed during this study are included in this published article.

Declarations

Conflict of interest The authors declare no competing interests.

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