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Influence of La\textsuperscript{3+} Induced Defects on MnO\textsubscript{2}-Carbon Nanotube Hybrid Electrode for Supercapacitor

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Abstract:

Here we report, the successful coupling of La doped MnO\textsubscript{2} nanorods (30 nm mean diameter and 1 \textmu m mean length) with multiwalled carbon nanotubes (CNTs) via a simple in situ hydrothermal method to form a La\textsuperscript{3+}:MnO\textsubscript{2}-CNT nanohybrid as well as a systematic investigation of the influence of the dopant concentration on its performance as electrode for supercapacitor. X-ray diffraction, electron microscopies and energy dispersive X-ray analysis revealed the formation of MnO\textsubscript{2} nanorods uniformly distributed within the CNT network. The electrochemical measurements revealed a strong positive influence of the La dopants on the performance of the MnO\textsubscript{2}-CNT nanohybrid for up to 2 mol\% La above which the performance degraded. Thus, 2 mol\% La\textsuperscript{3+}:MnO\textsubscript{2}-CNT nanohybrid sample was identified as the best electrode material in this study which exhibited a specific capacitance of \approx 1530 F/g at a current density of 1 A/g along with 92\% charge retention after 5000 cycles which are both much higher than those reported previously using MnO\textsubscript{2} based supercapacitor electrodes and thus, is a leap forward towards using MnO\textsubscript{2} as a low-cost electrode for supercapacitor. The enhanced performance of the optimised 2 mol\% La\textsuperscript{3+}:MnO\textsubscript{2}-CNT nanohybrid originated from the combinatorial influence of the material selection, the optimised concentration of La dopants and the synergistic influence of CNTs that resulted in its lowest charge transfer resistance and highest diffusion coefficient.

Keywords: Supercapacitor electrode; Carbon nanotubes; MnO\textsubscript{2} nanorods; La doping; hydrothermal synthesis;
Introduction:

As the demand for energy storage devices exhibiting high power density rises, research on supercapacitor has received huge attention over the past couple of decades due to its high power output, fast charging or discharging and long cycle life [1]. The combination of these features makes supercapacitor an effective component in modern electronic gadgets, electric vehicles, and industrial power set-ups. Of the two types of supercapacitors, electrical double layer capacitors (EDLCs) store energy on the electrode surface (typically using carbon nanomaterials such as CNTs, graphene, carbon aerogel, activated carbon etc.) whereas pseudocapacitors store it by Faradaic or redox reactions occurring at the electrode-electrolyte interface (typically uses transition metal compounds (TMCs) and conducting polymers)[2,3]. Both EDLCs and pseudocapacitors have their own advantages and disadvantages. Manganese dioxide (MnO$_2$) is a TMC that has been widely investigated as supercapacitor electrode owing to its high theoretical capacitance (1370 F/g), fast and reversible redox reaction, earthabundance, cost-effectiveness and eco-friendly nature [4-7] although its practical use has been limited due to poor electrical conductivity and poor capacity retention after large number of cycles.

In order to overcome these demerits, some researchers have induced artificial defects into the MnO$_2$ lattice by introducing dopants (like Ag, V, B, Fe, Cu and Zn)[8-13] to improve the electrical conductivity of MnO$_2$ but the problem of poor cyclic stability still remained. Due to their good electrical conductivity, mechanical and chemical stability, and large specific surface area, CNTs have found widespread applications [14-16] including in supercapacitors. Some researchers combined MnO$_2$ with multiwalled CNTs (MWCNTs) in order to improve both electrical conductivity and cycle stability of MnO$_2$ [17-23]. These reports showed some improvements in the electrode performance as a result of doping of cations into MnO$_2$ as well as for coupling with CNTs but the value of specific capacitance still did not cross beyond a few hundred F/g. Interestingly, although MnO$_2$ based electrode that is both doped with cations and coupled with CNTs is likely to have high performance due to synergistic influence on the electrical conductivity and cyclic stability, it has not been explored till date.

In view of the above, here we report a systematic investigation of the influence of La$^{3+}$ dopants on the electrochemical performance of MnO$_2$-CNT nanohybrid. A number of doped nanohybrid samples containing different concentrations of dopants were synthesized by a simple and low-cost hydrothermal method and the influence of dopants on their electrochemical performances were compared to identify the optimum dopant concentration.
2. Experimental

2.1 Materials Required

CNTs were procured from NanoAmor Inc., USA, >98% pure manganese sulphate monohydrate (MnSO$_4$.H$_2$O) purity), 99% pure ammonium peroxydisulphate (NH$_4$)$_2$S$_2$O$_8$ (APS) and 97% pure sodium hydroxide pellets (NaOH), were procured from Merck, India. 99.9% pure Lanthanum nitrate hexahydrate (La(NO$_3$)$_3$.6H$_2$O) was procured from Alfa Aesar. Nafion pellets (NR-50) were procured from Sigma Aldrich. All chemicals were used as received by the supplier without any purification.

2.2 Synthesis of MnO$_2$-CNT and La$^{3+}$: MnO$_2$-CNT nanohybrids

First, for the synthesis of MnO$_2$-CNT nanohybrid, 25 mg of CNT was dissolved in 35 mL of doubly distilled water and ultrasonicated for 1 h. 0.1M of MnSO$_4$.H$_2$O was then slowly introduced to the CNT suspension under constant stirring at 500 rpm. After 20 minutes, 35 ml of 0.1M of APS aqueous solution was then added to the MnSO$_4$-CNT suspension and stirred for another 1 h at 800 rpm. After stirring for another 30 min, the resulting solution was transferred to a 100 mL Teflon lined stainless steel autoclave and kept at 140 °C for 24 h followed by a natural cooling step to room temperature. The reaction mixture was subsequently washed with deionised water until pH 7 and filtered followed by a further wash with ethanol to remove any unreacted precursors (Schematic in Figure S1 of Supporting information). The final product was obtained as a powder of undoped MnO$_2$-CNT after drying the filtrate under an infrared lamp and named 0La-MnO$_2$-CNT.

To synthesize La$^{3+}$: MnO$_2$-CNT nanohybrids the same procedure was followed as above along with the addition of an appropriate amount of La(NO$_3$)$_3$.6H$_2$O to MnSO$_4$.H$_2$O-CNT suspension. Several nanohybrid samples were prepared by varying La(NO$_3$)$_3$.6H$_2$O content from 1, 2, 3 and 5 mol% with respect to MnSO$_4$.H$_2$O and named 1La-MnO$_2$-CNT, 2La-MnO$_2$-CNT, 3La-MnO$_2$-CNT and 5La-MnO$_2$-CNT, respectively.

2.3 Characterization Techniques

PANALYTICAL X Pert Pro diffractometer was used to carry out X-ray Diffraction (XRD) measurements for powder samples and Cu K$_\alpha$ radiation (1.5414Å) was employed as X-ray source. Raman spectra were recorded by a Raman Spectrometer (LabRAM HR JobinYvon) using an argon ion laser (514.5 nm) and were calibrated with respect to the position of the Raman shift at 520 cm$^{-1}$ originating from the Si wafer on which the sample was deposited.
Elemental mapping was carried out by using an Oxford Instruments energy-dispersive x-ray (EDX) analyser attached with the field emission scanning electron microscope (FESEM), (Carl Zeiss Supra 55, UK). JEOL 2100 transmission electron microscope was used to collect the high resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) pattern and their analyses were performed with ImageJ software. XPS measurements were carried out at a base pressure of $\sim 6 \times 10^{-8}$ mbar using an unmonochromated Mg K\textalpha radiation giving an overall energy resolution of 1eV. All spectra were calibrated by the position of the Au 4f peak originating from a gold foil in direct contact with the samples. The XPS peaks were fitted using CASA XPS software with a Shirley type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C 1s peak of adventitious carbon at 284.7 eV in accordance with literature.[24-25] The specific surface areas of the samples were estimated from their N2 adsorption isotherms at 77 K recorded using a BET surface analyzer (Nova 1000e, Quantachrome) after the samples were degassed at 300 °C for 3 h. The electrochemical testings were conducted with 1M sodium hydroxide (NaOH) as electrolyte in a three-electrode cell comprising a glassy carbon disc (3 mm dia) as working electrode, an Ag/AgCl as reference electrode and a Pt wire counter electrode using CHI 660E electrochemical workstation, USA. The working electrode was prepared by dropcasting a thick slurry of the active material (92%) and nafion (8% as a binder) dissolved in a mixture of water and isopropanol in 1:1 ratio (5 mg in 1 ml) on the glassy carbon disc followed by air drying. The estimation of diffusion co-efficient values and specific capacitance were carried out using standard literature methods[26]. The active material loading was 0.35 mg/cm².

3. Results and Discussion

3.1 XRD analysis

The XRD pattern of 0La-MnO$_2$-CNT sample presented in Figure 2 shows peaks corresponding to (110), (101), (011), (200), (112), (211), (220), (002) and (301) planes of tetragonal phase of $\beta$-MnO$_2$ (P 42/m n m , $a = 4.39$ Å, $b = 4.39$ Å and $c = 2.87$ Å) in accordance with JCPDS File no. 24-0735. A small peak at $2\theta = 26^\circ$ can be attributed to (002) planes of CNTs in accordance with their small weight fraction. The crystallinity is significantly reduced in the XRD patterns for La$^{3+}$ doped samples as evidenced from the presence of a few weak peaks corresponding to orthogonal phase of $\alpha$-MnO$_2$ (P n m a, $a = 9.32$ Å, $b = 2.85$ Å and $c = 4.46$ Å) in accordance with JCPDS file no 98-001-2177. The change in crystal structure from $\beta$-MnO$_2$ to $\alpha$-MnO$_2$ and the transformation of polycrystalline
\(\beta\)-MnO\(_2\) to nearly amorphous \(\alpha\)-MnO\(_2\) could be due to the mismatch in the ionic radius of La and Mn which is in accordance with previous literature [9].

![Figure 1: XRD pattern of undoped and La\(^{3+}\) MnO\(_2\)-CNT nanohybrid](image)

3.2 Raman Analysis

![Figure 2: Raman spectra of undoped and La doped MnO\(_2\)-CNT (a); Raman spectra showing D band and G band of undoped and La doped MnO\(_2\)-CNT (b).](image)

The Raman spectra of the doped nanohybrids presented in Fig. 2a show an intense peak at 635 cm\(^{-1}\) corresponding to the symmetrical stretching mode of Mn–O\(_8\) vibrational unit, a
Raman active mode for tetragonal structure of $\beta$-MnO$_2$. An additional peak was observed at around 350 cm$^{-1}$ for 3 mol% and 5 mol% La doping (inset of figure 2a) which can be attributed to the $E_{2g}$ band of La(OH)$_3$ [27]. Figure 2a also shows two other intense and sharp peaks at 1580 cm$^{-1}$, and 1351 cm$^{-1}$ due to G and D bands of MWCNT, respectively. [28-29] The G band or graphitic band arises because of in plane vibration of sp$^2$-bonded carbon atoms, whereas the D band arises because of structural defects such as change in bond angle and bondlength that can break the symmetry. The ratio of intensity of D band ($I_D$) to that of G band ($I_G$) is often used as a measure of defects in carbonaceous systems like MWCNT [30-31] and hence these values are also shown in the figure 2b. It is evident that the value of $I_D/I_G$ is increased from its value of 0.75 for undoped sample to about 0.81 upon incorporation of 2 mol% La dopant. Interestingly, further increase in dopant concentration did not cause significant change in this value. This can be understood by considering that at 2 mol% concentration, La$^{3+}$ ions are able to cause sufficient defects on MWCNT structure leading to the increase in the intensity of D band. However, further increase in La concentration cannot cause any further damage to the MWCNTs, as these may form La(OH)$_3$.

3.3 Surface analysis

Figure 3: XPS spectra of Mn 2p of 0La-MnO$_2$-CNT (a); and 2La-MnO$_2$-CNT (b).

XPS was performed on the undoped and 2La-MnO$_2$-CNT nanohybrid samples to identify the surface chemical states of various elements within the nanohybrid samples. The Mn 2p XPS spectra of the undoped MnO$_2$-CNT and 2La-MnO$_2$-CNT samples are presented in Figure 3(a) and (b), respectively whereas the XPS spectra due to all other elements are shown in Figure S2 and S3 of the Supporting information. It is evident from the deconvoluted spectra
presented in Figure 3 that both undoped and doped samples show the presence of a mixed Mn4+ and Mn3+ states in accordance with established literature[32-33]. In addition, for 2La-MnO2-CNT doped sample, the La 3d region showed a broad feature (due to low weight fraction of La) corresponding to La+3 states[34] (Figure S3c of Supporting information).

To assess the influence of dopants on the surface area of the MnO2-CNT nanohybrid, BET sorption isotherms were measured for both the undoped and the 2La-MnO2-CNT samples (Figure S4 of the Supporting information) which revealed a much larger value (99 m²/g) of specific surface area for the 2La-MnO2-CNT nanohybrid sample compared to that of the undoped MnO2-CNT sample (63 m²/g). The increased surface area of the 2La-MnO2-CNT clearly establishes the strong influence of the dopants on the surface area of the nanohybrid which is highly desirable for electrode application as larger surface area is likely to facilitate larger ion adsorption.

3.4 Electron microscopic analysis

![FESEM and elemental maps](image)

Figure 4: FESEM (a), and elemental maps of (b) Mn; (c) C, (d) O for 0La-MnO2-CNT.
FESEM image of the 0La-MnO$_2$-CNT nanohybrid is presented in Figure 4 (a) whereas Figures 4 (b,c,d) show the elemental mapping data as obtained by EDAX. The FESEM image of the 0La-MnO$_2$-CNT nanohybrid shows that MnO$_2$ rod-like structures of diameter 100 nm and 1µm long are anchored within the CNT network. From elemental mapping, it was further confirmed that the rods are indeed made of Mn and O only suggesting that the nanorods are made of MnO$_2$.

Fig. 5(a) represents a typical FESEM image of the 2La-MnO$_2$-CNT nanohybrid which shows that MnO$_2$ rod-like structures (diameter 90 nm and 1.2µm long) are attached to the CNT framework. The elemental mapping data further confirms (Figure 5 (b-e)) the presence of Mn, C, O and La.

![FESEM and EDAX images]( FESEM (a), and elemental maps of (b) Mn;(c) La;(d) C;(e) O for 2La-MnO$_2$-CNT.)

Figure 6(a) shows an image of a single nanorod of 30 nm diameter of α-MnO$_2$, whereas Figure 6(b) shows high resolution lattice resolved image of α-MnO$_2$ nanorods showing presence of (011) planes having $d$ value of 2.40 Angstroms (JCPDS card number 98-001-2177). From the TEM image (Figure 6(a)) it was clearly observed that the nanorods were
bundled together and because of this the average diameter of the nanorods came out to be around 90 nm (Figure 5 (a)). The SAED pattern (Fig. 6(c)) further shows concentric rings corresponding to (011), (210), (211), (402) and (112) planes of α-MnO$_2$ nanorods.

**Figure 6**: (a) TEM image; (b) HRTEM image showing a single 2 mol% La$^{3+}$:MnO$_2$ attached to CNT; (c) SAED pattern of 2La-MnO$_2$-CNT

### 3.5 CV Analysis

Figure 7(a) presents the CV curves obtained from 0La-MnO$_2$-CNT measured at different scan rates (10 mV/s to 200 mV/s) under the voltage window of -0.5 to 0.3 V whereas inset shows the CV curves at low scan rates (1mV/s to 5 mV/s). The rectangular shape of CV curves clearly indicates EDLC behaviour. Along with the presence of a weak pair of redox peaks which confirms the existence of some pseudocapacitance behaviour along with EDLC. The reduction (or cathodic) peak appears at -0.2 V and the oxidation (or anodic) peak appears at -0.1 V is the result of the reversible redox reaction of Mn$^{3+}$ to Mn$^{4+}$ [35]. Upon charging MnO$_2$ is oxidised to MnOOH at the electrode surface while MnOOH is reduced to MnO$_2$ during discharging. The charge storage mechanism of the nanohybrid is based on the surface adsorption of hydroxyl ions (OH$^-$) by the electrode material [36] as given below:

$$MnO_2 + OH^- \leftrightarrow MnOOH + H_2O + e^-$$  \hspace{1cm} (1)

The CV curves presented in figures 7(b-e) were measured using same measurement parameters for 1, 2, 3 and 5 mol% La$^{3+}$ doped MnO$_2$-CNT. With the increase in doping concentration of La, the shape of CV curves becoming more rectangular in shape as compared to that of the 0La-MnO$_2$-CNT which suggests great reversibility in capacitive behaviour for the doped samples. A comparative CV curve at 5 mV/s of all the nanohybridsis
presented in figure 7(f). It can be observed that the CV curve for 2La-MnO$_2$-CNT has the largest enclosed area and thus is expected to exhibit the highest specific capacitance.

Figure 7: CV curves of 0La-MnO$_2$-CNT (a), and various La doped MnO$_2$-CNT hybrids (b-e) at varying scan rates; (insets of a-eshow the curves at low scan rates); (f) Comparative CV curves for all the samples at 5 mV/s scan rate.
From the CV data (at 5 mV/s), the specific capacitances of 342 F/g, 707 F/g, 891 F/g, 594 F/g and 245 F/g for 0La-MnO$_2$-CNT, 1La-MnO$_2$-CNT, 2La-MnO$_2$-CNT, 3La-MnO$_2$-CNT and 5La-MnO$_2$-CNT, were estimated respectively. With the increase in doping concentration up to 2 mol% La, the specific capacitance increases and then decreases beyond 2 mol% which can be ascribed to the increase in the electrical conductivity of MnO$_2$ upon doping up to 2 mol% La. Beyond 2 mol% La doping, there is La(OH)$_3$ formation due to the excess amount of La precursor in the solution mixture during the synthesis process which is in good agreement with the Raman spectra (Figure 3a), XPS studies (Figure S1-S2) and our previous report on La doping [26]. For doping with low concentration (i.e., 2 mol% La), the mechanism is different as it does not form any additional La(OH)$_3$, rather its role is to create artificial defects within the MnO$_2$ lattice to enhance its surface area and electrical conductivity which synergistically improves the electrochemical performance. The specific capacitance of all the electrode materials decreases with the increase in scan rate due to reduced diffusion rates of OH$^-$ ions as the interaction time between the electrolyte ions and active electrode material gets shorter. Thus, only a small portion of the active electrode material takes part in the redox reaction, as a result of which lower specific capacitance values were obtained at high scan rates[26,37]. However, at low scan rates due to the increase in interaction time, the electrolyte ions gets a chance to enter into the pores of the active electrode material due to prolonged exposure. As a result the redox reaction is more efficient at lower scan rates leading to higher values of specific capacitance.

Figure 8: log of peak current ($I_{pc}$) vs log(v) plot (a); and $I_{pc}$ vs $v^{1/2}$ plot (b) of all the samples

The charge storage mechanism can be estimated using the power law, $I = a v^b$, where $b$ value determines the charge storage mechanism. The linear plots of the log ($I_{pa}$) versus log (v) were
generated using (Figure 8(a)) redox peak currents within the scan range 1-200 mV/s for all the samples confirms that the charge storage is controlled by both capacitive (b=1)(EDLC) and semi-infinite diffusion mechanism (b=0.5) (pseudocapacitance) as the ‘b’-value for all the nanohybrids lies in between 0.5-1 [38-42].

With the increase in scan rate, the cathodic ($I_{pc}$) and anodic peak ($I_{pa}$) current also increases and their ratio ($I_{pa}/I_{pc}$) was estimated ~1 indicating reversible redox reaction [43]. Both $I_{pa}$ and $I_{pc}$ are not linearly dependant with the square root of scan rates (figure 8(b)) but fits well with power law as shown in inset of figure 8(b), which represents capacitive behaviour. This further confirms that EDLC is dominant over pseudocapacitance which is consistent with the shape of the CV curves. Higher diffusion coefficient value of $D=4.27 \times 10^{-8}$ cm$^2$/s for the $2\text{La-MnO}_2$-CNT electrode was obtained as compared to that for $0\text{La-MnO}_2$-CNT sample ($D=9.49 \times 10^{-9}$ cm$^2$/s) which can be ascribed to the increase in mobility of electrolyte ions into the active electrode material due to the introduction of La$^{3+}$ dopants. Beyond 2 mol% La doping, the diffusion coefficient was found to decrease which might be due to the of aggregates of amorphous La(OH)$_3$ hindering the diffusion of electrolyte ions into the pores of the electroactive material.[26,44-45].

3.6 GCD Analysis

For $0\text{La-MnO}_2$-CNT and La doped samples the GCD measurements were carried out at different constant current densities ranging from 1 A/g to 5 A/g under the voltage window of -0.5-0.3 V which is presented in figure 9(a). The triangular shape of GCD profiles confirmed the dominance of EDLC behaviour. For $0\text{La-MnO}_2$-CNT nanohybrid the specific capacitance estimated at 1 A/g was 533 F/g which is comparable with that estimated from CV curve at 1 mV/s (515 F/g). The specific capacitance values estimated from CV curve and GCD profile can only be compared if the applied current density in GCD corresponds to that of peak current density obtained in the CV curve. Figure 9(b) presents a comparative GCD profiles of all the samples at constant current density of 1 A/g which shows clearly shows that the charging/discharging time increases with the introduction of La$^{3+}$ dopants upto 2 mol% beyond which it decreases, resulting in lower specific capacitance values for 3% and 5% La doped samples. Specific capacity as high as 1530 F/g was achieved at 1 A/g current density for $2\text{La-MnO}_2$-CNT. Figure 9(c) plots the GCD profiles for $2\text{La-MnO}_2$-CNT at different current densities whereas Figure 9(d) compares the cycling stability of $0\text{La-MnO}_2$-CNT and $2\text{La-}$
MnO$_2$-CNT over 5000 cycles at 5A/g which clearly confirmed the superiority of the 2 mol% La doped sample (92% retention) as compared to that of undoped sample (73%).

Figure 9: GCD profiles of 0La-MnO$_2$-CNT at different constant current densities (a); Comparative GCD profiles of undoped and La$^{3+}$MnO$_2$-CNT nanohybrids at 1 A/g (b); GCD profiles of 2La-MnO$_2$-CNT at 1 A/g (c); Cycle stability of 0La-MnO$_2$-CNT and 2La-MnO$_2$-CNT at 5 A/g upto 5000 cycles (d).

For convenience of the reader, specific capacitance estimated from CV at 5 mV/s and GCD at 1 A/g against doping concentration of La is presented in figure 10. One can see that both CV and GCD measurements confirm 2 mol% as the optimized concentration of La dopants for the best electrode performance. The large difference in the magnitudes of capacitance estimated from the two methods (CV and GCD) is not uncommon in the literature due to the mismatch in current density obtained from CV curve and applied current density to obtain the charge discharge plot.[19,23,33]
**Figure 10:** Specific capacitance vs doping concentration of La from CV curve at 5 mV/s and GCD curve at 1 A/g

### 3.7 EIS analysis

From the Nyquist plot presented in figure (11), the equivalent series resistance (ESR) and charge transfer resistance ($R_{ct}$) were estimated from the intercept and diameter of semi-circle in the Nyquist plot respectively [14,26]. The small changes in ESR values are due to differences in the conductivities caused by the structural variations from electrode to electrode. However, significant change in the $R_{ct}$ values were observed for La doped samples. The $R_{ct}$ values starts decreasing up to 2 mol% La and increases again upon further increase in doping concentration which is possibly due to the formation of amorphous La(OH)$_3$ having high electrical resistivity. It could be observed that though 1 mol% La nanohybrid has slightly higher current density than 3 mol% La, but the $R_{ct}$ value of 1 mol% La is higher than that of 3 mol% La which is possibly due to the occurrence of competing processes of defect induced positive effects and negative influence by formation of amorphous La(OH)$_3$ above 2 mol% La doping. The ESR and $R_{ct}$ values of undoped and La doped MnO$_2$-CNT hybrids are listed in the table 1 which also lists the diffusion coefficients of the nanohybrids as estimated from CV.
Figure 11: EIS spectra of undoped and La$^{3+}$: MnO$_2$-CNT nanohybrids

Table 1: ESR and $R_{ct}$ values for undoped and doped nanohybrids as obtained from the Nyquist plots. Also listed are the diffusion coefficients.

| Electrode Material | ESR ($\Omega$) | $R_{ct}$ ($\Omega$) | Diffusion coefficient (cm$^2$/s) |
|--------------------|----------------|---------------------|----------------------------------|
| 0La-MnO$_2$-CNT    | 3.49           | 33.4                | $9.49 \times 10^{-9}$            |
| 1La-MnO$_2$-CNT    | 1.81           | 23.4                | $3.16 \times 10^{-8}$            |
| 2La-MnO$_2$-CNT    | 1.85           | 15.8                | $4.27 \times 10^{-8}$            |
| 3La-MnO$_2$-CNT    | 1.66           | 16.8                | $2.33 \times 10^{-8}$            |
| 5La-MnO$_2$-CNT    | 1.49           | 24.9                | $9.82 \times 10^{-9}$            |

For better understanding of the reader of the importance of this work, we have compared the results of this work with previously published reports on MnO$_2$ based electrodes in Table 2. It is evident that the nanohybrid synthesized in this work shows much better performance in terms of specific capacitance and cycle stability as compared to the previous reports. The enhanced performance is due to appropriate choice of material combination and synergistic tailoring of the properties such as surface area and electrical conductivity of the optimised 2La-MnO$_2$-MWCNT sample.
Table 2: Comparison of the electrochemical performance of La\(^{3+}:\text{MnO}_2\)-CNT nanohybrids prepared in this work with that of MnO\(_2\) based electrodes reported by other researchers.

| Material          | Brief Synthesis Procedure | Electrolyte          | Specific Capacitance | Capacity retention | Ref |
|-------------------|---------------------------|----------------------|----------------------|--------------------|-----|
| MnO\(_2\)/MWCNT   | Wet Chemical route        | 1M Na\(_2\)SO\(_4\)  | 201 F/g at 1 A/g     | ~10000 cycles     | 17  |
| MnO\(_2\)/MWCNT   | Wet Chemical route        | 6M K\(_2\)SO\(_4\)   | Areal capacitance    | 85% @ 3000 cycles | 18  |
| Amorphous MnO\(_2\)/MWCNT | Wet Chemical route | 1M Na\(_2\)SO\(_4\)  | 145.6 at 5mV/s and 108.5 F/g at 0.7 A/g | ~1400 cycles | 19  |
| MnO\(_2\)/MWCNT core-shell | Hydrothermal @100°C for 12 h | 1M Na\(_2\)SO\(_4\)  | 223 F/g at 10 mV/s  |                  | 20  |
| MnO\(_2\)/MWCNT   | Wet Chemical route        | 1MNa\(_2\)SO\(_4\)   | 106 F/g at 0.5 A/g   | 95% @ 1000 cycles | 21  |
| MnO\(_2\)/MWCNT   | Electrodeposition         | 6M KOH               | 277F/g at 0.5 A/g    | 1000 cycles       | 22  |
| rGO/CNT/ MnO\(_2\) | Hydrothermal @150 °C for 6 h | 1M Na\(_2\)SO\(_4\)  | 319 F/g at 0.5 A/g   | 85% @ 3000 cycles | 23  |
| Ag doped MnO\(_2\) on carbon fiber | Electrochemical deposition | 0.5M Na\(_2\)SO\(_4\) | 825 F/g at 5 mV/s and 815 F/g at 0.5 A/g | ~ 3000 cycles | 46  |
| Ni doped MnO\(_2\)/ Carbon fiber | Carbonization followed by wet chemical route | 1M Na\(_2\)SO\(_4\)  | 445 F/g at 1 A/g     | 93% @ 1000 cycles | 47  |
| B doped MnO\(_2\)/ Carbon fiber | Wet chemical route | 0.5M Na\(_2\)SO\(_4\) | 364.8 F/g at 2 mV/s | 80% @ 1000 cycles | 48  |
| 2La-MnO\(_2\)-CNT nanohybrid | Hydrothermal route | 1M NaOH | 891 F/g at 5 mV/s and 1530 F/g at 1 A/g | 92% @ 5000 cycles | This work |

4. Conclusions

In summary, La\(^{3+}:\text{MnO}_2\)-CNT nanohybrids were prepared using a simple-hydrothermal method for its application as supercapacitor electrode. Several nanohybrids were prepared by varying the concentration of La precursor and the influence of dopant concentration on morphology, crystal structure and electrochemical properties was systematically investigated. XRD and electron microscopy revealed presence of rodlike MnO\(_2\) structures well distributed within the CNT network. The electrochemical studies showed that at 2 mol\% La doping, the 2La-MnO\(_2\)-CNT nanohybrid exhibited the best electrode behaviour with specific capacitance as high as ~1530 F/gm at 1 A/gm current density along with excellent cycle stability (92% retention of specific capacitance after 5000 cycles). The enhanced performance of the optimised 2La-MnO\(_2\)-CNT nanohybrid was ascribed to its lowest charge transfer resistance and highest diffusion coefficient compared to those of other samples containing lower or
higher dopant concentrations. Thus, the results shown in this report establishes 2La-MnO$_2$-CNT nanohybrid as a promising candidate for supercapacitor electrode.

**Conflicts of Interest**

There are no conflicts of interest to declare.

**Supporting Information**

Schematic of synthesis procedure, XPS spectra of C1s, O1s and La 3d$_{3/2}$ of 2 La-MnO$_2$-CNT, BET sorption and Ragone plot of undoped and 2 mol% La doped MnO$_2$-CNT can be found in the supporting information.

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First report of the hydrothermal synthesis 2 mol% La\textsuperscript{3+} doped MnO\textsubscript{2}-CNT nanohybrid exhibited specific capacitance of ~1530 F/g at 1 A/g and 92% capacity retention after 5000 cycles which is much higher than the performance of previous MnO\textsubscript{2} based electrodes.