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RESEARCH ARTICLE

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Preparation and characterization of WO_3 from ammonium paratungstate via hydrothermal method

Abstract Tungsten trioxide powder has been prepared from ammonium paratungstate via hydrothermal method using orthogonal and mono-level design of experiments. The effects of preparation process on particle size, specific surface area, crystal form and crystalline morphology of the tungsten trioxide was investigated by TEM and XRD *etc*. It was found that the optimum conditions of the preparation are hydrothermal crystallization for 8 h at 180°C, followed by vacuum drying at 45°C and calcination at 500°C for 2 h. The blank reference experiment shows that hydrothermal crystallization treatment favors the formation of hexagonal tungsten trioxide, and the tungsten trioxide powder sample prepared by this method has a high degree of crystallinity.

Keywords ammonium paratungstate, orthogonal design, tungsten trioxide, hydrothermal

1 Introduction

As an *n*-semiconductor and a kind of transition metal-oxide, tungsten trioxide (WO_3) is known as a multi-functional material with perfect performances of gas-sensitivity (for many gases such as NO_x, H_2S, NH_3 etc.), humidity-sensitivity, catalysis, electrochemical action, electrochromic capacity, electrochemical capacity and so on [1]. Hexagonal tungsten trioxide is of great interest in technology in particular because of its possibility to serve as an insertion host for lithium. As a result, lithium tungsten bronzes are found to be a useful cathode material for rechargeable lithium batteries [2]. It has been reported that hexagonal tungsten trioxide is formed by acidification of an Na_2WO_4 solution with a mineral acid (HCl) by hydrothermal method [4]. The calcination of Ammonium Paratungstate (APT) is one of the important processes in the preparation of WO_3, but little information has been accumulated on how to prepare WO_3 from APT in solution [5–8].

This paper aims at reporting the hydrothermal method-based preparation of WO_3 from APT. Orthogonal design of experiments is used to find the effects of the preparation process on particle size, specific surface area and the optimum conditions. Mono-level design of experiments is used to investigate the influence of hydrothermal treatment to product. The process of preparation of Hexagonal tungsten trioxide is primarily studied.

2 Experimental

2.1 Materials

Ammonium Paratungstate (APT) ($(NH_4)_{10}W_{12}O_{41}\cdot 11H_2O$) (white, 99.99% pure) and bi-distilled deionized water were used as raw materials.

2.2 Apparatus and procedures

For the hydrothermal synthesis of the WO_3, an APT aqueous solution was prepared as follows: powdered APT (3 g) was dispersed in 100 ml of bi-distilled, deionized water. The mixture was then introduced into a Teflon tube in an autoclave. The autoclave was sealed and heated from room temperature to 120–180°C and kept at the given temperature for 4–14 h according to the orthogonal design of experiments. After the reaction was complete, the products, i.e., tungsten

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trioxide powders precipitated in the bottom of the Teflon tube, were filtered off, washed with distilled water and alcohol, then calcined at a certain temperature for 2 h in air after ensuring sufficient dryness in air.

The optimum conditions obtained from the orthogonal of the experiments were improved by mono-level design of the experiments. The products of the hydrothermal treatment of APT were calcined at a certain temperature for 2 h after vacuum drying. The characteristic of the sample obtained without hydrothermal crystallization treatment was investigated by reference experiment.

2.3 Analysis and characterization of tungsten trioxide

The obtained samples were characterized by the X-ray powder diffraction (XRD) method. The XRD analysis was conducted on a Japan Rigaku D/MAX-RB Arotation anode X-ray diffractometer, using Ni-filtered CuK_{α} (λ=1.5417). The morphology of the tungsten trioxide was determined by using a Japan Hitachi H-600 transmission electron microscopy (TEM). The particle size was determined on a China ZhuHai OMEC LS-601 Laser Particle Sizer. The specific surface area of the obtained samples was measured by nitrogen absorption according to the BET method using an ST-08 instrument produced by China Beijing Analytical Instrument Factory.

3 Results and discussion

3.1 Orthogonal design of experiments

The $L_9(3^4)$ orthogonal arrays table was chosen for performing the experimental design. This investigation dealt with 4-dimension parameters with three levels for each factor. The variables included were crystallization time (A), crystallization temperature (B), dryness temperature (C) and calcinations temperature (D). The interaction between the design parameters was neglected in the present study. Only 9 experiments in Table 1 would be applied to conduct this experiment according to the $L_9(3^4)$ orthogonal arrays. The average particle size (D_{50}) and specific surface area (S_{BET}) of WO_3 were used as the output value. The experiment results of the three performance characteristics are also listed in Table 2.

The equilibration effect of each processing parameters on D_{50} and S_{BET} could be expressed as response table (K_1, K_2, K_3), which are shown in Table 2. The data shown in the bottom row of Table 2 were the difference between the maximum and minimum values among the three rows. This value related to the effect of that particular process parameter on D_{50} or S_{BET}, which was expressed as R.

3.2 Orthogonal test results and discussion

It can be noted from Table 2 that process parameter A (crystallization time) has the highest influence on D_{50}, while influence of the other parameters gradually decreases as follows: C (dryness temperature)> B (crystallization temperature) >D (calcinations temperature). Since a smaller D_{50} corresponds to a better property, the process parameter combination $A_2B_3C_3D_3$, i.e., hydrothermal crystallization for 8 h at 180°C, followed by air-drying at 180°C and calcination at 700°C for 2 h can get the smallest particle and can consider as the optimum conditions in this study.

Table 1 Results of orthogonal hydrothermal experiments

No.	A hydrothermal time/h	B hydrothermal temperature/°C	C drying temperature/°C	D calcinations temperature/°C	D_{50}/μm	S_{BET}/m^2·g^{-1}
1	1(4)	1(100)	1(100)	1(500)	24.07	9.87
2	1(4)	2(140)	2(140)	2(600)	12.86	4.11
3	1(4)	3(180)	3(180)	3(700)	0.98	4.08
4	2(8)	1(100)	1(140)	3(700)	0.83	3.22
5	2(8)	2(140)	2(180)	1(500)	1.08	11.93
6	2(8)	3(180)	1(100)	2(600)	1.16	4.71
7	3(14)	1(100)	3(180)	2(600)	6.72	5.00
8	3(14)	2(140)	1(100)	3(700)	16.96	2.65
9	3(14)	3(180)	2(140)	1(500)	1.24	11.95

Table 2 D_{50} and S_{BET} date of samples prepared by hydrothermal method

	D_{50}/μm				S_{BET}/m^2·g^{-1}			
	A	B	C	D	A	B	C	D
K_1	12.64	10.54	14.06	8.80	6.02	6.03	5.74	11.25
K_2	1.02	10.30	4.98	6.91	6.62	6.23	6.43	4.61
K_3	8.31	1.13	2.93	6.26	6.53	6.91	7.00	3.32
R	11.62	9.41	11.13	2.54	0.60	0.88	1.26	7.93

R: range, influence extent of factors on results; A–D see Table1

However, as to S_{BET} (the larger, the better), the best process parameter combination is $A_2B_3C_3D_1$, i.e., hydrothermal crystallization for 8 h at 180°C, followed by air-drying at 180°C and calcination at 700°C for 2 h. The influence of each parameter gradually decreases in the order D>C>B>A.

If the particle is approximately regard as spherical, the smaller D_{50} links with the larger S_{BET} in general. As can be seen from Table 1, the influence of process parameters A, B, C for D_{50} and S_{BET} are in correspondence. With the increasing of hydrothermal time (A), it favors transforming incompact amorphism morphology into crystalline morphology, forming pore and crack, which makes D_{50} decrease and consequently S_{BET} increase. But if the hydrothermal time increases too much, the D_{50} increases and consequently S_{BET} decreases because the longer time will favor the increase of the crystal nucleus and particle size, hence, the S_{BET} decreases. Therefore, there exists an optimal hydrothermal time (A) for both D_{50} and S_{BET}, which is determined to be 8 h. But as to B and C, the increase of hydrothermal and drying temperature is propitious to the transfer of internal water and degree of crystallinity of the particle, and reduces the soft agglomeration of small particles. As a result, with the increase of hydrothermal and drying temperature, the D_{50} decreases but the S_{BET} increases. The higher the hydrothermal and drying temperature are, the more degree of decrease in D_{50} and the larger the S_{BET} is.

Influence of calcination temperature (D) on D_{50} and S_{BET} is the opposite. Both the D_{50} and S_{BET} are observed to decrease when the calcination temperature is increased. This is possibly due to adequate vaporization of water at higher calcination temperature. This also favors the transformation of coarse grain into close grain, which leads to the decrease of particle size. A high calcination temperature also causes a high degree of crystallinity and low driving force for shrinking or sinking of the internal pore, which decreases the S_{BET}.

It is worth noting that when both the mean value of D_{50} and S_{BET} matches, the resulting optimal sequence is present among the combinations $A_2B_3C_3D_1$, appearing in Table 1 and planned for experimentation. The results show that when the sample is synthesized under this optimal condition, it can get the best results among the planned for experimentation, i.e., the numerical value for D_{50} and S_{BET} is 0.65 μm, 12.48 $m^2 \cdot g^{-1}$, respectively. It has a small average particle size (D_{50}) and a large specific surface area (S_{BET}).

3.3 Effect of drying-manner

It is known that water can be easily vaporized at low temperatures in vacuum drying, which favors the elimination of the induration phenomena in ambient pressure drying [9]. In order to get a good result, mono-level design of experiments is done to improve the result of the orthogonal design of experiments. Fig. 1 shows the SEM micrograph of sample A and sample B. Sample A is obtained from hydrothermal crystallization for 8 h at 180°C; Sample B is obtained without hydrothermal crystallization treatment. Both sample A and sample B are followed by vacuum drying at 45°C and calcination at 500°C for 2 h.

The tungsten trioxide with hydrothermal crystallization treatment (see Fig. 1A) is plate-like and column shaped. The ratio of length and diameter of the column shape is 8.23:1, the length of the particle with column shape is between 0.25–1.2 μm, which is well consistent with the obtained sample D_{50}, i.e., 0.58 μm, S_{BET} of sample A is 15.36 $m^2 \cdot g^{-1}$. It is obvious that drying-manner has a great effect on the particle size; vacuum drying is effective on the decrease of D_{50} and on the increase of S_{BET}. For comparison, the tungsten trioxide without hydrothermal crystallization treatment (see Fig. 1B) has an irregular granula shape with partial agglomeration, and its D_{50} is between 0.04–0.13 μm.

3.4 Identification of the phase formed of WO_3

The powders prepared in the above manner are analyzed by XRD; the obtained patterns are shown in Fig. 2. Tungsten

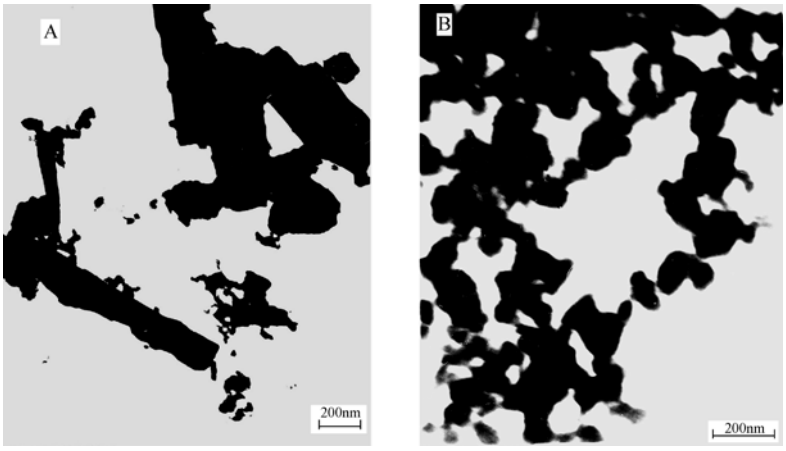

Fig. 1 TEM images of WO_3

A: Sample obtained from hydrothermal crystallization for 8 h at 180°C; B: Sample obtained without hydrothermal crystallization treatment

trioxide has several allotropic modifications, which differ structurally from each other. The prepared samples are compared to tungsten oxide JCPD files and those reported by others [7, 8]. The diffraction lines of sample A are designated as containing mainly triclinic WO_3 (JCPDS PDF 20-1323) and partially hexagonal WO_3 (JCPDS PDF 33-1387); The hexagonal WO_3 phase characteristically exhibits three peaks at 2θ=13.940, 28.160, 36.700°. The XRD pattern of sample B resembles those of WO_3 pure monoclinic structure (JCPDS PDF 43-1035).

It has been reported that when APT is heated in air, the test material shows two mass-loss steps at 60°C and 100°C, which are due most likely to elimination of NH_3 molecules and of water molecules (dehydration), respectively. It is shown from the TG curve that there is a plateau between 350 and 400°C. This corresponds to a product of mixture of crystalline ammonium tungsten bronze of the composition $(NH_4)_{0.33}WO_3$ and crystalline hexagonal WO_3 (JCPDS 33–1387). With the increase in heating temperature, the decomposition of $(NH_4)_{0.33}WO_3$ process is shown to be accompanied by phase transition of WO_3 from semi-stable hexagonal to stable monoclinic structure with no crystallinity. Further calcination at 500°C for 2 h resulted in complete transformation of $(NH_4)_{0.33}WO_3$ into a monoclinic WO_3. XRD of APT, which is obtained from hydrothermal crystallization for 8 h at 180°C, is given in Fig. 3. The diffraction pattern displayed matches well the pattern filed (JCPDS PDF 18–126) for triclinic $5(NH_4)_2{\cdot}12WO_3{\cdot}7H_2O$ and the pattern filed (JCPDS PDF 18–128) for monoclinic $(NH_4)_{10}{\cdot}H_2W_{12}O_{42}{\cdot}4H_2O$. It reflects clearly that the phase structure of sample A, which was obtained from hydrothermal crystallization for 8 h at 180°C, is a mixture of triclinic WO_3 (JCPDS PDF 20–1323) and partially hexagonal WO_3 (JCPDS PDF 33–138), but the phase structure of sample B, which was obtained without hydrothermal crystallization, is pure monoclinic structure. This phenomenon indicates that hydrothermal treatment favors the formation of hexagonal tungsten trioxide, but the mechanism needs further investigation.

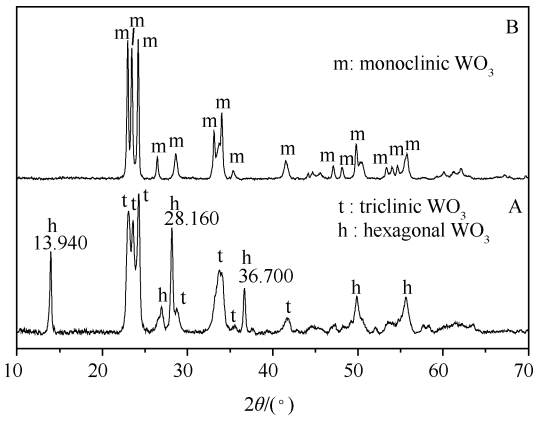

Fig.2 XRD patterns of WO_3

A: Sample obtained from hydrothermal crystallization for 8 h at 180°C; B: Sample obtained without hydrothermal crystallization treatment

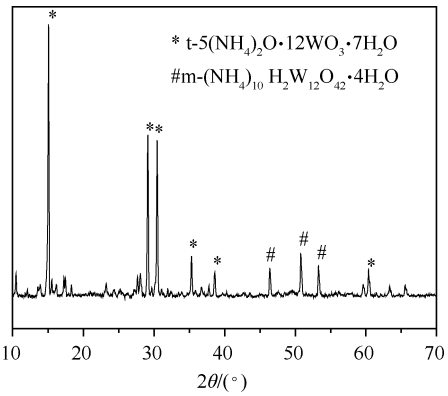

Fig.3 XRD pattern of sample obtained from hydrothermal crystallization for 8 h at 180°C (without calcinations)

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