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One step Hydrothermal Synthesize of nanostructures VO_2

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Abstract VO_2 nanostructures have been synthesized in a controlled manner via hydrothermal methods by using Cetyl Trimethyl Ammonium Bromide (CTAB) as surfactant, by adopting $NaVO_3$ and NH_4Cl as initial precursor and time as adjusting parameter. The products were characterized by scanning electron microscopy (SEM) images and X-ray diffraction (XRD) pattern. The evolution of composition and morphology during the time has been investigated. NaV_3O_8 was investigated as initial product and this precipitation turns to V_6O_{13} and VO_2 during the time.
The final products are nanolayers of VO_2 with 300 nanometer width and 30 nanometer thicknesses. This specific morphology is obtained due to the role of CTAB.
Key words: Hydrothermal; CTAB; vanadium dioxide; sodium metavanadate.

Introduction

Vanadium dioxide (VO_2), one of the important functional materials, exhibits four different polymorphic structures including VO_2 (R) with rutile structure, the monoclinic VO_2 (M), a tetragonal structure of VO_2 (A) and the metastable VO_2 (B) possessing a monoclinic structure[1,2].
VO_2(B) is an attractive material for various applications especially as an electrode material for lithium batteries due to its layered structure and distinctive redox properties. VO_2(B) exhibits a maximum reversible capacity of about 320 mAhg_1 in the range 4 to 1 V in lithium cells[1,3,4].
In recent researches the application of VO_2(B) in humidity sensors have been reported and it is observed that the VO_2(B) type sensor has a higher sensitivity at low RH, and can be used for low humidity detection, which is difficult for humidity sensors based on many other semiconductor oxides[1].
the phase change from metastable VO_2(B) to thermodynamically more stable rutile VO_2 will occur at $T>300^0C$ and the later shows no attractive electrochemical properties [5] and therefore, it is difficult to obtain by high temperature synthesize method.
In this paper in addition of the synthesize of the VO_2 by adopting sodium metavanadate as precursor, it is tried to reveal the evolution of the reactions and characterize the composition and morphology of the phases which are formed during the time.

Experimental procedure

A mixture of sodiummetavanadate and Ammoniumchloride with equal ratio was dissolved in 20 ml dionized H_2O at room temperature under stirring. 0.68mmol of CTAB solution were added to lateral solution under stirring conditions. Subsequently, solution was slowly acidified to pH=2 using sulfuric acid.
Samples were transferred to a 70 ml stainless steel autoclave. The autoclave was maintained at 180^0C for 3, 6, 14 and 24 hours in a preheated electric oven and then allowed to cool to room temperature.
Precipitation was separated by centrifuging. The obtained powder then washed with ethanol and distilled water to remove any other possible residues.
The synthesized powder were characterized using X-Ray diffractometer with Cu Kα radiation (λ=0.154 nm). The size and morphology of the particles were observed on scanning electron microscopy (XL30).

Results &discussion

Figure 1 show the XRD patterns of the samples with 0.68 mmol CTAB at 180^0C for 3,6,14 hours. The XRD patterns for 3 hours reaction time shows the presence of NaV_3O_8 as the main product and V_6O_{13} as a minority phase. The reaction which is taken place in autoclave in first stage can be suggested as below:

$$3NaVO_3+2NH_4Cl+H_2O \rightarrow NaV_3O_8+ 2NaCl+2NH_4OH$$

Corresponding SEM image (figure 2) includes a mixture of cubic, rods, unshaped and also flower shape parts which seems to make up of nanorods. XRD pattern after 6 hours reaction time represent the picks belong to NaV_3O_8 and V_6O_{13}. The intensity of NaV_3O_8 picks decrease compared with the last sample and new picks corresponding to V_6O_{13} appears. These results indicate the conversion of the NaV_3O_8 to V_6O_{13} which can occure according the following reaction:

$$2NH_4Cl+ 2NaV_3O_8 \rightarrow V_6O_{13}+ 2NaCl+ 2NH_4OH+ H_2O$$

SEM image of this sample is shown in figure 3. It consists mostly of ribbons with the thickness of about 80 nanometers and unshaped particles with low volume percent. By considering the XRD and SEM results of the samples with 3 and 6 hours reaction time it can be inferred that the cubic and unshaped particles are NaV_3O_8 and the rod shape particles that derived from cubes are V_6O_{13}.The rods grow during the time and turn to ribbons in figure 3.

The evaluation of morphology process in this stage is considered to be similar to that reported by Wu and co-workers, where used CTAB as a surfactant to produce the ZnO[6].

Due to the intrinsic amphiphilic character of the surfactant, CTAB molecules are adsorbed on the surface of initial precipitation with their hydrophobic groups pointed toward the initial products and their hydrophilic groups oriented toward the aqueous solution and make floatage products. Schematic illustration of this formation mechanism is shown in figure 4. Figure 5 shows high magnification image of the picture 1. It is observed clearly that the cubic particles convert to rods with the diameter of about 30 nanometers (The trace of the rods remained on cubes surface). This is another evidence for mentioned conclusions.

As a result in absence of CTAB the rate of the reaction would be controlled by the diffusion of the reactant ions into the solid products and it would take much longer time and also it would have no especial morphology. So, CTAB have a positive influence in the morphology as well as the rate of the reaction. According to XRD results the VO_2 phase also was investigated in 14 hours of reaction time. The fact that the peaks of VO_2 and V_6O_{13} are very close to each other make some wide peaks in the pattern. Figure 6 shows the microstructure of this sample; it has more homogenous morphology compared to those previously described.

The XRD pattern of the sample with 24 hours reaction time are presented in figure 8 and approximately pure VO_2 were characterized (JCPDS 31-1438).

Corresponding SEM image in figure 9 shows the nanoribbons with the dimension of about 400nm in width, 30nm thickness and thousands of nanometers length with rectangular flat tips and somewhat sharp corners and exhibit uniform width and thickness through their lengths.

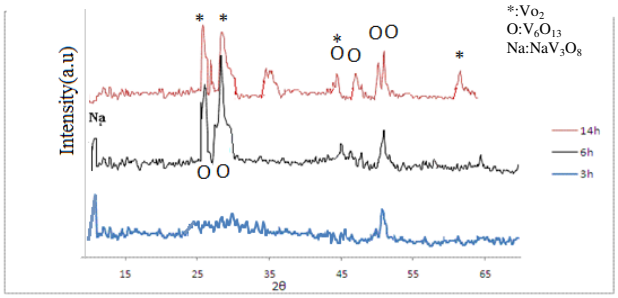

Fig. 1) XRD patterns of the samples with different reaction time

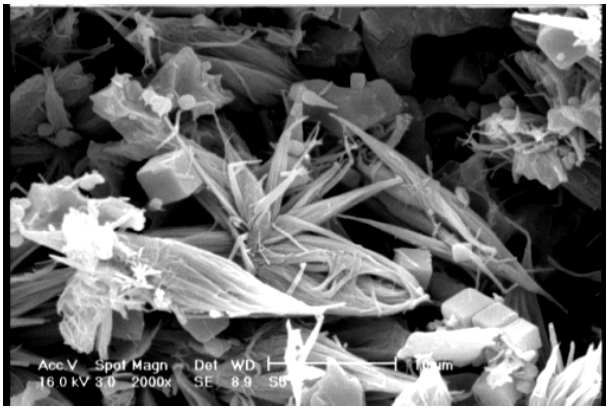

Fig.2) SEM images of sample with 0.68 mmol CTAB after 3 hours x1000.

Fig. 3) SEM image of sample with 0.68 mmol CTAB after 6 hours.

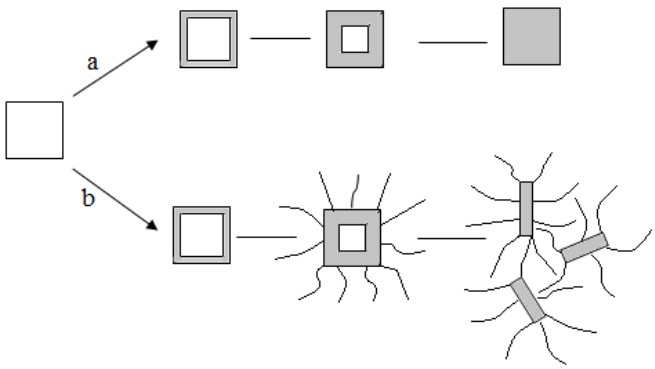

Fig.4) Schematic illustration of formation mechanism (a) without CTAB (b) in presence of CTAB

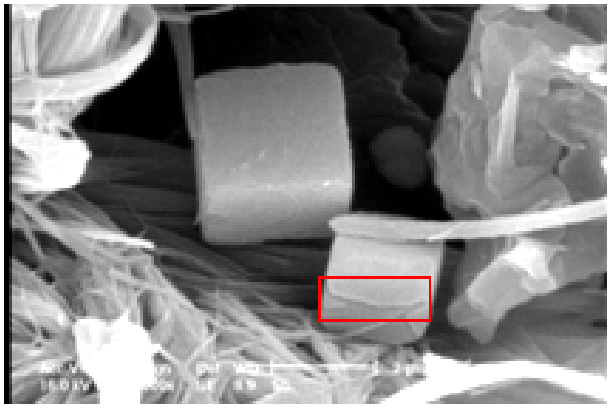

Fig.5) SEMimages of sample with 0.68 mmol CTAB after 3 hours with X15000 magnification.

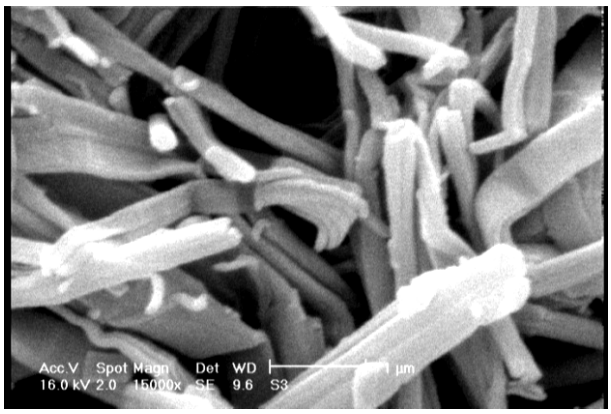

Fig . 6) SEM image of sample with 0. 68 mmol CTAB after 14 hours.

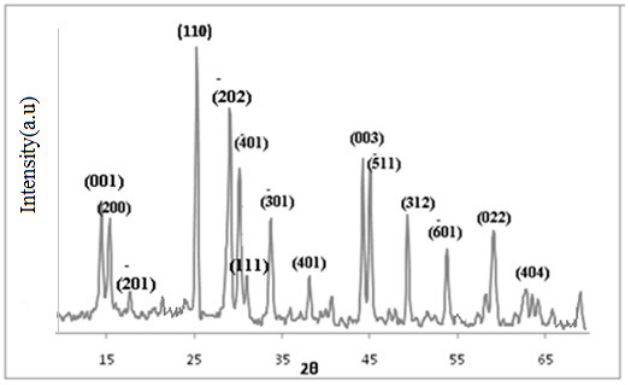

Fig.7) XRD pattern of the sample with 24 hours reaction time.

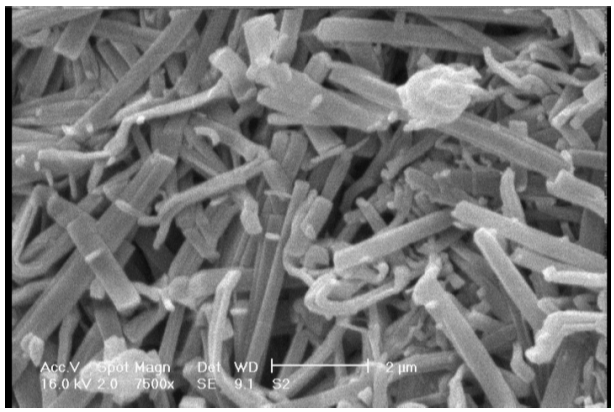

Fig .8) SEM image of sample with 0.68mmol CTAB after 24 hours.

Conclusion

In conclusion, VO_2 have been successfully synthesized with a simple hydrothermal method at 180^0C. The NaV_3O_8 was defined as an initial products. The cubic NaV_3O_8 produce the V_6O_{13} and VO_2 might have originated from this unstable oxide.

References

[1] H.Yin, K. Yu, Z. Zhang, M. Zeng, L. Lou, Z. Zhu, "Humidity Sensing Properties of Flower-Like VO2(B) and VO2(M) Nanostructures", Electroanalysis, 23(2011)1752.

[2] G. Zakharova, I. Hellmann, V. Volkov, Ch. Taschner, A. Bachmatiuk, A. Leonhardt, R. Klingeler, B. Buchner, "Vanadium dioxide nanobelts: Hydrothermal synthesis and magnetic properties", Materials Research Bulletin, 45(2010) 1118.

[3] P. Billik, M. Caplovicova, J. Manka, L. Caplovic, A. Cigan, A. Konakovsky, R. Bystricky, A. Dvurecenskij, "Synthesis and transport properties of nanostructured VO2 by mechanochemical processing" Measurement Science, 11(2011) 29.

[4] N. Chernova, M. Roppolo, A. Dillon and M. Whittingham, "Layered vanadium and molybdenum oxides: batteries and electrochromics", Journal of Material Chemistry, 19(2009) 2526.

[5] C. Tsang, A. Manthiram, "Synthesis of Nanocrystalline VO and Its Electrochemical Behavior in Lithium Batteries", J. Electrochem. Soc., 144(1997) 520.

[6] X. Sun, X. Chen, Z. Deng and Y. Li , A CTAB-assisted hydrothermal orientation growth of ZnO nanorods, Materials Chemistry and Physics, 78(2002) 99.