

TEMPLATE-FREE HYDROTHERMAL SYNTHESIS OF CeVO₄ FOR PHOTOCATALYTIC DEGRADATION OF INSECTICIDE DIAZINON

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The nut-like CeVO₄ microstructure was successfully synthesized by the template free hydrothermal process without chemicals assistance or calcination step. The effect of synthesis reaction time for photocatalytic activity was compared. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Fourier transform infrared spectroscopy (FT-IR). For evaluating photocatalytic activity under UV light irradiation, insecticide diazinon was used as a representative pollutant. The synthesized products were according to tetragonal CeVO₄ microstructure. CeVO₄ microstructure synthesized at 180 °C for 8 h and showed the highest photodegradation of 78.38% and the highest apparent rate constant of 0.0191 min⁻¹ within 90 min.

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1. Introduction

Agricultural residues are being considered to be highly toxic to the environment. Thailand is one of many major agricultural countries and it is a country with extensive use of pesticides. Organophosphorus is one of the most frequently used pesticides and is commonly detected in water sources. Diazinon (O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate) is a commonly used thionophosphorous organophosphate pesticide to control a variety of pests on different types of cultivation such as fruit trees, rice, sugarcane, corn, tobacco, horticultural plants and for other general purposes [1–3]. Once it goes into the water, the fate of diazinon depends on its volatilization, hydrolysis, and sorption to sediments and photolysis [4]. Many methods have been used to get rid of insecticide diazinon, such as ultrasonic treatment [5], ionizing radiation [6], adsorption and photocatalysis [7]. Advanced treatment technologies have been taken into account to eliminate pesticide residues because general treatment processes do not work under certain conditions. Photocatalysis has been considered an effective way to eliminate different pollutants in the environmental. Cerium vanadate (CeVO₄) is an important semiconductor with a wide band gap of 3.1–4.2 eV that has attracted a wide interest because of the suitability of its useful electronic and catalytic properties [8–9]. CeVO₄ exists as an interesting phase of the CeV–O ternary system, it has a tetragonal zircon-type structure and can stabilize Ce³⁺ ion even under oxidizing conditions. Thus, it has a wide potentiality of applications in different fields such as in laser host materials, luminescent materials, electrodes catalysts, oxidation catalysts and so on [10–11].

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In this research, nut-like CeVO_4 microstructure was synthesized using a single step hydrothermal method without template. The hydrothermal reaction time impacts crystalline size, morphology and photocatalytic activities. The photocatalysis of nut-like CeVO_4 microstructure was analyzed using the photodegradation of insecticide diazinon under the UV light irradiation.

2. Experimental

All chemicals in this experiment were used as analytical-grade reagents including: cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99%, Sigma Aldrich, USA), ammonium metavanadate (NH_4VO_3 , 99.5%, Ajax, Australia), sodium hydroxide (NaOH , 99%, Loba Chemie, India), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%, Liqueur Distillery Organization, Thailand) and diazinon (98.9%, Dr. Ehrenstorfer GmbH, Germany). For the hydrothermal synthesis process, appropriate 6.940 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1.872 g of NH_4VO_3 were respectively dissolved with 25 mL deionized water. Then, the Ce^{3+} solution was added to the NH_4VO_3 solution and stirred, then the precipitate appeared. After substantial stirring, the slurry was adjusted to pH 10 by NaOH . After that, the suspensions were transferred into a sealed Teflon autoclave and kept at 180 °C for the different reaction time of 4, 6 and 8 h, then cooled down to room temperature. They then were separated from the reaction medium by filtration and subsequently washed with deionized water and ethanol. Finally, the powders were dried at 80 °C for 12 h for further use. The products have been denoted by the time of hydrothermal reaction as CeVO_4 -4h, CeVO_4 -6h and CeVO_4 -8h. The final products were characterized by XRD (Bruker, Advance D-8, USA), SEM (JEOL/JSM-5410LV, Japan), EDS (Oxford/IncaPentaFETx3, UK) and FT-IR (PerkinElmer/Spectrum RX I, UK). The setup for photocatalytic degradation of diazinon was examined via a test tube reactor with 30 cm length and 2.5 cm width containing 50 mL of 10 ppm diazinon solution and 0.025 g of CeVO_4 photocatalyst. The reactor was kept by the black wall box to protect it from external radiation. Two tubes of 6 Watts short wave UV-C germicidal lamps (Kingrate, G6T5, China) were used as sources of 254 nm UV radiation. The light sources are placed vertically on both sides of the reactor. In each test, the reactor was allowed to equilibrium by ultrasonic for 30 min and then left for 30 min in the darkness. The solution in the reactor was constantly stirred by a magnetic stirrer. The degradation was determined by removing 3 mL of solution at different time intervals and filtered through the 0.22 μm syringe filter (MS® MCE Syringe filter, Membrane Solution, USA) to take the suspension out. A diazinon concentration was assessed at a wavelength of 247 nm using a UV-VIS spectrophotometer (PG Instruments/T90+, UK).

3. Results and discussion

The phase structure and phase purity of the as-synthesized products were examined using XRD technique. Fig. 1 shows the XRD patterns of as-synthesized CeVO_4 products at 180 °C under different hydrothermal reaction times. For the CeVO_4 -4h, there were three predominant peaks at $2\theta=24.1^\circ$, 32.5° and 48.2° due to the (200), (112) and (312) reflections of CeVO_4 present, other peaks are not apparent. All diffraction peaks can be readily indexed to that of the pure tetragonal CeVO_4 , in good accordance with the database of JCPDS No. 01-072-0282. No other impurity phases were detected. This demonstrated that tetragonal structure of CeVO_4 was obtained [11]. Except for the CeVO_4 -6h and CeVO_4 -8h, a small amount of $\text{Ce}(\text{OH})_3$ was detected as parent peaks at $2\theta=26.6^\circ$ and 29.4° [12]. The average crystallite size was measured from full width at half maximum (FWHM) of (200) peaks based on Scherrer's relation [13]:

$$t = 0.9\lambda/\beta\cos\theta \quad (1)$$

where t = crystallite size, λ = wavelength of X-ray employed, β = FWHM of the highest intensity peak and θ = Bragg angle of the X-ray peak chosen. Crystallite size of the particles obtained at different hydrothermal reaction times (4, 6, and 8) is 1.020, 0.97 and 0.93 μm , respectively.

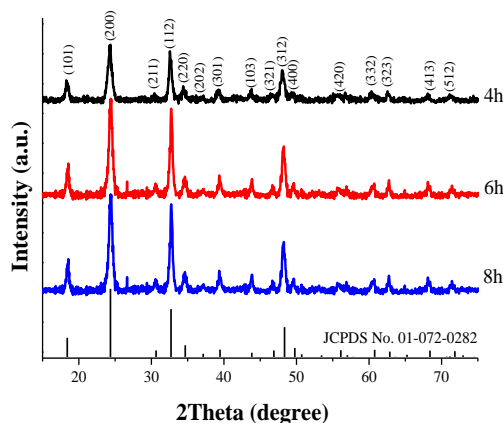


Fig. 1. XRD patterns of $CeVO_4$ synthesized via hydrothermal method at $180\text{ }^\circ\text{C}$ for 4–8 h.

Fig. 2 shows the SEM micrographs of the products synthesized via hydrothermal method with different reaction times of which the products exhibited nut-like microparticles with diameter from magnification bar of about 70, 30 and $10\text{ }\mu\text{m}$ for $CeVO_4$ -4h, $CeVO_4$ -6h and $CeVO_4$ -8h, respectively. Obviously, the size of the particle decreases as the hydrothermal reaction time increases.

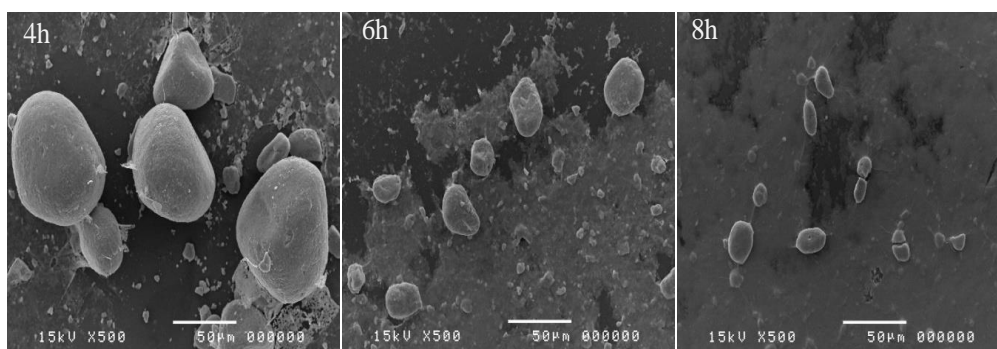
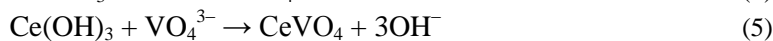


Fig. 2. SEM images of $CeVO_4$ synthesized via hydrothermal method at $180\text{ }^\circ\text{C}$ for 4–8 h.

From the above results we can see that the particle size of as-synthesized $CeVO_4$ products is responsive to the hydrothermal reaction time. The size of the sample synthesized at long hydrothermal reaction time is much smaller than those at short reaction time. The general reaction might occur through the hydrothermal process which would occur by Eq. 2 [11]. For the long hydrothermal reaction time in the basic media ($\text{pH}=9\sim 12$), cerium species firstly precipitates as $Ce(OH)_3$ particles while vanadium from NH_4VO_3 exists as the vanadate anion (Eq. 3–4). On the microscopic level, VO_4^{3-} was mobile species which incorporated into $Ce(OH)_3$ grains, resulted in the nucleation and growth of $CeVO_4$ (Eq. 5) [12,14].



The elemental compositions of nut-like $CeVO_4$ microstructure were identified using EDS studies and depicted in Fig. 3. The elemental maps of the selected area on $CeVO_4$ demonstrated homogeneous distribution of Ce, V and O constituting elements in the sample.

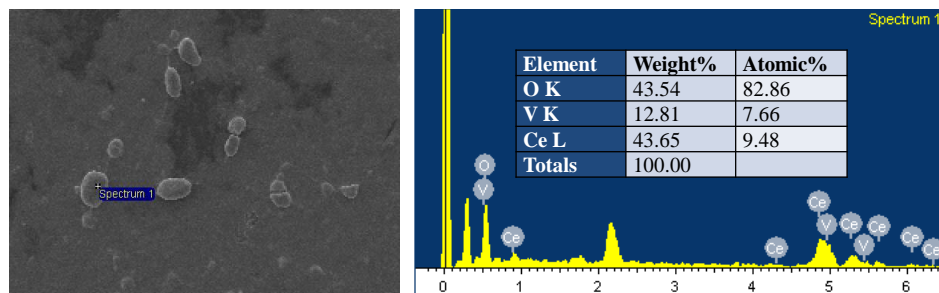


Fig. 3. EDS spectra of $CeVO_4$ synthesized via hydrothermal method.

The functional groups are identified using FT-IR spectroscopy as shown in Fig. 4. FT-IR spectrum of the as-synthesized $CeVO_4$ shows a strong absorption band at 795 cm^{-1} and a weak band at 447 cm^{-1} which are specified as the V-O bonding of VO_4^{3-} and Ce-O bonding, respectively. The obvious absorptions at 1623 cm^{-1} and $\sim 3200\text{ cm}^{-1}$ can be ascribed to bending and stretching vibrations of the adsorbed H_2O molecules, respectively [15–16]. The band at 1385 cm^{-1} may be assigned to NO_3^- vibrations which were also observed. This suggests that NO_3^- anions [17] remain on $CeVO_4$ surface as excess reaction precursor.

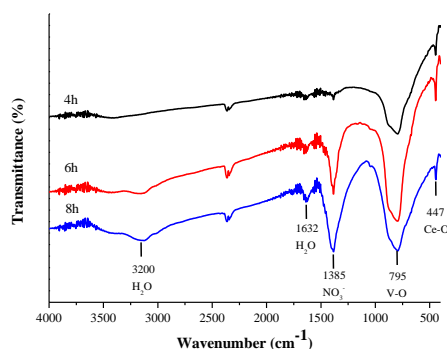


Fig. 4. FT-IR spectra of $CeVO_4$ synthesized via hydrothermal method at $180\text{ }^\circ\text{C}$ for 4–8 h.

In this research, photocatalytic performance of nut-like $CeVO_4$ microstructure for degradation of insecticide diazinon under UV light irradiation are presented in Fig. 5. Degradation efficiency of diazinon by photolysis, $CeVO_4$ -4h, $CeVO_4$ -6h and $CeVO_4$ -8h were 17.79%, 66.48%, 69.98%, and 78.38%, respectively. Among them, the $CeVO_4$ -8h showed the highest efficiency. Generally, degradation efficiency is impacted by crystalline degree, purity, shape, size, surface area, defects and others of the photocatalysts. Fortunately, the current synthetic medium is friendlier to the environment than the previous one.

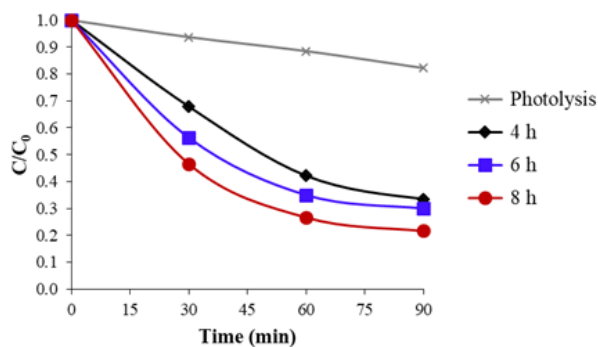
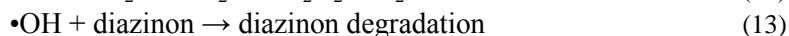
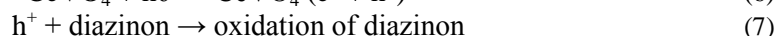
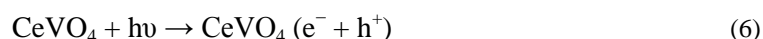


Fig. 5. Photocatalytic efficiency for the degradation of diazinon by $CeVO_4$ synthesized via hydrothermal method at $180\text{ }^\circ\text{C}$ for 4–8 h under UV light irradiation.

The mechanism of photocatalytic degradation of diazinon in the presence of CeVO_4 is described in equations 6–13. The first step in photocatalytic degradation is the photoexcitation of CeVO_4 , followed by the formation of an electron–hole pair (e^-h^+) on the CeVO_4 surface (Eq. 6). The high oxidative potential of positive holes (h^+) in the CeVO_4 allows the direct oxidation of diazinon to get into reactive intermediates (Eq. 7). Hydroxyl radicals in a very active state can also be formed either by the decomposition of water molecules (Eq. 8) or by the interaction between OH^- and holes (Eq. 9). The generated active hydroxyl radical is a greatly strong and non–selective oxidant that leads to degradation of diazinon [18]. Conduction–band electrons on the catalyst surface can minimize neutral oxygen to superoxide anion radicals (Eq. 10), which can form organic peroxides with diazinon (Eq. 11) or H_2O_2 (Eq. 12). Diazinon mineralization can be found by interaction with hydroxyl radicals (Eq. 13).



The degradation rate was calculated by pseudo–firstorder plotting. The apparent rate constant (k) can be determined from the regression line of $\ln(C_0/C)$ versus irradiation time (Fig. 6). In this research, the rate constant of nut–like CeVO_4 microstructure for 8 h (0.0191 min^{-1}) was the highest. Thus, the nut–like CeVO_4 microstructure have been proven to be a good photocatalyst for wastewater treatment [2]. The calculated k values are 0.0021, 0.0128, 0.0150 and 0.0191 in the case of photolysis, CeVO_4 –4h, CeVO_4 –6h and CeVO_4 –8h, respectively. These results indicate that the samples tested can be listed in descending order of efficiency as follows: CeVO_4 –8h > CeVO_4 –6h > CeVO_4 –4h > photolysis and this finding confirms that the efficiency of the catalyst is directly affected by the hydrothermal reaction time.

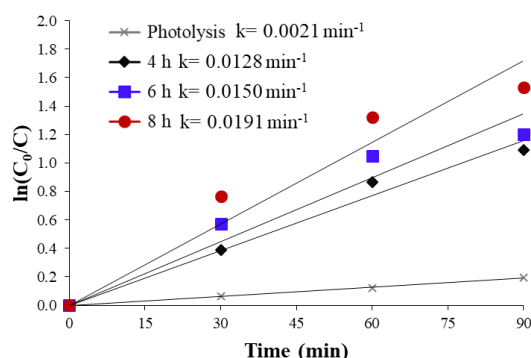


Fig. 6. First–order plot for the degradation of diazinon by CeVO_4 synthesized via hydrothermal method at 180°C for 4–8 h under UV light irradiation.

The crystallinity, phase purity and morphological uniformity of products were highly correlative with the hydrothermal reaction time. Based on the results of all these experiments, the reaction time required for synthesis of CeVO_4 by hydrothermal method affects the efficiency of the application. From what previously reported, the different reaction time for synthesis of CeVO_4 by hydrothermal with or without template method gives different results. For example, Phuruangrat et al. (2016) [15] said that the CeVO_4 nanostructures can be synthesized in 24 h and Shah et al. (2015) [19] reported that nanorods can be synthesized in 48 h. For the short reaction time, the microspheres [10] or microstructure [20] can be synthesized in 8–12 hours. However, the photocatalytic properties of synthesized CeVO_4 can be enhanced by calcination [10]. In addition,

the photocatalytic degradation of diazinon in the presence of synthesized CeVO_4 under UV light irradiation can be enhanced by adding electron acceptors such as H_2O_2 [21].

4. Conclusions

In this study, simple hydrothermal method was used in the synthesis of nut-like CeVO_4 microstructure. The influence of hydrothermal reaction time on the structure, morphology and particle size of products was studied. On the basis of the results presented, the hydrothermal reaction time had potential effects on the formation of nut-like CeVO_4 microstructure. The reaction time of simple hydrothermal synthesis method has a significant effect on the particle size and the crystalline size of nut-like CeVO_4 microstructure. For the environmental application, effective degradation of insecticide diazinon is possible via photocatalysis in the presence of synthesized CeVO_4 microstructure under UV light irradiation. The results indicated that the photocatalysis process in the presence of CeVO_4 synthesized at 180°C for 8 h offered the highest rate constant.

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