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

Gang Pang, a, b Changzhou Yuan, b Ping Nie, a Bing Ding a, Jiajia Zhu a and Xiaogang Zhang**

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A new solvothermal strategy combined with following calcination has been developed to synthesize NaTi$_2$(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 NaTi$_2$(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$_2$SO$_4$ aqueous electrolyte. The electrode delivers high specific capacities of 110, 85, 65, 40 mAh 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. Recent 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. A variety of anode materials including carbon-based compounds, organic compounds, oxides, sulfides and alloys 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, where the structure stands for a well-known family of Na$^+$ superionic conductors with an open 3D framework based on the formula of A$_2$M$_4$(XO$_4$)$_3$ (A = alkali, M = transition metal, X = Si$^{4+}$, P$^{5+}$, S$^{6+}$, Mo$^{6+}$, etc.). 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. In the structure, alkali ions occupy two different sites. At low alkali content (n ≤ 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. The NASICON-type structure can allow easy migration of the alkali ions between A(1) and A(2). 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 NaTi$_2$(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.

The electrochemical performance of the NASICON-type NaTi$_2$(PO$_4$)$_3$ electrode for sodium extraction/insertion has been firstly reported, 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 NaTi$_2$(PO$_4$)$_3$, such as applying nanostructured materials and surface coating with conductive materials. Recently, mechanical milling and carbothermal treatment have been used for improvement of the electric conductivity of NaTi$_2$(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$^{-1}$). 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. 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, ultra-thin thickness and structural flexibility. Among these applications, graphene has been approached by forming composites or hybrids as a highly

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electronic conductive network in the fields of rechargeable batteries. Recently, improvement on cycling stability and rate performance was reported when some anode materials and NaV$_2$(PO$_4$)$_3$ were supported by graphene.

In this work, we present the preparation of NaTi$_2$(PO$_4$)$_3$/graphene nanosheets (NaTi$_2$(PO$_4$)$_3$/GNS) nanocomposites through a solvothermal method for the first time, where highly crystalline NaTi$_2$(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 NaTi$_2$(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 SinopharmChemical Reagent Co., Ltd, China. Graphite oxide (GO) was synthesized from natural graphite powders (SP-1) by a modified Hummers method, in which pre-oxidation of graphite is followed by oxidation with Hummers’ method (see Electronic Supporting Information, ES1). For the synthesis of NaTi$_2$(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 NH$_4$H$_2$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 NH$_4$H$_2$PO$_4$ in 10 mL of distilled water and 265 mg of Na$_2$CO$_3$ 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 NaTi$_2$(PO$_4$)$_3$/GNS powders. The pure NaTi$_2$(PO$_4$)$_3$ was prepared in a similar manner to that of NaTi$_2$(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 Kα radiation and Sol-X detector from 2θ = 10° to 80° at 40 kV and 40 mA. The XRD profiles were refined by the Rietveld program RIETAN-FP. Schematic illustrations of the crystal structures of NaTi$_2$(PO$_4$)$_3$ phase were drawn using the program VESTA. 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.

3. Results and discussion

3.1 Physicochemical characterization

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

Fig. 1 shows the XRD patterns of pure NaTi$_2$(PO$_4$)$_3$ and NaTi$_2$(PO$_4$)$_3$/GNS. The pure NaTi$_2$(PO$_4$)$_3$ (Fig. 1a) has several very sharp diffraction peaks at 2θ = 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 NaTi$_2$(PO$_4$)$_3$/GNS (Fig. 1b). It confirmed the successful synthesis of highly crystalline NASICON-type NaTi$_2$(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 NaTi$_2$(PO$_4$)$_3$/GNS nanocomposites. It may be the low content of RGO and the high crystalline of NaTi$_2$(PO$_4$)$_3$ in the nanocomposites. Thermogravimetric (TG) analysis was used to determine the amount of GNS in the NaTi$_2$(PO$_4$)$_3$/GNS
nanocomposites (Fig. S1, ESI†). The result indicates that the hybrid materials have a chemical composition of 96.6 wt.% NaTi$_2$(PO$_4$)$_3$ and 3.4 wt.% GNS.

![Rietveld refinement of the observed XRD pattern for NaTi$_2$(PO$_4$)$_3$ phase.](image)

The Rietveld method was performed to refine the crystal structure of pure NaTi$_2$(PO$_4$)$_3$ by RIETAN0FP software. Initially, the common overall parameters, zero shift, unit-cell parameters, half-width, background, scale factor 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) Å$^3$ 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.

![Scheme 1 A schematic illustration of the NASICON-type structured.](image)

Table 1 Atomic coordinates, isotropic thermal parameters and occupation numbers for NaTi$_2$(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) Å$^3$ and $Z = 6$; $R_{wp} = 8.79$ %, $R_p = 6.73$ %, $R_I = 2.54$ %, $S = 1.44$.

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![Fig. 3 FESEM images of (a, b) pure NaTi$_2$(PO$_4$)$_3$, (c, d) NaTi$_2$(PO$_4$)$_3$/GNS, (e, f) TEM images of NaTi$_2$(PO$_4$)$_3$/GNS and (g) bright-field STEM image of NaTi$_2$(PO$_4$)$_3$/GNS, elemental mapping of the same region, indicating spatial distribution of C, P, O, Ti and Na, respectively and the EDS analytical results.](image)
The morphology of the synthesized samples was observed by FESEM. Fig. 3 displays the morphological features of pure NaTi$_5$(PO$_4$)$_3$ and NaTi$_5$(PO$_4$)$_3$/GNS. As observed from Fig. 3 (a, b), the NaTi$_5$(PO$_4$)$_3$ sample prepared in the absence of GNS were 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 NaTi$_5$(PO$_4$)$_3$/NPs were homogeneously anchored on conducting GNS forming two-dimensional (2D) nanostructure and the GNS were also separated by the NaTi$_5$(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 NaTi$_5$(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 NaTi$_5$(PO$_4$)$_3$/GNS more clearly, the sample was further investigated by TEM. As observed in Fig. 3 (e, f), a very large quantity of NaTi$_5$(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 NaTi$_5$(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 NaTi$_5$(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 NaTi$_5$(PO$_4$)$_3$/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 NaTi$_5$(PO$_4$)$_3$/GNS.

3.2 Formation mechanism of the NaTi$_5$(PO$_4$)$_3$/GNS nanocomposites

In order to investigate the formation mechanism of the NaTi$_5$(PO$_4$)$_3$/GNS nanocomposites, each process in the experiment was carefully conducted. The experimental details are presented in the materials synthesis. The overall fabrication procedures of NaTi$_5$(PO$_4$)$_3$/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, NH$_4$H$_2$PO$_4$ 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, NH$_4$H$_2$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 Ti$_5$P$_3$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 Ti$_5$P$_3$O$_{20}$ phase (Fig. S4a, ESI†). The Ti$_5$P$_3$O$_{20}$ NPs were also anchored on RGO by solvothermal treatment, and following calcination (Fig. S4b, ESI†). Finally, the intermediate Ti$_5$P$_3$O$_{20}$ production in situ transformed into the NaTi$_5$(PO$_4$)$_3$/GNS precursor (a quaternary Na-Ti-P-O) accompanied by adding Na$_2$CO$_3$ aqueous solution. In order to further investigate the mechanism of formation for the NaTi$_5$(PO$_4$)$_3$/GNS nanocomposites, off-stoichiometric Na$_2$CO$_3$ were taken into consideration in the process. Surprisingly, the main NaTi$_5$(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 Ti$_5$P$_3$O$_{20}$ and TiPO$_4$ phases is caused by Na$_2$CO$_3$. Similarly, The NaTi$_5$(PO$_4$)$_3$ and TiPO$_4$ NPs were also anchored on RGO by the same process (Fig. S5b, ESI†).

\[ \text{NaT}_{\text{i}}\text{Ti}_5\text{(PO}_4\text{)}_3 + 2\text{Na}^+ + 2e^- \xrightarrow{\text{charge}} \text{Na}_2\text{Ti}_5\text{(PO}_4\text{)}_3 ] \]

The smaller potential differences between oxidation-reduction peaks of NaTi$_5$(PO$_4$)$_3$/GNS compared with pure NaTi$_5$(PO$_4$)$_3$ could be attributed to the variation of cell impedance.

3.3 Electrochemical analysis

To examine the effectiveness of GNS on improving the electrochemical performance of the electrode, the Na$^+$ extraction/insertion properties of NaTi$_5$(PO$_4$)$_3$/GNS nanocomposites and pure NaTi$_5$(PO$_4$)$_3$ were investigated, respectively. Cyclic voltmametric measurements were taken in 1 M Na$_2$SO$_4$ 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 NaTi$_5$(PO$_4$)$_3$/GNS, and similar peaks were observed at -0.85 V (red.) and -0.79 V (ox.) for the pure NaTi$_5$(PO$_4$)$_3$, indicating the reversible insertion/extraction reaction of Na$^+$ in the NaTi$_5$(PO$_4$)$_3$ lattice. The redox potential was consistent with the previous report of NaTi$_5$(PO$_4$)$_3$.\(^38\) When NaTi$_5$(PO$_4$)$_3$ is charged and discharged, it undergoes the following reaction:

\[ \text{NaT}_{\text{i}}\text{Ti}_5\text{(PO}_4\text{)}_3 + 2\text{Na}^+ + 2e^- \xrightarrow{\text{charge}} \text{Na}_2\text{T}_{\text{i}}\text{Ti}_5\text{(PO}_4\text{)}_3 ] \]
Corresponding to the extraction/insertion process of Na\(^+\) in the NASICON-type structured NaTi\(_2\)(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 NaTi\(_2\)(PO\(_4\))\(_3\)/GNS,\(^{14,20}\) not for pure NaTi\(_2\)(PO\(_4\))\(_3\). The peak current of NaTi\(_2\)(PO\(_4\))\(_3\)/GNS are about 6.0 and 4.5 mA, which are much higher than those of pure NaTi\(_2\)(PO\(_4\))\(_3\). Indeed the Na\(^+\) diffusion coefficient is proportional to the square of the peak current (i\(^2\)) in the CV profiles, so higher peak current means higher Na\(^+\) ion diffusion coefficient and consequently, better electrochemical performance of the NaTi\(_2\)(PO\(_4\))\(_3\)/GNS anode material. The obvious peaks in the CV curves of NaTi\(_2\)(PO\(_4\))\(_3\)/GNS was due to functionality of GNS. Meanwhile, the good overlapping of the curves for the subsequent cycles suggests that NaTi\(_2\)(PO\(_4\))\(_3\)/GNS is more stable than pure NaTi\(_2\)(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\(_2\)SO\(_4\) 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 NaTi\(_2\)(PO\(_4\))\(_3\)/GNS as a promising anode material for Na-ion batteries.\(^{14,20,21,38}\)

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

Based on the above mentioned results, only the NaTi\(_2\)(PO\(_4\))\(_3\)/GNS electrode further investigated the charge-discharge cycling performance at 2 C for 100 cycles (shown in Fig. 4 (b)). The NaTi\(_2\)(PO\(_4\))\(_3\)/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 NaTi\(_2\)(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 NaTi\(_2\)(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 NaTi\(_2\)(PO\(_4\))\(_3\)/GNS,\(^{13,14}\) possessing the good crystallinity, the electronic conductivity of the GNS and high ionic conductivity,\(^{25}\) which was consistent with that of the extraction/insertion reaction in the aqueous electrolyte as expected in CV curves.

Fig. 5 FESEM image (a), TEM image (b) and (c) bright-field STEM image of NaTi\(_2\)(PO\(_4\))\(_3\)/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.

Meanwhile, the high-rate capabilities of the NaTi\(_2\)(PO\(_4\))\(_3\)/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 NaTi\(_2\)(PO\(_4\))\(_3\)/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 NaTi\(_2\)(PO\(_4\))\(_3\)/GNS exhibit excellent electrochemical performance with high-rate capability may be attributed to the NaTi\(_2\)(PO\(_4\))\(_3\) 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 NaTi\(_2\)(PO\(_4\))\(_3\) NPs composites 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 NaTi\(_2\)(PO\(_4\))\(_3\) 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

\(^{*}\) College of Material Science & Engineering and Key Laboratory for Intelligent Nano Materials and Devices of Ministry of Education, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P. R. China. E-mail: azhangxg@163.com; Fax: +86 025 52112626; Tel: +86 025 52112918

\(^{†}\) School of Material Science & Engineering and Anhui Key Laboratory of Metal Materials and Processing, Anhui University of Technology, Maanshan, 243002, P. R. China.

\(^{*}\) Electronic Supplementary Information (ESI) available: [Synthesis of Graphite oxide, TG curve of NaTi\(_2\)(PO\(_4\))\(_3\)/GNS, XRD patterns and morphology of GO, TiO\(_2\)/GNS, TiP\(_2\)O\(_5\)/GNS, and NaTi\(_2\)(PO\(_4\))\(_3\)/GNS]. See DOI: 10.1039/b000000x/