Research Article

Synthesis and Characterization of CeVO$_4$ by Microwave Radiation Method and Its Photocatalytic Activity

Nuengruethai Ekthammathat, Titipun Thongtem, Anukorn Phuruangrat, and Somchai Thongtem

1 Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
2 Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
3 Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
4 Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Correspondence should be addressed to Titipun Thongtem; ttpthongtem@yahoo.com and Anukorn Phuruangrat; phuruangrat@hotmail.com

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A general microwave synthesis method was developed to synthesize cerium orthovanadate (CeVO$_4$) nanostructures without the use of any catalysts or templates. This method is able to control the shape and size of the products by adjusting the pH of precursor solutions to be 1–10. Phase, purity, and different morphologies of the products were characterized by XRD, FTIR, SEM, and TEM. They showed that the as-synthesized products exhibited pure single crystalline CeVO$_4$ with tetragonal structure. Their morphologies developed in sequence as nanoparticles (pH = 4–10), nanorods (pH = 2, 3), and microflowers (pH = 1). UV-visible spectra were used to estimate the direct energy gaps of CeVO$_4$ nanorods and microflowers: 3.77 and 3.65 eV, respectively. Photoluminescence (PL) of CeVO$_4$ microflowers showed strong emission intensities at 578 nm. These results were in the range of possible application for photocatalysis, investigated by studying the degradation of methylene blue.

1. Introduction

In recent years, nanostructured rare earth orthovanadates (RVO$_4$), an important compound family of inorganic materials, have been widely studied due to their important properties [1, 2]. Generally, the RVO$_4$ structure has two polymorphs: a monoclinic monazite type and a tetragonal zircon type [2]. Phase of the individual RVO$_4$ was influenced by the ionic radii of rare earth elements. Due to the higher coordination number, the larger rare earth elements prefer to crystallize in the monazite type, as compared to the zircon one [2]. For CeVO$_4$, it is in between the boundary of the first and second types, controlled by the synthesis conditions [2]. Cerium orthovanadate (CeVO$_4$) is an interesting phase of the Ce-V-O ternary system and has a tetragonal zircon-type structure belonging to the space group I41/amd [3–6]. This tetragonal zircon-type structure stabilizes Ce$^{3+}$ cations even in an oxidizing condition [3]. The compound exhibits unique electronic [6–8], optical [6–10], magnetic [6–10], catalytic [9, 10], and luminescent [9, 10] properties. It has wide potential application in various fields, such as oxidative catalyst [7, 10, 11, 13], gas sensors [7, 11, 12], luminescence [7, 10], electrochromic material [9, 13], and components of solid oxide fuel cells (SOFCs) [11–13].

Photocatalysis by solar energy is of great importance in solving global energy and environmental crises [14, 15]. They have been applied in many fields like waste water treatment, air purification, water splitting to produce hydrogen gas, and other environmental problems [9, 15, 16]. It was also reported that lanthanide orthovanadates can be used as photocatalysts for the degradation of dyes and organic compounds [17]. Thus the particular 4f-5d and 4f-4f electronic transitions are different from other elements [7]. The photocatalytic activities of rare earth orthovanadates for the degradation of methylene blue were also reported by Mahapatra et al. [4] and Selvan et al. [2].

Most previous approaches for the synthesis of cerium orthovanadate were reported: hydrothermal method [1, 7, 13],
sol-gel [5], sonochemical method [2, 10], and microwave-assisted synthesis [9, 11]. Microwave-assisted synthesis is an interesting process and is a rapidly developing area of the research. Microwave has been in use to accelerate organic reaction rate since it is generally fast, simple, and consumes less energy. The energy transfer from microwave to the material is believed to be by resonance and relaxation, resulting in rapid heating [9, 11]. Moreover, microwave-assisted synthesis is unique in their potential for large-scale synthesis without suffering thermal gradient effect [18]. In this work, a simple microwave irradiation route was used to synthesize CeVO$_4$ nanorods and microflowers. The dependence of optical properties and photocatalytic application of CeVO$_4$ with different morphologies is reported.

2. Experimental Procedures

In a typical procedure, 0.005 mol Ce(NO$_3$)$_3$·6H$_2$O (cerium (III) nitrate hexahydrate, assay 99.50%, Acros) and 0.005 mol NH$_4$VO$_3$ (ammonium metavanadate, assay 100.3%, Baker analyzed A.C.S. Reagent) were dissolved in 80 mL DI water in a volumetric flask. The pH of the precursor solutions was adjusted to be 1–4 using HCl (assay 35.4%, BDH) and 5–10 using 3M NaOH (assay 90.0%, Solvay) under vigorous stirring. The mixed solutions were stirred for 15 min and they turned into transparency solutions at the pH 1–2, red-brown precipitate at the pH 3–4, and yellow precipitate at the pH 5–10. The ready-adj usted mixture was then placed in a home type microwave oven (Electrolux, EMS 2820, 2.45 GHz) at 180 W and processed for 120 min to form precipitates. The as-synthesized precipitates were filtered, rinsed with DI water and 95% ethanol several times, and dried at 70°C for 24 h.

Crystalline degree and phase identification were analyzed by X-ray diffractometer (XRD, Philips X’Pert MPD) using Cu-K$_\alpha$ radiation at 45 kV and 35 mA in the range of 10–60 deg. Size and morphology of the as-synthesized CeVO$_4$ were characterized by field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F) operating at 35 kV. A transmission electron microscopic image and selected area electron diffraction (SAED) patterns of the as-synthesized CeVO$_4$ products were taken using a transmission electron microscope (TEM, JEOL JEM-2100F) operating at 200 kV. Fourier transform infrared (FTIR) spectrometer was carried out by a Perkin Elmer RXS spectrometer in the range of 400–4000 cm$^{-1}$ at room temperature, with CeVO$_4$ tablets diluted 40-fold with KBr. The photoluminescence (PL) emission was studied by a LS 50B PerkinElmer fluorescence spectrophotometer using 420 nm excitation wavelength at room temperature. Absorbance spectra of a UV-visible spectrometer (Lambda25 PerkinElmer) were used to analyze energy gap of the products and to determine the degradation of methylene blue at room temperature.

Photocatalysis was proceeding in a photoreactor fitted with three 15 W of UV germicidal irradiation lamps. The lamp radiated predominantly at 365 nm (3.4 eV) and a photon flux of $5.8 \times 10^{-6}$ mol/s [4, 9]. The photocatalytic activities were evaluated by measuring the photocatalytic degradation of methylene blue (MB) in the aqueous solutions. In a typical degradation experiment, 100 mL of $10^{-5}$ M MB solution and 100 mg as-synthesized cerium orthovanadate were put in a 250 mL Pyrex Erlenmeyer flask and the mixture was continuously stirred in the dark for 30 min to attain adsorption-desorption equilibrium of MB on surface of the photocatalyst. The equilibrium concentration of MB was used as the initial value for the photodegradation process. The light was turned on to initiate the photocatalytic reaction. At certain time intervals, every 5 mL solution was sampled and centrifuged to remove particles inside. The degradation of organic dye was monitored by measuring the absorbance of
the solutions with DI water as a reference and the degradation efficiency was determined from the absorbance intensity at 665 nm wavelength.

3. Results and Discussion

Phase, purity, and crystallinity of the as-synthesized cerium orthovanadate were characterized by powder X-ray diffraction. Figure 1 shows the XRD patterns of CeVO₄ synthesized in the solutions with the pH of 1, 2, 4, 6, and 8 by a microwave irradiation method at 180 W for 120 min. The patterns fitted well with the tetragonal (zircon) type CeVO₄ with 141/amd space group, lattice constants \( a = b = 7.340 \) Å and \( c = 6.470 \) Å of the JCPDS no. 72-0282 [19]. The diffraction peaks were carefully indexed and assigned to the lattice planes of (101), (200), (112), (220), (301), (312), and (400), corresponding to the 2\( \theta \) values of 18.3, 24.2, 32.6, 34.5, 39.3, 48.2, and 49.6 deg., respectively. No other impurities were detected in these spectra. Upon increasing the acidity content of the precursor solutions, all the peaks became sharpened. Thus, they were concluded that the pH of the solutions plays an important role in the crystalline degree of pure CeVO₄ [3, 10, 11, 13, 17].

Figure 2 presents the FTIR spectra of CeVO₄ synthesized in the solutions with the pH of 1 and 2 by microwave radiation at 180 W for 120 min. The FTIR spectra were recorded over the range of 400–4,000 cm⁻¹. In this research, both spectra show sharp and broad bands around 460 cm⁻¹ and 786 cm⁻¹ due to the stretching vibration of VO₄ and V–O, respectively [2, 4, 5, 20, 21]. Other shallow bands of the O–H bending [2] and stretching [4, 20, 22] of water adsorbed on the surface of CeVO₄ were also detected at 1,620 and 3,420 cm⁻¹, respectively.

General morphologies and sizes of CeVO₄ were examined by FE-SEM technique. The FE-SEM images of the products (Figure 3) synthesized in the solutions with the pH of 1, 2, 3, 4, 5, and 6 showed different morphologies. The products exhibited microflowers at the pH 1 with diameters of about 10 µm, nanorods at the pH 2 and 3. For the pH 2, the product was nanorods about 600 nm long and about 50 nm in diameter. For the pH 3, the product was also nanorods but smaller and longer than those for the pH 2. They were about 30 nm in diameter and up to several micrometers. Most of the nanorods were straight and uniform along their axial axes. For the pH range of 4–10, the products were nanoparticles.

TEM image and SAED patterns of the products were characterized. Figure 4(a) shows a petal of CeVO₄ microflowers synthesized at the pH 1 by the microwave radiation. The SAED pattern (Figure 4(b)) shows a number of bright spots of fully concentric rings, which indicated the as-synthesized nanocrystals with different orientations. The rings correspond to the (101), (200), (202), and (321) planes and were specified as tetragonal structured CeVO₄. The SAED pattern (Figure 4(c)) confirmed that the petal was single nanocrystals of tetragonal structured CeVO₄ with the [–103] direction as zone axis. An electron diffraction pattern with the [–103] zone axis (Figure 4(d)), simulated using CaRIne Crystallography 3.1 [23], corresponds very well with that of Figure 4(c). In addition, the CaRIne Crystallography 3.1 [23] was used to simulate the crystal structure of tetragonal CeVO₄ as shown in Figure 5. The sites and fractional coordinates [24] are shown in Table I. The tetragonal CeVO₄ is composed of VO₄ tetrahedral sharing corners and edges with CeO₈ dodecahedral chains. The chains, interrupted by distorted VO₄ units, extended along the c-crystalline axis and were
favorable to stabilizing Ce$^{3+}$ cations even in an oxidizing condition [3, 6, 10].

Due to the above, the as-synthesized CeVO$_4$ was influenced by pH of precursor solutions, with the optimal pH of ≤10. This phenomenon was able to be used for explanation of the complex interaction and balance between the chemical potential and the rate of ionic motion [13]. The morphologies evolution of the products was developed in sequence, nanoparticles → nanorods → microflowers, by decreasing in the pH values of the solutions. Thus possible reactions could be discussed as follows. When cerium source was dissolved in water, Ce(OH)$_3$ formed in alkaline solutions. At high pH values, the formation of VO$_4^{3-}$ was favor, and CeVO$_4$ was synthesized under appropriate heating microwave condition. These led to favor the formation of CeVO$_4$ nanoparticles. In acidic solutions, vanadate species exist as anionic oligomers and Ce$^{3+}$ reactive species as cations. Ce$^{3+}$ existing as mobile cations incorporated with vanadate anions to synthesize CeVO$_4$ [11,17]:

\[
\begin{align*}
\text{Ce}^{3+} + 3\text{OH}^- & \rightarrow \text{Ce(OH)}_3 \quad (1) \\
\text{VO}_3^{2-} + \text{OH}^- & \rightarrow \text{VO}_4^{3-} + \text{H}^+ \quad (2) \\
\text{Ce(OH)}_3 + \text{VO}_4^{3-} & \rightarrow \text{CeVO}_4 + 3\text{OH}^- \quad (3) \\
\text{Ce(OH)}_3 + 3\text{H}^+ & \rightarrow \text{Ce}^{3+} + 3\text{H}_2\text{O} \quad (4)
\end{align*}
\]

The effect of pH on the morphologies of CeVO$_4$ is presented in Figure 6. It shows the probable growth mechanism of the nanostructures with different morphologies, explaining the structural evolution of CeVO$_4$ under the influence of pH of the precursor solutions. The chemical growth of materials related to the precipitation process of solids from solutions. Basically, they consisted of nucleation and growth stages [25], which balance between the kinetic and thermodynamic growth regimes and strongly control the final nanostructured morphologies [25]. The shapes of the crystals were determined by specific surface energies associated with the crystalline facets [26]. The further development of crystallites was controlled by the hindrance of H$^+$ on the facets [26]. In this experiment, Ce$^{3+}$ and
VO$_4^{3-}$ incorporated into crystal lattice of the as-synthesized crystallites which grew according to the anisotropic structure of CeVO$_4$ nanoparticles. Upon decreasing the pH values, the concentrations of H$^+$ ions were increased. At the pH 3, each facet of the crystallites has the probability to generate active sites by the adsorption of H$^+$ ions. Then CeVO$_4$ could be grown as 1D nanorods. Until at the pH 1, Ce$^{3+}$ and VO$_4^{3-}$ ions were able to incorporate into the active sites through the more hindrance of adsorbed H$^+$ ions, leading to the possible formation of microflowers [26].

The UV-visible absorption spectra of the as-synthesized CeVO$_4$ microflowers (pH = 1) and nanorods (pH = 2) are shown in Figure 7. By dispersing the as-synthesized products in ethanol and sonication of the mixtures for 30 min, the clear solutions formed. The results show strong absorption peaks at 253 and 248 nm for CeVO$_4$ microflowers and nanorods, respectively. A shoulder at 270 nm was also detected for the microflowers. These prominent peaks were attributed to the UV absorption of the VO$_4^{3-}$ of rare earth vanadates [1,2,10,22]. They attributed to the charge transfer from the oxygen ligands to the central vanadium atoms inside the VO$_4^{3-}$ groups of cerium orthovanadate [1,22]. Obviously, with the decreasing in sizes, the positions of absorption peaks of the as-synthesized CeVO$_4$ products significantly shifted to lower wavelength. It is a typical phenomenon of the quantum-size effect of nanostructured system. CeVO$_4$ has the potential to apply as counter electrodes in electrochromic devices. The blue shift of the absorption peaks affected the electrochromic property of CeVO$_4$-based devices [11]. From UV-visible spectroscopic results, the energy gaps were estimated to be 3.65 and 3.77 eV caused by the optical measurements of CeVO$_4$ microflowers and nanorods, respectively. In addition, optical property of the products was also analyzed by photoluminescence (PL) spectroscopy technique. Figure 8 shows two broad emission bands of CeVO$_4$ microflowers and nanorods centered at 578 and 582 nm, respectively. They could be specified as the electronic transitions from the lowest excited states arising from 5d$^1$ to the 4f$^2$ ground state ($^2$F$_{5/2}$ and $^2$F$_{7/2}$) of the Ce$^{3+}$ ions. The asymmetric emission band was possibly caused by the splitting of the 4f$^2$ ground state due to spin-orbital interaction [20].

The band gap values of CeVO$_4$ products obtained by the UV-vis spectroscopy technique are comparable to the band gap value of the well-known photocatalyst [2]. The orthovanadates were reported to act as photocatalysts under UV light [2,4]. Degradation of MB was used as an indicator to examine the photocatalytic activities of CeVO$_4$ under UV light. The degradation of MB specified from the absorbance spectra of the dye solutions recorded at different time intervals after the recovery of the photocatalyst. The highest intensities of the UV-visible spectra of MB at 665 nm wavelength for CeVO$_4$ synthesized in the solutions with the pH of 1 (microflowers) and 2 (nanorods) under UV light were monotonically decreased within 35 min. The reaction mechanism for the degradation of MB by pure CeVO$_4$ was discussed according to the following. When the solutions were irradiated by UV light, MB molecules were excited. Subsequently, the photoexcited electrons transferred to conduction band of CeVO$_4$ and further transferred to the adsorbed O$_2$ on the surface of CeVO$_4$ to form •O$_2$ negative superoxide radicals. At the same time, protonation of OH$^-$ or H$_2$O yielded •OH radicals, which were responsible for the degradation of MB molecules [27,28].

Figure 9 shows the MB degradation efficiency of CeVO$_4$ nanostructure under UV light within different lengths of
time, compared to the control or catalyst-free solution. Concentration of MB rapidly decreased to 63% and 45% for the as-synthesized CeVO₄ microflowers and nanorods, respectively. These show that CeVO₄ microflowers have 18% higher photocatalytic activity than CeVO₄ nanorods. The space between internanorods of CeVO₄ microflowers could function effectively in promoting reflection of trapped incident light, enhance light harvesting, and increase the quantities of photogenerated electrons and holes participating in the photocatalysis [29, 30]. Size and crystalline nature of the photocatalyst played a critical role in determining the photocatalytic activity of the present study. Shape of the crystals influenced the absorbance and direct energy gap, which reflected the photocatalytic performance due to the different activities of the dominant facets [31–33]. In this research, the energy gap of CeVO₄ microflowers synthesized at the pH of 1 is narrower than the energy gap of CeVO₄ nanorods synthesized at the pH of 2. The specific surface, controlled by structure and crystallite size, was an important factor to determine the reaction activity. The higher photocatalytic activity of CeVO₄ microflowers could pertain to defects containing in grain boundaries, surficial amorphous layers, and intergranular layers [34]. The present analysis is able to contribute to the potential application of CeVO₄ microflowers for waste water treatment.

4. Conclusions

In this paper, we have developed a microwave radiation method for synthesizing nanostructured cerium orthovanadate. This system is simple and efficient in controlling different morphologies of the products. The pH of the precursor solutions was the key factor to control the morphologies of CeVO₄: nanoparticles, nanorods, and microflowers. In this research, the growth mechanism was proposed the role of pH of the precursor solutions in synthesizing CeVO₄ nanostructures. Energy gaps of the as-synthesized CeVO₄ were 3.65 eV for microflowers and 3.77 eV for nanorods. The photocatalytic activity of these materials was identified by the degradation of MB. The activity of CeVO₄ microflowers was higher than that of CeVO₄ nanorods.

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