In situ Synthesis of V$_2$O$_3$-Intercalated N-doped Graphene Nanobelts from VO$_x$-Amine Hybrid as High-Performance Anode Material for Alkali-Ion Batteries

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V$_2$O$_3$ is a promising anode material for lithium- and sodium-ion batteries due to its high theoretical capacity and natural abundance. However, the low conductivity, sluggish ion reaction kinetics, and large volume change limit the rate and cycling stability in batteries. In this work, the V$_2$O$_3$-nanoparticles-intercalated N-doped graphene (V$_2$O$_3$/NG) hybrid is prepared by one-step controlled pyrolysis of inorganic-organic hybrid VO$_3$/3-phenylpropylamine nanobelts under Ar. The intercalated 3-phenylpropylamine molecules are carbonized in situ into the NG layers and the sandwiched VO$_3$ layers are converted into 10-20 nm V$_2$O$_3$ nanoparticles. The V$_2$O$_3$/NG nanobelts possess well-defined 0D-in-1D morphology and excellent electrochemical performance such as high reversible capacities of 435 mAh g$^{-1}$ at 100 mA g$^{-1}$ over 250 cycles for Li-ion storage and 154 mAh g$^{-1}$ at 500 mA g$^{-1}$ over 500 cycles for Na-ion storage. The well-defined 0D-in-1D hybrid V$_2$O$_3$/NG structure with small V$_2$O$_3$ nanoparticles, interconnected nanochannels, and conductive NG layers offer abundant electrochemical active sites leading to fast Li$^+$ and electron transport and excellent alkali-ion storage.

1. Introduction

On the heels of gradual depletion of fossil fuel and aggravation of environmental problems, renewable energy sources and high-efficiency electrochemical energy storage devices are highly desirable.$^{[1-6]}$ Rechargeable lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) are regarded as the most promising electrochemical energy storage systems because of the high energy densities, long cycle life, and environmental friendliness.$^{[7-16]}$ The charge storage performance of alkali-ion batteries depends on the electrode materials and so development of high-performance electrode materials is imperative to the success of advanced LIBs and SIBs.$^{[17-27]}$

V$_2$O$_3$ is a promising anode material for alkali-ion batteries due to the high theoretical capacity (1070 mAh g$^{-1}$ for Li-ion storage), low toxicity, and natural abundance.$^{[28-30]}$ However, the intrinsically low conductivity of V$_2$O$_3$, sluggish reaction kinetics, and large volume change during cycling lead to the poor rate capability and cycling deterioration thus hampering practical applications. The phenomenon pertaining to V$_2$O$_3$ is more critical for sodium-ion storage due to the 34% larger ionic radius of Na$^+$ (0.102 nm) compared to Li$^+$ (0.076 nm). To overcome these hurdles, conductive carbon materials have been introduced to produce nanostructured V$_2$O$_3$/C composites which show improved Li storage properties because of the enhanced electronic conductivity. For example, Gao et al.$^{[31]}$ designed and prepared LIBs with peapod-like V$_2$O$_3$ nanorods having a large capacity of 210 mAh g$^{-1}$ at 0.1 C (1 C = 1000 mAh g$^{-1}$) and high rate capability with 68% capacity retention when the current density was increased from 0.1 to 1 C. Liang et al.$^{[32]}$ reported that metal-organic framework-derived porous shuttle-like vanadium oxide had a capacity of 181 mAh g$^{-1}$ at 2000 mA g$^{-1}$ with a low capacity fading rate of 0.032% per cycle for over 1000 cycles for SIBs. However, despite recent progress, the preparing process of V$_2$O$_3$/C nanohybrids is complex and templates or surfactants are generally needed to control the morphology. Moreover, V$_2$O$_3$ nanoparticles coated on carbon can easily come off during cycling due to the large volume change resulting in poor cycle stability. To improve the electrochemical stability and electrochemical utilization ratio, alternatingly stacked carbon and V$_2$O$_3$ layers are desirable so that carbon is not only coated on the V$_2$O$_3$ surface, but also contacts the inner V$_2$O$_3$ matrix to improve the conductivity as well as electrochemical stability.

Herein, we describe a spatially confined strategy to synthesize V$_2$O$_3$-nanoparticles-intercalated N-doped graphene (V$_2$O$_3$/NG) nanobelts from inorganic-organic hybrid VO$_3$/amine nanobelts.$^{[33]}$ The V$_2$O$_3$/NG nanobelts are synthesized by one-step calcination of VO$_3$/3-phenylpropylamine hybrid nanobelts in Ar atmosphere. The intercalated amine molecules are in situ carbonized into NG layers and the sandwiched VO$_3$ layers are converted into small V$_2$O$_3$ nanoparticles and inserted into the NG interlayers forming a well-defined 0D-in-1D morphology.$^{[34]}$ The V$_2$O$_3$ nanoparticles intercalated NG nanobelts possess several advantages regarding alkali-ion storage. First, the small V$_2$O$_3$ nanoparticles offer a large electrode/electrolyte contact area.

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area and short path lengths for Li or Na ions diffusion. Secondly, the pillared lamellar structure and conductive NG matrix provide favorable ion and electron transport channels thus facilitating fast electron transport and lowering the charge transfer resistance. Thirdly, the NG layers buffer the strain produced by the volume change of the V$_2$O$_5$ nanoparticles during cycling yielding better structural and electrochemical stability. Fourthly, the synthesis is simple and effective without needing complex templates or surfactants and toxic precursors and the V$_2$O$_5$/NG hybrid nanobelts can be mass produced. Consequently, the V$_2$O$_5$/NG hybrid nanobelts have large potential in alkali-ion batteries. According to our investigation, the V$_2$O$_5$/NG nanobelts have a large capacity of 435 mAh g$^{-1}$ at 100 mA g$^{-1}$ and high rate capability of 201 mAh g$^{-1}$ at 2000 mA g$^{-1}$ for over 500 cycles in LIBs. When employed as anode materials in SIBs, the V$_2$O$_5$/NG nanobelts have a capacity of 154 mAh g$^{-1}$ at 500 mA g$^{-1}$ that is close to the initial discharge capacity. Moreover, the V$_2$O$_5$/NG nanobelts possess high rate capability with 52% capacity retention when the current density is increased from 50 mA g$^{-1}$ to 2000 mA g$^{-1}$. Electrochemical impedance spectroscopy (EIS) reveals a small charge transfer resistance confirming the high conductivity and rapid transfer of alkali ions. Our study suggests a promising electrode design and general strategy to prepare V$_2$O$_5$/NG nanobelts and the protocol can be extended to the production of high-performance metal oxides for alkali-ion batteries.

2. Results and Discussion

Figure 1a schematically illustrates the fabrication procedures of the V$_2$O$_5$/NG hybrid nanobelts. The inorganic-organic hybrid VO$_x$/3-phenylpropylamine nanobelts are synthesized by a low-temperature hydrothermal method with V$_2$O$_5$ and 3-phenylpropylamine as precursors. The X-ray diffraction (XRD) pattern of the as-obtained product is shown in Figure 1b and the small angle (00$l$) peaks (5°-20°) indicate a well-ordered layer structure. The peak with the highest intensity at a small diffraction angle reflects the distance between the vanadium oxide layers and the calculated interlayer spacing is about 1.69 nm, which is much larger than that of V$_2$O$_5$ (0.44 nm), suggesting a bilayer arrangement of 3-phenylpropylamine molecules in the interlayers of vanadium oxide considering the 0.9 nm length of 3-phenylpropylamine. The VO$_2$ peaks (JCPDS Card no. 81-2392) are identified besides the orthorhombic phase V$_2$O$_5$ (JCPDS Card no. 41-1426) due to reduction of V$_2$O$_5$ by organic amines during hydrothermal treatment.

The Fourier transform infrared spectroscopy (FTIR) in Figure S1 reveals the presence of N–H bonds (3060 cm$^{-1}$), C=C stretching mode of the quinoid ring (1585 cm$^{-1}$) and benzenoid ring (1488 cm$^{-1}$), as well as V=O$^{[41,42]}$ suggesting the formation of inorganic-organic VO$_x$/3-phenylpropylamine. Figure 1c and Figure S2a depict the typical scanning electron microscope (SEM) images of the hydrothermal product disclosing a nanobelt morphology with a width of 300–600 nm and thickness of 20–40 nm. The nanobelts have lengths up to ten micrometers. The transmission electron microscopy (TEM) image in Figure S2b shows a high-resolution view of the nanobelts suggesting a bilayer arrangement of 3-phenylpropylamine and V$_2$O$_5$.
confirms the 1D nanobelts structure and the interlayer lattice of 1.70 nm is identified from the high-resolution TEM (HR-TEM) image (Inset in Figure S2b) in agreement with XRD. These results indicate that 3-phenylpropylamine intercalated VOₓ nanobelts have been synthesized by hydrothermal treatment of organic 3-phenylpropylamine and V₂O₅ powder. After calcination of 3-phenylpropylamine intercalated VOₓ nanobelts under Ar at a high temperature, the interlayered 3-phenylpropylamine molecules are carbonized in situ into the NG layers while the sandwiched VOₓ layers are converted into small V₂O₅ nanoparticles which are inserted between the NG layers forming the pillared lamellar V₂O₅/NG hybrid nanobelts. The HR-TEM pattern of the annealed sample (Figure 1b) can be indexed to the hexagonal phase of V₂O₅ (JCPDS Card no. 34-0187), suggesting VOₓ is fully converted into V₂O₅ through carbon reduction during annealing in Ar. The NG peak is not observed possibly due to the poor crystallinity and no stacking of the graphene layers. The SEM images in Figure 1d and Figure S3 show that the annealed sample has a nanobelt morphology similar to that of the pristine VOₓ/3-phenylpropylamine nanobelts.

A representative TEM image of the V₂O₅/NG hybrid nanobelts is shown in Figure 2a, demonstrating the width of 300–600 nm, being agreement with SEM image shown in Figure 1d. The large-magnification TEM image in Figure 2b shows small V₂O₅ nanoparticles with a diameter of 10–20 nm embedded in the nanobelts. The HR-TEM image (Figure 2c) indicates that the V₂O₅ nanoparticles are crystalline and the lattice fringe spacing of 0.248 nm is ascribed to the (110) planes of hexagonal V₂O₅. The scanning TEM (STEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental maps are shown in Figure 2d. C and N are uniformly distributed throughout the nanobelts but V shows an island-like dispersed distribution corroborating the 0D-in-1D V₂O₅/NG structure. To further confirm the pillared lamellar nanobelts comprising sandwiched V₂O₅ nanoparticles and alternating NG layer, the V₂O₅/NG nanobelts were immersed in 6 mol L⁻¹ NaOH solution to remove the V₂O₅ nanoparticles. The TEM image (Figure 2e) shows that the remaining NG has a similar width and length as the V₂O₅/NG nanobelts. EDS (Figure 2f) confirms that the V₂O₅ nanoparticles have been removed completely and the content of nitrogen is 3.1 wt.%. The Raman spectrum (Figure 2g) of the NG nanobelts shows two obvious peaks at around 1343 and 1585 cm⁻¹ corresponding to the D-band and G-band of NG, respectively. The thickness of NG is further characterized by atomic force microscope (AFM). As shown in Figure S4, the thickness of NG is about 5.2 nm. However, it is worth noting that we could not conclude 5.2 nm is the precise thickness of NG in V₂O₅/NG because the in situ produced NG could be restacked resulting in the increased thickness. The NG content in the V₂O₅/NG hybrid nanobelts is measured to be 18.6 wt% (Figure S5) by thermogravimetric analysis (TGA). These results show successful synthesis of the pillared lamellar nanobelts of V₂O₅ nanoparticles intercalated NG nanobelts. For comparison, the V₂O₅ nanobelts and VOₓ nanoparticles are synthesized by heating VOₓ/3-phenylpropylamine in air at 320 °C to remove the 3-phenylpropylamine and then annealing in Ar/H₂ (95:5 v/v) at

![Figure 2](image-url)

**Figure 2.** (a) TEM image, (b) high-magnification TEM image, (c) HR-TEM image, and (d) EDS maps of the V₂O₅/NG hybrid nanobelts. (e) TEM image of the NG nanobelts obtained by removing the V₂O₅ from the V₂O₅/NG hybrid in a 6 mol L⁻¹ NaOH solution. (f) Corresponding EDS spectrum and element analysis result. (g) Raman scattering spectrum of the NG nanobelts.
600 °C for 5 h and 750 °C for 5 h, respectively. Then the mixture of V₂O₅ nanoparticles and NG was produced by mechanical mixing. The morphology of as-obtained V₂O₅ in Figure 5a reveals a nanobelt morphology and the corresponding XRD pattern in Figure 5b confirms the V₂O₅ nanobelts (ICPDS Card no. 34-0187). However, the V₂O₅ nanobelts have a rough surface and porous structure different from the V₂O₅/NG hybrid nanobelts, indicating the NG plays an important role in maintaining the structural stability of V₂O₅/NG nanobelts. The morphology of V₂O₅ nanoparticles is also shown in Figure 5c, the obvious conglomeration can be observed.

Figure 3a shows the X-ray photoelectron spectroscopy (XPS) full spectrum of the V₂O₅/NG hybrid nanobelts showing the presence of V, C, N, and O. The high-resolution V 2p in Figure 3b shows five peaks at 514.2 eV, 515.9 eV, 517.3 eV, 523.1 eV, 524.5 eV arising from V–C, V 2p½ V 2p½, V 2p½ V 2p½, V 2p½ V 2p½, and V 2p½ V 2p½, respectively.[15,46] The V–C bond indicates strong interaction between V₂O₅ and NG, which facilitates fast electron transfer and structural stability during cycling. The existence of V²⁺ stems from partial surface oxidation of V₂O₅. The C 1s spectrum in Figure 3c shows four peaks at 283.2, 284.6, 285.8, and 288.4 eV corresponding to V–C, C–C, C–N and C–O.[40] The N 1s spectrum in Figure 3d can be fitted to pyridinic (399.1 eV), pyrrolic (400.4 eV), and graphitic (401.7 eV) types.[50,51] Table S1 shows the XPS elemental analysis results of the V₂O₅/NG hybrid nanobelts and the atomic content of nitrogen is measured to be 2.9%. These promising results indicate the successful synthesis of pillared lamellar V₂O₅/NG hybrid nanobelts from the inorganic-organic VOₓ–amine hybrids.

The electrochemical performance of the V₂O₅/NG hybrid nanobelts is assessed with a coin-type half-cell using a lithium foil as the counter electrode. Figure 4a shows the representative cyclic voltammetry (CV) curves during the 1st–4th cycles in the potential range of 0.01–3 V at a scanning rate of 0.2 mV s⁻¹.

Figure 4. Lithium-ion storage properties of the V₂O₅/NG, the mixture of V₂O₅ nanoparticles and NG and V₂O₅ nanobelts: (a) CV curves of the V₂O₅/NG hybrid nanobelts at a scan rate of 0.2 mV s⁻¹ between 0.01 and 3.0 V; (b) GCD profiles of the V₂O₅/NG hybrid nanobelts at 100 mAh g⁻¹; (c) Cycling performance and rate performance of the V₂O₅/NG hybrid nanobelts, the mixture of V₂O₅ nanoparticles and NG and V₂O₅ nanobelts at various current densities; (d) Cycling performance of the V₂O₅/NG hybrid nanobelts at the current density of 100 mAh g⁻¹ and 2000 mAh g⁻¹ (the first 5 cycles were tested at a current density of 100 mAh g⁻¹ as an activation process and the following cycles were measured at 2000 mAh g⁻¹); (e) Electrochemical impedance spectra of the V₂O₅/NG hybrid nanobelts, the mixture of V₂O₅ nanoparticles and NG and V₂O₅ nanobelts in the frequency range between 0.01 Hz and 100 KHz. Inset of (e) is the fitted equivalent circuit.

The electrochemical reaction mechanism of V₂O₅ involves intercalation and conversion reactions as follows:[31]

\[
\text{V}_2\text{O}_5 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{V}_2\text{O}_5 \tag{1}
\]

\[
\text{Li}_x\text{V}_2\text{O}_5 + (6-x)\text{Li}^+ + (6-x) e^- \rightarrow 2\text{V} + 3\text{Li}_2\text{O} \tag{2}
\]

In the first cycle, the wide cathodic peaks at 1.45 V is ascribed to Li⁺ insertion into V₂O₅ as shown in Reaction (1).[51,52] The cathodic peak at 0.5 V arises from the formation of solid-electrolyte interface (SEI) layer during the first cycle[53] and this reduction peak disappears in the following cycles. In the anodic cycles, the peak at around 1.8 V arises from multistep oxidation of LiₓV₂O₅ to V₂O₅[54] in the subsequent cycles, the reduction peak at 0.48 V can be attributed to reduction of LiₓV₂O₅ to metallic vanadium (Reaction 2) and the peak at 0.75 V may be caused by oxidation of V[55]. The subsequent CV cycles overlap indicating good cycle stability and reversibility. The galvanostatic charging and discharging (GCD) curves of the V₂O₅/NG hybrid nanobelts and V₂O₅ nanobelts between 0.01 and 3.0 V are shown in Figure 4b and Figure 5b, respectively. The voltage in the discharging state below 1.4 V drops slowly in the first GCD cycle indicating a multistep reduction process of V₂O₅.[31] The plateaus are in good agreement with the cathodic/anodic
peaks in the CV. The charging and discharging capacities of the V$_2$O$_3$/NG hybrid nanobelts for the 1$^{st}$ cycle are 402.2 and 574.6 mAh g$^{-1}$, respectively, showing an initial Coulombic efficiency (CE) of 70%, which is higher than that of the V$_2$O$_3$ nanobelts (52.5%). The irreversible capacity in the initial cycles can be ascribed to the reduction of electrolyte and the formation of the SEI film. After five cycles, nearly 100% of CE can be achieved reflecting high reversibility. The cycle stability and rate performance of the V$_2$O$_3$/NG hybrid nanobelts is shown in Figure 4c. The assembled cell is cycled at a current density of 1000 mAh g$^{-1}$ for 200 cycles and then operated at different current densities from 100 mAh g$^{-1}$ to 2000 mAh g$^{-1}$. For comparison, the cycle and rate performances of V$_2$O$_3$ nanobelts and the mixture of V$_2$O$_3$ nanoparticles and NG are provided. The V$_2$O$_3$/NG hybrid has a high capacity of 256 mAh g$^{-1}$ at 1000 mAh g$^{-1}$, which is much higher than that of V$_2$O$_3$ nanobelts (112 mAh g$^{-1}$) and the mixture of V$_2$O$_3$ nanoparticles and NG (169 mAh g$^{-1}$). Moreover, the V$_2$O$_3$/NG hybrid exhibits higher capacities at all the measured current densities compared to V$_2$O$_3$ nanobelts and the mixture of V$_2$O$_3$ nanoparticles and NG. The V$_2$O$_3$/NG hybrid nanobelts show a high average capacity of 402 mAh g$^{-1}$ at 100 mAh g$^{-1}$. When the current density is increased to 2000 mAh g$^{-1}$, the capacity is about 210 mAh g$^{-1}$ showing 52% capacity retention. When the current density is returned to 100 mAh g$^{-1}$, the specific capacity recovers fully to 408 mAh g$^{-1}$ thus showing excellent reversibility. The good rate performance of the V$_2$O$_3$/NG hybrid nanobelts stems from the unique sandwiched hybrid structure and enhanced conductivity of V$_2$O$_3$/NG. The cycling stability of the V$_2$O$_3$/NG nanobelts at current densities of 100 mAh g$^{-1}$ and 2000 mAh g$^{-1}$ is presented in Figure 4d. The material shows a large capacity of 433 mAh g$^{-1}$ at 100 mAh g$^{-1}$ for over 250 cycles and 201 mAh g$^{-1}$ at 2000 mAh g$^{-1}$ for over 500 cycles. The increased capacity during cycling may be caused by the continuous activation process during cycling similar to that observed from other V$_2$O$_3$-based anode materials. For comparison, the cycling stability of the V$_2$O$_3$ nanobelts at 100 mAh g$^{-1}$ is also shown in Figure S9. A lower capacity of 241 mAh g$^{-1}$ is observed after 250 cycles. Figure 4e shows the EIS results of the V$_2$O$_3$/NG, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts after 250 cycles in the fully charged state. The equivalent circuit model is provided in the inset of Figure 4e, in which R$\text{e}$, R$\text{ct}$, and R$\text{f}$ represent the electrolyte resistance, resistance of the SEI film and charge transfer resistance, respectively. The R$\text{ct}$ of the V$_2$O$_3$/NG hybrid nanobelts is measured to be 71 $\Omega$, which is smaller than that of the mixture of V$_2$O$_3$ nanoparticles and NG (161 $\Omega$) and V$_2$O$_3$ nanobelts (289 $\Omega$), implying a faster charge transfer process. The slope in the low frequency region is related to diffusion of lithium ions in the electrode and the larger slope of the V$_2$O$_3$/NG hybrid nanobelts compared to V$_2$O$_3$ nanobelts indicates better ion diffusion. The enhanced Li-ion storage performance of V$_2$O$_3$/NG hybrid nanobelts stems from the synergistic roles of the small V$_2$O$_3$ nanoparticles and pillared lamellar structure enabling fast ion diffusion and electron transfer. The excellent cycle stability is also confirmed by morphological evolution characterized by TEM before and after 500 cycles at 2000 mAh g$^{-1}$. After 500 cycles, there is no substantial morphological change (Figure S10) confirming the good structural and electrochemical stability.

The Na-ion storage properties of the V$_2$O$_3$/NG hybrid nanobelts are also studied and presented in Figure 5. The half-cell is assembled with the Na foil as a counter electrode. Figure 5a shows the CV curves of the V$_2$O$_3$/NG hybrid nanobelts during the 1$^{st}$-4$^{th}$ cycles at a scanning rate of 0.1 mV s$^{-1}$ in the potential window between 0.01 and 3.0 V. The obvious reduction peak at around 0.98 V in the first cathodic scan arises from the formation of the SEI film but it disappears in subsequent scans. Figure 5b and Figure S11 shows the discharging/charging curves of the V$_2$O$_3$/NG hybrid nanobelts and V$_2$O$_3$ nanobelts at a current density of 50 mAh g$^{-1}$, respectively. The initial discharging capacity of the V$_2$O$_3$/NG hybrid nanobelts reaches 393 mAh g$^{-1}$ with a CE of 51%, which is higher than that of the V$_2$O$_3$ nanobelts (35%). The low initial CE is due to the formation of excessive SEI during sodiation process. Figure 5c displays the cycling stability of the V$_2$O$_3$/NG hybrid nanobelts, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts (first 2 cycles at 50 mAh g$^{-1}$ for activation and following cycles at 500 mAh g$^{-1}$). The V$_2$O$_3$/NG hybrid nanobelts have a capacity of 154 mAh g$^{-1}$ after 500 cycles which is higher than that of the mixture of V$_2$O$_3$ nanoparticles and NG (90 mAh g$^{-1}$) and the V$_2$O$_3$ nanobelts (62.5 mAh g$^{-1}$). Figure 5d shows the GCD profiles of the V$_2$O$_3$/NG hybrid nanobelts: (a) CV curves of the V$_2$O$_3$/NG hybrid nanobelts at a scanning rate of 0.1 mV s$^{-1}$ between 0.01 and 3.0 V; (b) GCD profiles of the V$_2$O$_3$/NG hybrid nanobelts at a current density of 50 mAh g$^{-1}$; (c) Cycling performance of the V$_2$O$_3$/NG hybrid nanobelts, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts at various current densities; (e) Electrochemical impedance spectra of the V$_2$O$_3$/NG hybrid nanobelts, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts in the frequency range between 0.01 Hz and 100 KHz. The inset of (e) is the fitted equivalent circuit.
shows the rate performance of the V$_2$O$_3$/NG hybrid nanobelts, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts. The V$_2$O$_3$/NG hybrid nanobelts have larger capacities than that of the V$_2$O$_3$ nanobelts and the mixture of V$_2$O$_3$ nanoparticles and NG at measured current densities. At current densities of 50, 100, 200, 500, 1000, and 2000 mA g$^{-1}$, the V$_2$O$_3$/NG hybrid nanobelts deliver a high capacities of 223, 193, 151, 150, 130, and 115 mAh g$^{-1}$, respectively. The EIS results of the V$_2$O$_3$/NG hybrid nanobelts, the mixture of V$_2$O$_3$ nanoparticles and NG and V$_2$O$_3$ nanobelts after 500 cycles in the charging state are shown in Figure 5e. All the EIS plots can be fitted with an equivalent circuit shown in the inset of Figure 5e.$^{[31]}$ $R_{ct}$ of the V$_2$O$_3$/NG hybrid nanobelts is 208 $\Omega$ which is smaller than that of the mixture of V$_2$O$_3$ nanoparticles and NG (280 $\Omega$) and the V$_2$O$_3$ nanobelts (426 $\Omega$) indicating much improved charge transport of V$_2$O$_3$/NG hybrid nanobelts. The TEM image (Figure S12) acquired after 500 cycles demonstrates that the morphology of the nanobelts is maintained corroborating the robust structure and stability of the V$_2$O$_3$/NG hybrid nanobelts during the sodiation and desodiation processes.

The long cycle life and excellent rate performance of the V$_2$O$_3$/NG hybrid nanobelts for LiBs and NiIBs originate from the pillared lamellar 0D-in-1D V$_2$O$_3$/NG nanostructure. As shown in Figure 6, the interlayered NG layers can effectively buffer the mechanical strain during cycling and provide excellent electrical conductivity. Moreover, the small V$_2$O$_3$ nanoparticles offer a large electrode/electrolyte contact area and short paths for Li or Na ions diffusion thereby giving rise to high charging-discharge rates and long cycle life.

3. Conclusions

Pillared lamellar 0D-in-1D V$_2$O$_3$/NG nanobelts suitable for anodes in high-performance LiBs and SiIBs are prepared by controlled one-step pyrolysis of inorganic-organic hybrid VO$_2$/3-phenylpropylamine nanobelts in an Ar atmosphere. The intercalated 3-phenylpropylamine molecules are carbonized in situ into the NG layers and the sandwiched VO$_2$ layers are converted into 10–20 nm V$_2$O$_3$ nanoparticles which are intercalated into the NG layers. The small V$_2$O$_3$ nanoparticles between the NG layers provide abundant electrochemical active sites for Li- or Na-ion storage and the NG layers buffer the strain caused by volume change of the V$_2$O$_3$ nanoparticles during cycling and provide fast electron transfer paths. The V$_2$O$_3$/NG hybrid nanobelts possess enhanced Li- and Na-ion storage properties compared to the V$_2$O$_3$ nanobelts. Our results reveal an effective and general strategy to design and develop high-performance transition metal oxides/carbon composites for alkaline-ion storage.

Experimental Section

Synthesis V$_2$O$_3$ and V$_2$O$_3$/NG Hybrid Nanobelts

The inorganic-organic hybrid VO$_2$/3-phenylpropylamine nanobelts were prepared by a previously described method.$^{[30]}$ The chemicals were purchased from Aladdin and used without purification. In a typical synthesis, 0.81 g of V$_2$O$_3$ powder and 0.6 g of 3-phenylpropylamine were added into 30 mL H$_2$O. The mixture was vigorously stirred for 30 min and transferred to a Teflon-lined autoclave which was sealed and heated to 180 °C for 48 h. After cooling to room temperature naturally, the inorganic-organic hybrid VO$_2$/3-phenylpropylamine nanobelts were collected by annealing the as-obtained VO$_2$/3-phenylpropylamine nanobelts under Ar at 450 °C for 6 h and then 750 °C for 4 h.

Materials Characterization

The morphology, structure, and composition of the samples were characterized by X-ray diffraction (XRD, Philips X’Pert Pro), field-emission scanning electron microscopy (FE-SEM, FEI NanoSEM 450), transmission electron microscopy (TEM, FEI Titan 60-300 Cs), high-resolution TEM (HR-TEM, Titan), energy-dispersive X-ray spectroscopy (EDS, Oxford INCA 200), Raman scattering (HR RamLab), X-ray photoelectron spectroscopy (XPS, ESCALAB250) and Fourier transform infrared spectroscopy (FTIR, NICOLET FT-IR spectrometer). The NG content in V$_2$O$_3$/NG was determined by thermogravimetric analysis (TGA, NETZSCH, TG 209 F3).

Electrochemical Measurements

To prepare the electrodes, the V$_2$O$_3$/NG or V$_2$O$_3$ nanobelts, carbon black, and poly (vinylidene fluoride) (PVDF) with a weight ratio of 80:10:10 were mixed in N-methylpyrrolidone (NMP) to form a slurry and then pasted onto a copper foil. The electrodes were dried at 120 °C in a vacuum oven for 12 h. The mass loading for all electrodes is 1.45–1.5 mg cm$^{-2}$. The electrochemical tests were performed using a coin-type half cell (CR 2025) assembled in an argon-filled glove box. For LiBs, a metallic lithium foil acted as the counter electrode and polypropylene (PP) microporous film (Celgard 2400) as the separator. The electrolyte was 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume). For SiIBs, the counter electrode was the Na foil and glass fiber (Whatman) was the separator. The electrolyte was 1 M NaClO$_2$ dissolved in propylene carbonate. The charging and discharging measurements were conducted on the MTTI automatic battery cyclers with a voltage cut-off between 0.01 and 3 V. Cyclic voltammetry (CV) was conducted on the CHI 760e electrochemical workstation and the electrochemical impedance spectra (EIS) were acquired on an Autolab electrochemical workstation between 0.01 Hz and 100 kHz.
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Conflict of Interest

The authors declare no conflict of interest.

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