General methods for large-scale production of nanostructured V_{2}O_{5} with controlled morphologies

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A B S T R A C T

V_{2}O_{5} especially in nano-size is widely applied in metallurgy, chemical industry, catalysis and energy storage. Great advances have been made in the area of fabricating nano-sized V_{2}O_{5} materials in bench scale recently. However, large-scale production of nano-sized V_{2}O_{5} materials remains a scientific and engineering challenge which hamper the corresponding commercialization process. Herein we report three facile methods for synthesizing V_{2}O_{5} nanomaterials with controllable morphologies such as nanobelts, nanorods and nanosheets through solution, thermal decomposition and hydrothermal processes, respectively. By optimizing previous methods, the V_{2}O_{5} products with controlled morphology were obtained in high yield. The morphologies and crystalline phases were characterized by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. Owing to the advantages of low-cost and high reproducibility, these methods can be potentially applied in large-scale production of nanostructured V_{2}O_{5} material for practical application.

1. Introduction

Vanadium pentoxide (V_{2}O_{5}), one of the vanadium oxides, holds great potential in electrochemical energy storage applications due to its excellent electrochemical properties lent by the unique layered framework structure [1–4]. Various forms of V_{2}O_{5} nanostructures with advanced electrochemical properties have been obtained, such as V_{2}O_{5} microspheres with uniform yolk-shelled and multi-shelled hollow structures [5], single-crystalline bilayered vanadium oxide nanobelts [6], 3D porous V_{2}O_{5} hierarchical microspheres [7] and cucumber-like coaxial nanowires vanadium pentoxide/poly (3,4-ethylenedioxythiophene) @ MnO_{2} [8]. There is still a technical gap, however, between the academic research, and industrial manufacturing of V_{2}O_{5} nanomaterials. Usually the reported methods are largely convoluted and time-consuming [9,10], which makes the large-scale production infeasible. Therefore, working out efficient strategies that are capable for mass production of V_{2}O_{5} nanomaterials for practical applications is of a significant importance.

Different V_{2}O_{5} nanostructures have their own advantageous characteristics in electrochemical applications. V_{2}O_{5} nanobelts can provide channels with high conductivity for electron transportation along the x–y plane during the charge/discharge processes because of their laterally confined structural features. Meanwhile, nanobelts have the advantages of low-cost and interconnected structure, making it flexible and a type of promising electronical material [11–16]. In another case, V_{2}O_{5} nanorods are desirable for their short Li-ion diffusion distance [17]. Apart from the two structures above, 2D nanosheet are the most widely used structure of V_{2}O_{5} material that possesses great surface area and ultra-thin texture. Such an appealing structure can reduce the diffusion distance for both electrons, leading to high capacitance, high rate-capability and excellent stability [18,19].

Here, we developed facile methods for large scale synthesis of morphologically controlled V_{2}O_{5} nanostructures, including nanobelts, nanorods and nanosheets. All the nanostructures were prepared through one-pot processing of commercial V_{2}O_{5} precursor. Specifically, V_{2}O_{5} nanobelts, with lengths up to tens of micrometers and width of 5–50 nm were synthesized by simply stirring NaCl contained V_{2}O_{5} solution; V_{2}O_{5} nanorods were prepared through thermal decomposition of V_{2}O_{5} precursors and oxalic acid (H_{2}C_{2}O_{4}); whilst V_{2}O_{5} nanosheets, several nanometers in thickness, were fabricated by a hydrothermal treatment. The synthesis process of previous researches are multi-step or time consuming, for example melt quenching and sol-gel process accompanied by a hydrothermal treatment are involved in one experiment of fabricating V_{2}O_{5} nanomaterial which is too complicated to carry out [20]; a template based method of synthesizing V_{2}O_{5} nanomaterial needs more than one week and follow-up template removal treatment which bring difficulties to large-scale production as well [21]. However, the synthesis methods here used avoid difficult
experiment conditions, complex and time consuming procedures, and the use and removal of templates (1-hexadecylamine (HDA) and PEO) [14,22–26], meanwhile these methods employ inexpensive commercial available V2O5 as vanadium source instead of expensive precursors (e.g., vanadyl trispropoxide and vanadium acetylacetonate) to save cost. Moreover, these preparation process with gram scale are likely to solve the remained problem of low throughput (in milligrams) [11–13,27,28]. Therefore the reported methods are cost-effective, environmentally friendly and expandable which have the potential to be widely applied in the industrialization of V2O5 nanomaterial.

2. Experimental

Commercial V2O5 powder (Alfa Aesar), oxalic acid (99%, Aldrich), NaCl (Alfa Aesar) and H2O2 (30%) (Alfa Aesar) were used as received without further purification.

2 g V2O5 powder was dissolved in 50 mL NaCl aqueous solution (5 M), followed by stirring at room temperature (∼25 °C) for 48 h. The obtained dark red mixture was washed and cut off by centrifugation–redispersion cycles with deionized water and ethanol for at least 10 times. Finally, the product was dried at 70 °C for 12 h.

2 g V2O5 powder and 2.96 g oxalic acid was dissolved in 30 mL deionized water, and then stirred at room temperature (25 °C) for 2 h. The as-obtained transparent blue solution was dried at 70 °C and the resulting blue powder was calcined at 400 °C in air for 2 h. After cooling down to room temperature, the sample with yellow color was collected.

2 g V2O5 powder was dispersed into a mixture of 12 mL H2O2 (30 wt %) and 60 mL deionized water under vigorous stirring at room temperature until the color of the solution turned red followed by seal of mixture in a 100 mL Teflon autoclave which had been maintained at 190 °C for 8 h. Subsequently, the as-prepared gel was dried at 70 °C.

The crystalline structure of the V2O5 samples were measured by X-ray diffraction (XRD) using Bruker D8 ADVANCE while the morphology were characterized by scanning electron microscopy (SEM) (JEOL 6700) respectively. The collection of Raman spectra of these samples were carried out with a WITEC CRM200 Raman system equipped with 532 nm laser source.

3. Results and discussion

3.1. V2O5 nanobelts

XRD measurement was applied to examine the phase purity and crystal structure. The XRD results of commercial V2O5 precursor in Fig. 1a and as-prepared V2O5 nanobelts sample in Fig. 1b were sufficiently agreed with each other, which indicated the absence of impurity in orthorhombic V2O5 structure (JCPDS no. 41-1426). The Raman spectrum of V2O5 nanobelts (curved in Fig. 2b) showed the same features as that of V2O5 precursor (Fig. 2a), designating the high purity of as-prepared V2O5 nanobelts sample. Different from the morphology of commercial V2O5 sample (Fig. 3a-c), the TEM images exhibited that the as-prepared V2O5 sample was 1D nanobelts structure in Fig. 3d-f with sizes of several micrometers in length and several nanometers in width, which evinced that the ideal morphology was obtained.

On the basis of the results above, the formation of V2O5 nanobelts can be summarized as followed. Considering from the standpoint of precedent studies, the formation of V2O5 nanobelts might relate to partial dissolution and recrystallization of V2O5 precursor [29]. The V2O5 precursor was irregular formed particles with size around 1–4 μm. At the initial stage of stirring, only a small part of the V2O5 particles dissolved in water and produced vanadium ions (like VO2+). Then the dissolved vanadium ions deposited on the surface of V2O5 particles which triggered the further dissolution of V2O5 precursor, while a few nanobelts with small size formed on the surface of V2O5 crystals. With the reaction proceeding, the V2O5 bulky particles became smaller and large amount of longer nanobelts being formed. Ultimately, large majority of V2O5 particles (yellow color) turned into V2O5 nanobelts (dark red color). Actually, the growth mechanism of V2O5 nanobelts from large crystal under such an experiment condition was quite different from the well-known Ostwald ripening process in which small particles grew to large species. The unique formation mechanism of V2O5 nanobelts in this work was due to the presence of NaCl which triggered the further dissolution of V2O5 precursor, while a few dissolved V2O5 precursor (without further treatment), as-prepared V2O5 nanobelts, as-prepared V2O5 nanorods, with standard orthorhombic V2O5 (JCPDS no. 40-1296), and (d) as-prepared V2O5 nanosheets with standard orthorhombic V2O5 (JCPDS no. 40-1296). The gray spectral lines are the measured XRD patterns, the red lines are the fitted results, and the blue vertical line corresponds to the standard JCPDS plots of V2O5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

![Fig. 1. XRD patterns of V2O5 materials with different morphologies: (a) V2O5 precursor (without further treatment), (b) as-prepared V2O5 nanobelts, (c) as-prepared V2O5 nanorods, with standard orthorhombic V2O5 (JCPDS no. 41-1426), and (d) as-prepared V2O5 nanosheets with standard orthorhombic V2O5 (JCPDS no. 40-1296). The gray spectral lines are the measured XRD patterns, the red lines are the fitted results, and the blue vertical line corresponds to the standard JCPDS plots of V2O5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).](image-url)
3.2. V$_2$O$_5$ nanorods

First, the crystal structure of V$_2$O$_5$ nanorods were determined by XRD (shown in Fig. 1c). All diffraction peaks could be indexed to the orthorhombic system (JCPDS no. 41-1426), which were in good agreement with the result of V$_2$O$_5$ precursor (in Fig. 1a) as well. No peaks of any other phases were detected, suggesting high purity of the product. Besides, the Raman spectrum of V$_2$O$_5$ nanorods (in Fig. 2c) exhibited same peak distribution as that of commercial V$_2$O$_5$ precursor (in Fig. 2a). The measured Raman peaks matched up with the corresponding vibration mode of V$_2$O$_5$ molecule without impurity. The SEM images in Fig. 3g-i revealed the uniform rod-like morphology of the as-prepared V$_2$O$_5$ nanorods. Compared with the commercial V$_2$O$_5$ powder (in Fig. 3a-c), the morphology of as-prepared was much smaller and uniform.

The formation process of the presented V$_2$O$_5$ nanorods was mainly related to thermal-decomposition of VOC$_2$O$_4$, which was originated from V$_2$O$_5$ precursor and H$_2$C$_2$O$_4$. First, the mixture (V$_2$O$_5$: H$_2$C$_2$O$_4$ stoichiometric ratio of 1: 5) was stirred for 2 h until its color became transparent blue from yellow indicating that the initial V$^{5+}$ turned to V$^{4+}$ accompanied by VOC$_2$O$_4·n$H$_2$O being formed. The reaction was illustrated in Eq. (1) [33,34]. The VOC$_2$O$_4$ blue powder was annealed at 400 °C for 2 h after dried and grounded. With the heat treatment processing, the transformation of VOC$_2$O$_4$ experienced three stages [34]. The dominant reaction of the first stage involved VOC$_2$O$_4·n$H$_2$O losing its crystal water accompanied with some physically absorption when the temperature was below 267 °C. Then during the second stage, with the temperature increasing to 292 °C, VOC$_2$O$_4$ turned to vanadium oxide of miscellaneous-valences (VO$_2$ and V$_2$O$_5$) through decomposition process. After that, at third stage, when the temperature went over 353 °C, VO$_2$ converted to V$_2$O$_5$ completely [35].

Upon the reaction’s completion, the obtained yellow sample was weighed up to 1.808 g (Fig. S1d) which was high yield compared to 2 g V$_2$O$_5$ precursor. The whole process only consumed about 6 h with cost-effective raw chemicals and simple steps, thus it held promises to be extended to large-scale production. On the other hand, the thermal treatment was of advantage to increase the crystallization degree of the product [36–38]. Same V$_2$O$_5$ nanorods material sizing over micrometre was also produced via electrosprun technique [40], but compared to electrosprun technique our method which involved only 400 °C annealing process was easier to be extended to large-scale production and the final product of V$_2$O$_5$ nanorods was much smaller and more uniform. In conclusion, this method was low-cost, environmentally-friendly, uncomplicated and highly yielding which could be potentially applied in practical production. Therefore the output can be expanded directly depending on customization requirements (in Fig. S1c).

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V_2O_5 + 3H_2C_2O_4 \rightarrow VCO_2O_3 + 3H_2O + 2CO_2
\]

(1)

3.3. V$_2$O$_5$ nanosheets

The XRD pattern (in Fig. 1e) of V$_2$O$_5$ nanosheets showed that the main peak of V$_2$O$_5$ architecture was located at 7.6°, and two weak peaks were located at 22.8° and 30.4°, corresponding to (001), (003), and (004) facets of orthorhombic V$_2$O$_5$ (JCPDS no. 40-1296), respectively. Thus the crystalline and phase purity of V$_2$O$_5$ nanosheets could be promised. Meanwhile Raman spectrum of V$_2$O$_5$ nanosheets was measured and shown in Fig. 2d. The vibration modes were labeled in the measured Raman spectrum taking off from previous research [41] and all the peaks were agreed well with that of commercial V$_2$O$_5$ precursor (in Fig. 2a). Also, from the SEM pictures in Fig. 3j-l, the 2D sheets morphology with thickness of about several nanometers could be distinct. Compared with the SEM images of commercial V$_2$O$_5$ (in Fig. 3a-c), the morphology of as-prepared V$_2$O$_5$ nanosheets sample had drastically changed.

Based on the former results, it is worth to further explore the reaction mechanism between H$_2$O$_2$ (30 wt %) and V$_2$O$_5$ precursor. The mixture of V$_2$O$_5$ and H$_2$O$_2$ was stirred for 1 h while the solution slowly turned transparent red (in Fig. 1c) in the wake of vigorous bubbles. This phenomenon was due to the intense reaction between V$_2$O$_5$ and H$_2$O$_2$ on the basis of the previous study [35,42], and the large amount of bubbles came from the generation of gas O$_2$. After that, V$_2$O$_5$ gel with typical layered structure was formed, which could act as hosts for the intercalation of water molecules [43]. Afterwards, the V$_2$O$_5$ gel was transferred into stainless steel autoclave for the subsequent hydrothermal treatment. While the reaction proceeding, V$_2$O$_5$ in the mixture preferably regrew along its [a] and [b] directions from VO$_2$ and was also produced via electrospun technique [40], but compared to electrospun technique our method which involved only 400 °C annealing process was easier to be extended to large-scale production and the final product of V$_2$O$_5$ nanorods was much smaller and more uniform. In conclusion, this method was low-cost, environmentally-friendly, uncomplicated and highly yielding which could be potentially applied in practical production. Therefore the output can be expanded directly depending on customization requirements (in Fig. S1c).

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V_2O_5 + 3H_2C_2O_4 \rightarrow VCO_2O_3 + 3H_2O + 2CO_2
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(1)
via a special molecular-level sol-gel chemistry. Although the morphology of mentioned V$_2$O$_5$ nanosheets materials were outstanding, the methods were time-consuming and accompanied with complex procedures which were hard to be followed. In present work, this method was easy to repeat, time-saving, and high-yield which made it possible to be industrialized. Besides, the yield only depended on the volume of autoclaves and the mass of reactants, thus the production could be reasonably enlarged to meet the demands for the mass markets.

4. Conclusion

In summary, three methods for controllable fabricating V$_2$O$_5$ nanostructured materials of various morphologies and high morphological uniformity have been exhibited. The advantages of low-cost, facile growth processes and high yield promise these methods a bright future for fundamental studies and more importantly practical applications. These results could accelerate the commercialization of V$_2$O$_5$ nanomaterials.

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References
