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Synthesis of Bi$_2$O$_3$-MnO$_2$ Nanocomposite Electrode for Wide-Potential Window High Performance Supercapacitor

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Received: 15 July 2019; Accepted: 24 August 2019; Published: 28 August 2019

Abstract: In this work, we report the synthesis of a Bi$_2$O$_3$-MnO$_2$ nanocomposite as an electrochemical supercapacitor (ES) electrode via a simple, low-cost, eco-friendly, and low-temperature solid-state chemical process followed by air annealing. This as-synthesized nanocomposite was initially examined in terms of its structure, morphology, phase purity, and surface area using different analytical techniques and thereafter subjected to electrochemical measurements. Its electrochemical performance demonstrated excellent supercapacitive properties in a wide potential window. Its specific capacitance was able to reach 161 F g$^{-1}$ at a current density of 1 A g$^{-1}$ and then showed a superior rate capability up to 10 A g$^{-1}$. Furthermore, it demonstrated promising cycling stability at 5 A g$^{-1}$ with 95% retention even after 10,000 charge–discharge cycles in a wide potential window of 1.3 V, evidencing the synergistic impact of both Bi$_2$O$_3$ and MnO$_2$ in the Bi$_2$O$_3$-MnO$_2$ ES electrode. Additionally, the practical reliability of the envisioned electrode was ascertained by the fabrication of a symmetric Bi$_2$O$_3$-MnO$_2$/Bi$_2$O$_3$-MnO$_2$ pencil-type supercapacitor device that displayed an energy density of 18.4 Wh kg$^{-1}$ at a power density of 600 W kg$^{-1}$ and a substantial cyclic stability up to 5000 cycles. Subsequently, an LED was also powered at its full brightness using three of these devices connected in series in order to demonstrate the real-time application of the Bi$_2$O$_3$-MnO$_2$ ES electrode.

Keywords: nanocomposite; Bi$_2$O$_3$-MnO$_2$; solid state synthesis; supercapacitor; wide potential window

1. Introduction

During the past few years, there has been a dramatic increase in research activities directed at developing high-performance energy storage devices due to their increasingly important role in our daily life and energy driven society [1–5]. Among the different available energy storage devices, electrochemical supercapacitors (ESs) have attracted considerable interest due to their myriad technological applications on account of their unique properties, i.e., fast charging and discharging, long cycle life, high reliability, and ability to deliver high power density than conventional batteries. In recent years, researchers have extensively worked to develop different ES electrode materials via several different synthesis methods such as dc-plasma reaction, solution-derived synthesis, molecular beam epitaxy, chemical vapor deposition, sputtering, thermal evaporation, and many others [6–10]. It should be noted that these synthesis methods are impressive but require specific experimental conditions, complicated and expensive instrumental setups, they involve strict environmental controls,
and also provide only limited yields of the synthesized product. Therefore, to enable the production of ES electrode materials on a large scale, it is highly desirable that a synthesis route should be adopted that is economically viable and facile. Among the different available routes fulfilling these requirements such as the sol-gel route [11] and the co-precipitation method [12], the solid state chemical synthesis route is one of the simplest and extensively used methods for developing various types of materials for different applications [13,14]. Importantly, this method has seldom been explored for the development of ES electrode materials.

Previously, the majority of the electrode materials envisaged fall mainly into three categories: Metal oxides or hydroxides, carbonaceous materials, and conducting polymers. By contrast, metal oxide/hydroxide-based electrode materials are relatively economic and eco-friendly. Especially, by virtue of their synergistic effects, nanocomposites of metal oxides/hydroxides have proven to be remarkable as ES electrode materials [15,16]. However, it is important to avoid the use of expensive rare earth metal oxides/hydroxides and those materials which have environmental hazards associated with them. Among the different types of metal oxide materials that can serve as ES electrodes, bismuth oxide (Bi$_2$O$_3$) is known to be a promising negative ES electrode material owing to its multiple oxidation states, biocompatibility, and non-toxicity [17,18]. Additionally, the alternating layered structure of Bi$_2$O$_3$ makes it an interesting host for ion storage, encouraging its employment for energy storage applications. On the other side, manganese dioxide (MnO$_2$) has drawn enormous research interest owing to its high theoretical capacitance, environmental friendliness, and great abundance [19–21]. More importantly, it also provides a wide positive potential window in an aqueous electrolyte, resulting in high-energy-density ES devices [22]. Looking at the intriguing properties of both these materials, it would be interesting to explore nanocomposites of these materials as ES electrodes, capitalizing on their dissimilar opposite electrochemical potential windows to form a single wide potential window. Previously, Ma et al. [23] reported bismuth oxide @ manganese oxide nanocomposite electrodes for ES applications. However, the obtained nanocomposite was unable to show any surprising supercapacitive performance. Similar work was reported by Chi et al., who also could not achieve excellent performance from their nanocomposites [24]. Moreover, in both the cases, there was a need for a special apparatus arrangement to synthesize the nanocomposites, inhibiting their facile and large-scale production.

We, therefore, in the present work, report a facile solid-state chemical synthesis approach to prepare Bi$_2$O$_3$-MnO$_2$ nanocomposite as an ES electrode with a wide potential window. This synthesis process is inexpensive, environmentally friendly, and easily scalable. The as-synthesized Bi$_2$O$_3$-MnO$_2$ nanocomposite was characterized to determine its phase purity, structure, morphology, and surface area. After different characterizations, electrochemical measurements were conducted using a three-electrode configuration to measure its specific capacitance, rate capability, and cycling stability. Further, Bi$_2$O$_3$-MnO$_2$ ES electrode was used to design a symmetric device, installed as a posistrode (i.e., positive electrode) and negatrode (i.e., negative electrode), offering a superior energy density of 18.4 Wh kg$^{-1}$ at a power density of 600 W kg$^{-1}$ with a cycling stability up to 5000 cycles retaining almost 96% of its initial energy density. The promising electrochemical performance obtained for this device and its successful use for powering an LED show the potential of the Bi$_2$O$_3$-MnO$_2$ nanocomposite as an ES electrode.

2. Experimental Details

2.1. Materials

All reagents used in the present work were of analytical grade and used without further purification. Bismuth chloride (BiCl$_3$ >98%), manganese chloride tetrahydrate (MnCl$_2$·4H$_2$O >98%), and sodium hydroxide (NaOH >98%) were purchased from Sigma Aldrich. Deionized (DI) water obtained from Millipore was used throughout the experiments as a solvent.
2.2. Method of Synthesis

The Bi$_2$O$_3$-MnO$_2$ nanocomposite was synthesized by using a solid-state chemical synthesis route in the presence of two readily available and low-cost reactants, i.e., BiCl$_3$, and MnCl$_2$·4H$_2$O, and NaOH. In a typical synthesis, 4 g of each metal precursor in powder form and 2 g of NaOH (2:1 w/w) were ground together using agate and mortar for 15–20 min. A thick, slurry kind of paste was obtained after completion of the reaction. The paste was washed grossly dispersing it into water, and then centrifuged for product separation. This process was repeated three times before the final product was obtained. After washing, the product was dried at 60 °C in oven and then annealed at 300 °C for 1 h in a horizontal tube furnace.

2.3. Fabrication of ES Electrode and Full-Cell Device Assembly

Fabrication of ES electrodes was done by mixing active material (final product obtained after annealing) with acetylene black and a polytetrafluoroethylene (PTFE) suspension (60 wt.%) as a binder at a weight ratio of 8:1:1, and then pressing this mixture onto a nickel foam substrate (20 MPa) serving as a current collector. The mass loading of the active material on the Ni foam was approximately 3 mg cm$^{-2}$. Thereafter, it was dried in a vacuum oven at 60 °C for 12 h before using it as a working electrode in a three-electrode configuration for electrochemical measurements. Later on, to fabricate a full-cell device configuration, two similar working electrodes were stacked together separated by a piece of filter paper soaked in 1 M NaOH liquid electrolyte. The prepared assembly is denoted as a Bi$_2$O$_3$-MnO$_2$ // Bi$_2$O$_3$-MnO$_2$ pencil-type symmetric ES device.

2.4. Material Characterizations

The X-ray diffraction (XRD) pattern used to characterize the Bi$_2$O$_3$-MnO$_2$ nanocomposite was obtained using a D8-Discovery Bruker diffractometer with a Cu-K$_\alpha$ source (λ = 1.5405 Å) operated at a voltage of 40 kV and a current of 40 mA. The surface morphology of the nanocomposite and the elements present therein were examined using a field-emission scanning electron microscope (FESEM, Hitachi, S-4800, 15 kV) equipped with an energy dispersive X-ray spectrometer (EDX). During EDX operation, the probe was focused to 0.2 nm and a camera length of 20 cm was used. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning TEM (STEM) images were also recorded using an FEI Tecnai F20. Brunauer–Emmett–Teller (BET) measurements were performed on a Micromeritics ASAP 2010 analyzer to confirm the type of porosity and the surface area of the nanocomposite. The pore size distributions of all the samples were confirmed from Barrett–Joyner–Halenda (BJH) plots. X-ray photoelectron spectroscopy, (XPS, VG Scientifics ESCALAB250) calibrated to a carbon peak (C 1s) located at 284.6 eV, was used to analyze the composition and valence states of the ions present over the surface of the Bi$_2$O$_3$-MnO$_2$ nanocomposite.

2.5. Electrochemical Measurements

Electrochemical measurements of the Bi$_2$O$_3$-MnO$_2$ ES electrode and its device assembly were carried out on an Ivium-n-Stat electrochemical workstation (Ivium, The Netherlands). The electrode was subjected to cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements, as the working electrode, in a three-electrode configuration containing 1 M aqueous NaOH electrolyte. A piece of platinum foil (facing towards the working electrode) and a saturated Hg/HgO electrode served as the counter and the reference electrodes, respectively. The distance between the working electrode and the counter electrode was fixed to be ~1 cm. The EIS response was recorded in the frequency range of 100 kHz–0.01 Hz with an AC voltage amplitude of 5 mV. Similarly, the constructed device was employed on the same station using two terminals for its electrochemical measurements. Calculations of the specific capacitance,
energy density, and power density were done similarly to the calculations in our previously reported paper [25] using the following equations:

\[
C_E = \frac{I \Delta t}{m \Delta V} \quad C_{device} = \frac{I \Delta t}{m_t V}
\]  

(1)

\[
E = \frac{1}{2} C_{device} V^2
\]  

(2)

\[
P = \frac{E}{\Delta t} \times 3600
\]  

(3)

where, \(C_E\) and \(C_{device}\) are the specific capacitances in F g\(^{-1}\) for the electrode and device calculated from their respective charge–discharge curves, \(I\) is the charge–discharge current, \(\Delta t\) is the discharging time, \(m\) is the mass of active material, \(m_t\) is the mass of total electrode material, \(\Delta V\) is the potential window of the half-cell, \(V\) is the voltage of the charge–discharge curve measured for the symmetric device, and \(E\) and \(P\) are the energy density and power density in terms of Wh kg\(^{-1}\) and W kg\(^{-1}\) of the symmetric device, respectively.

3. Results and Discussion

3.1. Structural Analysis

The structure and phases present in the Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite were confirmed from the XRD pattern shown in Figure 1 (4th from the bottom row). To clearly show the presence of MnO\(_2\) in the Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite, we also present the XRD pattern of Bi\(_2\)O\(_3\) prepared by the same solid-state synthesis route in Figure 1 (3rd from the bottom row). The XRD patterns of both samples have been indexed using Bi\(_2\)O\(_3\) and MnO\(_2\) standard reference patterns reported in JCPDS No: 027-0053 and JCPDS No: 053-0633, respectively, shown in Figure 1 (bottom row and 2nd from bottom row). The XRD pattern corresponding to Bi\(_2\)O\(_3\), scanned within the range of \(2\theta = 15–50^\circ\), matches well with its reported standard reference pattern. All the peaks are clearly visible and can be well indexed to a monoclinic phase with P21/c space group.

![Figure 1. The X-ray diffraction (XRD) patterns of Bi\(_2\)O\(_3\) and Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposites.](image)

The two most prominent peaks observed at 2\(\theta\) values of 27.3\(^\circ\) and 33.2\(^\circ\) exhibits \(d\)-spacings of 3.25 Å and 2.71 Å and therefore correspond to the (-121) and (-202) reflection planes of Bi\(_2\)O\(_3\), respectively. Further, the XRD pattern of Bi\(_2\)O\(_3\)-MnO\(_2\) was also scanned within the same 2\(\theta\) range and
matches well with the expected Bi$_2$O$_3$ reflection planes, except for one additional peak. This additional peak appearing at 2θ values of 30.1° is the peak of the Bi(OH)$_3$ phase present as an impurity in the synthesized material.

Moreover, we can also notice two peaks for MnO$_2$, among which one of the peaks at 27.3° coincides with the most prominent peak observed for Bi$_2$O$_3$, and exhibits d-spacings of 3.26 Å. The other peak appearing at 37.0° is the most prominent peak of MnO$_2$ according to the standard reference pattern in the respective JCPDS card exhibiting d-spacing of 2.42 Å. These peaks therefore correspond to the (310) and (330) reflection planes of MnO$_2$, respectively. The well matching peaks can be indexed to a tetragonal lattice system. Thus, the XRD pattern confirms the presence of two distinct phases, i.e., Bi$_2$O$_3$ and MnO$_2$, in the Bi$_2$O$_3$-MnO$_2$ sample, confirming the formation of a nanocomposite. Additionally, a larger full width at half maximum (FWHM) can be seen for the peaks in the XRD pattern of the Bi$_2$O$_3$-MnO$_2$ nanocomposite in comparison to the XRD pattern of Bi$_2$O$_3$, which suggests the nanocomposite has a finer crystallite size. Furthermore, no impurity phase peaks were found in the XRD pattern except one from the Bi(OH)$_3$ phase. Therefore, it confirms the phase purity of the nanocomposite.

3.2. Electronic States and Chemical Composition Confirmation

The surface electronic states and chemical compositions were obtained from XPS analysis, shown in Figure 2a, where the presence of Bi, Mn, and O is evidenced without any impurity elements, suggesting the formation of Bi–Mn–O based nanocomposite. The high-resolution XPS spectra of Bi 4f, Mn 2p, and O 1s are shown in Figure 2b–d. Figure 2b shows the Bi 4f core level spectrum with two spin–orbit doublet peaks (J = 5/2 and 7/2) centered at 164.2 (Bi 4f$_{5/2}$) and 158.9 eV(Bi 4f$_{7/2}$) with a peak separation of 5.3 eV, which is in accordance with the literature, clarifying the existence of Bi in the +3 oxidation state [26]. Further, deconvolution of the above doublet peaks resulted in two sub-peak in each. The pair of peaks at 164.3, and 159 eV with a peak separation of 5.3 eV is in correlation with the extant cited literature, confirming the presence of Bi$_2$O$_3$ phase in the sample. Additionally, the pair of peaks at lower binding energies 164 and 158.6 eV with the peak separation of 5.6 eV can be assigned to Bi$^0$ state of metallic Bi 4f [27].

![Figure 2. X-ray photoelectron spectroscopy (XPS) analysis, (a) full scan spectrum of Bi$_2$O$_3$-MnO$_2$, (b) narrow scan of Bi 4f, (c) Mn 2p, and (d) O 1.](image-url)
Similarly, Figure 2c shows the spin–orbit doublet of Mn 2p \((j = 3/2, 1/2)\) centered at 641.9 (Mn 2p3/2) and 653.7 eV (Mn 2p1/2) with a peak separation of 11.8 eV, indicating the existence of the Mn\(^{4+}\) oxidation state \([28,29]\). Again, the deconvolution of spin–orbit peaks indicate the co-existence of Mn\(^{4+}\) and Mn\(^{3+}\) valence state at 642.9 and 641.4 eV, respectively. However, higher peak intensity and larger area under the curve can be noticed for the peak corresponding to Mn\(^{4+}\) state in comparison to peak corresponding to Mn\(^{3+}\) state, confirms the presence of major phase as MnO\(_2\) along with partially surface oxidized Mn\(_2\)O\(_3\) phase in the sample \([30]\). Further, the deconvoluted O 1s spectrum presented in Figure 2d manifests two peaks located at 530.1 and 531.5 eV due to lattice oxygen and surface-adsorbed oxygen, respectively \([31–33]\). Thus, the XPS data confirms the chemical purity of the sample, and the electronic states of the elements are consistent with the formation of a Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite.

### 3.3. Structure–Morphology Correlation and Reaction Mechanism

The surface morphology of the as-prepared Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite was initially analyzed using SEM images like that shown in Figure 3a, which highlights the fine nanoplatelet-like structures fused to each other \([34]\). A magnified image of this morphology shows that these platelets exist in a cubic form (Figure 3a insert). However, agglomeration of nanoplatelets can also be seen, although to a moderate extent only in comparison to the Bi\(_2\)O\(_3\) sample prepared by same solid-state synthesis route (supporting information Figure S1). Again, the morphology and internal structure of these nanoplatelets were analyzed using TEM and HRTEM (Figure 3b) where a big faceted crystal along with a fine elongated nanoparticle were observed. A higher magnification image acquired specifically from the marked square portion is shown in Figure 3c, confirming that the as-formed crystals are highly crystalline and that they consist of two distinct sets of planes. The big faceted cubic-type crystals exhibit a lattice spacing of 2.71 Å corresponding to the (-122) plane of Bi\(_2\)O\(_3\) and a spacing of 2.98 Å corresponding to the (220) plane of MnO\(_2\), suggesting the involvement of both Bi\(_2\)O\(_3\) and MnO\(_2\) in the Bi\(_2\)O\(_3\)-MnO\(_2\) composite \([35]\). Figure 3d shows the high-angle annular dark field (HAADF) image from a particular imaging area of the nanocomposite with a changing brightness at different locations, suggesting the even distribution of the respective elements throughout the sample. The analogous EDX elemental mapping clearly agrees with the HAADF image, showing that the elements of the nanocomposite, i.e., Bi, Mn and O, are seemingly visible as a mixture of three different colors in Figure 3e. Further, the focused mapping of specific elements depicts the separate mapping of Bi in red (Figure 3f), O in blue (Figure 3g), and Mn in green (Figure 3h), affirming the locus of elemental distribution areas in the nanocomposite precisely. Thus, HRTEM analysis and EDX elemental mapping together confirm the formation of a Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite, which is in good agreement with XRD and XPS results. The surface area and porosity of the as-synthesized nanocomposite were also estimated, through BET and BJH measurements, presented in supporting information (Figure S2 and the inbuilt inset), exhibiting a type-IV isotherm and H\(_3\)-type hysteresis loop \((I/P_0 \sim 0.4)\).
The measured surface area was 27 m² g⁻¹, whereas the average pore diameter lies close to 74 Å, suggesting the mesoporous nature of the Bi₂O₃-MnO₂ nanocomposite, which is favorably a good signature since it exposes plenty of electroactive sites to the electrolyte and also facilitates easy migration of electrolyte ions into its near surface area region.

The formation mechanism of the Bi₂O₃-MnO₂ nanocomposite can be described as follows. Initially, NaOH reacts with the metal chloride salts in the presence of environmental moisture due to rigorous mixing of the precursor salt, resulting in the precipitation of metal hydroxides with the evolution of heat [14,36,37]

\[
\text{BiCl}_3 + 3\text{NaOH} \rightarrow \text{Bi(OH)}_3 + 3\text{NaCl} \quad (4)
\]

\[
\text{MnCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Mn(OH)}_2 + 2\text{NaCl} + 4\text{H}_2\text{O} \quad (5)
\]

Furthermore, after washing the yield several times, as detailed in the experimental section, a product powder free from reactant impurities is obtained after drying. After air annealing, this powder decomposes and is oxidized by the environmental oxygen, giving rise to the Bi₂O₃-MnO₂ nanocomposite. To ascertain the formation of the hydroxides in the intermediate state (i.e.,
before annealing) we also took the powder XRD of before annealed sample (supporting information Figure S3) which clearly confirms the presence of bismuth and manganese hydroxide in the sample.

$$2\text{Bi} (\text{OH})_3 + \text{Mn(OH)}_2 + x\text{O}_2 \xrightarrow{\Delta} \text{Bi}_2\text{O}_3 + \text{MnO}_2 + y\text{H}_2\text{O} \quad (6)$$

3.4. Electrochemical Performance Analysis

To highlight the benefits of Bi$_2$O$_3$-MnO$_2$ over the Bi$_2$O$_3$ ES electrode synthesized by the same solid-state synthesis route, their CV and GCD performances are compared at a scan rate of 50 mV s$^{-1}$ and current density of 1 A g$^{-1}$ in Figure 4a,b, respectively. For the full CV and GCD performances of the Bi$_2$O$_3$ ES electrode, refer to Figure S4 in the supporting information. A 1 M solution of sodium hydroxide (NaOH) was used throughout all the electrochemical measurements. As can be seen from the CV curves, the potential window of the Bi$_2$O$_3$-MnO$_2$ ES electrode was extended by an additional 0.3 V, ensuring that it has the potential to deliver high energy storage ability. Moreover, the same CV also encloses a larger area under its curve with a relatively higher current density response, signifying that the Bi$_2$O$_3$-MnO$_2$ ES electrode is endowed with rich electroactive sites as well as better conductivity. Certainly, this shows that combining Bi$_2$O$_3$ with MnO$_2$ induces a key influence to enhance significant level of capacitive ability in Bi$_2$O$_3$-MnO$_2$ ES electrode. This key influence could be understood more clearly in the Supporting information Figure S5, where, the comparative CV curves for Bi$_2$O$_3$, MnO$_2$ and Bi$_2$O$_3$-MnO$_2$ ES electrode has been presented. Importantly, the enhanced performance in Bi$_2$O$_3$-MnO$_2$ ES electrode doesn’t include any contribution from the Ni-foam, used as a current collector. To ascertain this, CV performance has been compared for Bi$_2$O$_3$-MnO$_2$ ES electrode and bare Ni-foam (supporting information Figure S6) measured in the same electrolyte. Comparison shows that the CV performance obtained for the Ni-foam is almost negligible in compared to CV performance seen for the Bi$_2$O$_3$-MnO$_2$ ES electrode. Therefore, the high electrochemical potential obtained for the Bi$_2$O$_3$-MnO$_2$ ES electrode is a clear vindication of synergistic inclusion of electrochemical performance from the MnO$_2$ ES material. CV and GCD performance of the MnO$_2$ ES electrode is shown in the supporting information Figure S7, evince the idea of individual capacitive as well as energy storage potential of MnO$_2$.

Further, the comparative GCD performances in Figure 4b are in good agreement with the discussed CV results, where a larger potential window and area under the GCD curve were again observed for the Bi$_2$O$_3$-MnO$_2$ ES electrode, confirming its higher energy storage ability. Nevertheless, the commonality between the performances of the two electrodes is their almost linear GCD curves, confirming their capacitive-type energy storage behavior. Figure 5a,b present detailed CV and GCD measurements of the Bi$_2$O$_3$-MnO$_2$ ES electrode. The shapes of the CV curves obtained at different scan rates ranging from 10 (low scan rate) to 100 mV s$^{-1}$ (high scan rate) demonstrate typical capacitive-type behavior due to impressive charge transport characteristics and easy migration of ions into the near surface.
region of the electrode material. With increasing scan rate, the shape of the CV curve deviates slightly from its near rectangular appearance, indicating the existence of partial diffusion resistance.

Moreover, despite this partial diffusion resistance evidenced by the CV curves, no significant deformation was observed in the shapes of CV curves obtained after cycling (supporting information in Figure S8a). The characteristics of these CV curves suggest that the capacitive activity originates mainly from the outer surface and near surface region of Bi$_2$O$_3$-MnO$_2$, where charge transfer occurs from the specifically adsorbed ions as well as counter balanced ions to the electrostatically polarized electrode [38]. Due to the involvement of the outer surface and near surface region, diffusion resistance encountered during the forward and backward scans is minimal, which allows the CV curves to retain their shape over a long period of time. Moreover, the CV curves enclose a prominent area within a wide potential range of 1.3 V, indicating the high energy storage ability of the Bi$_2$O$_3$-MnO$_2$ electrode. We can further validate this inference from the GCD curves (Figure 5b), measured by charging and discharging up to a current density of 10 A g$^{-1}$ without any reduction in the potential window marked for the CV curves.

The linear behavior of the charge-discharge curves is a clear indication of surface and near surface controlled capacitive behavior from the ES electrode. Intriguingly, this capacitive ability has emerged as a consequence of reversible electrostatic as well as Faradaic reactions originating from Bi$_2$O$_3$ and MnO$_2$ in the Bi$_2$O$_3$-MnO$_2$ composite [17,24,39].

\[
\text{MnO}_2 + \text{Na}^+ + e^- \leftrightarrow (\text{MnOO}^\cdot\text{Na}^+) \quad (7)
\]

\[
(\text{MnO}_2)_{\text{surface}} + \text{Na}^+ \leftrightarrow (\text{MnOO}^\cdot\text{Na}^+)_{\text{surface}} \quad (8)
\]

\[
\text{Bi}_2\text{O}_3 + x\text{Na}^+ + xe^- \leftrightarrow \text{Na}_x\text{Bi}_2\text{O}_3 \quad (9)
\]

Furthermore, the electrochemical behavior of the Bi$_2$O$_3$-MnO$_2$ electrode was also studied based on its EIS performance (Figure 5c), where a very small series resistance of about 0.9 $\Omega$ is evidenced from the intercept on the X-axis in the high frequency range. Moreover, the curvature diameter of 2.3 $\Omega$ seen in the magnified Nyquist plot corresponds to the interfacial charge–transfer resistance ($R_{\text{ct}}$) between the interface of the electrode and the electrolyte solution. This implies a rapid charge transfer
process across the electrolyte/electrode interface, ensuring a large capacitance and good rate capability up to 10 A g\(^{-1}\) from Bi\(_2\)O\(_3\)-MnO\(_2\) electrode.

In the low frequency region, the straight line exhibiting a slope of more than 45° can be attributed to the excellent capacitive behavior of Bi\(_2\)O\(_3\)-MnO\(_2\) on account of the surface redox reactions and electric double layer formation, consistent with the CV and GCD results. The rate capability performance of the as-fabricated Bi\(_2\)O\(_3\)-MnO\(_2\) electrode is presented in Figure 5d. A specific capacitance (SC) of 161 F g\(^{-1}\) at 1A g\(^{-1}\) was obtained from the GCD curves, sustaining an impressive SC up to 53 F g\(^{-1}\) at a relatively high current density of 10 A g\(^{-1}\). Such impressive rate capability performance is due to the fact that a large number of electroactive sites are exposed to the ions present in the electrolyte. However, the decrease in the value of the SC towards higher current density is possibly due to abated participation of electroactive sites in the near surface region during the quick charging-discharging process of the Bi\(_2\)O\(_3\)-MnO\(_2\) electrode.

Another important electrochemical aspect of any electrode material is its cycling stability, which is an essential criterion for establishing its endurance before it can be employed in the ES devices. Figure 5e shows the long-term cycling stability of the ES electrode up to 10,000 cycles of GCD @ 5 A g\(^{-1}\) current density. Stable capacitance retention with almost 95% of its initial capacitance was achieved after cycling while securing a 99.5% of columbic efficiency, indicating the excellent kinetic reversibility of the electrode. The stability of Bi\(_2\)O\(_3\)-MnO\(_2\) energy storage properties after cycling are well attested by its CV, GCD, and EIS performance, which are presented in detail in Figure S8a–c of the supporting information. Comparing the electrochemical performance of the as-synthesized Bi\(_2\)O\(_3\)-MnO\(_2\) nanocomposite with literature data (Table 1), several unique features can be observed: (i) Better cycling stability compared to other bismuth oxide electrodes, and (ii) a higher working potential window with excellent ES properties. [23] Meanwhile the synthesis technique used is comparatively cheaper, easily scalable, and facile. These unique features of the Bi\(_2\)O\(_3\)-MnO\(_2\) electrode and its high energy storage performance could possibly be attributed to: (i) The fused nanoplatelet-like morphology with multiple interconnecting points allowing fast electron transport, (ii) good crystallinity with reduced electronic resistance, (iii) a mesoporous structure allowing better ionic/mass transportation, and (iv) Chemically and mechanically stable nanomaterial providing its long-term usability. Further, to realize the application potential of the Bi\(_2\)O\(_3\)-MnO\(_2\) ES electrode, a Bi\(_2\)O\(_3\)-MnO\(_2\)/Bi\(_2\)O\(_3\)-MnO\(_2\) symmetric ES device was assembled and then subjected to CV and GCD measurements, as demonstrated in Figure 6a,b, respectively. The CV scanning performed from a low to high scan rate within a 0–1.3 V stable potential range confirmed the capacitive-type charge storage behavior of the symmetric ES device, which is almost similar to that of the individual Bi\(_2\)O\(_3\)-MnO\(_2\) in a three electrode configuration. While scanning, these curves retained their shapes under different scan rates, suggesting good reversibility of ion transport at the electrode/electrolyte interface. Charge-discharge measurements were carried out from low to high current density as shown in Figure 6b, to determine the real-time charge storage ability of the device. As can be seen from the GCD curves, there is a slight deviation from its linearity compared to the single-electrode GCD curves. We believe that this increased resistance observed in the charge–discharge performance is possibly due to inter-electrode separation.
Table 1. A summary of electrochemical performance for Bi$_2$O$_3$ based composite material.

| Sl. No. | Materials | Specific Capacitance | Electrolyte | Voltage Difference (in V) | Cycling Stability (Specific Capacitance Retention) | Ref. |
|--------|-----------|----------------------|-------------|--------------------------|---------------------------------------------------|-----|
| 1      | Bi$_2$O$_3$/HOMC | 232 F g$^{-1}$ @ 5 mV s$^{-1}$ | 6 M KOH | 1.0 V | 70% after 1000 cycles | [40] |
| 2      | AC–Bi$_2$O$_3$ composite | 332.6 F g$^{-1}$ @1 A g$^{-1}$ | 6 M KOH | 1.0 V | 60% after 1000 cycles | [41] |
| 3      | BiMn$_2$O$_6$/MWCNT | 6.0 F cm$^{-2}$ @ 2 mV s$^{-1}$ | 0.5 M Na$_2$SO$_4$ | 1.0 V | 90% after 1000 cycles | [42] |
| 4      | rGO-Bi$_2$O$_3$ composite | 216 F g$^{-1}$ at 1 A g$^{-1}$ | 1 M KOH | 1.0 V | Not mentioned | [43] |
| 5      | RGO-Bi$_2$O$_3$ composite | 94 F g$^{-1}$ @ 0.2 A g$^{-1}$ | 6 M KOH | 1.0 V | 90% after 3000 cycles | [44] |
| 6      | AC-Bi$_2$O$_3$ | 0.5127 F cm$^{-2}$ | 6 M KOH | 0.9 V | 92.2% after 20,000 cycles | [45] |
| 7      | Bi$_2$MoO$_6$ | 182 F g$^{-1}$ @ 1 A g$^{-1}$ | 3 M KOH | 0.5 V | 80% after 3000 cycles | [46] |
| 8      | Bi$_2$O$_3$@MnO$_2$ | 93.1 F g$^{-1}$ @ 1 A g$^{-1}$ | 1 M Na$_2$SO$_4$ | 1 V | 112% after 1000 cycles | [23] |
| 9      | Bi$_2$O$_3$/MnO$_2$ | 79.4 F g$^{-1}$ @ 1 A g$^{-1}$ | 1 M Na$_2$SO$_4$ | 1.0 V | 95% after 1000 cycles | [24] |
| 10     | Bi$_2$O$_3$-MnO$_2$ | 161 F g$^{-1}$ @ 1 A g$^{-1}$ | 1 M NaOH | 1.3 (GCD) | 95% after 10,000 cycles | This Work |

Figure 6. (a) CV, (b) GCD, (c) Rate capability, and (d) cycling performance of the Bi$_2$O$_3$-MnO$_2$ symmetric device.

Furthermore, the capacitance retention with increasing current density up to 10 A g$^{-1}$ (in Figure 6c) evidences the rate capability of the symmetric device. The SC values calculated at 1 A g$^{-1}$ and 10 A g$^{-1}$ reached 92 F g$^{-1}$ and 8 F g$^{-1}$, respectively. Long-term cycling stability is also a crucial parameter to assess the practical application of a symmetric ES device. Figure 6d presents cycling stability plot of the device, where, GCD cycling measurement was performed at 5 A g$^{-1}$, showing only 4% loss over 5000 cycles, with 99% of columbic efficiency.

To further understand the electrochemical performance of the device, EIS measurements were conducted. As can be seen from the Nyquist plot in the high-frequency region (Figure 7a), the Z$'$-intercept on the x-axis indicates a value of 0.6 Ω for the series resistance, indicating a favorable power density for the device. In the same figure, from the inserted magnified portion of the Nyquist plot, the charge transfer resistance can be estimated to be 3 Ω based on the curvature diameter, suggesting benign transport properties at the electrode/electrolyte interface, endowing substantial
charge storage ability to the device. Also, the slope of the straight line in the high frequency region being greater than 45° is a clear indication of surface-controlled device performance. Finally, Figure 7b shows the Ragone plot for the Bi$_2$O$_3$-MnO$_2$ symmetric device, where an energy density of about 18.4 W h Kg$^{-1}$ obtained at a power density of 600 W kg$^{-1}$ is higher than the previously reported device based on bismuth manganese composite [24,43], corroborating the synergistic influence of Bi$_2$O$_3$ and MnO$_2$ in the performance of symmetric Bi$_2$O$_3$-MnO$_2$ ES device. A single LED was also powered for several minutes using three symmetric Bi$_2$O$_3$-MnO$_2$ ES devices connected in series, as shown in Figure 7b (inset), giving us confidence in the possibility of commercial utilization of this material.

![Figure 7](http://www.mdpi.com/1996-1073/12/17/3320/s1)

**Figure 7.** (a) Nyquist plot for Bi$_2$O$_3$-MnO$_2$ ES electrode (inset—magnified plot in the high frequency range) and (b) Ragone plot for the symmetric device assembly (inset—demonstrating LED lighting).

4. Conclusions

In summary, our work provides an easily scalable, low-cost, and environment friendly solid-state chemical synthesis approach to prepare a Bi$_2$O$_3$-MnO$_2$ nanocomposite electrode material for high-performance ES applications. Due to the excellent synergy of Bi$_2$O$_3$ and MnO$_2$, the polycrystalline and mesoporous Bi$_2$O$_3$-MnO$_2$ nanocomposite electrode was able to deliver 161 F g$^{-1}$ specific capacitance @ 1 A g$^{-1}$. Moreover, the nanocomposite showed superior rate capability up to 10A g$^{-1}$ and cycling retention of nearly 95% for cycling over 10,000 charge-discharge cycles. Further, the as-assembled Bi$_2$O$_3$-MnO$_2$ // Bi$_2$O$_3$-MnO$_2$ symmetric device demonstrated 18.4 Wh kg$^{-1}$ energy density @ 600 W kg$^{-1}$ power density and rate capability up to 10 A g$^{-1}$. Later on, when the device was cycled 5000 times, it still retained nearly 96% of its initial energy density. Our work inspires the preparation of other metal oxide nanocomposites using a solid-state synthesis route for their application as high-performance ES electrode materials.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1073/12/17/3320/s1, Figure S1: SEM image of Bi$_2$O$_3$ nanostructure (a) Low magnification and (b) High Magnification, Figure S2. N2-adsorption/desorption isotherms including BJH pore size distribution curve (inset) for Bi$_2$O$_3$-MnO$_2$ nanocomposite powder, Figure S3. Powder XRD for Bi$_2$O$_3$-MnO$_2$ nanocomposite before annealing, Figure S4. (a) CV and (b) GCD performance of Bi$_2$O$_3$ ES electrode, Figure S5. CV performance comparison of Bi$_2$O$_3$, MnO$_2$, and Bi$_2$O$_3$-MnO$_2$ ES electrode, Figure S6. CV performance comparison of Bi$_2$O$_3$-MnO$_2$ ES electrode and bare Ni-foam, Figure S7. (a) CV and (b) GCD performance of MnO$_2$ ES-electrode in 1M NaOH electrolyte, Figure S8. (a) CV (b) GCD and (c) EIS performance of Bi$_2$O$_3$-MnO$_2$ ES electrode after cycling.

**Author Contributions:** Conceptualization, Methodology and Review by R.S.M., Electrochemical Measurement assistance by N.M.S., Characterization of Materials, Review and English Revision by J.M.Y., Experiments, Manuscript writing, Data presentation and Review by S.S., Data analysis, its Presentation Assistance, and Review by R.K.S., Formal Analysis and Supervision by K.H.K.

**Funding:** This research received no external funding.
Acknowledgments: We gratefully acknowledge the support of this work by the Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2013M3A6B10789874). The authors are very grateful to the members of the National Core Research Centre (NCRC) for their excellent experimental assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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