Microwave assisted growth of nanorods vanadium dioxide VO$_2$ (R): structural and electrical properties

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Abstract. Nanostructured metal oxides have attracted a lot of attention recently owing to their unique structural advantages and demonstrated promising chemical and physical properties for various applications. In this study, we report the structural and electrical properties of vanadium dioxide VO$_2$ (R) prepared via a single reaction microwave (SRC) synthesis. Our results are revealing that the components of VO$_2$ (R) films have a rod-like shape with a uniform size distribution. The nanorods with very smooth and flat surfaces have a typical length of up to 2μm and a width of about several nanometers. The structural investigations reveal the high crystallinity of VO$_2$ (R) ensuring good electrical contact and showing a high conductivity as a function of temperature. This synthesis method provides a new simple route to fabricate one-dimensional nanostructured metal oxides which is suitable for a large field of applications especially for smart windows.

1. Introduction

Among the transition metal oxides, nanostructured vanadium oxides materials, such as V$_2$O$_5$, V$_2$O$_3$, V$_3$O$_7$, VO$_2$ (B), VO$_2$ (M), VO$_2$ (R) and VO$_2$ (A) have been used in many fields due to their outstanding structural flexibility [1] and their wide range of oxidation states (from +2 to +5) in the vanadium-oxygen system [2]. Vanadium dioxide (VO$_2$) is the most well-known of many vanadium-related oxides and has been extensively investigated for its distinctive multifunctional including chemical, optoelectronic and electrochromic properties [3]. VO$_2$ nanoparticles have been brought into sharp focus with its different crystalline phases [4]. Because of these attractive properties they exhibit potential applications in many areas such as smart windows [5] and energy storage devices [6]. Vanadium dioxide with rutile-type structure VO$_2$ (R) undergoes first-order reversible metal-insulator transition (MIT) at around 68 °C. During the phase transition process, there is a structural phase transformation from high-temperature metallic tetragonal phase VO$_2$ (R) to low-temperature insulating
monoclinic phase VO$_2$ ($M_1$) [7]. The reversible transition in structure is accompanied by reversible changes in its optical and electrical properties [8]. Many different synthesis methods have been developed for the synthesis of vanadium oxide nanoparticles including sol–gel [9], vapor transport [10], pulsed laser ablation [11] and hydrothermal method [12].

There are few reports devoted to the synthesis of VO$_2$ (R) by microwave method. The microwave route for synthesizing vanadium oxide nanoparticles is particularly successful in terms of controlling every reaction by direct pressure and temperature control, with very high growth rate and small particle sizes as a consequence of fast homogenous nucleation [13]. To the best of our knowledge, this is the first study of the effect of the time and annealing treatment on the growth of the nanostructured vanadium dioxide VO$_2$ (R) prepared by microwave SRC.

In the present work, we investigate the structural and electrical properties of vanadium dioxide VO$_2$ (R). The structure and morphology of our nanoparticles are investigated in order to probe the effects of the time and annealing treatment on the morphology and size change of the nanostructured vanadium oxides. In this sense, X-ray diffraction (XRD), transmission electron microscopy (TEM) and electrical conductivity were investigated.

2. Experimental

2.1. Material preparation
Vanadium oxides nanoparticles VO$_2$ (R) were synthesized using a single reaction microwave synthesis.
In a typical synthesis, V$_2$O$_5$ (0.9g) was first stirred with 20 ml of deionized water to make a yellow suspension. Then 1.5 ml of sulphuric acid, H$_2$SO$_4$, was added to the suspension while heating at around 60 °C. 0.25 ml of hydrazine hydrate, N$_2$H$_4$·2H$_2$O, was added dropwise to the solution. Heat could also be applied to the solution while adding NaOH and hydrazine solution. The pH of the blue VO$_2^+$ solution was strongly acidic, then was weighed with a stir bar and placed on a rack. The rack is fitted to the chamber top with a mechanical stirrer, which is lowered automatically. The mixture was treated at 230 °C for 30, 60 and 90 minutes. When the program stops, a circulating water-cooling jacket rapidly cools the chamber, pressure is gently released, and gases and vapors are directed away to exhaust. The resulting suspensions were collected by centrifugation at 4500 rpm for 40 min to remove metal ions and impurities using distilled water and ethanol (figure 1). All of the chemical reagents were analytical grade. They were purchased from Acros Organics and used without further purification.

2.2. Material Characterization
To characterize the obtained samples, XRD patterns were obtained from a Rigaku Smart Lab system using Cu Kα (λ=1.54178 Å), scanning electron microscopy (SEM) is employed to observe the morphology of vanadium oxides nanoparticles. Finally, conductivity was measured with a Picoammeter/Voltage Source-Keithley Model 6487 system.

3. Results and discussions

3.1. X-ray diffraction

![XRD patterns](image)

**Figure 2.** XRD patterns of VO-NPs (a) synthesized at different time and (b) under annealing process for 3h at 90 min.

The XRD pattern of vanadium oxides nanoparticles synthesized at different time (figure 2 .(A). (a) - (b)) revealed an amorphous phases, this indicates that the vanadium oxide nanoparticles are not efficiently formed during the growth mechanism. However, after 90 minutes, all the peaks could be indexed as the tetragonal VO$_2$ (R) (JCPDS: 71-0291) with lattice constants: a = b = 4.5546 Å, c = 2.8528 Å and β = 90.00°. There are only the neat and narrow peaks without any outsider peaks or impurity, revealing that the V$^{5+}$ ions in V$_2$O$_5$ have been reduced to V$^{4+}$ ions by the hydrazine in the reaction. Figure 2 (B) shows the XRD pattern of VO$_2$ (R) under annealing process for 3h at 200, 300, 400 and 500 °C respectively. We observe that we have similar phase of monoclinic VO$_2$ (R) at 200 °C for 3h accompanied by a decrease in the intensity of XRD spectrum. However, for 300 °C the peaks of VO$_2$ (R) vanished which indicated that the phase was modified with the appearance of vanadium pentoxide picks. In addition, at 500 °C, all the peaks could be indexed as the orthorhombic V$_2$O$_5$ (Space group 59: Pmmm) with lattice constants a = 11.5160 Å, b = 3.5656Å and c = 4.3727 Å, and
β = 90.00°; this is compatible with the standard value of JCPDS: 41-1426 already described in the literature [14]. Hence, Vanadium oxides can be selectively synthesized with controllable phase structures VO₂ (R) and V₂O₅ with increasing synthesis time and annealing temperature which affect the stoichiometry and the arranged band.

3.2. SEM Measurements
The SEM images of our nanoparticles synthesized at different time (figure 3 (a) - (b)) revealed that vanadium oxides nanoparticles were not efficiently formed during growth mechanism indicating that the phase was amorphous even after 60 min. The SEM image in figure 3 (c) confirms rod-shaped morphology of VO₂ (R) nanoparticles and shows an important modification on the morphology of these nanostructures prepared at 90 min. The average diameter of the nanorods was from several tens to several hundred nanometers and the surface was very smooth. These results confirm that time is a principal parameter in the formation of VO-NPs.

Furthermore, figure 3 (d) confirms that the morphology was changed after annealing treatment, it can be observed that the transition of crystal phases from VO₂ (R) to V₂O₅ in our experiments occurred at 500 °C. The growth of VO-NPs, in this case, leads to a sphere-like shape with very smooth and flat surfaces and a typical width of about several nanometers.

Figure 3. SEM surface morphology: (a) amorphous phase at 30 min, (b) amorphous phase at 60 min, (c) VO₂ (R) nanorods at 90 min, (d) V₂O₅ nanospheres at 500 °C.

These results support the structural investigations and confirm the remarkable effect of time and annealing treatment on the growth of vanadium oxide nanostructures.
3.3. I-V Characterization

**Figure 4.** Conductivity measurement of VO-NPs nanostructures synthesized at different time: 30, 60 min (a, b) and the conductivity as a function of the time at the applied voltage (10 V) (c).

The I-V characteristics of VO-NPS nanostructures at different time are shown in figure 4. The representation of the I-V curves on the same figure makes it possible to better understand the influence of time on the electrical properties. As we can see (figure 4 (a) -( b)), the I-V curves of the VO-NPs obtained are linear indicating an ohmic behavior of the contact. At a negative voltage, for a period of 90 minutes, the value of the current at which the conductivity starts its linear behavior is -2 mA. Figure 4 (c) shows the conductivity as a function of the time at the applied voltage (10 V). It is observed that from 30 to 60 min there is no a great enhancement in the conductivity. However, the conductivity increases rapidly with an increase of the time from 60 to 90 min. The increment in the time reduces the occupancy of defect states, which is due to a large number of charge carriers available for conduction so that the mobility increases. Hence, this results shows that by increasing the time, the electronic conductivity can be increased by 3 orders of magnitude.

**Figure 5.** Conductivity measurement of VO-NPs nanostructures under annealing process for 3h at 90 min (a, b) and the conductivity as a function of the annealing treatment at the applied voltage (10 V) (c).

Figure 5 provides a comparison of the I-V characteristics of VO-NPs before and after the annealing treatment at 90 min. Earlier measurements show that by increasing the temperature, the electronic conductivity can be increased by 2 orders of magnitude [15-16]. In figure 5 (a)-(b), the measurement show that the conductivity increases with increasing temperature where the number of electronic defects decreases so the mobility increases. Figure 5 (c) shows the conductivity as a function of the temperature at the applied voltage (10 V). It is observed that the conductivity increases moderately with an increase of the annealing treatment from 0 °C to 300 °C. Then, we observed that above 400 °C the conductivity decreases slightly which may be due the change of the phases and morphology of VO-NPs [17]. However, for 400 to 500 °C we observed, that a large number of charge carriers available for conduction are accompanied by a greater increase of electrical conductivity. Our results show that the two main reasons for good electrical conductivity of VO-NP films are the increase in the time and annealing treatment.
4. Conclusion

The purpose of this study was to investigate the structural and electrical properties of vanadium oxides prepared by a single reaction microwave synthesis. The experimental results demonstrate that synthesis time and annealing treatment effecting on the growth of the nanostructured vanadium dioxide VO₂(R). Our result highlighted the modification of VO-NPs form, shape and phase after the time and annealing treatment showing that the annealing and time are two main factors in controlling the phase and morphology of vanadium oxides nanoparticles. The experimental measurement revealing that the annealing state and the increase in time are two crucial parameters for the improvement of the electrical conductivity. The use of these nanoparticles is promising way for the development of technological applications for smart windows as solar heat control.

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