An ultralight and flexible sodium titanate nanowire aerogel with superior sodium storage†

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An ultralight, conductive, and flexible 3D assembly of a metal oxide nanowire aerogel as an electrode for energy storage devices without additives and typically inconvenient flexible supported-substrates remains a challenge. Herein, we report a new 3D highly ordered layer-by-layer stacking sodium titanate@reduced graphene oxide core–shell (NTO@GCS) nanowire aerogel that has an ultra-high aspect ratio with a diameter of 30–50 nm and typical length up to 100 μm for a new class of convenient sodium-ion battery (SIB) anodes. The formation mechanism of the unique 3D NTO nanowire aerogel, the precursor of the NTO@GCS aerogel, was carefully proposed, demonstrating that the key challenge for this synthesis strategy was to form a stable and homogeneous ultrafine NTO nanotube gel suspension. In addition, for high performance sodium-ion storage, reduced graphene oxides (rGOs) were introduced into the NTO aerogel backbone. The critical role of the graphene structure between the NTO nanowires and rGO sheets in Na⁺ storage was systematically investigated. Compared to the 3D pristine NTO aerogel and 3D NTO nanowires on graphene sheet paper, the 3D interconnected NTO–GCS aerogel electrode facilitated rapid ion/electrolyte transportation, resulting in remarkably enhanced Na⁺ storage with a reversible capacity of 240 mAh g⁻¹ at 0.2C and durable cycling stability after 4900 cycles at a rate of 2 and 4C with nearly 100% coulombic efficiency.

Introduction

The discovery of three-dimensional (3D) aerogels representing a new class of nano-structure architecture materials with extremely low-density, large open pores, and a high specific surface area has resulted in a prominent class of porous materials for electronics, catalysis, sensors, membranes, and energy storage devices.1–4 Intense research efforts have successfully developed a variety of methods for the synthesis of 3D aerogels from metals,5,6 metal oxides,6–8 carbon-based materials,9–11 and semiconducting chalcogenides.12–14 Unfortunately, unlike 3D carbon-based material aerogels, there have been only a few achievements in the 3D assembly of metal oxide nanowire aerogels (MONAs), preventing the extensive study of their promising applications. In particular, 3D MONAs can be obtained through template synthesis using hierarchical soft organic templates.15–17 However, a subsequent template removal process is required, and the resulting porosity and mechanical properties are limited after template removal.18

Recently, some efforts to develop a facile method for improving the porosity of 3D MONA materials have been successful. In this regard, Jung et al.18,19 showed that a 3D K2–Mn3O8 and TiO2 nanowire aerogel can be directly achieved by self-assembling a high-aspect ratio nanowire into a cross-linked network via van der Waals interactions without using templates or supporting materials during a hydrothermal process. However, due to the poor intrinsic electrical conductivity of metal oxides and random self-assembly of a nanowire aerogel, their application is so far limited in the membrane absorption of heavy metal ions and toxic organic content for water treatment.17,18,20 Therefore, there is significant interest in the design of methods to synthesize highly ordered and flexible 3D MONAs and improve their electrical conductivity for various applications.

Flexible sodium ion batteries (SIB), which are considered alternative large-scale energy storage devices to their Li-ion counterparts, have drawn worldwide attention due to their promising application in next-generation portable and wearable electronic technologies.21–23 Previous studies showed that layered sodium titanate, Na2Ti3O7 (NTO), with a lowest charge/discharge voltage plateau of 0.3 V vs. Na⁺/Na and a high theoretical specific capacity of 178 mAh g⁻¹, could be considered an ideal anode material for SIBs.24–26 However, the inherent poor electrical conductivity and instable structure of NTO are major obstacles for its practical application in SIBs.25,27,28 Recently, several approaches have been dedicated to enhancing the electrical conductivity and optimal ion diffusion pathway through surface engineering28–30 and structure optimization,31–32...
respectively, resulting in significantly accelerated kinetic diffusion of sodium ions during charging/discharging. Alternatively, in addition to addressing the sluggish diffusion kinetics and large volume expansion during Na⁺ insertion/extraction, the development of a flexible, ultra-light, and high capacity material is required for flexible anode electrodes in real applications. Most of the current efforts are only focused on developing flexible electrodes by directly growing active materials or using traditional slurry-cast mixing of active material, a binder, and a conductive agent on flexible conductive substrate-supports such as metals,7–26 carbonaceous materials,14–36 paper,37 and cloth substrates,38 which have several drawbacks including a significant decrease in volumetric/gravimetric energy density, mechanical flexibility, and cycle stability, as well as the high cost of the electrodes.21 Therefore, searching for suitable electrode materials to satisfy the robust flexibility and high capacity requirements, and direct use without additives is very important not only for the development of efficient flexible SIBs, but also to simplify the preparation process of the electrode for energy storage devices.

Herein, we report an innovative strategy to synthesize a 3D highly ordered stacking layer-by-layer NTO@rGO core–shell (3D HOSLL NTO@GCS) nanowire aerogel via a facile pre-hydrothermal reaction that can be directly utilized as a binder-free and current collector-free anode for SIBs. Our main target is to simultaneously improve the flexibility, porous structure, and electrical conductivity of this electrode. For this purpose, we carefully designed a stable and high concentration (7.5 mg ml⁻¹) homogeneous ultrafine NTO nanotube gel suspension with a diameter of 8–10 nm and typical length of 80–100 nm through ultra-sonication, followed by a hydrothermal reaction to form a 3D HOSLL NTO nanowire aerogel. In addition, to enhance the electrical conductivity of the electrodes, different graphene structure configurations between the NTO–rGO hybrids, expected to produce different performances in Na⁺ storage, were further introduced for a comparative study. It is expected that a well-defined 3D HOSLL NTO@GCS nanowire aerogel can provide a higher specific capacity and rate capability and longer cycling stability than a 3D pristine NTO (3D pNTO) nanowire aerogel and 3D NTO nanowires on rGO paper sheets (3D NTO-GP) due to the higher electrical conductivity of the 3D HOSLL NTO@GCS nanowire aerogel.

**Experimental**

**Preparation of the 3D NTO nanowire hydrogel**

The 3D NTO nanowire hydrogel was synthesized through a simple hydrothermal method. In brief, commercial P25 (7.5 mg ml⁻¹) was dissolved in 10 M NaOH, followed by sonication for 5 days at 80 °C in a sonication bath. The mixture was then probe-sonicated for 4 h using a homogenizer with a power of 350 W. Next, 45 ml of the as-prepared mixture was transferred to a 60 ml Teflon-lined stainless autoclave, sealed, and maintained at 180 °C for 24 h. The autoclave was naturally cooled to room temperature, and the 3D NTO nanowire hydrogel was washed several times with excess DI water under gentle stirring at 200 rpm until pH ~7, followed by supercritical drying to obtain the 3D pNTO aerogel. For NTO nanowire paper preparation, the as-prepared 3D NTO nanowire hydrogel was pressed and rolled onto filter paper using a glass rod, followed by drying at RT for 24 h. The 25 μm-thick paper was obtained by peeling it from the filter paper.

**3D NTO@GCS nanowire aerogel**

Graphene oxide (GO) was first synthesized using a modified Hummers method. The synthesized GO was probe-sonicated in DI water for 2 h to produce a homogeneous GO solution (0.5 mg ml⁻¹). The as-prepared 3D pNTO aerogel was immersed in cetyltrimethylammonium bromide (CTAB) solution (1 mg ml⁻¹) with gentle stirring at 300 rpm for 2 h and then removed with tweezers and freeze-dried overnight to obtain the positively charged 3D CTAB-grafted pNTO aerogel. Next, the 3D NTO@GO core–shell nanowire aerogel was prepared by immersing the CTAB-grafted NTO NW aerogel in a natural, negatively charged GO solution with room temperature stirring at 300 rpm for 24 h. After freeze-drying, the 3D NTO@GO core–shell nanowire aerogel was thermally annealed in a horizontal tube furnace at 300 °C under Ar gas for 2 h to produce the 3D NTO@GCS aerogel.

**NTO-GP**

The as-prepared NTO nanowire paper was placed on a filter funnel, and the obtained homogeneous GO solution was poured onto its surface. The GO sheet solution was absorbed into the nanowire matrix paper through vacuum filtration using an oil pump. The obtained GO-NTO NW paper was then placed in a horizontal tube furnace and heated to 300 °C under Ar gas for 2 h to produce NTO-GP.

**Electrochemical characterization**

The obtained pNTO aerogel, NTO@GCS aerogel, and NTO-GP were directly used as a binder, conductivity additive, and metal current collector-free anode for NIBs, respectively. All the half-cell NIB tests were conducted using standard CR2032-type coin cells with Na metal foil as the counter and the reference electrode. The as-prepared samples were punched and compressed into 0.8 cm-diameter electrodes (1–1.5 mg cm⁻²) and immersed in an electrolyte overnight before assembly. The assembly of sodium coin-type cells was performed in an Ar-filled dry room using 1 M NaClO₄ in propylene carbonate with a 5 vol% fluoroethylene carbonate additive as an electrolyte and a glass fiber separator. Electrochemical measurements were performed using a VMP3 electrochemical workstation (Bio-logic Science Instruments, France) at room temperature.

**Material characterization**

X-ray diffraction was conducted by using a Rigaku Ultima IV to understand the crystal structure of the samples. The morphology of each sample was determined by using field emission scanning electron microscopy (FESEM, JEOL 7500F) and transmission electron microscopy (JEOL JEM-2100F). X-ray photoelectron spectroscopy and profile analysis were performed
using a thermo VG Microtech ESCA 2000. Raman spectroscopy was carried out by using a Witec, Alpha 300R with a 523 nm laser.

Results and discussion

Fig. 1 shows a schematic representation of the 3D pNTO aerogel, 3D NTO-GP, and 3D NTO@GCS aerogel. NTO nanowires can be easily produced by an alkaline hydrothermal reaction using TiO₂ nanoparticles; however, the scalable preparation of 3D highly ordered NTO nanowire aerogels has been extremely challenging due to the easy precipitation of TiO₂ nanoparticles during the reaction, resulting in random, non-uniform, and aggregated nanowires with a short length and low aspect ratios. To overcome this challenge, our strategy was to first synthesize a stable and high concentration homogeneous ultrafine NTO nanotube gel suspension to prevent the aggregation of NTO nanotubes. In addition, a high concentration of the NTO nanotube gel suspension was required to reach the gel formation concentration, followed by in situ 3D NTO nanowire hydrogel formation through self-assembly of the adjacent nanotubes during the hydrothermal reaction. For a typical synthesis, P25 nanoparticles were continuously sonicated in a 10 M NaOH solution at 80 °C for 5 days to obtain a homogeneous, ultrafine NTO nanotube gel suspension. The layered NTO nanosheets were first generated by reaction between P25 nanoparticles and NaOH at 80 °C, and then the NTO nanosheets were rolled-up to form nanotubes as reaction time increased. In addition, to prepare the homogeneous ultrafine NTO nanotube gel suspension, ultra-sonication during the reaction was employed to prevent the aggregation of the as-obtained NTO nanotubes. As shown in Fig. 2a, the bottles containing homogeneous ultrafine NTO nanotubes were very similar after several weeks without precipitation of nanotubes, indicating a highly stable gel suspension. From transmission electron microscopy (TEM) (Fig. 2a and b), it was evident that the homogeneous ultrafine NTO nanotube was composed of many uniform layered nanotubes with a diameter of 8–10 nm and a typical length of 80–100 nm. Moreover, the crystalline structure of the homogeneous ultrafine NTO nanotubes was further explored by XRD and is shown in Fig. 2c, which exhibited a crystalline Na₂Ti₃O₇ phase. The 3D, ordered, layer-by-layer,

![Fig. 1](image1.png)

**Fig. 1** Schematic illustration of the synthesis of the 3D pristine NTO (3D pNTO) aerogel, 3D NTO@rGO core–shell (3D NTO@GCS) nanowire aerogel, and 3D NTO nanowires on rGO paper sheets (3D NTO–GP).

![Fig. 2](image2.png)

**Fig. 2** (a and b) TEM images of the homogeneous ultrafine NTO nanotube gel suspension (inset shows the digital photographs of the pristine and 1 month old homogeneous ultrafine NTO nanotubes). (c) XRD of the homogeneous ultrafine NTO nanotube gel suspension. (d) The formation mechanism of the 3D NTO nanowire aerogel.
self-assembled NTO nanowire hydrogel was prepared via a hydrothermal reaction of the as-obtained homogeneous ultrafine NTO nanotube gel suspension at 180 °C for 24 h, followed by supercritical drying into an aerogel. Finally, the 3D NTO@GCS aerogel was obtained via coulombic self-assembly of positively charged-functionalized CTAB-grafted individual NTO nanowires and negatively charged GO sheets, followed by heat treatment at 300 °C in an Ar atmosphere. At the same time, large-scale and flexible 3D NTO-GP was also successfully fabricated by facile pressing and rolling and a subsequent vacuum filtration process. The digital photographs of the as-prepared samples are shown in Fig. 3a, illustrating a cylindrical 3D NTO hydrogel. After supercritical drying with liquid nitrogen, a fully integral aerogel monolith was observed and could rest on a dandelion, indicating a high porosity and light-mass material with a low density of 14.7 mg cm⁻³ (Fig. S2a†). More importantly, after hybridization with reduced graphene oxide, the body colour of the 3D NTO@GCS aerogel was changed from white to black, and its structure retained the original shape and volume of pristine 3D NTO hydrogels without the collapse of the 3D framework, indicating robust mechanical properties of the 3D aerogel. The morphological features of the as-prepared samples are shown in Fig. 3b–e. The cross-sectional SEM images (Fig. 3b and c) revealed that the pristine 3D NTO aerogel consisted of a well-defined self-assembly of NTO nanowire sheets, which is a uniform layer-by-layer material stacked to form a highly ordered 3D NTO framework. In addition, top-view SEM and TEM images (Fig. S1a–c†) further confirmed that a uniform and large-scale self-assembled NTO nanowire sheet was composed of dense nanowires with an average diameter of 20–50 nm and a typical length up to a few hundred microns. The high-resolution TEM image of the pristine 3D NTO nanowire aerogel in Fig. 3f shows evidence of a layered structure with a lattice spacing of 0.86 nm, corresponding to the (001) facet of monoclinic Na₂Ti₃O₇. After wrapping rGOs onto individual NTO nanowires, the morphology of the 3D NTO@GCS aerogel retained a layer-by-layer stacking, as shown in Fig. S1d.† Moreover, the TEM images (Fig. 3g and h) exhibited a thin layer of rGO with a thickness of 3–7 nm that was successfully coated along the NTO nanowire for a 3D NTO@GCS aerogel electrode. Alternatively, 3D NTO paper with a thickness of approximately 25 μm was also observed by using SEM images (Fig. 3d–e), and its structure of ordered, self-assembled NTO nanowire sheets was a layer-by-layer facially stacked film. The configuration between the rGO sheets and NTO nanowires of 3D NTO-GP was further tested by TEM as shown in Fig. 3i and j, which exhibited NTO nanowires on the rGO nanosheets.

To the best of our knowledge, compared with previous randomly oriented nanowire assembly to the 3D aerogel structure, this is the first report documenting the highly ordered, layer-by-layer self-assembly of a nanowire stacking aerogel structure, which can be beneficial for mechanical properties for various applications. The formation mechanism of this structure is depicted schematically in Fig. 2b. The key challenge for a different synthesis strategy in comparison with previous reports was the successful fabrication of a homogeneous

![Fig. 3](https://example.com/fig3.png)  
(a) Digital photographs of the as-prepared samples. (b and c) Cross-sectional SEM images of 3D pNTO. (d and e) Cross-sectional SEM images of the pristine 3D NTO paper. (f) HR-TEM of 3D pNTO. (g and h) HR-TEM images of the 3D NTO@GCS aerogel. (i and j) HR-TEM images of 3D NTO-G.
ultrafine NTO nanotube gel suspension. During the hydrothermal reaction, the self-assembly of the adjacent nanotubes allowed the formation of an ultra-long nanowire suspension. Based on Doi and Edwards's theory, due to the high concentration and ultra-high aspect ratio of the nanowire suspension, the rotation of each nanowire can be inhibited by adjacent nanowires, and the closest nanowires may have the tendency to self-assemble to form a sheet via physical bonding at the contact points between the nanowires by van der Waals forces.

The crystal structure of the as-prepared electrodes was characterized by X-ray diffraction (XRD). As shown in Fig. 4a, most of the diffraction peaks of the 3D NTO@GCS aerogel are well indexed to the layered structure of the Na2Ti3O7 phase (JCPDS no. 31-1329). The Raman spectrum of the 3D NTO@GCS aerogel electrode is shown in Fig. 4b. In addition to the typical characteristic peaks of Na–O–Ti and Ti–O–Ti stretching in monoclinic Na2Ti3O7, two peaks at 1350 and 1600 cm–1 were also clearly observed, corresponding to the D and G bands of rGO, respectively, demonstrating the presence of the rGO shell in the structure. Furthermore, the content of rGO in this electrode was approximately 13%, which was estimated by thermogravimetric analysis, as shown in Fig. S3.† The X-ray photoelectron spectroscopy (XPS) measurement of the 3D NTO@GCS nanowire aerogel was conducted to verify the composition and chemical state of different elements, as shown in Fig. 4c. According to Fig. 4d, the high resolution spectra of C 1s were resolved into four components at 284.6, 285.6, 287.2, and 288.9 eV corresponding to (C–C/C=C), (C=O), (C≡O), and (–COO), respectively. The Ti 2p spectra shown in Fig. 3e exhibited two peaks at 458.7 and 464.5 eV, assigned to Ti 2p3/2 and Ti 2p1/2, respectively, indicating the existence of Ti4+. The Brunauer–Emmett–Teller (BET) surface area of the as-prepared 3D NTO aerogel was 74.87 m2 g–1, as shown in Fig. 4f, nearly two times larger than that of previously reported nanowire membranes. The pore size of 3D NTO@GCS is confirmed by Barrett–Joyner–Halenda evaluation as shown in the Fig. 4f inset, which shows the features of a multimodal porous structure. The highly accessible surface area should be beneficial for ion/electrolyte diffusion, thus enhancing the sodium-ion storage performance.

It is well known that the 3D open-architecture offers several advantages including rapid ion transport in the electrolyte, short electron diffusion and charge transfer pathways in electrodes, and a high accessible surface area to enhance the electrochemical performance of the batteries. Therefore, to evaluate the application of 3D nanowire aerogels in energy storage devices, 3D pNTO, 3D NTO-GP, and 3D NTO@GCS aerogels were directly used as anode electrodes for SIBs without any additives or supported substrates. The electrochemical behaviours of the different electrodes were determined using a coin cell with sodium metal as the counter and reference electrodes in 1 M NaClO4 in propylene carbonate with 5% volume fluoroethylene carbonate electrolyte. Fig. 5a–c display the typical cyclic voltammetry (CV) curves for the different electrodes at a scan rate of 0.1 mV s–1 in the potential range between 0.01 and 2.5 V (vs. Na+/Na). Both exhibited typical CV curves of the Na2Ti3O7 anode for NIBs with redox peaks at 0.52 and 0.18 V (vs. Na+/Na), corresponding to the reversible reaction between Ti3+ and Ti4+ during Na+ insertion/extraction into the NTO crystal lattice. In addition, irrespective of the electrodes, the disappearance of the initial reduction peak at 0.7 V (vs. Na+/Na) occurred after the first cycle, which can be ascribed to the irreversible reaction of the formation of a solid electrolyte interphase (SEI) layer at the interface between the electrode and electrolyte.

**Fig. 4** (a) XRD pattern of the 3D NTO@GCS aerogel. (b) Raman spectra of the 3D NTO@GCS aerogel. (c) XPS spectra of the 3D NTO@GCS aerogel. (d and e) High-resolution XPS of C 1s and Ti 2p, respectively, of the 3D NTO@GCS aerogel. (f) BET surface area and BJH pore size distribution (inset) of the 3D NTO@GCS aerogel.
Importantly, the CV curve area of the 3D pNTO aerogel electrode gradually decreased with cycling, implying capacity fading due to the poor intrinsic electrical conductivity of NTO and volume expansion during Na$^+$ insertion/extraction in the NTO crystal lattice. Unlike the 3D pNTO aerogel, the intensity of the obvious cathodic/anodic peaks of the 3D NTO-GP and 3D NTO@GCS aerogel electrodes increased. As the cycles increased, the peaks were significantly enlarged, indicating improved kinetics of the Na$^+$ insertion/extraction in the NTO crystal lattice as well as excellent stability of the electrode reaction. However, compared to 3D NTO-GP, the 3D NTO@GCS aerogel electrode showed very good cycling stability with continuously increased intensity of the couple redox peaks up to 160 cycles. This phenomenon might be mainly attributed to the activation of the 3D macroporous architecture structure and configuration of the rGO nanosheets and the NTO nanowire. As indicated by the TEM results, the NTO nanowires were on the surface of the rGO sheets in 3D NTO-GP, whereas an individual NTO nanowire was fully wrapped with highly conductive rGO nanosheets in the 3D NTO@GCS aerogel, which enhanced the electrical conductivity of the individual NTO nanowire and prevented volume expansion during Na$^+$ insertion/extraction into the NTO nanowire, resulting in long-term cycling stability for Na$^+$ storage. Moreover, compared with naked NTO on the rGO sheet, more cycles were required for Na$^+$ ions to completely diffuse into the active NTO nanowire, as in the NTO@rGO core–shell nanowire. This argument was further confirmed by galvanostatic discharge/charge measurements in the voltage range of 0.01–2.5 V (vs. Na$^+$/Na) at different current densities. Fig. 5d shows the initial five charge/discharge curves of the 3D NTO@GCS aerogel electrode at a current density of 0.1C. The initial discharge and charge capacities of the first cycle were 880 and 284 mA h g$^{-1}$, respectively, with a low initial coulombic efficiency of 32.2%. The low coulombic efficiency can generally be attributed to the irreversible reaction of the formation of the SEI layer, resulting in lack of the amount of Na$^+$ ions in the electrolyte. Another possible reason for the low initial efficiency is the high porosity of the 3D aerogel structure. It is well known that the smaller the specific surface area of the electrode, the smaller the irreversible capacity loss, increasing the initial efficiency. The same tendency was observed for the 3D NTO-GP and 3D pNTO aerogel electrodes, as shown in Fig. S5a.† The rate-performance of the 3D NTO@GCS aerogel, 3D NTO-GP, and 3D pNTO aerogel at various current densities of 0.1, 0.2, 1, 2, and 4C is shown in Fig. S4a, c, and S5b, respectively. The rate-capability of the different electrodes at various current densities is summarized in Fig. 5e. The 3D NTO@GCS aerogel electrode demonstrated a reversible discharge capacity of 240 mA h g$^{-1}$ at a current density of 0.1C, and 238.6, 212, 159, and 105.9 mA h g$^{-1}$ at rates of 0.2, 1, 2, and 4C, respectively.

Fig. 5 (a–c) CV curves of the 3D pNTO aerogel, 3D NTO-GP, and 3D NTO@GCS aerogel. (d) Galvanostatic charge/discharge profile of the 3D NTO@GCS aerogel at a 0.1C current density. (e) Comparison of the rate-capability of the different electrodes. (f) Nyquist plots of the different electrodes. (g) Rate performance at various current densities and cycling performance of the 3D NTO@GCS aerogel at 0.2C. (h) Long-term cycling of 3D NTO-GP and 3D NTO@GCS aerogel at current densities of 2 and 4C.
which was greater than those of the 3D NTO-GP and 3D pNTO aerogel under the same conditions. Notably, this result was observed by directly using the as-prepared aerogels as working electrodes without a conductive additive or a metal current collector. In addition, compared to the 3D pNTO aerogel, the rate-capability of the other electrodes was significantly improved after hybridization with rGO, leading to the best performance for the NTO@GCS structure. To gain insight into the excellent sodium storage properties of the 3D NTO@GCS aerogel electrode, its electrochemical impedance spectroscopy (EIS) results were examined within the frequency range from 100 kHz to 0.01 Hz at an open circuit potential. As shown in Fig. 5f, the charge transfer resistance of the 3D NTO@GCS aerogel electrode (300 Ω) was the smallest compared to those of the 3D pNTO aerogel (685 Ω) and 3D NTO-GP (387 Ω), indicating that the rGO fully wrapped NTO nanowire could significantly accelerate the Na\(^+\) insertion/extraction kinetic process during the electrochemical reaction by enhancing the electrical conductivity, resulting in enhanced rate-capability. The increased electrical conductivity of the 3D NTO aerogel after hybridization with rGO was further confirmed by digital photographs, as shown in Fig. S2b.† Moreover, besides the increase of ion/electrolyte kinetic diffusion, the NTO@rGO core–shell nanowire structure could also prevent the volume expansion of the NTO nanowire during Na\(^+\) insertion/extraction, which significantly enhanced the cycling stability of the electrode. As shown in Fig. 5g, after charge/discharge at different current densities, the current rate was switched back and continuously showed charge/discharge at a very low rate of 0.2C, and the specific capacity of the 3D NTO@GCS aerogel electrode exhibited nearly no change after 500 cycles (230 days), with a coulombic efficiency of ~100%. In addition, the long-term cycle performance of the 3D NTO@GCS aerogel electrode was further confirmed at a high rate of 2 and 4C (Fig. 5h). Compared to 3D NTO-GP, the 3D NTO@GCS aerogel electrode showed very good cycling stability with small electrode capacity fading after 4900 cycles maintaining nearly 100% coulombic efficiency. Alternatively, the 3D pNTO aerogel electrode showed poor capacity retention with significant capacity fading after 180 cycles at a high rate of 2C (Fig. S5d†). The robust and durable cycling Na\(^+\) storage is ascribed not only to the high conductivity and negligible volume expansion of the NTO@rGO core–shell configuration, but also to the advantages of the unique aerogel structure. Compared with the current traditional electrode, our convenient anode electrode without additives or metal current collectors could prevent capacity fading during cycling due to the decomposition of inactive components such as the insulating polymer binder and metal current collector, contact loss between the active material and collector, and insufficient ion/electrolyte pathway diffusion caused by the polymer binder.

Conclusions

In summary, a well-defined large-scale 3D HOSLL NTO@GCS aerogel with robust flexibility, light mass, high porosity, and high conductivity was successfully prepared. The formation mechanism of this unique structure was carefully proposed. For high performance sodium-ion storage, a new class of SIB anodes was fabricated using an NTO@GCS aerogel without an insulating polymer, carbon black, or metal current collector. In addition, the critical role of the configuration between the rGO sheets and NTO nanowire backbone in Na\(^+\) storage was systematically investigated. A uniform 3–7 nm thick layer of rGO fully wrapped along a NTO nanowire increases the Na\(^+\) kinetic diffusion and significantly enhances long-term cycling stability. As expected, the 3D interconnected NTO–GCS aerogel electrode facilitated rapid ion/electrolyte transportation compared to NTO-GP, resulting in remarkably enhanced Na storage with a reversible capacity of 240 mA h g\(^{-1}\) at 0.2C and durable cycling stability for 4900 cycles at a rate of 2 and 4C, with nearly 100% coulombic efficiency. We strongly believe that this proposed electrode design will provide a breakthrough strategy for the development of efficient flexible SIBs and simplification of electrode preparation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was supported by the Institute for Basic Science of Korea (IBS-R011-D1).

References