Revisiting Li^+ intercalation into various crystalline phases of Nb_2O_5 anchored on graphene sheets as pseudocapacitive electrodes

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Abstract

Herein, polycrystalline Nb₂O₅ nanoparticles including pseudo-hexagonal (*TT*-), orthorhombic (*T*-), tetragonal (*M*-) and monoclinic (*H*-) phases are uniformly anchored onto graphene sheets through a polyol-mediated solvothermal reaction and post heat-treatment, enabling us to discuss the effect of Nb₂O₅ crystalline phases on Li⁺ intercalation process. Electrochemical results show that Li⁺ intercalation into *M*- and *H*-Nb₂O₅ are also capacitive behavior, exhibiting higher capacity of 650 C g⁻¹ and 615 C g⁻¹ than *T*- and *TT*-phases of 585 C g⁻¹ and 530 C g⁻¹ at 0.5 A g⁻¹. The higher capacity-retention is also obtained for *M*- and *H*-phases (509 and 452 C g⁻¹) compared to *T*- and *TT*-phases (305 and 207 C g⁻¹) at 20 A g⁻¹. The high rate performance of *H*-phase can be explained by higher Li⁺ diffusion coefficients (D_{Li}) of 1.6×10^{-12} cm² s⁻¹, which is almost two order of magnitude higher than *TT*-phase of 4.7×10^{-14} cm² s⁻¹. This results indicate that Nb₂O₅ with various crystal structures shows similar Li⁺ capacitive intercalation behavior, but more ordered arrangement of unit cell may provide more vacancy for Li⁺ with the lower diffusion barriers, thus leading to higher rate performance.

Keywords: Niobium pentoxide; Graphene; Intercalation pseudocapacitance; Capacitive behavior; Li-ion diffusion coefficient

1. Introduction

In the flourishing electronic age, electrochemical energy storage has a broader applications from the portable electronic products to the large-scale power grid [1, 2]. As typical electrochemical devices, battery and supercapacitor have achieved a notable improvement in electrochemical performance, but they still suffer various drawbacks [3, 4]. Lithium-ion batteries could provide high energy density (170 W h kg^{-1}) due to faradaic charge-storage, but their power density is limited by solid-state diffusion of electrolyte ions [5]. Electrochemical double-layer capacitors have high power densities (6 kW kg^{-1}) but poor energy density due to lower specific capacitance limited by surface area of carbon materials [6]. In contrast, the pseudocapacitive materials involving the surface or near surface faradaic reactions, could offer attractive capacitance and bring the energy density of supercapacitors significantly closer to that of batteries [7]. Accordingly, there is a growing need to develop the devices, which can provide both high energy and high power density in the same material for the current and near-future electrochemical energy storage devices.

Conway identified three faradaic mechanisms for pseudocapacitance, involving the reversible underpotential deposition on the electrode surface, redox reaction at the electrode surface and reversible ions intercalation into the bulk material [8]. Recently, Dunn et al. discovered the intercalation pseudocapacitive phenomenon and the high-rate capability of orthorhombic (*T*-) Nb_2O_5 [9]. They proposed the lithium-ion intercalation reaction was capacitive behaviour, which was ascribed to the unique crystal structure of Nb_2O_5 . The mostly empty octahedral sites between (001) plane provided natural tunnels for rapid Li^+ transport throughout the *a-b* plane. Calculations indicate that the (001) plane

allows degenerate pathways with low energy barriers for ion transport. Ganesh et al. further suggested that intrinsic high rates was due to the interconnected open channels from the quasi-2D NbO_x sheets, leading to low cost diffusion pathways and fast local charge transfer [10]. The $T\text{-Nb}_2\text{O}_5$ as the capacitive-type intercalation material could provide high capacity as much as batteries at high charge-discharge rates, which is closer to that of supercapacitors. This will give the hope to eliminate the gap between battery and supercapacitor to develop a new energy storage concept. Recent progress on Nb_2O_5 materials was majorly focused on nanostructure and nanocomposite technologies, to reduce the particle dimensions and to increase the conductivity of semi-conductive Nb_2O_5 electrode, thus improving the pseudocapacitive responses [11-13].

Dunn et al. have proposed that the capacitive behavior of Nb_2O_5 was highly dependent upon its crystalline structure [14]. They found that amorphous Nb_2O_5 aerogel with higher surface area exhibited lower capacity than T - and pseud-hexagonal (TT -) phases. They explained faradaic process occurred in crystalline phases leading to an additional capacitive storage mechanism which did not occur in amorphous phase. In addition, the capacity and rate-retention of T -phase were higher than that of TT -phase. Kumagai et al. suggested that (180) plane of T -phase may provide a favorable pathway for Li^+ transport, then Li^+ could occupy the vacant interstitial sites in (001) plane [15]. The absence of (180) plane in TT -phase may explain its smaller capacity than that of T -phase. Nb_2O_5 has a large band gap, thus, exhibits a relatively complicated structure that displays extensive polymorphism, and the most common crystal phases are TT -, T -, tetragonal (M -) and monoclinic (H -) phases [16-18]. We predict that the rich crystal structure of Nb_2O_5 would give rise to the different electrochemical properties. The prior researches have paid more attention to the synthesis and application of TT - and $T\text{-Nb}_2\text{O}_5$ /carbon composites as Li^+

intercalation pseudocapacitive electrodes [11, 12, 19-21]. Lu and Wang et al. physically mixed *TT*-Nb₂O₅ nanocrystals with CNTs which significantly improved the rate capability of the composites [22]. Simon et al. demonstrated intercalation pseudocapacitance in *T*-Nb₂O₅ was an intrinsic property of the material and can be extended to practical electrode structures [23]. The capacitive behavior of other crystallinity Nb₂O₅ especially for *M*- and *H*-phases structure is still not clearly investigated.

Thus, this paper intends to revisit the influence of Nb₂O₅ crystallinity on Li⁺ intercalation process. We present a solvothermal method to decorate ultrafine Nb₂O₅ particles onto the reduced graphene oxide (rGO) surface. After heat treating at different temperatures, various crystalline Nb₂O₅ (*TT*-, *T*-, *M*- and *H*- phases) with the nanoscale dimension are obtained, and all of them are homogeneously anchored on the enhanced conductive graphene sheets. When used as Li⁺ intercalation electrodes, all of them demonstrate the capacitive behaviour and the fast Li⁺ intercalation kinetics characteristics. Moreover, we found for the first time, the *M*- and *H*- Nb₂O₅ exhibited higher capacity and rate capability than *T*- and *TT*- Nb₂O₅, which should be due to more ordered crystal structure of *M*- and *H*- phases with the face-sharing large 2D connected channels that allow faster ion diffusion. The Li-ion diffusion coefficient in *M*- and *H*- phases is two orders of magnitude of *TT*-phase. These results are helpful to further understand the intercalation capacitive behaviour of Nb₂O₅ and provide the viable structure design scheme for pseudocapacitive materials.

2. Experimental

2.1 Preparation of Nb₂O₅/graphene composites

The various crystallographic Nb₂O₅/graphene composites were prepared through a solvothermal reaction, followed by heat treatment at different temperatures. Graphite oxide (GO) was synthesized from the natural graphite by a modified Hummers method [14]. In a typical process, 0.3 g GO was dispersed in 40 mL ethylene glycol (EG) with ultrasonic and 0.9 g NbCl₅ powders (99.99%, Sigma-Aldrich) was dissolved in 50 mL EG with magnetic stirring. Then, two solutions were mixed together under magnetic stirring for more than 1 h to obtain a homogenous solution. Transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After cooling down to room temperature, amorphous Nb₂O₅/rGO composites were obtained and washed with DI-water under centrifugal separation for several times. Finally, amorphous Nb₂O₅/rGO composites were heat-treated at 600, 800, 950, 1000 °C for 3 h in N₂ flow to form *TT*-Nb₂O₅/graphene, *T*-Nb₂O₅/graphene, *M*-Nb₂O₅/graphene and *H*-Nb₂O₅/graphene composites, respectively.

2.2 Material characterization

The crystalline structure was identified by powder X-ray diffraction (XRD) patterns with a RigakuD/max 2550 diffractometer operating at 40 kV and 20 mA using Cu K α radiation ($\lambda = 0.15406$ nm). The microstructure and morphology were observed on field emission scanning electron microscope (SEM, FEI-300) and transmission electron microscope (TEM, JEOL, 2100F). Thermogravimetric analysis was performed using a TA Instrument Q600 Analyser at 10 °C min⁻¹ from room temperature to 800 °C in 100 mL min⁻¹ air flow. Pore structure characterization was measured by N₂ adsorption-desorption isotherms at 77 K with a Quadrasorb SI analyser. Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. Barrett-Joyner-Halenda (BJH) model

was used to analysis the pore size distributions from the desorption branch. The total pore volume was calculated using a single point at a relative pressure of 0.985.

2.3 Electrode preparation

The electrode slurry was prepared by mixing the as-prepared various crystalline Nb₂O₅/graphene composites, carbon black (Timical super C65) and polyvinylidene fluoride (PVDF) binder in an 8:1:1 weight ratio in N-methyl-2-pyrrolidinone (NMP). Then the slurry was uniformly casted onto Cu foil, dried in a 110 °C vacuum oven overnight, and punched into electrodes with a diameter of 12 mm and a thickness of 50 µm. The counter electrode was prepared by commercial activated carbon, carbon black (Timical super C65), and PTFE (60 wt. % in H₂O) at a weight ratio of 85:10:5, then dried under vacuum at 110 °C for 12 h.

2.4 Electrochemical characterization

Electrochemical tests were performed using 3-electrode system with the prepared samples as working electrode, overcapacitive activated carbon and lithium foil used as the counter and reference electrode, respectively. 1 M LiPF₆ in EC/DMC/EMC (*V/V*, 1:1:1) was employed as the electrolyte, the separator was a microporous membrane (Celgard 2400). All the cells were assembled in an argon filled glove box at 25 °C and each cell need to be injected 0.5 mL electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on a PCI-4/300 potentiostat (Gamry, USA), galvanostatic charge-discharge (GCD) tests were conducted on the Arbin BT2000 system. The weight of active materials (Nb₂O₅) in electrode was used to calculate the gravimetrically normalized current and capacitance.

3. Results and discussion

3.1 Material synthesis

The synthesis strategy of various crystalline Nb₂O₅/graphene composites is illustrated in Fig. 1. Through a polyol-mediated solvothermal reaction of NbCl₅ and GO in ethylene glycol (EG) system, ultrafine Nb₂O₅ nanodots (inset in Fig. 1, TEM image) are homogeneously anchored on rGO surface. The EG not only function as the solvent, but also as a stabilizing agent that effectively restricts particle growth of Nb₂O₅ and hinder the aggregation of rGO during the reduction process. Further heat-treatment of as-prepared amorphous Nb₂O₅/rGO composites in N₂ flow at different temperatures, could achieve various crystalline phases of Nb₂O₅ including *TT*-, *T*-, *M*- and *H*- phases.

3.2 Nb₂O₅ crystal phase

The structure evolution of amorphous Nb₂O₅/rGO composites during heat treatment was monitored by *in situ* high-temperature XRD patterns, as shown in Fig. 2a. Various XRD patterns are observed indicating that the crystal phase transition of Nb₂O₅ is highly dependent up the heating temperature. The initial obtained Nb₂O₅/rGO composites only have a broad peak centred at $2\theta \approx 25^\circ$, which is corresponding to graphitic structure of rGO. No any Nb₂O₅ crystal peaks are observed indicating the completely amorphous feature. When heated to 300 °C, it is possible to confirm the beginning of the crystalized process, since two small broad peaks present at $2\theta \approx 22.6^\circ$ and 28.5° , respectively. Heated to 500 °C, the *TT*-phase is obtained due to the peaks at $2\theta \approx 22.6^\circ$, 28.3° , 36.6° , 46.2° , 50.3° and 55.2° can be attributed to (001), (100), (101), (002), (110) and (102) planes of *TT*-Nb₂O₅ (JCPDS No. 28-0317), respectively [17, 24]. Until heated to 800 °C, (100)

plane of *TT*-phase begin to separate into two peaks (180) and (200) of *T*-phase while (101) plane divide into (181) and (201) planes, and two typical characteristic peaks of (2100) and (2110) planes are observed at $2\theta \approx 42.6^\circ$ and 45.0° . All these peaks can be indexed to JCPDS No. 30-0873, demonstrating that *TT*-phase has successfully translated to *T*-phase [17, 25]. When heated to 950°C , *T*-phase is beginning to transform to *M*-phase (JCPDS No. 72-1484), due to the present of *M*-phase diffraction peaks at $2\theta \approx 18.2^\circ$, 23.8° , 25.1° , 32.2° , 39.1° and 48.1° [18, 26].

According to the results of *in situ* high-temperature XRD patterns, we heated Nb₂O₅/rGO composites at 600°C , 800°C , 950°C and 1000°C in N₂ flow for 3 h respectively. The corresponding XRD patterns of the heated samples are shown in Fig. 2b. The pure *TT*- and *T*- phases are obtained with heating at the temperature of 600°C and 800°C , respectively, because their peaks can be well indexed to their JCPDS (No. 28-0317 and No. 30-0873). The sample heat treated at 950°C demonstrate a dominated *M*-phase with a small amount of *T*-phase, while heated at 1000°C the sample show the pure *H*-phase (JCPDS No. 37-1468) [18, 27]. Furthermore, no any reduced phase is formed. In order to clearly distinguish the crystal phase, the reference spectra was given at the bottom of XRD patterns in Fig. S1. The relationship between the heating temperature and the average crystallite sizes of Nb₂O₅ calculated using the Debye-Scherrer method is shown in Table S1. The crystallite size increases generally from 13.5 to 64.6 nm with the heating temperature increasing, which is a common sintering phenomenon of crystal materials.

The Raman spectra of Nb₂O₅/graphene composites heated at 600, 800, 950, 1000 °C is shown in Fig. S2. The new graphitic domains with the smaller size are created in graphene during the heat treatment.

3.3 Nb₂O₅/graphene composite morphology

The evolution of morphology and crystallinity of Nb₂O₅ nanoparticles is clearly observed by SEM and TEM images in Fig. 3. The solvothermal product, amorphous Nb₂O₅/rGO shows plenty of Nb₂O₅ nanodots anchored on the surface of rGO (Fig. 1 insert, TEM image). After heat treatment, the Nb₂O₅ nanodots experience obvious growth, with the average sizes of *ca.* 15-70 nm at different temperatures, in good agreement with the calculation results from XRD patterns. It should be noted that even after high temperature sintering, the Nb₂O₅ nanoparticles are still homogeneously dispersed onto the surface of graphene sheets. This should be due to confinement effect of graphene sheets that hinders the aggregation of Nb₂O₅ nanoparticles. The high-resolution TEM images could provide some information about Nb₂O₅ crystalline structure. For sample heated at 600 °C, the image in Fig. 3c shows a lattice spacing of 0.31 nm corresponding to the (100) plane of *TT*-Nb₂O₅. The image of sample heated at 800 °C shows two lattice spacings of 0.39 nm and 0.31 nm, responding to (001) and (180) planes of *T*-Nb₂O₅, respectively. The image of sample heated at 950 °C shows a visible lattice spacing of 0.37 nm that can be ascribed to (110) plane of *M*-Nb₂O₅. And the image of sample heated at 1000 °C demonstrates the clearly monoclinic lattice fringe and a lattice spacing of 0.38 nm, in consistent with (110) planes of *H*-Nb₂O₅. These TEM images combined with the electron diffraction rings (the insets) could very confirm the crystal structure of these Nb₂O₅ nanoparticles obtained at different temperatures, which is consistent with the XRD results.

The contents of graphene in the Nb₂O₅/graphene composites were determined to be 18 wt. % by TG analysis in air flow (Fig. S3), regardless of the heat-treated temperature. The BET surface areas of these samples were investigated by a N₂ adsorption-desorption measurement (Fig. S4). With the increase of heat-treated temperature, the BET specific surface area of composites gradually decrease from 137.3 to 101.2 m² g⁻¹. The more information of pore structure parameters was given in Table S2.

3.4 Li⁺ intercalation behaviour of various crystalline Nb₂O₅

The Li⁺ intercalation behaviour of various crystalline Nb₂O₅ is examined using three-electrode system, using the as-prepared Nb₂O₅/graphene composites as the working electrode with the voltage window between 1.0-3.0 V (vs. Li/Li⁺). The intercalation pseudocapacitance contribution of graphene and conductive carbon black (Super C65) can be ignored, because the Li⁺ intercalation reaction of graphene and carbon black always occurred at the lower potential bellow 1.0 V (vs. Li/Li⁺). In addition, due to the low BET surface area (< 140 m²/g), the electrochemical double layer capacitance of these composites can also be neglected.

The effect of Nb₂O₅ crystallinity on the Li⁺ intercalation process is firstly characterized by cyclic voltammetric (CV) tests. The whole CV results in Fig. S5-S6 show that *TT*- and *T*- phases formed at mediate temperatures of 600 and 800 °C have broad Li⁺ intercalation peaks, which is obviously different with the shape of redox peaks of *M*- and *H*- phases formed at high temperatures of 950 and 1000 °C. For a facile comparison, the CV curves of *TT*-, *T*-, *M*- and *H*- phases at 1 mV s⁻¹ are shown in Fig. 4a-b. The *TT*- and *T*- phases show two broad Li⁺ intercalation peaks around 1.23 V and 1.43 V and broad Li⁺ extraction peaks around 1.53 V, which may indicate that the active sites of Li⁺ intercalation in *TT*- and *T*- crystals has a broad distribution of energy [10]. The CV curves of *M*- and *H*- phases (Fig. 4b) show a couple of sharp

cathodic and anodic peaks at around 1.36 and 1.44 V, indicating that Li^+ fast adsorb on the 2D NbO_x faces with the overlapping intercalation energy [10, 15]. The little voltage separation (< 0.08 V) between cathodic and anodic peaks and the reversible capacity from charge-discharge processes, suggest that the Li^+ insertion/extraction into/from *M*- and *H*- phases is highly reversible process without obvious change of crystal structure. The CV results suggest that the Li^+ intercalation process is highly sensitive to Nb_2O_5 crystal structure.

The capacity of these Nb_2O_5 are calculated by integrating the discharge portions of CV curves, as shown in Fig. 4c. At a low sweep rate of 1 mV s^{-1} , the capacity follows an order of *M*- (629 C g^{-1}) $>$ *H*- (610 C g^{-1}) $>$ *T*- (557 C g^{-1}) $>$ *TT*- (430 C g^{-1}). Combined with XRD crystallographic analysis, the difference in capacity of these Nb_2O_5 may be explained as the difference of Li^+ insertion sites. Kumagai et al. previously suggested that Li^+ would transport through (180) plane (served as a favourable pathway for Li^+) to occupy vacant interstitial sites in (001) plane in the three-dimensional framework of *T*-phase [18]. The *TT*-phase is believed to be a defect structure of *T*-phase, such as (100) plane of *TT*-phase was separated to (180) and (200) planes of *T*-phase. The absence of (180) plane in *TT*-phase may explain its smaller capacitance than that of *T*-phase. In contrast, Li^+ could enter the 2D interlayer channels of highly ordered *M*- and *H*- crystal structure, which exhibit weak expansion of the interlayer distance for accommodating more Li^+ ions [10, 18]. Indeed, the increased pseudocapacitive behaviour compared to *TT*- and *T*- phases, have been revealed by Ganesh et al. through simulation method. Moreover, the rate capability of these Nb_2O_5 nanocrystals have the same tendency with capacity, which are for 81.2%, 64.0%, 58.4% and 47.7%, respectively, at high sweep rate of 100 mV s^{-1} .

The kinetics of charge storage in *T*- Nb_2O_5 has been previously studied by plotting $\log(i)$ versus $\log(v)$ for cathodic and anodic peak currents at various sweep rates, while the Li^+

intercalation kinetics of *M*- and *H*- phases is not yet reported. According to the power relationship between the current (i , A) and the sweep rate (v , mV s⁻¹): $i = av^b$, the charge storage whether controlled by diffusion ($b=0.5$) or surface processes ($b=1$) can be reflected by the b -value [28-30]. As shown in Fig. 4d, the kinetics of various crystalline Nb₂O₅ are compared. For the sweep rates ranging from 1 to 50 mV s⁻¹, corresponding to the discharging times > 40 s, the b -value of all crystal phases for both cathodic and anodic peaks is equal to 1, indicating that the kinetics of Li⁺ intercalation into various crystallinity Nb₂O₅ are controlled by surface process with the capacitive behaviour.

The Li⁺ intercalation into various Nb₂O₅ crystal structure is further studied by galvanostatic charge-discharge (GCD) tests with the current densities ranging from 0.5 A g⁻¹ to 20 A g⁻¹, as shown in Fig. S7. A direct comparison of GCD curves at current density of 0.5 A g⁻¹ is shown in Fig. 5a-b. The charge-discharge potential of *TT*- and *T*- phases vary linearly with the charge-discharge capacity from 1.0-2.0 V, may indicating that the original crystal structure of *TT*- and *T*- phases is maintained during lithium intercalation without any new phase appearing, and the Li⁺ intercalation process is a capacitive behaviour. But in Fig. 5b, the *M*- and *H*- phases show a flat potential region at around 1.42 V in charge-discharge curves. The discharge capacity of *M*- and *H*- phases is about 173 and 164 mAh g⁻¹, corresponding to 1.73 and 1.64 Li⁺ inserted into the Nb₂O₅ host lattice, respectively. Kumagai et al. suggested that a new phase was formed to a small extent at $x \approx 1.2$ and the original structure of the monoclinic was mostly maintained during Li⁺ intercalation. This leads to a two-phase equilibrium being consistent with the appearance of a flat potential region. Although a little new phase was formed, the original structure of *M*- and *H*- Nb₂O₅ was mostly maintained during Li⁺ intercalation. Thus, the Li⁺ intercalation reaction has major contribution in the total electrochemical process, instead of a little phase transformation.

In addition, the rate capability of these Nb₂O₅ nanocrystals have the same tendency with the capacity, as shown in Fig. 5c. *M*-Nb₂O₅ always show the highest capacity at various current densities, which is slightly higher than that of *H*-Nb₂O₅ and much higher than these of *T*- and *TT*-Nb₂O₅. All other Nb₂O₅ crystals have the excellent cycling stability with the capacity retention up to 88%, and the *TT*-Nb₂O₅ shows the lowest capacity retention is 80% after 2000 cycles. The higher capacity and rate capability of monoclinic compared to orthorhombic have been proved by Ganesh et al. through simulation method. These NbO_x polyhedra are more regularly connected in monoclinic phase than in orthorhombic phase, long-range diffusion is expected to occur more easily in monoclinic phase.

3.5 Li⁺ diffusion coefficient

To understand why *M*- and *H*- phases exhibit higher rate capability than *T*- and *TT*- phases, in this work, the Li⁺ diffusion kinetics in various crystal structure is estimated by using a plane-sheet diffusion model [31, 32]. The relationship between the charge amount and the current density is straight line, shown in Fig. 6a, the chemical diffusion coefficient of Li⁺ was estimated assuming that Li⁺ diffusion coefficients (D_{Li}) does not depend on the Li⁺ concentration. The detailed calculation process of D_{Li} is given in Fig. S8. It should be noticed that the D_{Li} is not only affected by the crystal structure, but also the Nb₂O₅ particle size and the morphology of composites. As shown in Fig. 6b, the D_{Li} in *TT*-, *T*-, *M*- and *H*- phases are calculated to be 4.7×10^{-14} , 1.0×10^{-13} , 1.1×10^{-12} and 1.6×10^{-12} cm² s⁻¹, respectively. Apparently, the D_{Li} in Nb₂O₅ is increased with increasing the sintering temperature, and particularly the D_{Li} of *H*-phase is two order of magnitude higher than *TT*-phase. Such significant difference of D_{Li} in these Nb₂O₅ should be majorly due to their crystal structure.

The crystal structure of *TT*-, *T*-, *M*- and *H*- phases has been given in Fig. 6c-f. Typically, in the *TT*-phase unit cell, each Nb atom is at the centre of four, five or six oxygen atoms on the *ab*-plane and an Nb-O-Nb-O chain structure exists along the *c*-axis, without enough intervals for Li^+ transport [33]. In the *T*-phase unit cell, each Nb atom is surrounded by six or seven oxygen atoms, creating distorted octahedra or pentagonal bipyramids. The polyhedra are connected by edge- or corner-sharing in the *ab*-plane and by corner-sharing along the *c*-axis, as shown in Fig. 2d [34]. The *T*-phase is always thought to be a more ordered structure than the *TT*-phase. Moreover, only 5% Nb atoms occupy the vacant interstitial sites of *ab*-plane, the inserted Li^+ could occupy the rest of empty sites of *ab*-plane. The *H*-phase contains 3*4 and 3*5 blocks consisting of corner-sharing NbO_6 octahedra in the *ab*-plane and edge sharing with a shift of half a unit cell dimension along the *c*-axis [35]. The *M*-phase containing 4*4 blocks has the similarity crystal structure with the monoclinic phase, but more ordered two-dimensional channels [27, 36]. Thus, the continuous voids between these interconnected NbO_6 octahedra form the face-sharing 2D layer channels along the *c*-axis, which would be like nanoporous quasi-2D layer materials. The Li^+ insertion reaction is very similar to 2D surface adsorption reactions. The *M*- and *H*-phases therefore can be regarded as a nanoporous material permit ions fast adsorb and translate with sufficiently low energy barrier of 2D layer channels, giving rise to a high rate intercalation pseudocapacitive behaviour.

4. Conclusions

In this work, various crystalline Nb_2O_5 /graphene composites were synthesized through polyol-mediated solvothermal reaction and post heat-treatment process. All Nb_2O_5 nanocrystals are homogeneously anchored on graphene sheets. The Li^+ intercalation process in all crystal phases Nb_2O_5 is capacitive behaviour, but the Li^+ intercalation behaviour is highly depend upon crystal

structure. The *TT*- and *T*- phases have the similar unit cell arrangement and give the similar Li^+ intercalation/extraction process. But *T*-phase exhibits the higher capacity and better rate capability than *TT*-phase, due to that the *TT*-phase is a less crystalline form with the crystal defect comparing to *T*-phase. While, *M*- and *H*- phases have the similar crystal structure and give the similar lithiated process. The *M*-phase exhibited the highest capacity and rate capability than the others Nb_2O_5 crystals, because the *M*-phase has the more ordered NbO_6 octahedra arrangement. It seems that the two-dimensional nature of the structure of *M*- and *H*- phases is favourable for the reversible insertion of Li^+ into the structure compared with three-dimensional structure of *TT*- and *T*- phases. These findings are useful to understand the intercalation capacitive behaviour of Nb_2O_5 and will provide the viable structure design scheme for pseudocapacitive materials.

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Figure captions:

Fig. 1 Schematic of fabrication process for various crystalline Nb₂O₅/graphene composites.

Fig. 2 (a) *In situ* high-temperature XRD patterns of Nb₂O₅/rGO composites from room temperature to 950 °C in N₂ flow; (b) XRD patterns of various crystalline Nb₂O₅/graphene composites.

Fig. 3 SEM, TEM, HR-TEM images and Electron diffraction studies: (a-c) *TT*-Nb₂O₅/graphene; (d-f) *T*-Nb₂O₅/graphene; (g-i) *M*-Nb₂O₅/graphene; (j-l) *H*-Nb₂O₅/graphene.

Fig. 4 (a-b) CV curves of various crystallinity Nb₂O₅/graphene composites at 1 mV s⁻¹. (c) Specific capacity as a function of sweep rates and (d) *b*-value determination of the anodic and cathodic peak currents.

Fig. 5 (a-b) Charge-discharge curves of various crystallinity Nb₂O₅/graphene composites at 0.5 A g⁻¹; (c) Rate capability and (d) cycle performance at 1 A g⁻¹ for these Nb₂O₅/graphene composites.

Fig. 6 (a-b) Estimation of Li⁺ diffusion coefficient in *TT*-, *T*-, *M*- and *H*- Nb₂O₅. Crystal structure of (c) *TT*-, (d) *T*-, (e) *M*- and (f) *H*- phases.

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Fig. 6 (a-b) Estimation of Li^+ diffusion coefficient in $TT\text{-}$, $T\text{-}$, $M\text{-}$ and $H\text{-}$ Nb_2O_5 . Crystal structure of (c) $TT\text{-}$, (d) $T\text{-}$, (e) $M\text{-}$ and (f) $H\text{-}$ phases.

Graphical abstract

Revisiting Li^+ intercalation into various crystalline phases of Nb_2O_5 anchored on graphene sheets as pseudocapacitive electrodes

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