NANORODS SYNTHESIZED BY HYDROTHERMAL PROCESS USING V_2O_5 AS THE STARTING MATERIAL FOR THERMOCHROMIC APPLICATIONS

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ABSTRACT

Vanadium dioxide (VO_2) nanorods which are one of practical thermochromic materials were successfully synthesized via hydrothermal method using vanadium pentoxide (V_2O_5) as a starting material and *n*-butanol, acetylacetone as a reductant. The precursor was kept in stainless steel-autoclave at 120 °C for 48 h. The structural and morphological properties depended on the type of reductants were characterized by XRD, SEM and TEM. The XRD patterns indicated that the V_2O_5 was transformed to monoclinic VO_2 when the dual *n*-butanol and acetyacetone were used as a reductant. This synthesis method provides a simple route to fabricate one-dimensional VO_2 nanostructures which can be utilized as potentially practical thermochromic applications such as smart windows and optical switching.

KEYWORDS: nanorod, hydrothermal synthesis, VO_2, thermochromic material

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INTRODUCTION

In the past few decades, nanomaterials have received increasing attentions because of their fascinating properties that can be enhanced when their dimensions are in nanoscale. Numerous nanostructures are being investigated, including nanoparticles, nanosheets, nanotubes, nanowires and nanodots . Among nanomaterials, Vanadium dioxide (VO_2) has been intensively studied in the field nanomaterial due to its excellent properties for various applications such as sensors, catalysts, magnetic materials, storage material and thermochromic applications [1-2]. Previously, many kind methods have been developed to synthesize the VO_2 nanostructure such as ion beam sputtering, atmospheric chemical vapour deposition, co-precipitation and hydrothermal method [3-4]. Haihong Yin *et. al* [5] synthesized VO_2 by hydrothermal process and studied field emission properties of the nanostructure. V_2O_5 was selected as source material and oxalic acid as reductant. The results indicated that the nanostructure of this material can be changed with variation of oxalic acid concentration and the nanobundles have the best field emission performance. P. Evans *et. al*. [6] reported on thermochromic properties of VO_2 thin films prepared by atmospheric chemical vapour deposition and the corresponding results indicated that their transmission spectra in infrared region drastically reduced up to 80% when the films were heated at 65 °C. Graham Armstrong *et. al.* [7] reported on lithium intercalation electrochemistry of VO_2 synthesized by hydrothermal process. The results indicated that VO_2 nanowires were obtained after kept in stainless-steel autoclave at 180 ºC for 48 h and had a capacity to intercalate lithium of 265 $mAhg^{-1}$ at a rate of 10 mAg^{-1}. From literatures, the electrical and optical behaviors of these materials could be improved depending on sample size and morphology.

In this work, we report on the simple synthesis of VO_2 nanorods by hydrothermal method. The effect of reducing agent types on physical properties of as-prepared products were scrutinized and discussed.

MATERIALS AND METHODS

The VO_2 nanorods were synthesized by hydrothermal method using V_2O_5 as the source of vanadium and *n*-butanol, acetylacetone as the reducing agents. In a typical process, 1.81 g of commercial V_2O_5 powder, 10 mL of *n*-butanol, 10 mL of acetylacetone and 100 mL of deionized water were vigorously magnetic stirred at room temperature for 1 h, the suspension was transferred into a 250 mL Teflon-lined stainless autoclave, which was then filled with deionized water up to 200 mL of total volume. The autoclave was sealed and kept at 120 ºC for 24 h and then cooled down to room temperature for 24 h. The obtained dark blue precipitate was filtered and washed for several times with deionized water, acetone and absolute ethanol and dried in air at 80 ºC for several time.

The crystal structure and phase identification of the samples were investigated by X-ray diffracttion with a monochromatic source of Cu K_α (λ=0.15405 nm). Their morphologies were monitored with EVO® HD scanning electron microscope with an accelerating voltage of 10.0 kV. Transmission electron microscopy images and selected area electron diffraction (SAED) patterns were taken with TECNAI G2 20 transmission electron microscope, using an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

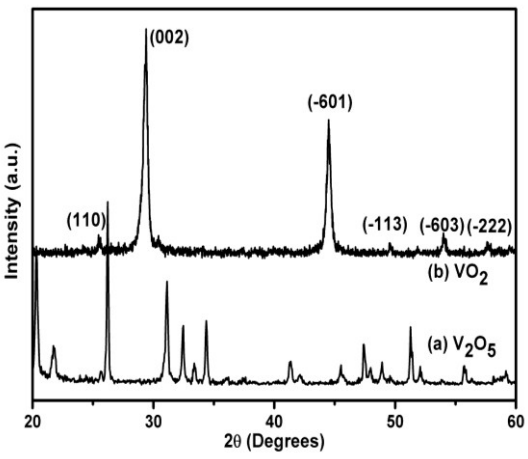

Fig. 1. XRD patterns of (a) commercial V_2O_5 powders and (b) As-synthesized VO_2 powders were synthesized by facile hydrothermal method at 120 ºC for 24 h.

XRD patterns of VO_2 powders synthesized by hydrothermal method are provided in Fig 1. The as-synthesized product thoroughly exhibits the diffraction peaks positions at 2θ = 25.55º, 29.34º, 44.51º, 49.59º, 54.05º and 57.70º attributed to (110), (002), $(\bar{6}01)$, $(\bar{1}13)$, $(\bar{6}03)$ and $(\bar{2}22)$ orientation plane of monoclinic structure of metastable phase VO_2 [JCPDS 81-2392]. This result indicated that the metastable phase VO_2 powder can be obtained by facile hydrothermal method. The interplanar space (*d*-spacing) could be determined by Bragg's law as follows ;

$$2d\sin\theta = n\lambda \quad (1)$$

where d is the interplanar space, θ is Bragg angle, λ is the wavelength of the X-ray source. From calculation, the calculated interplanars from XRD pattern are close to JCPDS file number 81-2392 as shown in Table 1.

Table 1. Comparison of *d*-spacing.

Orientation plane	*d*-spacing JCPDS file (Å)	*d*-spacing calculation (Å)
(110)	3.53	3.48
(002)	3.08	3.04
$(\bar{6}01)$	2.02	2.03
$(\bar{1}13)$	1.85	1.84
$(\bar{6}03)$	1.67	1.70
$(\bar{2}22)$	1.59	1.59

The SEM image of the commercial V_2O_5 powders is shown in Fig. 2(a). The form of the commercial V_2O_5 is the brain-like with the high density of aggregation. Fig. 2(b) shows the SEM image of V_2O_5 powders synthesized by facile hydrothermal method at 120 °C for 24 h. It is clearly observed that the uniform nanorod-liike VO_2 with diameter about 100-150 nm and 1.5-2 μm in length can be productively synthesized by hydrothermal method. High magnification and Selected Area Electron Diffraction (SEAD) mode of the as-synthesized VO_2 synthesized by hydrothermal method at 120 ºC for 24 h is illustrated in Fig 5. The results demonstrate that the nanorods consist of interplanar space along the length direction of 3.12 Å that is in good agreement with the values calculated from XRD patterns. From SEM and TEM images results, the one-dimensional VO_2 in form of short nanorod structure could be synthsized by single-step hydrothermal method without any further post-

treatment. It has been reported in previous literature carried out by R. Lopez and his group that the optical contrast between the semiconducting and metallic phases is dramatically enhanced in the visible region, presenting size-dependent optical resonances and size-dependent transition temperatures [8].

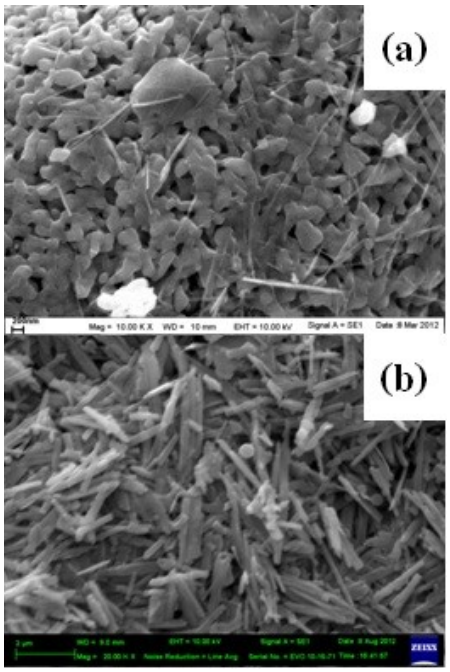

Fig. 2. SEM images of (a) commercial V_2O_5 powders and (b) As-synthesized VO_2 nanorods were synthesized by facile hydrothermal method at 120 ºC for 24 h.

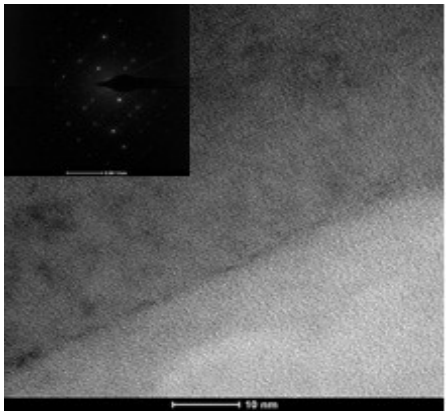

Fig. 3. TEM images of the As-synthesized VO_2 nanorods were synthesized by facile hydrothermal method at 120 ºC for 24 h (scale bar 10 nm ; the insert image is SEAD mode).

CONCLUSION

In summary, this work reports on the synthesis of VO_2 nanorods using V_2O_5 that can be carried out by facile hydrothermal method at 120 ºC for 24 h. The XRD results revealed that the as-synthesized VO_2 nanopowders have the pure monoclinic structure. SEM and TEM results shown that the the as-synthesized VO_2 nanorods have the 100-150 nm in daimeter and 1.5-2 µm in length, which are suitable applied for thermochromic and optoelectronic devices.

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REFERENCES

[1] Wentao, J., Juan, N., Ke, Y. and Ziqiang, Z. Hydrothermal synthesis and electrochemical characterization of VO_2 (B) with controlled crystal structures, Applied Surface Science 257, 2011, 3253–3258.

[2] J.B. Kana Kana., J.M. Ndjaka, P. Owono Ateba, B.D. Ngom, N. Manyala, O. Nemraoui, A.C. Beye and M. Maaza. Thermochromic VO_2 thin films synthesized by rf-inverted cylindrical magnetron sputtering, Applied Surface Science 254, 2008, 3959–3963.

[3] Sorapong, P., Yoshikazu, S., Athapol, K., Sommai, P. and Susumu, Y. Synthesis and characterization of vanadium oxides nanorods, Journal of Solid State Chemistry 178, 2005, 2152–2158.

[4] M. Benkahoul, M. Chaker, J. Margot, E. Haddad, R. Kruzelecky, B. Wong, W. Jamroz and P. Poinas. Thermochromic VO_2 film deposited on Al with tunable thermal emissivity for space applications, Solar Energy Materials & Solar Cells 95, 2011, 3504–3508.

[5] Haihong, Y., Juan, N., Wentao J., Zhengli, Z. and Ke, Y. Synthesis, field emission and humidity sensing characteristics of monoclinic VO_2 nanostructures, Physica E 43, 2011, 1720–1725.

[6] P. Evans, M.E. Pemble, D.W. Sheel and H.M. Yates. Multi-functional self-cleaning thermochromic films by atmospheric pressure chemical vapour deposition, Journal of Photochemistry and Photobiology A: Chemistry 189, 2007, 387–397.

[7] Graham, A., Jesus, C., A. Robert, A. and Peter, G. B. The synthesis and lithium intercalation electrochemistry of VO_2(B) ultra-thin nanowires, Journal of Power Sources 178, 2008, 723–728.

[8] R. Lopez, L. C. Feldman and R. F. Haglund, Jr. Size-Dependent Optical Properties of VO2 Nanoparticle Arrays, Physical Review Letters, 93, 2004, 1774031-4.