

MnO₂ as Super capacitor Material: A Comprehensive Review of Its Electrochemical Behaviour

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Abstract:

Thus MnO₂ is considered a suitable candidate for use as an electrode material in supercapacitors due to its low cost, high capacitance and non-toxicity to the environment. During the charge-discharge process, MnO₂ dissolve and hence it has low specific capacitance and it rarely in circulate in practice. In this study, diverse MnO₂ and MnO₂-based composites having distinct structures and their electrochemical properties, and synthesis techniques, have been well elaborated. Additionally, prospects for composites based MnO₂ have been given Further, directions for the creation of MnO₂-based composites have been discussed.

Keywords — MnO₂, Supercapacitors, Electrode material, High capacitance, Synthesis techniques, Electrochemical properties.

I. INTRODUCTION

Today, energy storage systems are expanding rapidly with the advancement of new technologies such as mobile devices that require fast charging, and battery electric vehicle (BEV) [. In this regard, supercapacitors have been paid much attention as a new electrochemical energy storage devices being intermediate between the DLC and secondary batteries. Among the many advantages, they possess a high power density, energy density as well as cycle life to which credit can be given [2]. It can be easily inferred from the equation that how well a particular device performs in the role of a supercapacitor is largely determined by the properties of the materials of the electrodes which it is made of. Oscillating between the charges that it holds, a supercapacitor's charging and discharging usually dictate how it can be classified into two types. Among them, there is one type of well-known EDLCs which uses the adsorption of ions on the surface of the active electrode material. The second is pseudocapacitors that charge energy through the ion adsorption and

desorption through reversible electrochemical means [3]. Thereafter, EDLCs possess lower values of power densities and cycling stability as compared to the pseudocapacitors which evidenced superior specific capacitance and energy densities. By achieving a high specific capacitance, the researchers focused on materials with pseudocapacitive characteristics. Various transition metal oxides have been synthesized for application as electrode materials up to the present time; RuO₂[4], TiO₂[5], SnO₂[6], V₂O₅[7], Co₃O₄[8], MoO₃ and MnOx. Some of the applications of manganese oxides and their derivatives include; molecular sieves, catalysts, and super capacitors as result of their structural versatility and physicochemical properties. Of the manganese oxide series, MnO₂ has recently received much attention from the researchers due to its α -, β -, γ -, and δ -type crystal structure, the highest theoretical specific capacitance of 1360 F g⁻¹, low cost, a relatively large working potential range of 0. 8-1. 1 V and eco-friendly nature.

However, when it comes to actual applications, MnO₂ fails to deliver promising electrochemical results. Low rate capability and long cycle life are normally associated with MnO₂-based electrodes and are likely to limit service because they degrade during the charge-discharge cycle. Moreover, the electrolyte cannot go further into its internal configuration due to a low ionic conductivity of 10⁻⁵-10⁻⁶ S cm⁻¹ which could affect its rate capability, specific capacitance, and structure. As of late, researchers understand that the crystal structure of materials and other little characteristics of the material (for instance, size, porosity and the like) might affect their electrochemical characteristics. Thus, to improve the performance, the MnO₂'s dimension, size and form should be controlled and more attention is paid to the synthesis of MnO₂. MnO₂ can be produced in the different crystallography types depending on the process of the redox reactions with MnO₄⁻ or Mn²⁺. Some of the processes that are used to create nanomaterials include electrochemical deposition, template, hydrothermal, sol-gel, among others. Later, Sun et al [9] introduced a Ni@MnO₂ structure with the nanoarchitecture of hollow Ni dendrites combined with MnO₂ nanowires developed on the Ni surface using the electrodeposition method for high-performance supercapacitors. These properties are attributed to the structure of Ni@MnO₂ with a large porosity and layering that allows the electrolyte to penetrate swiftly and establish a conductive pathway for electrons.

As mentioned earlier, Hydrothermal synthesis is easy, safe and cheap and, therefore, the most widely used synthesis technique from these. By applying the techniques mentioned above, researchers have achieved much during the last few decades for developing MnO₂ electrodes with various morphologies and structures to apply for the supercapacitor devices. Due to an enhancement of its energy storage mechanism, MnO₂ possesses the merits of a large specific surface area and a plentiful pore structure. An electrode with a high specific capacitance could be achieved because of several active sites due to the small size of the electrode's specific surface area. At the same time, the cycle

stability of electrode and the rate stability of this electrode might be enhanced by the electrolyte by the virtue of porous structure. A novel resealable bowl-shaped MnO₂ was constructed by a simple template-free hydrothermal method, and the prepared MnO₂ nanosheets was extremely thin, around 4 nm thick. In addition, the large surface area and short unblocked diffusion path which consists of nanostructure makes easy for ions and electrons to pass. It then delivers a high specific capacitance (358 F g⁻¹), achieves fine rate capability (59.5% capacity reloading rate at 0.4-10 A g⁻¹), and demonstrates great long-cycle performance (86.3% remaining capacitance after 4500 cycles).

The composites of MnO₂ with high electrical conducting materials including, conducting polymers, CNTs or rGO have been reported to have improved electrical properties than the pristine MnO₂ [10]. An individual freestanding flexible 3D graphene/MnO₂ composites in the form of network and can be used flexible electrode for flexible supercapacitors. This is due to remarkable characteristic of the developed hybrid flexible electrode material, including the electrochemical performance, specific capacitance, and the extended cycle performance. Front-line strategy for application of efficient flexible supercapacitors and a sheet of CNTs/MnO₂. Lithium-ion supercapacitors fabricated from the above flexible supercapacitors demonstrate better rate stability and area capacitance than previously reported flexible thin film electrodes based on MnO₂. In summary, this research has reviewed the state-of-the-art applicable to the incorporation of nanomaterials rooted from manganese dioxide in supercapacitors. This study statistically reviews the preparation methods and shapes of MnO₂ based nanomaterials in general. At the same time, it is necessary to discuss the advantages and the disadvantages of each considered approach and morphology. Lastly, we have outline some possible futures of MnO₂-based nanomaterials, possibly leading to new insights regarding their design.

II. PURE MnO_2 WITH DIFFERENT MORPHOLOGIES

MnO_2 has strengths such as availability, affordability, and environmental pleasantness. Nevertheless, the electrical conductivity of this compound is low and thus its utility is somewhat limited. However, MnO_2 is a complex structure and the formation of this morphology, is a rational design and synthesis method to deal with the above mentioned difficulty. Therefore, the MnO_2 with a number of kinds of structures has been developed by employing different kinds of methods in order to enhance the electrochemical performance, including nanowires, nanosheets, nanorods, nanotubes, and hollow sphere.

Lately, due to their special physical and chemical parameters, one dimension 1D nanomaterials are with extensive potential application value in many fields. Thus, many researchers are aimed at synthesizing and coating of 1D MnO_2 nanomaterials. Preparation of electrode material through electro deposition leading to the formation of MnO_2 nanowire like structure for supercapacitor application at ambient temperature. The outcome clearly indicates that the form of MnO_2 nanomaterials existed on the basis of the deposition potential. Deposition potential is a quantitative subspecies, which is calculated depression in terms of volts, so when the tension depression is in the region of 0 volts, then the deposition potential is also in the region of 0 volts. 2–0. 7 V, the morphology has begun to change from MnO_2 nanorods with diameters of several tens of nanometers to MnO_2 nanowires with diameters ranging from 9 to 17 nm. Because of the constructed nanorod structure, the Central material possesses a high specific capacitance, 340 F/g at 0. 1 mA/cm², and very stable in the rate capability, only 71. 42% decay in the current density range of 0. 1 mA/cm² to 10mA/cm² in Na₂SO₄ aqueous electrolyte. α - MnO_2 nanowires (sample 1 and α - MnO_2 nanorods (sample 2) thru using different reducing agent in one-pot hydrothermal process. If the reagent is urea, α - MnO_2 has a nanowire like morphology with the length of roughly 2 micrometers and the width of about 110nm. When the choice is made with ammonium persulfate

as a reagent, the formation of α - MnO_2 has a nanorod-like structure with the length of 2 μm and the diameter 110 nm. The cyclic voltammogram of both samples are almost rectangular as can be seen in Figure 1C indicating the material had electrical conductivity. As has been found earlier nanorods had several transport channels for electrons and protons but fractured nanowires along their longitudinal section may have several active sites. The discharge time of nanowire like α - MnO_2 is higher than that of the nanorod like α - MnO_2 as indicated from the GCD curves shown in Fig. 1D and E. Figure 1F also demonstrated that the specific capacitance of nanorod-like α - MnO_2 is at 105 F g⁻¹ whereas nanowire-like α - MnO_2 is at 157 F g⁻¹ at 4 A g⁻¹. Moreover, the nanostructure of the nanowire-like and nanorod-like α - MnO_2 facilitates long cycling stability since shortens the diffusion path length for ions and electrons. Due to the formation of 1D-structured nanomaterials, they can aggregate together in such a manner that may reduce their active sites and also reduce the rate of electrolyte transfer.

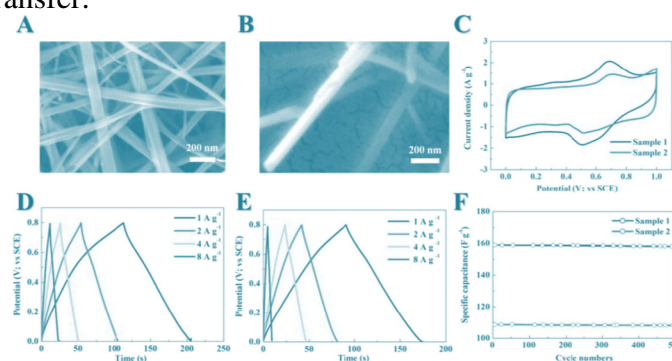


Fig. 1: SEM images of the synthesized nanomaterials: α - MnO_2 nanowires (A) and α - MnO_2 nanorods (B). Sample 1 and sample 2 were analyzed by performing CV tests, while the long-cycle stability of the α - MnO_2 nanowires and nanorods was examined for sample 2. The GCD curves of α - MnO_2 nanowires (D) and nanorods (E).

Because of such physical and chemical characteristics as high strength, excellent electrical and thermal conductivity, flexibility and other qualities which 2D nanomaterials might possess due to their unique structure, the scientists from all over the country enhanced interest. The oxidizer in hydrothermal procedure can be used to control the nanostructure of MnO_2 by varying the oxidizer. In terms of capacitance in aqueous solution and organic

electrolyte, the flake-shaped MnO₂ (with oxidizer NH₄Cl) showed higher capacitance than needle-shaped MnO₂ (with NH₄F), and nanorod-shaped MnO₂ (with KMnO₄), with the conclusion that the former may provide more active sites and better ion or electron transport channels. Moreover, the specific capacitance of the flake-shaped MnO₂ based electrode is higher in case of an LiPF₆ electrolyte (450 F g⁻¹) comparatively to the LiClO₄ (430 F g⁻¹) and NaOH (34 F g⁻¹) electrolytes. 2D MnO₂ nanoparticles are electrochemically unstable because they are able to combine and interrupt the straight ion or electron movement.

In terms of electrode materials, 3D structures are more efficient due to the higher specific surface area and the ability of the ions present in the electrolyte to diffuse rapidly. Two methods exist for creating three-dimensional nanomaterials: either perched onto three-dimensional conductive substrates or covalently bonded with one- or two-dimensional nanomaterials. Hydrothermally synthesized single-crystal birnessite-type MnO₂ nanoflowers self-assembled by petal-like nanosheets. Based on the material-derived electrode that proposed for its high specific capacitance (196.3 F g⁻¹ at 1 A g⁻¹) and long cycle life (capacitance retention of 93.6% after 1100 cycles). This self-assembly nanoscale structure with the multi-branch hierarchical structure may have many active sites and shorten the electron transmission route, which are the reasons that make their structure stable. Based on this self-assembly nanoscale structure with multi-branch hierarchical, many active sites, short electron transmission route, the authors synthesize ϵ -MnO₂ microspheres at ambient temperature by a direct reaction between MnCO₃ and KMnO₄. As depicted by the figure, the ϵ -MnO₂ microsphere that is obtained in the reaction has a homogeneous pore size distribution when the reaction duration is set at 3 minutes, implying that there could be adequate sites for the reaction. The synthesized material exhibits a large specific capacitance of 114 F g⁻¹ at 0.4 A g⁻¹ and exhibits long cycle stability in a capacitance of about 75% after 450 cycles.

It was possible to synthesise well-developed cauliflower like δ -MnO₂ particles with the help of

the above said MHT route. Cauliflower δ -MnO₂ ... The conditions for synthesizing α -MnO₂ nanorods include high temperatures of 140, 160 and 200 °C. The δ -MnO₂ electrode thus resembles cauliflower and it has a wide working window of -0.1 to 0. In a 1 M Na₂SO₄ electrolyte at 9 V, it achieves a high specific capacitance of 200 F g⁻¹ at 4 mV s⁻¹ and manifests high cycling stability, maintaining 93% of the initial capacitance after 900 cycles.

Metal oxide hierarchical 3D MnO₂ microspheres were synthesized using a simple and fast microwave recrystallization process. As seen in Figures 2F and B, all the synthesized materials possess a major surface area of 183. In terms of area density, the wear-resistant coatings of the obtained fibers are about 32 m² g⁻¹, indicating that they can form a large amount of active sites and possess a high specific capacitance. The good electroconductivity can be confirmed by the fact that all the CV curves in the form of rectangles for 3D hierarchical MnO₂-based electrode (Fig. 2C). Obtained material has a broad potential window (2.1 V), high specific capacitance (309.5 F g⁻¹ at the scan rate of 5 mV s⁻¹) more; and rate capability (the capacity retained ~50% from 5 to 90 mV s⁻¹) due to the special ionic electrolyte of 0.5 M 1-Ethyl-3-methyl imidazolium tetrafluoroborate/ N,N-dimethyl formamide (C₃H₇NO).

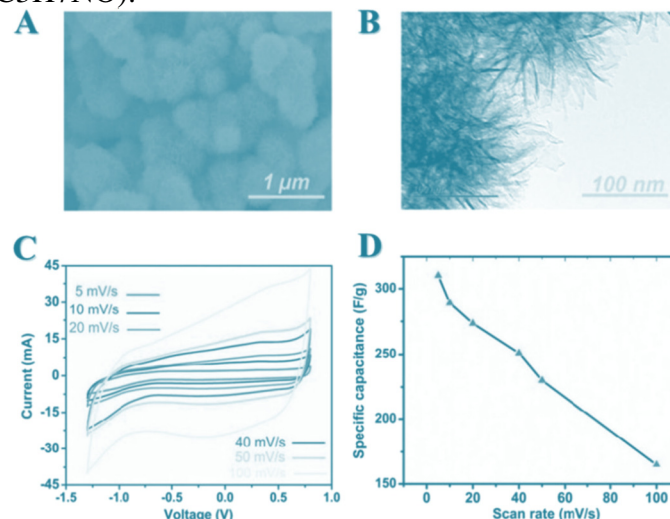


Fig 2: (A) A scanning electron micrograph and (B) a transmission electron micrograph of a three-Dimensional Hierarchical MnO₂ microsphere. Responding to task No: 7 (C) The three-dimensional hierarchical MnO₂ CV curves and (D) rate capability by a shift in the scan rate

The introduction of 3D-structured conducting material may enhance the dispersibility of MnO₂ and as the electrode possesses larger pore size as well as higher surface area, it may enhance the electron transfer capability of the electrode. For instance, the galvanostatic electrodeposition technique has produced MnO₂ nanoplates on the stainless steel (SS) substrates abbreviated as MnO₂/SS. Maximum specific capacitance is observed to be 800 F g⁻¹ at 5 mV s⁻¹ for MnO₂/SS based electrode which is higher than that of 1 M KOH electrolyte (590 F g⁻¹) and 1 M NaOH electrolyte (600 F g⁻¹). We propose that the lower ionic radius of Na₂SO₄ electrolyte makes the intercalation/de-intercalation process easier, which accounts for possessing a larger specific capacitance as compared to the other two electrolytes. In addition, the produced electrode material provides phenomenal long-term cycling stability recovering 84% of its capacity even after 1100 cycles. The preparation of δ-MnO₂ nanosheets on nickel foam (NF) substrate was based on the one-pot chelating method. However, NF possesses many other admirable characteristics apart from being a binder and conductive agent; it has a large specific surface area and pores. Subsequently, material that has been generated has a long cycle stability of 80% discharge capacity residual after 1100 cycles and maximum capacitance of 320 F g⁻¹ at current density of 1 A g⁻¹.

III. MnO₂-BASED NANOCOMPOSITES

When it came to the performance of the supercapacitor, the electrodes were always the king or queens of the jungle. Specifically, there are no many applications that have employed MnO₂ based electrodes mainly due to low energy density and conductivity. Two strategies to improve its electrochemical performance include the incorporation of carbon material and the coupling with other transition metals. Supercapacitor electrodes fabricated from manganese dioxide nanocomposites have been developed with electrodes.

IV. MnO₂/CARBON NANOCOMPOSITES

While carbon materials are known to exhibit high electrochemical stability and power density, they do not have a high CE or SC. The next task for the researchers lies in the development of new materials, which mean the creation of hybrids of carbon-based EDLCs and pseudocapacitive transition metal oxide materials. Graphene is basically an arrangement of carbon atoms in the form of honeycomb lattice in a single plane. Apart from that, it possesses very high SSA of 2500 m² /g besides having superior mechanical, thermal and electrical properties. [50]. Graphene nanosheet-MnO₂ composites at room temperature through the mechanism of the partial oxidation of the carbon atoms of the graphene nanoplatelet. It should also be noted that the graphene structure can be preserved within a short amount of time (< 3 h), which, in turn, can enhance the dispersion and conductivity of MnO₂ loading (Fig. 3A, B, E and F). The electrochemical performance could be lost due to the gradual destruction of the graphene structure for reaction times exceeding three hours (Fig. 3C, D, G and H). It can be observed from Fig. I-M that the material generated had a high specific capacitance of 308 for a reaction period of 3hr. 5 F g⁻¹ when the voltammogram was recorded with the scan rate of 5 mV s⁻¹. A rather direct method of generating three-dimensional hybrid structures of graphene and MnO₂.

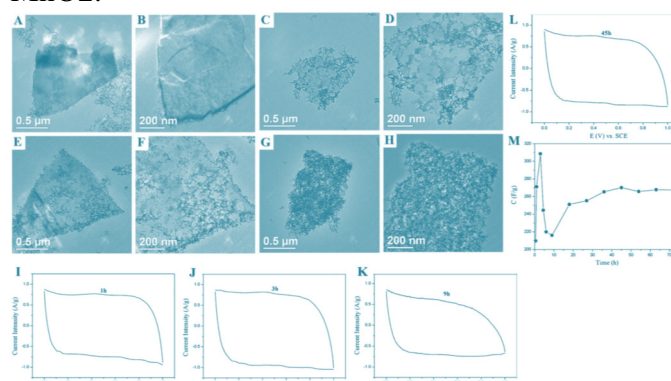


Fig 3: T – Scanning electron microscope images of graphene nanoplate composites incorporating MnO₂ at 1/2 an hour (A, B), 1/3 an hour (E,F), 9hours (C, D) and 45hours (G, H) after the reaction time. The specific capacitance and the corresponding CV curves of the composites of graphene nanoplate and MnO₂ after 1 h, 3 h, 9 h and 45 h; (M) the relationship between specific capacitance and reaction time of the composites; and (I), 3 h; (J) 9 h; (K) 45 h (L).

The specific capacitance of the composites prepared with graphene foam structures of MnO₂ was highest in the case of flower-like MnO₂/graphene foam composites, which is estimated to be 550 F g⁻¹. Furthermore, at 0.2 A g⁻¹, the specific capacitance of the electrodes decreased to 91 % of the original capacitance, which means that its capacity is faded by about 18 % after 1100 cycle. Supercapacitors with flexible electrodes wherein the electrodes are composed of 3D graphene networks, manganese oxide infused and electrodeposited. As for the developed flexible 3D graphene networks, the following advantages can be noted: The structures are self-standing, they work as light (0.75 mg cm⁻²), thin (<100 μm) and possess very high electrical conductivity equal to 55 S cm⁻¹. Graphene-based composites consist of flexible 3D graphene networks and possess the specific capacitance of 465 F g⁻¹ at 2 mV s⁻¹ due to its excellent physical and chemical characteristics.

Due to its several advantages like a high specific surface area, electrical conductivity, superior mechanical performance, and a synthesis method that can be scaled up, a big number of scientists is interested in Carbon Nanofibers (CNFs). It has become apparent that porosity the extent or the amount of pore space available as well as pore size distribution in the carbon based ultracapacitors do have a direct impact on the capacitance performance. Such a three-dimensional nanostructure of the interconnected CNFs promotes the transfer of the whole electrolyte and the provision of a large specific surface area to accommodate more active components. Two catalysts, MnO₂-CNFs and MnO₂-aCNFs, are prepared using electrospinning along with electrodeposition approaches. The etching of a layer of carbon (Fig. 4A and B) might contribute to the fact that the diameter of the aCNFs was slightly smaller than that of CNTs after acid treatment, and the average size of aCNFs is about 300 nm. A lesser quantity of aCNFs in the weight ratio of MnO₂ to aCNFs produced hence there is a direct relation between the mean diameter of aCNFs and MnO₂. As seen in Figure 4C, the SAED pattern of MnO₂-aCNFs with the outer layer supports the hypothesis that the MnO₂ which was formed is

amorphous. The composites obtained are represented by the symbol AC_x/MnO₂(y). In Figure 5B, the surface of the AC exhibits a uniform distribution of the produced MnO₂ nanoneedles of AC6/MnO₂ (3). Thus, the formation of MnO₂ has the ability to penetrate and infill the micro- and mesopores of AC, making it an important component of composites with superior electrochemical characteristics. In figure 5C it can be observed that the discharge time of the produced AC6/MnO₂(3) is much longer than other samples indicating a higher specific capacitance. Lastly, AC6/MnO₂(3) exhibited improved rate capability, cycling stability and high specific capacitance.

Carbon materials have attracted much attention due to their high conductivity, enhanced mechanical and chemical stabilities, and non-toxicity as MnO₂ loading substrates. Price and process difference between AC and other carbon compounds are huge. MnO₂ may destroy the pore structure of the AC and decrease the amount of active sites and the electrolyte transfer channel. Subsequently, AC is surpassed by graphene and CNFs in the aspects of electrical conductivity and surface area. However, the ability of graphene to aggregate may limit the number of nucleation sites for MnO₂ growth. Of all the MnO₂/carbon composites, the one with 3D graphene and paired with MnO₂ exhibited the highest electrochemical performance. The major drawback that still prevents 3D graphene from getting widespread usage is the challenging method of preparation.

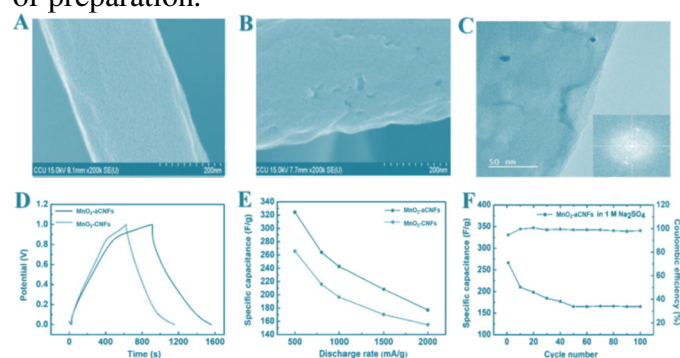


Figure 4: SEM of CNFs and aCNFs. Transmission electron micrograph of MnO₂-aCNFs is presented in (C). MnO₂-CNFs and MnO₂-aCNFs' specific capacitance, and (D) the GCD plots at 0.5 A g⁻¹. The specific capacitance and coulombic efficiency of MnO₂-aCNFs were evaluated after 100 cycles at 1 A g⁻¹.

V. SYMMETRIC SUPERCAPACITOR

The constructed MnO₂//MnO₂ based FSSSC exhibits high power density 15 kW kg⁻¹, energy density 51 Wh kg⁻¹ and potential window of 1.6 V. Because of its film structure, it is also very pliable; this tool can be twisted several times over at an angle of 180 degrees. Fabrication of carbon quantum dot manganese oxide (CQD-MnO₂) via hydrothermal method. The low resistance of CQD-MnO₂ enables the fabrication of the CQDMnO₂//CQD-MnO₂ supercapacitor which has high power density of 3370 W kg⁻¹, high denenergy density of 62 Wh kg⁻¹ and exceptional cycle stability since it still retained about 100% of its capacity after 2000 cycles. As shown in Fig. 6A, the electrochemical deposition method illustrated the MnO₂/CNT hybrid films' methodologies and highly loaded carbon nanotube. Such CNT produced has a mechanical strength of 30-50 MPa, electrical conductivity of 100 S m⁻¹ and typical thickness of 10 μm. The nanoflower-like MnO₂ was deposited over the hydrogel-like CNT film as depicted in Figure 6B. The electrode prepared therefore exhibits better electrochemical performance than the other samples when loading mass of MnO₂ is 92% (MnO₂ deposition period is 20 min). The aforementioned MnO₂-CNT nanomaterial therefore plays both the positive and negative role in the fabricated flexible supercapacitors. Specifically, the symmetric flexible supercapacitor that was produced outperforms both the pure CNT film (8.1 mF cm⁻²) and the MnO₂-CNT (≈100 mF cm⁻²) at 0. The HAc sensitivity increases to 2 mA cm⁻², as presented in Figure 6B. Besides, it has higher energy density, which is 40 μWh cm⁻² and power density of 2.4 mW cm⁻² as compared to the other two samples.

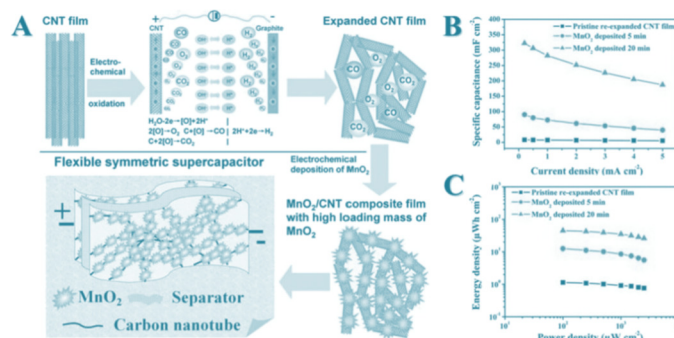


Fig 6 Carbon nanotube-manganese oxide composite films prepared by the sol-gel method are illustrated in cross-section in 6 (A). Venturing deeper into Ragone plots of the CNT-MnO₂ film at different electrodeposition time in the overall deposition process and rate performance comparison.

VI. ASYMMETRIC SUPERCAPACITOR

The electrodes of asymmetric supercapacitors are generally composed of divergent materials for the anode and cathode, so as to achieve better electrochemical performance than that of symmetric supercapacitors. 1D MnO₂ nanostructures in the form of nanorods, nanowires, and nanoneedles were synthesised through coprecipitation method. These were then used as the anode in the construction of all-solid-state supercapacitors. The maximum voltage in the asymmetric devices which can be fabricated using MnO₂ as the positive electrode material and rGO as the negative electrode material can be as high as 1.6V when it has been subjected to electrolysis using poly(vinyl alcohol) and phosphoric acid. For the asymmetrical device, the MnO₂ nanoneedles//rGO electrode has a higher specific capacitance of 98 F g⁻¹ at 9 mV s⁻¹ than MnO₂ nanorods//rGO and MnO₂ nanowires//rGO with 70 F g⁻¹ and 69 F g⁻¹, respectively, this is due to the larger surface area of nanoneedles. Subsequently, MnO₂ nanoneedles//rGO possesses a high power density of 7. This has been estimated at 8 kW kg⁻¹ and an energy density of 24.12 Wh kg⁻¹. The redox process was simple to produce highly ordered MnO₂ nanofibers on the surface of the GHCS (abbreviated as GHCS-MnO₂-z in which z is the mass ratio of MnO₂). The GHCSMnO₂-50 has the highest value of 260 m² g⁻¹ when the weight fraction of MnO₂ is 50. Subsequently, an asymmetric supercapacitor with GHCS as the anode and GHCS-MnO₂ as the cathode in 1 M Na₂SO₄ aqueous electrolyte possessed an enormously wide window voltage of 2.0 V, and an energy density of

21.1 W/kg and the peak power density of 7 W/kg. 0 kW kg⁻¹.

This might be due to the fact that GHCS//GHCS-MnO₂ has usual structure with well defined crystalline morphology which has more electrochemical performance. Run on the external surface of GHCS is frequently coated with ultra thin MnO₂ nanofibers which have been grown vertically. The presence of these nanofibers may enable a large number of redox active sites and facilitate the diffusion of electrons and electrolytes. More so, the coulomb efficiency of the device was 99% for GHCS/GHCS-MnO₂ and 98% for the GHCS/GHCS-MnO₂ with MnO₂ electrode during 1100 cycles. Hydrothermal precarbonization and pyrolysis carbonization technique and in-situ hydrothermal method to synthesized nitrogen-doped porous hollow carbon spheres (HCS) and MnO₂ nanowires on HCS surface and MnO₂/HCS-t described the concentration of KMnO₄ (Fig. 7A). It may be due to the greater MnO₂/HCS-30 electrode specific capacitance value of 255 F g⁻¹ compared to 210 F g⁻¹ obtained in case of MnO₂/HCS-20 and 137 F g⁻¹ for MnO₂/HCS-40, due to correct pore size and greater specific surface obtained by optimizing the reaction concentration of potassium permanganate. After that, employing MnO₂/HCS-30 as the positive electrode and HCS as the negative electrode to design an asymmetric supercapacitor as depicted in Fig. 7B,C&E). reaches a maximum specific capacitance of 74.5 F g at a rate of 0.8 Wg-equivalent⁻¹, and a maximum power density of 0.8 Wg⁻¹. Therefore, we achieved the power density of 5 kW kg⁻¹, and energy density of 41.4 Wh kg⁻¹. The capacitance also holds the value of approximately 92 and the number of switching cycles is approximately 400. even after 4900 cycles, the efficiency is maintained to be less than 9% (Figure 7D).

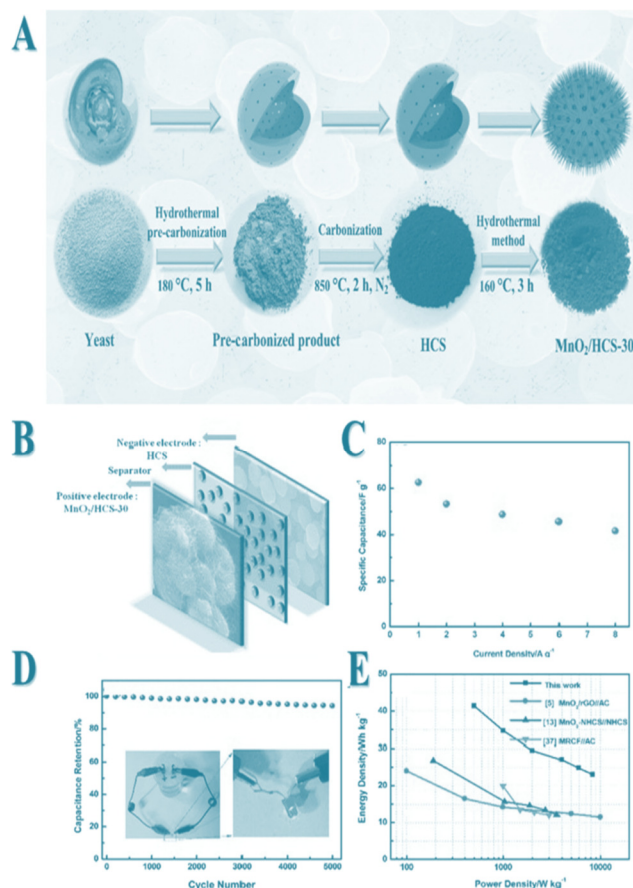


Fig 7: (A) illustrates the general synthesis steps for MnO₂/HCS-30 anode material. SevenThe asymmetric supercapacitor device (B) is schematically represented, (C) operating at the rated and (D) qualitatively cycled. Some of the information that would fit in this format include: (E) A Ragone plot that will set the technology proposed in this paper against other asymmetric supercapacitors.

Conclusion

The research work done on manganese dioxide has received considerable interest in investigation due to its potential application in variety fields. From such research, it is evident that the performance of nanomaterials in applied research is likely to stem from the nanoscale and chemical nature of the said materials. Then, each of the various morphology's of MnO₂ based nanomaterial described in this study have also been fabricated employing a range of techniques including electrodeposition, template, hydrothermal and sol-gel methods. Out of the common preparation methods hydrothermal is the most used because of the method's ease and a generally fast reaction. Besides, the nanomaterials could provide sufficient shape and structure, which might benefit the preparative strategy and the construction of nanomaterial with unique application

performance. Recently develop in MnO₂- based electrode and MnO₂- as a electrode for supercapacitor application has been enhanced. Nevertheless, due to the low electrical conductivity, problems are encountered in the density of power and the electrochemical stability of the material, and so its use is limited. Then, there are two major effective strategies to increase its electrochemical performance: Involving changes to its above mentioned requisite shape and structure or introduction of new material into the system.

The synthesis methods, structure and morphological features, together with the electrochemical properties of MnO₂ related composites nanomaterials in this context are also described and discussed. From mentioned above, the pure MnO₂-based electrode with 3-D nano structure could own more delightful electrochemical performance compared to 1-D and 2-D nano structure, might be ascribed to its larger exposed surface area and easier for the transport of the electrolyte. Then, depending on MnO₂- based composites electrode shape and the component of it, they could be adjusted. In conclusion, the MnO₂-based composites with the 3D nanostructure possess correct elemental content ratio and can reveal the superior electrochemical performance. Moreover, the electrolyt might also be another important element by the effects of which it could be possible to change the operating voltage of the electrode. Presumably, the electrode which is measured in organic electrolyte may have larger working voltage compared with in other electrolyte. Then, using organic electrolyte may be an efficient approach to

achieve a higher electrochemical performance of MnO₂-based composites.

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