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Original Article

Synthesis of Micro-/Nano Urchin-like VO_2 Particle and Its Decolorization of Methylene Blue

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Abstract: In this article, micro-/nano urchin-like VO_2 particles were successfully synthesized by hydrothermal method. Vanadium pentoxide (V_2O_5), oxalic acid ($C_2H_2O_4$) and sodium dodecyl sulfate (SDS) surfactant were used as reagents for the synthesis of VO_2. The article reports on the synthesis procedure of VO_2 nanorods and micro-/nano urchin-like VO_2 structure and evaluates the methylene blue (MB) adsorption properties. Morphology and particle size of VO_2 were observed by FE-SEM. The VO_2 formation phase was studied by XRD. Raman spectroscopy was also used for characterizing VO_2. Micro-/nano urchin-like VO_2 structure shows good MB adsorption properties that have potential applications in dye-contaminated water treatment.

Keywords: Micro-/nano-scale, nanoparticles, VO_2, methylene blue.

1. Introduction

In recent years, waters containing organic dyes coming from textile, leather, paper, and printing have become concerns in the environment and human health [1]. Many technologies are being applied for treatment of contaminated water such as chemical oxidation [2], ion exchange [3], biological

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treatment [4], and adsorption [5] to eliminate residual dyes in contaminated water. Among them, especially the adsorption method is regarded as the most effective method because of the simple treatment process, fast decolorization and low cost [6]. Many materials such as wheat shells [7], activated carbon [8], and biochar [9] have been widely used to adsorb organic dyes in water. Nano-structured transition oxide materials have attracted a lot of attention in dye contaminated water treatments because of the large surface contact area with high absorption capacity [6]. Vanadium oxide has attracted a lot of attention in engineerings such as electrodes for batteries [10], adsorption [11], sensors [12], and smart windows [13] because of its stable chemical and physical properties. VO_2 has several polymorphs: VO_2 (R), VO_2 (D), VO_2 (M), VO_2 (B), VO_2 (A) and VO_2 (C) [13,14]. Nevertheless, there are only a few reports on the adsorption of dye by using nanostructure VO_2 (D) [14] and VO_x Nanosheets [15]. In particular, in our knowledge, there are no reports on methylene blue (MB) decolorization using micro/nano urchin-like VO_2 particles. Therefore, this study proposes the attempt to synthesize micro/nano urchin-like VO_2 particles using the hydrothermal method in presence of sodium dodecyl sulfate (SDS) surfactants for potential treatment of MB dye in contaminated water. The microstructures of the micro/nano urchin-like VO_2 was characterized by field emission scanning electron microscopy (FE-SEM). Dye decolorization was determined by UV-Vis spectroscopy.

2. Experimental procedure

0.91 g of V_2O_5 (99.99 % purity, Aldrich) was put into 25 ml of distilled water, and then 25 ml of oxalic acid ($C_2H_2O_4$, 0.48 M, 99.99 % purity, Aldrich) was added under magnetic stirrer. At this, stage, the color of solution was changed from yellow to blue color. Then, 5 mL of 0.2 M SDS ($C_{12}H_{25}SO_4Na$, 99.99 % purity, Aldrich) solution was added to the above solution for 5 hours. The mixture solution was transferred into 200 ml Teflon-lined autoclave, after that the autoclave was sealed and maintained at 200 ºC for 12 h. The resulting particles were washed twice times and then dried at 70 ºC for 24h. The crystalline structures of the micro/nano urchin like VO_2 particles were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructure was determined by field emission scanning electron microscopy (JEOL, JSM-6700F, JEOL Techniques, Tokyo, Japan). Raman spectrometers of the particles were measured by Raman scattering (Renishaw) using 633 nm laser and 15mW power. Methylene blue (MB) decolorization test, 0.003 g of VO_2 nanowires or micro/nano urchin-like VO_2 particles were added into 30mL methylene blue solution (20 ppm) which was at pH value of 7 under 20 minutes. The degradation of methylene blue was determined by UV-Vis (Cary 500 spectroscopy).

3. Results and discussions

The microstructures of the VO_2nanorods and micro/nano urchin-like VO_2 particles synthesized without and with the application SDS surfactants are shown in Figs. 1 {(a)–(d)}. The VO_2 synthesized without SDS surfactant showed a nanorods structure, Fig. 1{(a), (c)} with the width of 150 nm and the length of ~ 800 nm, as is often the case with VO_2 particles synthesized by hydrothermal [16]. However, when an SDS surfactant was used, a number of nanorods with the width of 100 nm and the length of ~ 1,5 µm were uniformly formed within the grains of VO_2 with a diameter of 5 µm, Fig. 1 {(b), (d)}.

The micro/nano urchin-like VO_2 particles formation mechanism can be explained as following: SDS surfactant ($C_{12}H_{25}SO_4Na$) will be decomposed into $C_{12}H_{25}SO_4{}^-$ and Na^+ in solution. The $C_{12}H_{25}SO_4^-$ will create spherical micelles, with negative charge on the surface.

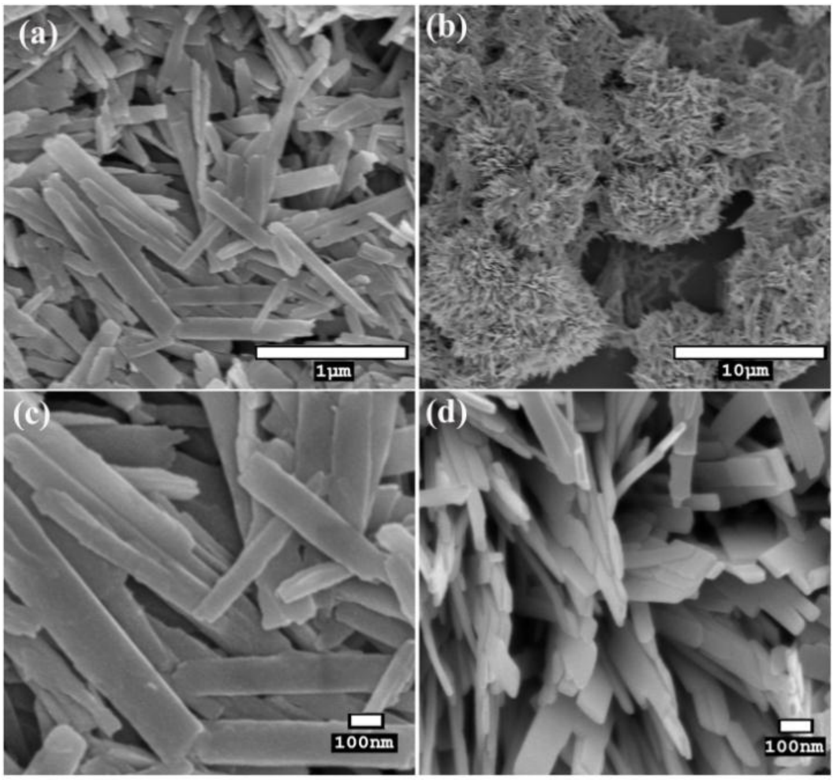

Figure 1: FESEM image of VO_2nanorods and micro/nano urchin-like VO_2 particles synthesized without {(a), (c)} and with {(b), (d)} SDS surfactant. (c) and (d) high magnification image.

Next, the positive charge VO^{2+} will be settled down on the negative charge $C_{12}H_{25}SO_4^-$, creating crystal seeds [17-21]. Then, the nucleation of VOC_2O_4 will take place and VOC_2O_4 seed will grow into nanowires on the spherical micelles template. Finally, VOC_2O_4 nanowires will be converted to VO_2 under high temperature and pressure hydrothermal condition. The reaction formation process for micro/nano urchin-like VO_2 can be illustrated as follows [21].

$$V_2O_5 + 3H_2C_2O_4 \leftrightarrow 2VOC_2O_4 + 3H_2O + 2CO_2 \quad (1)$$

$$V_2O_5 + H_2C_2O_4 \leftrightarrow (VO)_2C_2O_4 + H_2O \quad (2)$$

$$(VO)_2C_2O_4 + 2H_2C_2O_4 \leftrightarrow 2VOC_2O_4 + 2H_2O + 2CO_2 \quad (3)$$

$$2VOC_2O_4 \leftrightarrow VO_2 + 3CO_2 + C \quad (4)$$

Figure 2 (a) and (b) shows the typical XRD patterns of the VO_2 particles processed with and without the use of SDS during hydrothermal, respectively. The VO_2 particles synthesized with SDS surfactants showed a relatively strong peak at $2\theta = \sim 15{,}6^o$ $25{,}4^o$ $29{,}1^o$ $45{,}1^o$ $49{,}4^o$ $59{,}2^o$ corresponding to the (200) (110) (002) ($\bar{6}01$) (020) ($\bar{7}11$) plane. All of the peak can be indexed to the crystalline VO_2 (B) structure (JCPDS 81-2392), Fig. 2 (a). On the other hand, the VO_2 particles synthesis without SDS surfactants, the peak at ~$25{,}4^o$ and $49{,}4^o$ was shifted to longer angle and their intensity was decreased, Fig. 2 (b). These results indicate that the VO_2 particles synthesized with the use of SDS surfactants display an improving the crystallinity due to the preferential nuclear growth in the hydrothermal process. On the basis of these findings, the micro/nano urchin-like VO_2 particle synthesized with the use of SDS surfactant was used for further characterizations.

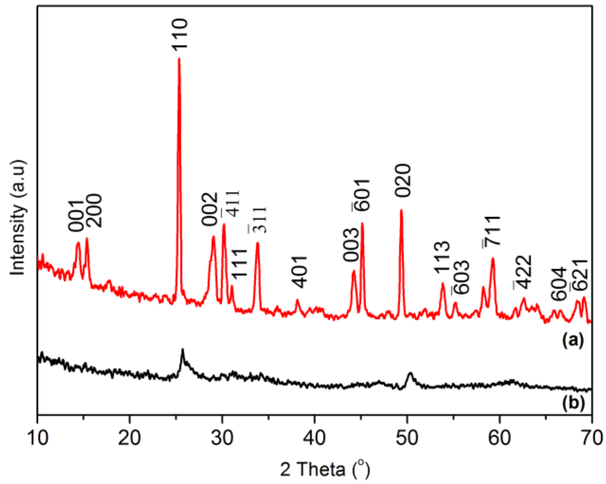

Figure 2. XRD patterns of the VO_2 particles (a) with and (b) without the use of SDS surfactant.

Figure 3 shows the Raman spectrum of micro/nano urchin-like VO_2 particles synthesized by hydrothermal with the use of SDS surfactant. As shown in Fig. 3, two spectrums, peaks at 283 cm^{-1} and 405 cm^{-1} correspond to flexural modes of V_2-O and V-O. The spectrum is in the range of 400-600 cm^{-1} is related to bridging modes of V_2-O and V_3-O. The Raman peak at 692 cm^{-1} corresponds to the stretching vibration mode of V_2-O. The peak appears at ~ 1000 cm^{-1} is assigned to stretching mode of V = O [16]. All the Raman peaks correspond to the characterization mode of VO_2 (B) without any evidence of impurities, indicating that VO_2 (B) has been synthesized successfully.

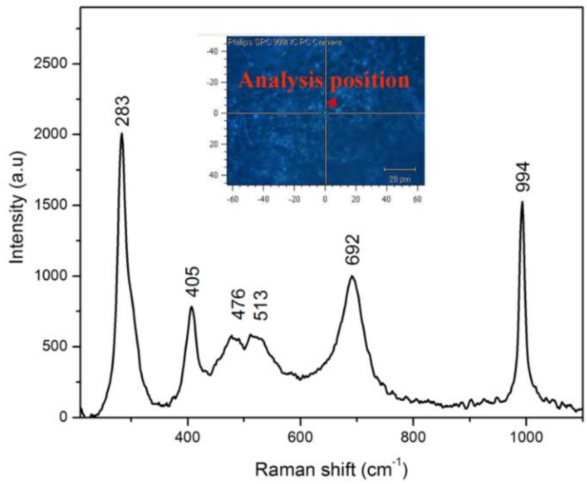

Figure 3. Raman spectra of micro/nano urchin-like VO_2 particles.

The typical UV-Vis absorption spectra of (the bare MB solution, VO_2nanorods and micro/nano urchin-like VO_2 particles synthesized without and with the use of SDS are shown in Figs. 4. Bare MB has a strong absorption peak at ~ 660 nm and one weak peak at ~ 630 nm. Compared to the bare MB, lower adsorption intensity was observed for the VO_2 particles at the same MB concentration, demonstrating the effective the decolorization of MB. However, it should be noted that the adsorption intensity of micro/nano urchin like VO_2 particles synthesized by the use of SDS surfactants was much lower than that of the VO_2 nanowires synthesized without SDS surfactants by a factor of ~2.1. This improvement of MB decolorization was mainly attributed to the achievement of micro/nano urchin-like VO_2 structure which is possessed highly contacting area for MB adsorption.

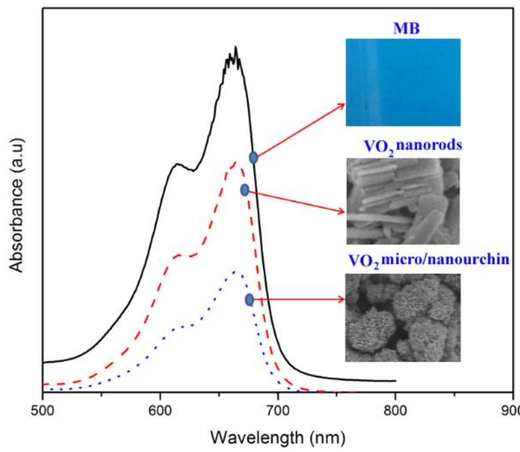

Figure 4. UV-Vis spectra showing the MB decolorization of the bare MB, VO_2nanorods and micro/nano urchin-like VO_2 particles.

In general, when the particles size of material is enough small, the specific surface area increases and adsorption efficiency increases. However, small particles size of materials will be suspended in the solution after the adsorption process which making the recovering of materials is difficult. Hybridization between adsorbent and iron oxide (GO – Fe_3O_4nanohybrid) can recover material by external magnetic field after the adsorption process [22]. This technique can be eliminated ~ 100% of adsorbent materials, but synthesis of nanohybrid materials is quite complicated which limiting its application. Therefore, the micro/nano material has a special structure, which does not require strict processing procedures, high efficiency of adsorption, easy recovery of materials after adsorption is currently an interesting research area. In this work, the micro/nano urchin-like VO_2 particles can be deposited at the bottom of the adsorption vessels after the adsorption processes, Fig. 5b. The micro/nano urchin-like VO_2 particles can be collected completely after centrifuging and transparent solution is observed, Fig. 5d. This is considered as one of the advantages of micro/nano urchin-like VO_2 material compared to the other material. Therefore, micro/nano urchin-like VO_2 particle is a promising material for MB contaminated water treatments.

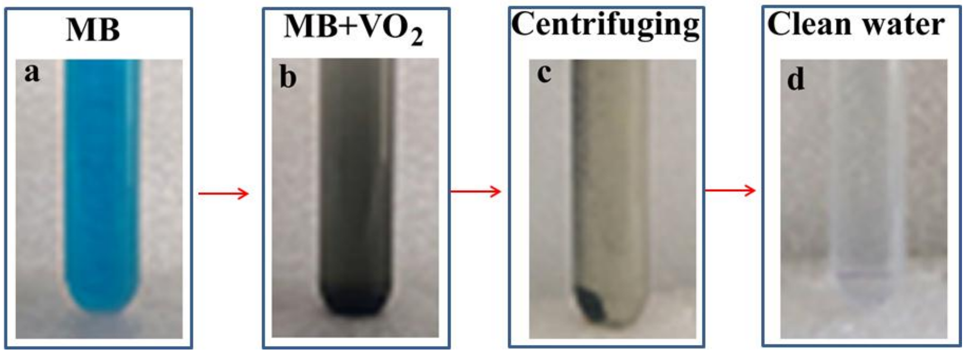

Figure 5. Methylene blue adsorption process of VO_2.(a) MB solution, (b) Mixture of VO_2 particles and MB, (c) centrifugal separation of VO_2 particles and MB solution. (d) Water after adsorption of MB.

4. Conclusions

Micro/nano urchin-like VO_2 particles have been synthesized successfully by hydrothermal method. In particular, The VO_2 particles synthesized without SDS showed nanorods structures. On the other hand, when SDS surfactants were used, a micro/nano urchin-like VO_2 particle was achieved. Micro/nano urchin-like VO_2 particle showed good MB decolorization which has a potential application in dye-contaminated water treatments.

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