Synthesis of $\text{V}_2\text{O}_5$ Nanoflakes on PET Fiber as Visible-Light-Driven Photocatalysts for Degradation of RhB Dye

Yim-Leng Chan, Swee-Yong Pung, and Srimala Sreekantan

Science and Engineering of Nanomaterials Team, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

Correspondence should be addressed to Swee-Yong Pung; sypung@usm.my

Received 26 May 2014; Revised 27 July 2014; Accepted 28 July 2014; Published 17 August 2014

1. Introduction

Water pollution is one of the most serious environmental problems. Many untreated organic effluents such as dyes from textile industries are being discharged into the ecosystem, creating severe environmental pollution by releasing toxic and potential carcinogenic substances into the environment [1]. Therefore, various wastewater treatment processes such as precipitation, adsorption by activated carbon, coagulation, and membrane ultrafiltration have been developed for the removal of these organic pollutants [2–5]. However, these wastewater treatment processes are simply transforming the pollutants from one phase to another, leading to secondary pollution problems.

Recently, there has been a growing interest in the utilization of advanced oxidation processes (AOPs) via semiconductor photocatalysts for the organic pollutants removal. In AOPs, highly reactive species such as hydroxyl radicals are generated to oxidize a broad range of organic pollutants rapidly and nonselectively. Semiconductor photocatalysts are widely used due to their unique strengths for complete mineralization of organic pollutants into less harmful byproduct such as water, CO$_2$, and mineral acids. For example, zinc oxide (ZnO) nanoparticles [6–10] and titanium oxide (TiO$_2$) nanoparticles [11–13] were frequently used by researchers as UV-driven photocatalysts to decompose organic compounds/pollutants because of their wide band gap.

Development of visible-light-driven semiconductor photocatalysts for organic compounds removal is our current research focus. This is because the visible light accounts for 45% of the total energy of solar spectrum, while UV light only represents less than 10%. Theoretically, the photodegradation efficiency of organic compounds by semiconductor photocatalysts in visible light irradiation could be further enhanced. Several methods have been explored to develop visible-light-driven semiconductor photocatalysts. This could be done by shifting the band gap absorption edge of wide band gap semiconductors to a longer wavelength via metal or nonmetal doping. For example, Cu doped ZnO nanorods [14] and Cd doped ZnO nanostructures [15] responded to visible light...
irradiation in degradation of organic dyes. Furthermore, narrow band gap semiconductor such as manganese oxide (MnO2) nanoparticles [16, 17] and vanadium dioxide (VO2) nanoparticles [18] could also be used as visible-light-driven photocatalysts. Normally, H2O2 chemical was required to improve the photodegradation efficiency of these semiconductor photocatalysts in degradation of organic compounds under visible light irradiation [19].

Regardless of UV- or visible-light-driven photocatalysts, most of the previous research used semiconductor in the form of nanoparticles for organic compounds removal. This is because semiconductor nanoparticles collectively have a high surface area, resulting in effective generation of free radicals and decomposition of organic compounds. The limitation of using semiconductor nanoparticles is that there is a need for the removal of nanoparticles from the slurry via centrifugation [20]. This addition step is time consuming and adds extra cost to the overall process. This additional processing step for the removal of semiconductor nanoparticles can be avoided by growing semiconductor nanostructures rigid substrates such as stainless steel wire [21].

In this work, vanadium pentoxide (V2O5) was selected as visible-light-driven semiconductor to be grown on flexible substrate, that is, polyethylene terephthalate (PET) fibre attributed to its narrow band gap (2.52 eV). There are various synthesis methods that could be used to produce the V2O5 nanostructures and thin films. For instance, Wei and Zhang synthesized V2O5 nanotubes using hydrothermal method [22] and Yin et al. grew porous V2O5 micro/nanotubes by chemical vapor deposition [23]. In addition, Blanquart et al. deposited V2O5 thin films using atomic layer deposition [24] and Gotič et al. synthesized V2O5 powder by sol-gel method [25]. As the V2O5 nanostructures used in this study

3. Results and Discussion

3.1. V2O5 Nanoparticles and Their Photocatalytic Activity. The XRD pattern of the nanoparticles is shown in Figure 1. The XRD pattern could be indexed to V2O5 (JCPDS no. 60-0767). The diffraction peaks at 15.6°, 20.4°, 21.9°, 26.3°, 31.2°, 32.6°, 34.5°, 41.4°, 42.3°, 45.6°, 47.5°, 49.0°, 51.4°, 52.3°, 55.8°, 61.2°, and 62.3° corresponded to (020), (011), (110), (040), (101), (130), (002), (012), (141), (060), (102), (200), (061), (201), (240), and (170) planes, respectively. No diffraction peaks for other elements were detected. The narrow and intense diffraction peaks reveal that the V2O5 nanoparticles were
highly crystalline. The calculated size of $V_2O_5$ nanoparticles based on Scherrer equation was 53.5 nm. The morphology of $V_2O_5$ nanoparticles was determined by SEM image as shown in Figure 2(a). The $V_2O_5$ nanoparticles were rod-like with average length of $231.9 \pm 14.9$ nm. The EDX analysis as shown in Figure 2(b) indicates that there are no other impurity elements, besides V and O elements. The atomic percentage of V and O is 32.82% and 67.18%, respectively, which is close to the stoichiometric ratio of $V_2O_5$.

The effectiveness of $V_2O_5$ nanoparticles to degrade RhB solution under visible light was evaluated and is shown in Figure 3. The degraded RhB solution by $V_2O_5$ nanoparticles was characterized by measuring the 553 nm absorption spectra of RhB using Cary 50 UV-Vis spectroscopy. The intensity of the 553 nm absorption peak decreased as a function of irradiation time from 1.293 a.u. (initial absorbance) to 0.849 a.u. after 15 min and further decreased to 0.518 a.u. after 60 min. The decrease of this absorption peak was due to the breaking of the conjugated $\pi$-system in RhB chain by free radicals. This phenomenon is known as cycloreversion.

According to Lambert-beer law, the concentration of the solution (C) is proportional to the absorption spectrum (A). Thus, this allows the data to be replotted as $\ln(C_o/C)$ versus irradiation time graph, as shown in Figure 4. The linear plot of $\ln(C_o/C)$ versus irradiation time indicates that degradation of RhB solution by $V_2O_5$ nanoparticles under visible light irradiation follows the first order kinetic. The rate constant of photodegradation of RhB by $V_2O_5$ nanoparticles under visible light irradiation, which could be determined from the slope of the graph, is $0.0149$ min$^{-1}$ (std. error = 0.0013 and $R$-square = 0.9611). This result suggests that $V_2O_5$ nanoparticles...
are visible-light-driven semiconductor photocatalysts. The photodegradation mechanism of RhB solution using \( V_2O_5 \) nanoparticles will be discussed in Section 3.3.

3.2. \( V_2O_5 \) Nanoflakes Grown on PET Fiber and Their Photocatalytic Activity. \( V_2O_5 \) nanoflakes were grown on PET fiber using the preestablished synthesis condition from Section 3.1. As shown in Figure 5(a), the PET fiber was fully covered by \( V_2O_5 \) nanoflakes. The thickness of the nanoflakes was in the range of 5–20 nm as shown in the inset of Figure 5(a). The EDX analysis in Figure 5(b) indicates that the main elements of the nanoflakes are V and O with the atomic percentage of 56.39% and 43.61%, respectively. No other impurity elements could be detected in the \( V_2O_5 \) nanoflakes.

The effectiveness of \( V_2O_5 \) nanoflakes grown on PET fiber to degrade RhB solution under visible light was evaluated. The color of RhB solution was faded gradually after being exposed to visible light as shown by the UV-Vis absorption spectrum of RhB solution in Figure 6(a). The intensity of the 553 nm absorbance peak of RhB decreased from 1.293 a.u. (initial absorbance) to 0.895 a.u. after 30 min irradiation. It is further reduced to 0.838 a.u. after 60 min and 0.608 a.u. after 120 min irradiation. The linear plot of ln(\( C_0/C \)) versus irradiation time in Figure 7(a) indicates that photodegradation of RhB by \( V_2O_5 \) nanoflakes under visible light irradiation follows the first order kinetic. The rate constant for \( V_2O_5 \) nanoflakes on PET fiber to degrade RhB solution under visible light irradiation is 0.0065 min\(^{-1}\) (std. error = 0.0006 and R-squared = 0.9842). Although the rate constant of using \( V_2O_5 \) nanoflakes on PET fiber to degrade RhB solution under visible light is smaller than the rate constant using \( V_2O_5 \) nanoparticles, the result proved that the \( V_2O_5 \) nanoflakes could still degrade the RhB solution after growing on the PET fiber. Thus, the application of \( V_2O_5 \) nanoflakes grown on PET
fiber to degrade organic pollutants in flowing water such as river is possible.

The photodegradation of RhB solution was deteriorated by \( V_2O_5 \) nanoflakes on PET fiber under visible light irradiation with the mixing of IPA as shown in Figures 6(b) and 7(b). The rate constant of the reaction with IPA is 0.0011 min\(^{-1}\) (std. error = 0.0002 and \( R^2 \)-square = 0.999). As IPA is known as an OH free radical scavenger [26, 27], the significant decrease of rate constant indicates that the photodegradation of RhB solution was dominant by the OH free radicals that were generated by \( V_2O_5 \) nanoflakes on PET fiber under visible light irradiation.

3.3. Photodegradation Mechanism of RhB Solution by \( V_2O_5 \) under Visible Light Irradiation. The photodegradation of RhB solution by \( V_2O_5 \) could be explained by adsorption-oxidation-desorption mechanism. The optical band gap of \( V_2O_5 \) nanoparticles measured by UV-Vis spectrometer is 2.41 eV as indicated in Figure 8. The \( E_v \) and \( E_c \) of \( V_2O_5 \) nanoparticles in NHE are 0.40 eV and 2.81 eV, respectively, as shown in Figure 9. This result is in good agreement with the reported values by Miyauchi et al. and Viswanathan [21, 28]. As illustrated in Figure 9, the band edge of conduction band (\( E_c \)) of \( V_2O_5 \) nanoparticles is more positive to the absolute electronegativity of oxygen (−0.046 eV). Thus, the excited electrons (\( e_{cb}^+ \)) in the conduction band do not favor for the reduction of oxygen molecules into \( O_2^- \) free radicals. However, the band edge of valence band (\( E_v \)) (2.81 eV) is more positive than the oxidation potential of water (1.99 eV). In this case, the holes (\( h_{vb}^+ \)) are able to produce OH free radicals [29–31]. These free radicals are responsible for the degradation of RhB dye into less harmful byproduct such as water as shown in (1)–(3). Generally, \( V_2O_5 \) nanoparticles and nanoflakes took a longer time to decolorize the RhB solution as compared to ZnO [6–10] and TiO\(_2\) [11–13]. The slower photodegradation efficiency was likely attributed to the limited number of free radicals produced by \( V_2O_5 \) as only the photogenerated holes were able to produce free radicals. Consider the following:

\[
\begin{align*}
V_2O_5 + h\nu &\rightarrow h_{vb}^+ + e_{cb}^- \quad (1) \\
h_{vb}^+ + H_2O &\rightarrow H^+ + OH^- \quad (2) \\
\text{RhB dye} + O_2^- + OH^- &\rightarrow \text{byproducts} \quad (3)
\end{align*}
\]

4. Conclusions

\( V_2O_5 \) nanoparticles and \( V_2O_5 \) nanoflakes on fiber were successfully synthesized via sol-gel method. The \( V_2O_5 \) nanoparticles were rod-like with average length of 231.9 ± 14.9 nm, whereas the thickness of the nanoflakes was in the range of 5–20 nm. The photocatalytic activities for both \( V_2O_5 \) nanoparticles and \( V_2O_5 \) nanoflakes grown on fiber were
0.0149 min\(^{-1}\) and 0.0065 min\(^{-1}\), respectively, under visible light irradiation. These results indicate that both V\(_2\)O\(_5\) nanostructures could be used as visible-light-driven photocatalysts to remove organic pollutants. The slow photodegradation rate of V\(_2\)O\(_5\) nanostructures to degrade RhB dye under visible light irradiation is proposed due to the slow free radicals (OH\(^{\cdot}\)) generation rate as only the photogenerated holes are positively enough to produce OH\(^{\cdot}\) based on the energy diagram.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Acknowledgments**

The authors would like to acknowledge the USM Postgraduate Research Grant Scheme (PRGS) (1001/PBAHAN/8036010) and the USM Research University Grant (RU) (1001/PBAHAN/814200) for the financial support to conduct this project.

**References**


Submit your manuscripts at http://www.hindawi.com