Leaf-Like V₂O₅ Nanosheets Fabricated by a Facile Green Approach as High Energy Cathode Material for Lithium-Ion Batteries

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Lithium-ion batteries (LIBs) have attracted considerable attention due to their wide applications, such as in portable electronic devices, implantable medical devices, and electric vehicles (EVs).[1] To meet the constantly increasing demands of upcoming electronic devices, new LIBs require substantial improvements in energy capacity, cycling stability, and rate capability of both the cathode and anode materials.[2,3] Among cathode materials for LIBs, orthorhombic vanadium pentoxide (V₂O₅) is the most stable form in the vanadium oxide family, has gained great interest due to its high energy density, low cost, abundant sources, and good safety properties.[4–7]

The theoretical capacity of V₂O₅ with two Li intercalations/deintercalations is about 294 mA h g⁻¹, much higher than those of more commonly used cathode materials, making it a very promising cathode material for next-generation LIBs. However, the practical use of V₂O₅ as cathode materials for LIBs has been hampered due to its poor cycling stability, low electronic and ionic conductivity, and slow electrochemical kinetics.[8–10] To overcome these problems, decreasing their particle size to nanoscale level is generally believed to be one of the most effective approaches due to the shorter transport lengths for both electrons and Li ions, larger electrode/electrolyte contact area, and better accommodation of the strain of Li intercalation/deintercalation in nanomaterials.[11,12] The unique performance of nanomaterials lies in their large specific surface area and favorable structural properties. 2D nanosheets often possess large exposed surfaces and specific facets, which make them more attractive in energy conversion devices.[13] 2D structures are ideal frameworks for fast Li storage, which requires stability, large active surface area, and short transport path for Li intercalation/deintercalation.[14] There have been many researches on nanstructured V₂O₅ materials for LIBs.[4–7,15–20] However, there are few reports on 2D nanostructured V₂O₅ for LIBs. The only report on 2D nanostructured V₂O₅ was that Zhang’s group prepared large-area pure V₂O₅ nanosheets by dissolution-splitting method from their parent bulk crystal using ammonium persulfate as intercalated compound.[15] The method is a typical top-down method. The as-prepared product exhibits enhanced lithium storage properties including high reversible capacity, good cycling, and rate performance.

In this communication, we demonstrate a novel and facile green method to prepare 2D leaf-like V₂O₅ nanosheets as illustrated in Figure 1. V₂O₅ powders were reacted with H₂O₂ in combination with ultrasonic treatment to generate V₂O₅ gel. Then the V₂O₅ gel was diluted, freeze-dried, and further treated at 450 °C in air to obtain V₂O₅ nanosheets. Used as cathode material for LIBs, this 2D leaf-like V₂O₅ nanosheets exhibits excellent Li storage properties, including high reversible capacity, high rate capability, and good capacity retention upon cycling. The low-cost raw materials (only commercial V₂O₅ powder and H₂O₂ without using any templates) and facile experimental procedures favorably enable the method suitable for large-scale production.

Figure 2 presents the FESEM and TEM images of the V₂O₅ nanosheets annealed at 450 °C for 1 h in air. It can be clearly seen that the prepared V₂O₅ has a large-area 2D leaf-like structure (Figure 2a). The thickness of the V₂O₅ nanosheets is 60–80 nm (Figure 2b). From the SEM image shown in Figure 2b, one can find that the V₂O₅ nanosheet actually is polycrystalline and consists of small nanorods. The TEM image (Figure 2c) further confirms the 2D sheet structure of the prepared V₂O₅. The high resolution (HR) TEM image (Figure 2d) of the V₂O₅ nanosheet displays clear lattice fringes with a spacing of 0.26 nm and is indexed to the (310) planes of orthogonal V₂O₅ (JCPDS

![Figure 1. Schematic illustration of the synthesis route of 2D leaf-like V₂O₅ nanosheets in this work.](image)
card No. 41-1426). The mechanism for the formation of this 2D V₂O₅ nanosheet can be described as follows. During the process of freeze drying, the ribbon-like V₂O₅ fibers intertwines into sheets V₂O₅ during the removal of solvent from the V₂O₅ gel. The freeze-dried V₂O₅ cryogel consists of long nanobelts which are less than 100 nm wide (see Supporting Information, Figure S2). These nanobelts morphology could be related to the formation of hydrous V₂O₅ as previously reported in literature,[22,23] and this is in good agreement with the XRD diffraction results (see Supporting Information, Figure S3). When the V₂O₅ cryogel are annealed in air at 450°C, the hydrous V₂O₅ nanobelts grow into small nanorods and formed orthorhombic leaf-like V₂O₅ nanosheets.

Figure 3a shows the XRD pattern of the V₂O₅ nanosheets annealed at 450 °C for 1 h in air. All the diffraction peaks can be indexed to an orthorhombic phase V₂O₅ (JCPDS card No. 41-1426) with the lattice parameters of a = 11.488 Å, b = 3.559 Å, c = 4.364 Å, agreeing well with literatures[5,17,18] No secondary phase is observed. The orthorhombic phase V₂O₅ has a layered structure consisting of V₂O₅ layers stacking along the c-axis (the inset of Figure 3a).[22] Nitrogen adsorption/desorption isotherm measurement was carried out and the results are shown in Figure 3b. The Barrett-Joyner-Halenda (BJH) pore size distribution obtained from the isotherm reveals that the sample contains relatively mesoscale pores. The Brunauer-Emmett-Teller (BET) specific surface area has been estimated to be 28 m² g⁻¹.

Figure 4a presents the cyclic voltammetry (CV) profiles of 2D leaf-like V₂O₅ nanosheets electrode for the first two cycles at a scan rate of 0.2 mV s⁻¹. In the first cycle, three intensive reduction peaks located at 3.30, 3.08, and 2.17 V correspond to the phase transitions ε/γ, ε/δ, and δ/γ, respectively.[24] Three obvious oxidation peaks appears during the anodic scanning, at 2.57, 3.35, and 3.48 V, respectively. An additional cathodic peak observed in the high potential region (at 3.56 V) can be ascribed to the irreversible phase transition of the γ/γ’ system.[25] The symmetrical feature of the CV curve suggests a good reversibility of the cycling process. Figure 4b gives the cycling response of 2D leaf-like V₂O₅ nanosheets electrode at various charge/discharge current densities. The discharge capacities measured in the voltage window from 2.0 V to 4.0 V are 303, 273, 251, 219, and 160 mA h g⁻¹ at the current densities of 50, 200, 500, 1000, and 2000 mA g⁻¹, respectively. Even at a very high current density of 5000 mA g⁻¹, the 2D leaf-like V₂O₅ nanosheets electrode can still deliver high capacity of 104 mA h g⁻¹. This rate capability is better than those of nanostructured V₂O₅ electrodes reported in literatures (see Supporting Information, Figure S5).[5,26-29] The results from this study show that the 2D leaf-like V₂O₅ nanosheets structure favorsly reduces the diffusion length for lithium ions and enables the high rate performance of LIBs. With the charge/discharge current density increasing from 50 to 5000 mA g⁻¹, the power density increases from 142 W kg⁻¹ to 8410 W kg⁻¹ (see Supporting Information, Figure S5). Compared to supercapacitors, which addresses the extremes of power density

![Figure 2](image2.png)

**Figure 2.** (a) Low- and (b) high-magnification FESEM images of V₂O₅ nanosheet; (c) TEM image of individual V₂O₅ nanosheet; (d) high resolution TEM (HRTEM) image of the selected area in Figure 2c.

![Figure 3](image3.png)

**Figure 3.** (a) XRD pattern of leaf-like V₂O₅ nanosheets. The vertical lines on the x-axis correspond to the standard XRD reflections of orthorhombic V₂O₅ and the inset shows crystalline structure of layered V₂O₅. (b) N₂ adsorption/desorption isotherm and corresponding BJH pore-size distribution curves (inset) of leaf-like V₂O₅ nanosheets.
It is noticeable that the capacity loss with the plateau of about 3.15 V is much larger than those of others. Therefore, it can be inferred that the 2D leaf-like V_2O_5 processes relatively poorer reversibility for Li intercalation/deintercalation with the voltage plateau of about 3.15 V, which is considered a main reason for capacity fading. The excellent high rate performance of 2D leaf-like V_2O_5 nanosheets is believed to be based on their unique architecture results from the following aspect: The large specific area of the 2D leaf-like V_2O_5 nanosheets facilitates the electrolyte to transport the intercalation and deintercalation of the lithium ions; the hierarchical porous structure of the 2D leaf-like V_2O_5 nanosheets could effectively relax the mechanical strain generated upon the charge/discharge cycling.

Figure 4. (a) CV curves of the first two cycles for leaf-like V_2O_5 nanosheets electrode at a scan rate of 0.2 mV s^{-1}. (b) Discharge capacities of leaf-like V_2O_5 nanosheets electrode at various current densities. (c) Charge/discharge curves of leaf-like V_2O_5 nanosheets electrode at various current densities. (d) Cycling performance of leaf-like V_2O_5 nanosheets electrode at a current density of 500 mA g^{-1}. Inset shows the charge/discharge curves correspond to different cycles.

Even at the 60th cycle. It is noticeable that the capacity loss with the plateau of about 3.15 V is much larger than those of others. Therefore, it can be inferred that the 2D leaf-like V_2O_5 processes relatively poorer reversibility for Li intercalation/deintercalation with the voltage plateau of about 3.15 V, which is considered a main reason for capacity fading. The excellent high rate performance of 2D leaf-like V_2O_5 nanosheets is believed to be based on their unique architecture results from the following aspect: The large specific area of the 2D leaf-like V_2O_5 nanosheets facilitates the electrolyte to transport the intercalation and deintercalation of the lithium ions; the hierarchical porous structure of the 2D leaf-like V_2O_5 nanosheets could effectively relax the mechanical strain generated upon the charge/discharge cycling.

Figure 5a gives the Nyquist plots of the 2D leaf-like V_2O_5 nanosheets electrode at various depth of discharge (DOD) after the electrode was activated at 20 mA g^{-1} for 4 cycles. The semicircle at the high frequency region relates to the combined process of surface film (R_d) and the charge transfer resistance (R_contrib). The low frequency semicircle (for 76%, 90%, and 100%...
DOD corresponds to the bulk phenomena, which arises from electronic conductivity of active material and ionic conductivity of the electrolyte filled in the pores of composite electrode.\cite{10,11} Figure 5b presents the calculated $R_{\text{ct}}$ values (diameter of semicircle at high frequency) under various DOD states. With DOD increasing from 0% to 62%, the $R_{\text{ct}}$ value initially decreases from 853 $\Omega$ to 637 $\Omega$ at 28% DOD and then slightly increases to 660 $\Omega$ at 62% DOD. Further increasing DOD from 76% to 100% leads the $R_{\text{ct}}$ value abruptly increases from 740 $\Omega$ to 1660 $\Omega$. Such a big increase of $R_{\text{ct}}$ value suggests that the electrochemical reaction under high DOD becomes much more difficult than under low DOD due to the change of phase structure. Another important feature of the EIS plots is the appearance of bulk resistance ($R_b$, the second semicircle at low frequency, see Supporting Information, Figure S6) under high DOD (76%, 90%, and 100% DOD) states. This suggests that under those states the electrode is a poor electronic conductor. While under low DOD (from 0% DOD to 62% DOD) states, the bulk resistance ($R_b$) is negligibly small, indicating that electrodes are good electronic conductors. This result is in good agreement with the four-probe current-voltage characteristics for Li$_x$V$_2$O$_5$ nanoribbons reported by Cui et al.\cite{34} Large changes in $R_b$ values have also been observed in other cathode materials,\cite{30–34} depending on the DOD, and are attributed to reversible semiconductor-metal transformations during cycling.

In summary, we have developed a facile, green, and low-cost synthesis of 2D leaf-like V$_2$O$_5$ nanosheets. The unique nanoscale characteristics, including 2D morphology, hierarchical porous structure, large specific surface, of these 2D V$_2$O$_5$ nanosheets leads to the superior electrochemical performance in terms of their specific capacity, rate capability, and cyclability when they are used as a cathode material for LIBs. The obtained excellent performance opens up new opportunities in the development of high performance next-generation LIBs used for alternative energy and electric transportation. The proposed synthetic method may be easily extended to other layered materials which can be used in broad fields including catalysis and sensors.

**Experimental Section**

Material preparation: Vanadium pentoxide gel was prepared using the method reported by Frontenot et al.\cite{33} In brief, V$_2$O$_5$ powders (99.8%, Alfa-AESAR) were added into de-ionized water and H$_2$O$_2$ (30 wt.% in H$_2$O, Sigma-Aldrich) to form a solution with a V$_2$O$_5$ concentration (C$_v$) of 0.3 M and n(H$_2$O$_2$), n(V) of 8:1. The resulting solution was stirred for 15 min while kept in water bath at a room temperature and then sonicated for 15 min for the reactions. This solution was later diluted to C$_v$ = 0.056 M and then sonicated for about 80 min until the solution turned into brownish red V$_2$O$_5$ gel. This gel was further dispersed and diluted to a C$_v$ of 0.03 M, and stirred in de-ionized water until a homogenous red-colored, viscous solution was formed. This solution was pre-frozen in a freeze dryer at −20 °C for 1 day and then freeze-dried under vacuum at −50 °C for 2 days in a Labconco FreeZone 1 L freeze dryer. After drying, the V$_2$O$_5$ cryogel was annealed in ambient atmosphere at 450 °C for 1 h to form 2D leaf-like V$_2$O$_5$ nanosheets.

Material characterization: The phase structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD, Philips 1820 X-ray diffractometer), field emission scanning electron microscopy (FESEM, JEOL, JSM-7000), and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin). The Brunauer-Emmet-Teller (BET) specific surface areas and pore size distributions were measured with Quantachrome NOVA 4200e analyzer (working gas N$_2$, 77 K).

Electrochemical measurements: The electrochemical properties of the 2D leaf-like V$_2$O$_5$ nanosheets were tested in coin-cells with metallic lithium as the anode and polypropylene (PP) film as separator. The coin-cells were assembled in an argon-filled glove-box. The cathodes were fabricated by mixing V$_2$O$_5$ nanosheets, super P carbon black, and poly(vinylidifluoride) (PVDF) at a weight ratio of 70:20:10 in n-methyl-2-pyrrolidone (NMP) solvent. The resulting mixture was then uniformly spread on an aluminum foil current collector. Finally, the electrode was dried at 80°C for 24 h. The electrode loading was about 2 mg cm$^{-2}$. The electrolyte solution was made of 1 M LiPF$_6$ in a 1:1 (V/V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were galvanostatically charged and discharged under different current densities between 2.0 V and 4.0 V (vs Li/Li$^+$) using Arbin BT-2000 battery tester at room temperature. Cyclic voltammetry (CV) studies were carried out on an electrochemical workstation (CHI 600C) between 2.0 and 4.0 V at a scan rate of 0.2 mV s$^{-1}$. Electrochemical impedance spectroscopies (EIS) were performed using the Solartron 1287A in conjunction with a Solartron 1260FRA/impedance analyzer. In EIS measurement, the frequency ranged from 100 kHz to 10 mHz and the AC amplitude was 5.0 mV.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
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