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Preparation of Porous Vanadium Pentoxide Nanotubes by Electrospinning

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Abstract: Porous vanadium oxide nanotubes (VNTs) were prepared by electrospinning technique and following sintering treatment. We chose commercial vanadium oxides and benzyl alcohol and Isopropanol as the raw materials to form low-cost inorganic vanadium sol solution followed by the appropriate addition of poly(vinylpyrrolidone) (PVP) as electrospinning vanadium precursor. Thus, we prepared the one-dimensional (1D) VNTs, which mainly contain V_2O_5-sol and PVP, followed by varying the holding time of sintering. Crystal structure and the morphology of electrospun VNTs were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) also displays carbon remains after PVP is sintered. Results show that the electrospun VNTs are about 400~700 nm in diameter, and 2~10 μm in length with various degrees of porous interconnected fibrous morphology which could be seen by SEM and TEM images. And the degrees of the fracture of the porous vanadium pentoxide nanotubes are various with different holding time at high temperature.

Key words: electrospinning; vanadium pentoxide nanotubes; nanofibers; nanostructures

Special properties and attractive applications in many areas have made 1D nanostructure, such as nanofibers (NFs), nanorods, and nanoribbons, more and more intensive research[1]. 1D nanostructures can be efficient in the power-density and energy-density. Because of these advantages: (1) the electron can transport along the longitudinal direction quickly; (2) some ion flux would be increased in the nanostructure of porous and hollow 1D morphology; (3) 1D nanostructure will improve the strain relaxation to withstand the volume expansion[2-4]. So, many start to try to fabricate and synthesize perfect 1D nanostructures by different ways in the forms of fibers, wires, rods, belts, tubes, spirals, and rings from different materials[5]. However, electrospinning may be a remarkably simple and cost-effective method to generate NFs with solid or hollow nanostructure[6,7]. This structure has long length, uniform diameter, and various composition[6]. The process of electrospinning is like this: high accelerating voltage is applied to a needle. This needle is connected to a syringe containing a polymeric precursor. A large electric field is added between the needle and collector to form electric force on the drop. Until the electric field is large enough to overcome the surface tension of the polymeric precursor, the NFs will be formed and meanwhile the solvent on the fibers will evaporate quickly during contacting with the ambient atmosphere. The morphology of these NFs can be controlled by adjusting the electrospinning parameters like the voltage applied, distance between the needle and the collector, viscosity of the solution, and the flow rate of the pump of pushing the solution[7]. Electrospinning uses the electrostatic among surface charges, rather than a mechanical or shear force, to continuously reduce the diameter of a viscoelastic jet or a glassy filament[8]. But electrospinning achieves continuous and much thinner NFs. The electrospinning is similar to electrostatic spraying (or electrospray) process. The common points of the two techniques are getting the fibers by inducing a high voltage driven liquid jets[8]. As for electrospray, varicose break-up of the electrified jet forms the small droplets or particles. This jet is usually from a solution with a not high viscosity. But electrospinning generates the solid fibers by electrostatic repulsions between the surface charges and the evaporation of solvent. These electrified jets have higher viscous polymer solution. Electrospinning technique was first patented in1934, and known by more people as electrostatic spinning in 1993[9,10]. Until 1990s, some research groups gained interest in generating fibers by electrospinning different viscosities of polymer solution.

As for the materials, we chose the vanadium pentoxide (V_2O_5) and PVP. Among them, PVP plays the role of template in final nanostructure. V_2O_5 is one of the most attractive materials in many applications, such as actuators1[11], catalysis[12],

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and sensors[13] and batteries[14]. Besides, V_2O_5 is low cost, and abundant in the nature and has the unique layer structure.

Herein, we fabricated the 1D nanostructures with the electro- spinning technique and controlling the morphology by setting the heating time. The precursor of V_2O_5 was prepared into vanadium sol with PVP to increase the viscosity. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM), Thermogravimetric Analysis (TGA) and X-ray diffraction (XRD) were employed to characterize the morphology and crystallinity of the VNTs.

1 Experiment

Vanadium oxide sol (V_2O_5 -sol) was synthesized according to our previous work[15], in which V_2O_5-sol was prepared from cheap commercial V_2O_5 powder, benzyl alcohol and Isopropyl alcohol through a reflux condensation-reflux extraction method. In this paper, PVP-ethanol solution was formed by dissolving polyvinylpyrrolidone (PVP, Mw=1300 000) in ethanol with the mass ratio of 10 wt% under vigorous stirring. Then V_2O_5-sol solution was appropriately added into PVP-ethanol solution under magnetic stirring to form a homogeneous viscous orange solution. Next, the viscous orange solution was loaded into a plastic syringe with stainless steel needle. The solution was electrospun at a DC voltage of 15 kV, and the distance between the needle tip and the collector is 12 cm. Finally, the as-spun NFs were annealed in a muffle furnace in air at 350 and 400 ℃ with the same heating rate of 1 ℃/min.

2 Result and Discussion

2.1 Morphology of the as-prepared vanadium nanotubes

Fig.1 shows the fabrication of porous VNTs based on the simple electrospinning method and subsequent annealing. Firstly, the light orange precursor was prepared by mixing V_2O-sol and PVP-ethanol solution. Then, the as-spun NFs were annealed at 350 ℃ and 400 ℃ to get the porous nanotubes which will be discussed in the later sections.

TGA was performed to investigate thermal decomposition of the as-spun NFs. As shown in Fig.2, the mass loss below the temperature of 200 ℃ is due to the evaporation of residual solvent. Until the 250~400 ℃, the mass loss becomes very fast with wide range which could be attributed to the degradation of V_2O_5-sol and PVP into carbon. At about 400 ℃, there is another mass loss which could be the carbon further oxidized into carbon dioxide (CO_2). When the temperature is up to 440 ℃, there is no mass loss which indicates all of the PVP and its decomposition is burned out completely.

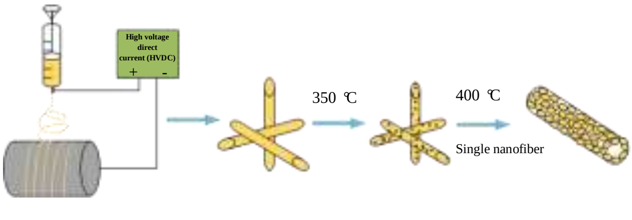

Fig.1 Electrospinning process and the formation of porous VNTs during sintering

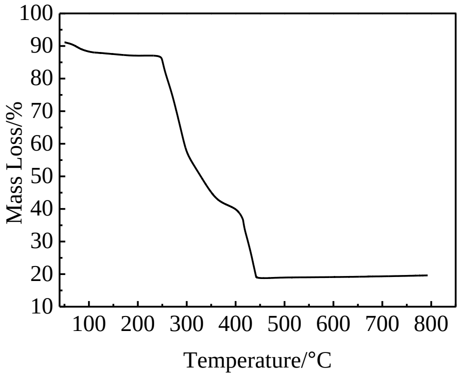

Fig.2 TGA curve of the as-prepared V_2O_5-sol/PVP nanotubes

From Fig.2, it could be known that the organics is totally degraded until the temperature is about 440 ℃. So, we chose 400 ℃ as the annealing temperature to obtain nanostructures with carbon which would enhance the frame stability and electrochemical conductivity when applied in electrical devices[8,15,16]. And to explore the influence of the annealing time on the raw NFs, we set the temperature gradient: 2, 4, and 6 h with the same slow heating rate of 1 ℃/min.

SEM images of precursor NFs with 10% PVP concentration and different annealing time are shown in Fig.3. The precursor NFs have a relatively smooth surface with no pores or other nanostructures (Fig.3a). Close observation reveals that the diameters of nanotubes are about 1 μm. The lengths are up to several millimeters (Fig.3a). After sintering at 400 ℃ for different time, a 1D, nanoparticles interconnect, and fibrous morphology is observed in Fig.3b~3e. The continuous 1 D nanostructures are retained, but there is a notable change to the morphologies of the NFs: many pores appear on the surface of the nanotubes. A comparison of 400 ℃ and 350 ℃ was conducted to investigate the influence of temperature on the morphology. Thus, the morphology of the NFs is not as smooth as the raw NFs but with small pores on them and some NFs are fractured. These as-prepared V_2O_5 have diameters in the range of 400~700 nm and there are many pores on the surface. As the holding time increases, the porous nanostructure is damaged more seriously than the less ones (Fig.3b~3e). The length is much shorter and the porous nanotubes are wrecked into pieces or particles.

TEM analysis was performed to gain the further insight into the morphology and structure of the VNTs which were heated for different time which is shown in Fig.4. The TEM images confirm that highly porous and hollow nanostructures are formed. When the calcination time increases, the organics is degraded gradually. The pores and the vanadium nanoparticles

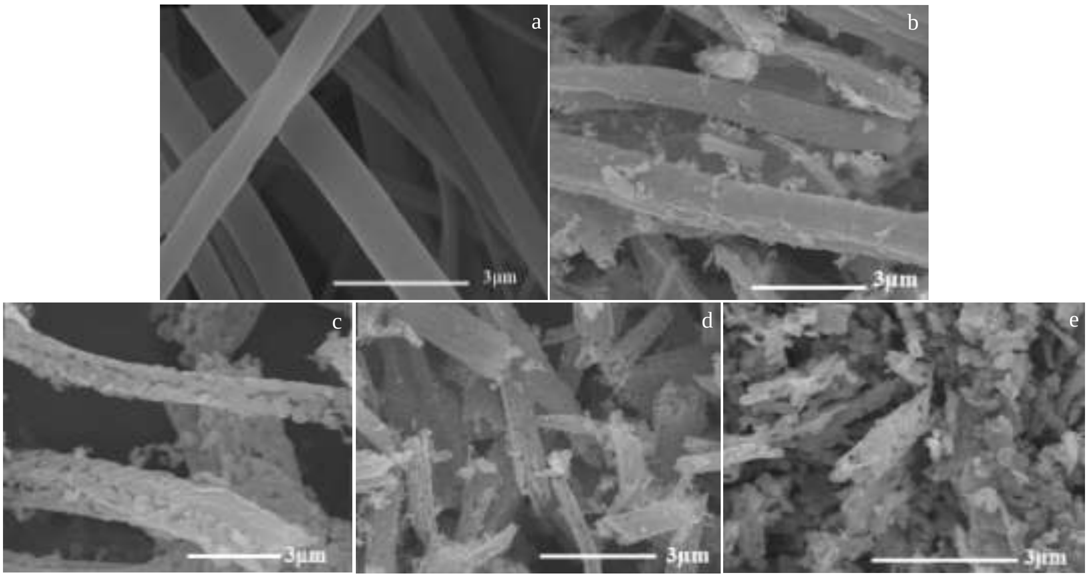

Fig.3 SEM image of the as-spun NFs (a); nanostructures of V_2O_5 at 350 ℃/2 h (b), 400 ℃/2 h (c), 350 ℃/2 h (d), and 400 ℃/6 h (e)

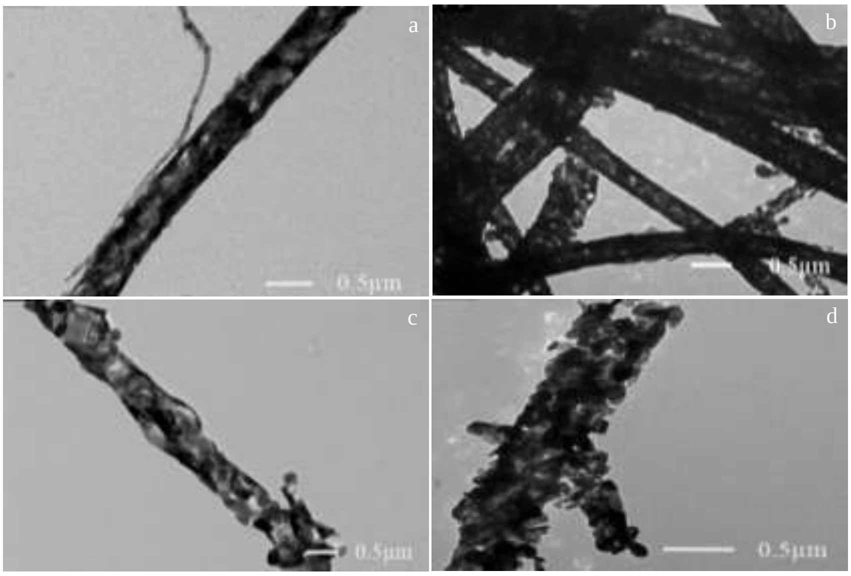

Fig.4 TEM images of VNTs: (a) 350 ℃/2 h, (b) 400 ℃/2 h, (c) 400 ℃/4 h, and (d) 400 ℃/6 h

become bigger which implies the V_2O_5 particles grow bigger after burning at 400 ℃ for several hours. And the nanostructure of 2 h is kept best among them which is consistent with SEM analysis.

The XRD patterns (Fig.5) is suggest that for all of the four samples, the width of the diffraction peaks is very big. That would be due to the PVP which is oxidized into carbon. With the temperature and the sintering time increasing, the intensity of these diffraction peaks gets stronger suggesting that the crystallization of V_2O_5 is enhanced. And this is in agreement with the TGA analysis (Fig.1) which shows that organic matter are incompletely removed at the temperature of 400 ℃. All the diffraction peaks are indexed to the pure orthogonal symmetry of V_2O_5 (JCPDS card no.:41-1426), which means that the V_2O_5 are all obtained.

To identify the existence of different forms of carbon, X-ray photoelectron spectroscopy (XPS) was displayed (Fig.6). The peaks in Fig.6 are corresponded to oxygen, vanadium, and carbon elements. And as the temperature gets higher, the intensity of C 1s peak is stronger which indicates that more carbon is acquired. Fig.6 shows in all the three samples the carbon element has been detected. This proves that the sample of 400-4 also has the carbon and PVP which is slowly oxidized into carbon when the temperature rises. So, we

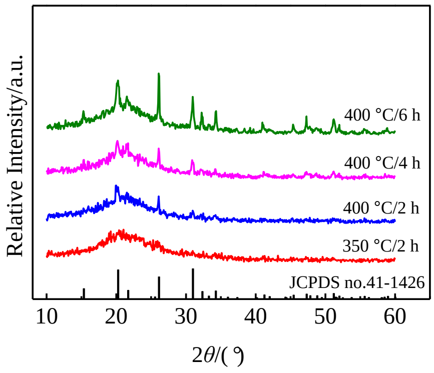

Fig.5 XRD patterns of V_2O_5-sol/PVP nanotubes annealed at different temperatures for different time

proved the guess of existing carbon due to the incomplete composition of PVP.

2.2 Formation mechanism of the porous vanadium nanotubes

The possible mechanism was proposed[17]. During the electrospinning process, the PVP forms a polymeric scaffold in which the droplets of dissolved V_2O_5-sol are evenly dispersed. The length of the NFs is not continuous which can be contributed to the inadequately decomposition of PVP and V_2O_5-sol. The V_2O_5 nanoparticles are adjusted during the annealing process and join to each other to get the resultant nanostructure: nanotube. Besides, slow heating rate can make sure the PVP gets enough time to degrade. Thus, the probably mechanism of the formation of V_2O_5 nanotubes would be like this: V_2O_5-sol close to the surface of the raw NFs is decomposed and then V_2O_5-sol inside the NFs will migrate to the surface because of the concentration gradient. And at the high temperature, PVP would be oxidized into CO_2 and volatilized rapidly. The outwards volatilization of CO_2 leads to many pores on the raw nanofiber. With the annealing temperature rising, PVP decomposes more and vanadium oxide nanoparticles grow larger gradually. Finally, these nanoparticles connect together to generate porous nanotubes. This formation process has been clearly denoted in Fig.1.

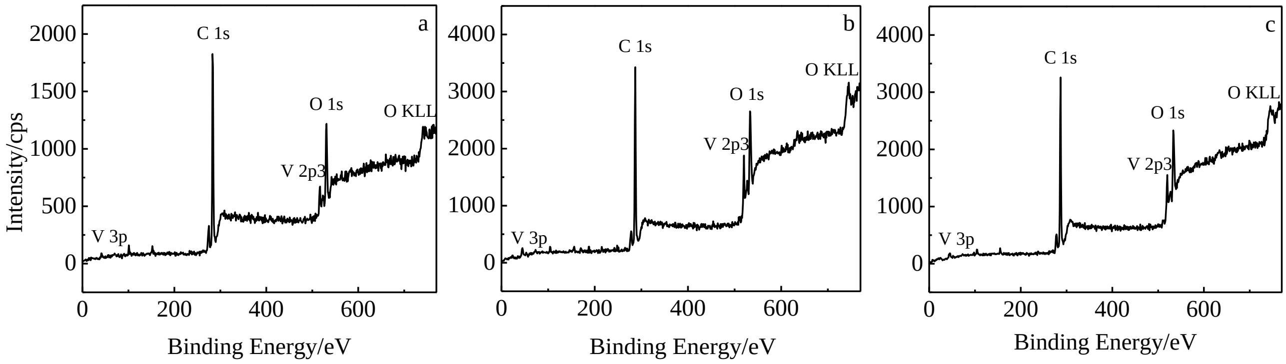

Fig.6 XPS spectra of VNTs: (a) 350 ℃/2 h, (b) 400 ℃/2 h, and (c) 400 ℃/6 h

3 Conclusions

1) 1D VNTs are prepared successfully by a simple electrospinning technique with cheap raw materials as precursor and subsequent annealing process.

2) PVP degrading into C causes the resultant nanotubes' pores. Higher temperature makes PVP decompose more to achieve bigger size nanoparticles and the nanotubes get more pores on the surface. When the temperature increases, the PVP starts to decompose into carbon and then CO_2 which would be the reducer of vanadium pentoxide and make the NFs porous.

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静电纺丝法制备多孔五氧化二钒纳米管

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摘　要：采用静电纺丝法制备多孔五氧化二钒纳米纤维，在经过后续的高温处理得到多孔洞的五氧化二钒纳米管结构。以商用五氧化二钒粉末，苯甲醇和异丙醇为原料制备氧化钒溶胶，添加聚乙烯吡咯烷酮（PVP）以增加前驱体的粘性，并以此为前驱体通过静电纺丝法制备超长五氧化二钒纳米纤维，通过改变热处理的时间来实现对纤维形貌的控制。所添加的 PVP 在整个溶液中的质量分数为 10%。使用 SEM、TEM 以及 XRD 来表征所制备的多孔五氧化二钒纳米管的形貌和结晶度。由热重分析仪（TGA）来测试静电纺丝设备制备得到的五氧化二钒纳米纤维的热分解，并以此选择高温处理温度。结果表明，静电纺丝得到的超长五氧化二钒纳米纤维的直径在 400~700 nm，长度为 2~10 μm。经过不同时间的高温处理后，所获得结构为不同完整程度的多孔洞五氧化二钒纳米管。

关键词：静电纺丝；五氧化二钒纳米管；纳米纤维；纳米结构

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