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Microstructure and luminescence of VO₂ (B) nanoparticle synthesis by hydrothermal method

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Abstract: This paper reports the way for the synthesis of nanoplate VO₂ (B) particles with controlled morphology. Nanoplate VO₂ (B) particle was synthesized by hydrothermal method. Microstructure of VO₂ (B) particles were controlled by hydrothermal temperatures and use of Zn doping into VO₂ (B) matrix. The microstructure of the particles was shifted from nanowires to nanoplate morphology by changing of hydrothermal temperatures. The doping of Zn into VO₂ nanoparticles resulted in an effective achievement of VO₂ (B) phase. In addition, luminescence of VO₂ (B) nanoparticle was also controlled by the use Zn doping. These results suggest that the potential application of Zn doped VO₂ (B) particles for potential application in optical and energy techniques.

Keywords: nano VO₂; luminescence; Zn; nanoparticle

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1 Introduction

Vanadium oxide (VO₂) has received considerable attention as a host material applications in data display, electrochromic devices, optical and thermal switching, to sensing and actuation based on specific VO₂ polymorphs [1,2]. In particular, different polymorphs of VO₂ is including VO₂ (B), VO₂ (M), VO₂ (R), VO₂, VO₂ (C), VO₂ (D) [3]. For example, monoclinic phase, VO₂ (M) is an interesting metal oxide that possesses thermochromism due to crystalline phase transition at about 68°C [4,5]. Doping of VO₂ (M) with W ion can be improved the thermochromism of materials significantly [6]. Another interesting polymorphs of VO₂, the VO₂ (B) has been widely researched in recent years as a great potentials candidate for the cathode in lithium-ion batteries due to its layered structure, high energy capacity along with moderate work potential [7,8]. VO₂ (B) metastable phase has a monoclinic layered structure (space group of C2/m) similar to that of V₆O₁₃ [9]. Functionalization of VO₂ (B) with carbon has been reported for improving the supercapacitors of materials [10,11]. Although the hydrothermal synthesis of VO₂ (B) are well documented, thus far, only a few papers have reported on the control the microstructure VO₂ (B) nanoparticles [12,13]. In particular, to the best of our knowledge, no attempts have been made to synthesize VO₂ (B) nanoparticles with a controlling the microstructure and luminescence by hydrothermal methods, which would open up new potential application of VO₂ (B) research field. Therefore, this study proposes a way of controlling the phase, microstructure and luminescence the VO₂ (B) nanoparticles, which can be achieved by changing the hydrothermal temperature and applying Zn doping. Phase and microstructure VO₂ (B) nanoparticles were characterized by X-ray diffraction and field emission scanning electron microscopy (FE-SEM), respectively. The luminescence was determined by photoluminescence spectrometer.

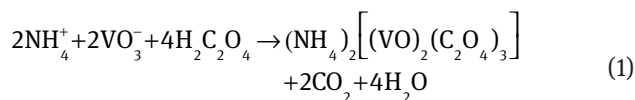
2 Experimental procedure

VO₂ (B) particle was synthesized through a hydrothermal method, as follows: an aqueous solution containing 1 M

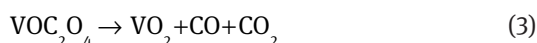
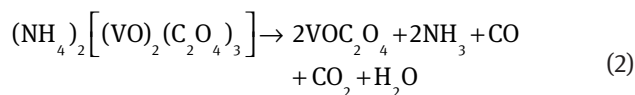
ammonium metavanadate NH₄VO₃ (99.99% purity, Aldrich) were added over an aqueous solution containing 2 M oxalic acid (H₂C₂O₄, 99.99% purity, Aldrich). For synthesis of Zn doped VO₂, an aqueous solution containing x mol of Zn(NO₃)₂·6H₂O (99.99% purity, Merck) x = 0, 1, 3, 5, and 8 were added over an aqueous solution containing 1 M NH₄VO₃ and 2 M oxalic acid. The solutions were stirred for 0.5 h at room temperature. The mixture was transferred into 200 mL Teflon-lined autoclave, and then the autoclave was sealed and maintained at 200°C for 12 h. The resulting precipitates were washed twice times, and then dried at 80°C for 2 h. The crystalline structures of the VO₂ (B) particles were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructure VO₂ (B) particles were determined by field emission scanning electron microscopy (JEOL, JSM-6700F, JEOL Techniques, Tokyo, Japan) and high resolution transmission electron microscope, HRTEM (JEM 2100, JEOL Techniques, Tokyo, Japan), respectively. X-ray photoelectron spectrometer (XPS, Multilab 2000, Thermo Fisher Scientific, USA) as used for analysis the chemical characteristic of VO₂ (B) particles. Luminescence spectra of the VO₂ (B) were recorded using NANO LOG spectrofluorometer (Horiba, USA) equipped with 450 W Xe arc lamp.

3 Results and discussion

In this paper, an ammonium metavanadate (NH₄VO₃) was used to synthesize doped VO₂ (B) by one step hydrothermal method. Firstly, (NH₄)₂[(VO)₂(C₂O₄)₃] can be obtained by a reaction using NH₄VO₃ and oxalic acid H₂C₂O₄, as shown in Eq. 1 [14].



Subsequently, the VO₂ nuclear occurred during the subsequent hydrothermal step and is expressed by the chemical reaction equation (Eq. 2 and 3) [14].



By changing experimental parameter in the hydrothermal process, different VO₂ morphology can be produced.

Figures 1a-d show the typical XRD patterns of VO₂ (B) nanoparticles synthesized with the variation

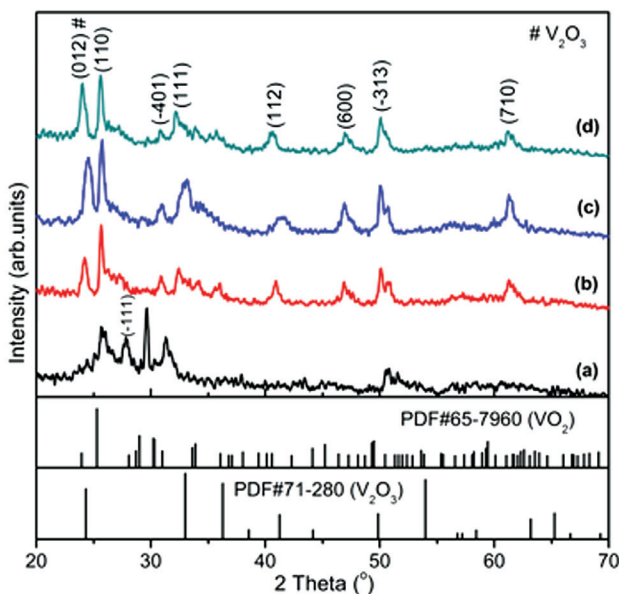


Figure 1: XRD patterns of VO₂ (B) nanoparticles synthesized at different temperatures: (a) 100°C, (b) 150°C, (c) 180°C and (d) 200°C.

of hydrothermal temperatures. As shown in Figure 1, all the XRD patterns of VO₂ (B) nanoparticles showed peaks matching the standard patterns of monoclinic VO₂ (B) (JCPDS, 65-7960) with an additional peak at 2θ = ~24.4° corresponding to the (012) plane of V₂O₃ (JCPDS, 71-280) [12,15,16]. It should be noted that intensity of XRD pattern peak was increased as hydrothermal temperature increase, suggesting that highly crystalline structure of VO₂ (B) could be obtained when a high hydrothermal temperature of 180-200°C was used.

Figures 2a-d show SEM image of VO₂ (B) nanoparticles synthesized by hydrothermal method with different temperatures. It can be seen that the VO₂ (B) nanoparticles had a nanowire shape when the VO₂ (B) was synthesized at hydrothermal temperature of 100-150°C (Figures 2a and 2b). However, a plate-like shape of VO₂ (B) nanoparticle was observed when a high hydrothermal temperature of 180°C was used. The development of a plate-like shape of VO₂ (B) nanoparticle became more vigorous as increases hydrothermal temperature to 200°C. The variation in the morphology of VO₂ (B) nanoparticle with increasing in hydrothermal temperature observed in the present studies can be explained in terms of the higher nucleation density during the hydrothermal process.

Figures 3a-e show the typical XRD patterns of VO₂ (B) nanoparticles synthesized with different mole fraction of Zn doping. The VO₂ (B) nanoparticles synthesized without doping Zn showed peaks matching the standard patterns of VO₂ (B) (JCPDS, 65-7960), as well as a peak at 2θ = ~24.4° corresponding to the V₂O₃ (JCPDS, 71-280), Figure 3a.

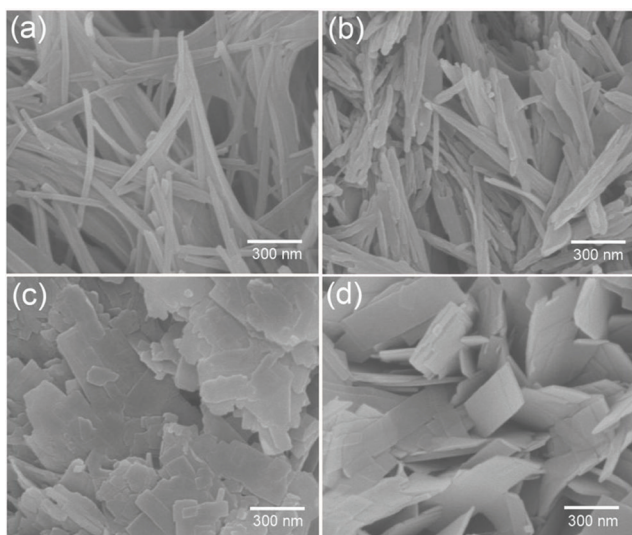


Figure 2: SEM images of VO₂ (B) nanoparticles synthesized at different temperatures: (a) 100°C, (b) 150°C, (c) 180°C and (d) 200°C.

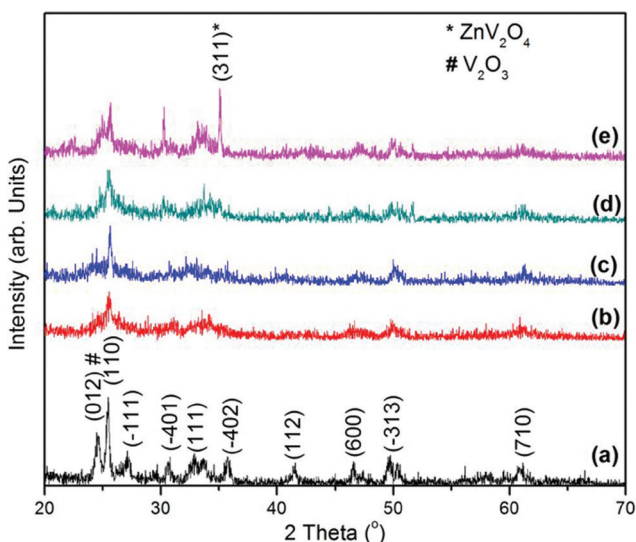


Figure 3: XRD patterns of VO₂ (B) nanoparticles synthesized at 200°C with different mole fraction of Zn. (a) 0% mol Zn, (b) 1% mol Zn, (c) 3% mol Zn and (d) 5% mol Zn and (e) 8% mol Zn.

On the other hand, only VO₂ (B) was observed in the specimen when the mole fraction of Zn in range of 1-5% (Figures 3b-d). When the mole fraction of Zn reached 8%, the XRD patterns showed all peaks corresponding to the crystalline VO₂ (B) with additional peak at $2\theta = \sim 35.1^\circ$ corresponding to the ZnV₂O₄ (JCPDS, 750318) [17]. These results indicate that the VO₂ nanoparticles synthesized without and with the application of Zn doping had the preferential phase of VO₂ (B) phase.

Figure 4 shows EDS analysis of Zn doped VO₂ (B) synthesis by hydrothermal method with 1% mole fraction of Zn. As shown in Figure 4, peaks corresponding to

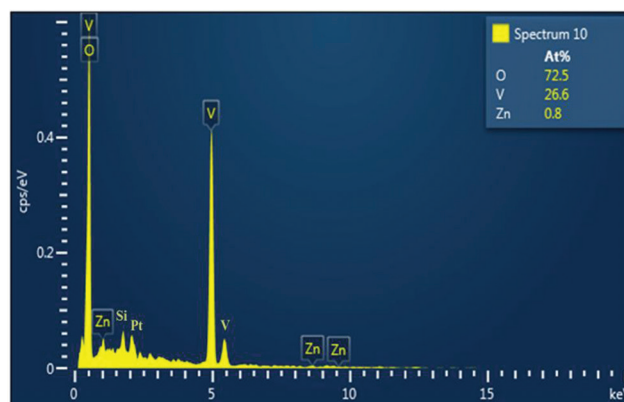


Figure 4: EDS patterns of VO₂ (B) nanoparticles synthesized at 200°C with 1% mol fraction of Zn.

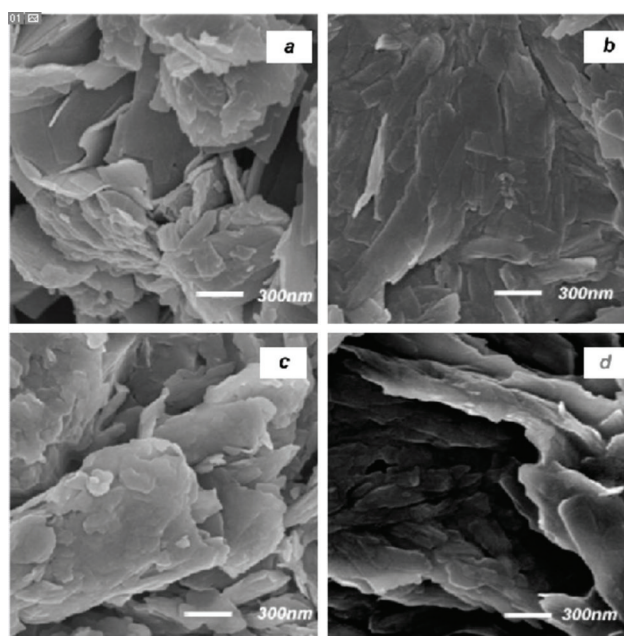


Figure 5: SEM images of VO₂ (B) nanoparticles synthesized at 200°C with different mole fraction of Zn: (a) 1% mol Zn, (b) 3% mol Zn, (c) 5% mol Zn and (d) 8% mol Zn.

the Zn element were observed, indicating the presence of the Zn in the VO₂. In addition, a calculated atomic concentration of the Zn incorporated was 0.8%, which would be permeably suggested to the successful doping of Zn in to the host VO₂. It can be seen that there are Si and Pt elements peak in the EDS spectrum because the Zn doped VO₂ (B) powders were attached on conductive Si wafer and Pt coating for SEM observation.

Figure 5 shows morphology of Zn doped VO₂ (B) nanoparticles with various mole fraction of Zn. As shown in Figure 5, irrespective of the mole fraction of Zn, the morphology of Zn doped VO₂ (B) nanoparticles display the same morphology. In other words, all the specimens

show nanoplate microstructure with a smooth surface, as is often the case with VO₂ (B) synthesized without surfactant [18,19].

Microstructures of the VO₂ (B) and Zn doped VO₂ was further studied by TEM, as shown in Figures 6a and 6b. It can be seen that nanoplate microstructure are obtained for both VO₂ (B) and Zn doped VO₂ nanoparticles which are very consistent with the observation from SEM images, Figure 5.

The survey XPS spectra of the VO₂ (B) are shown in Figure 7a. The elements C, O and V could be observed on the spectrum. The peaks for O and C are attributed to the O₂, CO₂ or H₂O absorbed in the sample. The peaks at 530.15 eV is assigned to the O1s. The V2p binding energies at ~516.57 and 523.7 eV are assigned to the characteristics of V⁴⁺ oxidation state, which are consistent with the values of VO₂ (B) reported in the literature [20,21] (Figure 7b).

Figure 8 shows luminescence of VO₂ (B) and Zn doped VO₂ (B) (1% mol Zn) nanoparticles under the excitation of the 325 nm. As shown in Figure 8, the PL of VO₂ (B) showed a sharp band at ~361 nm which can be assigned to free-excitation emission [22]. However, the PL of Zn doped VO₂ (B) showed the samples consist of ~361 nm bands with addition broad band at ~430 nm.

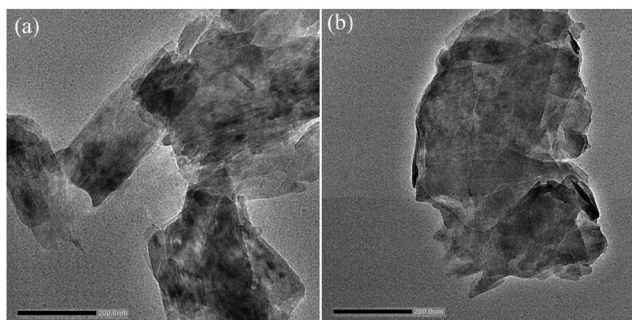


Figure 6: TEM images of VO₂ (B) nanoparticles synthesized at 200°C with different mole fraction of Zn: (a) 0% mol Zn, (b) 5% mol Zn.

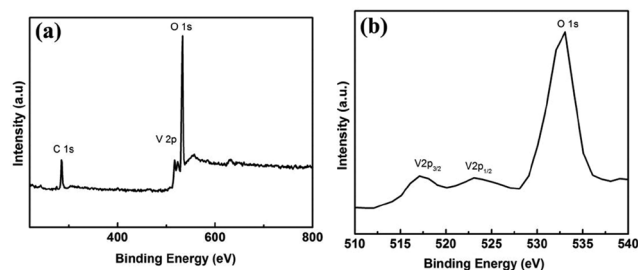


Figure 7: XPS analysis of VO₂ (B) nanoparticles: (a) survey XPS spectrum of VO₂ (B), (b) core level spectra of V2p.

The luminescent occurring at 430 nm was attributed to the electric charge transfer, corresponding to the weak energy of V = O bond [23,24].

Figure 9a shows luminescence of Zn doped VO₂ (B) with different Zn concentration under the excitation of the 350 nm. All the Zn doped VO₂ showed a broad band at ~430 nm, which can be attributed to the electric charge transfer, corresponding to the weak energy of V = O bond. However, it should be noted that the relative PL intensity of Zn doped VO₂ increased with the Zn concentration increases. Figure 9b shows the emission spectra of the Zn doped VO₂ with 5% mol Zn doping under different excitation wavelengths. Interestingly, when excitation wavelengths increased from 300 to 350 nm, the PL spectrum displayed one emission center at ~430 nm with an increase in the PL intensity.

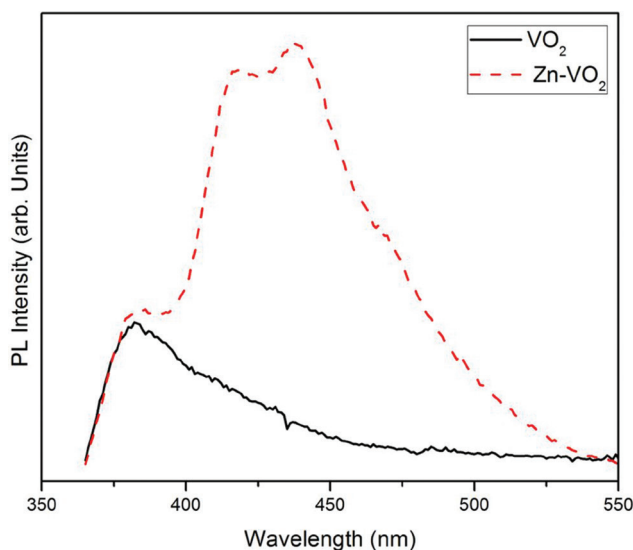


Figure 8: Luminescence of VO₂ (B) and Zn doped VO₂ (B) nanoparticles.

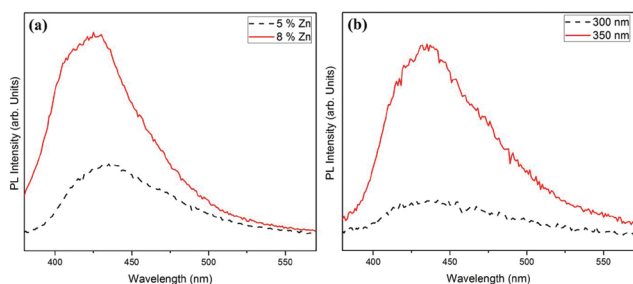


Figure 9: Luminescence of Zn doped VO₂ (B) nanoparticles: (a) effect of Zn concentration under excitation 350 nm, (b) effect of excitation in 5% mol Zn doped VO₂.

4 Conclusions

We herein demonstrated that the nanoplate VO₂ (B) nanoparticles could be obtained effectively by changing the hydrothermal temperature and Zn doping into VO₂ (B) matrix. In particular, the microstructure of the particles was shifted from nanowires to nanoplate morphology as changing the hydrothermal temperatures. Doping of Zn into VO₂ nanoparticles resulted in an effective achievement the VO₂ (B) phase. The luminescence of the VO₂ (B) particles was displayed strongest band at 361 nm, which was different from Zn doped VO₂ (B) particles. Zn doped VO₂ (B) emit dominant band at ~430 nm, which was attributed to the electric charge transfer. Thus, this approach showed promise technique to controlling the VO₂ (B) particles for potential application in optical and energy techniques.

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