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Controllable synthesis, characterization and photocatalytic studies on cadmium vanadate nanostructures

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ABSTRACT

Cadmium vanadate ($Cd_2V_2O_7$) nanocrystals have been successfully synthesized via simple coprecipitation method by using $Cd(NO_3)_2 \cdot 4H_2O$ and NH_4VO_3 as starting materials. Effects of various amines, temperature, reaction time, solvent, pH were investigated to reach optimum condition. It was found that particle size, morphology and phase of the as-prepared products could be greatly influenced via these parameters. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, energy dispersive X-ray microanalysis (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocatalytic activity of cadmium vanadate nanostructures was investigated by degradation of anionic dye of eosin Y in aqueous solution under visible light irradiation.

1. Introduction

In recent years, metal vanadates have attracted significant interest, due to their extensive technological importance in a wide range of applications, including catalysis [1], cathode materials in batteries [2], implantable cardiac defibrillators (ICDs) [3] and low-temperature magnetic devices [4]. Lots of research has been focused on the synthesis of metal vanadates of silver, copper, manganese, iron, bismuth and indium from different approaches. In this paper, Cadmium vanadate was selected as an interesting material to its excellent optical and chemical properties. Di li et al synthesized CdV_2O_6 and $Cd_2V_2O_7$ via hydrothermal method and investigated photocatalytic activity of CdV_2O_6 and $Cd_2V_2O_7$ samples for the degradation of methylene blue under visible-light irradiation [5]. Herein, we develop the precipitation method to synthesize of cadmium vanadate nanocrystals. The precipitation method is a suitable synthesis process for prepare of many nano products [6–8]. This method is simple, potential for large scale Production, convenient and cost effective synthetic procedure and provides an effective way to the synthesis of uniform nanocrystals. In this method, crystallization way is done at low temperature and design of reaction condition is very flexible. In this paper, $Cd_2V_2O_7$ nanoparticles were synthesized by a precipitation method using novel basic agents to adjust the pH value to 8–9. The purpose of this study is investigating the role of different amines on the size, morphology and uniformity of the pure $Cd_2V_2O_7$ nanocrystals. The selected amines are chosen in a way that we investigate the effect of different amines with different nitrogen active sites. The long carbon chain of amines can provide great steric hindrance to control the size of nanoparticles. Recently our team has focused on the effect of different amines as a basic and capping agent [9–11]. It has been demonstrated that these kinds of amines have an effective role on controlling size, shape, and optical properties of final products. The effects of different parameters such as Effects of various amines, temperature, reaction time, solvent and pH on the product size, morphology and uniformity were also investigated. Moreover, the photocatalytic degradation activity of anionic dye of eosin Y as water pollutant is performed to study the catalytic properties of *as*-produced $Cd_2V_2O_7$ nanostructures.

2. Experimental

2.1. Materials and physical measurements

$Cd(NO_3)_2 \cdot 4H_2O$, NH_4VO_3, NH_3, ethylenediamine (en), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) were purchased from Merck Company. All of the chemicals were used as received without further purifications. For characterization of the products, X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM. Transmission electron microscopy (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. GC-2550TG (Teif

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Gostar Faraz Company, Iran) were used for all chemical analyses. Optical analyses were performed using a V-670 UV–Vis–NIR Spectrophotometer (Jasco). Room temperature photoluminescence (PL) was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer.

2.2. Synthesis of cadmium vanadate nanoparticles

$Cd(NO_3)_2 \cdot 4H_2O$ was dissolved into deionized water to form a transparent solution. Then NH_4VO_3 with a molar ratio of Cd:V = 3:2 was dissolved into another deionized water at 80 °C. After that, the NH_4VO_3 solution was added slowly to the Cd solution under stirring. In this process, a yellow suspension appeared gradually. Finally, basic agent was added to adjust the pH value of the solution, after the mixture had been stirred for about 2 h. The final products were collected by centrifugation, washed with deionized water and ethanol. The as-obtained products were dried at 70 °C under vacuum for 2 h, then calcined at 600 °C for another 2 h. The effects of different basic agent, temperature, reaction time, solvent and pH on the morphology, particle sizes and the phase of cadmium vanadate samples were investigated and the results listed in Table 1.

2.3. Photocatalytic measurements

The photocatalytic activity of cadmium vanadate nanoparticles was tested by using eosin Y solution. The degradation reaction was carried out in a quartz photocatalytic reactor. The photocatalytic degradation was carried out with 2×10^{-5} M of eosin Y solution containing 0.05 g of nanostructures. This mixture was aerated for 30 min to reach adsorption equilibrium. The experiments were performed at room temperature and pH of the eosin Y solution was adjusted 3. Aliquots of the mixture were taken at periodic intervals during the irradiation, and after centrifugation they were analyzed with the UV–Vis spectrometer. The dyes degradation percentage was calculated as follows:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance value of solution at 0 and t min, respectively.

3. Results and discussion

3.1. X-ray diffraction patterns

XRD analysis, which is the most useful technique for characterization of crystalline structure, was employed to investigate the purity of the prepared products. The X-ray diffraction patterns of as-prepared products obtained from the precipitation reaction are shown in Fig. 1.

Table 1
Reaction conditions for cadmium vanadate nanostructures.

Sample no	Basic factor	Reaction time (h)	Reaction temperature (°C)	pH	Solvent
1	–	2	R.T	6	H_2O
2	NH_3	2	R.T	8	H_2O
3	en	2	R.T	8	H_2O
4	TETA	2	R.T	8	H_2O
5	TEPA	2	R.T	8	H_2O
6	en	20 min	R.T	8	H_2O
7	en	24	R.T	8	H_2O
8	en	2	3	8	H_2O
9	en	2	80	8	H_2O
10	en	2	R.T	10	H_2O
11	en	2	R.T	8	Methanol
12	en	2	R.T	8	PG
13	en	2	R.T	8	Butanol
14	en	2	R.T	8	Isobutanol

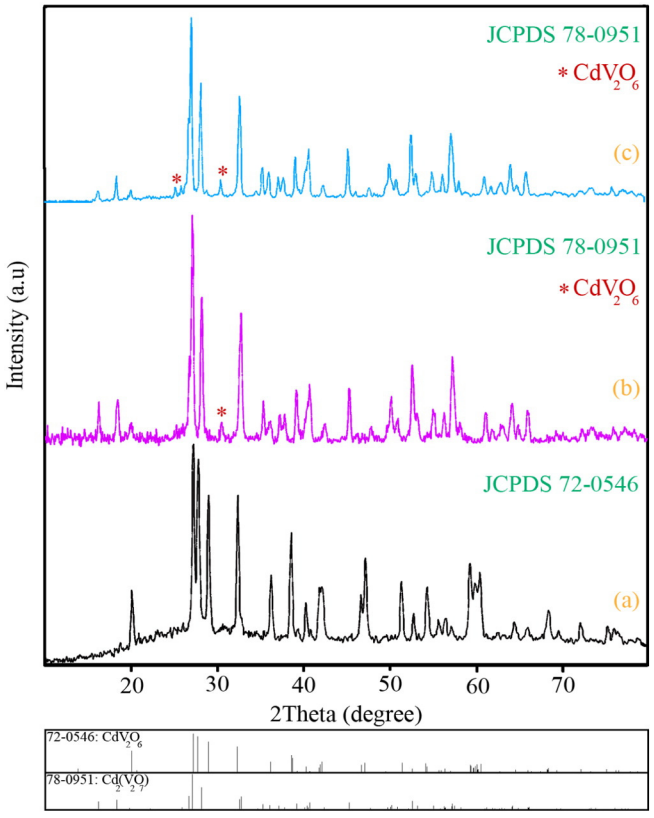

Fig. 1. XRD patterns of synthesized samples at different pH (a) 6, (b) 8 and (c) 10.

Fig. 1a–c show the XRD patterns of samples prepared at different pH (sample Nos. 1, 3 and 10), respectively. Fig. 1a shows the XRD patterns of samples prepared without adding of basic agent (pH = 6). All the diffraction peaks are assigned to monoclinic–CdV_2O_6 structure with space group of C2/m and cell constants a = 9.3590 Å, b = 3.5680 Å, and c = 6.9800 Å (JCPDS Card No. 72-0546). With an increase of the pH ranges to 8–10 (Fig. 1b, c), most of the reflection peaks can be attributed to the monoclinic phase $Cd_2V_2O_7$ (JCPDS card No. 78-0951) and some weak diffraction evidence of residual CdV_2O_6 phase (JCPDS card No. 72-0546). It was found that the CdV_2O_6 and $Cd_2V_2O_7$ phases are stable in acidic and basic environment, respectively. The crystallite diameter (D_c) of cadmium vanadate nanostructures obtained using the Scherrer equation [12,13]: $D = K\lambda/\beta\cos\theta$; where β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. Calculated crystalline domain sizes have been found to be 33, 27 and 29 nm for sample Nos. 1, 3 and 10, respectively.

3.2. SEM and TEM images

To examine the role of the different basic agents on the morphology and size of the products, cadmium vanadate nanostructures were synthesized by NH_3, en, TETA and TEPA. SEM images of synthesized product using different basic agents are illustrated in Fig. 2a–d, respectively. As shown in Fig. 2a–d, the morphology of the samples cadmium vanadate synthesized by NH_3, en, TETA and TEPA is spherical and ellipsoids nanoparticles. Although morphologies of the products are the same, the size and uniformity of nanoparticles are different. The cadmium vanadate product synthesized by en amine is optimum product because nanoparticles have smaller size and more uniformity. Schematic diagram of formation of cadmium vanadate products by different basic agent is depicted in Scheme. 1. The size and morphology of the products were analyzed by the TEM image (Fig. 2e). Fig. 2e reveals that the cadmium