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## Facile and creative design of hierarchical vanadium oxides@graphene nanosheets patterns

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We herein reported the design and facile synthesis of hierarchical graphene nanosheets/vanadium oxides (GNS/VO<sub>x</sub>) structures by creatively using the conventional and most convenient spin-coating approach. This traditional method can easily get the layer-by-layer structure and push forward the practical utilize of hierarchical structure in sodium-ion batteries. When used as the cathode for sodium-ion batteries, such hierarchical structures can greatly enhance the electrode cycle stability and provide high capacities in contrast with previous cases of single-phased vanadium oxides.

## 1. Introduction

Along with the continual economic development, contradictions between limited natural resources and growing human demands push scientists to develop new clean energy-harvest and energy-storage devices.<sup>1</sup> Compared with mainstream power suppliers, lithium-ion batteries (LIBs) are popular and particularly play dominant roles in electric vehicles.<sup>2,3</sup> As the most important and widely used rechargeable batteries, LIBs have higher capacities, lower toxicity, and relatively long cyclic lifetime.<sup>4-6</sup> However, there still remain formidable questions regarding the safety and cost of LIBs.<sup>7</sup> Since future use of LIBs tends to become more widespread, especially in fields of electrical automobile industries, the rapid increasing demand of Li combined with its very limited natural reserves on earth will lead to the exhaustion of Li minerals and drive up the battery price, which is foreseeable and drives worldwide researchers looking for novel and alternative battery systems. One of them is the sodium-ion battery (SIB). As known, the overall content of sodium element is very rich on earth.<sup>8</sup> Due to the low cost of sodium, SIBs have the great potential to meet the needs of large-scale grid energy storage. SIBs can provide alternative electrical energy storages to LIBs, and may become competitive to LIBs in other special markets.<sup>9</sup> Moreover, SIBs are much attractive because of their non-aqueous electrolyte cell commitment and enhanced stability (e.g., lower operating voltage). However, such a lower working voltage<sup>10</sup> will lead to a less energy density so that the electrode material of SIBs must have a high capacity. Besides, the radius of sodium is about 30% longer than lithium, which requires the cathode material having larger lattice spacing.<sup>11</sup> The cathode is one of the most important factors to push forward the research on SIBs. Vanadium oxides materials<sup>12, 13</sup> are considered as very suitable cathode materials for SIBs because of their wide lattice spaces. Also, graphene nanosheets,<sup>14</sup> the thinnest materials in the world and well-known as flexible and electronically conducting agents,<sup>15,16</sup> are noteworthy to be utilized as effective electrode additives to promise the comprehensive performance of SIBs. Various synthetic methods have been used in previous studies, involving sputtering, thermal

evaporation, thermal decomposition, electrophoretic deposition and many other chemical routes typically like hydrothermal approach, etc. We herein reported a facile and scalable way to prepare vanadium oxides@graphene nanosheets (GNS/VO<sub>x</sub>) multi-layers for SIBs. The spin-coating method,<sup>17</sup> as a traditional method, was creatively developed to build the multi-layer constructions for cathode materials of SIBs.

The GNS/VO<sub>x</sub> hybrid cathode exhibited high capacities and good stability during the whole battery testing. These GNS/VO<sub>x</sub> materials showed a high initial capacity<sup>18</sup> of 224 mA h g<sup>-1</sup> at a current density of 0.2 A g<sup>-1</sup> and kept for 200 cycles. After 500 cycles, the specific capacity was 145.1 mAh g<sup>-1</sup> and still retained 85% of the initial capacity (~171.2 mAh g<sup>-1</sup>), which may show great potential to push forward SIBs into practical applications. This preparation method is quite easy to realize multi-layer hybrid configurations, and can be readily extended to other significant applications.

## 2. Experimental section

### Preparation of hierarchical GNS/VO<sub>x</sub> materials

Raw materials of VO<sub>x</sub> were synthesized using a very facile approach.<sup>19</sup> In a typical synthesis, 0.364 g of commercial V<sub>2</sub>O<sub>5</sub> (99.6+%, Sigma-Aldrich) was initially dispersed into 20 mL of distilled water and then 4.0 mL of 30% H<sub>2</sub>O<sub>2</sub> was added under vigorous stirring. The above solution was kept for 2 h at room temperature. Graphene oxide (GO) was prepared in a chemical way. GO was synthesized from natural graphite by a modified Hummers method.<sup>20</sup> Before use, all the solution needs to be treated by ultra-sonication. The following spin-coating process involves two main procedures. First is to spin GO onto the base (aluminium foil). Second, spin colloidal solution of VO<sub>x</sub> onto GO layers and then repeat the first step (a sandwich-like layer was built up; See Fig. S1). Next, the materials were annealed at 120 °C for 12 h in vacuum to remove residual water. At last, the samples were annealed at 500 °C in a quartz tube-type furnace under N<sub>2</sub> flow for activation. The resulting products were called GNS/VO<sub>x</sub>-500 in short.

### Material characterizations and electrochemical measurements

The morphology of as-prepared materials was examined by field-emission scanning electron microscopy (FESEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100). Powders X-ray diffraction were performed using Cu K $\alpha$  radiation on a Bruker D8 Advance Diffractometer (XRD, Maxima-X XRD-7000), X-ray photoelectron spectroscopy (XPS) measurements were carried out on a spectrometer (Escalab 250xi, Thermo Scientific). The precursor was heated from 50 to 500 °C at a rate of 3 °C min<sup>-1</sup>.

Coin cells with a disk of sodium foil as the counter electrode were made to test the electrochemical and battery performance of the hierarchical materials. Cycle performance and rate performance tests were performed in the potential range of 2.0-4.5 V vs. Na/Na<sup>+</sup> at ambient temperature on a Land battery testing system (Wuhan, China). The cyclic voltammogram (CV) was measured at a scan rate of 0.1 mV s<sup>-1</sup> between 2.0 and 4.5 V using a CHI600D electrochemical analyser. V<sub>2</sub>O<sub>5</sub> and VO<sub>2</sub> (Fig. 4). The XPS graph of element V reflected that there were two valence states in the VO<sub>x</sub> mixture,<sup>22,23</sup> and the two peaks could be divided into two couple of peaks which stand for V<sup>5+</sup> and V<sup>4+</sup> respectively (Fig. 4a). The XPS spectra in Fig. 4b and Fig. 4c furthermore verified the existence of O and C elements in cathode electrodes. Prior to any battery testing, no Na<sup>+</sup> ions were detected (Fig. 4d).

### 3. Results and discussion

#### 3.1 Materials characterizations

Scanning electron microscopy (SEM) analysis (Fig.1) showed the surface morphology of as-prepared GNS/VO<sub>x</sub> cathode. SEM observations toward these multi-layer cathode materials were taken at different magnifications and orientations. The VO<sub>x</sub> exhibited a uniform nanoscale distribution (Fig.1b) and this layer was perfectly package with a fine graphene layer (Fig.1a). The multi-layer construction of GNS/VO<sub>x</sub>-500 was confirmed by the specific observation on fracture sections (Fig.1d). A magnification graph (Fig.1c) further reflected how graphene layer was covered on VO<sub>x</sub>.

In order to better understand the properties of this composite, X-ray diffraction

(XRD) patterns of GNS/VO<sub>x</sub>-500 and GO/VO<sub>x</sub> without annealing treatment were plotted in Fig. 2, respectively. After heating at 500 °C, this multi-layer material had a more orderly crystalline structure. The main diffraction peak positions of our products are well indexed with VO<sub>2</sub> (PDF NO. 44-0253). There still remain some impurity peaks, which eventually turn out to belong with V<sub>2</sub>O<sub>5</sub> (PDF NO. 11-0673). XRD patterns of single-phased VO<sub>x</sub> and GO samples were also characterized (Fig. S3). The broad peaks centered at 24.5° was attributed to the (002) plane of graphene nanosheets.<sup>21</sup> After comparing these XRD records, it is implied that the GO and VO<sub>x</sub> had influenced each other during the fabrication process of sandwich structures.

Fig. 3 showed a TEM image of the multi-layer materials annealed at 500 °C with a lateral size exceeding 100 nm. High-resolution TEM images exhibited that VO<sub>x</sub> had a highly ordered crystalline structure which was in agreement with above XRD results. The lattice space of VO<sub>x</sub> can be easily distinguished under a high-resolution display (3.39Å, 3.54 Å), which is quite in favor of Na<sup>+</sup> ions insertion. Combined with X-ray photoelectron spectra (XPS) analysis, it is determined that the inner part of V<sub>2</sub>O<sub>5</sub> and VO<sub>2</sub> (Fig. 4). The XPS graph of element V reflected that there were two valence states in the VO<sub>x</sub> mixture,<sup>22,23</sup> and the two peaks could be divided into two couple of peaks which stand for V<sup>5+</sup> and V<sup>4+</sup> respectively (Fig. 4a). The XPS spectra in Fig. 4b and Fig. 4c furthermore verified the existence of O and C elements in cathode electrodes. Prior to any battery testing, no Na<sup>+</sup> ions were detected (Fig. 4d).

### **3.2 Electrochemical behavior of the hierarchical vanadium oxides@graphene nanosheets patterns**

Aimed to evaluate the electrochemical performance of GNS/VO<sub>x</sub>-500 cathode, galvanostatic discharge/charge experiments were carried out in coin-type half cells and performed against sodium metal anodes (Fig. 5). The cyclic voltammetry (CV) curves showed that our batteries have a good reversible capability, as observed from the good overlap of two curves. Evidently, a pair of redox peaks was present. In the voltage range of 2.0-4.5 V, it was clear that an oxidation peak at 3.82 V and a reduction peak at 2.63 V were noticed.

In the second cycle, these two peaks had both increased just a little. It means that

the cell capacity was kept well<sup>24</sup> and the capacity should increase in the first few cycles; no notable irreversible side reactions between injected electrons and electrolyte were observed. The rate performance (Fig. 6a) was tested under various current densities from 0.1 to 1 A g<sup>-1</sup> for 20 cycles. The GNS/VO<sub>x</sub>-500 cathode materials delivered a specific capacity of 293.5, 241, 180.7 and 115.7 mAh g<sup>-1</sup> at 0.1, 0.2, 0.5 and 1 A g<sup>-1</sup>, respectively. When the current density turned back to 0.1 A g<sup>-1</sup>, the specific capacity can return to the level of 299.8 mAh g<sup>-1</sup>, which demonstrates the stable cycling performance of the GNS/VO<sub>x</sub>-500 cathode materials. The cycling test of GNS/VO<sub>x</sub>-500 cathode materials was examined in half cells against sodium metal at a current density of 0.2 A g<sup>-1</sup> (Fig. 6b).

These cathode materials had exhibited excellent cycling performance in battery testing. In the first 50 cycles, the cell showed an increasing capacity trend and then kept for nearly 200 cycles with a high specific capacity of 224 mA h g<sup>-1</sup>. The increasing capacity in the first 50 cycles was compliant with the CV curves. The multi-layer GNS/VO<sub>x</sub> electrodes needed more sodium ion insertions than pure multi-layer VO<sub>x</sub> electrodes to reach the electrodes fully activated level due to the GNS layers. And the GNS layers protected the constructions from crack during the insertions and extrusions. Besides, after 500 cycles the cathode materials still kept a capacity of 145.1 mA h g<sup>-1</sup> which was only 15% decreased from the initial 171.2 mA h g<sup>-1</sup>. The GNS layer prevented the overall structure from collapse during the Na-ion insertion. The large scale lattice structure of VO<sub>x</sub> provided a perfect sodium channel for Na-ion insertion and result in a high capacity. In contrast, the rate performance and cycle performance of 3-layer VO<sub>x</sub> without GNS was tested (Fig. S3) to show in what way the GNS layers had improved the electrodes' performance. With the GNS layers, the electrodes exhibited more stable cycling performance and higher capacity than the layered pure VO<sub>x</sub> electrodes when tested at the same current densities.

The contrast cycling tests of different concentration of GO and different layers of the materials (Fig. S4) were taken to find best condition for sodium batteries. These four materials showed the increasing capacities in the first 100 cycles and then the capacities stabilized. Without annealing, the multi-layer materials showed poor

electrical conductivity due to the GO existing. The 1 layer GNS/VO<sub>x</sub> with GO's concentrate of 4.5 mg/mL exhibited the highest capacity but worst stability among these samples. The 1-layer structural couldn't keep well during the Na-ion insertion and since the lower content of GO release the electrical resistance, the specific capacity climb to 268 mA g<sup>-1</sup> as the highest one. With more layers, the materials showed better stability during the cycling test. When raised the concentrate of GO to 9 mg/mL, the great increase of the electrical resistance led up a lowest capacity among these four different type samples (Fig. S5). Fig. S6 showed the charge and discharge performance at different rate of four different types of multi-layer GNS/VO<sub>x</sub>-500 cathode materials. Among them, the capacity of sample of 3-layer GNS/VO<sub>x</sub>-500 at various charge-discharge rate performances is the highest one, especially when at the high charge and discharge current. When changing to the low current charge and discharge, its capacity also showed an increase trend. The other layered materials (annealed at 500 °C) also showed good stability and large capacities, but lower than the 3-layer GNS/VO<sub>x</sub>-500 cathode materials. The 3-layer material without annealing exhibited the lowest capacity.

#### 4. Conclusions

In summary, we have provided a facile way to produce high performance cathode materials for sodium batteries. We used spin coating method to make up the multi-layer structure cathode materials for sodium batteries for the first time. These sodium ion battery cathode materials of multi-layer structure with a large scale lattice structure are more stable and thus more conducive to embed the amount of sodium ions and have good intercalation reversibility. These multi-layer structure cathode materials had exhibited good stability and high capacity in sodium batteries. We believe that these discoveries may push forward the practical application of sodium batteries. It is believed that this facile method for preparing multi-layer materials used as the sodium ion battery cathode materials would not only improve the actual capacity of the batteries and extending the cycle life of the batteries but also push forward the abundant practical application of sodium batteries.



## Acknowledgments

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### Figure caption

**Fig. 1** SEM characterization of the multi-layer GNS/VO<sub>x</sub> materials. (a) GNS covered on VO<sub>x</sub>. (b) VO<sub>x</sub>. (c) A magnification of the GNS on VO<sub>x</sub>. (d) Fracture surface of two layers.

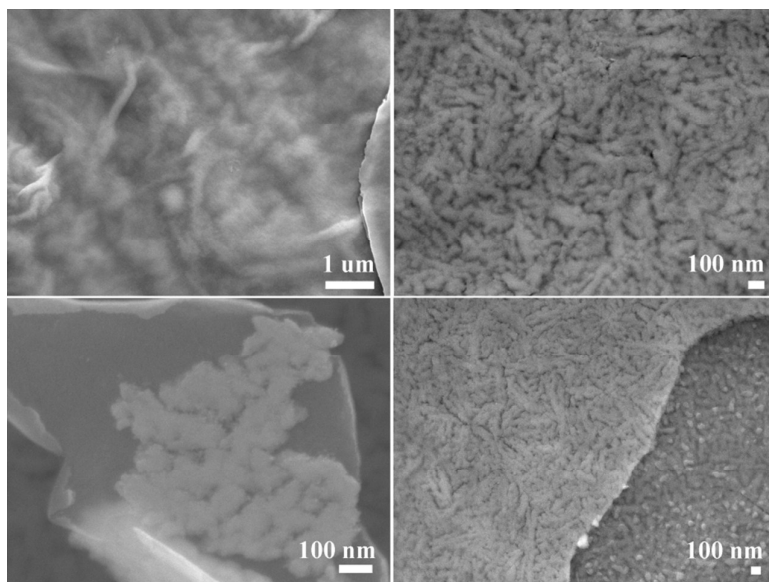
**Fig. 2** XRD image of GNS/VO<sub>x</sub>-500 °C and GO/VO<sub>x</sub> without annealing.

**Fig. 3** TEM of GNS/VO<sub>x</sub>-500 cathode materials.

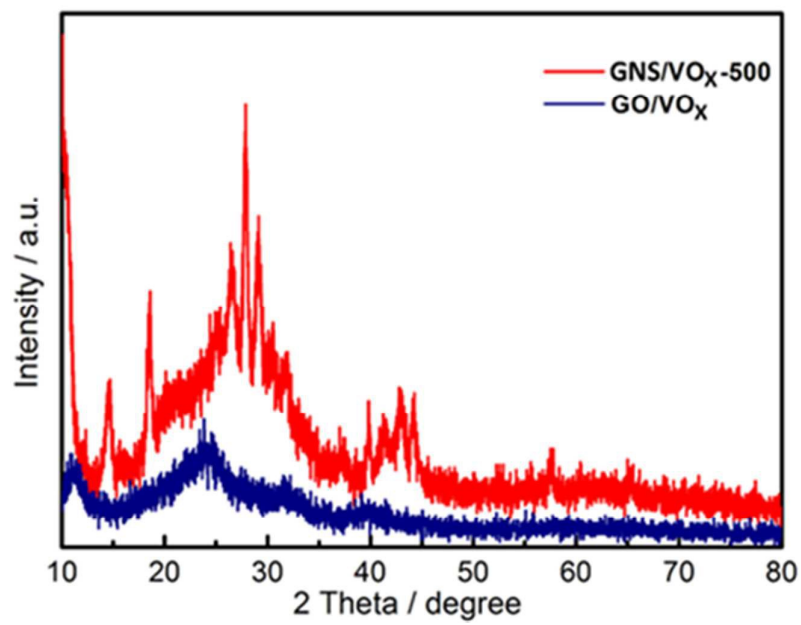
**Fig. 4** XPS spectra of the GNS/VO<sub>x</sub>-500. (a) V<sub>2P</sub>; (b) O<sub>1S</sub>; (c) C<sub>1S</sub>; (d) Na<sub>1S</sub>.

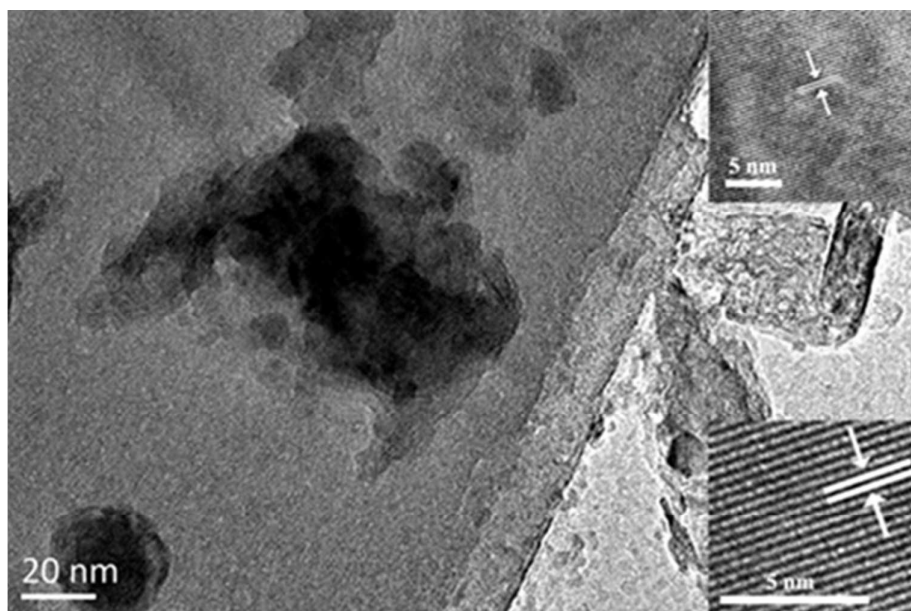
**Fig. 5** CV curves of the GNS/VO<sub>x</sub> of 3-layer-500 cathode materials. The scan potential region from 2.0 to 4.5 V at a scan rate of 0.1 mV/s versus Na/Na<sup>+</sup>.

**Fig. 6** Performance of 3-layer-500 GNS/VO<sub>x</sub> cathode materials. (a) Rate performance of 3-layer-500 GNS/VO<sub>x</sub> in the voltage range of 2.0-4.5 V versus Na/Na<sup>+</sup>; (b) Long-term cycling performance of 3-layer-500 GNS/VO<sub>x</sub> electrode at a current density of 0.2 A/g in the voltage range of 2.0-4.5 V versus Na/Na<sup>+</sup>.

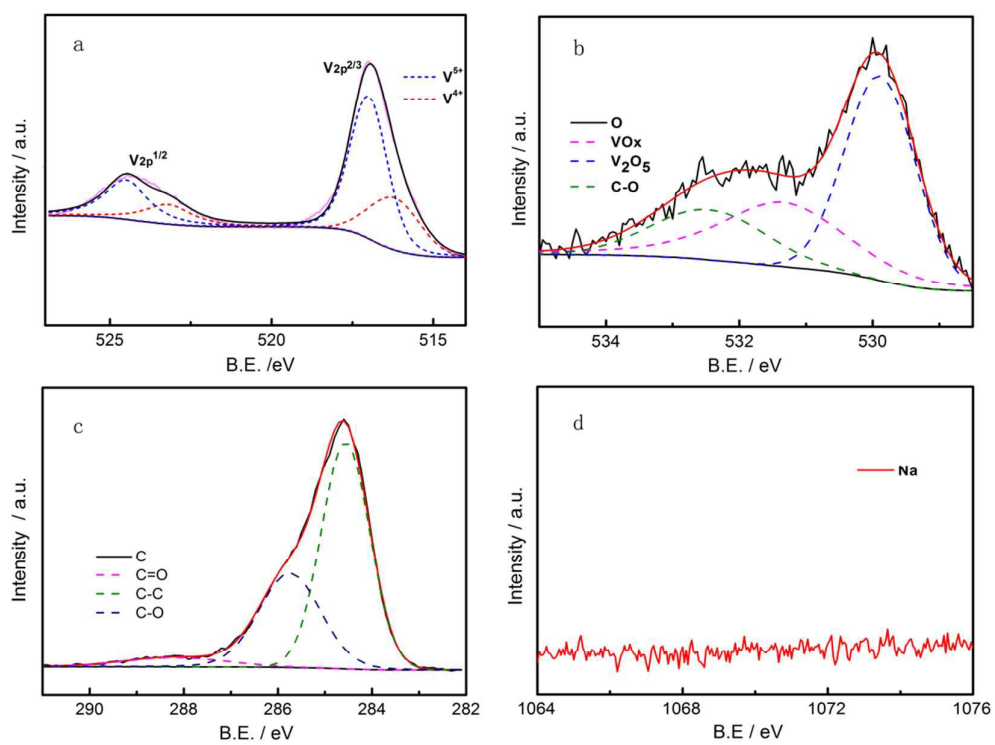


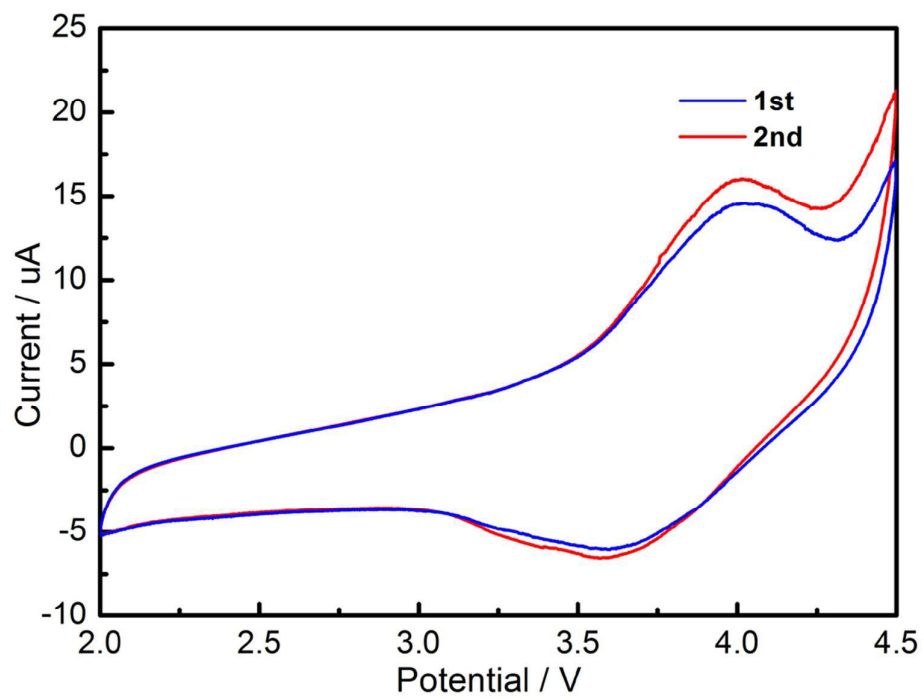
**Fig. 1**

**Fig. 2**



**Fig. 3**

**Fig. 4**

**Fig. 5**



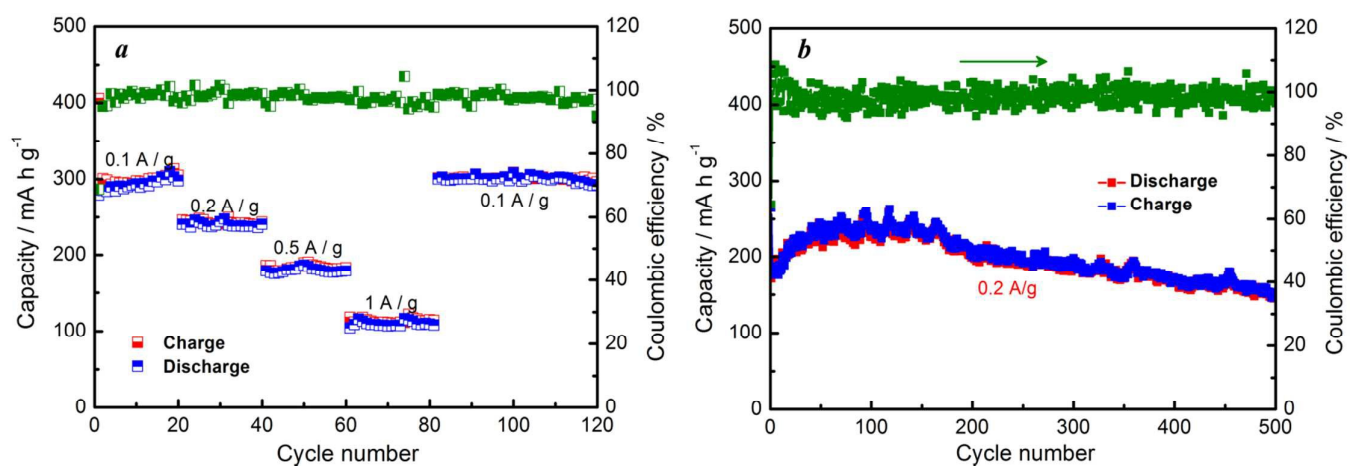


Fig. 6

## TOC

We make up the vanadium oxides@graphene nanosheets multi-layer structure cathode materials for sodium batteries by creatively using spin coating method. These multi-layer structure cathode materials had exhibited good stability and high capacity in sodium batteries.

