Graphene-Wrapped Anatase TiO₂ Nanofibers as High-Rate and Long-Cycle-Life Anode Material for Sodium Ion Batteries

Yeolmae Yeo¹, Ji-Won Jung¹, Kyusung Park² & Il-Doo Kim¹

Anatase TiO₂ has been suggested as a potential sodium anode material, but the low electrical conductivity of TiO₂ often limits the rate capability, resulting in poor electrochemical properties. To address this limitation, we propose graphene-wrapped anatase TiO₂ nanofibers (rGO@TiO₂ NFs) through an effective wrapping of reduced graphene oxide (rGO) sheets on electrospun TiO₂ NFs. To provide strong electrostatic interaction between the graphene oxide (GO) sheets and the TiO₂ NFs, poly(allylamine hydrochloride) (PAH) was used to induce a positively charged TiO₂ surface by the immobilization of the -NH₃⁺ group and to promote bonding with the negatively charged carboxylic acid (-COO⁻) and hydroxyl (-OH) groups on the GO. A sodium anode electrode using rGO@TiO₂ NFs exhibited a significantly improved initial capacity of 217 mAh g⁻¹, high capacity retention (85% after 200 cycles at 0.2C), and a high average Coulombic efficiency (99.7% from the second cycle to the 200th cycle), even at a 5C rate, compared to those of pristine TiO₂ NFs. The improved electrochemical performances stem from highly conductive properties of the reduced GO which is effectively anchored to the TiO₂ NFs.

Lithium-ion batteries (LIBs) have been widely used as power sources for portable electronic devices and hybrid electric vehicles. However, the growing usage and application of LIBs bring a fundamental question as to whether lithium resources on earth can cover future industrial demands. For this reason, many researchers have studied other energy-storage devices beyond LIBs. The sodium-ion batteries (NIBs) are a promising candidate because it is similar to the conventional LIB system in terms of the charge/discharge mechanism and the cell configuration. A number of notable studies of NIB have been conducted recently in search of cost-effective, high-capacity, and structurally/electrochemically stable sodium-ion electrode materials¹⁻⁴.

Recently, tin (Sn)⁵⁻⁶, antimony (Sb)⁷ and red phosphorus (red P)⁸⁻⁹ were reported as promising sodium-ion anode materials¹⁰. They have high theoretical specific capacities of 847 mAh g⁻¹ for Na₁₁Sn₄¹¹, 660 mAh g⁻¹ for Na₃Sb¹¹ and 2596 mAh g⁻¹ for Na₃P⁸. However, these high-capacity anode materials undergo large volume changes during cycling, which can generate pulverization or cracks, eventually leading to cell failure. For example, after sodiation, the theoretical volumetric expansions of Na₁₁Sn₄, Na₃Sb¹¹, and Na₃P⁸ were approximately 420%, 390% and 308%, respectively. As experienced in the LIB system, the volumetric expansion problem is difficult to solve because it stems from the intrinsic properties of the materials, which are related to structural changes during sodiation. Consequently, alternative anode materials which undergo minimal volume changes should be found for the practical application of NIBs.

¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea. ²Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States. Correspondence and requests for materials should be addressed to I.-D.K. (email: idkim@kaist.ac.kr)
In this regard, TiO$_2$ is a particularly interesting anode material. Xu et al. first reported anatase TiO$_2$ (hereafter, TiO$_2$) for a sodium-ion battery with a stable cycle life of 100 cycles$^{12}$. After this study, TiO$_2$ received much attention as a promising sodium-ion anode material$^{13}$. In-depth studies of the electrochemical reaction mechanism between the Na$^{+}$ and TiO$_2$ have also been conducted$^{14,15}$. It is believed that TiO$_2$ stores Na$^{+}$ below 0.8 V through the Ti$^{4+}/3+$ redox reaction, which is based on Na$^{+}$ insertion in the host structure. Then, the metastable sodium titanate phase is converted into metallic titanium, sodium superoxide and an amorphous sodium titanate phase at 0.3 V vs Na/Na$^{+}$ during cycling. One major concern about TiO$_2$ is its low electrical conductivity owing to its high bandgap of ~3.2 eV, which gives rise to the insulating nature of intrinsic TiO$_2$ without a dopant$^{16}$. In order to improve the electrical transport characteristics of TiO$_2$, several studies have been performed to achieve nanostructural TiO$_2$ (i.e., nanoparticles, nanorod, nanotube)$^{17–19}$ with advanced carbonaceous materials such as carbon nanotubes (CNTs)$^{20}$ or graphene$^{21}$. A carbon-modified TiO$_2$ composite showed a noticeable improvement in its electrochemical performance, but it still had problems such as a high cost and low productivity due to its complex manufacturing process.

In particular, for LIB applications, graphene-TiO$_2$ composite structures, including those with TiO$_2$ particles decorated onto the surface of graphene$^{22,23}$, stacked TiO$_2$ and graphene layers$^{24}$, structures with physically mixed TiO$_2$ particles and graphene$^{25}$, and those with TiO$_2$ particles wrapped with graphene$^{26}$ have been widely studied. However, a simple mixing route between carbon/graphene and zero-dimensional (0D) oxide nanoparticles often requires large amounts of carbon/graphene. Severe aggregation of the oxide nanoparticles or the graphene itself is easily observed during the mixing process. On the other hand, well-interconnected one-dimensional (1D) nanostructures can greatly improve the electrochemical kinetics owing to a reduced diffusion length to the fiber core ($t = L^2/D$; $t$: reaction time, L: ion diffusion length, D: diffusion coefficient)$^{27}$. For such a 1D nanostructure, intriguingly, the graphene-wrapping route offers significantly improved cycle performance and rate capability with a small amount of graphene and without the aggregation of the graphene sheets. In this study, we propose graphene-wrapped 1D TiO$_2$ nanofibers (hereafter, TiO$_2$ NFs) for the first time as a high-rate and long-cycling anode material for sodium-ion batteries. In this study, 1D TiO$_2$ NFs were prepared via an electrospinning method, and poly (allylamine hydrochloride) (PAH) was used as a surface modifier to induce a positively charged TiO$_2$ surface, i.e., -NH$_3^+$-grafted TiO$_2$ NFs$^{28}$. Then, the graphene-wrapping process was done to obtain graphene-wrapped TiO$_2$ NFs. The electrochemical sodiation/desodiation properties of the graphene-wrapped TiO$_2$ NFs and their reaction mechanism are discussed.

**Results**

**Schematic illustration of the electrospinning and graphene-wrapping process.** Figure 1 shows the processing steps for the synthesis of the reduced graphene-oxide-wrapped TiO$_2$ NFs (hereafter, rGO@TiO$_2$ NFs). The rGO@TiO$_2$ NFs were obtained by several synthetic steps, and the products in each step are shown in Fig. 1a. First, as-spun Ti precursor/polymer composite NFs were obtained via an electrospinning method. After high-temperature calcination, the TiO$_2$ NFs were formed by the thermal decomposition of the matrix polymer and the crystallization of the TiO$_2$ particles composing...
the NFs. With regard to the graphene-wrapping method, its mechanism is illustrated in Fig. 1b. In order to provide strong electrostatic interaction between the negatively charged graphene oxide (GO) and the as-prepared TiO$_2$ NFs above, (i) we grafted the surfaces of the TiO$_2$ NFs by using poly (allylamine hydrochloride) (PAH). TiO$_2$ NFs were positively charged by -NH$_3^+$ in the solution; (ii) Subsequently, GO sheets were added to the TiO$_2$ NF-dispersed solution, and the solution was mechanically agitated to ensure homogeneous mixing. GO sheets have sufficient functional groups such as carboxylic acid (-COOH) and hydroxyl (-OH) groups, which induce surface-negative charges (-COO$^-$ and -O$^-$) in the solution. Then, the positively charged TiO$_2$ NFs and the negatively charged GO are self-assembled; (iii) Crosslinking between GO and PAH arises due to ring-opening of the epoxy groups of GO as well as partial contribution of the carboxylic group, originated from the nucleophile reaction of the unpaired electrons of the amine groups$^{28}$; (iv) Finally, hydrazine was added to the mixed solution including the GO and PAH-modified TiO$_2$ NFs to transform the GO sheets into reduced GO (rGO) sheets. This graphene-wrapping mechanism was discussed in our previous report$^{29}$. As part of the processes above, proper centrifuging and drying were conducted.

**Characteristics of TiO$_2$ NFs and rGO@TiO$_2$ NFs.** Figure 2 shows the X-ray diffraction (XRD) patterns of the TiO$_2$ NFs and the rGO@TiO$_2$ NFs. The XRD patterns of both samples confirm that they have the original anatase TiO$_2$ structure (space group I4$_1$/amd, JCPDS PDF#21–1272). The main peak of the anatase TiO$_2$ at 25.2$^\circ$ indicates the crystal lattice plane (101), and other strong peaks at 37.8$^\circ$, 48$^\circ$, 54.8$^\circ$, and 55$^\circ$ present the (004), (200), (105) and (211) planes, respectively. Moreover, it is important to note that the graphene-wrapping process did not affect the crystal structure of the TiO$_2$. Using the Scherrer equation, $d = \frac{0.94\lambda}{\cos \theta w}$, we estimated the mean crystallite size of the nanoparticles comprising the polycrystalline TiO$_2$ NFs. In equation 1, $d$ is the mean grain size, $\lambda$ is the wavelength of the Cu K$_\alpha$ radiation (0.154 nm), $\theta$ is the Bragg angle considered, and $w$ is the line width at half-maximum intensity on the 2$\theta$ scale, in radians. From this calculation, we estimated the average crystallite size of the anatase TiO$_2$ to be 15.5 nm.

The morphological features of the TiO$_2$ NFs and rGO@TiO$_2$ NFs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. As shown in the SEM images in Fig. 3a,b, calcined TiO$_2$ NFs with a diameter of approximately 200–300 nm exhibited a wrinkled surface and a straight line shape. The high-resolution TEM (HRTEM) image of the calcined TiO$_2$ NFs clearly confirms that the Ti precursor was crystallized into polycrystalline TiO$_2$, which is composed of small nanoparticles (Fig. 3c,d). The lattice fringes of the TiO$_2$ (3.52 Å) NF correspond to the TiO$_2$ (101) plane (JCPDS PDF#21–1272). Figure 3e,f depict SEM images of the rGO@TiO$_2$ NFs. The rGO sheets cover all the surfaces of the TiO$_2$ NFs well and effectively interconnect the TiO$_2$ NFs to each other. Figure 3g exhibits a TEM image of the edge structure of the rGO@TiO$_2$ NFs. We note the HRTEM image in Fig. 3h, which is a highly magnified image of the yellow frame in Fig. 3g and which reveals that the thickness of the rGO sheets is approximately 3 nm.

To provide further investigation, we conducted Raman and FT-IR analyses of both the TiO$_2$ NFs and rGO@TiO$_2$ NFs. The Raman spectra of the TiO$_2$ NFs exhibit peaks which are located at approximately 145, 398, 520 and 640 cm$^{-1}$ (Fig. 4). These peaks correspond to the lattice vibrational model of the $E_g(1)$, $B_{1g}(1)$, $B_{1g}(2)$ + $A_{1g}$ and $E_g(3)$ bands of the anatase TiO$_2$, respectively$^{30}$. The Raman spectra of the rGO@TiO$_2$ NFs equally contain the $E_g(1)$, $B_{1g}(1)$, $B_{1g}(2)$ + $A_{1g}$ and $E_g(3)$ bands of the anatase TiO$_2$, which also confirms that the graphene-wrapping process does not cause any local structure changes. Likewise, the rGO@TiO$_2$ NFs show two peaks of rGO at 1349 and 1605 cm$^{-1}$. These two peaks denote the general G and D bands of rGO, respectively$^{31}$. The Raman analysis clearly verified that the structural properties of the TiO$_2$ NFs, which were well covered by rGO, did not change after the graphene-wrapping process.

Figure 5 presents the Fourier-transformed infrared (FT-IR) spectra of the TiO$_2$ NFs, the rGO@TiO$_2$ NFs, and GO in H$_2$O. The GO in H$_2$O was measured in the attenuated total reflection (ATR)
mode. Both the TiO$_2$ NFs and rGO@TiO$_2$ NFs showed Ti-O and Ti-O-Ti vibrations at 500–700 cm$^{-1}$, which provides evidence of the structural identity of these two materials. Furthermore, several bands located at a similar wavenumber in both the rGO@TiO$_2$ NFs and the GO in H$_2$O revealed that the graphene-wrapping process was successful. The broad band on the rGO@TiO$_2$ NFs overlaps with the C=O stretch of the carbonyl groups at the edges of GO at 740 cm$^{-1}$. Moreover, the C=C stretch at
1630 cm$^{-1}$ and the bending vibration O–H stretch at 3100–3500 cm$^{-1}$ are apparent in both the rGO@TiO$_2$ NFs and the GO in H$_2$O$^{31}$.

**Electrochemical reaction with Na$^+$.** Figure 6a,b show the cyclic voltammetry (CV) curves of the TiO$_2$ NFs and the rGO@TiO$_2$ NFs. A CV test was performed at a scan rate of 0.5 mV s$^{-1}$ at 0.01 ~ 2.5 V for six cycles.

In the first cathodic scan of the TiO$_2$ NFs and the rGO@TiO$_2$ NFs, first irreversible reduction peaks at approximately 0.84 V are assigned to the formation of a solid electrolyte interface (SEI), and the second reduction peaks and the third peaks near 0.26 V and 0.02 V are attributed to sodiation and electrolyte decomposition. With subsequent cyclic sweeps, for both the TiO$_2$ NFs and the rGO@TiO$_2$ NFs, the second cathodic peaks and anodic peaks shift to higher potentials (~0.5 V and ~0.75 V). These phenomena may be caused by redox couple of Ti$^{4+}$/Ti$^{3+}$. Such results were already observed in previous study reported by Wu et al.$^{33}$ Upon further cathodic and anodic voltage sweeps, broad cathodic and anodic peaks near 0.5 V and 0.75 V were reversely observed in both electrodes. This result reveals that both anode materials present the same electrochemical characteristics, especially in terms of reversibility.

**Discussion**

**Ex-situ analysis of a plausible reaction mechanism.** The charge-discharge voltage curves of the electrodes using TiO$_2$ NFs and rGO@TiO$_2$ NFs at a 1C rate (335 mA g$^{-1}$) were measured after one cycle at 10 mA g$^{-1}$ (Supplementary Figures S1a,b). During the first cycle at 10 mA g$^{-1}$, the voltage curves of the two electrodes showed two plateau regions near 1.25 V and 0.2 V while discharging. These two plateau regions are ascribed to the formation of a SEI layer, which is in good agreement with the results of the initial CV curves in Fig. 6. In the 1$^{st}$, 2$^{nd}$, 100$^{th}$, and 200$^{th}$ cycle during the following 1C rate charge/discharge, most of the capacities of the TiO$_2$ NFs and rGO@TiO$_2$ NFs are below 0.6 V vs. Na/Na$^+$ (Fig. 7a,b). The rGO@TiO$_2$ NFs showed enhanced capacity levels at all cycles and greatly improved capacity retention as compared to the TiO$_2$ NFs after 200 cycles; these results were 90% and 58% in the rGO@TiO$_2$ NFs and TiO$_2$ NFs, respectively. From the voltage profiles, we found that no voltage plateau appears in any of the cycles, which differs from the reported voltage profile of anatase TiO$_2$ for LIBs$^{34}$. 

![Figure 6](image6.png)

**Figure 6.** Cyclic voltammetry of (a) TiO$_2$ NFs and (b) rGO@TiO$_2$ NFs tested at a scan rate of 0.5 mV s$^{-1}$ for six cycles.

![Figure 7](image7.png)

**Figure 7.** Charge and discharge curves of (a) TiO$_2$ NFs and (b) rGO@TiO$_2$ NFs at a 1 C (335 mA g$^{-1}$) rate.
In typical anatase TiO₂, the redox potential for Li⁺ insertion/deinsertion is about 1.6 V versus Li/Li⁺; this can be written as follows:

\[ \text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \]

In this regard, we studied the charge/discharge behaviors using TiO₂ NFs and rGO@TiO₂ NFs as anodes for LIBs to determine whether the smooth voltage profiles are caused by our choice of materials. The experiment using lithium metal as a counter electrode was performed at 1C rate after pre-cycling at 10 mA g⁻¹ (Supplementary Figure S2). In this experiment, both the TiO₂ NFs and rGO@TiO₂ NFs exhibited a Li⁺ ion insertion plateau near 1.6 V, as reported previously[35]. This finding verifies that the reaction mechanism of TiO₂ NFs and rGO@TiO₂ NFs for lithium insertion is based on insertion, as predicted. However, in the sodium insertion case, the TiO₂ NFs and rGO@TiO₂ NFs indicate smooth charge/discharge voltage behaviors, which is fundamentally different from the case of lithium insertion. Although the effect of the particle size could cause some difference in the plateau length, generally the size effect does not eliminate this plateau. Therefore, it is important to note that the reaction mechanism of TiO₂ for NIBs may differ from that of LIBs.

To confirm the plausible reaction mechanism of anatase TiO₂ for sodium insertion/extraction, we performed ex-situ XRD and ex-situ TEM analyses. Figure 8a presents the first cycle voltage profile at a 0.2C rate. Each Roman numeral indicates the cut-off voltage for the ex-situ analyses. Figure 8b shows ex-situ XRD patterns of pristine TiO₂ NFs at 1 V, 0.1 V and 0.01 V while discharging and at 0.1 V and 2.5 V while charging. We could not find any significant structural decomposition through the ex-situ XRD analysis, and thus this may be interpreted as that the anatase structure was maintained during cycling. An ex-situ TEM analysis was performed to determine the structural stability. Figure 8c,d indicate selected-area electron diffraction (SAED) patterns in fully discharged and fully charged states, respectively. Our results rather coincide with a recent report by Kim et al.[36] Kim reported that the anatase structure is maintained during extensive cycling and suggested that the reaction mechanism is insertion through an X-ray absorption spectroscopy (XAS) analysis. This may differ from the results reported by Wu et al., who claimed that the XRD reflections of the anatase phase disappear in the discharged state. Although we observed that the (004) and (200) reflections at 38° and 48° still exist after a full discharge in our case, the results in here remain controversial. Therefore, a further elaborate analysis is necessary for a precise investigation of the reaction mechanism of graphene/TiO₂ hybrid materials.

**Electrochemical performances.** The galvanostatic cycles of Na-anode electrodes using TiO₂ NFs and rGO@TiO₂ NFs were tested at rates of 0.2C (67 mA g⁻¹), 1C (335 mA g⁻¹) and 5C (1.675 A g⁻¹) for 200 cycles (Fig. 9a–c). All cycle tests were performed after an initial charge/discharge process at 10 mA g⁻¹. During the galvanostatic cycles, the rGO@TiO₂ NFs maintained significantly higher specific
capacities than those of the TiO$_2$ NFs. For example, at the rates of 0.2C, 1C, and 5C, the rGO@TiO$_2$ NFs exhibit initial discharge capacities of 217, 165 and 124 mAh g$^{-1}$, respectively. Previously, Cha et al. showed through cyclic voltammetry that sodium ions could be stored in graphene$^{21}$. In other words, graphene could serve as an electrochemically active material. However, in this study, we found through an elemental analysis (EA) that the detected carbon element in rGO@TiO$_2$ NFs was only 1.85 wt% (Supporting Information, Table S1). This negligible amount of carbon coming from graphene sheets may not appreciably contribute to the capacity of a cell. The rGO@TiO$_2$ NFs show very stable cycle lifetimes with high coulombic efficiency ($>98\%$). They show high capacity retention of about 90% after 200 cycles at 1C. Moreover, at 5C, the cycling capacities of the rGO@TiO$_2$ NFs increase for about 70 cycles, which indicates a gradual improvement of the electrode kinetics or an increase in the active area. However, the TiO$_2$ NFs show a considerably low initial discharge capacity of 131 mAh g$^{-1}$ at 0.2C. Unfortunately, at higher rates, although this 1D nanostructured TiO$_2$ may make it possible effectively to transport Na$^+$ with regard to the diffusion length, the original insulating property of the TiO$_2$ NFs markedly limited the electron transport (47 mAh g$^{-1}$ at a 1C rate and 12 mAh g$^{-1}$ at a 5C rate). For a comparison of the TiO$_2$ NFs and rGO@TiO$_2$ NFs in light of the power density, the rate performances are shown in Fig. 9d. The rGO@TiO$_2$ NFs exhibited high reversible capacities of 217, 182, 164, 146, 119, 87 and 197 mAh g$^{-1}$, while the TiO$_2$ NFs showed reversible capacities of 101, 56, 36, 21, 8, 2 and 68 mAh g$^{-1}$ at rates of 0.2C, 0.5C, 1C, 2C, 5C, 10C and recovering rate of 0.2C, respectively. The rGO@TiO$_2$ NFs showed 91% of initial capacity at 0.2C when the current density was reversed back to 0.2C, whereas the TiO$_2$ NFs exhibited 67% of initial capacity under same condition. The rGO@TiO$_2$ NFs clearly show significantly improved rate performances compared to those of the TiO$_2$ NFs at all rates. The higher reversible capacities and better cycle performances are evidences that wrapped graphene sheets significantly increase the electrical conduction of TiO$_2$ NFs and offer higher electrode conductivity levels with their three-dimensionally interconnecting nanofibers in a complementary manner.

In summary, TiO$_2$ NFs with a wrinkled surface and a uniform diameter (200–300 nm) were synthesized via an electrospinning method. To improve the electrical conductivity of the TiO$_2$ NFs, rGO sheets were effectively wrapped onto PAH-grafted TiO$_2$ NFs. We verified that the sodiation mechanism is clearly based on an insertion process by conducting ex-situ XRD and ex-situ TEM analyses. The Na anode electrode with rGO@TiO$_2$ NFs delivered a high reversible capacity of 217 mAh g$^{-1}$ at 0.2C, excellent cycle performance at 1C (90% capacity retention during 200 cycles) and superior rate capability of 124 mAh g$^{-1}$ at a 5C rate (1.675 A g$^{-1}$). The graphene-wrapping assisted by the surface grafting of the TiO$_2$ NFs offers a versatile way to improve the electrical conductivity and electrochemical stability of TiO$_2$ NFs for application to Na ion batteries.
Methods

Materials. The titanium (iv) isopropoxide (C₄H₂₈O₆Ti, 98%), polyvinylpyrrolidone (PVP, M₀ = 1,300,000), dimethylformamide (DMF, anhydrous, 99.8%), GO solution (2 ml mg⁻¹) and Poly(allylamine hydrochloride) (PAH, Mₚ = 900,000) were purchased from Sigma-Aldrich. Acetic acid (CH₃COOH, 99.9% (m/m)) was purchased from Junsei. We used all materials without further purification.

Synthesis of TiO₂ nanofibers. In a typical process, TiO₂ NFs were fabricated via electrospinning. First, 2g of titanium (iv) isopropoxide and 1g of acetic acid, as a precursor and a dissolving catalyst, respectively, were dissolved in 7g of DMF. Then, 1.2g of PVP as a sacrificial template was added to the solution. After stirring the precursor solution at 500rpm for 12h, the solution was sequentially loaded into a plastic syringe. Under a voltage of 17kV and a flow rate of 0.3ml min⁻¹, as-spun Ti precursor/PVP composite NFs were obtained. Here, the feeding rate of the solution was 10μl/min, and a 25-gauge needle was used in the electrospinning condition. Finally, to decompose the matrix polymers and obtain TiO₂ NFs, the collected as-spun nanofibers were heat-treated at 500°C for 1h to decompose the matrix polymer and crystallize the TiO₂ NFs.

PAH functionalization and graphene-wrapping. rGO@TiO₂ NFs were synthesized by the following three methods. First, 1g of PAH was dissolved into 25ml of DI water, and an amount of 0.13g of TiO₂ NFs was added to this aqueous solution. This solution was mildly stirred for 1h to functionalize the surface of the TiO₂ NFs homogeneously into an amine end group. Then, centrifuging, washing and vacuum drying at 80°C for 6h followed. Second, an amount of 0.11g of prepared PAH-TiO₂ NFs was dispersed in 10ml of DI water, and 3200μl of aqueous GO solution was added to this mixture to synthesize GO-coated TiO₂ NFs as a hybrid anode material. Third, the GO-wrapped TiO₂ NFs were dispersed in 10ml of DI water, and 1.5g of hydrazine monohydrate was added to this solution to obtain rGO@TiO₂ NFs by reducing GO to rGO.

Material characterization. The anatase structure of TiO₂ was investigated by X-ray diffraction (XRD, D/MAX-RB (12KW) and D/MAX-RC (12KW), Rigaku). The morphologies of the TiO₂ NFs and rGO@TiO₂ NFs were observed by a scanning electron microscope (SEM, Philips). The lattice fringe and selected-area electron diffraction (SAED) patterns were obtained by a transmission electron microscope (TEM, Tecnai F30 S-Twin, FEI). Raman spectroscopy was carried out using a LabRAM HR UV/Vis/NIR PL device by Horiba Jobin Yvon, France. The Fourier-transform infrared spectroscopy (FT-IR) analysis was performed using the attenuated total reflection (ATR) method for the GO solution and the KBr-pellet method for the TiO₂ NFs and the rGO@TiO₂ NFs in transmission mode on an IFS66V/S & Hyperion 3000, Bruker Optiks, Germany. Carbon contents were measured by an element analysis (EA, Flash 2000 series, Thermo Scientific).

Electrochemical measurements. The composition of the slurries was 75 wt% active materials, 15 wt% Super P and 10 wt% polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP). The loading of the active material was about 0.85 mg cm⁻². Super P, and 10 wt% polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP). The loading of the active material was about 0.85 mg cm⁻². Using a doctor blade technique, the slurry was coated onto Cu foils to a thickness of 90 μm. Then, overnight vacuum drying at 80°C followed. Second, an amount of 0.11g of prepared PAH-TiO₂ NFs was dispersed in 10 ml of DI water, and 3200μl of aqueous GO solution was added to this mixture to synthesize GO-coated TiO₂ NFs as a hybrid anode material. Third, the GO-wrapped TiO₂ NFs were dispersed in 10ml of DI water, and 1.5g of hydrazine monohydrate was added to this solution to obtain rGO@TiO₂ NFs by reducing GO to rGO.

References
1. Palomares, V., Casas-Cabanana, M., Castillo-Martínez, E., Han, M. H. & Rojo, T. Update on Na-based battery materials. A growing research path. Energy Environ. Sci. 6, 2312–2337 (2013).
2. Slater, M. D., Kim, D., Lee, E. & Johnson, C. S. Sodium-Ion Batteries. Adv. Funct. Mater. 23, 947–958 (2013).
3. Yabuuchi, N., Kubota, K., Dahbi, M. & Komaba, S. Research Development on Sodium-Ion Batteries. Chem. Rev. 114, 11636–11682 (2014).
4. Porouch, A., Marchante, E., Courty, M., Tarascon, J.-M. & Palacin, M. R. In search of an optimized electrolyte for Na-ion batteries. Energy Environ. Sci. 5, 8572–8583 (2012).
5. Han, X., Li, T. & Hu, L. Tin Anode for Sodium-Ion Batteries Using Natural Wood Fiber as a Mechanical Buffer and Electrolyte Reservoir. Nano Lett. 13, 3093–3100 (2013).
6. Wang, J. W., Liu, X. H., Mao, S. X. & Huang, J. Y. Microstructural Evolution of Tin Nanoparticles during In Situ Sodium Insertion and Extraction. Nano Lett. 12, 5897–5902 (2012).
7. Darwiche, A. et al. Better Cycling Performances of Bulk Sn in Na-Ion Batteries Compared to Li-Ion Systems: An Unexpected Electrochemical Mechanism. J. Am. Chem. Soc. 134, 20805–20811 (2012).
8. Kim, Y. et al. An Amorphous Red Phosphorus/Carbon Composite as a Promising Anode Material for Sodium Ion Batteries. Adv. Mater. 25, 3045–3049 (2013).
9. Li, W. et al. SnₓPᵧ@amorphous Sn-P composites as anodes for sodium-ion batteries with low cost, high capacity, long life, and superior rate capability. Adv. Mater. 26, 4037–4042 (2014).
10. Dahbi, M., Yabsuchi, N., Kubota, K., Tokiya, K. & Komaba, S. Negative electrodes for Na-ion batteries. Phys. Chem. Chem. Phys. 16, 15007–15028 (2014).
11. Xiao, L. et al. High capacity, reversible alloying reactions in SnSb/C nanocomposites for Na-ion battery applications. Chem. Commun. 48, 3323–3325 (2012).

12. Xu, Y. et al. Nanocrystalline anatase TiO2: a new anode material for rechargeable sodium ion batteries. Chem. Commun. 49, 8973–8975 (2013).

13. Wu, L., Buchholz, D., Bresser, D., Gomes Chagas, L. & Passerini, S. Anatase TiO2 nanoparticles for high power sodium-ion anodes. J. Power Sources 251, 379–385 (2014).

14. González, J. R., Alcántara, R., Nacimiento, E., Ortiz, G. F. & Tirado, J. L. Microstructure of the epitaxial film of anatase nanotubes obtained at high voltage and the mechanism of its electrochemical reaction with sodium. Cyst Eng Comm 16, 4602–4609 (2014).

15. Wu, L. et al. Unfolding the Mechanism of Sodium Insertion in Anatase TiO2 Nanoparticles. Adv. Energy Mater, 5, 1–11 (2014).

16. Hanaor, D. A. H. & Sorrell, C. C. Review of the anatase to rutile phase transformation. J. Mater. Sci. 46, 855–874 (2011).

17. Su, X. et al. Advanced titania nanostructures and composites for lithium ion battery. J. Mater. Sci. 47, 2519–2534 (2012).

18. Kim, J. & Cho, J. Rate Characteristics of Anatase TiO2 Nanotubes and Nanorods for Lithium Battery Anode Materials at Room Temperature. J. Electrochem. Soc. 154, A542–A546 (2007).

19. Wu, Q. L. et al. Aligned TiO2 Nanotube Arrays As Durable Lithium-Ion Battery Negative Electrodes. J. Phys. Chem. C 116, 18669–18677 (2012).

20. Wang, B. et al. Mesoporous CNT@TiO2-C Nanocable with Extremely Durable High Rate Capability for Lithium-Ion Battery Anodes. Sci. Rep. 4, 3729 (2014).

21. Cha, H. A., Jeong, H. M. & Kang, J. K. Nitrogen-doped open pore channeled graphene facilitating electrochemical performance of Li-ion batteries. J. Mater. Chem. A 2, 5182–5186 (2014).

22. Ding, S. et al. Graphene-supported anatase TiO2 nanosheets for fast lithium storage. Chem. Commun. 47, 5780–5782 (2011).

23. Yang, S., Feng, X. & Müller, K. Sandwich-Like, Graphene-Based Titania Nanosheets with High Surface Area for Fast Lithium Storage. Adv. Mater. 23, 3575–3579 (2011).

24. Qu, Y. et al. Synthesis of Size-Tunable Anatase TiO2 Nanoparticles and their Assembly into Anatase/Titanium Oxynitride/Titanium Nitride-Graphene Nanocomposites for Rechargeable Lithium Ion Batteries with High Cycling Performance. ACS Nano 4, 6515–6526 (2010).

25. Li, N. et al. Battery Performance and Photocatalytic Activity of Mesoporous Anatase TiO2 Nanospheres/Graphene Composites by Template-Free Self-Assembly. Adv. Funct. Mater. 21, 1717–1722 (2011).

26. Chen, J. S., Wang, Z., Dong, X. C., Chen, P. & Lou, X. W. D. Graphene-wrapped TiO2 hollow structures with enhanced lithium storage capabilities. Nanoscale 3, 2158–2161 (2011).

27. Bruce, P. G., Scrosati, B. & Tarascon, J.-M. Nanomaterials for Rechargeable Lithium Batteries. Angew. Chem. Int. Ed. Engl. 47, 2930–2946 (2008).

28. Satti, A., Larrentz, P. & Gun’ko, Y. Improvement of mechanical properties of graphene oxide/poly(allylamine) composites by chemical crosslinking. Carbon 48, 3376–3381 (2010).

29. Shin, J., Park, K., Ryu, W.-H., Jung, J.-W. & Kim, I.-D. Graphene wrapping as a protective clamping layer anchored to carbon nanofibers encapsulating Si nanoparticles for a Li-ion battery anode. Nanoscale 6, 12718–12726 (2014).

30. Zhang, W. F., He, Y. L., Zhang, M. S., Yin, Z. & Chen, Q. Raman scattering study on anatase TiO2 nanocrystals. J. Phys. D. Appl. Phys. 33, 912–916 (2000).

31. Guo, H.-L., Wang, X.-F., Qian, Q.-Y., Wang, F.-B. & Xia, X.-H. A Green Approach to the Synthesis of Graphene Nanosheets. ACS Nano 3, 2653–2659 (2009).

32. Goh, G. K. L., Han, X. Q., Liew, C. P. K. & Tay, C. S. Crystallinity and Orientation of Solution Deposited Anatase TiO2 Films. J. Electrochem. Soc. 152, C532–C535 (2005).

33. Wu, L., Buchholz, D., Bresser, D., Chagas, L. G. & Passerini, S. Anatase TiO2 nanoparticles for high power sodium-ion anodes. J Power Sources 251, 379–385 (2014).

34. Koudriachova, M., Harrison, N. & de Leeuw, S. Orthorhombic Distortion on Li intercalation in Anatase. Phys. Rev. B 69, 1–6 (2004).

35. Sudant, G., Baudrin, E., Larcher, D. & Tarascon, J.-M. Electrochemical lithium reactivity with nanotextured anatase-type TiO2. J. Mater. Chem. 15, 1263–1269 (2005).

36. Kim, K. T. et al. Anatase Titania Nanorods as an Intercalation Anode Material for Rechargeable Sodium Batteries. Nano Lett. 14, 416–422 (2014).

Acknowledgements
This work was supported by a grant from the Korea CCS R&D Center (KCRC) funded by the Korean government (Ministry of Science, ICT & Future Planning) (No. NRF-2014M1A8A1049303).

Author Contributions
Y.Y. and J.W.J. contributed to conceiving the concept. Y.Y. established nearly all parts of the experimental system and carried out the measurements and characterizations, and J.W.J. assisted with some parts. Y.Y., J.W.J. and K.P. wrote the text of the entire manuscript and prepared all figures together, J.W.J. drew the Fig. 1. K.P. provided research advice, and I.D.K. oversaw the project and led the effort to completion. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yeo, Y. et al. Graphene-Wrapped Anatase TiO2 Nanofibers as High-Rate and Long-Cycle-Life Anode Material for Sodium Ion Batteries. Sci. Rep. 5, 13862; doi: 10.1038/srep13862 (2015).