Rapid redox kinetics in uniform sandwich-structured mesoporous Nb_2O_5/graphene/mesoporous Nb_2O_5 nanosheets for high-performance sodium-ion supercapacitors

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ABSTRACT

Sodium-ion hybrid supercapacitors have received great attracts for next-generation energy storage applications due to their high energy and power densities, as well as the abundant sodium resource. However, electrodes based on transition-metal oxides often suffer from low reversible capacity and sluggish redox kinetics, which seriously constrains the rate and cycling performance of the devices. Herein, a facile two-step hydrolysis synthesis is used to prepare uniform sandwich-like mesoporous Nb_2O_5/graphene/mesoporous Nb_2O_5 (G@mNb_2O_5) nanosheets as sodium storage materials. The mesoporous Nb_2O_5 layers on graphene are constructed by several nanometer-sized Nb_2O_5 particles. In virtue of the structural features, the G@mNb_2O_5 nanosheets electrode demonstrates high-rate capacity (293 and 125 mA h g\textsuperscript{-1} at 50 and 2000 mA g\textsuperscript{-1}, respectively) and stable cycling performance due to the rapid redox kinetics, including significantly increased surface pseudocapacitive contribution, improved sodium-ion diffusion coefficient, and short characteristic relaxation process. By employing activated carbon as cathode, a full sodium-ion hybrid device successfully demonstrates a high energy density of 56.1 Wh kg\textsuperscript{-1} at 120 W kg\textsuperscript{-1}, and 9.7 Wh kg\textsuperscript{-1} at 7200 W kg\textsuperscript{-1}, as well as a stable capacitance retention of ~ 89% at 1 A g\textsuperscript{-1}. The availability of capacitive Na-ion storage system presented here is attractive for cost-effective energy storage applications.

1. Introduction

Electrochemical supercapacitors (ESCs) hold tremendous promise for next-generation energy storage applications, such as electronic devices, electric vehicles, and uninterruptible power supply (UPS) [1–4]. Among various kinds of ESCs, hybrid ESCs with faradic materials as the anodes, carbonous materials as the cathodes, and non-aqueous electrolytes are extraordinarily attractive [2,5,6]. These ESCs deliver high energy/power densities and long lifetime due to the integrated merits of wide cell operation potential range, redox-based energy storage in anodes, as well as fast ion adsorption/desorption kinetics in cathodes [1]. While high-performance lithium-ion (Li-ion) hybrid ESCs have been successfully proposed [7–10], developing sodium-ion (Na-ion) hybrid ESCs are much economically favorable for large-scale applications due to the low cost and abundant resource [11,12]. Up to now, several Na-ion hybrid ESCs have been fabricated [13–20]. Those cells demonstrated reasonable energy and power density comparable to Li-ion hybrid ESCs. However, they suffered from poor cycling performance. In addition, Na-ion hybrid ESCs with higher power density are also avidly exploited to meet various practical applications. Therefore, fabrication of sodium-based hybrid devices with high energy/power densities and long cycle life are still urgent.

It is believed that the larger diameter of Na-ions (1.02 Å) has strong adverse impacts on the redox kinetics [3,11,12]. First, in contrast to Li ions (0.76 Å), the Na-ions are much harder to be inserted into the inner parts of the electroactive particles [11,12,21–23], not only restricting the effective utilization of the electrode materials, but also impeding the Na-ion extraction process. Second, for some Na-ion host materials, amorphization occurs during the first discharge process [9,24–27]. Compared to pristine crystalline materials, the decreased conductivity
of amorphized layer is unfavorable to the sodium-ion redox kinetics to some extent. To solve the above problems, fabrication of metal oxide@carbonaceous material nanocomposites where the metal oxide is in mesoporous nature with ultra-short ion diffusion distance, is rather desirable [28,29]. The advantages include: (1) Significantly decrease in energy storage contributed from the sluggish redox taking place in the inner parts of the electroactive oxides; (2) Good electroactive materials/electrolyte contact arising from the mesopores; (3) Efficient electron transport pathway due to the high electrical conducting carbonous materials; (4) The emerging accelerated Na-ion redox kinetics, such as enhanced pseudocapacitive effect and improved sodium-ion diffusion coefficient [1,17,23,27].

Niobium pentoxide (Nb2O5) has been explored as one ideal high-rate Li-ion storage material for hybrid supercapacitors because it is intrinsic pseudocapacitive material [8–10,30,31]. However, rapid sodiation/desodiation of Nb2O5 for high rate capability is thought to be more challenging due to the larger radius of Na-ions and decreased electrical conductivity derived from the amorphization during the first discharge [27,32]. Furthermore, unlike to the cases of lithium storage [2,29–31], insertion/deinsertion behavior of Na-ions in Nb2O5-based materials also shows high dependency on the micro/nanostructures of the materials [25,32–34]. To develop Na-ion hybrid ESCs more commercially available, researches should be further conducted to obtain more enhanced specific capacity, charge/discharge rate, and cycling stability of Nb2O5 materials by facile preparation approach.

In this work, we report uniform sandwich-like mesoporous Nb2O5/graphene/mesoporous Nb2O5 (denoted as G@mNb2O5) nanosheets in which the Nb2O5 layer is composed of numerous nanometer-sized particles, for high specific capacity and high-rate capability of sodium storage. These G@mNb2O5 nanosheets were prepared by a facile two-step hydrolysis method. The G@mNb2O5 nanosheets electrode delivered much enhanced specific capacity and rate performance (293 and 125 mAh g\(^{-1}\)) at 50 and 2000 mA g\(^{-1}\)) with good cycling stability. Electrochemical analysis indicated the structural and compositional features-derived rapid redox kinetics, including enhanced electrical conductivity, significantly increased surface pseudocapacitive contribution, improved Na-ion diffusion coefficient, and short characteristic relaxation process, were the important origins. Coupling with an activated carbon cathode, a full Na-ion hybrid ESC provided both high energy and power densities (56.1 and 9.7 Wh Kg\(^{-1}\) under 120 and 7200 W Kg\(^{-1}\), respectively). After initial 800 cycles, the assembled hybrid cells delivered a stable capacity with high retention of ca. 89% at 1 A g\(^{-1}\).

2. Experimental section

2.1. Synthesis of G@mNb2O5 nanosheets

Concentrated H\(_2\)SO\(_4\), concentrated ammonia solution (28–30 wt %), KNO\(_3\), KMnO\(_4\), Nb2O5 powders (denoted as Com-Nb2O5) and ethanol were of analytical grade and purchased from Sinopharm Chemical Reagent Corp. Niobium ethoxide, pure ethanol and graphite were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Deionized water was used for all experiments.

First, graphene oxides were synthesized via a Hummer’s method. To realize the two-step hydrolysis approach for preparation of G@mNb2O5 nanosheets, the graphene oxide suspension was transferred into ethanol and sonicated in an ultrasound bath for 6 h, centrifuged and re-dispersed in pure ethanol with a concentration of ~0.08 mg/mL. Then, 0.45 mL of niobium ethoxide was added dropwise into 100 mL of the graphene sheets ethanol suspension with stirring at 45 °C. After being stirred for 15 min, 0.2 mL of concentrated ammonia solution was added. The mixture was then stirred for 24 h. The products were collected by centrifugation, followed by immersing into 30 mL distilled water and then being treated by ultrasound bath for 6 h at 25 °C. The final samples were collected by centrifugation, followed by washing with distilled water and then dried by freeze-drying method. Annealing process at 600 °C for 3 h in Ar was used to make Nb2O5 crystalize and reduce the graphene oxides. Mesoporous Nb2O5 nanosheets (denoted as mNb2O5 nanosheets) were obtained by annealing treatment of as-hydrolyzed products in air. Nb2O5 nanopowders (denoted as Nano-Nb2O5) were prepared in the pure ethanol without graphene oxides.

2.2. Physical characterization

The crystalline and morphology information are collected by X-ray diffraction (XRD, Rigaku D/MAX2000pc), transmission electron microscopy (TEM, FEI Tecnai G2F30, 300 kV), high-resolution TEM (HRTEM), atomic force microscopy (AFM, Bruker, Dimension Icon) and scanning electron microscopy (SEM, FEI Helios Nanolab 600i) examinations. The chemical elements and binding characters were investigated by X-ray photoelectron spectroscopy test (XPS, PH 5700 ESCA System using Al \(K\alpha\) radiation) and Raman spectra (JY Co. LABRAM-HR). The content of the Nb2O5 and decomposition performance were determined thermogravimetrically using a TGA analyzer (Netzsch STA449F3) in air. The nitrogen physisorption measurements were performed on a Quantachrome QDS-MP-30 analyzer (USA) at 77 K.

2.3. Electrochemical characterization

The Na-ion storage performance of Nb2O5-based materials was investigated by half-cell standard CR2032 configuration with glass microfiber filters as separators. The working electrodes for half cells were prepared by mixing the active material, acetylene black and poly(vinylidene fluoride) (PVDF) at a weight ratio of 70:20:10, coated uniformly on Cu foil. The electrodes were dried at 80 °C for 12 h under vacuum, and then pressed to enhance the film stability. The average loading density of the active materials was around 0.92 mg cm\(^{-2}\). For the assembly of half-cell Na-ion battery, pure sodium foil was used as the counter electrode, and a solution of 1 M NaClO\(_4\) in ethylene carbonate(EC)/propylene carbonate (PC) (1:1 by volume) with 5% fluoroethylene carbonate (FEC) as the electrolyte. The charge/discharge measurements were carried by a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurement were performed by a CHI660C electrochemistry work station (Shanghai Chenhua, China) within the range from 0.01 to 2.5 V. A sodium-ion hybrid supercapacitor was constructed using Nb2O5-based materials as the anode and the activated carbon as the cathode materials in a CR2032 coin type cell with the same electrolyte and separator. The energy and power densities of full-cells were calculated according to the following equations:

\[
E = \int_{t_1}^{t_2} P dt = \Delta V \times \frac{I}{m} \times t
\]

(1)

\[
P = \frac{E}{t}
\]

(2)

where \(I\) is the charge/discharge current, \(V\) is the working voltage, \(t_1\) and \(t_2\) are the start/end-of-discharge time (s), respectively, and \(t\) corresponds to the discharge time.

3. Results and discussion

Fig. S1 schematically illustrates the typical synthetic procedure of mesoporous G@mNb2O5 nanosheets prepared by a controlled two-step hydrolysis of metal alkoxide. In this approach, it is believed that the oxygen-containing groups on GO initiated the hydrolysis of Nb-ethoxide to produce the nuclei, while the ammonia molecules and water can accelerate the hydrolysis, further generating tremendous
polycondensation of metal oxide precursors which can tightly bond on the GO surface and preformed nuclei \[35,36\]. The advantages of such kind of two-step hydrolysis mainly includes: (1) The generation of polycondensations can uniformly cover the entire surface, even on the hydrophobic sites where the oxygen-containing groups are absent ("A" sites pointed in GO) \[35,36\]; (2) The size of the produced metal oxides particles can be controlled easily in the range of several nanometers. The freeze-drying and then annealing treatments lead to the dark fluffy products (Fig. S2a), which are beneficial for good electrode materials/electrolyte contact. Mesoporous Nb₂O₅ (mNb₂O₅) nanosheets (Fig. S2b) prepared by annealing treatment of as-hydrolyzed products in air exhibit white color, indicating that the graphene sheets are wiped out. The morphology of the prepared G@mNb₂O₅ nanosheets was investigated by SEM, TEM, HRTEM, and AFM. Fig. 1a shows that the nanosheets are well dispersed and no aggregations due to the freeze-drying treatment. Magnified SEM image of a nanosheet clearly demonstrates that both sides of the graphene are uniformly covered by the Nb₂O₅ nanoparticles, forming sandwich-like nanosheets (Fig. 1b). As shown in the bright-field TEM image of Fig. 1c, the homogenous contrast of the entire nanosheet confirms the uniform distribution of Nb₂O₅ nanoparticles on graphene. A higher-magnification TEM image further verifies the uniform cover of the Nb₂O₅ nanoparticles on graphene due to the controlled hydrolysis (Fig. S3). It is evident that these Nb₂O₅ nanoparticles are very uniform with an average diameter lower than 10 nm. Such several nanometer-sized nanoparticles are believed to be able to provide the ultra-short Na-ion diffusion for feasible ion insertion/extraction process, as well as the high surface pseudocapacitive energy storage \[1,17,23,27\]. In addition, existence of the mesopores could be verified by the contrast difference between the nanoparticles. Remarkably, TEM image reveals that the graphene sheet is uniformly covered by Nb₂O₅ nanoparticles but with exposed edges, which may be originating from the framework shrinkage of the covered Nb₂O₅ layers during the annealing process (Fig. 1d). Furthermore, cross-sectional HRTEM image of a G@mNb₂O₅ nanosheet clearly shows the typical sandwich-like structure in which a graphene sheet composed with several carbon atom layers is uniformly covered by Nb₂O₅ but with exposed edges (Fig. 1e). As shown in the HRTEM image (Fig. 1f), spacing of 0.24 and 0.31 nm are well matched to the \(d_{181}\) and \(d_{180}\) of orthorhombic Nb₂O₅. A mesopore with a diameter of ca. 5 nm (appointed by the red dotted line circle) is also found in the HRTEM image.

The uniform coating nature of the G@mNb₂O₅ nanosheets can be further unraveled by the typical scanning TEM image as well as the corresponding element mapping images because of the highly homogeneous distribution of carbon, niobium, and oxygen in the nanosheets (Fig. 1g). The AFM and thickness analyses (Fig. 1h,i) reveal the same morphology and structure as the observations from the SEM and TEM images. It directly indicates that the G@mNb₂O₅ nanosheets are constructed by two uniform Nb₂O₅ layers, and the total thickness of the nanosheets is ca. 24 nm. On the other hand, as shown in SEM and TEM figures of mNb₂O₅ nanosheets (Fig. S4a-S4c), it is interesting to find that the annealing removal of embedded graphene sheet in air does not lead the collapse of nanosheet morphology of the loaded Nb₂O₅ layer, indicating the stable and strong physical interaction.
among the as-hydrolyzed Nb$_2$O$_5$ nanoparticles. The Com-Nb$_2$O sample demonstrates a bulk character within scale of several microns and low specific surface area of 4.3 m$^2$ g$^{-1}$ (Fig. S4d, S4e). To further confirm the chemical constituents in the G@mNb$_2$O$_5$ nanosheets, XPS examinations of the same chemical elements detected in G@mNb$_2$O$_5$ nanosheets and mNb$_2$O$_5$ nanosheets show no impurities in the samples (Fig. S5a), while the pure C–C bond signals detected in the G@mNb$_2$O$_5$ nanosheets indicate the embedded graphene oxides are fully reduced to graphene (Fig. S5b), leading them to be the effective electron transport pathway when redox occurs in Nb$_2$O$_5$.

By using the nitrogen physisorption measurements (Fig. 2a), it further confirms the existence of mesopores in the G@mNb$_2$O$_5$ nanosheets from the type-IV hysteresis loop. The Brunauer-Emmett-Teller (BET) calculation demonstrates that the specific surface area of the G@mNb$_2$O$_5$ nanosheets is as high as 366 m$^2$ g$^{-1}$, which is much higher than that of mesoporous Nb$_2$O$_5$/carbon composites (96 m$^2$ g$^{-1}$) [27], Nb$_2$O$_5$/graphene mesoporous nanocomposites (158 m$^2$ g$^{-1}$) [32], and Nb$_2$O$_5$@C nanoparticles/rGO composites (253 m$^2$ g$^{-1}$) [33]. As shown in the pore size distribution inserted in Fig. 2a, the G@mNb$_2$O$_5$ nanosheets possess rich mesopores with pore diameter approximately from 1 to 4 nm. In addition, the mNb$_2$O$_5$ nanosheets exhibit similar nitrogen adsorption-desorption loop, pore size distribution, and specific surface area (315 m$^2$ g$^{-1}$) to G@mNb$_2$O$_5$ nanosheets, further indicating the stable physical interactions among the Nb$_2$O$_5$ nanoparticles. The crystallographic information of G@mNb$_2$O$_5$ nanosheets and mNb$_2$O$_5$ nanosheets are collected by XRD. As shown in Fig. 2b, both the diffraction patterns of the two samples match well with the orthorhombic Nb$_2$O$_5$ (JCPDS card no. 30-0873), which has been reported to deliver a superior lithium storage rate performance in regard to other Nb$_2$O$_5$ phases [8]. On the other hand, the existence of graphene can be verified by the Raman signals of D and G bands (Fig. 2c) [37]. The same intensity of these two bands shows that the graphene oxides are almost completely reduced during the annealing process [38], which fits well with the XPS examination results. The absence of D and G bands belonging to graphene in the mNb$_2$O$_5$ nanosheets further verifies the embedded graphene sheets are almost completely removed by annealing. Meanwhile, the Raman band locating at 707 cm$^{-1}$ corresponds to the symmetric stretching mode of the NbO$_6$ octahedra [39]. Thermogravimetric analysis (TGA) of the G@mNb$_2$O$_5$ nanosheets reveals that the weight fraction of graphene in the as-prepared products is about 13.8% by mass with a weight loss of ca. 3.2% derived from absorbed water [32] (Fig. 2d).

The electrochemical behavior of the G@mNb$_2$O$_5$ nanosheets was investigated in a Na-ion half-cell using sodium foil as both the counter and reference electrodes. Fig. 3a demonstrates the comparison of cyclic voltammetry (CV) data of G@mNb$_2$O$_5$ nanosheets, mNb$_2$O$_5$ nanosheets, and Com-Nb$_2$O$_5$ at a sweep rate of 3 mV s$^{-1}$ in the potential range from 0.01 to 2.5 V (vs. Na+/Na$^+$). The three electrodes exhibit obvious cathodic redox peaks at almost same potential of approximately 0.54 V, indicating that the Nb$_2$O$_5$-based sodiation makes a major energy storage contribution in these electrodes. However, difference arises as to the anodic redox peaks. Compared to the apparent desodiation peaks of G@mNb$_2$O$_5$ and mNb$_2$O$_5$ nanosheets electrodes, the bulk character of Com-Nb$_2$O$_5$ hinders the Na-ion extraction kinetics, giving rise to an anodic redox wave. In another aspect, the largest CV curve area of G@mNb$_2$O$_5$ nanosheets electrode indicates their superior energy storage performance and fast Na-ion redox kinetics in the three samples. We believe that the improved Na-ion insertion/extraction and the enhanced surface redox contribution are two main positive factors. The increased current response between 0.01 and 1 V derives from the first factor, while the second factor leads to the enlarged CV curve area in the remained potential range from 1 to 2.5 V, where both the mNb$_2$O$_5$ nanosheets and Com-Nb$_2$O$_5$ electrodes exhibit relatively low current response. By calculating the charge storage ($Q$) of the three electrodes according to the equation:

$$Q = \int i dV/v(2v)$$

where $i$ is the current, $V$ is the potential, and $v$ presents the sweep rate.

It can be calculated that the G@mNb$_2$O$_5$ nanosheets electrode provides a capacity of ~ 440 C g$^{-1}$, which is higher than the mNb$_2$O$_5$ nanosheets (~ 240 C g$^{-1}$) and Com-Nb$_2$O$_5$ (~ 102 C g$^{-1}$) electrodes, and is comparable to other high-performance Li-ion electrodes [8,30,31]. As shown in Figs. 3b, 8e, for the G@mNb$_2$O$_5$ nanosheets electrode, the
cathodic peak shift (the potential difference between anodic peak and cathodic peak) is ≤0.1 V at the sweep rates below 1 mV s⁻¹. Additionally, the nanosheets electrode exhibits a good CV curve shape maintenance even when the sweep rate increases to 100 mV s⁻¹. These phenomena imply that G@mNb₂O₅ nanosheets electrode captures highly reversible Na-ion redox kinetics.

Fig. 3c compares the charge storage capability of the three electrodes at sweep rates from 0.1 to 100 mV s⁻¹. For a typical voltage window at 0.01–2.5 V, these rates correspond to a charge/discharge time between 24.9 and 24900 s. Among the three electrodes, the Com-Nb₂O₅ electrode exhibits the lowest charge storage capacity at any charge/discharge time due to the bulk nature. The mNb₂O₅ nanosheets electrode without embodied graphene exhibits a fast capacity degradation. The electrode holds 119 and 32 C g⁻¹ when the charging time decreases to 2490 and 24.9 s (corresponding to sweep rate of 1 and 100 mV s⁻¹, respectively). In contrast, the G@mNb₂O₅ nanosheets electrode exhibits a substantially higher capacity of 543 and 148 C g⁻¹ at 2490 and 24.9 s, respectively. The substantial charge storage occurring in the order of a few minutes or less is a characteristic feature of capacitive storage.[1,13,30] Galvanostatic charge/discharge measurements were used to further investigate the sodium storage properties from 0.01 to 2.5 V (vs. Na/Na⁺). The G@mNb₂O₅ nanosheets electrode delivers a high capacity of ~293 mAh g⁻¹ at 50 mA g⁻¹ after the first Na-ion charge/discharge process of amorphization, indicating that the redox occurring in the G@mNb₂O₅ nanosheets is highly reversible (Fig. 3d). And this capacity value is comparable to that of graphene-silica template-assistant prepared Nb₂O₅/graphene mesoporous nanocomposites (ca. 300 mAh g⁻¹ at 50 mA g⁻¹) [32] and multi-step hydrothermally prepared Nb₂O₅@C nanoparticles/rGO composites (285 mAh g⁻¹ at 25 mA g⁻¹) [33], but is much higher than that of P123-assisted prepared mesoporous Nb₂O₅ (175 mAh g⁻¹ at 50 mA g⁻¹) [27] and hydrothermally prepared self-assembled Nb₂O₅ nanosheets (165 mAh g⁻¹ at 50 mA g⁻¹) [34]. Meaningfully, compared to the first-circle discharge curves of other Nb₂O₅-based nanomaterials [27,32,33], the much shorter constant-voltage region of G@mNb₂O₅ nanosheets indicates the high surface redox contribution and the undergoing rapid redox kinetics [1,40]. The charge/discharge curves of the G@mNb₂O₅ nanosheets electrode at various current densities from 50 to 4000 mA g⁻¹ maintain almost the same profile, as shown in Fig. 3e, indicating its sustainable Na-ion energy storage behavior in a wide operation current range. Moreover, the charge/discharge profiles of the G@mNb₂O₅ nanosheets electrode exhibit a featureless slope nature, which might imply that the sodiation/desodiation process occurring in the G@mNb₂O₅ nanosheets is mainly capacitive.[1,30,40].

The variations of the specific capacity with the current density of
the G@mNb2O5 nanosheets, mNb2O5 nanosheets, and Com-Nb2O5 electrodes were plotted in Fig. 3f. It is noted that the specific capacity of the three electrodes decreases with the increase of the current density due to the increased electrochemical polarization and limited redox time [28,40]. However, the maintained capacity of the G@mNb2O5 nanosheets electrode under high current densities is rather superior. For the G@mNb2O5 nanosheets electrode, the specific capacity decreases from 293 to 183 mAh g\(^{-1}\) as the current density goes from 50 to 500 mA g\(^{-1}\). Even when the current density is as high as 2000 and 4000 mA g\(^{-1}\), a high specific capacity of 125 and 98 mA h g\(^{-1}\) could be maintained, respectively. Although the mNb2O5 nanosheets electrode captures a similar specific surface area and mesopore distribution to those of the G@mNb2O5 nanosheets, it exhibits a poor rate performance. The mNb2O5 nanosheets electrode shows a similar specific capacity to that of G@mNb2O5 nanosheets electrode during the first two cycles at 50 mA g\(^{-1}\), but it decays fast in the following three cycles. In addition, the mNb2O5 nanosheets electrode only delivers a low specific capacity of 48 and 40 mA h g\(^{-1}\) at 2000 and 4000 mA g\(^{-1}\), respectively. However, these values are still twofold higher than those of the Com-Nb2O5 electrode (25 and 20 mA h g\(^{-1}\) at 2000 and 4000 mA g\(^{-1}\), respectively). The G@mNb2O5 nanosheets electrode also exhibited better rate performance than electrodes of Nb2O5 nanopowders (Nano-Nb2O5) and Nb2O5 nanosheets with 17% reduced graphene oxide addition (denoted as G@mNb2O5 nanosheets), indicating the electrochemical superiority of G@mNb2O5 nanosheets. Thus, we can conclude that both incorporation of graphene and mesopores Nb2O5 with ultra-short diffusion distance are vital merits to obtain superior performance sodium storage G@mNb2O5 nanosheets. The G@mNb2O5 nanosheets electrode also exhibits high cycling stability. As shown in Fig. 5g, although there is an undesired small degradation during the initial several tens of cycles, a high and stable specific capacity maintains with a Coulombic efficiency of 100% at a high current density of 2000 mA g\(^{-1}\) for 2000 cycles. Furthermore, as exhibited in the HRTEM image of one nanosheet after long-term cycling test in Fig. S8, although the amorphization during the discharge processes destroys the regular atomic arrangement of crystalline Nb2O5 to some extent. The nanosheet still possesses a mesoporous structure, demonstrating the structural stability of G@mNb2O5 nanosheets. Such desirable structural stability is favorable to the long-term cycling stability of G@mNb2O5 nanosheets electrode.

To better understand the influence of the nanostructure on sodiation/desodiation kinetics of the G@mNb2O5 nanosheets electrode, various electroanalytical methods were used. Fig. 4a shows the plot of normalized capacity versus \(v^{1/2}\) in the two electrodes. It demonstrates that the capacity of the G@mNb2O5 nanosheets electrode does not vary significantly as the sweep rate varies in the range of 0.1–1 mV s\(^{-1}\). It indicates that capacitive energy storage is independent of the sweep rate and makes the main contribution to the total energy storage in the electrode [17,30,40]. Such stable capacitive contribution is consistent with the small cathodic peak shift in the same sweep rate range in the CV examinations. In contrast, the mNb2O5 nanosheets electrode demonstrates fast capacity degradation, indicating the occurrence of strong rate-limited diffusion process. The relatively acceptable normalized capacity retention of Com-Nb2O5 electrode is due to the intrinsic low energy storage character.

The surface redox contribution to the total energy storage was further investigated. Assuming that the peak current (i) in the CV curves obeys a power-law relationship to the sweep rate (v), it exhibits the following relation [29,40–42]:

\[
i = av^b
\]

(4)

where \(a\) and \(b\) are adjustable values. A \(b\)-value of 0.5 indicates a diffusion-controlled current response, whereas a value of 1 represents the surface-controlled current, namely capacitive. Figs. 4b, S9 present the plots of \(\log i\) vs \(\log v\) for both cathodic and anodic peaks, respectively. The significant difference about \(b\)-values of the G@mNb2O5 nanosheets, mNb2O5 nanosheets, and Com-Nb2O5 electrodes clearly indicates the micro/nanostructure-dependent sodiation/desodiation kinetics of Nb2O5-based materials [27,32–34]. For both cathodic and anodic peaks, the G@mNb2O5 nanosheets electrode exhibits high and same \(b\)-value of 0.92, indicating that the majority of the Na-ion storage is capacitive. In addition, the \(b\)-values of G@mNb2O5 nanosheets electrode is higher than that of the mNb2O5 nanosheets electrode (0.88 and 0.9 for cathodic and anodic peaks, respectively), which could be attributed to the integration with graphene sheets. Although different factors such as an increase of the ohmic contribution and diffusion constraints would lead to the decrease of \(b\)-values, when the sweep rate is higher than 10 mV s\(^{-1}\) [29,41–43]. The G@mNb2O5 nanosheets electrode still presents a higher anodic \(b\)-value of 0.64 than that of mNb2O5 nanosheets electrode (0.47). These high \(b\)-values further confirm that the integration with high electrical conducting graphene sheets is an important factor for the high-rate capability of G@mNb2O5 nanosheets electrode. In addition, compared to mNb2O5 nanosheets electrode, the bulk Com-Nb2O5 electrode demonstrates much lower cathodic \(b\)-value of (0.7), indicating that nanostructure engineering treatment is another non-substitutable factor to realize the high-rate capability of Nb2O5 materials.

It is possible to quantitatively separate the capacitive \((k_1v)\) and diffusion-controlled charge \((k_2v^{1/2})\) at a fixed voltage (V) within the following equation [41–43]:

\[
\text{i(V)} = k_1v + k_2v^{1/2}
\]

(5)

where \(i(V)\) is the measured current at a fixed potential (V) under a certain sweep rate, \(k_1\) and \(k_2\) are adjustable values. As shown in Fig. 4c, for G@mNb2O5 nanosheets electrode at 0.2 mV s\(^{-1}\), the diffusion-controlled charge is mainly generated around the cathodic peak in the potential range from 0.01 to 0.4 V, whereas the capacitive contribution arises predominately in the following potential range. Furthermore, the diffusion-controlled current response significantly decreases when the sweep rate increases to 1 mV s\(^{-1}\) (Fig. S10). The results indicate the sodiation/desodiation process in G@mNb2O5 nanosheets is feasible [41–43]. Based on the quantification, 48.2% of the total charge (therefore, the capacity) is capacitive in G@mNb2O5 nanosheets electrode at a sweep rate of 0.2 mV s\(^{-1}\), whereas the capacitive contributions of mNb2O5 nanosheets and Com-Nb2O5 electrodes are only 17.5% and 9.8%, respectively (Fig. 4d). At 10 mV s\(^{-1}\), the capacitive contribution of G@mNb2O5 nanosheets electrode increases up to 93.4%, whereas the mNb2O5 nanosheets and Com-Nb2O5 electrode exhibit values of 59.2% and 19.7%, respectively. The high \(b\)-values and capacitive contribution of G@mNb2O5 nanosheets electrode are related to its high-rate capability.

Electrochemical impedance spectroscopy (EIS) measurement was performed to further investigate the sodiation/desodiation kinetics. According to the Nyquist plots illustrated in Fig. 5a and the modeling results (Table S1) based on the equivalent circuit in Fig. S11, the as-prepared G@mNb2O5 nanosheets electrode demonstrates a lower charge-transfer resistance \((R_{ct})\) and a higher exchange current density \((i_0)\) than those of the mNb2O5 nanosheets and Com-Nb2O5 electrodes due to the integration with high electrical conducting graphene, as well as mesoporous character of the loaded Nb2O5 layers. Moreover, the distinctly different slopes of the curves in the low frequency region show that these electrodes possess different solid-state ion diffusion behaviors (Fig. 5b). From the fitting plots of \(Z'\) vs \(\omega^{-1/2}\) (Here \(Z'\) is the respective real parts of the complex impedance \(Z\). \(\omega\) is the angular frequency), it is found that the G@mNb2O5 nanosheets electrode exhibits lower \(Z'\) vs \(\omega^{-1/2}\) slope than those of the mNb2O5 nanosheets and Com-Nb2O5 electrode, indicating its faster Na-ion diffusion process. The Na-ion diffusion coefficients \((D_{Na-ion})\) of these electrodes are calculated according to the following equation [32,44]:

\[
D_{Na-ion} = \frac{RT^2}{(2\pi^2n^4F^4C^2\sigma^4)}
\]

(6)
where \( R \) is the gas constant, \( T \) presents the absolute temperature, \( A \) is the electrode surface area, \( n \) is the number of redox electrons, \( F \) is the Faraday constant, \( C \) is the molar concentration of Na-ion in the Nb2O5 crystal, and \( \sigma_w \) is the Warburg impedance. As a result, the \( G@m\text{Nb}_2\text{O}_5 \) nanosheets electrode possesses a \( D_{\text{Na-ion}} \) of \( 9.86 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \), which is much higher than that of the \( \text{mNb}_2\text{O}_5 \) nanosheets and \( \text{Com-Nb}_2\text{O}_5 \) electrode (\( 1.03 \times 10^{-16} \text{ and } 2.17 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \), respectively). The enhanced \( D_{\text{Na-ion}} \) of \( G@m\text{Nb}_2\text{O}_5 \) nanosheets electrode confirms the importance of integration with the high electrical conducting graphene sheets.

EIS measurements also provide the complementary information about the frequency response of the electrode materials in supercapacitors, the capacitance of which changes with the operating frequency can be estimated [43]. The complex form of capacitance is dependent on frequency, which is defined as the following formulae:

\[
C(\omega) = C'(\omega) - jC''(\omega)
\]

(7)

\[
C'(\omega) = -Z'/\{\omega |Z(\omega)|^2\}
\]

(8)

\[
C''(\omega) = -Z''/\{\omega |Z(\omega)|^2\}
\]

(9)

where \( C'(\omega) \) and \( C''(\omega) \) are the real part and imaginary part of the
complex capacitance $C'(\omega)$, respectively. $Z' (\omega)$ and $Z'' (\omega)$ are the respective real and imaginary parts of the complex impedance $Z(\omega)$. At low frequency, $C'(\omega)$ corresponds to the capacitance of the electrode material and $C''(\omega)$ is ascribed to the energy dissipation by an irreversible process that leads to a hysteresis. Figs. 5c, d, S12 demonstrate the normalized real and imaginary part capacitance as a function of frequency for the G@mNb2O5 nanosheets, mNb2O5 nanosheets, and Com-Nb2O5 electrodes, respectively. By comparing the frequencies at which the capacitance drops to 50% of its maximum value ($f_0$), it is found that the G@mNb2O5 nanosheets electrode demonstrates a fastest frequency response with $f_0$ of 0.43 Hz among the three samples, indicating the superior Na-ion and electron transport speed, and better accessibility of the electrolyte ions. On the other hand, the characteristic relaxation time constant ($\tau_0$) can be calculated from the plots of $C''$ vs. $f$. Typically, a long $\tau_0$ suggests that a larger part of energy is dissipated as resistive losses [45,46]. As shown in the figures, the obvious inflection point of the G@mNb2O5 nanosheets electrode indicates the reversible Na-ion redox kinetics in it. Furthermore, $\tau_0$ of the G@mNb2O5 nanosheets electrode is 383 ms, which is lower than that of the mNb2O5 nanosheets and Com-Nb2O5 electrodes (682 and 460 ms, respectively). This value of G@mNb2O5 nanosheets electrode is much lower than that of the carbonaceous materials in organic electrolytes ($\tau_0 \geq 1$ s) [47,48], and comparable to the values of many metal oxide nanostructures in high-mobility aqueous electrolytes, such as Ni(OH)$_2$/graphene composites and Ni(OH)$_2$ nanoflakes (392 and 1239 ms, respectively) [49], NiCO$_3$O$_4$ nanoparticles (250 ms) [50], and RuO$_2$/Carbon nanofibers composites (230 ms) [51]. These faster frequency response and lower characteristic relaxation time constants correlate with the better capacitance retention at high sweep rates in the CV measurements or higher current densities in charge/discharge tests for the G@mNb2O5 nanosheets electrode.

Based on the above results, it is found that the G@mNb2O5 nanosheets are ideal anode material candidate for Na-ion hybrid supercapacitors due to the high specific capacity, high-rate performance, and desirable cycling stability. The excellent electrochemical performances can be ascribed to its rapid Na-ion redox kinetics, including significantly increased surface pseudocapacitive contribution, improved sodium-ion diffusion coefficient, and short characteristic relaxation process. In addition, the embedded graphene sheets provide effective electrical conducting pathways for the stable and high-rate sodium storage performance.

Coin-type asymmetric supercapacitors employing the G@mNb2O5 nanosheets as anode materials were assembled to assess the feasibility for practical sodium-ion energy storage devices. A commercial activated carbon (AC, BET specific surface area of 2084.15 m$^2$ g$^{-1}$, XinSen Carbon Industry Co., Ltd) was used as the cathodic material. The assembled devices are named as G@mNb2O5//AC Na-ion hybrid ESCs. Fig. S13a shows typical CV curves of the AC electrode in NaClO$_4$ electrolyte between 2.3 to 3.8 V (vs Na/Na$^+$) from 2 to 30 mV s$^{-1}$. The featureless rectangle shape indicates an ideal behavior of the electrochemical double layer capacitance. The specific capacity of the AC electrode was determined by galvanostatic charge-discharge test, and the results are shown in Fig. S13b. For the assembly of hybrid supercapacitors, the optimum mass ratio of anode and cathode is calculated using the specific capacity at 0.5 A g$^{-1}$, based on balancing the charge storages in cathode and anode. The mass ratio of G@mNb2O5 nanosheets and AC is set as 1:4.4. The reason of using specific capacity obtained at 0.5 A g$^{-1}$ is because that the assembled cells mainly operate under high current densities.

Hybrid cells operate with Na-ion insertion into the anode and perchlorate anion absorption onto the carbon cathode during charging process, while the discharge involves Na-ion extraction and perchlorate anion desorption. Such working mechanism could deliver high-energy and high-power energy storage performance [1–5]. The devices show an open circuit potential of ~0.1 V. Therefore, the galvanostatic charge-discharge tests were performed from 0.1 V to different cut-off voltages to identify a suitable operating window. Fig. 6a presents the charge/discharge curves of the G@mNb2O5//AC Na-ion hybrid ESCs at 0.05 A g$^{-1}$ with different cut-off voltages from 2.1 to 2.7 V, namely cell voltage from 2.0 to 2.6 V. These curves exhibit an almost triangular shape with small deviations from linearity, indicative of pseudocapacitive energy storage nature of Nb$_2$O$_5$. In addition, the chronopotentiometric profiles of the charge process approximately follow the same
trace under the cut-off voltage of 2.5 V, suggesting that both sodiation/desodiation on anode and perchlorate anion absorption/desorption on cathode are rather stable and reversible under cell voltage of 2.4 V, which can also be verified by the high Coulombic efficiency over 93.1%. Further increasing the cell voltage causes appreciable irreversible capacitance with decreased Coulombic efficiency (88.2% and 79.2% for cell voltage of 2.5 and 2.6 V, respectively), which should be avoided for long-term device operation. Therefore, the cut-off voltage is controlled at 2.5 V for the device configuration. Furthermore, the G@mNb2O5//AC device delivers a high specific capacitance (C_s) of 34 F g⁻¹ at current density of 0.05 A g⁻¹ (capacitance is calculated based on the total mass of cathode and anode active materials), giving an energy density of 56.1 Wh kg⁻¹ and a power density of 120 W kg⁻¹.

The charge/discharge curves of G@mNb2O5//AC, mNb2O5//AC (mNb2O5 nanosheets as anode materials), Com-Nb2O5//AC (Com-Nb2O5 as anode materials), and AC//AC Na-ion ESCs at 0.05 A g⁻¹ in the voltage range of 0.1–2.5 V are illustrated in Fig. 6b. Accompanying with decreased Coulombic efficiency of 77% and C_s of 21 F g⁻¹, the charge/discharge profile of mNb2O5//AC device demonstrates more apparent deviations from linearity than that of the G@mNb2O5//AC device. It indicates the relatively poor reversibility of Na-ion insertion/extraction and perchlorate anion absorption/desorption process in mNb2O5//AC device due to the lack of graphene as efficient electron transport pathway. In another aspect, the much lower C_s of 9 F g⁻¹ obtained in the commercial Com-Nb2O5//AC devices is due to the bulk character. Finally, the perfect symmetric shape of the charge/discharge curve with no deviations from linearity in AC//AC Na-ion ESCs is consistent with the pure electrochemical double layer ion absorption/desorption-based energy storage mechanism in AC. Furthermore, the G@mNb2O5//AC device also exhibited higher C_s than the Na-ion hybrid ESCs respectively fabricated by using Nano-Nb2O5 (14 F g⁻¹) and G-mNb2O5 nanosheets (23 F g⁻¹) as anode materials (Fig. S14).

Fig. 6c presents the representative galvanostatic charge/discharge curves for the G@mNb2O5//AC device at different current densities from 0.1 to 3 A g⁻¹. At a discharge time of 11.2 min (0.1 A g⁻¹), the devices provide an overall cell capacitance of ca. 28 F g⁻¹, leading to an energy density of 49.5 Wh kg⁻¹ and a power density of 240 W kg⁻¹. The energy density is close to that of the lithium-ion asymmetric devices [7–10]. Even at a power density of ~7200 W kg⁻¹ (charge and discharge time of 4.9 s at 3 A g⁻¹), the devices still provide a desirable cell capacitance of ~6.1 F g⁻¹, corresponding to an energy density of ~9.7 Wh kg⁻¹, indicative of the high power performance. The Ragone plots of the G@mNb2O5//AC, mNb2O5//AC, Com-Nb2O5//AC, AC//AC, and several representative Na-ion ESCs [13–19] are compared in Fig. 6d. The as-assembled devices offer significantly higher energy and power than that of AC-based symmetric cells and the current state-of-the-art electrical double-layer capacitors fabricated with commercial high-performance AC materials [13]. Moreover, the higher energy/power densities of the as-assembled cell are favorably compared with many reported Na-ion ESCs [7–9,13–19], indicating the energy storage superiority of the as-developed G@mNb2O5//AC ESCs.

The cycling performance of the G@mNb2O5//AC Na-ion ESC was evaluated with galvanostatic charge/discharge tests at 1 A g⁻¹ for 4500 cycles. As shown in Fig. 6e, the device demonstrates high and stable capacitance retention of ~89% after initial 800 cycles. Additionally, the Coulombic efficiency stays at around 100% during the course of measurement, indicating the excellent reversibility of the assembled device. After 4500 cycles, the charged device can still lighten four red LEDs for a long time (Inset photos in Fig. 6e), confirming its electrochemical stability. Such long-term cycling performance makes the as-fabricated G@mNb2O5//AC ESC device possess promising potential for practical applications. In contrast, both mNb2O5//AC and Com-Nb2O5//AC Na-ion ESCs display a continuous capacitance degradation during the cycling tests, reaching to a low capacitance retention of 45.3% and 24.6% after 4000 cycles (Fig. S15).

4. Conclusions

In summary, we demonstrated a facile two-step hydrolysis approach to prepare uniform mesoporous Nb2O5/graphene/semimoporous Na2O2 (G@mNb2O5) nanosheets as sodium-ion host material. The as-prepared nanosheets possess large specific surface area (366 m² g⁻¹) and mesoporous Nb2O5 layers formed by stack of several nanometer-sized Nb2O5 particles for ultra-short Na-ion diffusion distance, leading to a reversible specific capacity of 293 mAh g⁻¹ at 50 mA g⁻¹, and a high-rate capability 125 mAh g⁻¹ at 2000 mAh g⁻¹ with an excellent cycling stability over 2000 cycles. Kinetics analysis reveals that the integration of high electrical conducting graphene, significantly increased surface pseudocapacitive contribution, improved sodium-ion diffusion coefficient, and short characteristic relaxation process are vital origins. By employing the G@mNb2O5 nanosheets as anode and activated carbon as cathode, a novel sodium-ion hybrid supercapacitor exhibits a high energy density of 56.1 Wh kg⁻¹ at a power density of 120 W kg⁻¹, and 9.7 Wh kg⁻¹ at a high power output of 7200 W kg⁻¹. Moreover, the device also exhibits high and stable capacitance retention of ~89% after initial 800 cycles at 1 A g⁻¹. The results demonstrate the feasibility of G@mNb2O5 nanosheets using as the electrode for cost-effective long-term sodium-ion hybrid supercapacitors with high energy and power densities. In addition, the presented synthesis method can be used as guidelines for the development of functional materials for energy storage devices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.12.005.

References


