Abstract: Carbon encapsulated Fe$_2$O$_3$ nanoparticles (C@Fe$_2$O$_3$) were successfully synthesized via a facile and environmentally friendly hydrothermal method and prototyped in anode materials for sodium ion batteries (SIBs). High-resolution transmission and scanning electronic microscopy observations exhibited the formation of a highly core-shelled C@Fe$_2$O$_3$ composite consisting of carbon layers coated onto uniform Fe$_2$O$_3$ nanoparticles with a median diameter of 46.1 nm. This core-shell structure can repress the aggregation of Fe$_2$O$_3$ nanoparticles, preventing the harsh volume change of the electrode, enhancing the electric conductivity of the active materials, and promoting Na-ion transformation during cycling. The electrochemical performances of the C@Fe$_2$O$_3$ composite, as anodes for SIBs, retained a reversible capacity of 305 mAh g$^{-1}$ after 100 cycles at 50 mA g$^{-1}$ and exhibited an excellent cyclability at various current densities due to the synergistic effect between the carbon layers and Fe$_2$O$_3$. These results suggest that C@Fe$_2$O$_3$ composites present much potential as anode materials for rechargeable SIBs.

Keywords: C@Fe$_2$O$_3$ composite; anode; sodium ion battery

1. Introduction

Recently, sodium-ion batteries (SIBs) have attracted intensive attention as an alternative to lithium-ion batteries (LIBs). This interest can be attributed to the fact that sodium is abundantly available and is economically cheaper than lithium [1,2]. Graphite was established as the gold-standard anode material for lithium ion batteries (LIBs) due to their modest reversible capacity (372 mAh g$^{-1}$), superior cycling behavior, high Coulombic efficiency, low cost, and low and flat potential plateaus, which provide a decent voltage window [3]. However, conventional graphite is not suitable for SIB anodes because the larger atomic radius of sodium requires intercalation hosts, with larger diffusion channels [4]. In recent years, the researched anode materials for SIBs transition metal oxides, such as TiO$_2$, ZnO, and Co$_3$O$_4$, were found to hold the greatest potential for anode materials in SIBs due to their exceptional theoretical capacities, good versatility, and cost advantages [5–10]. In general, these anodes face severe challenges in poor electronic conductivity and huge volume changes during cycling. Therefore, the development of anode materials with excellent electrochemical performances is crucial. In particular, Fe$_2$O$_3$, which possess a lofty theoretical specific capacity (1007 mAh g$^{-1}$) [11], has garnered much attention in recent years [8–11]. However, the cycling stability of the Fe$_2$O$_3$ anode is significantly hindered by the harsh volume expansion/contraction during the Na alloying/dealloying process.
Metals 2018, 8, 461 2 of 10

processes. To boost the stability of the Fe₂O₃ anode and better the capacity retention and cycle life, an effective strategy, which has been previously investigated, is to combine Fe₂O₃ nanoparticles with carbonaceous substances. For example, Wang’s group reported the preparation of α-Fe₂O₃/RGO composites via microwave autoclave, with the resulting nanocomposites delivering a capacity of 310 mAh g⁻¹ after 150 cycles at 100 mA g⁻¹ [12].

In lithium-ion batteries, the carbon encapsulated Fe₂O₃ nanoparticles (C@Fe₂O₃) as anode materials attract special interest of researchers since this core-shell structured nanocomposite exhibits enhanced physical and chemical properties [13]. Coating layers of carbon onto a Fe₂O₃ core will simultaneously improve the electric conductivity and act as a buffer layer to mitigate the mechanical strain and improve the mechanical integrity due to the ductile and elastic nature of carbonaceous materials [14,15]. All these merits are beneficial for the development of electrochemical performance. Encouraged by these promising and interesting works, herein, we prepared core-shell structure C@Fe₂O₃ composites by a one-step hydrothermal procedure. Carbon layers were homogeneously coated on the Fe₂O₃ nanoparticles, with a median diameter of 46.1 nm. From this unique design, the C@Fe₂O₃ composites exhibit an impressive Na-ion storage performance with a high capacity and good cycles.

2. Materials and Methods

2.1. Materials Preparation

The C@Fe₂O₃ composites with a core-shell structure were synthesized by the hydro-thermal method. Glucose (0.3 g) and iron nitrate hydrate (0.4 g) were dispersed in distilled water (40 mL) using a thermostatic magnetic mixer (Zhengzhou Teer Instruments, Zhengzhou, China) for 0.5 h to form a uniform suspension. Subsequently, the mixed solution was displaced to reaction still after 0.25 h sonication using an ultrasonic cell disruptor (Ningbo Scientz Biotechnology Co., Ningbo, China), then heated in a 40 mL Teflon-lined stainless-steel autoclave for 9 h at 190 °C, and then left in ambient conditions. After cooling to room temperature, the products were washed thoroughly via centrifugal with deionized water. Finally, the washed products were dried under vacuum at 80 °C for 24 h to prepare carbon encapsulated Fe₂O₃ nanoparticles in a core-shell structure.

2.2. Materials Characterization

The crystal phase of C@Fe₂O₃ composites was analyzed by Rigaku D/Max 2500V/pc X-ray diffractometer (XRD) (Rigaku-TTRIII, Tokyo, Japan) with Cu Kα (λ = 1.5406 Å) in scanning step of 0.02°. The morphology was observed by a JEOL JSM-6700F scanning electron microscope (SEM, equipped with EDX elemental analysis, JEOL, Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEOL, Tokyo, Japan) from a JEOL JEM-2100F instrument with 200 kV acceleration voltage. Brunauer Emmett Teller (BET) (V-Sorb 2800P) tests were conducted to investigate the specific surface area of the composites. X-ray photoelectron spectroscopy (XPS) data was obtained with a PHI 5000 Versa Probe system (Ulvac-Phi, Kanagawa, Japan). The carbon content was estimated by thermo gravimetric analysis (TGA, SDTQ600, TA Instruments-Waters LLC, Newcastle, PA, USA). Raman spectroscopy analysis was examined on Raman spectroscopy (LabRAM Hr 800, HORIBA Jobin Yvon, Paris, France) with the laser wavelength of 514 nm.

2.3. Electrochemical Measurements

The electrochemical measurements were conducted at room temperature using coin cells (CR2025), with a sodium foil as the counter and reference electrode. The working electrode consisted of a C@Fe₂O₃ slurry, acetylene black, and sodium alginate binder combined at a weight ratio, 7:2:1, and evenly applied onto copper foil with 15 mm in diameter. The as-prepared working electrodes were dried in a vacuum oven at 80 °C for over 12 h to remove any residual moisture. The electrolyte was comprised of 1 M NaClO₄ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume),
and the separator used was a glass fiber film. The electrochemical performances were probed between 0.01 and 3.0 V (vs. Na/Na⁺) with a battery testing system (BTS-5V5 mA, Neware, Shenzhen, China). The specific capacity was calculated in reference to the mass of the total active material.

### 3. Results and Discussion

The crystalline structure of the C@Fe₂O₃ composite was characterized by XRD. Figure 1 shows that the typical diffraction peaks at 30.3°, 35.7°, 57.4°, and 63.1°, which correspond to the reflections of (2 0 6), (1 1 9), (1 1 15), and (4 0 12) planes of the Fe₂O₃ structure (JCPDS No. 25-1402), respectively. There is no evident carbon peak due to the presence of amorphous carbon.

![X-ray diffractometer (XRD) patterns of the C@Fe₂O₃ composite.](image1)

Raman spectra further confirmed the presence of carbon in the composites. As shown in Figure 2, two obvious bands at 1350 and 1586 cm⁻¹ are assigned to typical D and G bands of carbon, respectively. A 2D band of 2693 cm⁻¹ is also observed, confirming the presence of carbon from the hydro-thermal process of glucose in the composites.

![Raman spectrum of the C@Fe₂O₃ composite.](image2)

The morphology and particle sizes of C@Fe₂O₃ composites were characterized by SEM measurements. As shown in Figure 3a,b, the C@Fe₂O₃ composites are uniform spheres, with a median diameter of approximately 50 nm. The inset in Figure 3b depicts the average diameter of the C@Fe₂O₃ composites was 46.1 nm. The structure of the C@Fe₂O₃ composite was further investigated by TEM. Figure 3c illustrates carbon wrapping of Fe₂O₃ nanoparticles, which possess an average diameter of ~10 nm, confirming a core-shell structure. The HRTEM analysis, shown in Figure 3d, reveals the lattice fringe, with a distance spacing of 0.238 nm, corresponding to the (2 2 6) plane of Fe₂O₃.
illustrates that the thickness of the carbon layer was approximately 0.83 nm. The energy dispersive spectrometer (EDS) element mapping, shown in Figure 4, clearly demonstrates that the C@Fe₂O₃ composite mainly consist of C, Fe, and O, with a uniform distribution.

![Figure 3](image1.png)

**Figure 3.** SEM images (a,b) and corresponding median diameter (inset) and TEM images (c,d) of the C@Fe₂O₃ composites.

![Figure 4](image2.png)

**Figure 4.** SEM image (a) of the C@Fe₂O₃ composite and corresponding carbon (b), iron (c), and oxygen (d) element mapping.

The chemical composition and chemical bonding were further investigated by XPS, shown in Figure 5. As shown in Figure 5a, the peaks of Fe 2p, C 1s, and O 1s were detected in the C@Fe₂O₃ composite. Figure 5b delivers two peaks located at 724.7 and 711.1 eV in the high-resolution Fe 2p spectra, corresponding to Fe 2p1/2 and Fe 2p3/2, respectively. In addition, two weak satellite peaks at 733.3 and 719.5 eV can be attributed to the Fe 2p1/2 and Fe 2p3/2, respectively. This phenomenon
indicates that the composite was composed of Fe$^{3+}$ only. Figure 5c shows three peaks at 288.6, 286.6, and 284.8 eV in the C 1s spectra, corresponding to the C=O, C–O–C, and C–C, respectively. Figure 5d shows two peaks located at 531.8 and 529.8 eV in the O 1s spectra, which is attributed to Fe–O–H and Fe–O, respectively. Overall, the results indicate the successful transformation of glucose and iron nitrate hydrate into C@Fe$_2$O$_3$ composite.

![Figure 5. XPS full spectra (a), Fe 2p (b), C 1s (c), and (d) O 1s of the C@Fe$_2$O$_3$ composite.](image)

The carbon content of the C@Fe$_2$O$_3$ composites was tested by thermogravimetric (TG) analysis. From the TG curve in Figure 6, the weight fraction of the carbon was recorded to be 46%. The specific surface area and pore size distribution of the C@Fe$_2$O$_3$ composite was obtained from nitrogen adsorption-desorption measurements. From Figure 7a, the isotherms indicate type IV hysteresis loops, with a marked hysteretic loop in a desorption branch between relative pressures $P/P_0$ of 0.8 and 0.95, corresponding to the mesoporous nature of the sample. In general, the type IV hysteresis loop typically occurs due to the aggregated nanoparticle structure. The BET surface area for the C@Fe$_2$O$_3$ composite was calculated at 85.56 m$^2$ g$^{-1}$. Figure 7b shows the Barrett-Joyner-Halenda (BJH) pore size adsorption plot for C@Fe$_2$O$_3$ sample, highlighting a bimodal-pore size centered at 3.7 nm and 49.9 nm. This further confirms the mesoporous morphology of C@Fe$_2$O$_3$ composites.

![Figure 6. Thermogravimetric (TG) curve of the C@Fe$_2$O$_3$ composite.](image)
The electrochemical behavior of the C@Fe₂O₃ composite with Na-ion insertion-extraction was tested by cyclic voltammetry (CV) analysis as shown in Figure 8. In the cathodic scan, an irreversible peak is observed at around 0.75 V (vs. Na/Na⁺), corresponding to the formation of a solid electrolyte interface (SEI) layer [16]. The pronounced reduction peak occurs near 0.08 V, which results in the reduction of the Fe₂O₃ [17]. In the anodic scan, two broad oxidation peaks are located at 0.46 V and 1.71 V, corresponding to the reversible oxidation of Fe⁰ to Fe³⁺ [18]. The reversible electrochemical reaction can be described as [19]:

\[ \text{Fe}_2\text{O}_3 + 6\text{Na} \leftrightarrow 2\text{Fe} + 3\text{Na}_2\text{O} \]  \hspace{1cm} (1)

Figure 7. (a) Nitrogen adsorption/desorption isotherms and (b) the pore size distributions of C@Fe₂O₃ composites.

Figure 8. Cyclic voltammetry (CV) curve of the C@Fe₂O₃ composite at the initial cycle.
Figure 9 illustrates the charge–discharge profiles for the initial three cycles of the C@Fe$_2$O$_3$ composites at a current density of 50 mA g$^{-1}$ and at a potential window between 0.01 and 3.0 V. As observed, the C@Fe$_2$O$_3$ composite delivers an initial discharge capacity of 709 mAh g$^{-1}$ and a charge capacity of 415 mAh g$^{-1}$, which mainly originates in the first cycle, partially from the inevitable formation of the SEI film on the surface of the C@Fe$_2$O$_3$ electrode and the unique core-shell structure, which possesses a high specific surface area [20]. SEI films are generated from the decomposition of electrolyte, which produces a large amount of sodium ions and irreversibly intercalate into the crystal lattice [21]. In addition, no obvious voltage plateaus can be observed in Figure 9, which is accepted of Fe$_2$O$_3$ as is reported in the literature. Lastly, the capacity of the C@Fe$_2$O$_3$ composite quickly faded in the subsequent cycles because of the drastic volume change and the aggregation of Fe$_2$O$_3$ nanoparticles during charge–discharge processes [22].

![Figure 9](image_url)

**Figure 9.** The charge–discharge profiles of the C@Fe$_2$O$_3$ composites at the initial three cycles at 50 mA g$^{-1}$ between 0.01 and 3.0 V.

At a current density of 50 mA g$^{-1}$ for 100 cycles, the cycling performances of C@Fe$_2$O$_3$ composite are shown in Figure 10. In the first cycle, the C@Fe$_2$O$_3$ composite manifests a high irreversible discharge capacity of 709 mAh g$^{-1}$ and a relatively low initial coulombic efficiency of less than 60%. Subsequently, excellent cycle performance is maintained delivering a reversible capacity of 305 mAh g$^{-1}$ for 100 cycles. Furthermore, along with a high reversible discharge capacity, excellent cyclability was demonstrated as well, and the capacity decay was only 0.22% in per cycle. Complimentarily, the C@Fe$_2$O$_3$ electrode delivers a coulombic efficiency of over 99%. In summary, these results imply an excellent reversibility of sodium insertion/deinsertion in the C@Fe$_2$O$_3$ composites.

![Figure 10](image_url)

**Figure 10.** Cycling performance and coulombic efficiency of the C@Fe$_2$O$_3$ composites.
Figure 11 exhibits the rate capabilities of the C@Fe₂O₃ composite electrode at different current densities, spanning from 50 mA g⁻¹ to 1000 mA g⁻¹. The C@Fe₂O₃ composite electrode demonstrates excellent rate performance and reversible capacities of 364, 291, 245, 206, and 150 mAh g⁻¹ at current densities of 50, 100, 200, 500, and 1000 mA g⁻¹, respectively. Lastly, the C@Fe₂O₃ composite delivered a reversible capacity of 302 mAh g⁻¹ when returning the current density back to the initial 50 mA g⁻¹. These results reveal that the stable core-shell structure of the carbon encapsulated Fe₂O₃ nanoparticles can effectively sustain the large volume change, alleviate the aggregation of Fe₂O₃ nanoparticles, and improve electronic transports during sodium insertion [16,23,24].

Electrochemical impedance spectroscopy (EIS) measurements were measured to compare the Nyquist plots of C@Fe₂O₃ when fresh and after 100 cycles, as shown in Figure 12. The C@Fe₂O₃ composite, after 100 cycles, had much lower charge transfer resistance, corresponding to the smaller semicircle at high to middle frequency. As a result, the C@Fe₂O₃ composite exhibits a favorable electrochemical performance during cycling processes.

The electrochemical performance of C@Fe₂O₃ composites obtained in this paper is better than those of previously reported results with Fe₂O₃ (Table 1) [12,25]. Compared with Fe₂O₃, the cycling performance of the C@Fe₂O₃ composites is much better, showing that the carbon contributes to the capacity of the C@Fe₂O₃ composites and the carbon is taking a positive effect.
Table 1. Comparison of the electrochemical performances of Fe$_2$O$_3$ and C@Fe$_2$O$_3$ composite for sodium-ion batteries.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Discharge Capacity (mAh g$^{-1}$)</th>
<th>Cycle Number</th>
<th>Current Density (mAh g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>16</td>
<td>10</td>
<td>50</td>
<td>[25]</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>[12]</td>
</tr>
<tr>
<td>C@Fe$_2$O$_3$</td>
<td>305</td>
<td>100</td>
<td>50</td>
<td>This study</td>
</tr>
</tbody>
</table>

4. Conclusions

In summary, we reported a facile hydrothermal approach to fabricate a stable core-shell structure composed of carbon encapsulated Fe$_2$O$_3$ nanoparticles and investigated its application as anode materials for SIBs. A reversible capacity of 305 mAh g$^{-1}$ can be obtained at 50 mA g$^{-1}$ for up to 100 cycles for the C@Fe$_2$O$_3$ composites and it delivered a reversible capacity of 150 mAh g$^{-1}$ at a current density of 1000 mA g$^{-1}$. When the current rate returned to 50 mA g$^{-1}$, the reversible capacity could recover up to 302 mAh g$^{-1}$, indicating high rate capabilities even at very high current densities. The electrochemical results demonstrated that the C@Fe$_2$O$_3$ composites feature excellent cycling performance and good rate capability due to the unique core-shell structure of the SIB anode.

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