Controllable synthesis, characterization and photocatalytic studies on cadmium vanadate nanostructures

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Abstract

Cadmium vanadate ($\text{Cd}_2\text{V}_2\text{O}_7$) nanocrystals have been successfully synthesized via simple coprecipitation method by using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 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.

Keywords: $\text{Cd}_2\text{V}_2\text{O}_7$; Nanostructures; Optical properties; Photocatalytic activity; Electron microscopy.

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 $\text{Cd}_2\text{V}_2\text{O}_7$ via hydrothermal method and investigated photocatalytic activity of CdV_2O_6 and $\text{Cd}_2\text{V}_2\text{O}_7$ 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, $\text{Cd}_2\text{V}_2\text{O}_7$ 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 $\text{Cd}_2\text{V}_2\text{O}_7$ 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 kind 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 $\text{Cd}_2\text{V}_2\text{O}_7$ nanostructures.

2. Experimental

2.1. Materials and Physical Measurements

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 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 K α 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 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

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 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 hours. 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 2h. 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. Fig. 1a–c show the XRD patterns of samples prepared at different pH (sample No. 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 $a = 9.3590 \text{ \AA}$, $b = 3.5680 \text{ \AA}$, and $c = 6.9800 \text{ \AA}$ (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 $\text{Cd}_2\text{V}_2\text{O}_7$ (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 $\text{Cd}_2\text{V}_2\text{O}_7$ 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 vanadate nanoparticles (sample No. 3) prepared with en basic and capping agent via precipitation method consisting sphere-like nanoparticles with average particle size of 20 to 130 nm. In order to investigate the effect of reaction time in synthesis of cadmium vanadate products, the reaction is done at 20 min and 24 h. Fig. 3a, b show the effect of time on the morphology and size of products. Optimum time for synthesis of fine and uniform cadmium vanadate nanoparticles is 2 h (sample No. 3). Size of the microstructures produced after 20 min are not very homogeneous. By increasing the reaction time to 24 h, nanoparticles with larger size are achieved. Fig. 3c, d show cadmium vanadate samples synthesized at different reaction temperatures of 3 and 80 °C, respectively. Room temperature is optimum temperature for synthesis of uniform nanostructures (Fig. 1b). Fig. 3e, f show the SEM images of samples prepared at pH of 6 and 10, respectively. Cadmium vanadate microstructures synthesized at acidic and basic environments (pH=6 and 10) are agglomerated. Therefore, concentration of

OH⁻ has an important role on size and morphology of prepared products. The effect of different solvents in synthesis of cadmium vanadate structures were investigated. Fig. 4a-d show SEM images of cadmium vanadate products prepared in presence of methanol, propyleneglycol, butanol and isobutanol, respectively. As-prepared products in presence of all of them were agglomerated. Water solvent is suitable solvent for synthesis of cadmium vanadate nanostructures (Fig. 2b).

3.3. FT-IR and EDS spectra

The surface conditioning of as-prepared cadmium vanadate nanoparticles was recorded using FT-IR spectrum in order to detect the residual organic compounds. Fig. 5a shows FT-IR spectrum of sample No. 3. The absorption bond centered at 3431 and 3252 cm⁻¹ can be assigned to the stretching vibrations of the hydrogen-bonded OH and NH groups, respectively. The vibration bonds at 876 and 668 cm⁻¹ are attributed to tetrahedral VO₄ vibration modes in the network. The absorption around 408 cm⁻¹ correspond to the stretching vibration Cd-O band, which is consistent with octahedral CdO₆ [14, 15]. The absorption peaks at 1334 and 1577 cm⁻¹ can ascribe to the overtone of VO₄. Very weak peaks around 2937 cm⁻¹ can be attributed to the asymmetric and symmetric stretching vibrations of aliphatic groups (-CH₂-)_n, respectively [16]. From the FT-IR result, it can be concluded that probably a small amount of ethylenediamine is attached to the surface of cadmium vanadate nanoparticles which may have a well role in preventing nanoparticles agglomeration. EDX further confirmed that the nanoparticles are composed of cadmium vanadate. The EDX of the sample No. 3 is shown in Fig. 5b. Peaks associated with Cd, V and O are clearly observed and provide strong evidence that the nanocrystals are composed of only Cd₂V₂O₇.

3.4. Optical and photocatalytic properties

The UV-Vis Diffuse Reflectance spectroscopy of sample No. 1 and 3 are shown in Fig 6a, b. As shown in this figure the position of absorption edges are various. In comparison to the blank product without basic agent in acidic environment (sample No.1), the absorption edge of sample prepared with ethylenediamine

shift to blue region. The fundamental absorption edge in most semiconductors follows the exponential law.

Using the absorption data, the band gap was estimated by Tauc's relationship:

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \quad (2)$$

where α is absorption coefficient, $h\nu$ is the photon energy, α_0 and h are the constants, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can be any value between $\frac{1}{2}$ and 3 [17]. The energy gaps of the samples have been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis (Fig. 6 c and d). The E_g values are calculated 3.2 and 3.3 eV for the samples No. 1 and 3, respectively. The difference of band gap values have been attributed to variations in the impurities content, the crystalline size and the type of electronic transition [18, 19]. Optical properties of cadmium vanadate nanocrystals are of great importance as they provide information for the uses of these materials in photocatalytic applications. The photocatalytic activity of cadmium vanadate nanoparticles (sample No. 1, 3) was investigated by monitoring the degradation of eosin Y as water pollutant in an aqueous solution under visible light irradiation. The obtained results are shown in Fig. 7. According to photocatalytic calculations by Eq. (1), the eosin Y degradation was about 57 (sample No. 1) and 47% (sample No. 3) after 200 min irradiation of visible light. By decreasing of particles size, energy gap and UV irradiation absorption increased and as a result visible light absorption decreased. These results indicated that cadmium vanadate nanocrystals are suitable photocatalyst under visible light in the short time.

4. Conclusions

We employed a facile precipitation method to synthesize cadmium vanadate nanostructures with aid of different amines as a novel basic agent and size controller. The effect of different parameters such as reaction time, temperature, pH and solvent on the size, morphology and uniformity of products were investigated. Cadmium vanadate nanocrystals were characterized by XRD, SEM, TEM, EDS, FT-IR and DRS. Different

157 morphology and size of products were prepared. The photocatalytic behavior of nanoparticles was evaluated
158 using the degradation of eosin Y aqueous solution under visible light irradiation.

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References

- [1] M. Masato, M. Yui, M. Yuichi, I. Keita, Chem. Commun. 47 (2011) 9591-9593.
- [2] L. Q. Mai, L. Xu, C. H. Han, X. Xu, Y. Z. Luo, S. Y. Zhao, Y. L. Zhao, Nano. Lett. 10 (2010) 4750–4755.
- [3] A. M. Crespi, S. K. Somdahl, C. L. Schmidt, P. M. Skarstad, J. Power Sources. 96 (2001) 33-38.
- [4] G. Liu, J. E. Greedan, J. Solid. State. Chem. 114 (1995) 499–505.
- [5] D. Li, X. Bai, C. Pan and Y. Zhu, Eur. J. Inorg. Chem. 2013 (2013) 3070–3075.
- [6] Z. Shahri, A. Sobhani, M. Salavati-Niasari, Mater. Res. Bull. 48 (2013) 3901–3909.
- [7] F. Beshkar, S. Zinatloo-Ajabshir, M Salavati-Niasari, Chem. Eng. J. 279 (2015) 605–614.
- [8] G. Kianpour, M. Salavati-Niasari, Emadi H, Superlattice. Microst. 58 (2013) 120-129.
- [9] F. Mazloom, M. Masjedi-Arani, M. Salavati-Niasari, J. Mater. Sci. 10.1007/s10854-015-3980-5 (2015) 1-9.
- [10] F. Mazloom, M. Masjedi-Arani, M. Ghiyasiyan-Arani, M. Salavati-Niasari, J. Mol. Liq. 214 (2016) 46–53.
- [11] N. Mir, M. Salavati-Niasari, Electrochim. Acta. 102 (2013) 274–281.
- [12] M. Masjedi-Arani, M. Salavati-Niasari, Ultrason. Sonochem. 29 (2016) 226–235.
- [13] M. Masjedi-Arani, M. Salavati-Niasari, J. Mater. Sci. 26 (2015) 2316-2322.
- [14] P. Huang, X. Zhang, J. Wei, J. Pan, Y. Sheng, B. Feng, Mater. Chem. Phys. 147 (2014) 996-1002.

- 181 [15] R. Lozada-Morales, A. Cid-Garcia, G. López-Calzada, M. E. Zayas, O. Zelaya-Angel, J. Carmona-
182 Rodriguez, E. Rubio-Rosas, R. Palomino-Merino, O. Portillo-Moreno and S. Jiménez-Sandoval, Phys.
183 Status. Solidi. A. 209 (2012) 2281–2285.
- 184 [16] M. Masjedi-Arani, N. Mir, E. Noori, T. Gholami, M. Salavati-Niasari, Superlattice. Microst. 62 (2013)
185 30–38.
- 186 [17] J. Tauc, R. Grigorovici, A. Vancu, J. Phys. Status. Solidi B. 15 (1966) 627–637.
- 187 [18] M. Hidalgo, M. Aguilar, M. Maicu, J. Navio, G. Colon, J. Catal. Today. 129 (2007) 50-58.
- 188 [19] F. Hossain, L. Sheppard, J. Nowotny, G. Murch, J. Phys. Chem. Solids. 69 (2008) 1820-1828.
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190 **Figure Captions:**

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

192 **Fig. 2.** SEM images of $\text{Cd}_2\text{V}_2\text{O}_7$ nanostructures prepared by different amines (a) NH_3 , (b) en, (c) TETA, (d)
193 TEPA and (e) TEM image of optimum sample (sample No.3).

194 **Fig. 3.** SEM images of cadmium vanadate nanostructures prepared in different conditions (a-d) sample No.
195 6-9, (e) sample No. 1 and (f) sample No. 10.

196 **Fig. 4.** SEM images of cadmium vanadate nanostructures prepared by different solvents (a) Methanol, (b)
197 PG, (c) Butanol and (d) Isobutanol.

198 **Fig. 5.** (a) FT-IR spectrum and (b) EDS spectrum of sample No. 3.

199 **Fig. 6.** (a, b) UV–Vis diffuse absorption spectra and (c, d) plot of $(\alpha h\nu)^2$ versus $(h\nu)$ of sample No.3 and 1,
200 respectively.

201 **Fig. 7.** Photocatalytic eosin Y degradation of cadmium vanadate nanoparticles under visible light (a) sample
202 No. 1 and (b) sample No. 3.

203 **Scheme. 1.** Schematic diagram of formation of cadmium vanadate nanostructures by different basic and
204 capping agent.

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Sample no	Basic factor	Reaction time (h)	Reaction temperature (°C)	pH	Solvent
1	-	2	R.T	6	H ₂ O
2	NH ₃	2	R.T	8	H ₂ O
3	en	2	R.T	8	H ₂ O
4	TETA	2	R.T	8	H ₂ O
5	TEPA	2	R.T	8	H ₂ O
6	en	20 min	R.T	8	H ₂ O
7	en	24	R.T	8	H ₂ O
8	en	2	3	8	H ₂ O
9	en	2	80	8	H ₂ O
10	en	2	R.T	10	H ₂ O
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

Table 1. Reaction conditions for cadmium vanadate nanostructures.

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211 Scheme. 1.

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214 Fig. 1.

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Fig. 4.

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232 Fig. 7.
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