A simple and steerable method was adopted to synthesize well-distributed rutile TiO$_2$ nanobundles on reduced graphene oxides through two-step hydrothermal methods. The rutile TiO$_2$–RGO composites were used as the anode materials in lithium ion batteries for investigation, which had an original morphology and a reversible capacity of 300 mA h g$^{-1}$ at 0.6 C and 200 mA h g$^{-1}$ at 1.2 C after 500 cycles.

Lithium ion batteries (LIBs) have gained tremendous interest for use in portable electronics, electric vehicles and smart grids because of their high capacity, long lifespan and environmental friendliness.\textsuperscript{1–3} Especially, nanostructured TiO$_2$ has been attracting much attention as LIB anode material,\textsuperscript{4,5} and the reaction is as follows: TiO$_2$ + xLi$^+$ + xe$^-$ $\leftrightarrow$ Li$_x$TiO$_2$ ($0 \leq x \leq 0.5$); during the reaction, Li$^+$ ions insert/extract in the TiO$_2$ matrix, accompanied by electron transfer between Ti(III) and Ti(IV).\textsuperscript{6,7} The reversible process provides a considerable capacity of 167.5 mA h g$^{-1}$ with only a small volume variation (<4%), which is critical for a high rate capability and long cycle life.\textsuperscript{8}

However, TiO$_2$ anode nanomaterials are severely hindered by their agglomeration and dissolution during charge–discharge cycles, thus leading to the decrease of electroactive sites and the fading of specific capacities.\textsuperscript{9} In order to solve this problem, the addition of conductive phases such as carbon, polymers, and metals is always necessary. Compared with conventional conductive additives,\textsuperscript{10} graphene, with ultrathin thickness, superior electronic conductivity, chemical stability, structural flexibility and high surface area, is expected to be an excellent substrate for anodes.\textsuperscript{9,11–15} As a typical example, Wang and co-workers prepared rutile TiO$_2$ nanorod-graphene and anatase TiO$_2$ spherical nanoparticle graphene hybrids, which displayed good capacity retention close to 180–160 mA h g$^{-1}$ over 100 cycles at 1 C rate (167.5 mA h g$^{-1}$).\textsuperscript{10} Other attempts mainly focused on hydrothermal–solvothermal processes; however, the as-prepared TiO$_2$–graphene composites demonstrated poor electrochemical performance for lithium storage owing to the unsatisfactory distribution of TiO$_2$ nanocrystals on graphene nanosheets.\textsuperscript{17–19} To date, anatase TiO$_2$–RGO composites have been widely investigated for Li storage. Rutile TiO$_2$–RGO composites could also be used as anode materials. However, the synthesis of highly crystalline rutile TiO$_2$–RGO composites with high Li storage capacity and good stability has met with limited success so far.

In this work, a simple and steerable method was adopted to synthesize well-distributed rutile TiO$_2$ nanobundles growing on RGO through two-step hydrothermal methods. Compared with the reported hydrothermal–solvothermal routes, the current preparation was performed without high-temperature calcination and addition of any surfactants. More significantly, the obtained rutile TiO$_2$–RGO composites possessed a highly crystallized bundle morphology, excellent high-rate performance and ultralong cycle life. This work is favorable to explore advanced TiO$_2$-based composites as anode materials for LIBs with high power density.

The preparation of TiO$_2$ nanobundles on RGO nanosheets can be schematically illustrated in Scheme 1. GO nanosheets were
synthesized by a modified Hummers method first. Atomic force microscopy (AFM) displayed the 2D features of GO nanosheets with a thickness of 0.7–1.1 nm (Fig. S1, ESI†), corresponding to 2–3 layer GO nanosheets. These GO nanosheets were dispersed in the HCl–Li2SO4/H2O–tetrabutyl titanate (TBT) mixture as the ideal substrates for the growth of TiO2 nanobundles during the hydrothermal process (150 °C for 6 h). After the addition of ascorbic acid (AA) as an effective reduction reagent, the solution was kept at 150 °C for another 4 h, during which GO nanosheets were reduced to RGO.

The X-ray diffraction (XRD) patterns of the samples are shown in Fig. 1. The characteristic peak (\(2\theta = 10^\circ\)) of GO can be clearly observed in the XRD patterns, corresponding to the (001) plane of GO. After the hydrothermal reduction, this peak entirely disappears and a broad peak at \(2\theta = 25^\circ\) appears instead, indicating that –OH, –COO, and –COOH groups have been removed from GO to a great extent. All the peaks of TiO2–RGO and pure TiO2 can be well assigned to the standard card (JCPDS 4-551) of rutile TiO2.

All TiO2 crystal structures consist of TiO6 octahedra. Because rutile octahedra show linear chains parallel to [001] while anatase octahedra arrange in zigzag chains along [221], the distribution of the third octahedron significantly determines the polymorphs.20 The importance of solution pH and supporting anions in the phase selective crystallization of TiO2 has been demonstrated.21,22 Cl– has a weak steric effect because of its small radius, which led to the formation of the octahedron with Cl– and another octahedron combined along the straight direction, and the orientation of the third octahedron promoted the formation of a rutile nucleus. Meanwhile, the existence of a large amount of Cl– under highly acidic conditions generally promoted the formation of rutile crystallites.24 In our preparation, the experimental system contained a high concentration of hydrochloric acid which led to the preferential formation rutile phase TiO2. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the TiO2–RGO composites are shown in Fig. 2. The samples display a bundle-like structure with a uniform morphology and dimension, growing directly on RGO nanosheets. High-resolution TEM (HRTEM) images further confirm the morphology and crystal characteristics of the rutile TiO2 crystals in the TiO2–RGO composites (Fig. 2e and f). The crystalline lattice distance is 3.25 Å, corresponding to the (110) planes of rutile TiO2 which is consistent with the XRD results.

To probe the electrochemical performances of TiO2–RGO composites and pure TiO2, the samples were assembled as electrodes for LIBs. These electrodes showed the plateau at \(\sim 1.1\) V of the first discharge curve and appeared as a sloping region at the second discharge curve, which is typical for rutile electrodes.23 The initial discharge–charge capacities of pure TiO2 were 247/171 mA h g\(^{-1}\) at 1.2 C and rapidly deceased to only 134 mA h g\(^{-1}\) after 100 cycles (Fig. S4b, ESI†). By sharp contrast, TiO2–RGO composites exhibited a higher discharge–charge capacity of 436/237 mA h g\(^{-1}\) at the initial cycle (Fig. 3b). The irreversible capacity can be attributed to the formation of solid-electrolyte interface (SEI) films, which can be confirmed

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**Fig. 1** XRD patterns of GO, RGO, pure TiO2 and TiO2–RGO composites.

**Fig. 2** SEM (a and b), TEM (c and d) and HRTEM (e and f) images of TiO2–RGO composites. The lattice distance in the black region is 3.25 Å.

**Fig. 3** Discharge–charge profiles of TiO2–RGO composites (a and b) and cycling performance of TiO2–RGO composites (c and d) at 0.6 C and 1.2 C.
by electrochemical impedance spectroscopy (EIS) (see details below). More importantly, the TiO2–RGO composites exhibited a higher capacity of 200 mA h g\(^{-1}\) at 1.2 C even after 500 cycles (Fig. 3c and d). This stabilized capacity was much higher than that of pure TiO2 (Fig. 3c and d, ESI†). Taking the thesis of Wang et al.\(^{24}\) as a typical example of recent progress, the anatase TiO2, nanosheet–reduced graphene oxide composite was synthesized through a hydrothermal reaction and the product exhibited relatively lower capacity and weaker cycling stability (180 mA h g\(^{-1}\) at 1 C after 200 cycles). Compared with previous work, our rutile TiO2–RGO exhibits a highly crystalline bundle morphology, higher rate performance and ultralong cycle life for lithium storage.

Profiting from the favorable features of the superior hybrid nanostructures, TiO2–RGO composites also exhibited excellent performances at high rates. When cycled at 0.6 C, 1.2 C, 3 C, 6 C and 12 C, the reversible capacities were 292, 190, 133, 101 and 78 mA h g\(^{-1}\), respectively (Fig. 4a). More importantly, no obvious capacity loss occurred when the rate reduced to 3 C and 0.6 C, indicating very good reversibility. These performances were superior to other TiO2–graphene composites prepared through the hydrothermal–solvothermal route.\(^{13,19,25}\) As a typical example, Lee et al. synthesized TiO2 nanorod arrays on RGO as LIB anodes, and the capacity was only 94 mA h g\(^{-1}\) at 5 C.\(^{19}\)

To better understand the high-rate electrochemical behaviors of TiO2–RGO composites, cyclic voltammetry (CV) was performed between 0 and 3.0 V at different scanning rates from 0.5 to 5 mV s\(^{-1}\) (Fig. S5, ESI†). After the initial 4 cycles, a pair of redox peaks can be observed at 1.75 and 1.95 V at the low scanning rate of 0.5 mV s\(^{-1}\). Only one pair of distinct cathodic (insertion)/anodic (extraction) peaks can be observed at all scan rates.\(^{26}\) In contrast, the voltage hysteresis became serious at higher scanning rates owing to the dramatically increasing polarization. The linear relationship between the peak current and scanning rate (the inset in Fig. S5, ESI†) suggests obvious surface lithium storage, i.e., the faradic pseudocapacitance effect, which occurs at the interface between active particles and electrolytes.\(^{8}\)

To gain insight into the influence of RGO nanosheets, we conducted EIS on the cells comprising the TiO2–RGO composites and pure TiO2 as the working electrodes (Fig. 4b). The samples show only one semicircle in the high-frequency range and an inclined line in the low-frequency range. The high frequency semicircle is assigned to the charge-transfer impedance in the electrode/electrolyte interface, and the inclining line corresponds to the Li+ diffusion process. However, the EIS profile displays two semicircles after the first lithiation (iv); the high frequency semicircle is attributed to the formation of the SEI film, which mainly grows in the initial discharge process.\(^{8}\) After 3 cycles, the EIS profile (v) of TiO2–RGO nanocomposites exhibits a smaller semicircle in the high-frequency range and an inclining line with a larger slope than that (ii) of pure TiO2 and the corresponding equivalent circuit mode is shown in the inset. In this equivalent circuit, \(R_s\) and \(R_{ct}\) represent electrolyte resistance and charge-transfer resistance respectively,\(^{27}\) the two indices were calculated by the equivalent circuit in Table 1. The \(R_s\) values of the two samples show little distinction, due to the usage of identical electrolyte system. The \(R_s\) value of the TiO2–RGO nanocomposites is only 43.09 \(\Omega\) lower than that of the pure TiO2 (119.53 \(\Omega\)). Moreover, the Li+ ion diffusion behavior within the solid-state electrode materials can be represented by the linear Warburg regions at a low frequency (from 0.2 to 0.01 Hz) in Nyquist plots.\(^{28}\) And the formula of the Li+ diffusion coefficient is shown as follows (eqn (1)).

\[
D_{Li} = \frac{1}{2} \left( \frac{V_m}{FA\sigma_w} \right)^2 \frac{dE}{dx} \tag{1}
\]

In the equation, \(V_m, F, A\) and \(\sigma_w\) represent the molar volume of rutile TiO2, the Faraday constant, the total contact surface area between the electrolyte and the electrode, and the Warburg prefactor arising from the Warburg region of impedance response, respectively.\(^{28}\) The Li+ diffusion coefficient of TiO2–RGO composites (\(ca. 8.03 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}\)) is 2 times of that pure TiO2 (\(ca. 3.65 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}\)). Compared with pure TiO2, TiO2–RGO composites possess a smaller \(R_s\) value and higher Li+ diffusion coefficient, indicating that the incorporation of TiO2 and RGO nanosheets can effectively improve the electron transport and Li+ diffusivity, and leads to higher discharge–charge capacities of TiO2–RGO composites than pure TiO2.

The excellent performance of the TiO2–RGO composites can be attributed to several possible reasons. First, in nanometer-sized rutile TiO2, more than 0.5 Li+ per TiO2 can be inserted/extracted in the discharge–charge process and the electrochemical behavior of rutile TiO2 was greatly dependent on the particle size.\(^{29–32}\) It is commonly agreed that Li diffusion in rutile TiO2 is highly anisotropic, which proceeds through rapid diffusion along \(c\)-axis [001] channels. More importantly, HRTEM shows that the TiO2 nanocrystal growing on RGO was along the [110] plane (Fig. 2f), and the building units (the width and length are smaller than 10 nm) of nanobundles shorten the Li+ ion diffusion length in the nanocrystals which could accelerate Li+ insertion and extraction.\(^{31,13}\) Second, some studies proposed that SEI

![Image of Table 1](https://example.com/table1.png)

<table>
<thead>
<tr>
<th>Samples</th>
<th>(D_{Li}) (EIS) (\text{cm}^2 \text{ s}^{-1})</th>
<th>(R_s) ((\Omega))</th>
<th>(R_{ct}) ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2–RGO</td>
<td>(8.03 \times 10^{-15})</td>
<td>3.34</td>
<td>43.09</td>
</tr>
<tr>
<td>Pure TiO2</td>
<td>(3.65 \times 10^{-15})</td>
<td>4.15</td>
<td>119.53</td>
</tr>
</tbody>
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films contain various inorganic–organic compounds,\textsuperscript{34,35} which can participate in the reaction to form various compounds under suitable potentials and contribute to much higher capacity than that of the counterpart oxides. In addition, graphene nanosheets have significant disorder/defects, this also contributes to the extra lithium storage capacity.\textsuperscript{36} Third, during the cycle, the crystallized TiO\textsubscript{2} may change increasingly to become amorphous which makes more and more accessible active sites available for Li\textsuperscript{+} insertion.\textsuperscript{36} In addition, anchoring TiO\textsubscript{2} nanobundles onto RGO nanosheets minimizes TiO\textsubscript{2} agglomeration and RGO restacking, which helps keep high stability and large surface area during lithium insertion/extraction.\textsuperscript{37}

In summary, we adopted two-step hydrothermal methods without using any surfactants and high-temperature calcination to fabricate rutile TiO\textsubscript{2} nanobundles on RGO with the desired dimension and morphology. Different from previous hydrothermal/solvothermal products, the obtained rutile TiO\textsubscript{2}–RGO composites possessed a highly crystalline bundle of morphology, higher rate performance and ultralong cycle life for lithium storage. This work enlightens us on preparing nanobundles on graphene nanosheets for energy storage.

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Notes and references