Silver Nanoparticle Decorated on Reduced Graphene Oxide-Wrapped Manganese Oxide Nanorods as Electrode Materials for High-Performance Electrochemical Devices

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Abstract: In this work, silver nanoparticles decorated on reduced graphene oxide (rGO) wrapped manganese oxide nanorods (Ag-rGO@MnO 2 ) were synthesized for an active electrode material. MnO 2 nanorods were synthesized via a hydrothermal route, and their coating with GO and subsequent reduction at a higher temperature resulted in rGO@MnO 2 . A further addition of Ag on Ag-rGO@MnO 2 was performed by dispersing rGO@MnO 2 in AgNO 3 solution and its subsequent reduction by NaBH 4 . X-ray diffraction (XRD) analysis showed peaks corresponding to MnO 2 and Ag, and the absence of a peak at 2θ = 26° confirmed a few layered coatings of rGO and the absence of any graphitic impurities. Morphological analysis showed Ag nanoparticles anchored on rGO coated MnO 2 nanorods. Apart from this, all other characterization techniques also confirmed the successful fabrication of Ag-rGO@MnO 2 . The electrochemical performance examined by cyclic voltammetry and the galvanic charge–discharge technique showed that Ag-rGO@MnO 2 has a superior capacitive value (675 F g −1) as compared to the specific capacitance value of rGO@MnO 2 (306.25 F g −1) and MnO 2 (293.75 F g −1). Furthermore, the electrode based on Ag-rGO@MnO 2 nanocomposite showed an excellent capacity retention of 95% after 3000 cycles. The above results showed that Ag-rGO@MnO 2 nanocomposites can be considered an active electrode material for future applications in electrochemical devices.

Keywords: manganese oxide; reduced graphene oxide; silver nanoparticles; electrochemical properties

1. Introduction

Day by day, worldwide, energy consumption is continuously increasing, and current energy resources are insufficient to sustain our energy demands. Therefore, there is a great need to develop a novel alternative energy source and store this energy for a long time. Electrical energy storage devices such as electrostatic capacitors, fuel cells, batteries, and supercapacitors are being widely researched, as they are efficient, low cost, easy to manufacture, and environmentally friendly. For example, fuel cells can use fossil fuel to generate energy that pollutes the environment, but low-power density limits their practicality. In this context, supercapacitors are promising, owing to their excellent properties such as long cycle life, high-power density, fast charging/discharging rate, and eco-friendly nature. Due to these excellent properties, supercapacitors are used in different applications, such as hybrid electric vehicles, instant switches, portable electronic devices, motor starters, industrial power, and energy management [1–3].
An electrochemical device such as a supercapacitor can be categorized into two major parts on the basis of its charge–discharge mechanisms or electrochemical processes: first, electrical double-layer capacitors (EDLCs) and second, Faradaic pseudocapacitors [4,5]. In EDLCs, the electrochemical process occurs at the electrode–electrolyte interface, and electrical energy is stored through adsorption/desorption at the same interface. The active materials for fabricating the electrode for such types of capacitors are graphene oxide (GO), carbon black, and activated carbon. However, pseudocapacitors depend upon the Faradaic process between the surface of the electrode and the electrolyte, and charge accumulates through reversible redox reactions. Therefore, an electrode based on a conducting polymer and a transition metal oxide is ideal for such capacitors. However, various literature reports show that the electrode material often possesses low electrical conductivity and suffers from a very small specific surface area due to its semiconducting character [6,7]. Therefore, by incorporating metal oxides, sulfides, and conducting polymers in carbon materials, the electrical conductivity of the electrodes based on carbon materials can be enhanced, which, in turn, increases the specific surface area as well as the energy-storage capacity through pseudocapacitance [8].

In recent years, electrodes of high-performance energy storage devices have been fabricated using metal oxides (NiO, Co$_3$O$_4$, MnO$_2$, Fe$_2$O$_3$, and MoO$_2$) [9]. Among them, manganese oxide (MnO$_2$) is exciting owing to its theoretically high capacitive value, low cost, naturally abundance in large quantities, and eco-friendly nature. This makes it suitable for fabricating electrodes for high-performance supercapacitors [10]. Naturally occurring as a transition metal element, manganese has different stable phase oxide structures, such as MnO, MnO$_2$, Mn$_2$O$_3$, and Mn$_3$O$_4$. In general, MnO$_2$ has a theoretical specific capacitance value of 1370 Fg$^{-1}$, but its experimental value ranges from 50–200 Fg$^{-1}$ in aqueous electrolyte, which shows that the experimental specific value is much lower than the theoretical capacitative value [11]. Additionally, MnO$_2$ is poorly conductive, which results in a low capacitance value of MnO$_2$-based supercapacitors. Therefore, for highly conductive MnO$_2$-based electrodes with a high capacitance and charge storage capacity, their composite can be prepared with other highly conductive materials. Among different conductive materials, carbon-based materials such as graphene (GN) and multiwalled carbon nanotubes (MWCNTs) are highly promising, owing to their exceptional electrical, thermal, and mechanical properties. They can facilitate the charge transfer mechanism, which increases electrochemical characteristics such as capacitance, power density, and cycling stability [12].

GN has a two-dimensional structure that consists of a single layer of sp$^2$ carbon atoms closely packed in a honeycomb-like structure [13–15]. Thin sheets of GN show excellent thermal stability, mechanical strength, and optoelectronic properties, making it a promising material for many different devices [16–18]. Further, GN structures can be produced on a large scale, are low in cost, possesses high specific area and high thermal conductivity even at room temperature [18–21]. GN is synthesized by a physically powerful exfoliation method, in which a single layer of graphite oxide as GO is separated from stacked layers of graphite oxide [22,23]. It is an ideal material to fabricate positive electrodes for supercapacitors due to its rich electrochemistry, high specific surface area (2630 m$^2$g$^{-1}$), and high electrical conductivity (5 × 10$^{-3}$ Scm$^{-1}$) [24–27]. Theoretically, the maximum specific capacitance value (550 Fg$^{-1}$) can be obtained using the whole surface area of GN sheets [28]. However, unfortunately, in various literature, the specific capacitance values of GN and reduced GO (rGO) are 80–264 Fg$^{-1}$ in aqueous electrolyte [22–30]. The reduction in the specific capacitance is due to its small electrochemically active surface area, which might be due to the restacking or agglomeration of the ultra-thin rGO nanosheets. Therefore, researchers are trying to develop new composite materials by incorporating transition metal oxides or pseudocapacitive materials, such as Co$_3$O$_4$, Fe$_2$O$_3$, SnO$_2$, ZnO, and MnO$_2$, with GN for supercapacitor electrodes [31–35]. The pseudocapacitive materials act as a spacer between the GN sheets, which increases electrochemical surface area for the redox process in the electrolyte by reducing agglomeration and restacking GN sheets.
Furthermore, GN materials have limited double-layer capacitive charge storage, but they have a high electrical conductivity by providing a conductive platform to accelerate electron transport, whereas pseudocapacitive materials possesses a low conductivity but a high specific capacitance [36,37]. Both materials complement each other; therefore, combining both into a composite might provide an ideal electrode material. Additionally, pseudocapacitive materials have a low potential cycle that degrades after long potential cycling. Therefore, this intense GN can offer a high potential route to pseudocapacitive materials through a non-Faradaic energy storage mechanism. Furthermore, due to the hydrophilic nature of GO, MnO$_2$ nanorods can be grafted onto GO through a reaction between layers of GO sheets and Mn ions.

In various studies, it has been reported that MnO$_2$ discharges very quickly during the electrochemical process due to its low electrical conductivity; therefore, loading a highly conducting noble metal such as silver (Ag) nanoparticles onto a MnO$_2$ nanostructure should improve the MnO$_2$ electrical conductivity by providing extra channels to conduct the electrons during the electrochemical process [38,39]. Moreover, the electrical conductivity of rGO can be enhanced or improved by decorating Ag nanoparticles on its surface [40]. Therefore, based on the above idea, binary rGO/MnO$_2$ composite was decorated by Ag nanoparticles to produce Ag-rGO@MnO$_2$ ternary composite with improved conductivity and capacitive performance.

2. Materials and Methods

2.1. Materials

Silver nitrate (AgNO$_3$), sodium borohydride (NaBH$_4$), activated carbon (AC), absolute ethanol (C$_2$H$_6$O), hydrogen peroxide (H$_2$O$_2$), potassium permanganate (KMnO$_4$), anhydrous 1-methyl-2-pyrrolidinone (NMP), sulfuric acid (H$_2$SO$_4$), analytical-grade phosphoric acid (H$_3$PO$_4$), hydrochloric acid (HCl), and potassium hydroxide (KOH) were obtained from Sigma-Aldrich (Burlington, Massachusetts, MA, USA). High purity polyvinylidene fluoride (PVDF) was obtained from Daejung Chemicals and Meal Co, Ltd. (Gyeonggi, South Korea), and graphite flakes were procured from Asbury Inc. (Asbury, NJ, USA). High-quality nickel foam was bought from MTI Corporation (Richmond, CA, USA).

2.2. Synthesis of Electrode Materials

A modified Hummers method was employed to prepare GO using natural graphite flakes [41,42]. A simple hydrothermal method was used to synthesize pure MnO$_2$ nanorods, in which KMnO$_4$ (0.658 g) was dispersed in 75 mL of deionized water, and 1.5 mL of HCl (36%) was added dropwise under stirring conditions. The whole system was left under stirring conditions for 15 min, and the subsequently obtained dark-brownish mixture was transferred into a Teflon-lined hydrothermal reactor and heated at 140 °C for 24 h. After completion of the reaction, the hydrothermal reactor was allowed to cool to room temperature, and the obtained resulting mixture solution was washed several times with ethanol and DI water using a centrifuged system. The washed precipitate was annealed at 80 °C for 12 h to obtain MnO$_2$ nanorods. To prepare rGO@MnO$_2$ nanocomposite, 2 mL of GO solution (5 mg mL$^{-1}$) was added dropwise to the MnO$_2$ nanorods (300 mg) and mixed properly. The resulting mixture was annealed at 400 °C for four hours to further reduce the GO in GO@MnO$_2$ and to obtain the rGO@MnO$_2$ nanocomposite.

For the ternary Ag-rGO@MnO$_2$ nanocomposite, in 90 mL of 0.0020 M NaBH$_4$, 305 mg of rGO@MnO$_2$ nanocomposite was added, and the solution was kept under stirring conditions. To the above solution, 30 mL of 0.0010 M AgNO$_3$ was added dropwise, which resulted in the solution turning dark yellow due to the formation of Ag. Thus, prepared Ag-rGO@MnO$_2$ was separated by centrifugation, washed with an excess of water and ethanol, and annealed at 80 °C for 12 h. Figure 1. represents a schematic illustration for the synthesis of Ag-rGO@MnO$_2$. 
2.3. Characterization Technique

The crystallinity and phases of as-prepared samples were analyzed using X-ray powder diffractometer (Rigaku, Ultima IV XRD, Tokyo, Japan). The surface morphological studies as well as elemental analysis were carried out through field emission scanning electron microscopy (JEOL, JSM-7600F, FESEM, Tokyo, Japan). A transmission electron microscope (JEOL ARM-200F, HRTEM, Tokyo, Japan) was employed to measure the particle size and shape. Raman spectroscopy (DXR 532 Raman Microscope, Thermo scientific, Madison, WI, USA) was employed to examine the composition of the nanocomposites. The electrochemical analysis of prepared materials was performed using an electrochemical workstation Versa STAT 3 (AMETEK, Oak Ridge, TN, USA).

2.4. Development of Electrodes and Electrochemical Measurements

To fabricate the working electrode, a slurry of active material was prepared by adding Ag-rGO@MnO₂ nanocomposite (80 wt.%), activated carbon (10 wt.%), and PVDF (10 wt.%), in anhydrous NMP and mixing properly using a magnetic stirrer at ambient temperature for 12 h. Then, a chemically cleaned nickel foam of 1 × 1 cm² area was coated with the slurry and annealed at 90 °C for 12 h for complete drying. The average weight of active material was 1.5 mg. The same methodology was used to fabricate the working electrode of the MnO₂ nanorods and the rGO@MnO₂. The electrochemical measurements such as cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) was performed in 2 M KOH electrolyte using a three-electrode system.

3. Results and Discussion

3.1. X-ray Diffraction Analysis

The XRD technique was employed to evaluate the crystallinity and phase of the synthesized samples, as shown in Figure 2. All the samples showed sharp peaks, which suggested that the samples were polycrystalline in nature. The pure MnO₂ rods showed prominent peaks at 2θ = 12.73°, 18.00°, 25.70°, 128.68°, 37.42°, 42.01°, 49.74°, 60.02°, 65.53°, and 69.40°, corresponding to the (110), (200), (220), (310), (211), (301), (411), (521), (002), and (541) planes, respectively, which perfectly matched with the α-MnO₂ planes (JCPDS card No. 44-0141). The binary rGO@MnO₂ showed similar peaks to the MnO₂ rods but with a slightly lower intensity due to the introduction of rGO. In the Ag-rGO@MnO₂ nanocomposite, the additional intensity peaks were observed at 2θ = 38.13°, 44.23°, and 77.67°, corresponding to (111), (200), and (311) crystallographic planes, respectively, which confirmed that Ag nanoparticles with a cubic structure were present in the nanocomposite.

**Figure 1.** Schematic illustration for the synthesis of Ag-rGO@MnO₂ nanocomposite.
Crystals 2022, 12, x FOR PEER REVIEW 5 of 17

Figure 2. XRD of prepared MnO2 rods, rGO@MnO2, and Ag-rGO@MnO2 nanocomposite. The asterisk (*) shows the peak positions of Ag.

3.2. FESEM and EDX Analysis

The surface morphological analysis of the prepared MnO2 nanorods, rGO@MnO2, and Ag-rGO@MnO2 nanocomposites was performed by FESEM at different magnifications (Figure 3). The pure MnO2 exhibited a rod-type structure with sharp and broken edges, with a diameter in the range of ~50–70 nm and length in micrometers, as shown in Figure 3a,b. In Figure 3c,d large sheets of rGO covering a large number of MnO2 nanorods can be evidently seen and in Figure 3e,f clusters of Ag nanoparticles on rGO, bare MnO2, and rGO-coated MnO2 can be evidently seen.

The EDX spectrum of the MnO2 rod shows the presence of Mn, O, and Pt. The binary rGO@MnO2 shows Mn, O, C, and Pt, and the ternary Ag-rGO@MnO2 nanocomposites show C, O, Mn, Ag, and Pt (Figure 4a–c). The observed additional elemental peak of Pt is due to the coated Pt to avoid charging during the scanning process, as shown in Table 1. Furthermore, the EDX mapping images confirmed the uniform distribution of C, O, Mn, and Ag in the Ag-rGO@MnO2 nanocomposite (Figure 5a–f).
Figure 3. FESEM images of (a,b) pure MnO$_2$ rods, (c,d) rGO@MnO$_2$, and (e,f) Ag-rGO@MnO$_2$ nanocomposite at various magnification.

The EDX spectrum of the MnO$_2$ rod shows the presence of Mn, O, and Pt. The binary rGO@MnO$_2$ shows Mn, O, C, and Pt, and the ternary Ag-rGO@MnO$_2$ nanocomposites show C, O, Mn, Ag, and Pt (Figure 4a–c). The observed additional elemental peak of Pt is due to the coated Pt to avoid charging during the scanning process, as shown in Table 1.

Furthermore, the EDX mapping images confirmed the uniform distribution of C, O, Mn, and Ag in the Ag-rGO@MnO$_2$ nanocomposite (Figure 5a–f).

Figure 4. EDX spectrum of (a) pure MnO$_2$, (b) rGO@MnO$_2$, and (c) Ag-rGO@MnO$_2$ nanocomposite.
Table 1. EDX analysis showing the elemental composition of Ag-rGO@MnO₂ nanocomposite.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>1.93</td>
<td>5.44</td>
</tr>
<tr>
<td>O K</td>
<td>30.20</td>
<td>63.85</td>
</tr>
<tr>
<td>Mn L</td>
<td>34.93</td>
<td>21.51</td>
</tr>
<tr>
<td>Ag L</td>
<td>24.89</td>
<td>1.81</td>
</tr>
<tr>
<td>Pt M</td>
<td>8.05</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Figure 4. EDX spectrum of (a) pure MnO₂, (b) rGO@MnO₂, and (c) Ag-rGO@MnO₂ nanocomposite.

Figure 5. EDX mapping image (a) scan area, (b) C, (c) O, (d) Mn, (e) Ag, and (f) mixture of all elements in Ag-rGO@MnO₂ nanocomposite.

3.3. TEM Analysis

TEM was employed to determine the size and shape of MnO₂, rGO@MnO₂, and rGO@MnO₂ nanocomposite, as shown in Figure 6a–d. Pure MnO₂ nanorods with a length in the micrometer range and a diameter <100 nm can be evidently seen, and in rGO@MnO₂, sheets of rGO can be seen. In rGO@MnO₂, apart from these, well-dispersed Ag can also be seen coated on the MnO₂ nanorods or dispersed therein. The results are in agreement with the SEM analysis that the diameter of the MnO₂ nanorods ranged between 50 and 70 nm, and the Ag nanoparticles’ sizes ranged between 15 and 50 nm.

3.4. Raman Analysis

The Raman spectra of prepared electrode materials is shown in Figure 7. In all prepared samples, a Raman shift appeared at 643 cm⁻¹ for pure MnO₂, which is attributed to A₁g spectroscopic species due to the vibrations of MnO₆ octahedra [44]. Raman spectra of GO in the inset show highly intense peaks at 1359 and 1604 cm⁻¹, known as the D and G bands, where the D band represents the disorder/defect, and the G band denotes the graphitization of GN-based materials, respectively. Similarly, the rGO@MnO₂ and Ag-rGO@MnO₂ nanocomposite have prominent peaks at 1363, 1362, and 1595, and 1594 cm⁻¹ for the D and G bands, respectively. The intensity ratio (I_D/I_G), representing the GN quality, was calculated to be 1.03, 0.99, and 0.98 for GO, rGO@MnO₂, and Ag-rGO@MnO₂, respectively. The drop in the I_D/I_G ratio intensity confirms the presence of rGO in the binary rGO@MnO₂ and the ternary Ag-rGO@MnO₂ composite [45]. Furthermore, the intensity peak of the G band appears slightly higher as compared to the D band in both nanocomposites, which is another confirmation of the existence of rGO.
3.3. TEM Analysis

TEM was employed to determine the size and shape of MnO$_2$, rGO@MnO$_2$, and rGO@MnO$_2$ nanocomposite, as shown in Figure 6a–d. Pure MnO$_2$ nanorods with a length in the micrometer range and a diameter <100 nm can be evidently seen, and in rGO@MnO$_2$, sheets of rGO can be seen. In rGO@MnO$_2$, apart from these, well-dispersed Ag can also be seen coated on the MnO$_2$ nanorods or dispersed therein. The results are in agreement with the SEM analysis that the diameter of the MnO$_2$ nanorods ranged between 50 and 70 nm, and the Ag nanoparticles’ sizes ranged between 15 and 50 nm.

![Figure 6. TEM image of (a) MnO$_2$ rod, (b) rGO@MnO$_2$, (c) Ag-rGO@MnO$_2$ nanocomposite at magnification 40k×, and (d) TEM image of Ag-rGO@MnO$_2$ at high at magnification 200k×.](image)

3.4. Raman Analysis

The Raman spectra of prepared electrode materials is shown in Figure 7. In all prepared samples, a Raman shift appeared at 643 cm$^{-1}$ for pure MnO$_2$, which is attributed to Ag spectroscopic species due to the vibrations of MnO$_6$ octahedra [44]. Raman spectra of GO in the inset show highly intense peaks at 1359 and 1604 cm$^{-1}$, known as the D and G bands, where the D band represents the disorder/defect, and the G band denotes the graphitization of GN-based materials, respectively. Similarly, the rGO@MnO$_2$ and Ag-rGO@MnO$_2$ nanocomposite have prominent peaks at 1363, 1362, and 1595, and 1594 cm$^{-1}$ for the D and G bands, respectively. The intensity ratio (ID/IG), representing the GN quality, was found to be consistent with the results of TEM analysis.

3.5. Electrochemical Analysis

The electrochemical studies were carried out through a three-electrode system in an alkaline-medium (2M KOH) electrolyte. As prepared electrodes with pure MnO$_2$ nanorods, binary rGO@MnO$_2$ and ternary Ag-rGO@MnO$_2$ were used as working electrodes, whereas platinum (Pt) and Ag/AgCl (immersed in 2M KCL) acted as reference and counter electrodes, respectively. The cyclic voltammetry curve of all the prepared electrodes based on pure MnO$_2$ nanorods and their composites are shown in Figure 8a–c at varying scan rates of 10–70 mVs$^{-1}$ in the potential range 0.0–0.5V. All prepared electrodes exhibited reduction and oxidation peaks or redox activity on the electrode surface, which indicates that they possess pseudocapacitor behavior. Furthermore, the rectangular curve (characteristic of EDLCs) was not displayed by a CV curve, which further confirms the electrodes’ pseudocapacitor behavior. The chemical reaction occurring between the electrode and the electrolyte was based on Equation (1) [46,47] and Equation (2) [48]:

\[(\text{MnO}_2) + \text{K}^+ + e^- \leftrightarrow \text{MnO} \cdot \text{OK} \quad (1)\]

\[\text{Ag}^0 \leftrightarrow \text{Ag}^+ + e^- \quad (2)\]
voltammetric current. Figure 8a displays the CV curve of pure MnO$_2$ nanorods with Ag [52,53]. Similar observations have also been reported by other authors in their nanocomposites. In the MnO$_2$ nanocomposite, due to the high reduction peak at ~0.05 V, the peak at ~0.35 V is not distinct.

The drop in the ID/IG ratio intensity confirms the presence of rGO in the binary composite rGO@MnO$_2$. Furthermore, the intensity of the D band appeared slightly higher as compared to the D band in both nanocomposites, which is another confirmation of the existence of rGO.

The GCD has been studied to analyze the electrochemical behavior of the prepared electrodes. The electrochemical studies were carried out through a three-electrode system in an alkaline-medium (2M KOH) electrolyte. As prepared electrodes with pure MnO$_2$ nanorods, rGO@MnO$_2$, and the Ag-rGO@MnO$_2$ nanocomposite at different current densities are shown in Table 2.

It was observed that, with an increase in the scan rates, there is an increase in the voltammetric current. Figure 8a displays the CV curve of pure MnO$_2$ nanorods at various scan rates. The current densities appeared to increase linearly as scan rates increased, and they showed excellent electrode material behavior. Additionally, at a lower scan rate (10 mVs$^{-1}$),...
a maximum current density of 2 mAg\(^{-1}\) was achieved due to its nano size structure, which is also in good agreement with excellent electrode material [49]. However, in pure metal oxide in the nanoscale regime, the particles are aggregated, reducing the electrochemically active sites and ultimately reducing the electrode materials’ electrochemical performance. The CV curve of binary composite rGO@MnO\(_2\) showed a maximum current density of 4 mAg\(^{-1}\) at a lower scan rate, which was much higher than the MnO\(_2\) nanorods, as displayed in Figure 8b. It also shows that, with an increase in the scan rate, the current density linearly increases, and the highest current density is attained at a higher scan rate, indicating good reversibility [50]. On the other hand, in the case of the Ag-rGO@MnO\(_2\) nanocomposite in Figure 8c, at the lowest scan rate, the maximum current density was found to be 9 mAg\(^{-1}\) due to the synergistic effect of incorporating Ag nanoparticles that were much higher than their counterparts [51]. In the CV result of the Ag-rGO@MnO\(_2\) nanocomposite, due to the high reduction peak at ~0.05, the peak at ~0.35 V is not distinct. Similar observations have also been reported by other authors in their nanocomposites with Ag [52,53].

The GCD has been studied to analyze the electrochemical behavior of the prepared electrodes, as shown in Figure 9a–c, at current densities (0.5–10 Ag\(^{-1}\)). The highest discharge time was achieved by the Ag-rGO@MnO\(_2\) composite as compared to MnO\(_2\) rods and the rGO@MnO\(_2\) composite. Additionally, the GCD curve of all prepared electrodes does not show a triangular curve, suggesting that the electrodes possessed a non-electrostatic or pseudocapacitor behavior. Equation (3) has been used to calculate the specific capacitance \(C_{sp}\) of the prepared electrode with the help of the GCD curve:

\[
C_{sp} = \frac{I \cdot \Delta t}{m \cdot \Delta V}
\]  

where \(I\) represents current density (Ag\(^{-1}\)), \(m\) is the mass of active material (mg), and the derivative \(dt/dv\) represents the discharge time. The obtained capacitive values of the MnO\(_2\) rods, rGO@MnO\(_2\), and the Ag-rGO@MnO\(_2\) nanocomposite at different current densities are shown in Table 2.

![Figure 9. GCD curve of (a) pure MnO\(_2\) rods, (b) rGO@MnO\(_2\), (c) Ag-rGO@MnO\(_2\) at different current densities.](image-url)
The Ag-rGO@MnO$_2$ composite exhibited the largest integration capacitive area as compared to the rGO@MnO$_2$ composites and the MnO$_2$ nanorods. The specific capacitance value of an electrode depends upon the area enclosed by its CV curve, i.e., a CV curve with a large, enclosed area has a high capacitive value. Therefore, Ag-rGO@MnO$_2$ composite have a high capacitive value (a large area enclosed by the CV curve) in comparison to rGO@MnO$_2$ composite and MnO$_2$. Furthermore, the electrode based on the ternary Ag-rGO@MnO$_2$ nanocomposite has many active sites that provide better charge transfer kinetics during the redox process, and thus it shows excellent electrochemical performance. Figure 10b shows the comparative GCD curve for all variants at a fixed current density of 0.5 Ag$^{-1}$ and a potential difference of 0.0–0.4 V. The calculated specific capacitance value (C$_{sp}$) of pure MnO$_2$ rods, rGO@MnO$_2$, and Ag-rGO@MnO$_2$ nanocomposite were ~293.75, ~306.25, and ~675 Fg$^{-1}$, respectively. Based on the specific capacitance, the ternary Ag-rGO@MnO$_2$ nanocomposite shows the highest capacitive value compared to the rGO@MnO$_2$ composite and the MnO$_2$ rods. Table 3. shows the specific capacitance of MnO$_2$-based composites in previously published papers. The combination of higher capacitance, cyclic stability, and retention, in contrast to the previously reported work on MnO$_2$-based composites, suggest that the Ag-rGO@MnO$_2$ nanocomposite is an ideal material for fabricating an electrode for electrochemical devices.

![Figure 10](image_url)

**Figure 10.** Comparative (a) CV curve of pure MnO$_2$ rods, rGO@MnO$_2$, and Ag-rGO@MnO$_2$ at fixed scan rate 10mVs$^{-1}$ within potential window 0.0–0.5 V and (b) GCD curve at fixed current density 0.5 Ag$^{-1}$ with potential difference 0.0–0.4 V.

Table 2. Capacitive values of MnO$_2$ rods, rGO@MnO$_2$, and Ag-rGO@MnO$_2$ at different current densities.

<table>
<thead>
<tr>
<th>Current Density (Ag$^{-1}$)</th>
<th>MnO$_2$ rods</th>
<th>rGO@MnO$_2$</th>
<th>Ag-rGO@MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>293.5</td>
<td>305.25</td>
<td>675</td>
</tr>
<tr>
<td>1</td>
<td>287.5</td>
<td>293.5</td>
<td>600</td>
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<tr>
<td>2</td>
<td>280</td>
<td>290</td>
<td>575</td>
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<tr>
<td>4</td>
<td>260</td>
<td>275</td>
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<tr>
<td>5</td>
<td>181.25</td>
<td>200</td>
<td>250</td>
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<td>7</td>
<td>143.5</td>
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</tr>
<tr>
<td>10</td>
<td>100</td>
<td>110</td>
<td>120</td>
</tr>
</tbody>
</table>
and shows the potential ability to be used as electrode material for various electrochemical applications. The comparative specific capacitance of MnO$_2$ based nanocomposites from previously published works compared to the Ag-rGO@MnO$_2$ in this work is displayed in Figure 11b.

**Table 3.** The comparative specific capacitance of pure MnO$_2$ and its composites with the prepared electrode based on Ag-rGO@MnO$_2$ nanocomposite in previously published papers.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode Material</th>
<th>Electrolyte</th>
<th>Current Density (Ag$^{-1}$)</th>
<th>Specific Capacitance (C$_{sp}$) Fg$^{-1}$</th>
<th>No. of Cycles</th>
<th>Retention%</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>MnO$_2$ NR</td>
<td>1M Na$_2$ SO$_4$</td>
<td>1</td>
<td>362</td>
<td>5000</td>
<td>83</td>
<td>[54]</td>
</tr>
<tr>
<td>2.</td>
<td>MnO$_2$ nanoparticles</td>
<td>1M Ca(NO$_3$)$_2$</td>
<td>0.5 mA cm$^{-2}$</td>
<td>283</td>
<td>1000</td>
<td>78</td>
<td>[55]</td>
</tr>
<tr>
<td>3.</td>
<td>MnO$_2$/g-C$_3$N$_4$</td>
<td>1M Na$_2$ SO$_4$</td>
<td>1</td>
<td>211</td>
<td>1000</td>
<td>90</td>
<td>[56]</td>
</tr>
<tr>
<td>4.</td>
<td>MnO$_2$/EG</td>
<td>1M Na$_2$ SO$_4$</td>
<td>2 mV s$^{-1}$</td>
<td>358</td>
<td>1000</td>
<td>87</td>
<td>[57]</td>
</tr>
<tr>
<td>5.</td>
<td>α-Fe$_2$O$_3$/MnO$_2$</td>
<td>1M KOH</td>
<td>1</td>
<td>216</td>
<td>1000</td>
<td>89.2</td>
<td>[58]</td>
</tr>
<tr>
<td>6.</td>
<td>rGO/MnO$_2$</td>
<td>6KOH</td>
<td>0.85</td>
<td>486.48</td>
<td>2000</td>
<td>75.8</td>
<td>[59]</td>
</tr>
<tr>
<td>7.</td>
<td>CNT/rGO/MnO$_2$</td>
<td>2M Na$_2$ SO$_4$</td>
<td>1</td>
<td>404</td>
<td>5000</td>
<td>70</td>
<td>[60]</td>
</tr>
<tr>
<td>8.</td>
<td>MnO$_2$/PANI/GN</td>
<td>1M Na$_2$ SO$_4$</td>
<td>1</td>
<td>472</td>
<td>5000</td>
<td>79.7</td>
<td>[61]</td>
</tr>
<tr>
<td>9.</td>
<td>MnO$_2$/PPy/rGO</td>
<td>1M Na$_2$ SO$_4$</td>
<td>0.25</td>
<td>404</td>
<td>5000</td>
<td>91</td>
<td>[62]</td>
</tr>
<tr>
<td>10.</td>
<td>Ag-rGO@MnO$_2$</td>
<td>2M KOH</td>
<td>0.5</td>
<td>675</td>
<td>3000</td>
<td>90</td>
<td>Present case</td>
</tr>
</tbody>
</table>

**Figure 11.** (a) Calculated specific capacitance versus current density plot of prepared electrode based on pure MnO$_2$ rods and their composites, (b) comparative specific capacitance graph of MnO$_2$-based nanocomposites in further published papers.

Life-cycle study is a necessary requirement for electrochemical devices. Therefore, GCD analysis was used to test the cyclic stability of the Ag-rGO@MnO$_2$ composite at a fixed current load of 0.5 Ag$^{-1}$ between 0 and 1.5 V, as shown in Figure 12a. The Ag-rGO@MnO$_2$ nanocomposite showed outstanding electrochemical stability and retained 90% of its initial capacitance value after 3000 cycles. Figure 12b shows the comparative cycle stability graph of MnO$_2$ based nanocomposites from previously published papers. It can be seen that the ternary composite Ag-rGO@MnO$_2$ has the highest cycle stability. The energy density (E) and power density (P) of the Ag-rGO@MnO$_2$ nanocomposite were evaluated using Equations (4) and (5) as follows:

\[ E(\text{Wh/kg}) = \frac{1}{2}CV^2 \]  
\[ P(\text{W/kg}) = \frac{E}{t} \]
Crystals 2022, 12, x FOR PEER REVIEW 14 of 17

Figure 12. (a) Cycle stability of Ag-rGO@MnO2 nanocomposite, (b) comparative cycle stability graph of MnO2-based nanocomposites in further published papers, and (c) Ragone plot of Ag-rGO@MnO2 nanocomposite.

Ragone plots were constructed by plotting the curve between energy density versus power density, as displayed in Figure 12c. It shows the Ag-rGO@MnO2 nanocomposite stored a maximum energy density of 15 Whkg⁻¹ at a power density of 100 Wkg⁻¹ for a current density of 0.5 Ag⁻¹. Furthermore, when the current density was increased to 10 Ag⁻¹, the values of the energy density was 3 Whkg⁻¹ and power density of 2700 Wkg⁻¹ were recorded. The energy density was observed to increase when the value of power density decreased. Similarly, the value of energy density decreased as the value of power density increased. Therefore, energy density was found to be inversely proportional to power density.

4. Conclusions

In this work, a ternary Ag-rGO@MnO2 nanocomposite was successfully synthesized by hydrothermal and chemical reduction methods, confirmed by different analytical techniques. The Ag-rGO@MnO2, rGO@MnO2 and MnO2 were tested as electrode material using a three-electrode system in 2M potassium hydroxide electrolyte. The results showed that electrodes based on the Ag-rGO@MnO2 nanocomposite had a higher capacitive value than the rGO@MnO2 composite and the MnO2 rods. The electrochemical behavior of MnO2 rods improved by incorporating it with rGO, which increased the active sites on the surface of the electrode to facilitate the redox reaction by reducing the restacking or aggregation. Furthermore, the highly conductive noble metal Ag anchored on the rGO@MnO2 nanocomposite surface further enhanced its electrochemical properties. The ternary Ag-rGO@MnO2 nanocomposite achieved a high energy density (15 Whkg⁻¹) at a power density (100 Wkg⁻¹) and showed excellent long cyclic stability with a retention value of 90% of the initial value. Therefore, the nanocomposite Ag-rGO@MnO2 with high capacitive value and excellent cyclic stability could be used as an electrode material for fabricating high-performance electrochemical devices and applications.
Author Contributions: Conceptualization, A.R.A., M.O.A. and Z.O.; methodology, A.R.A., S.A.A., N.P. and Z.O.; writing—original draft preparation, A.R.A., M.O.A. and S.A.A.; writing—review and editing, N.P. All authors have read and agreed to the published version of the manuscript.

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