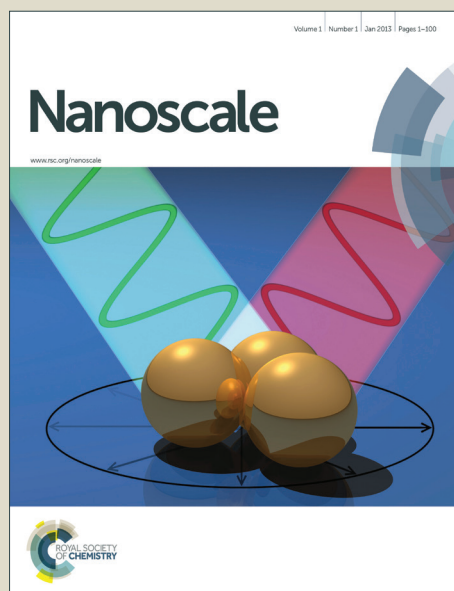


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ARTICLE TYPE

Synthesis of NASICON-type structured $\text{NaTi}_2(\text{PO}_4)_3$ -graphene nanocomposite as an anode for aqueous rechargeable Na-ion batteries

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A new solvothermal strategy combined with following calcination has been developed to synthesize $\text{NaTi}_2(\text{PO}_4)_3$ -graphene nanocomposites. X-ray diffraction, thermogravimetric analysis, field-emission scanning electron microscopy and transmission electron microscopy were performed to characterize their microstructures and morphologies. It was found that NASICON-type structured $\text{NaTi}_2(\text{PO}_4)_3$ nanoparticles (NPs) with highly crystalline homogeneously anchored on the surface of conducting graphene nanosheets (GNS), forming two-dimensional hybrid nanoarchitecture. A possible growth mechanism was further discussed based on the time-dependent experiments. When used as anode materials for Na-ion batteries, the nanocomposites exhibit excellent electrochemical performance with high-rate capability and excellent cycling stability in 1 M Na_2SO_4 aqueous electrolyte. The electrode delivers high specific capacities of 110, 85, 65, 40 mA h g^{-1} at 2, 5, 10 and 20C rates, respectively, and still remains of 90 % of the initial capacity after 100 cycles at 2C.

1. Introduction

Li-ion batteries have become the prime candidates from portable electronics to large scale applications, in particular, for electric vehicles, owing to their high energy density and output voltage of all rechargeable battery technologies in use.¹⁻⁴ Recently, Na-based compounds have made a comeback because of controversial debates regarding the basis of elemental abundance in the Earth's crust and higher cost.⁵⁻⁷ A variety of anode materials including carbon-based compounds,⁸ organic compounds,⁹ oxides,¹⁰ sulfides¹¹ and alloys¹² have been reported for application in Na-ion batteries. However, only a few reports were published for sodium storage properties of NASICON-type titanium phosphate,^{13,14} where the structure stands for a well-known family of Na^+ superionic conductors with an open 3D framework structure based on the formula of $\text{A}_n\text{M}_2(\text{XO}_4)_3$ (A = alkali, M = transition metal, X = Si^{4+} , P^{5+} , S^{6+} , Mo^{6+} , etc.).^{7,15} The NASICON-type phase consists of an open 3D framework of TiO_6 octahedra and PO_4 tetrahedra, where 2 TiO_6 octahedra separated by 3 PO_4 tetrahedra, with which they have no shared edges or shared faces, just shared all their corner oxygens. The structure model can form the so-called "lantern" units, all along the c-axis direction and the conduction channels are generated along the same direction.^{13,16} In the structure, alkali ions can occupy two different sites. At low alkali content ($n \leq 1$) in an octahedral site, A(1), it is preferably occupied, whose coordinates are 6b (0, 0, 0) position. When $n > 1$, the alkali ions are distributed among the A(1) and three 8-coordinate sites A(2), whose coordinates are 18e (x, 0, 1/4) position.^{7,17-19} The NASICON-type structure can allow easy migration of the alkali ions between A(1) and A(2).^{7,13-19} Although the open 3D

framework of NASICON-type structure is suitable for Na^+ diffusion, the poor electronic conductivity restrains slow transport of Na^+ . To improve the electrochemical performance of $\text{NaTi}_2(\text{PO}_4)_3$, two common methods of tailoring the particle size of electroactive materials to reduce both the ionic and electronic transporting path and enhancing their electronic conductivity with surface carbon-coating layers were tried.^{14,20,21} The electrochemical performance of the NASICON-type $\text{NaTi}_2(\text{PO}_4)_3$ electrode for sodium extraction/insertion has been firstly reported,¹³ where the large voltage difference between charge and discharge curves indicate that strong polarizations occur, partially due to low electronic conductivity. Tremendous efforts have been made to overcome the obstacles of $\text{NaTi}_2(\text{PO}_4)_3$, such as applying nanostructured materials and surface coating with conductive materials.^{14,20,21} Recently, mechanical milling and carbothermal treatment have been used for improvement of the electric conductivity of $\text{NaTi}_2(\text{PO}_4)_3$, which have a similar positive effect on the initial specific capacity (approx. 143.0 mAh g^{-1}), compared with that of bulk samples (only 129.3 mAh g^{-1}).¹⁴ Nanostructured materials lead to a decrease of the current density per unit surface area and an increase in the charge/discharge rate because the high surface areas increases the electrolyte/electrode contact areas; Meanwhile, nano-size provides a shorter path for ion and electron transport, which facilitates improved kinetic.²² Graphene, a new two-dimensional carbon material, has been considered to be a potential material for use in energy conversion and storage because of its superior electrical conductivity, high surface area, chemical tolerance, ultrathin thickness and structural flexibility.^{23,24} Among these applications, graphene has been approached by forming composites or hybrids as a highly

electronic conductive network in the fields of rechargeable batteries.²⁰⁻²² Recently, improvement on cycling stability and rate performance was reported when some anode materials²⁵⁻²⁸ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ²⁹ were supported by graphene.

In this work, we present the preparation of $\text{NaTi}_2(\text{PO}_4)_3$ /graphene nanosheets ($\text{NaTi}_2(\text{PO}_4)_3$ /GNS) nanocomposites through a solvothermal method for the first time, where highly crystalline $\text{NaTi}_2(\text{PO}_4)_3$ NPs with an optimal particle size are homogeneously anchored on surface of conducting GNS. The effect of different reaction times on the physico-chemical properties of $\text{NaTi}_2(\text{PO}_4)_3$ was studied, and a possible growth mechanism was further proposed. Electrochemical results show that only 3.4 wt.% of graphene in the nanocomposites leads to remarkable improvement of specific capacity, the rate performance and cycling stability.

2. Experimental Section

2.1 Materials synthesis

All the reagents were of analytical grade purity from Sinopharm Chemical Reagent Co., Ltd, China. Graphite oxide (GO) was synthesized from natural graphite powders (SP-1) by a modified Hummers method,³⁰ in which pre-oxidation of graphite is followed by oxidation with Hummers' method (see Electronic Supporting Information, ESI†). For the synthesis of $\text{NaTi}_2(\text{PO}_4)_3$ /GNS nanocomposites, 100 mg of GO was dispersed well into 40 mL of ethylene glycol (EG) after ultrasonication for 4 h to form the mixture. Then, 10 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ (28 wt.%) and 3.4 mL of tetrabutyl titanate (TiOB) were added to the above mixture under constant agitation (donated as Ti-O/GNS). After stirring for 1 h, 1725.5 mg of $\text{NH}_4\text{H}_2\text{PO}_4$ in 10 mL of distilled water and 265 mg of Na_2CO_3 in 10 mL of distilled water were added, respectively (donated as Ti-P-O/GNS and Na-Ti-P-O/GNS, respectively). The resulting white gel was then transferred into 80 mL Teflon-lined stainless steel autoclave and kept at 140 °C for 24 h. After cooled to room temperature (RT) naturally, the obtained product was separated by centrifugation, washed with de-ionized (DI) water and ethanol several times respectively to remove an excess of hydroxides before drying at 80 °C for 12 h. Subsequently, the dried sample was calcinated at 700 °C for 2 h by using a heating rate of 2 °C/min in a nitrogen atmosphere to obtain highly crystalline $\text{NaTi}_2(\text{PO}_4)_3$ /GNS powders. The pure $\text{NaTi}_2(\text{PO}_4)_3$ was prepared in a similar manner to that of $\text{NaTi}_2(\text{PO}_4)_3$ /GNS, except for the absence of GNS in the process.

2.2 Materials characterization

The crystalline phase of the prepared samples was characterized by powder X-ray diffraction (XRD) (Bruker D8 advance) with Cu K α radiation and Sol-X detector from $2\theta = 10^\circ - 80^\circ$ at 40 kV and 40 mA. The XRD profiles were refined by the Rietveld program RIETAN-FP.³¹ Schematic illustrations of the crystal structures of $\text{NaTi}_2(\text{PO}_4)_3$ phase were drawn using the program VESTA.³² Microstructural properties were obtained using field-emission scanning electron microscopy (FESEM, FEI Nova Nano SEM 430), scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS, JEM-2100, JEOL), and atomic force microscopy (AFM, Seiko Instrument, SPA-300HV). Thermo gravimetric (TG) analyses were performed on a

TG instrument (NETZSCH STA 409 PC) using a heating rate of 5 °C/min in an air atmosphere from 50 °C to 800 °C.

2.3 Electrochemical tests

The electrochemical performances of the synthesized samples were measured with a beaker-type three-electrode cell. The working electrode was fabricated by compressing a mixture of 80 wt.% active materials, 15 wt.% acetylene black and 5 wt.% polytetrafluoroethylene binder by weight onto a graphite electrode with 1 cm² area. Graphite electrode was selected as the current collector because of its high overpotential for hydrogen evolution. A commercial saturated calomel electrode (SCE) was used as the reference electrode while a piece of platinum foil (1 cm²) was used as counter electrode in a 1 M Na_2SO_4 aqueous solution purged with N_2 before use as electrolyte (made from DI water with 18 M Ω /cm electrical resistivity). Cyclic voltammetry (CV) was carried out on a CHI 660E electrochemical workstation (ChenHua, Shanghai, China). Galvanostatic charging-discharging experiments were conducted on LAND tester (Wuhan, China) at RT.

3. Results and discussion

3.1 Physicochemical characterization

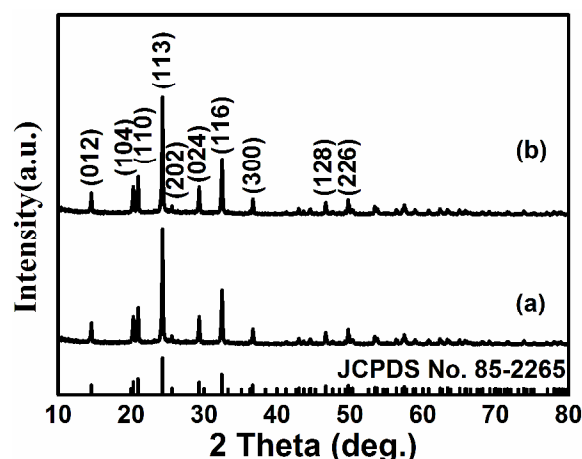


Fig. 1 XRD patterns of (a) pure $\text{NaTi}_2(\text{PO}_4)_3$ and (b) $\text{NaTi}_2(\text{PO}_4)_3$ /GNS. (The vertical lines for the standard pattern of JCPDS No. 852265 for the $\text{NaTi}_2(\text{PO}_4)_3$ phase.)

Fig. 1 shows the XRD patterns of pure $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{NaTi}_2(\text{PO}_4)_3$ /GNS. The pure $\text{NaTi}_2(\text{PO}_4)_3$ (Fig. 1a) has several very sharp diffraction peaks at $2\theta = 14.52, 20.28, 20.98, 24.30, 25.60, 29.30, 32.44, 36.68, 46.70$ and 50.36 , corresponding to (012), (104), (110), (113), (202), (024), (116), (300), (128) and (226) planes of well-crystallized rhombohedral, space group: R-3c (167), respectively, which was the same to that of the $\text{NaTi}_2(\text{PO}_4)_3$ /GNS (Fig. 1b). It confirmed the successful synthesis of highly crystalline NASICON-type $\text{NaTi}_2(\text{PO}_4)_3$ (JCPDS NO. 85-2265) phase through the solvothermal method combined with a short post-annealing. However, the typical diffraction peaks of reduced graphite oxide (RGO) were not observed in the XRD pattern of the $\text{NaTi}_2(\text{PO}_4)_3$ /GNS nanocomposites. It may be the low content of RGO and the high crystalline of $\text{NaTi}_2(\text{PO}_4)_3$ in the nanocomposites. Thermogravimetric (TG) analysis was used to determine the amount of GNS in the $\text{NaTi}_2(\text{PO}_4)_3$ /GNS

nanocomposites (Fig. S1, ESI†). The result indicates that the hybrid materials have a chemical composition of 96.6 wt.% $\text{NaTi}_2(\text{PO}_4)_3$ and 3.4 wt.% GNS.

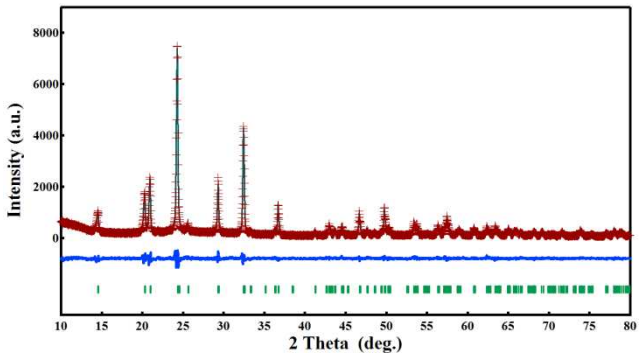
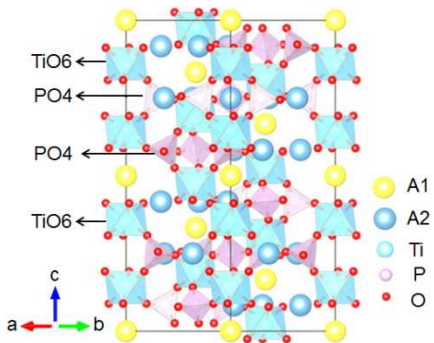


Fig. 2 Rietveld refinement of the observed XRD pattern for $\text{NaTi}_2(\text{PO}_4)_3$ phase. (Calculated (line) and observed (+) X-ray diffraction patterns for pure $\text{NaTi}_2(\text{PO}_4)_3$. Vertical bars below the pattern show the positions of all possible reflection peaks of the $\text{NaTi}_2(\text{PO}_4)_3$ phase.)

The Rietveld method was performed to refine the crystal structure of pure $\text{NaTi}_2(\text{PO}_4)_3$ by RIETAN-FP software. Initially, the common overall parameters, zero shift, unit-cell parameters, half-width, background, scale fact and pseudo-Voigt coefficient were refined. The atomic positions of Ti, P and O atoms were refined in the 12c (0, 0, z), 18e (x, 0, 1/4) and 36f ((x, y, z), (x, y, z)) Wyckoff positions, respectively. Na^+ was all assumed to occupy the A1 site (6b (0, 0, 0) position). Then, all refinements give a small value of factors R_{wp} , R_p and S, indicative of a good and reliable structural analysis. The resulting Rietveld refinement pattern and the resultant parameters are shown in Fig. 2 and Table 1, respectively. The NASICON-type phase has the lattice parameters of $a = 8.4845$ (3) Å, $c = 21.8117$ (5) Å, $V = 1359.809$ (8) Å³ and the atomic positions of Ti (0, 0, 0.1451), P (0.2873, 0, 1/4), O1 (0.1738, 0.9715, 0.1921), and O2 (0.1941, 0.1652, 0.0859) were obtained from the refinement, close to the values reported in earlier references.³³

Table 1 Atomic coordinates, isotropic thermal parameters and occupation numbers for $\text{NaTi}_2(\text{PO}_4)_3$ phase refined from X-ray powder diffraction data. NASICON-type structure in space group R-3c (No. 167); cell parameters: $a = 8.4845$ (3) Å, $c = 21.8117$ (5) Å, $V = 1359.809$ (8) Å³ and $Z = 6$; $R_{\text{wp}} = 8.79$ %, $R_p = 6.73$ %, $R_t = 2.54$ %, $S = 1.44$.

Atom	Site	g	x	y	Z	B (Å ²)
Na	6b	1	0	0	0	1.1(2)
Ti	12c	1	0	0	0.1451(1)	1.9(3)
P	18e	1	0.2873(3)	0	1/4	0.8(1)
O1	36f	1	0.1738(4)	0.9715(5)	0.1921(1)	0.9(2)
O2	36f	1	0.1941(4)	0.1652(4)	0.0859(1)	0.9(1)



Scheme 1 A schematic illustration of the NASICON-type structured.

Schematic illustration of the NASICON-type structure was given. As shown in Scheme 1, two positions of interstitial spaces (A1, A2) where conductor cations are distributed inside the channels can be distinguished: one (A1) in elongated octahedral oxygen environment at the intersection of three conduction channels, and the other (A2) among the (A1) and three 8-coordinate sites environment at each bend of the conduction channels.¹³⁻¹⁹ In the absence of motion, Na^+ preferably occupy octahedral A1 site, whose coordinates are 6b (0, 0, 0); Chemical intercalation of Na^+ in $\text{NaTi}_2(\text{PO}_4)_3$, Na^+ actually occupy octahedral A2 site, whose coordinates are 18e (0.6368, 0, 0.25).¹⁷⁻¹⁹ Two Na^+ can be reversibly intercalated in the 3D framework of $\text{NaTi}_2(\text{PO}_4)_3$. As a matter of fact the $\text{NaTi}_2(\text{PO}_4)_3$ phase could be considered as the charged form of a positive intercalation electrode, $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ playing the role of the discharge species.

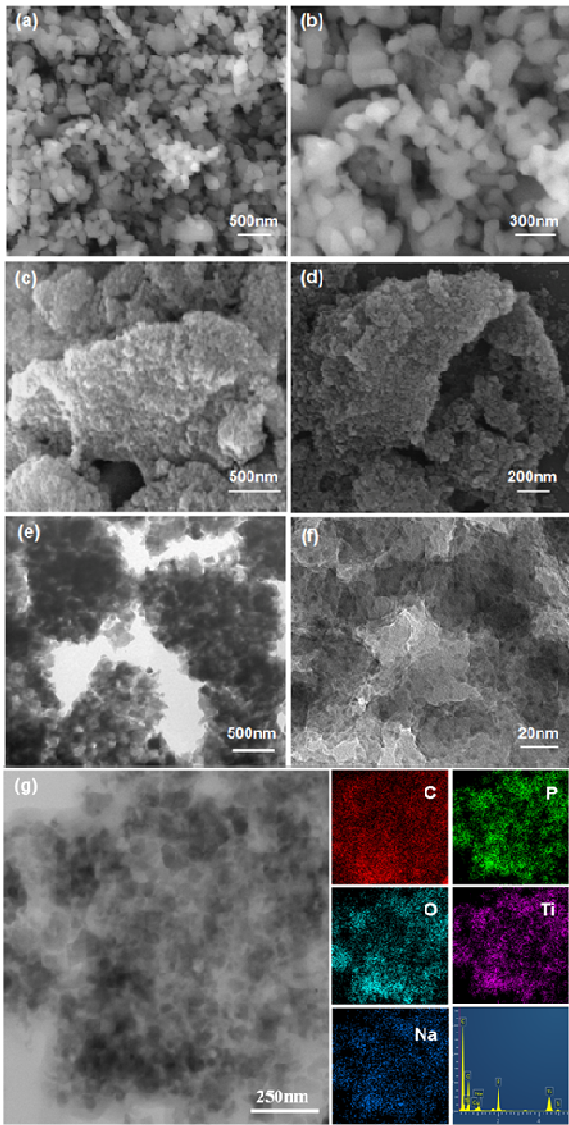


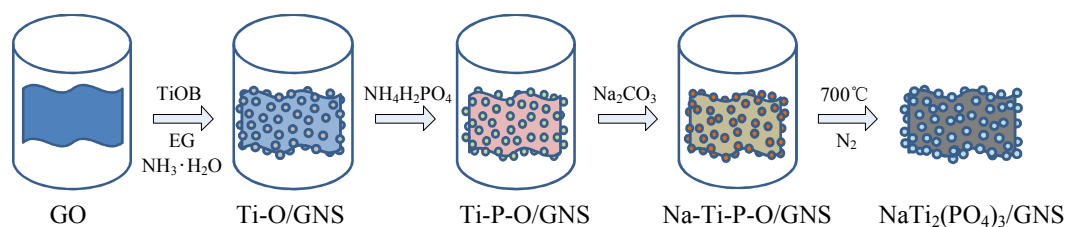
Fig. 3 FESEM images of (a, b) pure $\text{NaTi}_2(\text{PO}_4)_3$, (c, d) $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$, (e, f) TEM images of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ and (g) bright-field STEM image of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$, elemental mapping of the same region, indicating spatial distribution of C, P, O, Ti and Na, respectively and the EDS analytical results.

The morphology of the synthesized samples was observed by FESEM. Fig. 3 displays the morphological features of pure $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$. As observed from Fig. 3 (a, b), the $\text{NaTi}_2(\text{PO}_4)_3$ sample prepared in the absence of GNS consisted of irregular aggregated NPs with the size in the range of 100-200 nm. These irregular NPs interconnected each other and formed numerous inter-particle mesopores and/or macropores. From Fig. 3 (c, d), it can be seen that $\text{NaTi}_2(\text{PO}_4)_3$ NPs were homogeneously anchored on conducting GNS forming two-dimensional (2D) nanostructure and the GNS were also separated by the $\text{NaTi}_2(\text{PO}_4)_3$ NPs. It is worth noting that such a combination will perfectly facilitate the transport of Na^+ and increase the electrolyte/electrode contact area.³⁴ Meanwhile, it should be pointed out that during the solvothermal process, the NPs are still strongly anchored on the surface of GNS with a high density, suggesting a strong interaction between NPs and GNS. The strong anchoring of $\text{NaTi}_2(\text{PO}_4)_3$ NPs on GNS enables rapid electron transport through the underlying GNS to NPs, resulting in superior rate capability.³⁵ To examine the microstructure of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ more clearly, the sample was further investigated by TEM. As observed in Fig. 3 (e, f), a very large quantity of $\text{NaTi}_2(\text{PO}_4)_3$ NPs with a size of ~50 nm are uniformly dispersed onto the GNS, and some of them aggregate together, which is in good agreement with the SEM observation (Fig. 3 (c, d)). This result strongly indicates that the GNS play a significant role in controlling the morphology by acting as the nucleation site for deposits through interaction with metal ions.^{36,37} For further investigation the distribution of $\text{NaTi}_2(\text{PO}_4)_3$ NPs and GNS, a bright field STEM image and elemental mapping of the corresponding region were shown in Fig. 3 (g), indicating spatial distribution of C, P, O, Ti and Na, respectively. The P, O, Ti and Na were uniformly distributed over the surface of the $\text{NaTi}_2(\text{PO}_4)_3$ NPs and the images were overlapped with each other. Meanwhile, the distributions of these chemical elements were in the range of the EDS mapping of C, which were consistent with targeted $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ structure. EDS mapping indicated that the atomic ratio of Na to Ti is 1:2. The

Na/Ti ratio of the NPs is the same as that of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$.

3.2 Formation mechanism of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ nanocomposites

In order to investigate the formation mechanism of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ nanocomposites, each process in the experiment was carefully conducted. The experimental details are presented in the materials synthesis. The overall fabrication procedures of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ nanocomposites are schematically illustrated in Scheme 2. Firstly, GO with a thickness of 2.0 nm (Fig. S2, ESI†) was dispersed into the EG under ultrasonication. Next, $\text{NH}_3 \cdot \text{H}_2\text{O}$ and TIOB were successively added to the solution under constant agitation. The anatase and rutile TiO_2 phases (Fig. S3a, ESI†) can be detected for the product obtained after solvothermal treatment and then following calcination at 700 °C for 2 h. Thus, TiO_2 NPs were anchored on RGO by controlled hydrolysis of TIOB in the presence of GO (Fig. S3b, ESI†). Then, $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution was added subsequently. It can be found that the typical diffraction peaks of anatase and rutile TiO_2 phases disappear while the $\text{Ti}_5\text{P}_4\text{O}_{20}$ phase (JCPDS No. 49-1139) appears after following calcination, which indicates that the starting TiO_2 completely in situ converted into a ternary $\text{Ti}_5\text{P}_4\text{O}_{20}$ phase (Fig. S4a, ESI†). The $\text{Ti}_5\text{P}_4\text{O}_{20}$ NPs were also anchored on RGO by solvothermal treatment, and following calcination (Fig. S4b, ESI†). Finally, the intermediate $\text{Ti}_5\text{P}_4\text{O}_{20}$ production in situ transformed into the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ precursor (a quaternary Na-Ti-P-O) accompanied by adding Na_2CO_3 aqueous solution. In order to further investigate the mechanism of formation for the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ nanocomposites, off-stoichiometric Na_2CO_3 were taken into consideration in the process. Surprisingly, the main $\text{NaTi}_2(\text{PO}_4)_3$ phase (JCPDS No. 85-2265) and the small amount of TiPO_4 phase (JCPDS No. 38-1468) can be detected in the product (Fig. S5a, ESI†). The difference in the structures of the ternary $\text{Ti}_5\text{P}_4\text{O}_{20}$ and TiPO_4 phases is caused by Na_2CO_3 . Similarly, The $\text{NaTi}_2(\text{PO}_4)_3$ and TiPO_4 NPs were also anchored on RGO by the same process (Fig. S5b, ESI†).

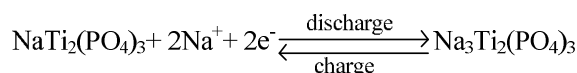


Scheme 2 Schematic illustration of the synthesis of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$.

3.3 Electrochemical analysis

To examine the effectiveness of GNS on improving the electrochemical performance of the electrode, the Na^+ extraction/insertion properties of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ nanocomposites and pure $\text{NaTi}_2(\text{PO}_4)_3$ were investigated, respectively. Cyclic voltammetric measurements were taken in 1 M Na_2SO_4 in a voltage range of -1.0 to -0.5 V at a scan rate of 0.5 mV s^{-1} . As shown in Fig. 4 (a), a pair of redox peaks located at -0.89 (red.) and -0.75 V (ox.) (vs. SCE) were observed for $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$, and similar peaks were observed at -0.85 V

(red.) and -0.79 V (ox.) for the pure $\text{NaTi}_2(\text{PO}_4)_3$, indicating the reversible insertion/extraction reaction of Na^+ in the $\text{NaTi}_2(\text{PO}_4)_3$ lattice. The redox potential was consistent with the previous report of $\text{NaTi}_2(\text{PO}_4)_3$.³⁸ When $\text{NaTi}_2(\text{PO}_4)_3$ is charged and discharged, it undergoes the following reaction:



The smaller potential differences between oxidation-reduction peaks of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ compared with pure $\text{NaTi}_2(\text{PO}_4)_3$ could be attributed to the variation of cell impedance.

Corresponding to the extraction/insertion process of Na^+ in the NASICON-type structured $\text{NaTi}_2(\text{PO}_4)_3$, a couple of strong and well-defined oxidation-reduction peaks for Ti^{3+} and Ti^{4+} can be easily observed for the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$,^{14,38} not for pure $\text{NaTi}_2(\text{PO}_4)_3$. The peak current of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ are about 6.0 and 4.5 mA, which are much higher than those of pure $\text{NaTi}_2(\text{PO}_4)_3$. Indeed the Na^+ diffusion coefficient is proportional to the square of the peak current (i_p^2) in the CV profiles, so higher peak current means higher Na-ion diffusion coefficient and consequently, better electrochemical performance of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ anode material. The obvious peaks in the CV curves of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ was due to functionality of GNS. Meanwhile, the good overlapping of the curves for the subsequent cycles suggests that $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ is more stable than pure $\text{NaTi}_2(\text{PO}_4)_3$ in aqueous electrolyte.

In addition, it was found that the redox reaction could take place at the potentials much more positive than the H_2 evolution potential of water in 1M Na_2SO_4 electrolyte at pH=7, which occurs below -1.16 V vs. SCE.¹⁴ The low Na^+ insertion/extraction potential is located at the lower limit of the electrochemical window of the aqueous electrolyte. Thus, it should be suitable to use the NASICON-type $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ as a promising anode material for Na-ion batteries.^{14,20,21,38}

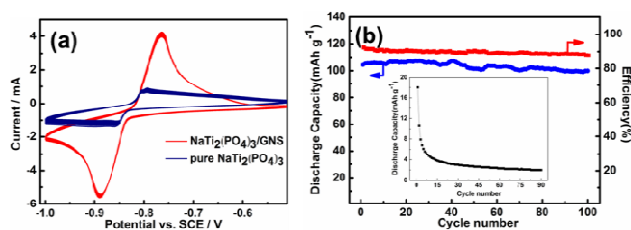


Fig. 4 Electrochemical performances of pure $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ electrodes in 1M Na_2SO_4 : (a) The first ten cycle profiles of cyclic voltammograms at 0.5 mV s^{-1} sweep rate. (b) Galvanostatic charge/discharge curves for $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ at 2 C. Inset shows discharge capacity profile for pure $\text{NaTi}_2(\text{PO}_4)_3$ at 2 C.

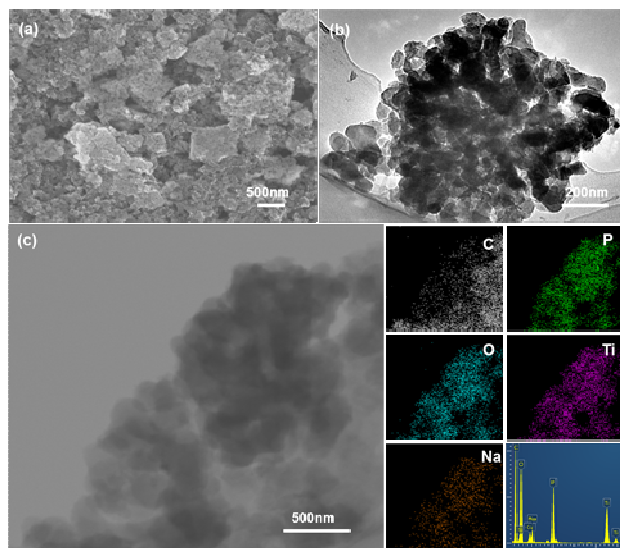


Fig. 5 FESEM image (a), TEM image (b) and (c) bright-field STEM image of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ after discharged, elemental mapping of the corresponding region, indicating spatial distribution of C, P, O, Ti and Na, respectively and the EDS analytical results.

Based on the above mentioned results, only the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$

electrode further investigated the charge-discharge cycling performance at 2 C for 100 cycles (shown in Fig. 4 (b)). The $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ exhibited excellent cycling performance. The discharge capacity in the first cycle was 104.4 mAh g^{-1} , and after 100 charge-discharge cycles, the capacity remained at 99.9 mAh g^{-1} , which was less than 4.3 % discharge capacity loss. However, the pure $\text{NaTi}_2(\text{PO}_4)_3$ samples synthesized in the absence of GNS presented a bad electrochemical performances (the inset in Fig. 4b). The discharge capacity of pure $\text{NaTi}_2(\text{PO}_4)_3$ in the first cycle was only 18.1 mAh g^{-1} and decreased steeply with increasing the cycle number. Calculated from the discharge capacity/charge capacity, the coulombic efficiency in this long cycle period almost kept constant at about 90 %. This result may be attributed to the stability of NASICON-type crystal structure of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$,^{13,14} possessing the good crystallinity, the electronic conductivity of the GNS and high ionic conductivity,²³ which was consistent with that of the extraction/insertion reaction in the aqueous electrolyte as expected in CV curves.

Above 100 cycles at 2 C, the morphology of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ samples after discharged was observed. As can be seen in Fig. 5 (a, b), the samples were maintained the previous morphological features that the $\text{NaTi}_2(\text{PO}_4)_3$ NPs, in sizes in the range 40 ~60 nm, were still strongly anchored on the surface of GNS with a high density. To further examine the architecture of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$, the samples were investigated by STEM and EDS mapping, shown in Fig. 5 (c). The results suggested that the chemical elements of P, O, Ti and Na were homogeneously distributed over the range of C element after 100 cycles. In addition, the EDS analysis indicated that the atomic ratio of Na to Ti is close to 3:2, which was consistent with the reaction mechanism mentioned above. The discharge product of $\text{NaTi}_2(\text{PO}_4)_3$ was also in accordance with previous reports.^{13,20}

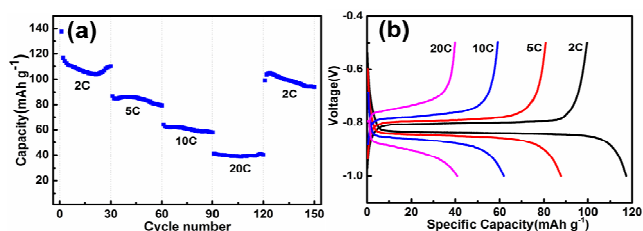


Fig. 6 Cycle performance (a) and capacity-voltage profiles (b) of $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ at different current densities.

Meanwhile, the high-rate capabilities of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ electrode was investigated (Fig. 6a). The electrode was progressively charged-discharged in serial stages with the different current rates from 2 to 20 C. A specific discharge capacity is around 110 mAh g^{-1} obtained at a rate of 2 C, and the specific discharge capacity reduced to 85 and 65 mAh g^{-1} at rates of 5 and 10 C, respectively. At the high rate of 20 C, the specific discharge capacity decreased to about 40 mAh g^{-1} . After 120 cycles, the electrode can still deliver a reversible capacity of 105 mAh g^{-1} , which was further charged-discharged at 2 C for another 30 cycles.

The galvanostatic charge-discharge curves of the $\text{NaTi}_2(\text{PO}_4)_3/\text{GNS}$ electrode at different current rates from 2 to 20 C were shown in Fig. 6 (b). The charge and discharge capacity were approximately 100 and 117 mAh g^{-1} at a rate of 2 C, respectively. In addition, the electrode had clear discharge

voltage plateau at a potential of around -0.85V vs. SCE, which was consistent with the CV curves shown as in Fig. 4 (a). With increasing current density, the electrode voltage decreased steeply and the specific discharge capacities were 86.7, 62.4 and 41.5 mAh g⁻¹ at rates of 5, 10 and 20 C, respectively. The NaTi₂(PO₄)₃/GNS exhibit excellent electrochemical performance with high-rate capability may be attributed to the NaTi₂(PO₄)₃ NPs are well dispersed onto GNS as spacers to effectively prevent the agglomerative NPs in the nanohybrids and consequently keep their large active contact area between the electrode and electrolyte.²⁴

4. Conclusions

In summary, we report a simple solvothermal route to fabricate NaTi₂(PO₄)₃ NPs composited with RGO and their use as advanced anode materials for Na-ion batteries. Benefited from the good conductivity, high surface area of GNS and the good stability of NASICON-type NaTi₂(PO₄)₃ NPs with highly crystalline, the unique structures endow the composites with ultra-fast charge capability, high reversible capacity and long cycle life. Furthermore, the characteristics of naturally abundance and operating in safe, inexpensive and highly conductive aqueous electrolytes make the nanocomposites especially desirable for use in high performance energy storage devices.

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Notes and references

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