Synthesis and Characterization of Nanoparticulate $CeVO_4$ by Ultrasound Method and its Photocatalytic Activity

Yi Zheng
Department of Materials Chemistry
Huzhou University
Huzhou 313000, P. R. China
e-mail: ZhengYi@163.com

Qian Yang
Department of Materials Chemistry
Huzhou University
Huzhou 313000, P. R. China
e-mail: yq127@outlook.com

Jiqi Jiang
Department of Materials Chemistry
Huzhou University
Huzhou 313000, P. R. China
e-mail: JiangJiqi@163.com

Peisong Tang
Department of Materials Chemistry
Huzhou University
Huzhou 313000, P. R. China
e-mail: tangps@163.com

Abstract—A simple and efficient method has been established for the synthesis of cerium orthovanadate ($CeVO_4$) nanoparticles without the use of any catalysts or templates. Using $Ce(NO_3)_3·6H_2O$ and NH_4VO_3 as main material, the $CeVO_4$ nanoparticles were synthesized by ultrasound method at 60°C and different pH conditions, The samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and UV-visible diffuse reflectance spectroscopy (DRS). The results showed that the pure $CeVO_4$ of tetragonal structure was successfully synthesized at the pH=4, 6 and 8. The $CeVO_4$ nanoparticles which were prepared at the pH=8 had an average grain size of 10~20 nm in diameter and the optical absorption onset of 355 nm, indicating the optical band gap of 3.49 eV. The photocatalytic activities of the $CeVO_4$ nanoparticles have been evaluated by studying the degradation of methyl orange (MO). The results showed that $CeVO_4$ nanoparticles appeared high photocatalytic activity for the decomposition of MO.

Keywords-cerium orthovanadate; ultrasound method; photocatalysis; thermal stability; nanomaterials.

I. INTRODUCTION

As one of the rare earth vanadate, the $CeVO_4$ was widely used in light-emitting materials, gas sensors, photocatalysis, lubricating additive and batteries fields[1-6]. Considering $CeVO_4$ excellent physical and chemical properties, it was particularly important to seek a preparation method of simple, efficient, energy-saving and environmental. At present, the methods of preparing $CeVO_4$ were mainly solid state reaction method[1-3], sol-gel method[4-5], hydrothermal method[6-9], microwave assistant method[10-12] and sonochemical assistant method[13-15]. However, these methods were all complicated, time-consuming and high energy consumption. Moreover, it was rarely reported that the $CeVO_4$ was synthesized by the quick and efficient ultrasound method. In this paper, we rapidly synthesized $CeVO_4$ nanoparticles by the ultrasound method under the condition of 60°C and given pH. The $CeVO_4$ samples were characterized by XRD, SEM, FTIR and DRS et al. The photocatalytic activity of the $CeVO_4$ nanoparticles were investigated by degradation simulation sewage containing 20 mg/L MO.

II. EXPERIMENTAL SECTION

A. Synthesis of $CeVO_4$

All reagents with analytical purity were purchased from Aladdin Co. and used as received without further purification. The $CeVO_4$ nanoparticles were prepared by ultrasound processing. In a typical synthesis, 1mmol $Ce(NO_3)_3·6H_2O$ and 1mmol NH_4VO_3 were dissolved in 30 mL distilled water at room temperature. Using 1mol/L HCl or NaOH to adjust solution pH, the mixture was stirred for 10 min to obtain the reaction liquid. The resulting solution was transferred to the ultrasound instrument, and the ultrasound processing was carried out 120 min at 60°C. The resulted products were centrifugally separated, washed by water and ethanol three times. Finally, the $CeVO_4$ nanoparticles were gotten after being dried in a 60°C oven.

B. Characterization

The X-ray diffraction patterns of the prepared products were measured with XD-6 X-ray diffraction (Beijing Purkinje General Intstrument Co., Ltd.) using Cu Kα (λ=1.5418 Å) radiation operated at 36 kV and 20 mA. The morphology of prepared products were observed using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) with an accelerating voltage of 5 kV. Fourier transform infrared spectra (FTIR) were recorded with a Nicolet 5700 infrared spectrometer on KBr pellets in the region of 400–4000 cm-1 with a 4cm-1 resolution under ambient conditions. The thermogravimetric and differential thermal analysis (TG-

DTA) were performed on a HCT-2 thermal analyzer with a heating rate of 10°C/min in air. UV-visible diffuse reflectance spectra (DRS) were taken with a Hitachi UV-4100 spectrometer. $BaSO_4$ was used as a reflectance standard in the UV-visible diffuse reflectance spectrum measurement.

C. *Photocatalytic activity testing*

Photocatalytic degradation experiment was carried out in a homemade photocatalytic reaction device. The light source was a 150W high pressure mercury lamp. Typically, 20 mg of $CeVO_4$ photocatalyst powders was suspended in 10 mL aqueous solution containing 10 mg/L methyl orange (MO). Then, the suspensions were stirred for 30 min in the darkness to get the adsorption-desorption equilibrium and followed by the light irradiation for a given time. Finally, the suspensions were centrifuged, and the upper transparent solution was subjected to the UV-visible absorption spectra measurement. The concentration of the residual MO was evaluated by the absorbance at 464 nm, then finding its degradation rate by its standard curve method.

III. RESULTS AND DISCUSSION

A. *Synthesis of $CeVO_4$ nanoparticles and structure analysis*

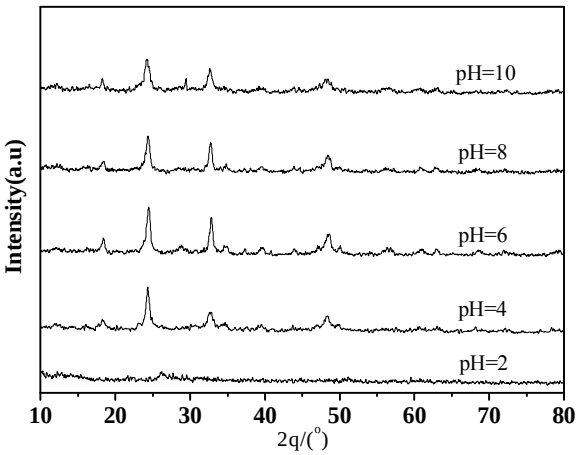

Figure 1. XRD patterns of the prepared samples under different pH

The tetragonal structure $CeVO_4$ which has average grain size of 50~100 nm was prepared by sonochemical processing and calcination at 500°C[8]. Using Na_3VO_4, HNO_3, $Ce(NO_3)_3$ and NaOH as main material, the $CeVO_4$ was prepared by two step sonochemical processing[9-10]. However, we prepared nanoparticulate $CeVO_4$ by a simple ultrasound route with $Ce(NO_3)_3 \cdot 6H_2O$ and NH_4VO_3 as raw materials in this work. The present method was simple, time-saving, and does not require the complicated operation and expensive high temperature calcination process.

Fig.1 showed the XRD patterns of the prepared samples under different pH conditions. As can be seen from Fig.1, the prepared samples at pH=2 has poor crystallinity so that there was no sharp XRD peak observed. However, the diffraction peaks of prepared $CeVO_4$ at pH=4, 6 and 8 matched well with the standard sample of tetragonal structure of $CeVO_4$ (JCPDS:12-0757), without other impurity phase peaks. The diffraction peaks of prepared $CeVO_4$ at pH=10 matched good with the standard sample of tetragonal structure of $CeVO_4$ except a small diffraction peak at around $2\theta=29.4^o$. It suggested that we successfully synthesized $CeVO_4$ by convenient ultrasound method at pH=4, 6 and 8.

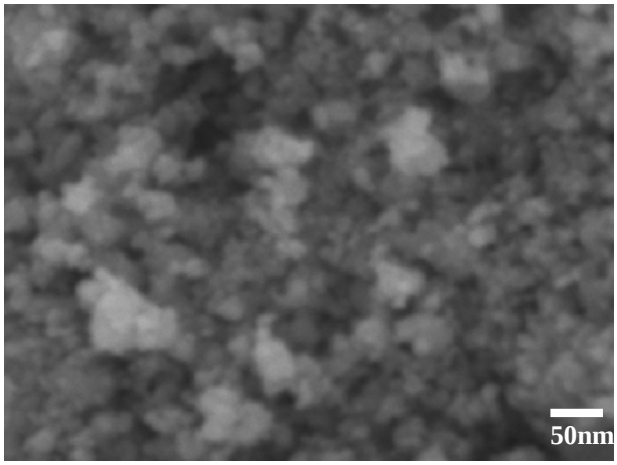

Figure 2. SEM photograph of the prepared CeVO4 at pH=8

Fig.2 showed that SEM photograph of the prepared $CeVO_4$ at pH=8. It can be seen that the average crystal grain size of the sample was mainly 10~20 nm except slightly agglomerated from Fig.2. This result exceed to the literature result which tetragonal structure $CeVO_4$ was prepared by sonochemical processing and calcination at 500°C[8].

B. *Surface chemistry and DRS spectrum*

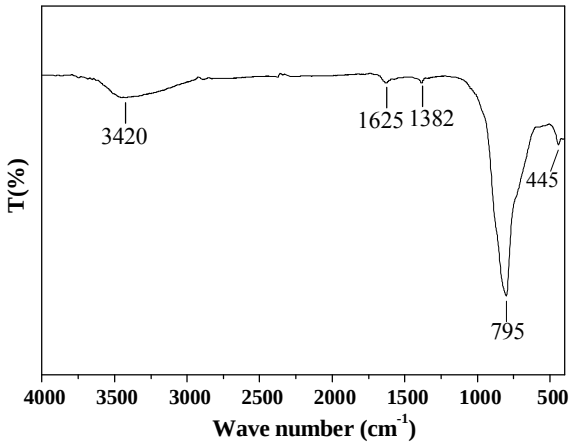

Figure 3. FTIR spectrum of the prepared $CeVO_4$ at pH=8

Fig.3 showed that FT-IR spectrum of the prepared $CeVO_4$ at pH=8. It can be seen that the 795 cm-1 and 445 cm-1 peaks were assigned to the stretching vibration of the V–O and Ce–O [8,10], respectively. Another small band were observed for the sample at 3420 cm-1, 1625 cm-1and 1382 cm-1 corresponding to the bending vibration of H_2O molecules[8,10]. It suggested that the $CeVO_4$ was successfully synthesized by convenient ultrasound method.

The optical property of prepared single phase $CeVO_4$ was investigated by the UV-visible DRS spectrum.

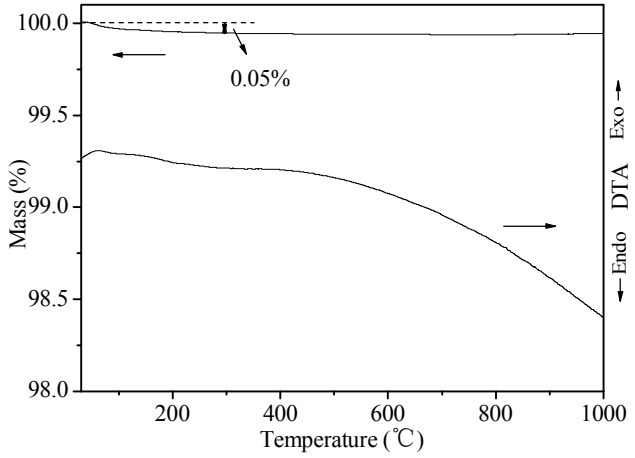

Figure 4. TG- DTA curve of the prepared $CeVO_4$ at pH=8

Thermal analysis of the prepared $CeVO_4$ was carried out in air to examine the stability of the resulting sample and the phase transformation process (Fig. 4). The TG and DTA curves reflect the thermal decomposition of organic species and the phase transformation of materials. It can be clearly seen that only 0.05% mass losse was observed from 30 °C to 300 °C at TG curve. However, the endothermic peak and exothermic peak were not obvious from 30 °C to 1000 °C at DTA curve. These results showed that the prepared $CeVO_4$ had good thermal stability.

Fig.5 showed the DRS of the prepared $CeVO_4$ under the condition of pH=8. It showed that the absorption onset of $CeVO_4$ was about 355 nm. According to the formula $E(eV)=1240/\lambda$, the band-gap width of $CeVO_4$ was 3.49 eV, belonging to a relatively wide band-gap semiconductor material. According to energy band theory and principle of semiconductor photocatalysis, the UV-light irradiation can excite the the present $CeVO_4$ nanoparticles, which makes it the potential UV-light-driven photocatalyst.

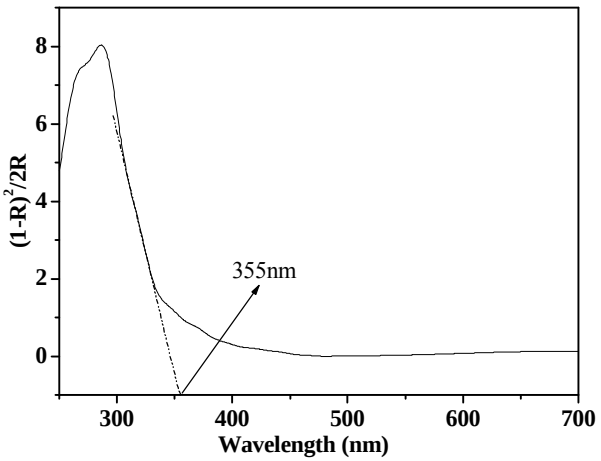

Figure 5. DRS of the prepared $CeVO_4$ at pH=8

C. Photocatalytic activity

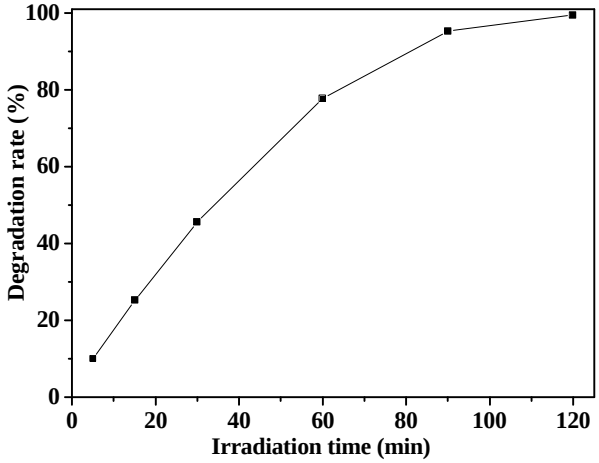

Figure 6. Plot of photocatalytic degradation rate of methyl orange in the presence of the prepared $CeVO_4$ at pH=8 under light irradiation

The photocatalytic activity was evaluated by the degradation of MO under the UV-light irradiation, as shown in Fig.6. As seen from Fig.6, it showed that the degradation rate of MO rapidly increased almost linearly with time increasing when the lighting time less than 90 min. When the lighting time was 120 min, the degradation rate of MO had reached about 100%. The $CeVO_4$ nanoparticles showed high photocatalytic activity for MO degradation.

IV. CONCLUSIONS

Using $Ce(NO_3)_3 \cdot 6H_2O$ and NH_4VO_3 as raw materials, the $CeVO_4$ nanoparticles was quick-step synthesized by ultrasound method. The synthesis of $CeVO_4$ was affected by solution pH. The prepared $CeVO_4$ had average crystal grain size of 10~20nm, and band-gap width of 3.49eV. The photocatalytic experiment indicated that $CeVO_4$ nanoparticles showed high activity for decomposition of MO. Therefore, our present work offers effective synthesis of $CeVO_4$ nanoparticles photocatalysts.

ACKNOWLEDGMENT

The research work were supported by the New Talents Program for Undergraduates of Zhejiang Province (No.2014R425002) and Zhejiang Province Natural Science Foundation of China (No.Y4100471).

REFERENCES

[1] M.V. Martí nez-Huerta, J.M. Coronado, M. Fernández-García, A. Iglesias-Juez , G. Deo, J.L.G. Fierro and M.A. Bañares, "Nature of the vanadia–ceria interface in V^{5+}/CeO_2 catalysts and its relevance for the solid-state reaction toward $CeVO_4$ and catalytic properties," Journal of Catalysis, vol. 225, Apr. 2004, pp.240-248, doi:10.1016/j.jcat.2004.04.005.

[2] J. Matta, D. Courcot, E. Abi-Aad, and A. Aboukaïs, "Identification of Vanadium Oxide Species and Trapped Single Electrons in Interaction with the $CeVO_4$ Phase in Vanadium−Cerium Oxide Systems. ^{51}V MAS NMR, EPR, Raman, and Thermal Analysis Studies," Chemistry of Materials, vol. 14, Oct. 2002, pp. 4118–4125, doi: 10.1021/cm010396t.

[3] W. Akiteru, "Highly Conductive Oxides, $CeVO_4$, $Ce_{1-x}M_xVO_{4-0.5x}$(M=Ca, Sr, Pb) and $Ce_{1-y}Bi_yVO_4$, with Zircon-Type Structure Prepared by Solid-State Reaction in Air," Journal of Solid State Chemistry, vol. 153,Aug. 2000, pp. 174-179, doi:10.1006/jssc.2000.8773.

[4] U. O. Krašovec, B. Orel, A. Šurca, N. Bukovec and R. Reisfeld, "Structural and spectroelectrochemical investigations of tetragonal $CeVO_4$ and Ce/V-oxide sol-gel derived ion-storage films," Solid State Ionics, vol. 118, Mar. 1999, pp. 195-214, doi:10.1016/S0167-2738(98)00456-1.

[5] G. Picardia, F. Varsanoa, F. Deckera, U. Opara-Krasovecb, A. Surcab,and B. Orelb, "Electrochemical characterization of optically passive $CeVO_4$ counterelectrodes," Electrochimica Acta, vol. 44, May 1999, pp. 3157–3164, doi:10.1016/S0013-4686(99)00033-X.

[6] L. Fengzhen, S. Xin, Y. Yibin, Z. Limin, S. Zhuwei, L. Xuehua, M.Xianhua, "Shape controlled synthesis and tribological properties of $CeVO_4$ nanoparticles as lubricating additive," Journal of Rare Earths, vol. 29, Jul. 2011, pp. 688-691, doi:10.1016/S1002-0721(10)60523-6.

[7] F. Luo, C. L. Jia, W. Song, L. P. You and C. H. Yan, "Chelating ligand-mediated crystal growth of cerium orthovanadate," Crystal Growth and Design, vol. 5, Jan. 2005, pp.137-142, dio: 10.1021/cg049940b.

[8] L. M. Chen, "Hydrothermal synthesis and ethanol sensing properties of $CeVO_4$ and $CeVO_4$–CeO_2 powders," Materials Letters, vol. 60, Jul. 2006, pp. 1859-1862, doi:10.1016/j.matlet.2005.12.037.

[9] X. Zhenhe, L. Chunxia, H. Zhiyao, P. Chong, and L. Jun, "Morphological control and luminescence properties of lanthanide orthovanadate $LnVO_4$ (Ln = La to Lu) nano-/microcrystals viahydrothermal process," CrystEngComm, vol. 13, Sep. 2010, pp. 474-482, doi:10.1039/C0CE00161A.

[10] S. Mahapatra, G. Madras and T.N.G. Row, "Synthesis, characterization and photocatalytic activity of lanthanide (Ce, Pr and Nd) orthovanadates," Industrial & Engineering Chemistry Research, vol. 46, Feb. 2007, pp. 1013-1017, doi: 10.1021/ie060823i.

[11] H. Wang, Y.Q. Mengy and H. Yan, "Rapid synthesis of nanocrystalline $CeVO_4$ by microwave irradiation," Inorganic Chemistry Communications, vol. 7, Mar. 2004, pp. 553-555, doi:10.1016/j.inoche.2004.02.017.

[12] E. Nuengruethai, T. Titipun, P. Anukorn and T. Somchai, "Synthesis and characterization of $CeVO_4$ by microwave radiation method and its photocatalytic activity," Journal of Nanomaterials, vol. 2013, Jan. 2013, pp. 434197-434203, doi:10.1155/2013/434197.

[13] R. Kalai Selvan, A. Gedanken, P. Anilkumar, G. Manikandan and C. Karunakaran, "Synthesis and characterization of rare earth orthovanadate (RVO_4; R=La, Ce ,Nd, Sm, Eu and Gd) nanorods /nanocrystals /nanospindles by a facile sonochemical method and their catalytic properties," Journal of Cluster Science, vol. 20, Jun. 2009, pp. 291-305, doi:10.1007/s10876-008-0229-y.

[14] B. G. Xie, G. Z. Lu, Q.G. Dai, Y.Q. Wang, Y. Guo and Y. L. Guo, "Synthesis of $CeVO_4$ crystals with different sizes and shapes," Journal of Cluster science, vol. 22, Dec. 2011, pp. 555-561, doi:10.1007/s10876-011-0396-0.

[15] B. G. Xie, "Preparation of rare earth orthovanadates and their luminescent and catalytic performances," Shanghai: doctoral dissertation of East China University of Science and Technology, 2011.