

Article

Facile Hydrothermal Synthesis of Binder-Free Hexagonal MnO₂ Nanoparticles for a High-Performance Supercapacitor's Electrode Material

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Abstract: Manganese dioxide (MnO₂)-based nanostructures are promising electrode materials for supercapacitors (SCs) due to their low cost, eco-friendly nature, and high theoretical capacitance. However, the conductivity of MnO₂ is poor, which is a big problem when trying to achieve the desired capacitance value. Herein, hexagonal-phase MnO₂ nanoparticles (NPs) are directly grown on a 3D conductive carbon cloth (CC) (denoted as MnO₂-NPs@CC) as a binder-free electrode through a simple and scalable hydrothermal strategy. The results show that MnO₂-NPs@CC with a large specific surface area and high porosity could be employed as a positive electrode material for high-performance SCs. Owing to these attractive properties, the MnO₂-NPs@CC electrode delivers a high specific capacitance of 660 F/g at a current density of 2 A/g in 6 M KOH aqueous electrolytes. Moreover, the MnO₂-NPs@CC electrode demonstrates excellent cycling stability with high capacitance retention of 92.8% over 10,000 cycles. Such remarkable findings suggest that MnO₂-NPs@CC with enhanced electrochemical performance is a favorable electrode material for next-generation high-performance SCs.

Keywords: manganese dioxide; hydrothermal; hexagonal MnO₂; carbon cloth; supercapacitor

1. Introduction

The rapidly growing technological and scientific requirements for renewable and green energy sources have drawn great attention to the design of ultramodern energy devices with higher specific energy and power density levels [1,2]. Supercapacitors (SCs) are attractive as energy storage devices owing to their high capability and long life span [3,4]. SCs have two major categories based on the charge storage mechanism: electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs). The EDLCs operate via the adsorption or desorption of electrolyte ions at the electrode–electrolyte interface [5–7]. On the other hand, to construct PCs, mostly transition metal oxides (TMOs) and conducting-polymer-based materials are used, which operate through Faraday redox reactions at the electrode surface, thereby exhibiting much higher energy density levels compared to EDLCs.

As compared to carbon-based materials [8] and conducting polymers [9], TMOs show remarkably high capacitance levels due to the rapid Faraday redox reactions; thus, TMOs

are the best choice for electrode materials in SCs [10]. Furthermore, TMOs, such as NiO [11], Fe₂O₃ [12], RuO₂ [13], Co₃O₄ [14], and MnO₂ [15], have been widely explored for use in SCs. Among them, MnO₂ has the characteristics of being eco-friendly, cost-effective, as well as having a high theoretical capacitance (~1380 F/g). Recently, different types of MnO₂ crystal structures have been prepared and examined for SC applications. The electrochemical performance of such materials depends on the crystal structure, grain size, morphology, and surface area [16]. Out of the various polymorphs of MnO₂, hexagonal MnO₂ (δ -MnO₂) has garnered much interest due to its layered architecture and excellent electrochemical performance [17,18]. The hexagonal δ -MnO₂ can effectively improve the electrochemical performance due to the rapid charge transport within the nano-architecture during the charge or discharge process. For example, δ -MnO₂/C has been synthesized and employed as an electrode for SCs, and displayed a specific capacitance of 520 F/g at 5 mV/s, with a remarkable cycling performance of 80.1% for 5000 cycles [19]. However, δ -MnO₂ is limited in SC electrodes due to its bad cycling performance, low specific capacitance, and low conductivity (about 10^{-5} – 10^{-6} S/cm) [20,21]. The low surface area (due to MnO₂ agglomeration) and low conductivity of MnO₂ ultimately limits the specific capacitance of MnO₂-based electrodes for SCs [22]. Enhancing the conductivity and maximizing the MnO₂ utilization, as well as maintaining the MnO₂ nanoparticles; (MnO₂-NPs) unique morphology, have become the basic criteria in the design of electrodes for SCs with remarkable performance [23]. In addition, an efficient method used to enhance the conductivity of MnO₂ is to directly grow in into conducting substrates and avoid the use of binders, which block the active sites and reduce the electrical conductivity [24].

Herein, we designed hexagonal-phase MnO₂-NPs that were directly grown on a carbon cloth using a simple and scalable hydrothermal strategy with an appropriately controllable size, morphology, and large surface area, along with better conductivity as an SC electrode. MnO₂-NPs incorporated on CC can produce more electrochemically active sites, which can support the electron and ion transport in the charging–discharging process, thus providing excellent cycling performance. Furthermore, the MnO₂-NPs contributing significantly to enhancing the capacitance. The present MnO₂-NPs@CC as a positive electrode for SCs delivers an excellent gravimetric capacitance of 660 F/g at 2 A/g and retains 92.8% of the capacitance over 10,000 cycles. These excellent results indicate that MnO₂-NPs@CC with boosted electrochemical properties is a promising cathode choice for next-generation SCs.

2. Experimental Section

2.1. Pre-Treatment of CC

The piece of CC was washed ultrasonically first in acetone, ethanol, and distilled water for 10 min to completely abolish the layer of oxides and oil stains on the CC. To dry the CCs, the cleaned CCs were then left for 12 h at 60 °C for further use.

2.2. Synthesis of MnO₂-NPs@CC

The MnO₂-NPs precursor was synthesized through a simple and scalable hydrothermal strategy, in which the CC was used as a substrate, and MnO₂-NPs were grown on the CC surface. Figure 1 shows a schematic illustration of the fabrication process of MnO₂-NPs. Initially, 3 mg of KMnO₄ was dissolved in 30 mL of distilled water, then 10 mL of hydrochloric acid (HCl) was slowly added. Afterwards, the above solution was sonicated and a purple solution was obtained. The cleaned CC substrate was put with the side wall of the Teflon-lined stainless steel autoclave and the purple solution was moved into a 70 mL autoclave that was sealed and then left for hydrothermal reaction for 12 h in an oven at 135 °C. After cooling down, the resulting precipitate was washed many times with distilled water and dried for 12 h at 90 °C.



Figure 1. Schematic representation of a typical synthesis procedure of MnO₂-NPs@CC.

2.3. Physical Characterizations

The morphology of MnO₂-NPs@CC was investigated using a field-emission scanning electron microscope (FESEM, HITACHI SU8220, Hillsboro, OR, USA). An X-ray diffractometer (X'Pert Pro Analytical) with monochromatic radiation (Cu-K α ; $\lambda = 0.15406$ nm, step speed 0.02°) was used to investigate the crystal structure. The Raman spectrum (HJY Lab RAM Aramics 70 France) with a wavelength of 514.5 nm was used to investigate the chemical bonds. The BET surface area and N₂ adsorption–desorption were measured at 77.5 K using Micromeritics (ASAP2460, Version 5.12, Boynton Beach, FL, USA).

2.4. Electrochemical Characterization

The electrochemical performance investigations were conducted using an electrochemical work station (CHI 660E, Wuhan, China) in a three-electrode configuration in a 6 M KOH aqueous electrolyte solution. The as-prepared MnO₂-NPs@CC measuring 1×1 cm² (1.0 mg/cm² mass loading density) was employed as the working electrode. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively. The cyclic voltammetry (CV) was measured at a potential window range of 0.0–0.8 V, the galvanostatic charge–discharge (GCD) measurements were performed in the same voltage range (0.0–0.8 V) with diverse current rates (2 to 32 A/g), and the electrochemical impedance spectroscopy (EIS) was performed using a fresh electrode in the frequency range of 0.001 to 100 kHz in open-circuit conditions with an applied amplitude of 5 mV. ZSim-view software was used to simulate the electrical equivalence circuit.

3. Results and Discussion

The morphological architecture of the as-prepared MnO₂-NPs@CC was investigated via FE-SEM. The low magnification FE-SEM images (Figure 2a,b) indicate that the interconnected nanoparticles with higher density and rough textures are uniformly distributed onto the cylindrical surface of every fiber of the CC. The high magnification FE-SEM image (Figure 2c) further confirms and provides the detailed architecture of the regular distribution of the well-established MnO₂-NPs with an average size of 26 nm.

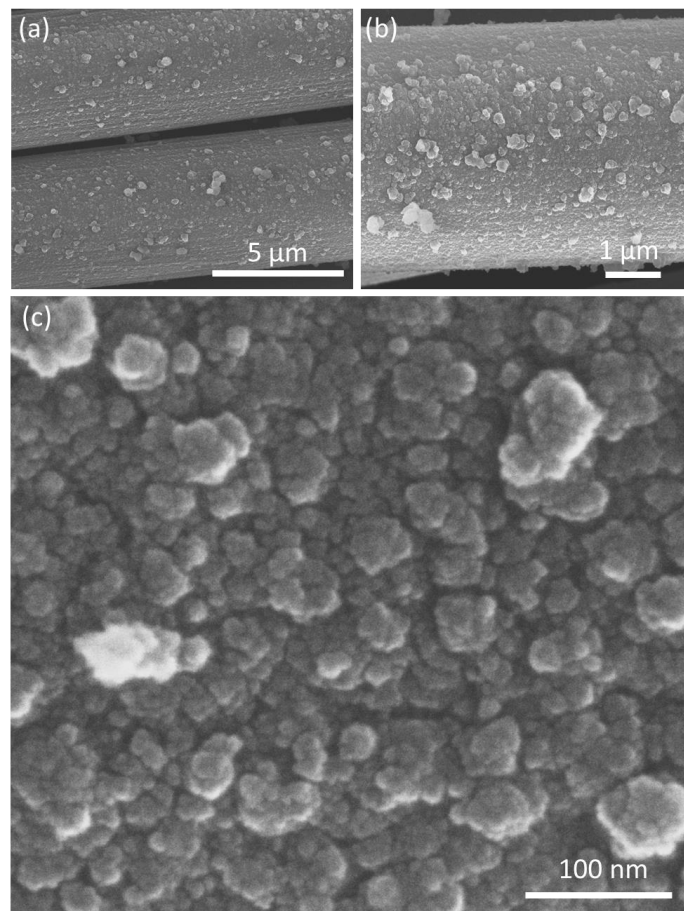


Figure 2. FESEM images of $\text{MnO}_2\text{-NPs@CC}$. (a,b) low- and (c) high-magnification.

The XRD spectrum of $\text{MnO}_2\text{-NPs@CC}$ is shown in Figure 3a. The characteristic peaks belong to the hexagonal phase of MnO_2 , with sharp and intense peaks that are well matched with JCPDS No. 71-0071, which shows the successful formation of hexagonal $\text{MnO}_2\text{-NPs}$ onto the CC. The broad residual peak that appears at about $2\theta = 26.5^\circ$ is related to the carbon cloth substrate, which corresponds to JCPDS No. 41-1487. Figure 3b shows the crystal structure of the as-prepared MnO_2 , in which every Mn atom is strongly bonded to six O-atoms and also connected to another Mn atom to form a hexagonal structure. The hexagonal structure with 2×2 tunnels is beneficial for fast ion and electron transfer and enhances the stability of the electrode [25].

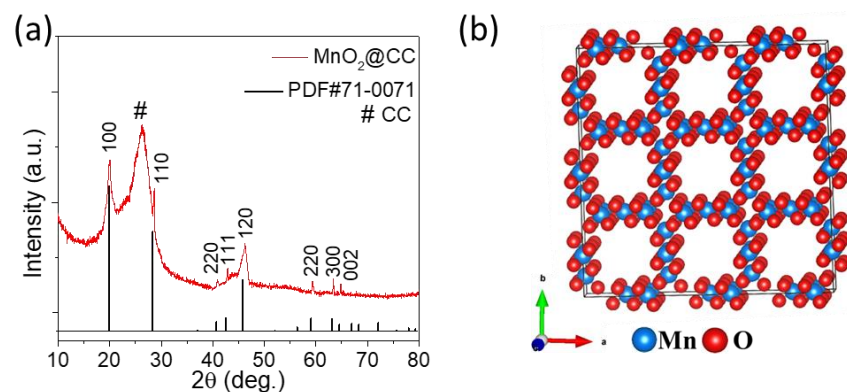


Figure 3. (a) XRD spectrum of $\text{MnO}_2\text{-NPs@CC}$. (b) Hexagonal crystal structure of MnO_2 with 2×2 tunnels.

To further study the chemical bonds, Raman spectroscopy was performed, and Figure 4 exhibits the Raman spectrum of MnO₂-NPs@CC. The location of the band at 647 cm⁻¹ is associated with oscillations of the lattices of Mn-O and is consistent with the previous reports [26,27]. In addition, the Raman spectrum shows two more peaks corresponding to the higher-intensity G-band along with the lower-intensity D-band, which demonstrate the excellent graphitization degree of the CC substrate. In the present case, the G-band (1598 cm⁻¹) is more intense than the D-band (1313 cm⁻¹); thus, the homogeneous and dominant contents of the graphitic structure exist. The I_D/I_G ratio of MnO₂-NPs@CC is 0.68, indicating that the carbon in the MnO₂-NPs@CC is coupled with a partial graphitic layer and provides excellent conductive support to MnO₂-NPs. Thus, the MnO₂-NPs@CC electrode shows better conductivity and enhanced electrochemical performance [28].

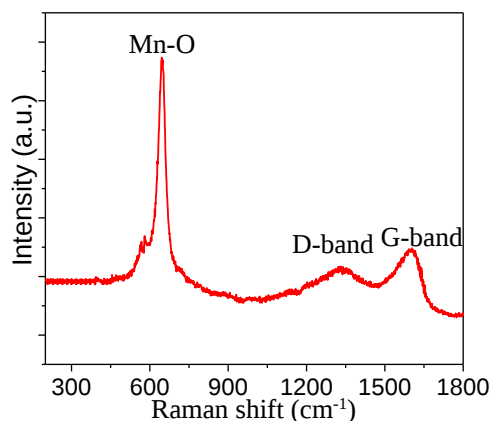


Figure 4. Raman spectrum of MnO₂-NPs@CC.

The specific surface area of MnO₂-NPs@CC was investigated via nitrogen (N₂) sorption measurements. The adsorption–desorption isotherms of MnO₂-NPs@CC show a type IV curve with a clear hysteresis loop in the of range 0.4–1.0 (P/P₀), as shown in Figure 5a. The figure shows typical characteristics of capillary condensation due to the mesopores in MnO₂-NPs@CC [29]. The surface area of the mesoporous MnO₂-NPs@CC computed using the BET method was 29 m²/g; thus, MnO₂-NPs@CC may show excellent electrochemical performance because of its large surface area, meaning it can offer a better active site for the occurrence of redox reactions. The BJH profile for porosity is illustrated in Figure 5b, where the mean size of the pores was estimated to be 12.46 nm, demonstrating the presence of large pores. This porous architecture is believed to be beneficial for storing more energy due to the mesoporous channels and large surface area being suitable for ion diffusion, which are the two main characteristics needed for electrode materials to achieve better electrochemical performance.

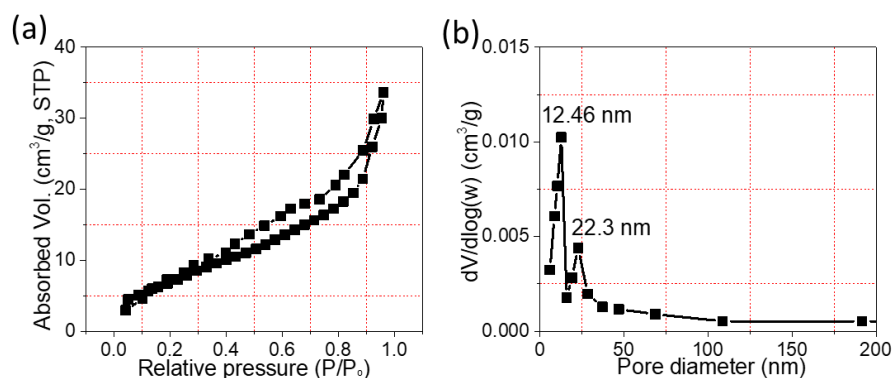


Figure 5. (a) The N₂ sorption isotherms of MnO₂-NPs. (b) BJH profile of the pore size distribution.

The MnO₂-NPs@CC was investigated as an electrode for SC, and the electrochemical behavior was examined in a 6 M potassium hydroxide (KOH) solution in a three-electrode configuration. First, we tested the pristine CC substrate to find the effect on the performance of the MnO₂-NPs@CC electrode. The comparative CV curves of the pristine CC and MnO₂-NPs@CC electrode are displayed in Figure 6a. The area under the CV curve of the pristine CC is much lower than that of the MnO₂-NPs@CC electrode at the same scan rate (5 mV/s). Furthermore, the GCD measurements were conducted and the comparative GCD curves are displayed in Figure 6b, which indicates that the capacitance generated from the pristine CC is tiny. Based on the CV and GCD results, we neglected the capacitance of the CC in the calculation. The CV curves for the MnO₂-NPs@CC electrode within a voltage range of 0.0–0.8 V and at various scan rates (5–30 mV/s) are exhibited in Figure 6c. The CV profiles reveal rectangular shapes without additional redox peaks, even when scan rate was increased to 30 mV/s, which indicates the excellent electrochemical performance of the MnO₂-NPs@CC [30]. The wide open spaces in the MnO₂-NPs@CC electrode provide easy paths to diffuse the electrolyte ions in the interior section of the active material. The NPs grown on the CC surface offer a good surface area and rapid electron transfer channels. The GCD measurements of the MnO₂-NPs@CC electrode at various current rates (2–32 A/g) are exhibited in Figure 6d. The linear and symmetric shapes of the GCD curves further confirm the good charge–discharge features and excellent reversibility. In addition, IR drops of 0.025 and 0.15 V were observed at 2 and 32 A/g, which indicated the quick I–V response with a small internal resistance from the active material. The major cause of an IR drop may be possibly due to charge transfer resistance or internal resistance of the active material or contact resistance at the electrode–electrolyte interface. The specific capacitance (C_{sp}) for the MnO₂-NPs@CC electrode was determined from the GCD profiles using Equation (1):

$$C_{sp} = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where m (g) indicates the mass, I (A) represents the current, Δt (s) indicates the discharge time, and ΔV (V) represents the potential window [31]. The specific capacitance was 660 F/g with a current rate of 2 A/g (Figure 6e). By increasing the current rate from 2 to 32 A/g, the MnO₂-NPs@CC electrode showed 58% capacitance retention, which indicated the excellent rate capability. The capacitance decreased at higher current rates owing to the short time for the diffusion of electrolyte ions into the interior section of the electrode material, so the reduced diffusion decreased the capacitance. The electrochemical impedance spectroscopy (EIS) experiment was performed to investigate the conductivity and diffusion performance of the MnO₂-NPs@CC electrode. The Nyquist plot consists of a semi-circular portion in a high-frequency region and a quasi-vertical line in a low-frequency region (Figure 6f). This linear portion corresponds to the remarkable electrochemical capacitive response of MnO₂-NPs@CC and the semicircle's radius indicates the charge transfer resistance ($R_{ct} = 2.52 \Omega$). The intercept with the horizontal axis depicts the combination of equivalent series resistance and the electrode's intrinsic and electrolytic resistance ($R_s = 0.69 \Omega$). The electrical equivalent circuit diagram consists of the resistor in series with the parallel combination of the resistor and the capacitor and simulates a semicircle, while the Warburg element (W) shows a low-frequency linear part (Figure 6f, inset). These results demonstrate that the MnO₂-NPs@CC electrode has remarkable electrochemical properties.

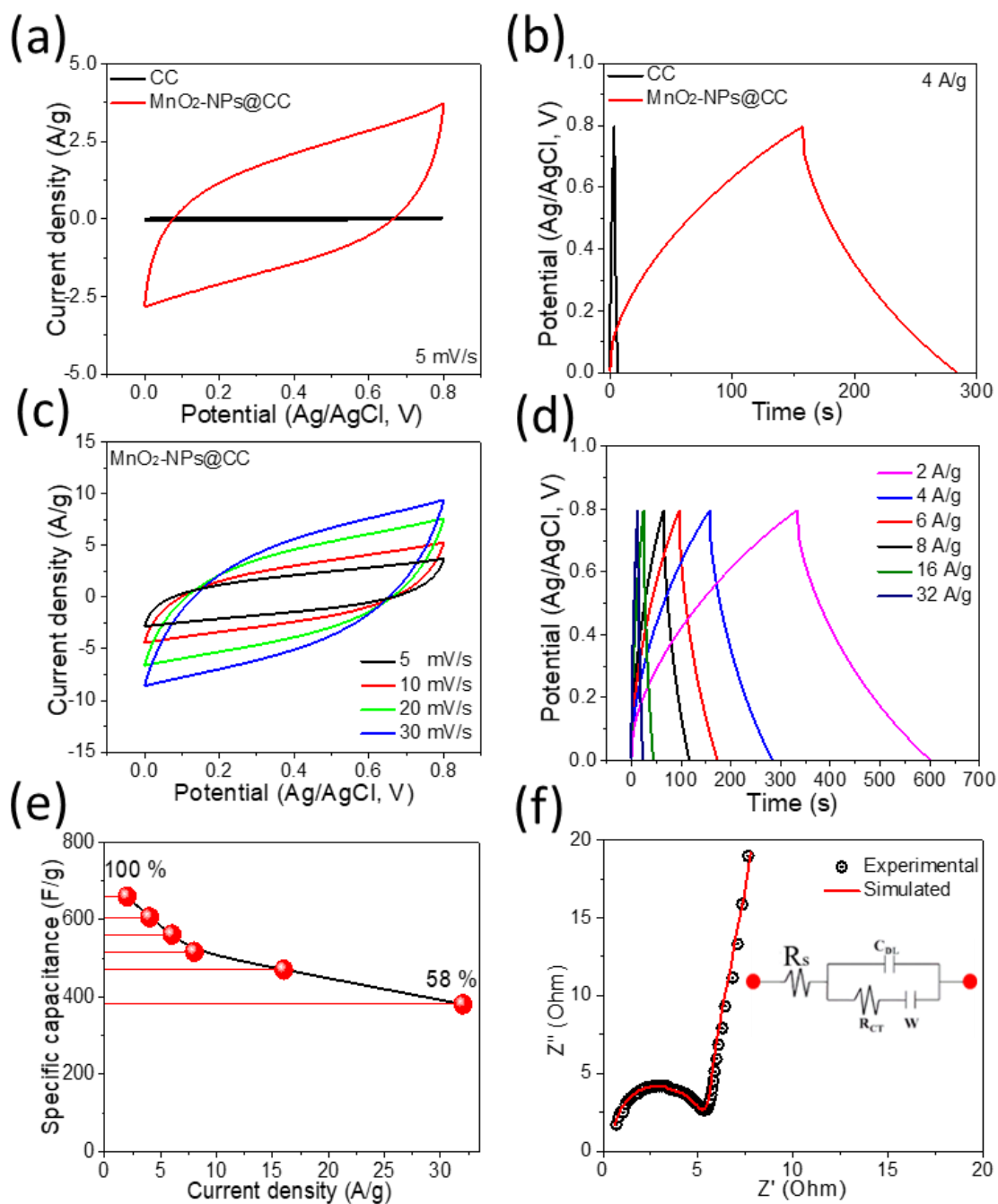


Figure 6. The electrochemical measurements of the $\text{MnO}_2\text{-NPs@CC}$ electrode: (a,b) comparative CV and GCD curves of $\text{MnO}_2\text{-NPs@CC}$ and pristine CC; (c,d) CV and GCD curves of $\text{MnO}_2\text{-NPs@CC}$; (e) capacitance as a function of the current density; (f) Nyquist plot with an electrical equivalent circuit.

The cycling performance is also a paramount parameter for the characterization of SC electrodes. A long-term cyclic performance measurement of the $\text{MnO}_2\text{-NPs@CC}$ cathode was studied at a current density of 16 A/g (Figure 7a). The capacitance decreased slowly and reached 92.8% of the initial value after 10,000 GCD cycles, showing excellent electrochemical stability.

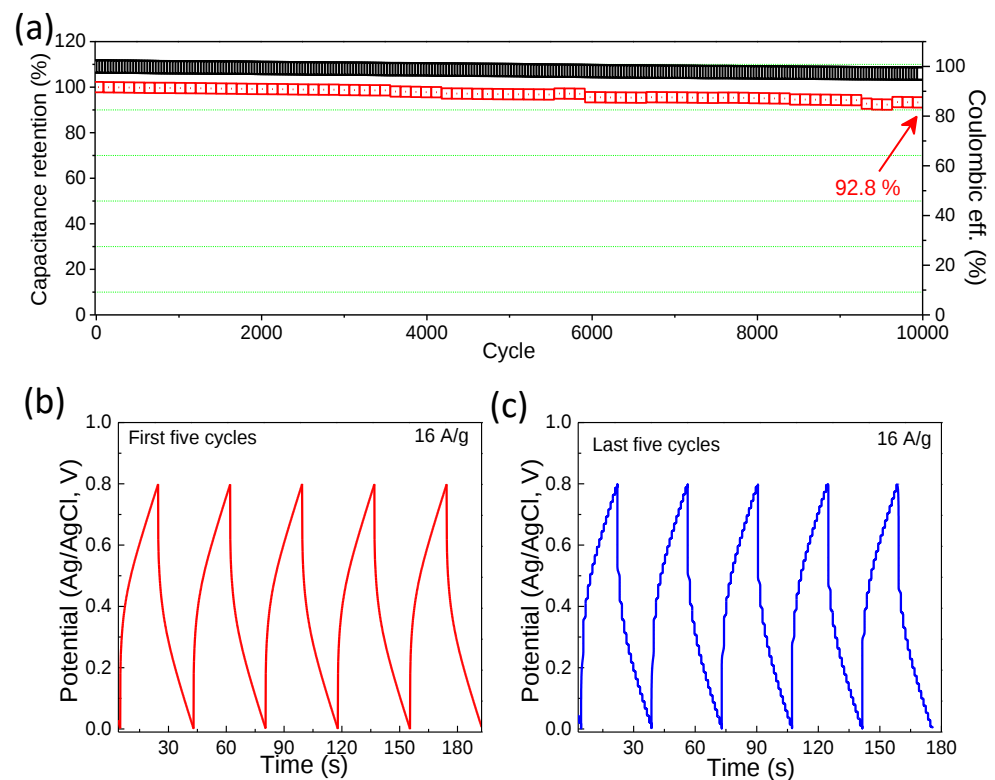


Figure 7. (a) Cycling performance of MnO₂-NPs@CC and CD characteristics for the (b) initial five cycles and (c) last five cycles.

In addition, typical GCD curves for the initial and last five cycles are displayed in Figure 7b,c, respectively, which demonstrate stable and similar shapes for both the initial and last cycles and the excellent stability of the MnO₂-NPs@CC electrode. Such exceptional contributions are mainly associated with prominent nanoparticles, such as the morphology of the hexagonal-phase MnO₂. Table 1 shows a comparison of the overall performance of the MnO₂-NPs@CC electrode, which was compared with similar cathode materials reported previously based on the various forms of MnO₂ and its composites with carbon and graphene.

Table 1. A comparison of MnO₂-based supercapacitor electrodes reported in previously published studies.

Sr. No	Electrode Material	Electrolyte	Specific Capacitance (F/g)	Current Density (A/g)	Capacitance Retention (%)	No. of Cycles (n)	Ref.
1.	α -MnO ₂	Na ₂ SO ₄	200	1	87.6	1000	[32]
2.	MnO ₂ @NGO	KOH	360	0.5	90	6000	[33]
3.	MnO ₂ -CNFs	Na ₂ SO ₄	324.55	0.5	62	1000	[34]
4.	MnO ₂ /PANI/GN	Na ₂ SO ₄	472	1	79.7	5000	[35]
5.	MnO ₂ /RGO	Na ₂ SO ₄	347	1	93.1	2500	[36]
6.	rGO/MnO ₂	KOH	486.48	0.85	75.8	2000	[37]
7.	α -Fe ₂ O ₃ /MnO ₂	KOH	216	1	89.2	1000	[38]
8.	α -MnO ₂ nanowires	Na ₂ SO ₄	362	1	83	5000	[39]
9.	MnO ₂ /g-C ₃ N ₄	Na ₂ SO ₄	211	1	90	1000	[40]
10.	MnO ₂ /MnCo ₂ O ₄	KOH	497	0.5	60	5000	[41]
11.	MnO ₂ -NPs@CC	KOH	640	2	92.8	10,000	This work

PANI (polyaniline); RGO (reduced graphene oxide); CNFs (carbon nanofibers); NGO (nitrogen-doped graphene oxide).

4. Conclusions

In summary, the hexagonal-phase MnO_2 -NPs supported on CC were synthesized via a simple and scalable hydrothermal strategy and their electrochemical performance in aqueous KOH electrolyte solution was investigated. The MnO_2 -NPs@CC, with its large surface area combined with a highly conductive CC support, provides an efficient path for electron and ion transfer and more electrochemical reaction sites. Owing to these characteristics, the MnO_2 -NPs@CC cathode shows a high specific capacitance of 660 F/g at 2 A/g and an excellent rate capability of 58% at a 32-fold current density. Furthermore, the MnO_2 -NPs@CC exhibits remarkable cycling stability performance of 92.8% over 10,000 GCD cycles. These results prove that the MnO_2 -NPs@CC-based electrode is promising and has tunable electrochemical performance, highlighting its potential for SC applications.

Author Contributions: Conceptualization, Q.A. and M.S.J.; methodology, Q.A.; software, A.M.; validation, N.U.H., A.I. and Z.U.R.; formal analysis, N.U.H., A.I. and Z.U.R.; investigation, M.A.B., N.U.H.; resources, A.I.; data curation, Z.U.R.; writing—original draft preparation, Q.A. and M.S.J.; writing—review and editing, M.A.B., N.U.H., A.I. and Z.U.R.; visualization, M.A.B.; supervision, M.S.J. and L.W.; project administration, L.W., M.S.J.; funding acquisition, M.A.B., M.S.J. and L.W.; All authors have read and agreed to the published version of the manuscript.

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