Two-Dimensional Core-Shell Structure of Cobalt-Doped@MnO$_2$ Nanosheets Grown on Nickel Foam as a Binder-Free Battery-Type Electrode for Supercapacitor Application

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Abstract: Herein, we present an interfacial engineering strategy to construct an efficient hydrothermal approach by in situ growing cobalt-doped@MnO$_2$ nanocomposite on highly conductive nickel foam (Ni foam) for supercapacitors (SCs). The remarkably high specific surface area of Co dopant provides a larger contacting area for MnO$_2$. In the meantime, the excellent retentions of the hierarchical phase-based pore architecture of the cobalt-doped surface could beneficially condense the electron transportation pathways. In addition, the nickel foam (Ni foam) nanosheets provide charge-transport channels that lead to the outstanding improved electrochemical activities of cobalt-doped@MnO$_2$. The unique cobalt-doped@MnO$_2$ nanocomposite electrode facilitates stable electrochemical architecture, multi-active electrochemical sites, and rapid electro-transport channels; which act as a key factor in enhancing the specific capacitances, stability, and rate capacities. As a result, the cobalt-doped@MnO$_2$ nanocomposite electrode delivered superior electrochemical activities with a specific capacitance of 337.8 F g$^{-1}$ at 0.5 A g$^{-1}$; this is greater than pristine MnO$_2$ (277.9 F g$^{-1}$). The results demonstrate a worthy approach for the designing of high-performance SCs by the grouping of the nanstructured dopant material and metal oxides.

Keywords: cobalt-doped manganese oxides; electrode; supercapacitors; energy storage; hydrothermal method

1. Introduction

The intemperate exploitations of fossil fuels have led us to energy consumption limits and unsustainable environmental difficulties [1–3]. Supercapacitors (SCs) are a new type of greener energy storing devices among batteries and capacitors that have the benefits of higher efficiency, larger power density, environmental protections, longer cycles, etc. [4–6]. However, the low energy densities of SCs limit their large-scale configuration commercially. An efficient route to enhance this energy density is to make asymmetric SCs [7–9].

Electrodes are one of the crucial elements influencing the performances of SCs [10]. Different types of material samples have been developed so far for achieving better energy densities, such as doped materials [11–13], metal hydroxides/oxides [14,15], composite electrodes [16–19], and conductive polymers [20–23]. From this perspective, MnO$_2$ becomes a favored source for making pseudocapacitor (PCs) electrodes due to their superior theoretical capacities (~1370 F g$^{-1}$), cheaper prices, and eco-friendliness [24]. MnO$_2$ would...
deliver excellent capacities and characteristic features in neutral electrolytes, which do not need stronger acids or alkalic-type environments; in turn, this is good for the environment [25]. However, the MnO$_2$ conductivity is still poor; this issue can be solved by combining MnO$_2$ with a dopant material, which enables larger specific surface areas and excellent conductivities [26,27].

Cobalt-doped electrodes have features such as excellent electrical conductivities, good chemical stabilities, superior surface interfaces, and a cheaper price. Thus, it could be contemplated as an absolute candidate for supporting MnO$_2$ in forming a composite electrode sample [28]. The fabrication of cobalt-doped materials on nickel foam skeleton has attracted a lot of interest so far [4,29–31]. Nickel foam is safer, greener, and plentiful; thus, it became favorable for renewable energy developments. Cobalt-doped material on the nickel foam skeleton generally consists of superior surface area and porosities, which would efficaciously shorten the ion/electron transportation intervals. Nickel foam with cobalt-doped material handled with alkali or acids also has a plentiful functional surfacing group, which are favored for electrochemical activities [32–35]. Thus, the use of cobalt-doped material with nickel foam and MnO$_2$ has been anticipated to enhance the performances of both MnO$_2$ and cobalt-doped materials.

Herein, we developed a unique cobalt-doped MnO$_2$ with the conductive skeleton of nickel foam via a hydrothermal technique. The composite of cobalt-doped@MnO$_2$ delivers excellent energy storing performance. This would be ascribed to the excellent retention of the conductive way and uniformly loaded MnO$_2$. Cobalt-doped@MnO$_2$ facilitated the self-assembly of the composites with nickel foam; meanwhile, the metal oxides constructively enhanced the capacities by transmitting the composite with PCs. The energy storage performances of the cobalt-doped@MnO$_2$ nanosheets were synergistically developed, providing multiple chemical states of Co-existences in the electrode. The results manifested the specific capacitance of the cobalt-doped@MnO$_2$ nanosheets is 337.8 F g$^{-1}$ at 0.5 A g$^{-1}$; this surpasses composites in recently reported literature.

2. Experimental Procedure

2.1. Synthesis of Cobalt-Doped@MnO$_2$ Composite Nanosheets

Before synthesis, nickel foam ($2 \times 1$ cm$^2$) was carefully cleaned with a 6.0 M HCl solution in an ultrasound bath for 30 min to remove and eliminate the influence of the NiO layer from the surface; it was then rinsed with deionized water and absolute ethanol several times; and finally, dried in a vacuum oven at 50 $^\circ$C. Cobalt nitrate hexahydrate (3 g) was added to 65 mL of MnCl$_2$ solution with a concentration of 0.034 mol L$^{-1}$. Then, the precursor solution was continuously treated with ultrasound for 20 min to permit the complete adsorption of Mn$^{2+}$ on cobalt nitrate hexahydrate. In due course, the supernatant liquids were detached by centrifugation; and 65 mL of KMnO$_4$ solutions (0.069 M) were added to the mixtures. After stirring at 115 $^\circ$C for 3 h, the precursor mixtures were washed with DI water continuously; and finally, dried at 130 $^\circ$C for 12 h to gain the cobalt-doped@MnO$_2$ nanosheets composite.

For comparison, pure MnO$_2$ electrodes were also fabricated by a similar reaction process without adding Cobalt nitrate hexahydrate into the MnCl$_2$ solution.

2.2. Characterizations

The electrode morphology was investigated by scanning electron microscopy (FE-SEM, S-4800, Hitachi, Busan, Korea) and transmission electron microscopy (HRTEM, CJ111). The elemental compositions and chemical states of the spectroscopic procedures of the electrode were studied by X-ray photoelectron spectroscopy (XPS, VG Scientific—ESCALAB 250, Busan, Korea.). The electrode sample structure of the crystal was perceived by X-ray diffraction (XRD, D/Max-2400, Rigaku, Tokyo, Japan, Cu Ka) at an acceleration voltage of 40 kV using Cu Ka ($\lambda = 0.154$ nm) radiation.
2.3. Electrochemical Measurement

The electrochemical activities of the electrode composites (MnO$_2$ and cobalt-doped@MnO$_2$) were investigated by a three-electrode configuration operating an electrochemical workstation (SP-150 Biologic instrument, Busan, South Korea) in a 2 M KOH electrolyte. The Pt wire (2 cm × 2 cm) and Hg/HgO electrode were employed as the counter and reference electrodes, respectively. The galvanostatic charge/discharge (GCD), cyclic voltammetry (CV) tests quantifications, and electrochemical impedance spectroscopy (EIS) analysis were captured with a counter and reference electrode. The EIS result was processed by operating AC potentials of 10 mV amplitude (versus Hg/HgO) in the ranges of 200 mHz to 200 kHz frequencies at open-circuit potential (OCP). For a three-electrode system, the AC potential of 10 mV was applied versus RE. The mass loading of the working sample on each electrode is ~3.4 mg. The specific capacitance ($C_s$, F g$^{-1}$) was calculated from the charge–discharge curve by using the following equation [34]:

$$C_s = (I \times \Delta t)/(m \times \Delta V)$$

(1)

where $C_s$, $I$, $\Delta t$, and $m$ are the specific capacitance (F g$^{-1}$), current (A), discharge time (s), and mass (g) of the active materials, respectively.

3. Results and Discussion

Figure 1 is a brief illustration of the preparation procedures for the cobalt-doped MnO$_2$ nanosheets composite. During the following hydrothermal procedures, the cobalt gradually transformed into a porous nickel foam structure. The cobalt dope supports the enhancement of the pore structures and provides the cobalt doping of the nickel form [29]. After a post in-situ hydrothermal deposition procedure, densely MnO$_2$ nanoparticles were grown on the nickel foam. The chemical reactions involved in the procedure are as follows:

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$

(2)

Figure 1. Schematic diagram of the cobalt-doped@MnO$_2$ nanosheets composite.

Figure 2a indicates a typical SEM image of the MnO$_2$ nanoparticle material. The MnO$_2$ nanoparticle appears with distinct porous architecture. The internally networked porous construction not only supplies a channel for quick electron transportations, but also acts as a well-being skeleton for the MnO$_2$ loading. Afterward, the SEM images of the cobalt-doped@MnO$_2$ nanosheets composite (Figure 2b) exhibits excellent dispersed MnO$_2$ nanoparticles uniformly coating on the interfaces of the nickel foam. Figure S1 shows the
SEM image of cobalt-doped@MnO₂ nanosheets composite well-distributed on the nickel foam. It is visible that the porous nature of the nickel foam is well-retained; this not only encourages the electrolyte ion transportations, but also produces a superior contacting surface for the MnO₂. The SEM structure analysis investigation obviously indicates that the cobalt-doped@MnO₂ nanosheets structure was facilitated by the excellent electron transportations between the electrode surface area and electrolyte interface to enhance the electrochemical performance. The different crystalline faces with polycrystalline characterization exist; and there was an observable grain boundary among the MnO₂ and cobalt dope in the structure of the cobalt-doped@MnO₂. TEM images (Figure 1) display the surface of the cobalt-doped@MnO₂ nanosheets composite, obviously disposing of dense nanoparticles loaded on the interfaces of the nickel foam. In addition, the HRTEM images (Figure 2d) of the MnO₂ nanoparticles disclose spacing fringes of 0.25 nm; this correlates to the (006) MnO₂ spacing planner. Further, the cobalt dope consists of numerous MnO₂ that connect to form a highly porous network structure; which helps the electrolyte ions penetrate during the charge–discharge process.

Figure 2. (a) SEM images of the MnO₂ sample; (b) an SEM image of the cobalt-doped@MnO₂ nanosheets composite; (c) a TEM image of the cobalt-doped@MnO₂ nanosheets composite; and (d) an HRTEM image revealing the crystalline structure of the MnO₂ nanosheets.

The crystalline structures of MnO₂ and the cobalt-doped@MnO₂ nanosheets composite were analyzed by XRD analysis, as depicted in Figure 3a. For the binary MnO₂ material, two sharp peaks are visible around 22° and 43.5°; these are similar to that of the nickel foam [34,35]. For the cobalt-doped@MnO₂ nanosheets composite, the three broader peaks at 12.3°, 36.8°, and 65.8° are correlated with (002), (006), and (119) planners of the birnessite category-MnO₂ (JCPDS 18-802), respectively [36,37]. It is known that binary MnO₂ is similar to MnO₂ in the composite through comparisons.
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**Figure 3.** The XRD patterns (a) and wide-scan XPS spectra (b) of the cobalt-doped@MnO$_2$ nanosheets composite, respectively. (c,d) The high-resolution XPS spectra for the cobalt-doped@MnO$_2$ nanosheets composite of Co 2p and Mn 2p.

XPS investigations were further employed to obtain information on elemental structure compositions, and the chemical molecular states of the surfaces of the electrode. Figure 3b is the general mapping of the XPS spectrum. The cobalt-doped@MnO$_2$ nanosheets composite depicts the peaks of Co 2p, Mn 2p, C, and O elements. Furthermore, due to the loading of MnO$_2$, the Mn peaks are visible in the spectra of the cobalt-doped@MnO$_2$ nanosheets composite; and the C peaks decrease sharply. For the Co 2p XPS spectrum (Figure 3c), the spin-orbit split results of Co 2p$_{3/2}$ (centered at 795 eV) and Co 2p$_{1/2}$ (centered at 781 eV), transgression 15 eV; this reveals the coexistences of Co$^{3+}$ and Co$^{2+}$ cations [38,39]. By a Gaussian fitting method, the Co spectrum was fitted to four peaks, including the Co$^{3+}$ peaks located at 780.8 eV and 781.1 eV and another peak located at 785.1 eV and 802.5 eV, which was assigned to Co$^{2+}$. For the Mn 2p pattern (Figure 3d), the two peaks at 643.5 eV and 655.6 eV correspond to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively [40–42]. The fitting peak at 637.7 eV is particularly characteristic of Mn$^{2+}$, and the peaks located at 642.9 eV and 653.6 eV ascribed to Mn$^{3+}$. The spin separations energies were 11.9 eV, which reveals that the Mn valence states were +4 [34,43,44]. The O 1s spectra would be deconvoluted into O-C (531.5 eV), C-O-C/C-OH (533.4 eV), and O–Mn (530.2 eV) bondings, respectively (as showed in Figure S2). The presence of the cobalt dope group was favored for the enhancement of electrochemical capabilities [32].
Electrochemical Properties of Electrode Materials

The electrochemical capabilities of binary MnO$_2$ nanoparticles and the cobalt-doped@MnO$_2$ nanosheets composite were investigated using a three-electrode setup. The CV and GCD data values of the cobalt-doped@MnO$_2$ nanosheets composite were depicted in Figure 4a,b, respectively. As the scan rates expand between 5 to 200 mV s$^{-1}$, the CV plots remain in almost rectangular shapes; manifesting that the sample material consists of excellent reversibility and absolute capacitance nature. There were not any apparent redox peaks under the voltage windows of 0.0–0.6 V; which illustrates the behavior of the PCs of MnO$ _2$(Figure S3a) of the binary MnO$ _2$ nanoparticles composite. At various current densities between 0.5 A g$^{-1}$ to 15 A g$^{-1}$, the GCD pattern shows close symmetrical charge/discharges (Figure 4b). At a 0.5 A g$^{-1}$ current density, we performed the comparison of both binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$ nanosheets composite electrodes (Figure 4c). We also investigated the CV curve of binary MnO$_2$ electrodes, as illustrated in Figure S3b. The CV curves comparison (Figure S3a) of the binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$ nanosheets composite also display rectangular-type shapes. It is visible from the regions of the CV plots that the specific capacitances of the cobalt-doped@MnO$_2$ nanosheets composite are greater than that of binary MnO$_2$.

![Figure 4](image_url)

Figure 4. Electrochemical performances with the three-electrode system. (a) CV and (b) GCD curves of the cobalt-doped@MnO$_2$ nanosheets composite. (c) GCD curves at a current density of 0.5 A g$^{-1}$ of binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$ nanosheets composite electrode materials. (d) The Nyquist plots of binary MnO$_2$ and cobalt-doped@MnO$_2$ nanosheets composite electrode materials.

The data of EIS (Figure 4d) further evidenced that the cobalt-doped@MnO$_2$ nanosheets composite consists of good electrochemical performances. The range in the frequencies of the pattern was from 0.02 Hz to 200 KHz. The Nyquist diagrams of binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$ nanosheets composite electrode materials achieve the same small semicircles in the higher-frequency ranges (the semicircle diameter reveals charge transfer resistances ($R_{ct}$)); manifesting that they have smaller charge transfer resistances. The $R_{ct}$ of the cobalt-doped@MnO$_2$ nanosheets composite was slightly greater than that of binary MnO$_2$ nanoparticles. This was due to the charge transfer of cobalt-doped@MnO$_2$ nanosheets presuming redox reactions, which were more moderate than the surface des-
The sorption/adsorption nature of the sample PCs [38]. In addition, it would be obvious that the cobalt-doped@MnO$_2$ nanosheets composite effectively enhances the conductivities of binary MnO$_2$ nanoparticles. The ideal capacitance character is apparent from the almost vertical linear plots in the lower frequency area. Thus, the cobalt-doped@MnO$_2$ nanosheets sample reveals a much more oblique plot; this signifies the foremost performances of the PCs.

Figure 5a displays the comparison of binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$ nanosheets composite GCD plots at 0.5 A g$^{-1}$, respectively. The specific capacitance of binary MnO$_2$ nanoparticles was calculated to be 277.9 F g$^{-1}$, which is approximately only 1/3 of the cobalt-doped@MnO$_2$ nanosheets composite. These results illustrate that the porous behavior of the cobalt-doped@MnO$_2$ nanosheets composite is advantageous to the electrolyte ions of diffusion. While conserving binary MnO$_2$ nanoparticles' PC capacitance, the cobalt-doped@MnO$_2$ nanosheets composite electrode also expands PC capacitances.

According to the cycling test (Figure 5b), binary MnO$_2$ nanoparticles consist of well-cycled stabilities; and the capacity retention rate residues ∼76.4% after 3000 long cycles. Whereas, for the cobalt-doped@MnO$_2$ nanosheets composite, the electrode remains ∼82.5% after 3000 long cycles; manifesting that the nickel foam effectively enhances the cycling capabilities of MnO$_2$. Surprisingly, both binary MnO$_2$ nanoparticles and cobalt-doped@MnO$_2$
nanosheets composite electrodes have excellent retention stabilities. The specific capacitance performances of the MnO₂-based composite samples reported in previous studies are displayed in Table 1. The specific capacitances of the cobalt-doped@MnO₂ nanosheets composite electrode are much higher than that of some nickel foam-based MnO₂ composite materials and other MnO₂-based composites. Figure 5c illustrates the SEM image of the cobalt-doped@MnO₂ nanosheets composite material after 3000-long cycling stability. The SEM image shows a good surface structure and super-wettability, indicating a vital role in keeping faradaic redox and energy storage reactions. Figure 5d shows the impedance plots of the binary MnO₂ nanoparticles and cobalt-doped@MnO₂ nanosheets composite electrodes after 3000 cycles. There were no obvious changes of Rₑ after 3000 long cycles, manifesting a rapid electron/ion transfer. Surprisingly, the higher performances of the cobalt-doped@MnO₂ nanosheets composite with hierarchical structure on nickel foam is beneficial; owing to the larger surface area accessing point for ions that enhance the wettability of the composite and accelerate electron transfer.

| Electrode                        | Electrolyte    | Specific Capacitance (F g⁻¹) | Current Density (A g⁻¹) | Ref.  |
|----------------------------------|----------------|------------------------------|-------------------------|-------|
| MnO₂/rice husk-derived composite | 0.5 M Na₂SO₄  | 210.3                        | 0.5                     | [30]  |
| Holey reduced graphene oxide/MnO₂ composites | 1 M Na₂SO₄ | 192.2                        | 0.5                     | [37]  |
| MnO₂@CCNs                       | 1 M Na₂SO₄  | 262                          | 0.2                     | [38]  |
| CNT@NCT@MnO₂                    | 1 M Na₂SO₄  | 210                          | 0.5                     | [40]  |
| δ-MnO₂(4.0)/HRGO                | 1 M Na₂SO₄  | 245                          | 1                       | [45]  |
| α-MnO₂ NWs@δ-MnO₂ NSs           | 6 M KOH      | 310.2                        | 0.5                     | [46]  |
| PPy/mesoporous MnO₂             | 1 M Na₂SO₄  | 320                          | 0.5                     | [47]  |
| D-MNS-A@MnO₂                    | 1 M Na₂SO₄  | 231                          | 1                       | [48]  |
| cobalt-doped@MnO₂ nanosheets    | 2 M KOH      | 337.8                        | 0.5                     | This Work |

4. Conclusions

In summary, cobalt-doped nanoparticles were uniformly grown on MnO₂ with a large specific surface region and unique pore construction to form a cobalt-doped@MnO₂ nanosheets composite. The improved electrochemical performances of the cobalt-doped@MnO₂ nanosheets composite are ascribed to the higher electrical conductivities, enlarged surface region, ample working electrochemical sites, and rapid charging-transfer channels. The cobalt-doped@MnO₂ nanosheets composite achieved extraordinary electrochemical capabilities. At a current density of 0.5 A g⁻¹, the specific capacitance is 337.8 F g⁻¹. Moreover, the cobalt-doped@MnO₂ nanosheets composite electrodes exhibit excellent cycling stabilities of 82.5% capacity retention at 3000 GCD long cycles. The results of this research support the use of metal oxides as conductive bases and expand the scope of dopant-based material applications. Finally, the cobalt-doped@MnO₂ nanosheets with the above unique physicochemical characteristics can have numerous good functionalities for other applications, such as biosensors, electrocatalysts, and batteries.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12183187/s1. 1. Materials and Reagents; Figure S1. SEM image of cobalt-doped@MnO₂ nanosheets well distributed on nickel foam; Figure S2. XPS spectra of O 1s; Figure S3a. CV comparison of binary MnO₂ nanoparticles and cobalt-doped@MnO₂ nanosheets composite; Figure S3b. CV curves of binary MnO₂ nanoparticles. All authors have read and agreed to the published version of the manuscript.
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