Original Article

Synthesis of Micro-/Nano Urchin-like VO₂ Particle and Its Decolorization of Methylene Blue

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Abstract: In this article, micro-/nano urchin-like VO₂ particles were successfully synthesized by hydrothermal method. Vanadium pentoxide (V₂O₅), oxalic acid (C₂H₂O₄) and sodium dodecyl sulfate (SDS) surfactant were used as reagents for the synthesis of VO₂. The article reports on the synthesis procedure of VO₂ nanorods and micro-/nano urchin-like VO₂ structure and evaluates the methylene blue (MB) adsorption properties. Morphology and particle size of VO₂ were observed by FE-SEM. The VO₂ formation phase was studied by XRD. Raman spectroscopy was also used for characterizing VO₂. Micro-/nano urchin-like VO₂ structure shows good MB adsorption properties that have potential applications in dye-contaminated water treatment.

Keywords: Micro-/nano-scale, nanoparticles, VO₂, 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
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. Nanostructured 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. $\text{VO}_2$ has several polymorphs: $\text{VO}_2\ (\text{R}), \text{VO}_2\ (\text{D}), \text{VO}_2\ (\text{M}), \text{VO}_2\ (\text{B}), \text{VO}_2\ (\text{A})$ and $\text{VO}_2\ (\text{C})$ [13,14]. Nevertheless, there are only a few reports on the adsorption of dye by using nanostructure $\text{VO}_2\ (\text{D})$ [14] and $\text{VO}_2\ \text{Nanosheets}$ [15]. In particular, in our knowledge, there are no reports on methylene blue (MB) decolorization using micro/nano urchin-like $\text{VO}_2$ particles. Therefore, this study proposes the attempt to synthesize micro/nano urchin-like $\text{VO}_2$ 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 $\text{VO}_2$ 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$_2$O$_5$ (99.99 % purity, Aldrich) was put into 25 ml of distilled water, and then 25 ml of oxalic acid (C$_2$H$_2$O$_4$, 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$_4$Na, 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 °C for 12 h. The resulting particles were washed twice times and then dried at 70 °C for 24h. The crystalline structures of the micro/nano urchin like $\text{VO}_2$ 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 $\text{VO}_2$ nanowires or micro/nano urchin-like $\text{VO}_2$ 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 $\text{VO}_2$nanorods and micro/nano urchin-like $\text{VO}_2$ particles synthesized without and with the application SDS surfactants are shown in Figs. 1 {(a)–(d)}. The $\text{VO}_2$ 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 $\text{VO}_2$ 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 $\text{VO}_2$ with a diameter of 5 µm, Fig. 1 {(b), (d)}.

The micro/nano urchin-like $\text{VO}_2$ particles formation mechanism can be explained as following: SDS surfactant (C$_{12}$H$_{25}$SO$_4$Na) 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.
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$_2$O$_4$ will take place and VOC$_2$O$_4$ seed will grow into nanowires on the spherical micelles template. Finally, VOC$_2$O$_4$ 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].

\[
V_2O_5 + 3H_2C_2O_4 \leftrightarrow 2VOC_2O_4 + 3H_2O + 2CO_2 \\
V_2O_5 + H_2C_2O_4 \leftrightarrow (VO)_2C_2O_4 + H_2O \\
(VO)_2C_2O_4 + 2H_2C_2O_4 \leftrightarrow 2VOC_2O_4 + 2H_2O + 2CO_2 \\
2VOC_2O_4 \leftrightarrow VO_2 + 3CO_2 + C
\]

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 20 = ~ 15.6° 25.4° 29.1° 45.1° 49.4° 59.2° corresponding to the (200) (110) (002) (601) (020) (711) 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° and 49.4° 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$_2$nanorods 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.

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$_3$O$_4$nanohybrid) 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 4. UV-Vis spectra showing the MB decolorization of the bare MB, VO$_2$nanorods and micro/nano urchin-like VO$_2$ particles.

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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