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# Enhanced capacitive performance of cathodically reduced titania nanotubes pulsed deposited with $\text{Mn}_2\text{O}_3$ as supercapacitor electrode

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A facile and simple pulse electrodeposition method was employed to deposit  $\text{Mn}_2\text{O}_3$  nanoparticles on cathodically reduced titania nanotubes (R-TNTs) at different deposition time in the range of 3–15 min to investigate the influence of mass loading of  $\text{Mn}_2\text{O}_3$  on the electrochemical performance of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  nanocomposite for supercapacitor application.  $\text{Mn}_2\text{O}_3$  nanoparticles were deposited on circumference of R-TNTs as well as in the nanotubes as revealed by FESEM images for all the deposited time. XPS result confirmed the presence of  $\text{MnO}_2$  ( $\text{Mn}^{4+}$ ) and  $\text{MnO}$  ( $\text{Mn}^{2+}$ ) on the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite which provide pseudocapacitive behaviour for the electrode. Mass loading of  $\text{Mn}_2\text{O}_3$  increased linearly with deposition time as confirmed by EDX analysis. The sample deposited for 12 min exhibits the highest areal capacitance of  $51 \text{ mF cm}^{-2}$  (which is 22 times enhancement over R-TNTs) at a current density of  $0.1 \text{ mA cm}^{-2}$  and specific capacitance of  $325 \text{ F g}^{-1}$  at  $6 \text{ A g}^{-1}$ . The sample also show a high-rate capability by retaining 80% of its capacitance even at higher current density of  $30 \text{ A g}^{-1}$ . Interestingly, it retained 98% of the capacitance over 5000 charge discharge cycles at  $10 \text{ A g}^{-1}$  after initial drop to 95% at 200th cycles suggesting an excellent long-term chemical stability. A considerably low equivalent series resistance (ESR) and charge transfer resistance ( $R_{ct}$ ) of  $9.6 \Omega$  and  $0.4 \Omega$  respectively was deduced from electrochemical impedance spectroscopy (EIS) analysis indicating good conductivity and improved charge transfer efficiency of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  nanocomposite.

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## Introduction

There is a rapidly increasing demand for energy conversion and storage devices such as supercapacitors, batteries, and fuel cells due to environmental issues posed by fossil fuels and the appearance of serious energy crisis.<sup>1,2</sup> Supercapacitors have attracted a wide research attention because of their unique properties, such as fast charge–discharge rates and longer cycle life than batteries, and higher energy density than conventional capacitors. Based on their charge–discharge mechanism, supercapacitors can be majorly categorised into electrochemical double layer capacitors (EDLCs) in which charge storage occurs at the electrode–electrolyte interface and pseudocapacitors where charge storage occurs *via* fast and reversible surface reactions.<sup>3–5</sup> In general, carbon-based materials such as graphene, activated carbon, carbon nanotubes (CNTs), are the most employed electrode material in EDLCs whereas metal

oxides such as  $\text{MnO}_2$ ,  $\text{RuO}_2$ ,  $\text{NiO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_2$ ,  $\text{SnO}_2$  are the frequently used materials in pseudocapacitors.<sup>6–14</sup>

Among the pseudocapacitive material,  $\text{MnO}_2$  has attracted a great deal of attention because of its low cost, availability, wide electrochemical potential window, environmentally-friendly and high theoretical capacitance value ( $1370 \text{ F g}^{-1}$ ).<sup>5,15,16</sup> However, the practical capacitance value of  $\text{MnO}_2$  has deviated far from the theoretical value because of its poor electrical conductivity of  $10^{-5}$  to  $10^{-6} \text{ S cm}^{-1}$  and densely packed nonporous structure.<sup>17,18</sup> To overcome this drawback, considerable efforts were devoted to synthesised nanoscale  $\text{MnO}_2$  and incorporate it into a more electrically conductive, stable, and highly surface area nanostructured materials such as CNTs,<sup>19</sup> carbon nanofibers,<sup>20</sup> and titania nanotubes (TNTs).<sup>17</sup>

Highly ordered TNTs synthesized by the electrochemical anodization method, have received great attention due to their simple fabrication method, excellent controllability, high electrical conductivity ( $10^{-5}$  to  $10^{-2} \text{ S cm}^{-1}$ ), good chemical stability, and most importantly it offers an extremely large and solvated ions accessible surface area in addition to acting as a binder-free electrode as well as a substrate to support electroactive materials such as  $\text{MnO}_2$  nanoparticles.<sup>5,16,21</sup>

Deposition of nanosized  $\text{MnO}_2$  onto TNTs have numerous advantages to the electrochemical performance of the  $\text{MnO}_2/\text{TNTs}$  composite. Contrary to the planar substrate, the

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nanotubular structure of TNTs offers unique properties conducive for rapid transfer of electrolytes ions during charge discharge processes in the electrode/electrolyte interface. It also provides an increased electronic and ionic sites that will enhance energy density of the  $\text{MnO}_2/\text{TNTs}$  composite.<sup>4,5</sup>

However, it was established that TNTs suffer from a very low areal capacitance less than  $1 \text{ mF cm}^{-2}$  due to its n-type semiconductor nature.<sup>6</sup> Several strategies have been employed to improve the capacitive performance of the TNTs electrode *via* thermal treatments to change the amorphous phase to anatase or rutile,<sup>22</sup> hydrogenation to increase the donor densities,<sup>23</sup> and electrochemical cathodic polarization to induced oxygen vacancies and reduced  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ .<sup>24</sup> Significant enhancement in the conductivity and capacitance of TNTs have been achieved through these various modifications which make it a suitable substrate or current collector that could serve as an easy path for fast transportation of ions and electrons, resulting in a reduced internal resistance and improved pseudocapacitive performance.<sup>25–27</sup> Thus, attempts on the deposition of  $\text{MnO}_2$  onto the modified TNTs have been made by hydrothermal,<sup>8</sup> sonochemical,<sup>10</sup> and chemical bath deposition,<sup>15,21</sup> these methods involved intensive control conditions such as high temperatures or longer preparation time.

Electrodeposition is advantageous compared to chemical solution methods as a facile, simple, and single step method, it can control the composition and thickness of the thin film with good adhesion to the current collector. Moreover, the desired morphology can be easily controlled by adjusting the deposition parameters.<sup>4,28</sup> For electrodeposition of  $\text{MnO}_2$  onto the TNTs, many studies have focused on potentiostatic (chronoamperometry), galvanostatic (chronopotentiometry) or cyclic voltammetry modes of electrodepositions.<sup>5,19,20,29,30</sup> However, these approaches resulted in the deposition of  $\text{MnO}_2$  species only on the top of the TNTs and in some cases causing the deposits to cover the nanotubes openings. This leads to non-utilization of the entire surface of the nanotubes which result in low coverage and specific capacitance values.<sup>4,31</sup> Pulse electrodeposition (PED) is another mode of electrodeposition that is considered as a useful technique for the synthesis of novel electroactive materials.<sup>32</sup> Smooth, homogenous, and uniform deposits along the elongated tube walls can be obtained by this technique. The physico-chemical properties of materials (such as morphology, electrical conductivity, porosity, adhesion, and compound content) can be controlled through modifying pulse parameters.<sup>12</sup> Zhou *et al.*<sup>3</sup> reported pulse current electrodeposition of  $\text{MnO}_2$  onto cathodically polarized TNTs with the deposit along the nanotubes wall has achieved a specific capacitance of  $425 \text{ F g}^{-1}$ . Samsudin *et al.*<sup>13</sup> have successfully deposited  $\text{Mn}_2\text{O}_3$  onto reduced TNTs *via* the reverse pulse potential electrodeposition with areal capacitance of  $18.32 \text{ mF cm}^{-2}$ .

In this study, PED was employed to deposit  $\text{Mn}_2\text{O}_3$  nanoparticles onto the R-TNTs. The influence of deposition time on the mass loading of  $\text{Mn}_2\text{O}_3$  on R-TNTs which in turn affects the morphology and electrochemical performance of the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite as electrode in supercapacitor application has been investigated. To specifically demonstrate the role of TNTs in electrochemical performance of the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite,  $\text{Mn}_2\text{O}_3$  was also deposited on the planar Ti foil without the nanotubes.

## Materials and methods

### Preparation of reduced titania nanotubes (R-TNTs)

Titanium foil (0.25 mm thickness, 99.7% purity, Sigma Aldrich) was cut into  $1 \times 1 \text{ cm}^2$  and cleaned by series of sonication in acetone, isopropanol and deionized (DI) water, for 15 min each followed by chemical etching in 3 M  $\text{HNO}_3$  (65%, MERCK) for 10 min, and finally rinsed with excess DI water and dried in air. The synthesis of TNTs by anodization was conducted in two-electrode electrochemical cell with titanium foil as the anode and high-density graphite as the cathode at room temperature. The electrolyte used was a mixture of glycerol (99.8% purity, initial water content 0.03 wt%, Fisher Scientific), 0.5 wt%  $\text{NH}_4\text{F}$  (FLUKA) and 25 v/v% water. The anodization was carried out at constant voltage of 30 V for 1 h using a DC power supply (Consort Mini, Cleaver Scientific Ltd). A distance of 2 cm was maintained between the two electrodes in all the experiments. Immediately after the anodization, the samples were rinsed with DI water, dried in air, and then calcined at  $500^\circ\text{C}$  under air atmosphere for 2 h at a heating rate of  $2^\circ\text{C min}^{-1}$ . Electrochemical reduction of the sample was conducted in the same electrochemical cell with the anodized sample as the cathode and high-density graphite as anode in 0.5 M  $\text{Na}_2\text{SO}_4$  solution as supporting electrolyte at constant voltage of 5 V for 30 s. The sample was rinsed with DI water and dried at room temperature.

### Preparation of $\text{Mn}_2\text{O}_3/\text{R-TNTs}$

PED mode was used for deposition of  $\text{Mn}_2\text{O}_3$  onto the R-TNTs. This was conducted in a three-electrode electrochemical cell by employing R-TNTs, Ag/AgCl (3 M KCl) and Pt wire as working, reference and counter electrode respectively using potentiostat-galvanostat (Autolab PGSTAT204/FRA32M module). 5 mM  $\text{MnSO}_4$  containing 40 mM  $\text{Na}_2\text{SO}_4$  was used as deposition electrolyte. Prior to the PED, cyclic voltammetry of the electrolyte was run from  $-1.0 \text{ V}$  to  $1.0 \text{ V}$  to determine the deposition potential of the  $\text{Mn}_2\text{O}_3$ . In the PED, one pulse consisted of applying a cathodic potential of  $-0.6 \text{ V}$  for 1 s and  $-0.2 \text{ V}$  for 9 s representing 10% duty cycle. The deposition was conducted for 3, 6, 9, 12 and 15 min and finally the samples were dried in an oven at  $80^\circ\text{C}$ .

### Material characterization and electrochemical measurements

The morphology and microstructure of the prepared samples were examined by field emission scanning electron microscopy (FESEM, JSM-7600F, JOEL, Japan) equipped with an energy dispersive X-ray spectrometer (EDS). Phase identification and chemical states of the samples were investigated using X-ray diffraction (XRD, Shimadzu, D60000, Japan) with  $\text{Cu K}_\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation and X-ray photoelectron spectroscopy (XPS, PHI Quantera II) respectively. The electrochemical performance of the electrode was investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and EIS using a conventional three-electrode cell (Auto lab PGSTAT204/FRA32M) in 1 M KCl aqueous solution as electrolyte at room temperature. EIS was conducted at open circuit potential (OPC) in the frequency range of 0.01 Hz to 1 MHz with a perturbation amplitude of

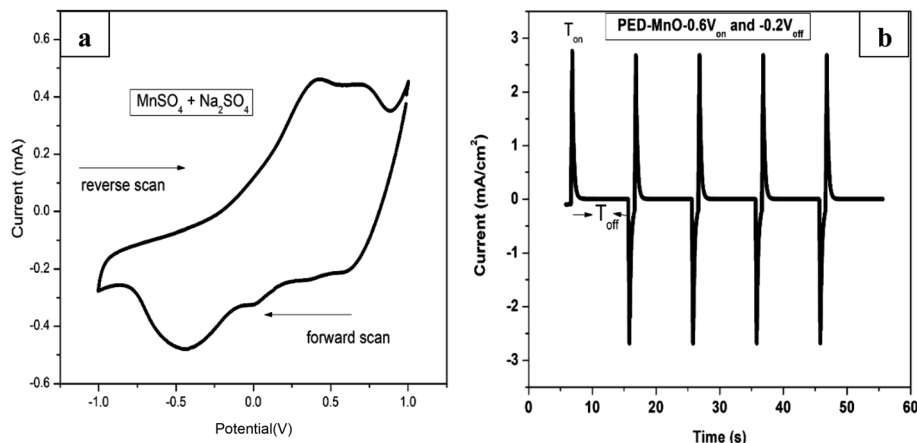


Fig. 1 (a) Cyclic voltammogram of  $\text{MnSO}_4$  containing  $\text{Na}_2\text{SO}_4$  at a scan rate of  $20 \text{ mV s}^{-1}$  (b) the output of pulse deposition graph for a few selected cycles.

5 mV. The areal capacitance ( $C_A$ ) and specific capacitance (SC) of the samples was calculated based on the GCD curves using eqn (1) and (2), respectively:<sup>4,33</sup>

$$C_A = \frac{I\Delta t}{\Delta EA} \quad (\text{F cm}^{-2}) \quad (1)$$

$$SC = \frac{I\Delta t}{\Delta Em} \quad (\text{F g}^{-1}) \quad (2)$$

where  $I$  is the discharge current in amperes,  $\Delta t$  is the discharge time in seconds,  $\Delta E$  is the difference in discharge voltage in volts,  $A$  is the area of the active electrode in  $\text{cm}^2$  and  $m$  is the mass of the active electrode material in gram.

## Results and discussion

Fig. 1a shows a CV voltammogram for  $\text{MnSO}_4$  containing  $\text{Na}_2\text{SO}_4$  swept from  $-1.0$  to  $1.0 \text{ V}$  at a scan rate of  $20 \text{ mV s}^{-1}$ . A broad reduction peak on the forward scan with a maximum cathodic current at around  $-0.5 \text{ V}$  is associated with the deposition of Mn. Meanwhile on the reverse scan, the highest anodic peak was observed at around  $0.40 \text{ V}$  which is due to the dissolution of the Mn. Based on the cathodic reduction peak from the CV,  $-0.6 \text{ V}$  was selected as the deposition potential ( $V_{\text{on}}$ ) of Mn. On the other hand, the dissolution potentials ( $V_{\text{off}}$ ) applied was  $-0.2 \text{ V}$  which is the onset of Mn dissolution corresponding to zero current. Fig. 1b presents a few selected pulses from PED experiment.

### Morphology and composition analyses

Phase identification and elemental composition of the prepared samples were investigated by XRD and XPS. Fig. 2a shows the XRD patterns of TNTs, R-TNTs, and  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  samples. Peaks at around  $35.1^\circ$ ,  $38.4^\circ$ ,  $40.2^\circ$ ,  $53.2^\circ$ ,  $63.0^\circ$ ,  $71.0^\circ$ ,  $76.2^\circ$  and  $77.4^\circ$  corresponding to hexagonal Ti substrate (JCPDS: 00-044-1294) and peaks at  $25.7^\circ$  and  $48.5^\circ$  which are indexed to (101) and (200) planes of pure anatase phase (JCPDS: 01-075-1537) were found in all the samples. After cathodic reduction, the XRD pattern of the R-TNTs remained the same as the calcined TNTs with slight increment in the intensity of anatase peak. No prominent peak corresponding to the  $\text{Mn}_2\text{O}_3$  was observed which may be ascribed to the dominant peaks from the substrate (R-TNTs) which retained its crystalline phase as reported elsewhere.<sup>15,21,27</sup>

$\text{Mn}_2\text{O}_3/\text{R-TNTs}$  sample was further characterized by XPS, the survey spectra of the sample depicted in Fig. 2b indicates the presence of four elements (Ti, O, Mn, C) in the sample. The Mn 2p spectra in Fig. 2c shows the presence of two spin-orbit doublets, where one pair of peaks at  $640.8$  and  $651.9 \text{ eV}$  are associated with  $2p_{3/2}$  and  $2p_{1/2}$  spectra of MnO, another pair of peaks centred at  $642.2$  and  $653.4 \text{ eV}$  are associated with  $2p_{3/2}$ , and  $2p_{1/2}$  spectra of  $\text{MnO}_2$ , respectively.<sup>15,18,30,34</sup> This confirmed that there are two types of Mn oxidation states ( $\text{Mn}^{2+}$  &  $\text{Mn}^{4+}$ ) in the sample as reported elsewhere.<sup>35–38</sup> The peak at around  $646 \text{ eV}$  could be assigned to MnO satellite feature.<sup>14</sup> To confirm the variation of oxidation state of Mn during redox reaction, the O 1s core level spectra was analysed. The O1s spectra deconvoluted into three peaks as shown in Fig. 2d, at around  $529.1$ ,

$$\text{Oxidation state} = \frac{[(IV(\text{SMn} - \text{O} - \text{Mn} - \text{SMn} - \text{OH})) + (III(\text{SMn} - \text{OH}))]}{\text{SMn} - \text{O} - \text{Mn}} \quad (3)$$



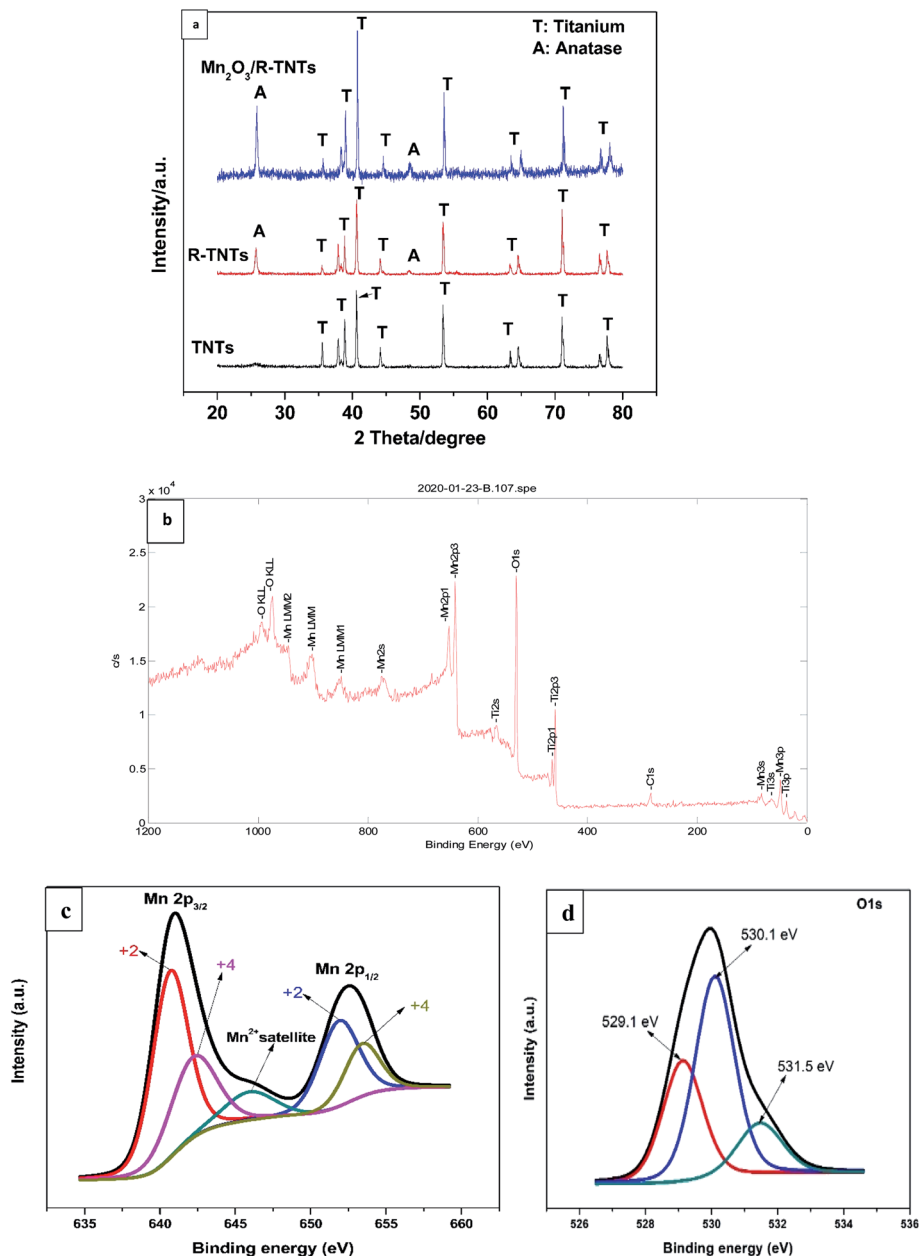
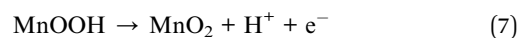


Fig. 2 (a) XRD pattern of TNTs, R-TNTs, and  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$ . XPS spectra of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  (b) survey spectra (c) Mn 2p and (d) O 1s spectra.

530.1 and 531.5 eV which can be attributed to Mn–O–Mn, Mn–OH, and H–O–H bonds signals, respectively.<sup>32,39</sup> The oxidation state of Mn can be determined from the intensities of Mn–O–Mn and Mn–OH signals by the following equation.<sup>40</sup> where S is the bond corresponding to the signals from O 1s spectra. The average Mn oxidation state obtained from the equation is 2.99 (~3) for  $\text{Mn}_2\text{O}_3$  nanoparticles. From this, the overall oxidation states of Mn are  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . The possible synthesis mechanisms of  $\text{Mn}_2\text{O}_3$  by PED involved reduction and oxidation reactions during the  $V_{\text{on}}$  and  $V_{\text{off}}$ . In the first pulse cycle,  $\text{Mn}^{2+}$  is reduced when  $V_{\text{on}}$  is applied to the system, as below:



During  $V_{\text{off}}$ , the remaining  $\text{Mn}^{2+}$  in the solution is oxidized to  $\text{Mn}^{3+}$  and subsequently, the metastable  $\text{Mn}^{3+}$  is transformed into an intermediate  $\text{MnOOH}$  by hydrolysis. Consequently,  $\text{MnOOH}$  is oxidized to  $\text{MnO}_2$ .



As the pulse cycle continues,  $\text{MnO}_2$  may be reduced to intermediate product  $\text{MnOOH}$  and further to  $\text{MnO}$ . But  $\text{MnO}$  is



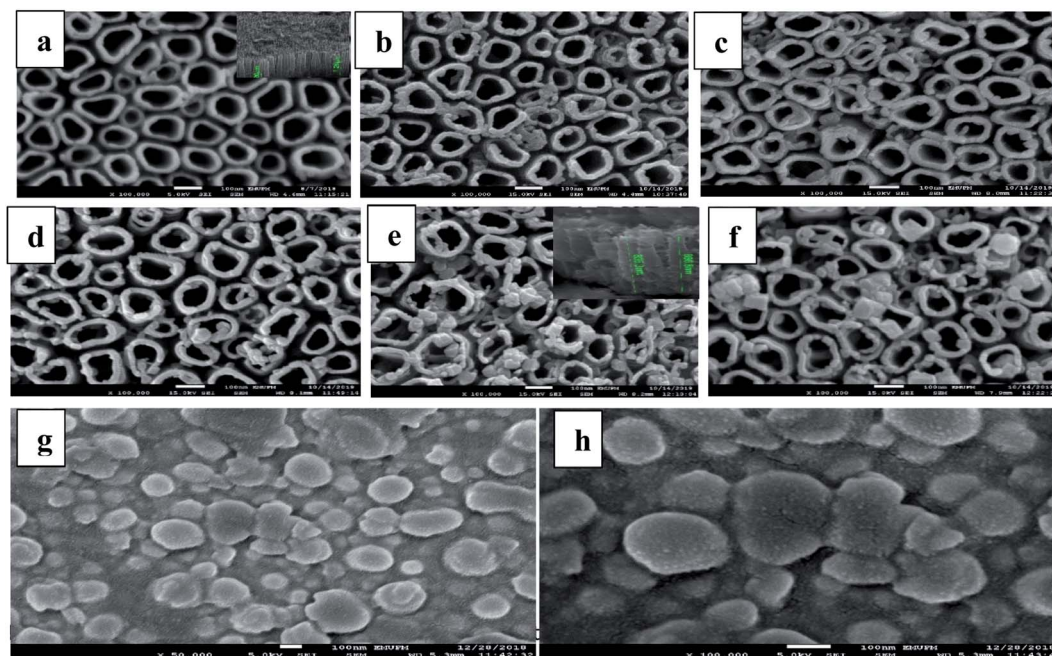


Fig. 3 Top view FESEM images of (a) R-TNTs and cross-sectional view (inset), and  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  electrodeposited at (b) 3 min, (c) 6 min, (d) 9 min, (e) 12 min (inset is cross-sectional view) and (f) 15 min.  $\text{Mn}_2\text{O}_3$  deposited on Ti foil for 12 min (g) lower magnification, and (h) higher magnification.

unstable in the presence of oxygen and combine with  $\text{MnO}_2$  to form  $\text{Mn}_2\text{O}_3$ .

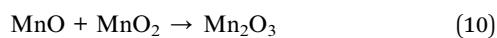


Fig. 3a presents the FESEM images of R-TNTs with average inner diameter, wall thickness and tube length (inset) of 86 nm, 21 nm and 1.2  $\mu\text{m}$ , respectively.  $\text{Mn}_2\text{O}_3$  was successfully deposited onto the circumference as well as inside the R-TNTs for all the deposition times investigated as shown in Fig. 3b–f. The distinctive change in surface morphology before and after electrodeposition of  $\text{Mn}_2\text{O}_3$  can be clearly observed. Obviously, as the deposition time increased the inner diameter of the nanotubes decreases while the wall thickness increases. The tube length become shorter after electrodeposition, for example at 12 min deposition time the average tube length is 850 nm. This may be due to the dense deposit of  $\text{Mn}_2\text{O}_3$  formed on the nanotube circumference as the amount and size of  $\text{Mn}_2\text{O}_3$  deposit increased with deposition time. For comparison,  $\text{Mn}_2\text{O}_3$  was deposited on planar Ti for 12 min. As seen in Fig. 3g and h, the morphology and dimension of  $\text{Mn}_2\text{O}_3$  is comparable to the one deposited on top of R-TNTs at 12 min deposition time even though the shape and structure of  $\text{Mn}_2\text{O}_3$  deposits are more visible on the planar Ti. However, more uniform distribution of  $\text{Mn}_2\text{O}_3$  deposits was obtained on R-TNTs as compared to Ti. This can be ascribed to the nanotubular structure of larger surface area that provides more nucleation sites than the Ti

substrate. EDX analysis of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  samples deposited at different times revealed the presence of four elements (Ti, O, C, Mn) in the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite as confirmed by the XPS. The amount of each element in weight% is presented in Table 1.

The carbon present in the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  sample is from the residual of glycerol used in anodization. The amount of Mn increases as the deposition time is increased as shown in Table 1. This is because of more pulse deposition cycles are applied as deposition time increases which leads to the increase in the amount of Mn deposits.

### Electrochemical measurements

The electrochemical measurements of all the synthesised samples were conducted in 1 M KCl within the potential window of 0.0 to 0.8 V vs. Ag/AgCl. The CV profiles for R-TNTs recorded at different scan rates are displayed in Fig. 4a. It shows a symmetrical rectangular curves at all the scan rate measured and maintained the same shape even at high scan

Table 1 Elemental analysis for  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  as a function of deposition time

Deposition time (min)	Weight%			
	C	O	Ti	Mn
3	3.25	46.85	48.18	1.71
6	3.13	52.36	41.93	2.58
9	5.48	51.70	39.40	3.42
12	3.37	51.93	38.80	5.90
15	4.04	52.10	35.96	7.90



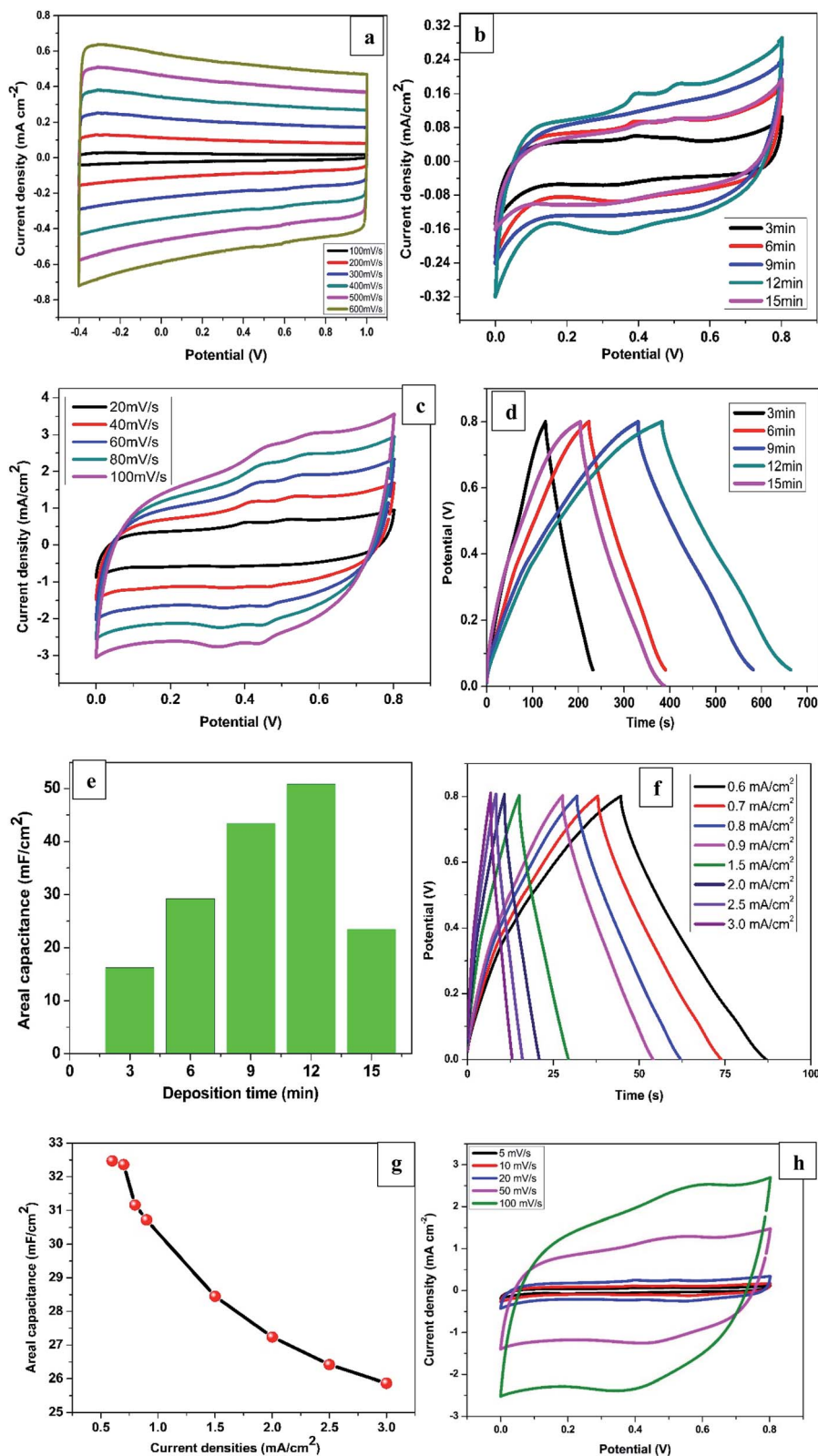


Fig. 4 CV curves of (a) R-TNTs at different scan rate,  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  (b) at different deposition time (c) as a function of scan rate for  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  synthesised for 12 min. (d) GCD curves of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  at different deposition time. (e) Areal capacitance as a function of deposition time. (f) GCD curves of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  synthesised for 12 min at different current densities, (g) areal capacitance as a function of current densities and (h) CV curves of  $\text{Mn}_2\text{O}_3/\text{Ti}$  at different scan rate.

rate of  $600 \text{ mV s}^{-1}$ . This is a typical characteristics of EDLC that exhibits excellent reversibility. The areal capacitance of R-TNTs evaluated at  $100 \text{ mV s}^{-1}$  is  $3.82 \text{ mF cm}^{-2}$ . The CV curves of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  synthesised at different deposition time, measured at a scan rate of  $5 \text{ mV s}^{-1}$  are presented in Fig. 4b. All the cyclic voltammograms display near symmetrical rectangular shape, which is a typical of a mixture of EDLC and pseudocapacitive behaviour of the electrodes. The redox waves are obvious at 0.35, 0.40 and 0.52 V were due to the transition between  $\text{Mn}^{4+}/\text{Mn}^{2+}$  on the surface of the electrode.<sup>26,37</sup> The presence of both ions was confirmed by XPS. The  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  sample synthesised for 12 min shows higher integrated area and current response than the other samples which implies higher capacitive performance, therefore, was selected for further evaluation. CV at varying scan rates from  $20 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$  was performed as shown in Fig. 4c. The CV curves show an increased current density with the increase in scan rate, indicating the quasi-reversibility of the redox reactions and thus excellent capacitive behaviour. Even at high scan rate of  $100 \text{ mV s}^{-1}$  it still retains its shape and symmetry, indicating good ions diffusion into the electrode material from the electrolyte.

To further confirmed the capacitive performance of the samples, GCD measurement was performed at current density of  $0.1 \text{ mA cm}^{-2}$  as presented in Fig. 4d. All the GCD curves are linear and triangular suggesting good capacitive behaviour and coulombic efficiency. The sample synthesised for 12 min shows a longer discharging time indicating a higher capacitive performance which agrees with the result from the CV

measurement. The areal capacitance as a function of deposition time is shown in Fig. 4e. The value increases from  $16.2 \text{ mF cm}^{-2}$  to  $50.8 \text{ mF cm}^{-2}$  as deposition time was increased from 3 min to 12 min due to the increase in mass loading of the  $\text{Mn}_2\text{O}_3$  as confirmed by EDX. However, the areal capacitance for a sample synthesised for 15 min decreased by more than half ( $23.5 \text{ mF cm}^{-2}$ ) despite an increase in  $\text{Mn}_2\text{O}_3$  mass loading. This can be ascribed to the increase in size of Mn deposits at 15 min deposition time which leads to partial coverage of nanotubes openings thereby reducing the electrolyte ions diffusion into the film.<sup>13</sup>

Fig. 4f displays the GCD curves of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  synthesised for 12 min at different current densities. The GCD curves retained its shape even at high current density of  $3.0 \text{ mA cm}^{-2}$  with small IR drop ( $0.08 \text{ V}$ ) indicating excellent capacitive behaviour and good reversibility.<sup>41</sup>

Interestingly, the sample retained about 80% of the initial capacitance even at high current density of  $3.0 \text{ mA cm}^{-2}$  proving high-rate capability.<sup>21,28</sup> The areal capacitance as a function of current densities are depicted in Fig. 4g, the decrease in capacitance at higher current densities is as a result of inability of the electrolyte ions to fully accessed the electrode material.<sup>15</sup>

Fig. 4h displayed the CV curves at different scan rates for  $\text{Mn}_2\text{O}_3$  deposited on planar Ti substrate for 12 min to further study the role of the nanotubes in electrochemical performance of the  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite. The areal capacitance of the sample measured at a scan rate of  $5 \text{ mV s}^{-1}$  is  $35.51 \text{ mF cm}^{-2}$  which is about 30% decrease in capacitance compared to the same sample deposited on R-TNTs. This indicates a superior capacitive

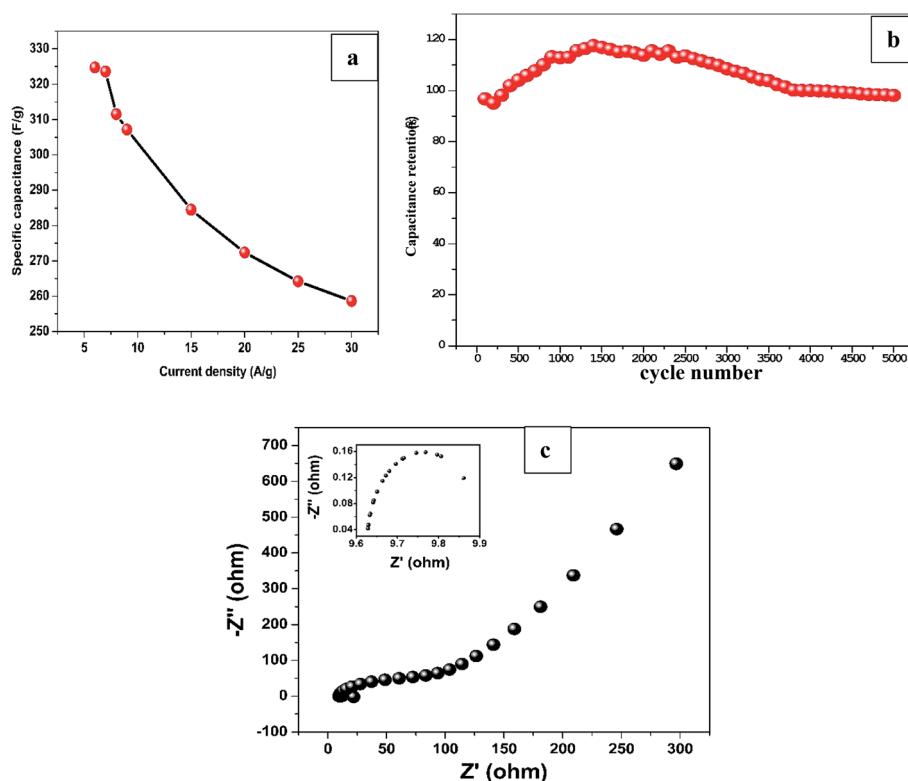


Fig. 5 (a) Specific capacitance of  $\text{Mn}_3\text{O}_4/\text{R-TNTs-12}$  as a function of current density. (b) Cyclic stability of  $\text{Mn}_3\text{O}_4/\text{R-TNTs-12}$  over 5000 cycles at  $1 \text{ mA cm}^{-2}$ . (c) Nyquist plot of  $\text{Mn}_3\text{O}_4/\text{R-TNTs-12}$  with inset showing magnified high frequency region.



performance due to the nanotubular channels that enhanced diffusion of electrolytes ions to the current collector. Furthermore, the CV curve at higher scan rate of  $100 \text{ mV s}^{-1}$  for  $\text{Mn}_2\text{O}_3/\text{Ti}$  deviated slightly from rectangular compared to  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  sample measured at the same scan rate. This can be attributed to good reversibility of the sample due to the rapid electrons transfer across electrode/electrolytes interface as reported elsewhere.<sup>16</sup>

On the other hand, specific capacitance based on the mass of  $\text{Mn}_2\text{O}_3$  obtained by average weight difference using analytical balance (0.1 mg accuracy) before and after electrodeposition for 12 min was evaluated at different current densities. The specific capacitance decreased from  $324.7 \text{ F g}^{-1}$  at  $6 \text{ A g}^{-1}$  to  $258.7 \text{ F g}^{-1}$  at  $30 \text{ A g}^{-1}$  as shown in Fig. 5a. The values are greater than most of the previously reported capacitances for  $\text{Mn}_x\text{O}_x$  for different composite materials as shown in Table 2.

**Table 2** A comparison of electrochemical performance of various  $\text{MnO}_2$  and its composites materials as electrode for supercapacitor

Material	Preparation method	Areal/specific capacitance	Current density/scan rate	Electrolyte	Capacitance retention	Ref.
Graphene/CNT/ $\text{MnO}_x$	Dispersion & hydrothermal	$210 \text{ F g}^{-1}$	Not mentioned	1 M $\text{Na}_2\text{SO}_4$	91% after 1000 cycles	2
$\text{MnO}_2$ nanoparticles	Precipitation method	$250 \text{ F g}^{-1}$	$1 \text{ mA cm}^{-2}$	1 M $\text{Ca}(\text{NO}_3)_2$	67% after 1000 cycles	17
$\text{Mn}_3\text{O}_4$ nanoparticles	Cathodic electrodeposition	$416 \text{ F g}^{-1}$	$1 \text{ A g}^{-1}$	1 M NaOH	47.1% after 1000 cycles	15
$\text{MnO}_2/\text{PEDOT}$	Anodic electrodeposition	$159 \text{ F g}^{-1}$	$5 \text{ mV s}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	91% after 500 cycles	45
$\text{TiO}_2@\text{MnO}_2$	Hydrothermal	$320 \text{ mF cm}^{-2}$	$2 \text{ mA cm}^{-2}$	1 M $\text{Na}_2\text{SO}_4$	17.7% after 1000 cycles	18
$\text{MnO}_2\text{-TNTAs}$	Galvanostatic electrodeposition	$40.4 \text{ mF cm}^{-2}$	$0.032 \text{ mA cm}^{-2}$	0.1 M KOH	85.6% after 100 cycles	19
$\text{MnO}_2\text{-TiO}_2$	SCBD	$175 \text{ mF cm}^{-2}$	$10 \text{ mV s}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	82.5% after 1000 cycles	16
$\text{MnO}_2\text{-TNTAs}$	Pulse current electrodeposition	$425 \text{ F g}^{-1}$	$0.5 \text{ A g}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	71.4% after 3000 cycles	3
PPy/ $\text{MnO}_2$	Cyclic voltammetry	$596.3 \text{ F g}^{-1}$	$0.5 \text{ A g}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	87.6% after 1000 cycles	20
$\text{TiO}_2@\text{MnO}_2$	Hydrothermal	$22.19 \text{ mF cm}^{-2}$	$5 \text{ mV s}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	85% after 4000 cycles	21
$\text{MnO}_2/\text{GA}$	Potentiostatic electrodeposition	$410 \text{ F g}^{-1}$	$2 \text{ mV s}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	95% after 50 000 cycles	22
$\text{MnO}_2$ nanoparticles	Pulse current electrodeposition	$290 \text{ F g}^{-1}$	$5 \text{ mV s}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	72% after 250 cycles	11
$\text{Mn}_2\text{O}_3$ nanoparticles	Pulsed laser deposition	$210 \text{ F g}^{-1}$	$1 \text{ mV s}^{-1}$	0.1 M $\text{Na}_2\text{SO}_4$	Not mentioned	46
$\text{MnO}_2\text{-TiO}_2$ NTs	SILAR	$436.2 \text{ mF cm}^{-2}$	$0.1 \text{ mA cm}^{-2}$	0.5 M $\text{Na}_2\text{SO}_4$	85.7% after 3000 cycles	5
$\text{MnO}_2$ microspheres	Solvothermal	$190 \text{ F g}^{-1}$	$0.5 \text{ A g}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	~100% after 1000 cycles	47
$\text{MnO}_x/\text{TiO}_2/\text{CFP}$	Galvanostatic electrodeposition	$327 \text{ mF cm}^{-2}$	$0.25 \text{ mA cm}^{-2}$	1 M $\text{Na}_2\text{SO}_4$	96% after 5000 cycles	23
$\text{MnO}_2\text{-TNT}$	Sono-chemical	$65 \text{ mF cm}^{-2}$	$1 \text{ mV s}^{-1}$	1 M KCl	95% after 2500 cycles	10
$\text{MnO}_2/\text{C}$	Dispersion	$205 \text{ F g}^{-1}$	$50 \text{ mV s}^{-1}$	2 M NaCl & 0.5 M TBAP/ACN	98% after 300 cycles	24
$\text{MnO}_x\text{-CDGs}$	Sonication & chemical reduction	$280 \text{ F g}^{-1}$	$1 \text{ A g}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	94.7% after 10 000 cycles	48
$\text{MnO}_2/\text{AC}$	Grafting oxidation	$332.6 \text{ F g}^{-1}$	$2 \text{ mV s}^{-1}$	0.5 M $\text{Na}_2\text{SO}_4$	87% after 2000 cycles	25
CQDs/ $\text{MnO}_2$	Sono-chemical	$210 \text{ F g}^{-1}$	$20 \text{ A g}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	90.3% after 10 000 cycles	49
$\text{MnO}_2$ microspheres	Ultrasonic spray pyrolysis	$320 \text{ F g}^{-1}$	$2.5 \text{ mA cm}^{-2}$	1 M LiClO	98% after 1000 cycles	50
H- $\text{TiO}_2/\text{C}/\text{MnO}_2$	Hydrothermal	$299.8 \text{ F g}^{-1}$	$0.5 \text{ A g}^{-1}$	1 M $\text{Na}_2\text{SO}_4$	87% after 2000 cycles	8
$\text{Mn}_2\text{O}_3/\text{R-TNTs}$	Pulse reverse electrodeposition	$18.32 \text{ mF cm}^{-2}$	$0.1 \text{ mA cm}^{-2}$	1 M KCl	Not mentioned	13
$\text{MnO}_x$	Pulse current electrodeposition	$252 \text{ F g}^{-1}$	$10 \text{ mV s}^{-1}$	3 M KCl	Not mentioned	12
$\text{Mn}_2\text{O}_3/\text{R-TNTs}$	Pulse electrodeposition	$324.72 \text{ F g}^{-1}$	$6 \text{ A g}^{-1}$	1 M KCl	98% after 5000 cycles	Present work





To evaluate long-term cycling stability of the sample, GCD test was performed at  $1 \text{ mA cm}^{-2}$  which is  $\sim 10 \text{ A g}^{-1}$  current density for 5000 cycles as shown in Fig. 5b. The GCD curves maintained its triangular shape even at 5000th cycle demonstrating excellent capacitive performance and superior reversibility. The sample retained 98% of the capacitance at the end of 5000 cycles after initial decrease to 95% at  $\sim 200$ th cycle which can be ascribed to the surface activation of the nanostructured material in the electrode induced by electrolyte ions penetration.<sup>42,43</sup>

EIS was conducted to explore the kinetic properties of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  electrode as represented by a Nyquist plot in Fig. 5c. The intercept at real axis at high frequency region represents equivalent series resistance (ESR) which corresponds to the combination of bulk electrolyte resistance, contact resistance at the interface between current collector and active material and internal resistance of the active material. At mid frequency region, the diameter of the semicircle (shown as inset in Fig. 5c) represents the charge transfer resistance ( $R_{\text{ct}}$ ) at the electroactive material/electrolyte interface, while the linear part at low frequency region corresponds to the combination of ion diffusion from electrolyte to the active material and accumulation of charges at the electrode surface.<sup>20,44</sup> The sample exhibits ESR and  $R_{\text{ct}}$  of  $9.6 \Omega$  and  $0.4 \Omega$  respectively, these considerably low resistance values indicate improved conductivity and charge storage capability of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  sample.

## Conclusion

A facile and cost-effective PED method was successfully used to deposit  $\text{Mn}_2\text{O}_3$  nanoparticles onto R-TNTs at different deposition time to investigate the mass loading of  $\text{Mn}_2\text{O}_3$  and its effect on the electrochemical performance of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$ .  $\text{Mn}_2\text{O}_3$  nanoparticles have been uniformly deposited at the nanotubes circumference as shown by FESEM images which allowed for maximum utilization of the nanotubes surface area as pathway for ion diffusion across the current collector–electrolyte interface. The sample exhibited superior capacitive performance over the  $\text{Mn}_2\text{O}_3$  deposited on planar Ti at the same deposition time. The mass loading and size of  $\text{Mn}_2\text{O}_3$  deposits for  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  increased with increase in deposition time as revealed by EDX and FESEM analysis, respectively. However, the sample deposited for 12 min recorded the highest capacitance. CV and GCD measurement at different scan rates and current densities revealed pseudocapacitive characteristics, excellent rate capability and good reversibility of  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  and interestingly, a superior stability of 98% retention over 5000 long-term charging discharging cycles with considerably low ESR and  $R_{\text{ct}}$  values as deduced from EIS analysis. Therefore, these good electrochemical properties suggest that  $\text{Mn}_2\text{O}_3/\text{R-TNTs}$  composite can serve as a potential electrode for supercapacitor application.

## Conflicts of interest

There are no conflicts to declare.

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