Free-Standing Sandwich-Structured Flexible Film Electrode Composed of Na$_2$Ti$_3$O$_7$ Nanowires@CNT and Reduced Graphene Oxide for Advanced Sodium-Ion Batteries

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ABSTRACT: A free-standing flexible anode material for sodium storage with sandwich-structured characteristics was fabricated by modified vacuum filtration, consisting of stacked layers of Na$_2$Ti$_3$O$_7$ nanowires@carbon nanotubes (NTO NW@CNT) and graphene oxide. The NTO NWs have a larger specific surface area for Na$^+$ insertion/extraction with shortened ion diffusion pathways, accelerating the charge transfer/collection kinetics. The added CNTs both facilitate the uniform dispersion of the nanowires and nanotubes and also contribute to the connectivity of the nanowires, improving their conductivity. More importantly, the unique sandwich-like layered-structured film not only provides large numbers of electron-transfer channels and promotes the reaction kinetics during the charging and discharging process but also ensures the structural stability of the NTO NWs and the electrode. Electrochemical measurements suggest that this rationally designed structure endows the electrode with a high specific capacity and excellent cycling performance. A satisfactory reversible capacity as high as 92.5 mA h g$^{-1}$ was achieved after 100 cycles at 2C; subsequently, the electrode also delivered 59.9 mA h g$^{-1}$ after a further 100 cycles at 5C. Furthermore, after the rate performance test, the electrode could be continuously cycled for 100 cycles at a current density of 0.2C, which demonstrated that durable cyclic capacity with a high reversible capacity of 114.1 mA h g$^{-1}$ was retained. This novel and low-cost fabrication procedure is readily scalable and provides a promising avenue for potential industrial applications.

INTRODUCTION

In modern society, portable and wearable electronics, such as flexible sensors and hand-held displays, are highly desired, which has motivated research into the necessary lightweight and flexible high-performance power sources. 1–3 At present, the study of flexible power sources is mainly focused on lithium-ion batteries (LIBs)4–6 and supercapacitors (SCs). In the energy-storage field, great attention has been focused on flexible SCs because of their convenient processability, fast charging and discharging ability, excellent rate capability, and their superior cycle lifetime. 7–9 However, the energy density of SCs is not very high considering the need for long-term resilience, and thus flexible LIBs perhaps hold greater promise for smart electronics, rollup displays, wearable devices, and other applications. 10–12 Flexible LIBs are of particular interest due to their higher energy storage densities. However, at present, with the commercialization of electric vehicles powered by LIBs, the limited availability of lithium storage will progressively increase its cost. As a result, low-cost sodium ion batteries (SIBs) have become a very popular topic in the research field of energy storage and conversion devices.

Sodium ion batteries have attracted interesting attention because they have similar electrochemical properties to LIBs in addition to their low cost and environmental friendliness. 13,14 However, flexible SIBs are still rarely reported at present. It is well-known that characteristics of batteries, such as flexibility, specific capacity, and rate capability, are mainly determined by their electrode materials. 15 Therefore, it is highly desirable to search for suitable electrode materials with appropriate flexibility for use in SIBs. Actually, some endeavors have been made to study flexible electrode materials for flexible SIBs, such as MoS$_2$, 16,17 Sb, 18 and Li$_4$Ti$_5$O$_12$. 19 Among the various anode materials, Na$_2$Ti$_3$O$_7$ (NTO) has been most promising on account of its high specific capacity (177 mA h g$^{-1}$) and its low charging/discharging voltage plateau of 0.3 V versus Na/Na$^+$. 20

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Nevertheless, the structural instability and the low electronic conductivity of Na$_2$Ti$_3$O$_7$ limit its further practical application. To solve these problems, lots of efforts have been made to design and fabricate Na$_2$Ti$_3$O$_7$ nanostructures, including nanorods, nanoparticles, microspheres, nanotubes, and nano-composites with carbon. However, the design and fabrication of reliable flexible electrodes with high storage capacity, high rate capability, and excellent stability remain challenging.

For the fabrication of SIB electrodes, conventional methods usually involve mixing, casting, and pressing the mixed compounds. These compounds comprise a cathode or an anode material for sodium storage, the metal current collectors, a conductive agent to maintain the electrode conductivity onto the metal current collectors, and a binder to inhibit the shedding of the active materials from metal current collectors. Such electrodes usually have little flexibility due to their rigid structure. Moreover, they contain a significant amount of inert components (e.g., binders) and cumbersome current collectors are used in the electrodes, inevitably compromising the energy density of the devices. Lightweight flexible substrates, such as textiles or plastics, have been proposed as replacements for metal substrates. To address sluggish Na reaction kinetics, Li et al. first designed the surface-engineered Na$_2$Ti$_3$O$_7$ nanoarrays on flexible Ti substrates by using the atomic layer deposition and hydrogenation process, through which the Na-ion batteries demonstrated the high-rate and long-cycled operation. Zhang et al. reported that NTO nanosheet array/carbon textiles exhibited excellent performance when used as the anode materials of sodium-ion pseudocapacitors. Our previous work also showed that ultralong NTO nanowires@carbon cloth as a binder-free flexible electrode demonstrated a large capacity and long lifetime for sodium-ion batteries. However, the preparation of these flexible electrodes usually requires a substrate, such as carbon cloth, carbon paper, etc., and they are difficult to
develop for large-scale production. In addition, the loading mass of the active material in these flexible electrodes is limited and difficult to control.

Herein, by introducing an architectural design strategy, a hybrid free-standing and sandwich-structured electrode was developed, which is a combination of one-dimensional nanowires together with nanotubes and two-dimensional graphene sheets in hierarchically structured composites. In this work, we demonstrate a simple method of hydrothermal-assisted vacuum filtration to prepare Na$_2$Ti$_3$O$_7$ nanowires@CNT@reduced graphene oxide (NTO NW@CNT@rGO) sandwich-structured flexible film electrodes for flexible SIBs for the first time. The unique sandwich-structured NTO NW@CNT@rGO flexible electrode materials were prepared by layer-by-layer vacuum filtration. This not only affords stability and robustness in the electrodes but also facilitates the diffusion of the electrolyte and improves the ion conductivity of the electrode material, thereby improving the electrochemical properties of Na$_2$Ti$_3$O$_7$.

■ RESULTS AND DISCUSSION

The free-standing and sandwich-structured flexible NTO NW@CNT@rGO film electrode was prepared using a two-step fabrication method. First, NTO NW@CNT was synthesized by a hydrothermal method. In the hydrothermal process, the carbon nanotubes are combined with Na$_2$Ti$_3$O$_7$ nanowires and can be used as bridges between nanowires to improve the conductivity of the nanowires. NTO NW@CNT@rGO flexible electrode materials with a sandwich structure were then prepared via layer-by-layer vacuum filtration (Figure 1). The graphene therein has a large specific surface area and good electrical conductivity. The NTO NW@CNT layer is sandwiched between graphene layers during the process of vacuum filtration. On the one hand, this method is beneficial as it increases the contact area between nanowires and graphene and improves the electrical conductivity of the material. On the other hand, it can improve the infiltration of the electrolyte and increase the ion conductivity of the electrode material, thereby improving the electrochemical properties of Na$_2$Ti$_3$O$_7$.

Meanwhile, the great flexibility of the film can be clearly observed in Figure 2a. The as-prepared electrodes can remain stable while being folded, which show great potential for use in highly flexible devices. To investigate the morphological and structural characteristics of the film, scanning electron microscopy (SEM) was employed. SEM images showing cross-sectional and top views of the S–NTO NW@CNT@rGO film are presented in Figure 2b–e. Figure 2b,c shows cross-sectional SEM images of the as-formed S–NTO NW@CNT@rGO film and the corresponding EDX mapping. As can be seen from Figure 2b, the thickness of the film is about 20 μm and the structure of the cross section is clearly considered as a layer-by-layer structure. Energy-dispersive X-ray (EDX) spectrometry mapping analysis was further employed for one layer of the film, and the results are shown in Figure 2e. The main elements of this layer are C (red), O (green), Na (cyan), and Ti (pink) and are shown in Figure 2c. C refers to the graphene on the upper surface and is evenly distributed. The shallow red color indicates that the graphene layer is relatively thin. Na, Ti, and O are the main elements of NTO and are evenly distributed. The color of the elements is deep, indicating that NTO is the main constituent of this layer. The structure of each
layer is similar to the sandwich structure, which is consistent with the effect we expect to achieve by layered titration and filtration. Subsequently, the upper surface of the film was observed and is shown in Figure 2d,e. The top-view SEM image reveals that the thin graphene layer is uniformly distributed on the upper surface of the film on a large scale and through the graphene layer, interdigitated NTO nanowires can be clearly seen. At a greater magnification shown in Figure 2e, the graphene layer is indeed observed, and NTO NW@CNT composites exist under the graphene layer. Thus, it can be seen that in the as-formed S−NTO NW@CNT@rGO film, the CNT of the NTO NW@CNT layer serves mainly to increase the connections between nanowires, thus extending the pathway of electron transfer of the NTO nanowires. The upper and lower graphene layers serve mainly to increase the contact area with the NTO nanowires and improve the electrical conductivity of the crossed nanowires.

In addition, in Figure 2b, we also see that there is a certain gap between the layers in the as-formed S−NTO NW@CNT@rGO film, which can facilitate the penetration of the electrolyte. But how did these gaps form? To illustrate the problem, the graphene film and the NTO NW@CNT film were prepared by the same process and then observed and analyzed by SEM. Figure S1 shows the SEM images of NTO NW@CNT. It can be seen in Figure S1a that NTO nanowires with the large aspect ratio are very uniform on the upper surface of the film. The distributions of NTO nanowires and CNT are also uniform. It is regrettable that after vacuum filtration the NTO NW@CNT film does not form a multilayer structure that could be seen in the cross section. However, multilayer graphene is clearly observed in the cross section of the film after vacuum filtration, as shown in Figure S2b, which means that the formation of the multilayered S−NTO NW@CNT@rGO film may be related to the graphene itself. After filtration, graphene oxides are formed in the film and then undergo a high-temperature process where some of the oxygen-containing functional groups between the layers become vaporized oxygen, leading to the emergence of a gap between the layers, as shown in Figure S2. Therefore, the gaps in the as-prepared sandwich-structured film containing the graphene oxide occur due to the volatilization of oxygen after the high-temperature treatment. It is precisely because the film prepared by our method exhibits a certain gap that the film both improves the electrical conduction of the electrode and facilitates the penetration of the electrolyte.

To further understand the structure of the S−NTO NW@CNT@rGO film electrode, transmission electron microscopy (TEM) was applied to observe the Na2Ti3O7 nanowires, CNT, and rGO of the film. As shown in Figure 3a,b, the interdigitated long NTO nanowires, including several hundred nanometers or even up to several micrometers in length, form a three-dimensional (3D) network structure, resulting in lots of porous structures. As we all know, these porous structures of the electrode materials likely facilitate the penetration of the electrolyte and also promote sufficient contact between the NTO nanowires and the electrolyte, providing shortened ionic diffusion pathways that may contribute to the improvement of the electrochemical performance in sodium storage. At the same time, it is clear that the distribution of the homogeneous NTO nanowires and the CNT is very uniform. CNT wrapped around the NTO nanowires increases the connectivity between the nanowires and improves their electrical conductivity.
Figure 3b, the graphene above the NTO nanowires and CNT can be seen to completely cover the nanowires having a large contact area with nanowires that greatly improves the conductivity of the nanowires. Figure 3c shows an HRTEM image of the NTO nanowires. The lattice fringes show interplanar spacings of 0.84 and 0.35 nm, corresponding to the distances of the (001) and (102) lattice planes in the NTO structure. The figure also shows that the NTO nanowires have good crystallinity, which is beneficial to the electrochemical performance of NTO. The colored diagrams in Figure 3d show the EDX mapping of NTO nanowires. It can be seen that the distribution of Na (cyan), O (green), and Ti (red) comprising Na$_2$Ti$_3$O$_7$ is consistent with the orientation of the nanowires, indicating that the nanowires are made of sodium trititanate.

To quantify the amount of NTO and carbon in the flexible film, TGA was carried out in air. The sample was heated from 25 to 800 °C at a rate of 10 °C min$^{-1}$. Figure 4a shows the TGA curve of the S–NTO@CNT@rGO film. The weight loss of the sample is about 16.3%, indicating that the carbon content of the film is about 16.3%, in line with the requirements for the carbon content of a flexible film material. In contrast, the NTO nanowires comprise approximately 83.6% of the mass and are the main component of the film. This shows that the as-prepared film has a certain flexibility, the key being that the nanowires themselves are also easily prepared as part of a flexible film. To gain further knowledge of the crystallographic phase and structure of the different samples, X-ray diffraction (XRD) tests were performed. As can be seen in Figure 4b, all of
the diffraction peaks of NTO NW@CNT powder correspond to those of layered Na2Ti3O7 (JCPDS card no. 31-1329). In addition, for the as-prepared NTO NW@CNT@GO film and the NTO NW@CNT@rGO film, the sharp and well-defined peaks correspond to those of Na2Ti3O7 according to the standard PDF card data. However, compared to that of the NTO NW@CNT sample, the intensity of the diffraction peak of NTO NW@CNT@GO becomes stronger at 10.5° and weaker near 25 and 30°. The reason for this phenomenon is that graphene oxide has a strong diffraction peak at 10.5°, as shown in Figure 4c.36 The diffraction peaks of Na2Ti3O7 and graphene oxide are superimposed at 10.5°, consistent with that of NTO NW@CNT powder. Figure 4d displays the Raman scattering spectra of the rGO film and the NTO NW@CNT@rGO film. Two distinctive characteristic carbon bands between 1200 and 1700 cm−1 can be observed. The asymmetrical shape of the carbon characteristic bands implies the existence of two types of bonding states of carbon.37 The Raman scattering spectra near 1300 and 1600 cm−1 are the characteristic bands of the C-atom crystals corresponding to the disorder-induced phonon mode (D band) and the graphite band (G band) of the sp2 carbon, which represents the lattice defect of the carbon atom and the in-plane stretching vibration of the sp2 hybrid of the carbon atom, respectively.38,39

To quantify the excellent electrochemical performance of the free-standing sandwich-structured film prepared by vacuum filtration, the electrochemical sodium storage characteristics of the flexible S–NTO NW@CNT@rGO film were evaluated by assembling an appropriate mass of the material in a Na-haft cell. The electrical energy storage capability of the film electrode was first examined using cyclic voltamograms (CVs). Figure 5a shows the CV curve at a scanning rate of 0.02 mV s−1 in the potential range between 2.5 and 0.01 V versus Na/Na+. A couple of redox peaks located at 0.25 V (cathodic peak) and 0.63 V (anodic peak) versus Na/Na+ can be observed, representing typical Na+ insertion/extraction in the Na2Ti3O7 crystal lattice. The distinct and well-defined redox peaks of Na2Ti3O7 indicate its excellent kinetics performance in the S–NTO NW@CNT@rGO film electrode. Moreover, the CV of the S–NTO NW@CNT@rGO electrode in a voltage window of 0.01–2.5 V at various sweep rates ranging from 0.01 to 0.1 mV s−1 is presented in Figure S3. The redox peaks in the potential range of about 0.2–0.6 V in the CV data could be attributed to the redox of the Ti4+/Ti3+ couple. With increasing cycles and increasing scanning rates, the peak current and the voltage of the electrodes increased continuously, which is consistent with the characteristics of the electrode material itself, indicating the great stability of the as-prepared electrode materials and the good reversibility of the de/intercalation of sodium ions. The charge/discharge curves of S–NTO NW@CNT@rGO electrode were calculated at 1C in the voltage range 0.01–2.5 V for 1st, 10th, 20th, 50th, 70th, and 100th cycles, as shown in Figure 5b. The initial discharge and charge capacities of the S–NTO NW@CNT@rGO film were calculated at 1C in the voltage range 0.01–2.5 V for 1st, 10th, 20th, 50th, 70th, and 100th cycles, as shown in Figure 5b. The initial discharge and charge capacities of the S–NTO NW@CNT@rGO film were calculated at 1C in the voltage range 0.01–2.5 V for 1st, 10th, 20th, 50th, 70th, and 100th cycles, as shown in Figure S3. The redox peaks in the potential range of about 0.2–0.6 V in the CV data could be attributed to the redox of the Ti4+/Ti3+ couple. With increasing cycles and increasing scanning rates, the peak current and the voltage of the electrodes increased continuously, which is consistent with the characteristics of the electrode material itself, indicating the great stability of the as-prepared electrode materials and the good reversibility of the de/intercalation of sodium ions. The charge/discharge curves of S–NTO NW@CNT@rGO were calculated at 1C in the voltage range 0.01–2.5 V for 1st, 10th, 20th, 50th, 70th, and 100th cycles, as shown in Figure S3. The redox peaks in the potential range of about 0.2–0.6 V in the CV data could be attributed to the redox of the Ti4+/Ti3+ couple. With increasing cycles and increasing scanning rates, the peak current and the voltage of the electrodes increased continuously, which is consistent with the characteristics of the electrode material itself, indicating the great stability of the as-prepared electrode materials and the good reversibility of the de/intercalation of sodium ions. The charge/discharge curves of S–NTO NW@CNT@rGO were calculated at 1C in the voltage range 0.01–2.5 V for 1st, 10th, 20th, 50th, 70th, and 100th cycles, as shown in Figure S3.
To investigate the cycling stability of the film electrodes, a cycling performance test was performed at different current densities. Figure 5c–f shows the cycling performance of the S−NTO NW@CNT@rGO film when the current densities were 0.5C, 1C, 2C, and 5C, respectively. As can be seen from Figure 5c–e, the film electrodes show good discharge specific capacity and Coulombic efficiency. At lower current densities 0.5C, 1C, and 2C, S−NTO NW@CNT@rGO delivers a high initial discharge capacity, and capacities of 419, 372.2, and 380.5 mA h g\(^{-1}\) can be respectively achieved. Remarkably, after 100 cycles, the electrode retains high capacities of 107.2, 101, and 97.9 mA h g\(^{-1}\), respectively, which confirms the excellent properties of Na storage capacity and cycling stability. For the NTO@CNT film electrode, its initial discharge capacity is only 141.7 mA h g\(^{-1}\), and after 70 cycles, a capacity of 34.2 mA h g\(^{-1}\) is retained, which confirms the excellent properties of Na storage capacity and cycling stability. For the NTO@CNT+rGO electrode, its initial discharge capacity is 65.3 and 26.5 mA h g\(^{-1}\) at 0.5C and 1C, respectively, after 100 cycles. On the other hand, the most impressive observation is that the S−NTO NW@CNT@rGO film electrode delivers discharge capacities of 204.8, 162, 115.5, 86.5, 56, and 31.9 mA h g\(^{-1}\) at current densities of 0.2C, 0.5C, 1C, 2C, 5C, and 10C, respectively. When cycled back to 5C, 2C, 1C, 0.5C, and 0.2C from 10C, the discharge capacity of the electrode can still reach up to 59.7, 91.7, 133.6, 166, and 196.8 mA h g\(^{-1}\), indicating the excellent reversibility of the S−NTO NW@CNT@rGO electrode. To further confirm the excellent electrochemical performance of the film, the electrode was even continuously cycled for 100 cycles at a current density of 0.2C, which showed that durable cyclic capacity with a high reversible capacity of 114.1 mA h g\(^{-1}\) was retained. The above results indicate that the S−NTO NW@CNT@rGO electrode has a significant advantage in terms of lifetime and capacity retention.

To further explore the effectiveness of the sandwich-structured film in improving the electrochemical performance of Na\(_2\)Ti\(_3\)O\(_7\), electrodes, the long-term cycling performance and the rate capability were investigated, as shown in Figure 6. In Figure 6a, the S−NTO NW@CNT@rGO film electrode starts at 363.8 mA h g\(^{-1}\) and maintains at 105.7 mA h g\(^{-1}\) after initial precycling. From 11 cycles, the discharge capacity has remained in a stable range at 2C, and it is satisfactory that a reversible capacity as high as 92.5 mA h g\(^{-1}\) is still achieved after 100 cycles. Subsequently, the S−NTO NW@CNT@rGO electrode also delivers 59.9 mA h g\(^{-1}\) after a further 100 cycles at 5C. This experiment fully demonstrates that the as-prepared S−NTO NW@CNT@rGO electrode possesses better capacity retention and longer lifetime. Figure 6b shows the rate capabilities of S−NTO NW@CNT@rGO at various current densities. For each stage, the process was taken from 0.2C to 10C over five cycles. Compared with the S−NTO NW@CNT+rGO electrode (Figure S6), the S−NTO NW@CNT@rGO electrode delivers discharge capacities of 204.8, 162, 115.5, 86.5, 56, and 31.9 mA h g\(^{-1}\) at current densities of 0.2C, 0.5C, 1C, 2C, 5C, and 10C, respectively. When cycled back to 5C, 2C, 1C, 0.5C, and 0.2C from 10C, the discharge capacity of the electrode can still reach up to 59.7, 91.7, 133.6, 166, and 196.8 mA h g\(^{-1}\), indicating the excellent reversibility of the S−NTO NW@CNT@rGO electrode. To further confirm the excellent electrochemical performance of the film, the electrode was even continuously cycled for 100 cycles at a current density of 0.2C, which showed that durable cyclic capacity with a high reversible capacity of 114.1 mA h g\(^{-1}\) was retained. The above results indicate that the S−NTO NW@CNT@rGO electrode has a significant advantage in terms of lifetime and capacity retention.

Figure 7. (a) XRD patterns of the NTO NW@CNT@rGO film electrode before and after the cycling test and morphology and structure of the NTO NW@CNT@rGO film electrode after the cycling test: (b, c) SEM images of the cross section and (d, e) SEM images of the upper surface.
From the above results, it can be seen that the as-prepared S–NTO NW@CNT@rGO flexible electrode materials have excellent electrochemical performance, which is mainly attributed to the design strategy and fabrication method of the electrodes. First, the absence of a binder is beneficial because of the increased electrical conductivity of the electrodes. The conventional electrode preparation process involves mixing the active materials, the electronic conductor, and the binder with the n-methyl-2-pyrrolidone solvent and coating the resultant slurry on copper foil as a current collector. However, our film electrode without the binder or current collector can not only improve the electrical conductivity but also effectively decrease the weight of the SIB system and enhance its energy density. Second, the Na$_2$Ti$_3$O$_7$ nanowires grown in situ using the hydrothermal method have many advantages, including a larger specific surface area for Na$^+$ insertion/extraction and shortened ion diffusion pathways that promote the charge transfer/collection kinetics. In addition, many porous structures are formed by intertwined nanowires, which are more conducive to the infiltration of the electrolyte, increasing the ion diffusion rate. Third, in the hydrothermal process, the added nanotubes not only facilitate the uniform dispersion of nanowires and nanotubes but also contribute to the formation of Na$_2$Ti$_3$O$_7$ nanowires, in which the nanotubes wrap around the nanowires or connect them, improving the conductivity of the nanowires themselves. Fourth, to ensure the largest contact area between the graphene and Na$_2$Ti$_3$O$_7$ nanowires, the process of the as-prepared film is repeated first with the filtration of graphene and then with that of the NTO NW@CNT. If this step is not performed, the contact area between graphene and nanowires is very small because most of the nanowires are inside the graphene layer rather than lying on the graphene surface, as seen in Figure S7b,c, leading to the poor conductivity of the material even with the addition of graphene. Fifth, the sandwichlike layered-structured film is formed via vacuum filtration. As can be seen in Figures 2b and S2, there is a certain gap between two layers because of the volatilization of oxygen in the reduction process of graphene oxide, which is beneficial to the infiltration of the electrolyte. Of course, the gap does not exist for the NTO NW@CNT@rGO sample in Figure S7a. Finally, the biggest advantage of sandwich-structured NTO NW@CNT@rGO is its ability to improve the electrical conductivity itself. Figure 1 shows the schematic representation and ideal electrotransfer pathway for the as-prepared S–NTO NW@CNT@rGO film. It can be seen that the electrons can transfer at will in the graphene layer and between the graphene layer and NTO NW@CNT layers. In addition, in the NTO NW@CNT layer, CNT connecting the nanowires can allow the electrons to move freely, implying that many electron-transfer channels are added. All of these benefits endow the electrode with the proposed flexible, current-collector-free, binder-free, and sandwich-structured anode configuration, which significantly improve the cycling performance and the rate capability of the electrode.

To further confirm the structural integrity of the electrodes, the battery was disassembled after the charge and discharge cycles and the electrode material was analyzed by both XRD and SEM (Figure 7). In Figure 7a, compared with the diffraction peaks before cycling, the diffraction peak of the electrode material after charging and discharging is very obvious at 10.5°, which is the typical peak of the Na$_2$Ti$_3$O$_7$ pattern corresponding to JCPDS no. 31-1379. This proves that the electrode material itself does not change after undergoing a rigorous process of intercalation and deintercalation of sodium ions. SEM images of a cross section of the S–NTO NW@CNT@rGO film electrode after cycling are shown in Figure 7b,c. The hierarchical structure is still obviously maintained, and the graphene and NTO nanowires of the interlayer are still observed, indicating that the sandwich-structured film is very stable. Meanwhile, as seen in the top view in Figure 7d,e, the morphology of the NTO nanowires remains intact, and there is still a graphene layer covering the surface of the NTO nanowires. This means that the graphene layer not only protects the multilayer structure of the electrode from damage and improves the electrode conductivity but also ensures that the NTO nanowires are not destroyed during the charging and discharging process.

**CONCLUSIONS**

In summary, we have presented a facile approach to produce free-standing and sandwich-structured NTO NW@CNT@rGO flexible film anode electrodes for high-performance sodium ion batteries by hydrothermal-assisted modified vacuum filtration. The as-obtained S–NTO NW@CNT@rGO flexible electrodes are not only binder-free and current-collector-free but also exhibit excellent electrochemical performances with a long cycle lifetime and large capacity for NIBs. At current densities of 0.5C, 1C, and 2C, the discharge capacities of the electrodes can be maintained at 107.2, 101, and 97.9 mA h g$^{-1}$ after 100 cycles, respectively. The S–NTO NW@CNT@rGO electrode still retain a discharge capacity of 80.6 mA h g$^{-1}$ after 150 cycles at a higher current density of 5C. During a long-term cycling performance test, after 100 cycles at a current density of 2C, a reversible capacity of 92.5 mA h g$^{-1}$ was achieved; the discharge capacity could reach 59.9 mA h g$^{-1}$ at 5C after 100 cycles. More importantly, after the rate performance test, a high reversible capacity of 114.1 mA h g$^{-1}$ was retained after a further 100 cycles at 0.2C. The superior electrochemical performance of the electrodes is believed to be in connection with the unique sandwich architecture formed by the ultralong Na$_2$Ti$_3$O$_7$ nanowires@CNT layer and highly conductive graphene layer. Furthermore, this general strategy explores exciting new methods for the design and fabrication of other flexible films applying to catalysis, energy storage, and other energy transformation processes.

**EXPERIMENTAL SECTION**

**Synthesis of Graphene Oxide (GO).** GO was prepared from natural graphite by a modified Hummers method. Briefly, 3 g of graphite powder was slowly added into a mixture of 50 mL 98% H$_2$SO$_4$, 3 g of K$_2$S$_2$O$_8$, and 3 g of P$_2$O$_5$ and then the solution was stirred continuously at 80 °C for 5 h. The prepared preoxidized product was cleaned using deionized water and dried in a vacuum oven at 80 °C for 12 h. Afterward, it was mixed with 150 mL of 98% H$_2$SO$_4$, forming a black uniform dispersion. KMnO$_4$ (15 g) was slowly added at a temperature below 20 °C, then the ice bath was removed, and the mixture was stirred at room temperature for 1 h. After slowly heating to 35 °C for 2 h, additional ice-water mixture and 20 mL of 30% H$_2$O$_2$ were slowly added into the mixed solution to completely react with the excess KMnO$_4$. After 10 min, a bright yellow solution appeared. The resulting mixture was washed with diluted aqueous HCl (1/10 v/v) solution and
H$_2$O. Graphite oxide was prepared after freeze-drying in a vacuum oven.

**Synthesis of Na$_2$Ti$_3$O$_7$ Nanowires@CNT (NTO NW@CNT).** Na$_2$Ti$_3$O$_7$ nanowires@CNT was synthesized via a simple hydrothermal process. In brief, 20 mL of 0.2 M tetrabutyl titanate ([CH$_3$CH$_2$O]$_4$Ti) solution in ethanol was mixed with 20 mL of 10 M aqueous NaOH solution. After adding 0.0403 g of CNT into the solution, the mixed solution was magnetically stirred and then transferred into a Teflon-lined stainless steel autoclave. It was heated in an oven at 190 °C for 12 h. After being air-cooled to room temperature (25 °C), the precipitate was collected by centrifugation, washed with deionized water and ethanol several times, and dried in air at 80 °C for 24 h, finally obtaining Na$_2$Ti$_3$O$_7$-nanowires@CNT.

**Fabrication of Free-Standing and Sandwich-Structured Na$_2$Ti$_3$O$_7$ Nanowires@CNT @Reduced Graphene Oxide (S–NTO NW@CNT@rGO) Flexible Film Electrode.** The flexible S–NTO NW@CNT@rGO film was fabricated by the vacuum filtration method. Typically, 20 mg of GO and 10 mg of NTO NW@CNT were respectively dispersed in 50 mL ethanol and then sonicated for 8 h to form solutions A and B. Subsequently, a sandwich-structured film was prepared by adding the solution dropwise to a vacuum filter with a 0.2 μm porous PTFE membrane according to the order “ABAB⋯”. Finally, the obtained filter film was peeled off from the microporous membrane and vacuum-dried at 100 °C for 12 h to obtain a free-standing film. The film was cut into pieces with a diameter of 10 mm and vacuum-dried at 200 °C for 4 h to convert graphene oxide to reduced graphene oxide.

For comparison, a Na$_2$Ti$_3$O$_7$ nanowires@CNT (NTO NW@CNT) film and a Na$_2$Ti$_3$O$_7$ nanowires@CNT+rGO (NTO NW@CNT+rGO) film were also prepared by vacuum filtration. A dispersion with Na$_2$Ti$_3$O$_7$ nanowires@CNT powder dispersed in ethanol by ultrasonication was filtered to produce a NTO NW@CNT film. The NTO NW@CNT+rGO film was obtained by filtering a mixture of the ethanol solution with Na$_2$Ti$_3$O$_7$ nanowires@CNT powder and graphene oxide.

**Material Characterization.** The X-ray diffraction patterns of the prepared samples were obtained using a Bruker D8 advance instrument at 40 kV and 40 mA with Cu Kα radiation (λ = 0.154 nm) (the scanning rate: 3 min$^{-1}$, the 20 range: 5–70°). The morphology and particle size of the samples were investigated using field-emission scanning electron microscopy (FESEM, JSM-7800F) and energy-dispersive X-ray spectroscopy (EDX). TEM and HRTEM images were obtained using a JEM-2100F instrument under a different resolution transmission electron microscope. Raman spectra were recorded on a PerkinElmer system at a laser wavelength, $λ$, of 532 nm. Thermogravimetric analysis (TGA) was carried out using a STA409 PC thermogravimetric analyzer to determine the carbon content in the flexible samples.

**Electrochemical Measurements.** The electrochemical performance of the as-prepared samples was investigated by CR2016-type coin half-cells using Na metal foil as the counter electrode. The free-standing and flexible S–NTO NW@CNT@rGO films were directly used as the working electrodes without the involvement of any metal current collector, conductive additive, or polymeric binder. The half-cells were assembled in an argon-filled glove box. The mass loading of the active material in each coin cell was typically 1.0–1.5 mg cm$^{-2}$. NaClO$_4$ (1 M) in a mixture (1:1, volume) of propylene carbonate (PC) and ethylene carbonate (EC) was used as the electrolyte, and a glass microfiber filter (Whatman GF/D) was used to separate the contacts of the cathode and anode electrode materials. Galvanostatic charge/discharge measurements were conducted using a LAND CT2001A test system (Wuhan, China) under various current densities in the potential range 0.01–2.5 V (vs Na$^+$/Na) at room temperature. Cyclic voltammetry (CV) measurements were performed using a CHI650D (Chenhua, Shanghai) electrochemical workstation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01051.

SEM images of the as-formed NTO NW@CNT film electrode and as-formed GO film, CV curves of the S–NTO NW@CNT@rGO electrodes at various sweep rates, cycling performance of the as-formed NTO NW@CNT film electrode at the current density of 0.2 C, cycling performance of the as-formed NTO NW@CNT@rGO film electrode at current densities of 0.5 C and 1 C, rate performance of the as-formed NTO NW@CNT@rGO film electrode, SEM images of the as-formed NTO NW@CNT@rGO film electrode (PDF).

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**Notes**

The authors declare no competing financial interest.

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