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Synthesis of nanostructured hollow microspheres of vanadium (III, V) oxides

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Vanadium oxides V_2O_5 and V_2O_3 have been synthesized by ultrasonic spray pyrolysis in the form of nanostructured spherical agglomerates with an average diameter of 0.5–1.5 μm. By changing the synthesis conditions, the vanadium oxidation state and microspheres surface morphology can be varied. The microspheres of V_2O_5 are formed during aerobic synthesis, while V_2O_3 microspheres are produced under an atmosphere of argon. An increase in the concentration of the initial solution leads to an increase in both size of V_2O_5 nanoparticles and the diameters of the V_2O_5 microspheres. Long-term storage of V_2O_3 in air results in morphological degradation of the microspheres.

Keywords: nanostructured microspheres, ultrasonic spray pyrolysis, solutions, vanadium oxides.

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1. Introduction

It is known [1] that a number of oxides of 3d-, 4d- and 5f- elements, including vanadium, are capable for metal-dielectric phase transition (MDPT) under the influence of temperature and pressure. This phase transition leads to changes in the structural, thermophysical, optical, magnetic and electrical properties of the compound and finds wide practical application. Thus, for V_2O_3, a phase transition at 150–160 K is observed from a low-temperature monoclinic (space group I2/a) to a rhombohedral (space group R3c) modification, which is accompanied by an increase in the electrical conductivity by seven orders of magnitude and a change in magnetic behavior from antiferromagnetic to paramagnetic [2, 3]. Therefore, materials based on vanadium (III) oxide are widely used for the manufacture of thermistors with a sharp change in resistance [4], which are used in electronic and electrical devices as breakers and inrush current limiters. In order to control the temperature of the V_2O_3 phase transition, the influence of deformation, pressure and doping is studied [5–9]. Several vanadium oxides and vanadium oxide-based compounds have a layered or tunnel type of crystal structure of V-O polyhedra, which provides significant mobility of metal cations embedded in crystallographic lattice [10]. This property makes these compounds a promising material for use as sensor materials and electrodes for intercalation batteries. Therefore, vanadium oxides with mixed valence and their derivatives have recently attracted attention as chemical sensors, nanoscale magnets, and electrical and optical devices [11–13]. The specific interest is the practical application of V_2O_5-based solid solutions as highly efficient cathode materials for metal-ion batteries, which demonstrates a high energy density (with charging capacity up to 650 mAh/g) and significant cycle stability [14–16]. The nanostructured V_2O_5-based materials obtained in the last decade demonstrate an high rate of the intercalation and deintercalation of M^{n+} ions compared to commercial ones [17]. A large amount of experimental results has been accumulated on the hierarchical structures of nanocrystalline vanadium (V) oxide [18]. Information on the features of the formation of V_2O_3 in the nanocrystaline state is scarce and contradictory. Significant differences in the character of MDPT in nanodispersed V_2O_3 in comparison with bulk crystalline samples were found [19]. Due to the synergetic effect, three-dimensional (3D) hierarchical nanostructures have a stable structure, a developed surface, and a large number of active centers. Such structures are intensively studied and applied in the field of optics, catalysis, and energy conservation [20]. The morphological features of nanocrystaline samples are varied by the preparation conditions. There are several ways to synthesize vanadium oxides in the 3-D state: hydrothermal method [17], thermal decomposition of complexes with an organic ligand [21], and spray pyrolysis method [22–25]. The production of oxide materials in the form of hollow microspheres is a challenging task, since these objects combine the advantages of 3-D structures and thin films. This work describes the most promising method of ultrasonic spray pyrolysis (USP). Previously, using the USP method, hollow microspheres of multiferroics $BiFe_{1-x}Mn_xO_3$ were obtained and studied [26, 27]. The USP method makes it possible to control the conditions for the formation of a single-phase oxide from an aqueous aerosol with a radial distribution of dissolved components in the droplet volume, which subsequently determines the formation of spherical agglomerates of a given diameter [26]. By varying the intensity of ultrasonic exposure, the temperature and atmosphere of aerosol thermolysis, it seems possible to obtain vanadium oxide in the expected valence and morphological state.

The aim of this study is to obtain vanadium (III and V) oxides in the form of nanostructured hollow microspheres using the USP method in a controlled gas atmosphere.

2. Experimental

Ammonium metavanadate NH_4VO_3 was used as a vanadium-containing precursor. Oxalic $C_2H_2O_4$ acid was added to an aqueous solution of NH_4VO_3 in a molar ratio of ammonium metavanadate:acid equal to 1:2. The vanadyl ions VO^{2+} solution with concentration of 0.10–0.30 mol/l was subjected to ultrasonic spraying in a vertical tube furnace at a temperature of 550–800°C. Air or argon was used as a carrier gas at a rate of 0.10–0.20 m/s. The resulting oxide was collected by an electrostatic precipitator.

The use of the V^{4+} precursor for the synthesis of vanadium oxides in different oxidation states excludes the stage of reduction of the formed V_2O_5 by hydrogen. It is known that the addition of carboxylic acids to the ammonium metavanadate solution ensures the reduction of VO_3^- ions to VO^{2+} and stabilizes the vanadyl ion in an aqueous medium in the form of a complex [19]:

$$VO_3^- + 2H_2C_2O_4 \rightarrow VO^{2+} + 2CO_2 + C_2O_4^{2-} + 2H_2O$$

$$VO^{2+} + C_2O_4^{2-} \rightarrow [VO^+(C_2O_4)_2]^{3-}.$$

USP synthesis was carried out using gas carrier: air or Ar. The synthesis temperature in both cases was 600°C. Aerosol was fed into the reaction zone at a rate of 0.2 m/s, corresponding to a synthesis time of 5 sec. A schematic diagram of the of vanadium oxide (III or V) synthesis is shown in Fig. 1.

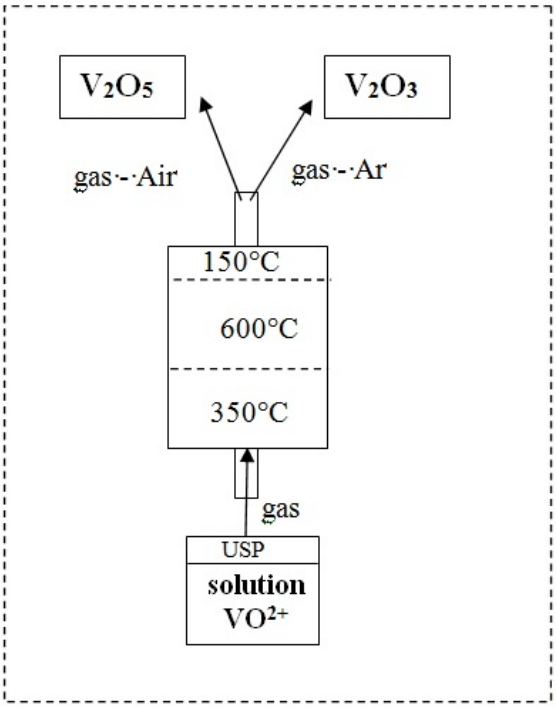

FIG. 1. A schematic diagram of the V_2O_n synthesis

X-ray phase analysis was carried out on an XRD-7000 diffractometer (SHIMADZU) with a secondary monochromator in CuKα radiation in the 2θ angle range from 20° to 80° with a step of 0.03°. X-ray diffraction analysis was performed using the PowderCell software. The morphology of the samples, their chemical composition and the uniformity of the distribution of chemical elements were studied using a JEOL JSM-6390LA scanning electron microscope (SEM) equipped with an EDS Inca Enegy 250 X-ray spectrometer.

3. Results and discussion

Under the described conditions, the single-phase samples of vanadium oxides were obtained. When carrying out the USP process in air the only product was V_2O_5. And using Ar s a gas carrier the final product was V_2O_3.

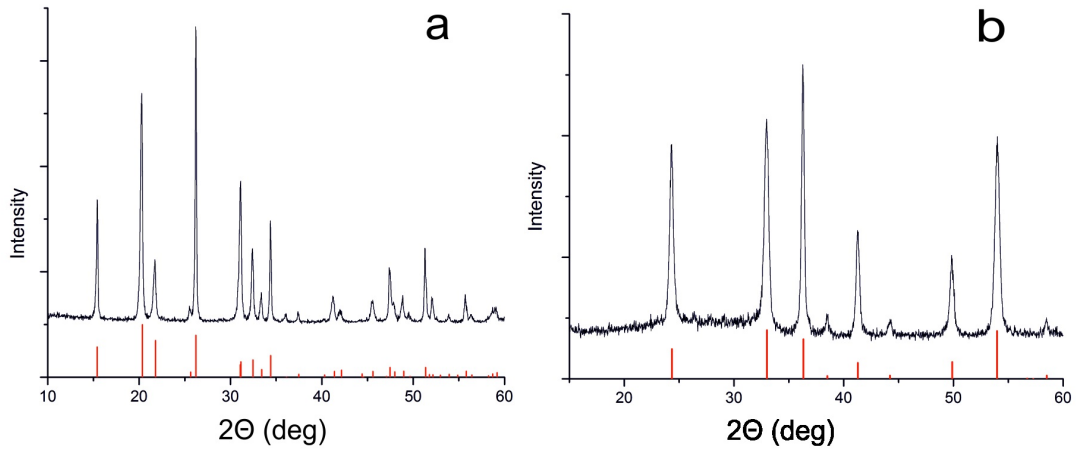

FIG. 2. X-ray diffraction patterns of samples obtained by USP VO^{2+} solution: in air (a), in Ar (b)

The diffraction patterns of the samples have a profile characteristic of the corresponding vanadium oxide (ICSD Collection Code 15299) (Fig. 2). During the USP the aerosol particles get directly into the drying zone with a temperature of 250–350 °C, and then into the calcination zone with a temperature of 600 °C (Fig. 1). The parameters and conditions of USP, i.e. the concentration of vanadyl ion C^{2+}_{VO} and the suppling rate of solution to the drying zone. These parameters ensure the production of hollow microspheres observed experimentally. The Table 1 shows the effect of the synthesis conditions of V_2O_n (C^{2+}_{VO}) on the parameters of unit cells and the size of coherent scattering regions D (Table 1).

TABLE 1. Characteristics of samples obtained from solution

Sample	Synthesis conditions	Oxide composition	Unit cell parameters	D, μm	CSR, nm
I	air $C_{VO^{2+}}$=0.04 mol/l	V_2O_5	a = 11.4807 c = 3.5636 b = 4.3989	0.45	50
II	air $C_{VO^{2+}}$=0.3 mol/l	V_2O_5	a = 11.4863 c = 3.5561 b = 4.3792	0.65	62
III	Ar $C_{VO^{2+}}$=0.3 mol/l	V_2O_3	a = 4.94498 b = 14.0123	0.45	36

The complex mechanisms of aerosol droplet formation, drying, and thermolysis in a dynamic mode were studied in detail in [26]. It was shown that the morphology of particles when using the USP process is formed during drying and is retained during the subsequent calcination.

It has been experimentally established that the diameter of a spherical particle formed by USP process d_g can be expressed by the following theoretical relationship:

$$d_g = d_D = \sqrt{\frac{C_V}{\rho_p}},$$

where C_V is the vanadium concentration, ρ_p is the vanadium oxide density, d_D is the average aerosol droplet size.

The droplet size is inversely proportional to the frequency of ultrasonic action on the solution during spraying. The intensity of US-vibrations is determined by the viscosity and surface tension of the liquid used as a precursor.

According to SEM and X-ray phase analysis the average diameter of the regular V_2O_5 microspheres obtained from dilute solutions of vanadium in air is 0.45 μm of (Fig. 3a). The surface of the spheres is dense, without pores and faults. With an increase in the vanadium concentration in the solution up to 0.3 mol/l, the average diameter of the resulting spheres grows insignificantly (Table 1, Fig. 2b), and the lattice parameters do not undergo noticeable changes.

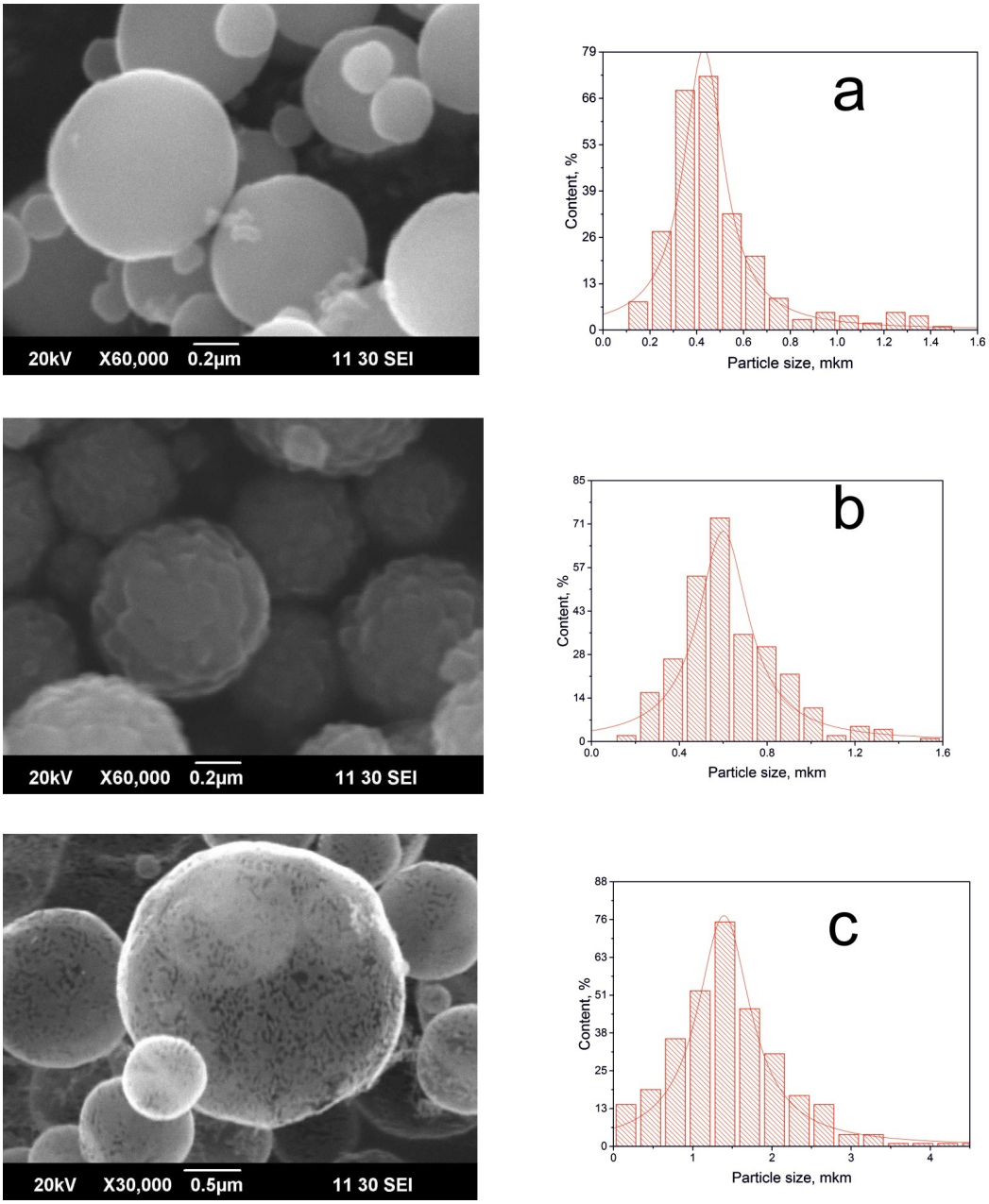

FIG. 3. SEM image and particle size distribution of V_2O_5 samples obtained from a solution with a concentration of 0.04 mol/l (a) and 0.3 mol/l (b) and V_2O_3 (c)

The main difference between obtained V_2O_5 microspheres is the surface type morphology. The surface of V_2O_5 microspheres obtained from concentrated solution is formed by flat scaly crystals closely adjacent to each other (Fig. 3b). In the case of USP under an Ar atmosphere, the V_2O_3 microspheres with an average diameter of 1.5 μm were obtained (Fig. 3c). The surface of the spheres is loose, formed from one layer of nanosized crystallites. It is known that vanadium (III) oxide is metastable and over time it undergoes spontaneous oxidation to V_2O_5 [27, 28]. The process of partial morphological and structural degradation characteristic of V_2O_3 was observed after 12 months of storage of the sample in air (Fig. 4).

The so-called "aging" of spherical samples is observed in a significant broadening of diffraction peaks characteristic to the V_2O_3 structure (Fig. 4). At the same time, no peaks of the V_2O_5 impurity were found in the diffraction patterns. According to SEM data (Fig. 4), the surface of the aged V_2O_3 samples is formed by lamellar aggregates connected weakly to each other. Therefore, the shell was easily destroyed and the spheres were completely degraded.

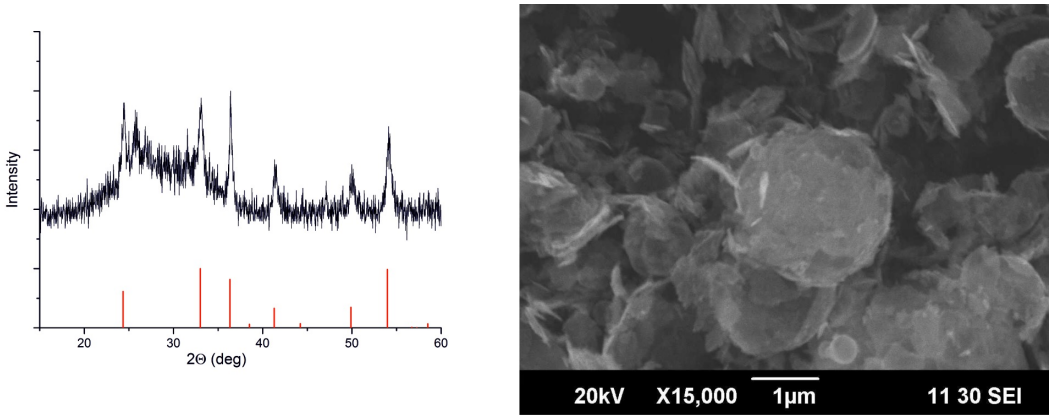

FIG. 4. V_2O_3 sample after storage in air: diffraction pattern and SEM image

4. Conclusion

Vanadium oxide (III or V), in the form of hollow microspheres, was obtained by the method of ultrasonic spray pyrolysis (USP) in the controlled gas atmosphere at one stage. The size of the microspheres and the main properties of their surface are establish to be dependent on the concentration of the precursor in an aqueous solution and thermolysis atmosphere. Thus, the average diameter of microspheres can be experimentally varied in the range 0.45–1.5 μm. The surface of V_2O_3 spheres obtained in an Ar atmosphere is formed by one layer of crystallites with an average size of 36 nm. Spontaneous oxidation of spherical V_2O_3 leads to complete degradation of its surface.

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