Research paper

Direct synthesis of vanadium oxide nanopowders by the combustion approach

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ABSTRACT

In the paper, VO_2 and V_2O_3 nanopowders were prepared via one-step solution combustion synthesis method. The properties of products can be tunable by adjusting the combustion parameters, such as fuel type, fuel-to-oxidizer ratio and atmosphere. Detailed combustion reaction mechanisms have been discussed. When glycine as fuel, the average particle size of VO_2 product is 40 nm. When citric acid and glycine as the mixture fuels, the VO_2 product with the average particle size of 20 nm show typical temperature-driven semiconductor to metal transition. The V_2O_3 product with the average size of 70 nm could be synthesized in an inert atmosphere.

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1. Introduction

During the last few years, metal oxides have been extensively studied and play important roles in a wide range of applications [1–4]. Vanadium, an abundant element in the earth crust, has variable oxidation states from +2 to +5 (VO, V_2O_3, VO_2, and V_2O_5) [5]. As the significant transition metal oxides, vanadium oxides have plenty of scientific and industrial applications. For example, vanadium dioxide (VO_2) has four polymorphic modifications: $VO_2(R)$, $VO_2(M)$, $VO_2(B)$, and $VO_2(A)$. Among them, $VO_2(M)$ exhibits a characteristic of temperature-driven semiconductor to metal (s–m) transition, which could be applied in the smart window coatings, field-effect transistors, sensors, and switches [6–8]. Also, vanadium trioxide (V_2O_3) has a wide range of potential applications in intelligent window, optical device, temperature sensor, conductive composite polymer, and catalyst [9–12].

To obtain the above corresponding functions, it is very necessary to synthesize the vanadium oxide powders with single phase composition. However, many possible vanadium oxide phases exist in the binary phase diagram of vanadium and oxygen, so the pure phase could only be formed in a narrow stoichiometric range. Currently, some methods have been made to synthesize vanadium oxide, including hydrothermal techniques, chemical vapour deposition, sol–gel, powder metallurgy and so on [13–15]. These methods require complex procedures, long reaction time, or special instrumentations. Therefore, an economically viable synthesis technique is greatly needed. Solution combustion synthesis (SCS) is emerging as a promising method for the preparation of nanopowders [16–19]. The SCS method is essentially a redox reaction between the oxidants and the reducing reagents, usually employing metal salts (nitrates) as oxidants, and fuels (urea, glycine or citric acid) as reducing reagents [16]. As the redox reaction is an exothermic reaction, the released heat can meet the energy requirement for the synthesis of target oxides. The products can be formed in several minutes. Time- and energy-efficiency are the most obvious advantages of SCS. Besides, there are several other advantages of SCS [16,19–21]: (1) simplicity and low cost of instrumentation; (2) the raw materials are mixed on the molecular level, guaranteeing a good chemical homogeneity of the combustion system; (3) the composition and microstructural characteristic of products can be simply tailored by varying the combustion parameters. In addition, both of fuels and reaction atmospheres play important roles in determining the phase, morphology, specific surface area and size distribution of the final products. Pawar et al. [22] reported the effect of fuel on the preparation of nano-sized cobalt ferrite powders by the SCS method. Varma et al. [23] synthesized a magnetite (Fe_3O_4) phase of iron oxide in an inert atmosphere.

In the present work, the experimental results of as-synthesized vanadium oxides with different fuels and in different atmospheres are presented. Since the metal resource (vanadium) didn't have the metal nitrate, we used metal acid radical ion ($[VO_3]^-$) as vanadium source, ammonium nitrate as oxidizer, and fuels (glycine and citric acid) as reducing reagents. The properties of products are sensitive

to the combustion parameters and can be tunable by adjusting the fuel and atmosphere. Reaction mechanisms of various combustion systems were characterized in detail. When citric acid and glycine as the mixture fuels, VO_2 product with the average particle size of 20 nm could be synthesized and show typical temperature-driven semiconductor to metal transition. In an inert atmosphere, the V_2O_3 product with the average size of 70 nm could be synthesized. These results can extend the theory of SCS with metal acid radical salt as the metal source and provide guidance for preparing other transition metal-oxide nanopowders.

2. Experimental procedure

2.1. Synthesis

All reagents were of analytical grade and used as received without further purification. ammonium metavanadate (NH_4VO_3, vanadium source), ammonium nitrate (NH_4NO_3, oxidizer), glycine ($C_2H_5NO_2$, fuel) and citric acid ($C_6H_8O_7$, fuel) were used. In the combustion process, firstly, dissolving all reactants with a sufficient addition in 150 ml deionized water in a 500 ml glass to obtain the starting solution at room temperature. Then the glass was placed on an atmosphere -controlled muffle furnace. All experiments were conducted in air, unless noted otherwise. The furnace could be heated up to 200 °C. Once the majority of the water was evaporated and the solution became a sticky paste, an instantaneous combustion occurred. The combustion process only took less than one minute and a foamy product was synthesized.

2.1.1. Glycine- ammonium metavanadate system

In the system, the additive amount of NH_4VO_3 and NH_4NO_3 was 0.05 mol and 0.4 mol, respectively. The $C_2H_5NO_2$ was used as fuel and its additive amount was various. The tunable parameter, φ_g, is the molar ratio between $C_2H_5NO_2$ and NH_4VO_3 (φ_g = 1.5, 2, 4 and 8). The experiment was conducted in air.

2.1.2. Citric acid - ammonium metavanadate system

In the system, the additive amount of NH_4VO_3 and NH_4NO_3 was 0.05 mol and 0.4 mol, respectively. The $C_6H_8O_7$ was used as fuel and the molar ratio between $C_6H_8O_7$ and NH_4VO_3 was 4. The experiment was conducted in air.

2.1.3. Mixture fuels - ammonium metavanadate system

In the system, the additive amount of NH_4VO_3 and NH_4NO_3 was 0.05 mol and 0.4 mol, respectively. The $C_2H_5NO_2$ and $C_6H_8O_7$ were used as mixture fuels, and the molar ratio between mixture fuels and NH_4VO_3 was 4. The tunable parameter, x_c, is the molar ratio between $C_6H_8O_7$ and $C_2H_5NO_2$ (x_c = 0.25, 1 and 4). The synthesis experiment of VO_2 and V_2O_3 was conducted in air and in an inert atmosphere, respectively.

2.2. Characterization

The thermogravimetric and gas-phase analysis of reactive gels before being ignited were performed by a thermogravimetry (TG)-differential scanning calorimetry (DSC) device (NETZSCH-Gerätebau GmbH, Germany) with a mass spectrometer (MS) (QMS403C) at a heating rate of 5 °C min^{-1} in air/argon atmosphere. The compositions of the products were studied by X-ray diffraction (XRD, MXP21VAHF) in reflection mode at room temperature, in which the 2θ angle varied from 10° to 90° in 0.02° increments and the sample support is square groove. The morphology of the as-synthesized powders was analyzed by the scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN). The automated Surface Area

& Pore Size Analyzer (QUADRASORB SI-MP, Quantachrome Instruments, BoyntonBeach, FL) was used to study the specific surface area of the samples.

3. Results and discussion

In the research, we investigated a variety of combustion systems to determine the conditions for direct synthesis of vanadium oxide nanopowders with pure phase compositions (VO_2 and V_2O_3). All experiments discussed below were conducted in air, unless noted otherwise.

3.1. Glycine-ammonium metavanadate system

Glycine, the simplest amino acid, is widely used in the SCS method [24,25]. During the experiments, the ratio between glycine and ammonium metavanadate, φ_g, varied in the range from 1.5 to 8. As reported in our previous work, the changes of this parameter have great influences in the properties (e.g., phase composition, purity, and morphology) of the synthesized powder [26,27].

XRD patterns of the four products are shown in the Fig. 1(a). It is obvious that the product (φ_g = 1.5) is a mixture of $(NH_4)_2V_6O_{16}$, VO_2, V_2O_5 and V_5O_9, indicating the fuel scarce and the combustion procedure inadequacy. Increasing the φ_g to 2, the product is consisted of VO_2, V_2O_5 and V_5O_9. When $\varphi_g \geq 4$, the two products have well-crystalline structures of the monoclinic VO_2 phase (JCPDS No. 76-0456). The diffraction peak intensity of VO_2 rises with the increase of glucose additives, indicating an increasing degree of crystallinity. In the case of φ_g=4, the average crystallite size calculated by the Debye–Scherrer method [28] (D_{XRD}) was 43 nm (Table 1).

Fig. 1(b)–(e) show the SEM images of the four products. The product (φ_g = 1.5) consist of irregular blocks. When φ_g is increased to 2, 4 and 8, all the three products show similar flake-like structure. These holes exhibited on the surface can be attributed to the strong dispersant effect of gases generated during the SCS process. As shown in the TEM image (Fig. 1(f)), the flake (φ_g = 4) comprise of nanoparticles with average particle size of 40 nm, consistent with the calculated D_{XRD} results (Table 1). The clear lattice fringes with an interlayer spacing of 0.3315 nm (Fig. 1(g)) correspond well with the distance of $(-1\ 1\ 1)$ planes, indicating the crystalline VO_2 structure. However, when φ_g is increased to 8, the phenomenon of spontaneous ignition occurs and the particle size is increased to 60 nm (Fig. 1(h)), which could be ascribed to the rich fuel system.

To better elucidate the formation of VO_2 (φ_g = 4) during the SCS process, we characterized this reaction by using TG-DSC coupled with MS analysis. Because of the polymeric structure of the anion, NH_4VO_3 is insoluble in water at room temperature [18]. However, when it is continually warmed with water, and glycine with COOH groups is added, NH_4VO_3 dissolves easily and completely [29–31]. At initial stage (below 115 °C), there is an endothermic peak accompanied with ~28% weight loss and the released gases of NH_3 and H_2O, which can be due to the water evaporation and rapid decomposition of NH_4NO_3 and NH_4VO_3 (Eqs. (1)-(3)) (Fig. 2) [26]. This decomposition phenomenon in the solution leads to the formation of NO_x species which would react with glycine later (Eq. (4)) [4,26]. Around 157 °C, a huge exothermic peak accompanied with abrupt weight loss occurs, caused by the redox reaction of the gel [23]. During the redox process, the adsorbed and released gases include O_2, NH_3, H_2O, NO, NO_2, CO and CO_2 (Fig. 2(b)), originated from the intermolecular complex reactions of decomposition and redox (Eqs. (5)-(8)). The possible equations of reactions are presented as follows:

$$NH_4NO_3 \rightarrow NH_4^+ + NO_3^- \tag{1}$$