Synthesis and Characterization of Nanoparticulate CeVO₄ by Ultrasound Method and its Photocatalytic Activity

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Abstract—A simple and efficient method has been established for the synthesis of cerium orthovanadate (CeVO₄) nanoparticles without the use of any catalysts or templates. Using Ce(NO₃)₃·6H₂O and NH₄VO₃ as main material, the CeVO₄ 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 CeVO₄ of tetragonal structure was successfully synthesized at the pH=4, 6 and 8. The CeVO₄ 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 CeVO₄ nanoparticles have been evaluated by studying the degradation of methyl orange (MO). The results showed that CeVO₄ 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 CeVO₄ was widely used in light-emitting materials, gas sensors, photocatalysis, lubricating additive and batteries fields[1-6]. Considering CeVO₄ 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 CeVO₄ 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 CeVO₄ was synthesized by the quick and efficient ultrasound method. In this paper, we rapidly synthesized CeVO₄ nanoparticles by the ultrasound method under the condition of 60°C and given pH. The CeVO₄ samples were characterized by XRD, SEM, FTIR and DRS et al. The photocatalytic activity of the CeVO₄ nanoparticles were investigated by degradation simulation sewage containing 20 mg/L MO.

II. EXPERIMENTAL SECTION

A. Synthesis of CeVO₄

All reagents with analytical purity were purchased from Aladdin Co. and used as received without further purification. The CeVO₄ nanoparticles were prepared by ultrasound processing. In a typical synthesis, 1 mmol Ce(NO₃)₃·6H₂O and 1 mmol NH₄VO₃ were dissolved in 30 mL distilled water at room temperature. Using 1 mol/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 CeVO₄ 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 Instrument 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. BaSO₄ 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 CeVO₄ 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 CeVO₄ nanoparticles and structure analysis

The tetragonal structure CeVO₄ which has average grain size of 50–100 nm was prepared by sonochemical processing and calcination at 500°C[8]. Using Na₂VO₃, HNO₃, Ce(NO₃)₃ and NaOH as main material, the CeVO₄ was prepared by two step sonochemical processing[9-10]. However, we prepared nanoparticulate CeVO₄ by a simple ultrasound route with Ce(NO₃)₃·6H₂O and NH₄VO₃ 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 CeVO₄ at pH=4, 6 and 8 matched well with the standard sample of tetragonal structure of CeVO₄ except a small diffraction peak at around 2θ=29.4°. It suggested that we successfully synthesized CeVO₄ by convenient ultrasound method at pH=4, 6 and 8.

Fig.2 showed that SEM photograph of the prepared CeVO₄ 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 CeVO₄ was prepared by sonochemical processing and calcination at 500°C[8].

B. Surface chemistry and DRS spectrum

Fig.3 showed that FT-IR spectrum of the prepared CeVO₄ 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 H₂O molecules[8,10]. It suggested that the CeVO₄ was successfully synthesized by convenient ultrasound method.

The optical property of prepared single phase CeVO₄ was investigated by the UV-visible DRS spectrum.
Thermal analysis of the prepared CeVO₄ 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 loss 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 CeVO₄ had good thermal stability.

Fig.5 showed the DRS of the prepared CeVO₄ under the condition of pH=8. It showed that the absorption onset of CeVO₄ was about 355 nm. According to the formula $E(eV) = \frac{1240}{\lambda}$, the band-gap width of CeVO₄ 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 present CeVO₄ nanoparticles, which makes it the potential UV-light-driven photocatalyst.

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 CeVO₄ nanoparticles showed high photocatalytic activity for MO degradation.

IV. CONCLUSIONS

Using Ce(NO₃)₃·6H₂O and NH₄VO₃ as raw materials, the CeVO₄ nanoparticles was quick-step synthesized by ultrasound method. The synthesis of CeVO₄ was affected by solution pH. The prepared CeVO₄ had average crystal grain size of 10–20nm, and band-gap width of 3.49eV. The photocatalytic experiment indicated that CeVO₄ nanoparticles showed high activity for decomposition of MO. Therefore, our present work offers effective synthesis of CeVO₄ nanoparticles photocatalysts.

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