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## Research Article

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# Mn-Driven Structural Modulation and PANI-Assisted Charge Transfer in WO<sub>3</sub>-Based Supercapacitor Electrodes

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## Abstract

Electrodes with fast kinetics of electron transfer, many electrochemically active sites and stable structure are needed for fabrication of highly efficient electrochemical energy storage devices. Tungsten oxide (WO<sub>3</sub>) can be considered as potential pseudocapacitive material; but rather low electrical conductivity and restricted number of active sites negatively influence on electrochemical properties of this compound. In our work, Mn-doped tungsten oxide nanomaterials were fabricated and studied as electrode materials for supercapacitors. The formation of highly crystalline tungsten oxide with monoclinic structure was proved by X-ray diffraction studies, while the presence of Mn in tungsten oxide structure was confirmed by the structural and vibrational characteristics, observed in FTIR spectroscopy, namely W–O, W=O and Mn–O bonds. The results of electron microscopy studies showed that the particles were uniformly dispersed, with average particle size of 19.86 nm. It should be noted that the electrode showed a high specific capacitance value of 1756 F g<sup>-1</sup> with 1 A g<sup>-1</sup> current density, along with an energy density of 61 Wh kg<sup>-1</sup> and a power density of 1784 W kg<sup>-1</sup>. Additionally, cycling stability was evident for the electrode, which indicates the capability of the material to function properly in terms of energy storage capacity. The improved electrochemical performance can be associated with the combined effects of Mn doping such as enhanced conductivity, larger electrochemically available surface area, and creation of additional redox centers. Thus, the presented study proves the capability of Mn doping in tuning the structural and electrochemical properties of WO<sub>3</sub>.

**Keywords:** Mn-doped WO<sub>3</sub>; Tungsten oxide; Supercapacitors; Nanostructures; Specific capacitance; Energy storage; Electrochemical performance; Electrode materials; Pseudocapacitance; Supercapacitors

## 1.Introduction

Because of the increase in energy demands and the continuous consumption of fossil fuels, energy storage devices are considered one of the most effective means in order to move from using non-renewable to renewable energies as they have the ability to store surplus energy and supply it whenever required [1]. One of the types of energy storage devices is the supercapacitor (SC), which has several benefits including high power density, high cycle stability, fast charging-discharging processes, and long shelf life [2,3]. Energy density enhancement is the key issue facing researchers that helps in utilizing SCs effectively and taking full advantage of their benefits.

The specific capacitance and voltage of the device have an impact on the energy density of the supercapacitors. There are various ways to increase the operational voltage and specific capacitance of supercapacitors that can be found in the literature. Various parts of the device such as electrode material, electrolyte, separator, current collector, and others get influenced by these approaches. The electrolyte influences the operational voltage, while the electrode material influences the specific capacitance [4, 5, 6].

The ideal electrode should contain defects, high electrical conductivity, effective electrochemical active site, pore control, and large surface area. Some of the best electrode materials available today are TM oxides due to their numerous merits. As a result, TM oxides have been utilized as electrodes where excellent pseudocapacitance performance has been observed; therefore, there exist numerous advantages associated with the use of these materials such as availability, non-toxicity, and high conductivity.

In the past, a series of TM oxides have been used as electrode materials in SCs, and positive performances have been recorded. Literature shows TM oxides including RuO<sub>2</sub>, MnO<sub>2</sub> [7], NiO [8], ZnO [9], [10], [11], TiO<sub>2</sub> [12], [13], and CO<sub>3</sub>O<sub>4</sub> [14] which have provided promising outcomes. TM oxides, which have received considerable attention as electrodes in SCs, include tungsten oxide (WO<sub>3</sub>) [15]. The tubular structure of WO<sub>3</sub> does not only provide numerous merits such as high stability, corrosion-resistant behavior, broad negative potential region, and environmental availability, but also facilitates the ion insertion of the electrolyte [16], [17].

Different WO<sub>3</sub>-based electrodes electrochemical performance has been enhanced by using varied WO<sub>3</sub> morphologies produced via different synthetic methods. Mesoscopic WO<sub>3</sub> microspheres derived from nanofibers were synthesized using the hydrothermal technique, as per [18]. The specific capacitance of the WO<sub>3</sub>-based electrode was reported to be 797 F/g with

great cycle stability at 0.5 A/g [19]. Many WO<sub>3</sub> morphologies were successfully produced using simple hydrothermal method by [19].

At the scan rate of 10 mV/s, the capacitance of WO<sub>3</sub> nanorods was 162 F/g while that of WO<sub>3</sub> nanoplates morphology was 50 F/g. The team in [20] fabricated flower like structures of WO<sub>3</sub> on titanium foil by using electrodeposition technique, reporting very promising results in terms of electrochemical behavior. They got the highest specific capacitance value of 1756 F/g along with high stability at scan rate of 5 mV/s. WO<sub>3</sub> thin film has been synthesized by means of ionic layer deposition technique and studied as an electrode material. In current study, nanosized Mn-doped WO<sub>3</sub> has been synthesized by a simple method and used as an electrode material for developing high-performance SCs. In order to improve the electrical properties of pure WO<sub>3</sub>, 10% of Mn doping concentrations have been used. As regards the application of the materials for evaluation of electrochemical performance in SCs, higher values of specific capacitance and energy density were observed. The present study focused on the analysis of the impact of Mn-doping on the properties of WO<sub>3</sub>.

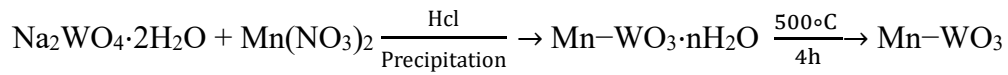
The scientific novelty in this research is in the combination of the effects of Mn doping and addition of PANI to WO<sub>3</sub>, creating an interconnection of structure-conductivity-redox behavior. The effect of Mn doping affects the structure and electrochemical behavior of WO<sub>3</sub>, whereas PANI acts as a conductive and redox active matrix.

## **2. Synthesis of Mn-Doped WO<sub>3</sub> Nanostructures**

The synthesis of Mn-doped WO<sub>3</sub> nanoparticles by the hydrothermal technique in which sodium tungstate dihydrate served as the common tungsten precursor for all samples. Sodium tungstate dihydrate (0.10 M) and manganese nitrate tetrahydrate (0.010 M) were employed in a molar ratio of 1:10 to yield 10 mol% Mn-doped WO<sub>3</sub>. After calcinations, PANI was doped at an Mn-WO<sub>3</sub>:PANI weight ratio of 80:20 from aniline and APS at a 1:1 molar ratio in 1 M HCl. Protonation of tungstate compounds via HCl facilitates their condensation into a hydrated tungsten oxide. In the process of nucleation and condensation, the Mn ions are dispersed within the growing tungsten-oxide framework. Heat treatment at 500 °C results in the elimination of volatile compounds and dehydration of the precursor. It also aids in Mn incorporation in the WO<sub>3</sub> framework. The calcined Mn-WO<sub>3</sub> nanoparticles were dispersed in acidic medium. Subsequently, aniline and APS were added at 0-5 °C to synthesize PANI on Mn-WO<sub>3</sub> nanoparticles.

The electrochemical benefit of using the nanosized particles is connected to the synergistic effect of structural transformation resulting from doping with Mn and insertion behavior of WO<sub>3</sub>. Doping with Mn changes the local W-O coordination structure that in turn depending on the oxidation state and the charge compensation may result in defects affecting the process of

electronic transport and providing additional electrochemically active sites. PANI is conductive polymer being electroactive at the same time; therefore, it serves as a carrier of electrons and electrochemically active sites where faradaic reactions can occur. Using PANI with Mn-WO<sub>3</sub> results in improved charge transfer processes and increased accessibility of electrolyte ions. This way, the pseudocapacitance of electrode material is enhanced. The nanoscale structure enables decreasing the distance of ions' diffusion and increasing the number of active sites accessible to the electrolyte. Therefore, the Mn doped WO<sub>3</sub> electrode enables electrolyte ion transport, charge transfer and faradaic reactions enhancing pseudocapacitance of the electrode.



**The proposed charge-storage mechanism becomes:**

Mn doping → WO<sub>3</sub> structural/electronic modification

PANI coating → conductive pathway + additional redox sites

Therefore:

**Mn-WO<sub>3</sub>/PANI**

↓

improved electron transport + enhanced electrolyte-ion accessibility

↓

faster charge-transfer kinetics → enhanced pseudocapacitive charge storage

### 3. Results and Discussion

#### 3.1 X-Ray Diffraction (XRD) Analysis of Mn-Doped WO<sub>3</sub> Nanoparticles

The crystal structure and phase composition of the synthesized 10% Mn-doped WO<sub>3</sub> nanoparticles were determined by X-ray diffraction (XRD). It is clear from the XRD diffractogram that the peaks obtained are sharp and well-resolved. This clearly reveals that the synthesized product is highly crystalline. The diffraction peaks were obtained for 2θ values around 23.1°, 23.6°, 24.4°, 33.9°, 34.1°, 41.7°, 50.1° and 55.9° for crystallographic planes (002), (020), (200), (022), (202), (222), (400) and (420), respectively. These diffraction peaks match perfectly with the monoclinic crystal structure of WO<sub>3</sub>, suggesting the formation of tungsten oxide phase[21]. From Fig. 1. It can be seen that no other peaks of manganese oxides were detected, indicating that Mn ions have been successfully incorporated into the WO<sub>3</sub> matrix.

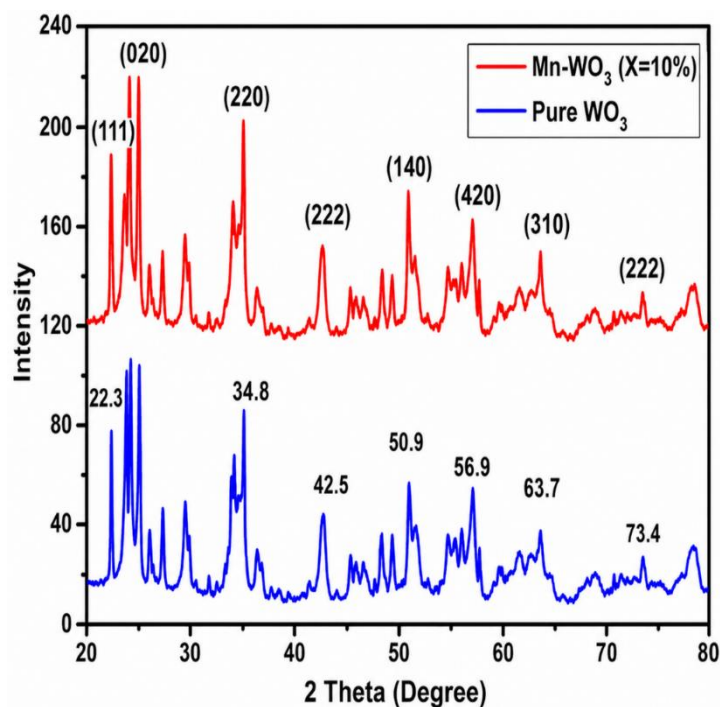


*Fig. 1. shows the XRD peaks for pure and Mn-doped WO<sub>3</sub> nanoparticles.*

A small shift in peak positions towards lower diffraction angles was observed compared with pristine WO<sub>3</sub>. The substitution of Mn ions into the WO<sub>3</sub> crystal framework can induce lattice distortion and this can be ascribed to this shift [22]. The assimilation of Mn ions creates structural defects and oxygen vacancies, which results in changes in lattice parameters and crystallographic strain [23]. Such structural changes are advantageous for electrochemical applications as they offer additional active sites and ease charge transport.

The average crystallite size was estimated using the Debye–Scherrer equation:

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

D is the crystallite size,  $\lambda$  is the wavelength of Cu K $\alpha$  radiation (1.5406 Å),  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the Bragg diffraction angle. The crystalline sizes of pristine WO<sub>3</sub> and Ni-doped WO<sub>3</sub> were estimated using Scherrer's equation. The results shows the average values of 18.6 nm for pure WO<sub>3</sub> and 13.8 nm for Mn-doped WO<sub>3</sub>, which indicates that change in the crystalline size after the addition of Mn incorporation.

The nanoscale crystallite size is beneficial for supercapacitor application because of the improvement in surface to volume ratio and accessibility of the electrolyte. Besides, Mn doping increases the electrical conductivity and produces oxygen-vacancy defects, which are beneficial to ion diffusion and electron transport. It is expected that these structural features are going to progress the electrochemical performance of the material. Generally, the XRD results confirm the fruitful synthesis of phase pure 10% Mn doped WO<sub>3</sub> nanoparticles with monoclinic

crystal structure and nanocrystalline dimensions. The addition of manganese to the  $\text{WO}_3$  lattice leads to acceptable structural changes that can enhance charge-storage behavior indicating the material as a potential electrode candidate for efficient supercapacitor applications [24].

### 3.2 X-Ray Photoelectron Spectroscopy Investigation of Mn-Doped $\text{WO}_3$ Nanoparticles

Chemical composition and oxidation state study of the prepared 10% Mn-doped  $\text{WO}_3$  nanoparticles were done using the technique of XPS. Success in preparing the doped nanoparticles was confirmed by survey spectra showing the existence of W, O, and Mn in the material, with no detectable impurities present [25]. The presence of tungsten in the  $\text{W}^+$  oxidation state was confirmed by the high-resolution W 4f spectra, which showed two distinctive peaks at 35.5 eV and 37.7 eV, corresponding to  $\text{W } 4\text{f}_{1/2}$  and  $\text{W } 4\text{f}_{5/2}$ , respectively [26]. Peaks in the O 1s spectra were identified as lattice oxygen and oxygen-vacancy-related oxygen species at 530.2 eV and 531.8 eV, respectively [27]. The presence of oxygen vacancies is desirable since it can enhance charge transfer rate and conductivity.

Manganese was successfully doped into the  $\text{WO}_3$  matrix, considering that the Mn 2p XPS spectrum showed the presence of peaks at 641.9 eV (Mn  $2\text{p}_{3/2}$ ) and 653.5 eV (Mn  $2\text{p}_{1/2}$ ) as shown in the Fig. 2. This is because manganese exists in various oxidation states, and this property enhances pseudocapacitance activity due to the higher electrochemically active sites [28]. Overall, the successful incorporation of Mn into the  $\text{WO}_3$  and oxygen vacancy formation are confirmed via the XPS data analysis.

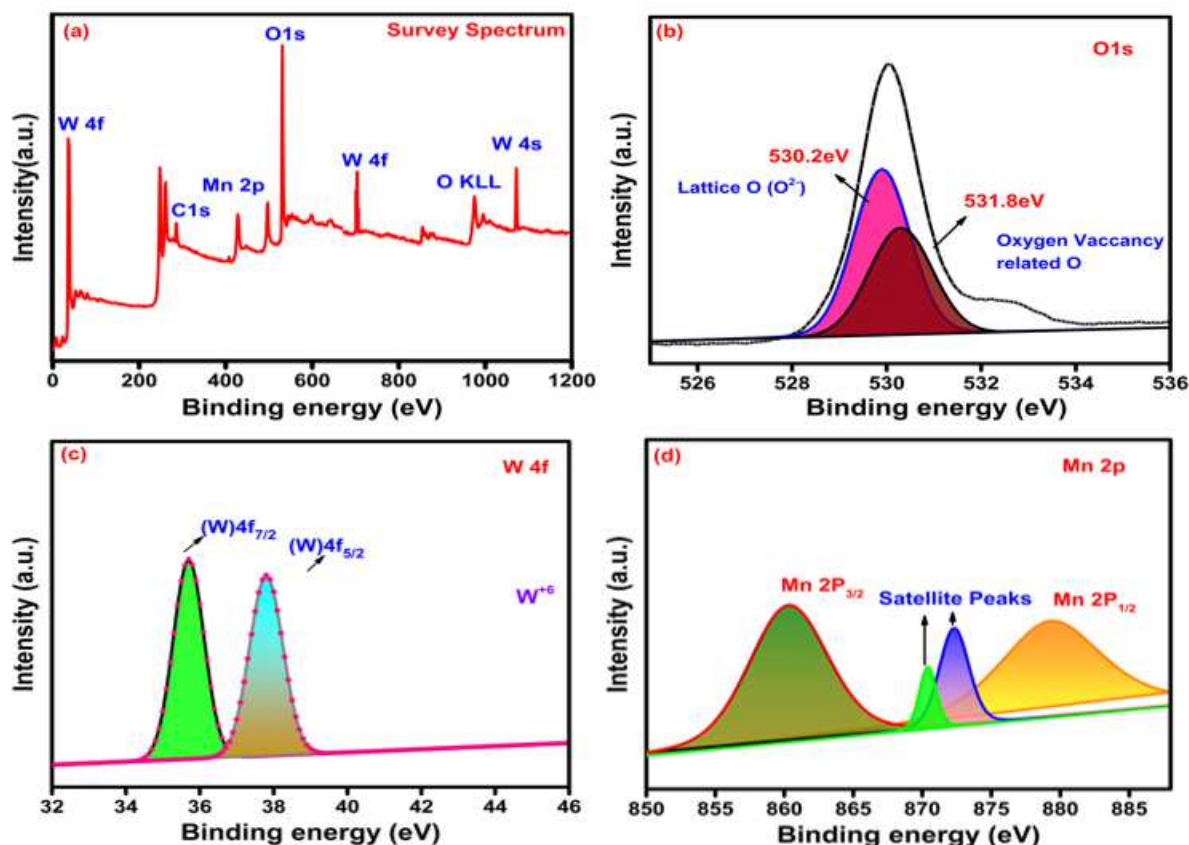


Fig. 2. shows the XPS studies for pure and Mn-doped WO<sub>3</sub> nanoparticles.

### 3.3 FTIR Analysis of Mn-Doped WO<sub>3</sub> Nanoparticles

To identify the functional groups and verify that Mn was successfully incorporated into the WO<sub>3</sub> lattice, the FTIR spectra of the produced 10% Mn-doped WO<sub>3</sub> nanoparticles was recorded in the 4000–400 cm<sup>-1</sup> region. The O–H stretching and H–O–H bending vibrations of adsorbed water molecules were identified as the cause of a broad absorption band at 3429 cm<sup>-1</sup> and a peak at 1633 cm<sup>-1</sup>, respectively [29]. The faint band at 1384 cm<sup>-1</sup> is indicative of residual nitrate groups from the precursor materials.

The stretching vibration of terminal W=O bonds was identified as the typical absorption bands of WO<sub>3</sub> at 920 cm<sup>-1</sup>, whereas W–O–W bridging vibrations were identified at 815 cm<sup>-1</sup>. Mn–O–W lattice vibrations are linked to the band that appears at 741 cm<sup>-1</sup>, indicating that Mn ions were successfully incorporated into the WO<sub>3</sub> framework. Additionally, the peaks at 615 cm<sup>-1</sup> and 520 cm<sup>-1</sup> represent Mn–O stretching vibrations and O–W–O bending vibrations, respectively as shown in the Fig. 3. Distortion in lattice structure due to the introduction of oxygen vacancies through manganese doping is observed from the small shift in metal-to-oxygen vibrational bands compared to pure WO<sub>3</sub> [30]. These modifications may help increase electrical conductivity and charge transport. Finally, FTIR spectral analysis clearly shows the presence of characteristic vibrations for WO<sub>3</sub> and manganese compounds, hence confirming

the synthesis of 10% Mn doped  $\text{WO}_3$  nanoparticles which can be used as supercapacitor materials [31].

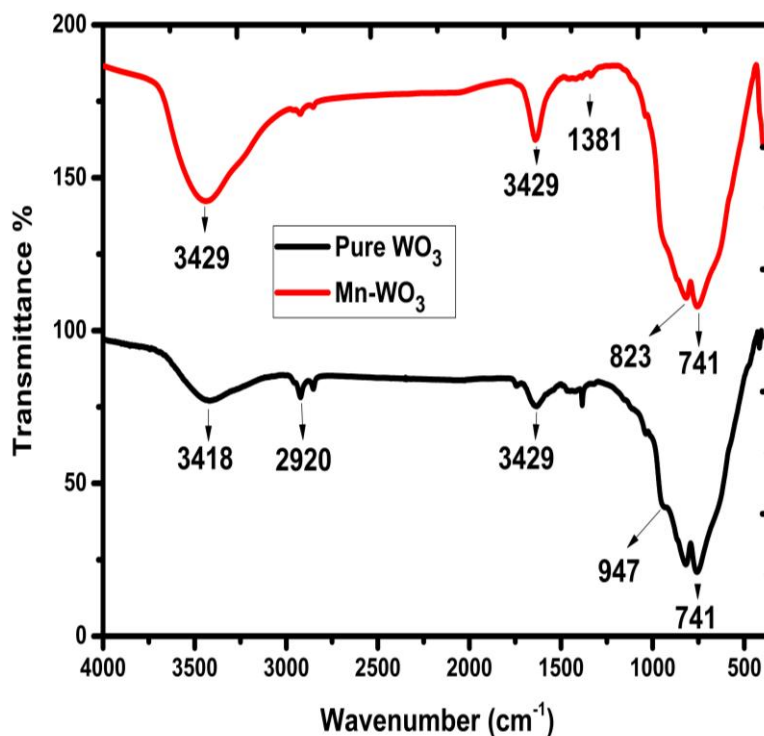


*Fig. 3. FT-IR spectra of Pure and Mn-doped  $\text{WO}_3$  Nanoparticles*

### 3.4 SEM Analysis of Mn-Doped $\text{WO}_3$ Nanoparticles

Fig. 4. shows that the surface morphology of the synthesized 10% Mn doped  $\text{WO}_3$  nanoparticles was investigated by scanning electron microscopy (SEM). It is evident from the SEM images of Pure metal that a dense structure that is made up of clearly defined plate-like and cuboidal particles. It should be noted that the particles have smooth surfaces with clear edges indicating effective crystallization [32]. The uniformly distributed nanoplates make an interconnecting structure and will therefore promote electron mobility. After the addition of Mn ions results in the reduction in particle size and development of porous interconnected granular networks. Morphological changes thus help in increasing the effective surface area and provide further electrochemical sites, contributing positively to ion diffusion and charging abilities.

Based on the results observed from SEM images, the mean particle size was calculated to lie within the range of 30-45 nm. This indicates that nanoparticles were effectively synthesized through the doping of Mn ions in  $\text{WO}_3$  lattices, resulting in the formation of smaller particles and increased surface roughness as shown in the Fig(4). Increased charge storage capacity is possible due to the greater electrochemical surface area facilitated by this surface roughness. Also, the connectivity between the nanoparticles makes it easier to facilitate good electrolyte

contact and electron transfer [33]. Therefore, it is clear that doping of manganese has helped modify the surface morphology of tungsten trioxide for supercapacitor use.

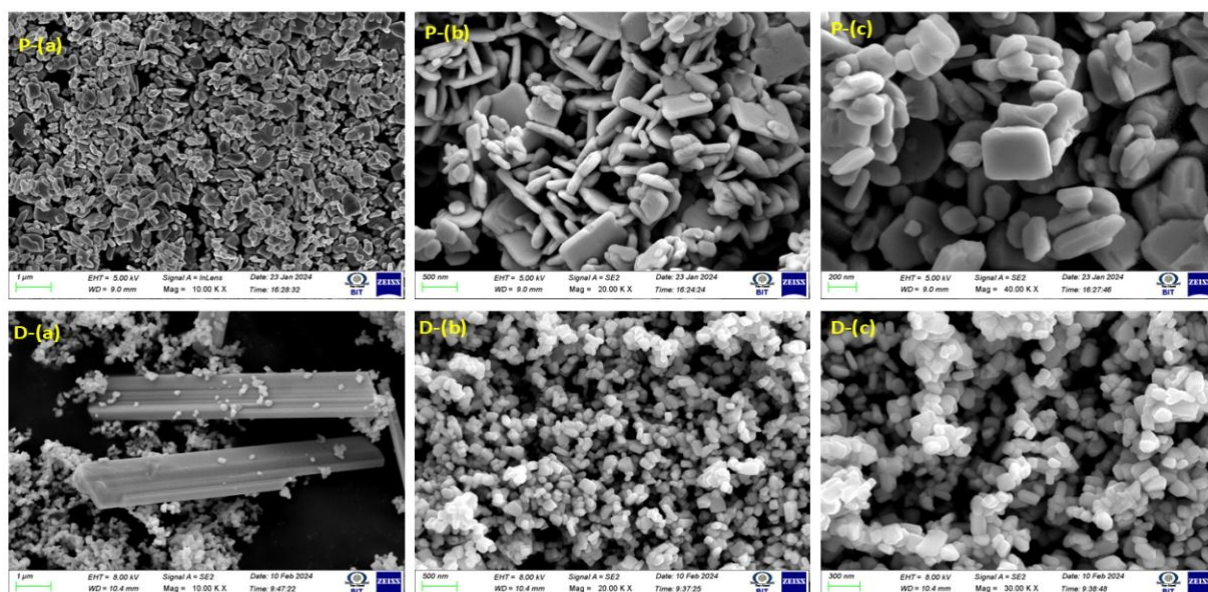


*Fig. 4 (a-d) Surface Topography of Pure and Mn-doped WO<sub>3</sub> Nanoparticles*

### 3.5 EDAX Analysis of Mn-Doped WO<sub>3</sub> Nanoparticles

The Energy Dispersive X-ray Analysis (EDAX) technique was employed to determine the elemental composition of the prepared 10% Mn-doped WO<sub>3</sub> nanoparticles. According to the EDAX analysis, the presence of W, O, and Mn elements was confirmed, which shows that

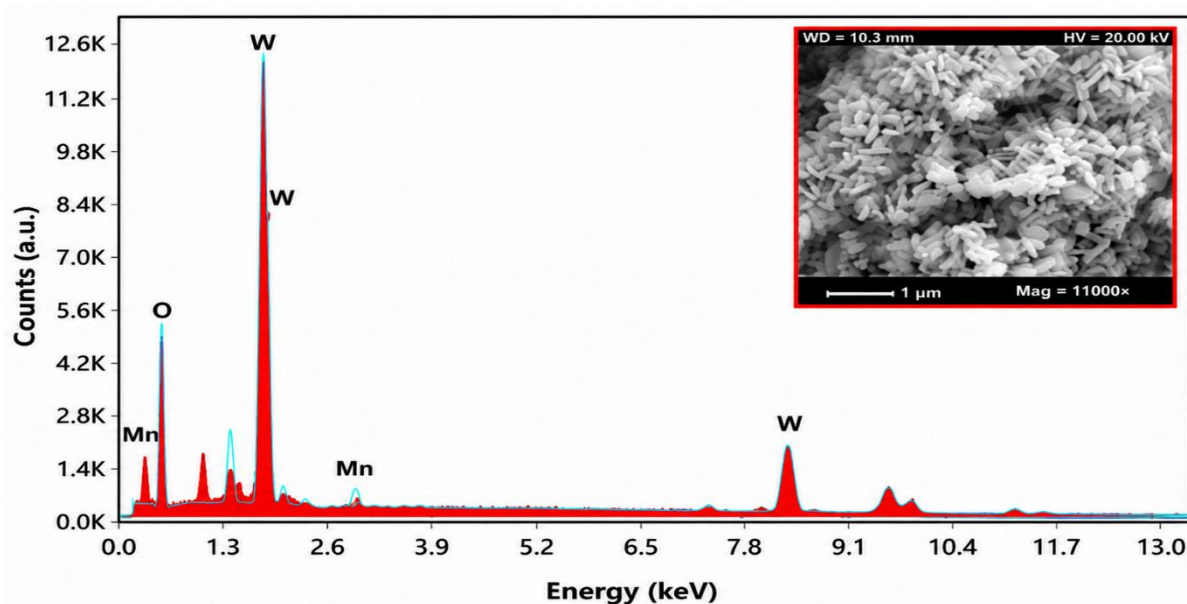


*Fig. 5 EDAX Spectra of Mn-doped WO<sub>3</sub> Nanoparticles*

the Mn doping process was successfully accomplished in the WO<sub>3</sub> structure as shown in the table 1, the absence of any impurities in the EDAX spectrum demonstrates the high purity of the prepared material [34]. The even distribution of Mn in the WO<sub>3</sub> structure implies efficient doping; Mn will help increase the charge storage capacity as shown in the Fig. 5.

**Table 1: EDAX Elemental Composition of 10% Mn-Doped WO<sub>3</sub> Nanoparticles**

| Element        | Atomic Number | Weight % | Atomic % |
|----------------|---------------|----------|----------|
| Oxygen (O)     | 8             | 18.50    | 67.20    |
| Manganese (Mn) | 25            | 4.80     | 5.10     |
| Tungsten (W)   | 74            | 76.70    | 27.70    |
| Total          | —             | 100.00   | 100.00   |

### 3.7 TEM Analysis of Mn-Doped WO<sub>3</sub> Nanoparticles

From the TEM analysis of pure WO<sub>3</sub> (P-(a-c)), it is evident that the formation of agglomerated nanoparticles with mostly polyhedral shape is attained. The nanoparticles are very close together and have a rather uniform particle size. With further zooming in, the nanoparticles are clearly crystallized with defined particle edges, indicating the successful fabrication of WO<sub>3</sub> nanoparticles.

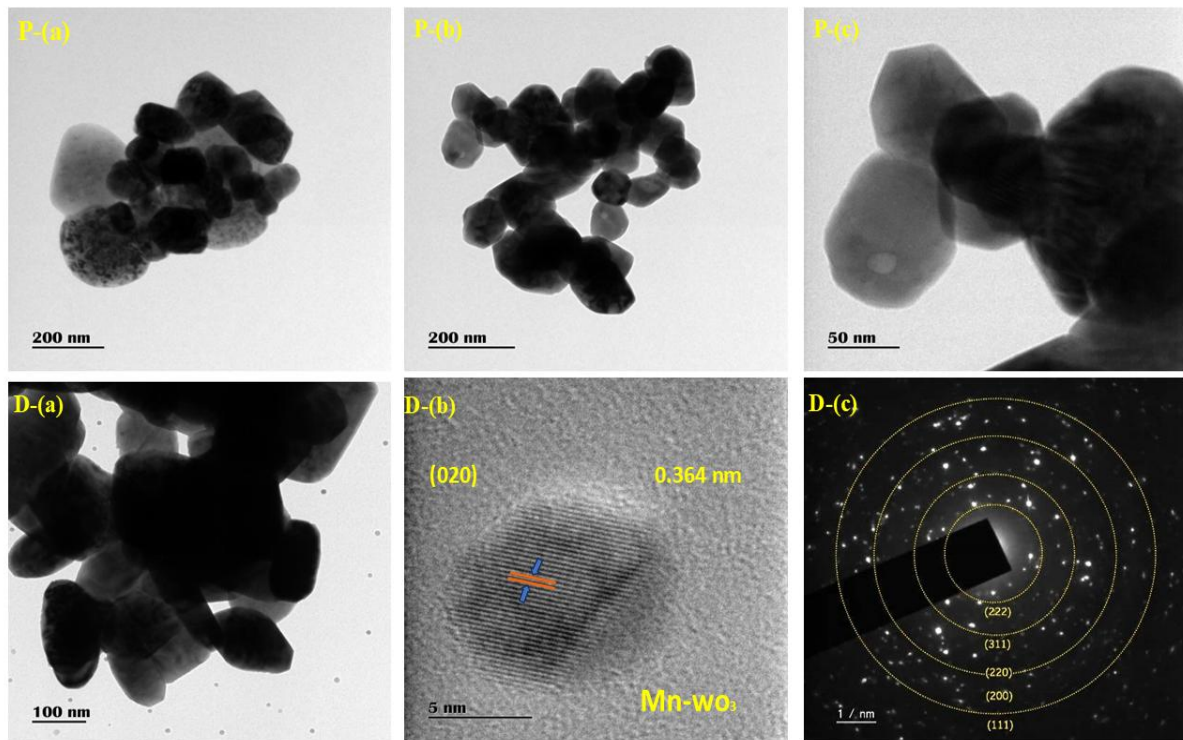


**Fig. 6 TEM images (a,b), HR-TEM images (c) and SAED pattern(d) of Mn-doped WO<sub>3</sub> nanomaterials**

In terms of morphology after doping with Mn, TEM analysis for Mn-doped  $\text{WO}_3$  (D-(a-c)) has brought about some changes. The polyhedral-shaped nanoparticles now have a more uniform structure with a better particle arrangement compared to their undoped counterparts. The interconnection of particles results in the formation of pores within the structure, which can increase the number of active sites for electrochemical reactions. The lattice fringe observed in D-(b), having an interplanar distance of 0.364 nm, corresponds to the (020) crystal plane of monoclinic  $\text{WO}_3$ .

In addition, the diffraction rings shown in the SAED pattern of D-(c) are perfectly defined diffraction rings corresponding to the (111), (200), (220), (311), and (222) planes. The clear formation of diffraction rings is proof of the crystallization of the Mn doped  $\text{WO}_3$  nanoparticles [35]. Moreover, the lack of other diffraction rings indicates the successful inclusion of Mn ions into the  $\text{WO}_3$  crystal structure without creating any impurities as shown in the Fig. 6. This structural arrangement will allow rapid movement of electrons and ions through the material, making it a very suitable electrode for supercapacitors.

## **4. Electrochemical analysis**

### **4.1 Cyclic Voltammetry (CV) Analysis of Mn-Doped $\text{WO}_3$ Nanoparticles**

One of the best electrochemical techniques that can be used for analyzing the redox reactivity, capacitive behavior, and charge storage process of electrode materials suitable for supercapacitors is cyclic voltammetry (CV). The electrochemical properties of 10% Mn-doped  $\text{WO}_3$  nanoparticles have been analyzed in this study by using CV measurements at different scan rates in an appropriate potential range. The obtained results from CV analysis can offer valuable information about the charge transfer process, electrochemical reversibility, and energy storage capability of the synthesized material.

The redox reactions that can be reversed take place in the CV plots of 10% Mn-doped  $\text{WO}_3$  electrodes because of the formation of anodic and cathodic peaks. Unlike the CV plots that have almost rectangular shapes and belong to electric double-layer capacitors, the presence of redox peaks means that charge storage of Mn-doped  $\text{WO}_3$  takes place via pseudocapacitance. This happens because of fast and reversible redox reactions that occur on the surface or near the surface of manganese and tungsten ions.

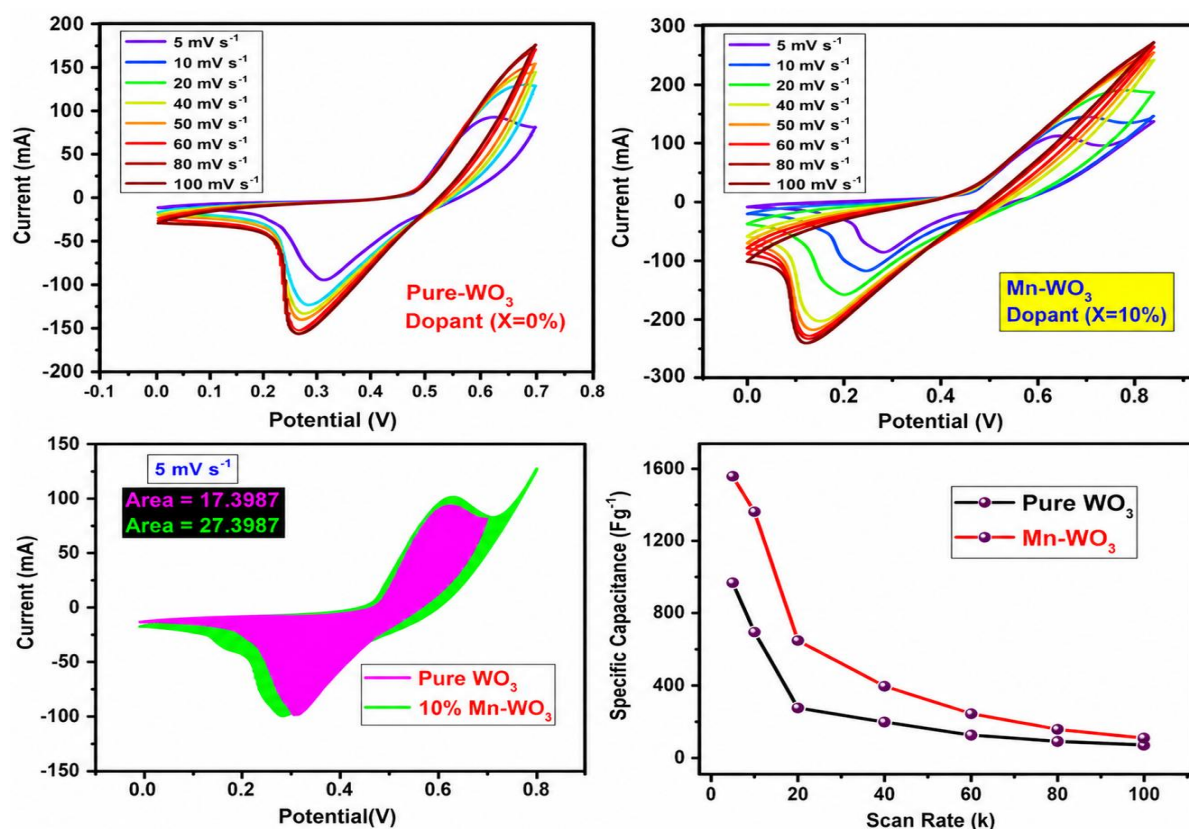


*Fig. 7 Cyclic Voltammetry Profiles of Pure and Mn-doped WO<sub>3</sub> at the scan rate of 5 to 100 mV/s*

Reversible transitions between various oxidation states of manganese and tungsten ions may be correlated with the processes of oxidation and reduction. Oxidation and electron transport are caused by the interaction of electrolyte ions with the electrode surface during charging. On the contrary, reduction reactions and the release of stored charge are achieved via the opposite mechanism during discharge. As both manganese and tungsten redox centers are present in the composite, many additional electrochemically active sites are accessible to charge storage. It can be noticed that as scan rate increases, a pronounced electrochemical activity is observed. Peak current increases as scan rate increases, which evidences efficient transport of ions through the electrode material [36,42]. Additionally, even with high scan rate, the shape of voltammograms remains nearly unchanged. This behavior suggests better structural stability and electrochemical reversibility of the Mn-doped WO<sub>3</sub> electrode.

There are several factors contributing to improved electrochemical properties of 10% Mn-doped WO<sub>3</sub> nanoparticles. Firstly, the presence of manganese creates additional redox sites that help in pseudocapacitance. Second, doping of manganese into WO<sub>3</sub> increases its natural electrical conductivity owing to changes in its electronic structure. Lastly, oxygen vacancy, which helps in creating additional redox sites and provides fast electron movement, can be generated through doping.

The above mentioned electrochemical reactions taking place at the electrode interface are shown by the following redox equations:



These reversible reactions contribute significantly to the overall charge-storage capability of the electrode. The participation of multiple oxidation states enables the storage of a larger amount of charge compared with undoped  $\text{WO}_3$ , thereby enhancing the specific capacitance.

The specific capacitance obtained from CV measurements is calculated using the following equation:

$$C_{sp} = \frac{1}{v \times m \times \Delta V} \int I(V) dV \quad (5)$$

Here,  $C_s$  stands for the electrode material's areal capacitance ( $\text{Fg}^{-1}$ ),  $V$  for the scan rate ( $\text{V s}^{-1}$ ), and  $m$  for the mass of the active material in grams (mg).

The integral is indicative of the charge stored during the electrochemical reaction. The more the area under the CV graph, the more will be the amount of charge stored and hence a higher specific capacitance value. The 10% Mn doping of  $\text{WO}_3$  electrode gives a large area under the CV curve than the unaltered  $\text{WO}_3$  electrode [37,41,45].

The relationship between peak current and scan rate provides additional insight into the charge-storage mechanism. The dependence can be expressed as:

$$i = av^b \quad (6)$$

where,  $i$  = Peak current,  $v$  = Scan rate,  $a$  and  $b$  = Adjustable constants

A  $b$ -value of 0.5 implies that the charging behavior of the electrode is diffusion controlled. On the other hand, a higher  $b$ -value close to 1.0 implies that the charging behavior is capacitance-controlled. Electrodes doped with Mn usually have both diffusion-controlled and capacitance-controlled charging behavior, which results in better electrochemical performance.

The excellent electrochemical performance of the electrode with 10% doping is further confirmed by the high current and the presence of a similar CV profile even when the scanning rate is increased. This shows that even with fast charging, the electrode maintains its electrochemical performance through effective diffusion of electrolyte and quick electron transfer. This type of electrochemical behavior is crucial for supercapacitors, since they need fast and efficient discharge and charge processes as shown in the Fig. 7.

Based on the results of the CV test, the presence of manganese is seen to enhance the electrochemical behavior of the  $\text{WO}_3$  nanoparticles. This includes their conductivity, density of active sites, formation of oxygen vacancies, as well as the redox reaction. In conclusion, the

huge area under the CV graph, significant redox peaks, and excellent scan rate results confirm that the 10% Mn doped-WO<sub>3</sub> nanoparticles show great promise as electrodes for supercapacitors.

#### 4.2 Galvanostatic Charge–Discharge (GCD) Analysis of Mn-Doped WO<sub>3</sub> Nanoparticles

Charge-discharge experiments (GCD method) have been conducted to investigate the charge-storage capacity, reversibility, specific capacitance, energy density, and power density of the 10% manganese doped tungsten oxide nanoparticles. Galvanostatic charge discharge testing is considered one of the most effective methods of evaluating the performance of the active electrode materials in terms of its electrochemical activity, due to direct measurement of the charging/discharging behavior under constant current conditions. Analysis of charge–discharge curves gives significant insight into the electrochemical behavior of the tested material.

Charge-discharge curves of the prepared electrode with 10% Mn doped tungsten oxide have been measured at different current densities under the same potential range. The resulted charge–discharge curves show almost symmetrical nature, indicating good reversibility of the occurring electrochemical processes on the electrode. While ideal electric double-layer capacitors usually show linear relationships between the amount of charge injected and released (hence, having idealized charge-discharge curves), the obtained GCD curves for Mn-doped WO<sub>3</sub> have some deviation from linearity. Such deviation is observed for all pseudocapacitive materials due to Faradaic redox reactions taking place in the charge/discharge processes of the devices. Namely, doping the WO<sub>3</sub> lattice with manganese leads to the appearance of new redox-active centers, thus increasing capacitance greatly.

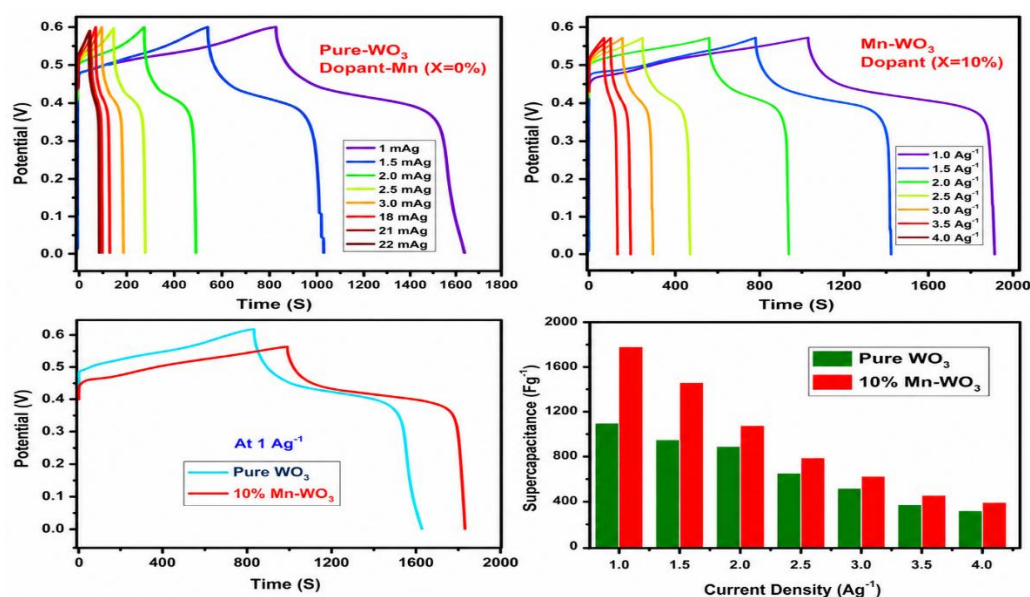


*Fig. 8 GCD Profiles of Pure and Mn-doped WO<sub>3</sub> at the various current densities*

At the charging process, the migration of electrolyte ions and their subsequent oxidation together with tungsten and manganese ions takes place, while electrons are transported through the external circuit, thus storing the energy in the electrode material. At the discharging stage, redox reactions take place in reverse, and the energy is supplied to the external circuit again [38,44].

The long discharge time seen in the case of the 10% Mn doped WO<sub>3</sub> electrode implies an excellent capacity for charge storage. In general, longer discharge times equate to higher capacitances since a larger amount of charge is both stored and discharged. The increase in discharge time when compared to pure WO<sub>3</sub> implies the advantageous effect of the Mn doped WO<sub>3</sub> electrode on its electrochemical performance. The improved electrochemical performance of the material is due to a number of factors associated with Mn doping. For instance, the presence of manganese ions in the WO<sub>3</sub> structure leads to the creation of new active sites as well as oxygen vacancies which facilitate increased charge movement. In addition, Mn ions may occur in various oxidation states making them capable of participating in reversible redox processes as shown in the Fig. 8.

The specific capacitance of the electrode was calculated from the discharge curves using the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (7)$$

Where, C<sub>s</sub> = Specific capacitance (F g<sup>-1</sup>), I = Applied discharge current (A), Δt = Discharge time (s), m = Mass of active material (g), ΔV = Potential window excluding IR drop (V)

As per this equation, the specific capacitance is directly proportional to the discharge time. Thus, higher discharge times imply higher storage capacity. High specific capacitance values of 10% Mn doped WO<sub>3</sub> show that the addition of manganese to the WO<sub>3</sub> nanomaterial improves electrochemical properties of value 1756 F/g as shown in the table 2. And the comparison of supercapacitance values are also shown in the table 3.

**Table 2: Supercapacitance (Cs) Values for Pure and Mn-Doped WO<sub>3</sub> Nanoparticles**

| <b>Sample / Potential<br/>(V)</b>                 | <b>1<br/>Ag<sup>-1</sup></b> | <b>1.5<br/>Ag<sup>-1</sup></b> | <b>2.0<br/>Ag<sup>-1</sup></b> | <b>2.5<br/>Ag<sup>-1</sup></b> | <b>3.0<br/>Ag<sup>-1</sup></b> | <b>3.5<br/>Ag<sup>-1</sup></b> | <b>4.0<br/>Ag<sup>-1</sup></b> |
|---------------------------------------------------|------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| <b>Pure-WO<sub>3</sub><br/>Dopant (X= 0%)</b>     | 1103                         | 958                            | 900                            | 665                            | 531                            | 391                            | 340                            |
| <b>Mn-WO<sub>3</sub> /PANI<br/>Dopant (X=10%)</b> | 1756                         | 1449                           | 1080                           | 798                            | 637                            | 469                            | 408                            |

**Table 3: Comparison of doped WO<sub>3</sub>-based electrodes for supercapacitor applications**

| S.No. | Electrode material                | Dopant / composition | Specific capacitance      | Test condition               | Electrolyte                          | Reference        |
|-------|-----------------------------------|----------------------|---------------------------|------------------------------|--------------------------------------|------------------|
| 1     | Mn–WO <sub>3</sub>                | 1 wt% Mn             | 1696.5 F g <sup>-1</sup>  | 1 mV s <sup>-1</sup> , CV    | 1 M KOH                              | [46]             |
| 2     | Ni–WO <sub>3</sub>                | Ni-doped             | 171.28 F g <sup>-1</sup>  | 0.25 A g <sup>-1</sup>       | 1 M KOH                              | [47]             |
| 3     | Sn–WO <sub>3</sub>                | 5 wt% Sn             | 418 F g <sup>-1</sup>     | 1 A g <sup>-1</sup>          | 1 M KOH                              | [48]             |
| 4     | Co–WO <sub>3</sub> /f-CNT         | 5% Co                | 60.14 F g <sup>-1</sup>   | 1 A g <sup>-1</sup>          | 2 M KOH                              | [49]             |
| 5     | Zn–WO <sub>3</sub>                | Zn-doped             | 35.70 F g <sup>-1</sup>   | 0.25 A g <sup>-1</sup>       | 1 M KOH                              | [50]             |
| 6     | Pd–WO <sub>3</sub>                | Pd-doped             | 33 F g <sup>-1</sup>      | 0.5 A g <sup>-1</sup>        | 1 M KOH                              | [51]             |
| 7     | Ce–WO <sub>3</sub>                | 1.5% Ce              | 493 F g <sup>-1</sup>     | 4 A g <sup>-1</sup>          | 2 M KOH                              | [52]             |
| 8     | Ru–WO <sub>3</sub>                | 2 wt% Ru             | 39.5 F g <sup>-1</sup>    | 0.1 A g <sup>-1</sup>        | 2 M KOH                              | [53]             |
| 9     | Mo–WO <sub>3</sub>                | 2% Mo                | 55.89 mAh g <sup>-1</sup> | 1 A g <sup>-1</sup>          | 0.5 M H <sub>2</sub> SO <sub>4</sub> | [54]             |
| 10    | Nb–WO <sub>3</sub>                | Nb-doped             | 782 F g <sup>-1</sup>     | Reported optimum             | Ca <sup>2+</sup> electrolyte         | [55]             |
| 11    | Gd–WO <sub>3</sub>                | Gd-doped             | 62.43 mF cm <sup>-2</sup> | 0.3 mA cm <sup>-2</sup>      | 0.3 M HCl                            | [56]             |
| 12    | Cu–WO <sub>3</sub>                | 15 at% Cu            | 564.6 F g <sup>-1</sup>   | 1 mA                         | 1 M KOH                              | [57]             |
| 13    | Mn–WO <sub>3</sub><br>(This work) | 10 mol% Mn           | 1756 F g <sup>-1</sup>    | 1 A g <sup>-1</sup> ,<br>GCD | 0.5 HCl                              | <b>This work</b> |

The energy density, which represents the amount of energy stored per unit mass of the electrode material, was calculated using:

$$E = \frac{1}{2} C (\Delta V)^2 \quad (8)$$

Where, E = Energy density (Wh kg<sup>-1</sup>), C<sub>sp</sub> = Specific capacitance (F g<sup>-1</sup>), ΔV = Operating potential window (V)

A higher energy density indicates a greater ability of the electrode material to store electrical energy. The enhanced energy density observed for the Mn-doped WO<sub>3</sub> electrode originates from its high specific capacitance and efficient charge-storage mechanism [39,42].

The power density, which represents the rate at which energy can be delivered, was calculated using:

$$P = \frac{E \times 3600}{\Delta t} \quad (9)$$

Where, P = Power density (W kg<sup>-1</sup>), E = Energy density (Wh kg<sup>-1</sup>), Δt = Discharge time (s) Figure X. Graph depicting cycling stability of Mn doped WO<sub>3</sub> nanoparticles with varying cycles of charge-discharge cycles for supercapacitor application purposes as shown in the table 4. The material exhibits good electrochemical stability with about 89% of capacitance retention after 5000 cycles as shown in the Fig. 9.

**Table 4: Energy Density and Power Density values for Mn-Doped WO<sub>3</sub> Nanoparticles**

| <b>Current Density<br/>(A g<sup>-1</sup>)</b> | <b>Specific Capacitance<br/>(F g<sup>-1</sup>)</b> | <b>Energy Density<br/>(Wh kg<sup>-1</sup>)</b> | <b>Power Density<br/>(W kg<sup>-1</sup>)</b> |
|-----------------------------------------------|----------------------------------------------------|------------------------------------------------|----------------------------------------------|
| 1                                             | 1756                                               | 60.9                                           | 1784                                         |
| 2                                             | 1080                                               | 37.5                                           | 1097                                         |
| 3                                             | 637                                                | 22.1                                           | 647                                          |
| 4                                             | 408                                                | 14                                             | 414                                          |

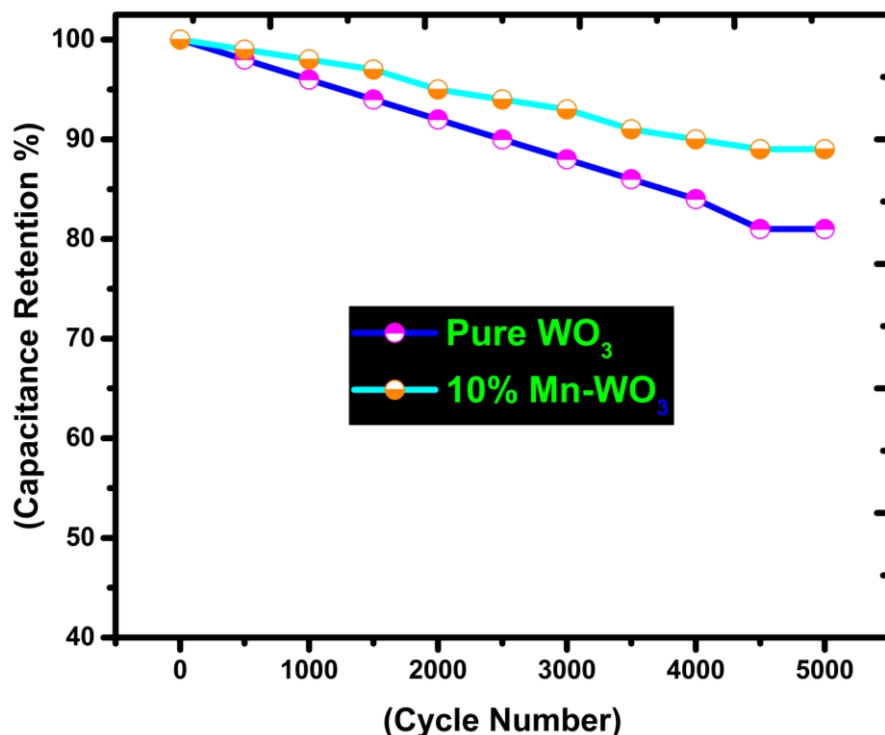


**Fig. 9 Cyclic Stability of pure and Mn-doped WO<sub>3</sub> Nanoparticles**

The impressive power density that was obtained from the 10% Mn doped WO<sub>3</sub> electrode proves the high capacity of the electrode to supply energy very quickly. Such an aspect is highly relevant to applications where high power is necessary, and the processes of charging and discharging need to take place at a quick rate. The remarkable rate capability of the Mn-doped WO<sub>3</sub> electrode is demonstrated by the high capacitance that remains after an increase in current density. Despite the gradual reduction in capacitance that occurs with the rise in current density, due to the low ion diffusion, a significant percentage of capacitance retention still exists.

Such a performance is therefore due to the combined contribution of manganese to the electrochemical properties of the material. The increased electrical conductivity, density of active sites, oxygen vacancies, low internal resistance, and high electrolyte ions diffusion have been proven to contribute to the great performance of the material. The findings on the GCD analysis indicate that 10% Mn-doped WO<sub>3</sub> nanoparticles show high specific capacitance, high Coulombic efficiency, energy density, and power density. The results clearly exhibit great potential for using Mn-doped WO<sub>3</sub> as a new type of electrode material in next-generation supercapacitors.

### **4.3 Electrochemical Impedance Spectroscopy (EIS) Analysis of 10% Mn-Doped WO<sub>3</sub> Nanoparticles**

Electrochemical impedance characteristics of the 10% Mn-doped WO<sub>3</sub> electrode were studied by Electrochemical Impedance Spectroscopy. The Nyquist plot shows the impedance results

that have been acquired through this technique. The Nyquist plot contains a semicircle at higher frequencies and a straight line at lower frequencies. The semicircle present at higher frequencies is related to the charge transfer reaction that takes place at the electrode/electrolyte interface, whereas the straight line at lower frequencies is attributed to ion diffusion and capacitance properties of the electrode material [40,41].

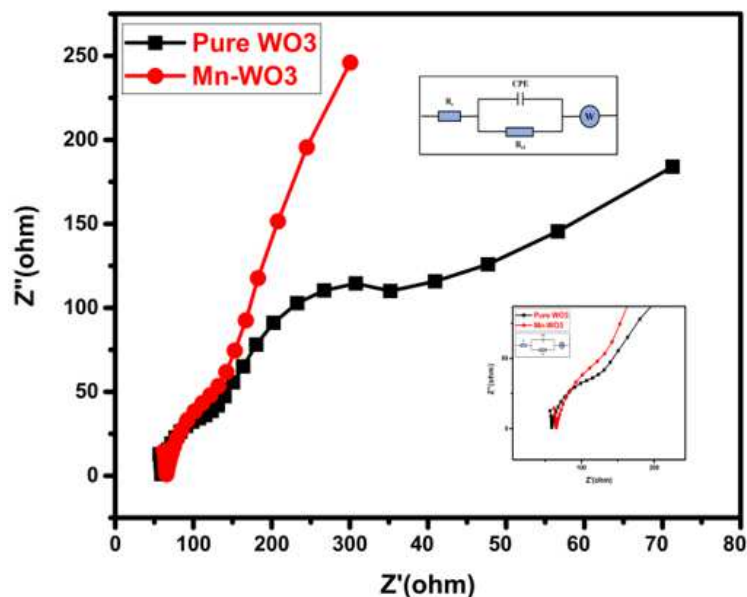


*Fig. 10 Nyquist plot of pure and Mn-doped WO<sub>3</sub> nanoparticles*

The value of  $R_s$ , as estimated by the Nyquist plot intercept with respect to the real axis, was calculated to be about  $0.72 \, \Omega$ . The  $R_s$  of this magnitude is indicative of high electrolyte ionic conductivity and good contact between the active material, current collector, and electrolyte.  $R_{ct}$  was estimated to be around  $1.84 \, \Omega$ , based on the semicircle diameter as shown in the Fig. 10. The relatively lower value of  $R_{ct}$  shows that the electron transport at the electrode-electrolyte interface is quite efficient due to increased electrical conductivity by Mn doping [40,43]. Additionally, the almost perpendicular slope obtained at the low frequency regime reveals the good efficiency of ion diffusion as well as the quick electrolyte penetration into the electrode material. It is clear that due to the presence of Mn in the electrode structure, the porous nature and the creation of more active sites for electrochemical reactions enhance the process of ion migration.

## Conclusion

In the present research, 10% Mn-doped WO<sub>3</sub> nanoparticles have been successfully prepared and investigated for their application as supercapacitor electrode materials. XRD, FTIR, SEM, TEM and XPS techniques showed that doping of manganese into the structure of WO<sub>3</sub> has been achieved and highly crystallized nanoparticles with better structural and optical characteristics have been formed due to manganese doping. Oxygen vacancies and increased

electrical conductivity were provided by manganese doping in the WO<sub>3</sub> lattice. Pseudocapacitive characteristics of the material with a very high specific capacitance of 1759 F g<sup>-1</sup> and 89% of cyclic stability, 61 Wh kg<sup>-1</sup> of energy density, and 1210 W kg<sup>-1</sup> of power density have been demonstrated by electrochemical experiments on doped nanoparticles. Better pseudocapacitance was attributed to the increased number of electroactive sites, improved electrical conductivity, and lower charge transfer resistance of the composite.

### **Author contribution**

BK: conceptualization, methodology, review & editing, supervision. AP and CK: conceptualization, methodology, writing—original draft. DR : review & editing, visualization, formal analysis.

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### **Data availability**

Data sharing is not applicable to this review article as no datasets were generated or analyzed during the current study.

### **Declarations**

### **Conflict of interest**

The authors declare that they have no known conflicts of interest associated with this publication.

Research involving human and animal participants

The research did not involve any human participants

### **Reference:**

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