Novel Schiff base ligand-assisted in-situ synthesis of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles via a simple precipitation approach

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Abstract

The effect of different Schiff-base ligands on size, morphology and uniformity of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles prepared via a simple in-situ precipitation route was investigated. Different calcination temperatures were applied and the as-prepared products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectrum, Electron Dispersive X-ray spectroscopy (EDX) and ultraviolet–visible (UV–Vis) spectroscopy. Vibrating sample magnetometer (VSM) was used to study the magnetism properties of $\text{Cu}_3\text{V}_2\text{O}_8$ sample. According to the obtained results, using the appropriate amount of Schiff-base ligand is a crucial parameter for control in particle size. The photocatalytic activity of $\text{Cu}_3\text{V}_2\text{O}_8$ nanostructures were evaluated by degradation of methylene blue in aqueous solution under UV and visible light irradiation.

Keywords: Nanostructure; Chemical synthesis; Photocatalytic activity; Magnetic property; Optical property; Electron microscopy.

1. Introduction

The nanoparticles have received considerable attention due to their wide range of applications in various fields like catalysis, solar cells, batteries, photocatalysis and sensors. Transition metal vanadates, as a considerable class of materials, have been intensively pursued in recent years because of their applications in optical devices [1], catalysis [2], paramagnetic materials [3, 4], lithium batteries [5, 6], etc. Among transition metal vanadates, $\text{Cu}_3\text{V}_2\text{O}_8$ with crystal structure of porous consisting Cu-O octahedra and V-O tetrahedra has been studied as a material with good photocatalytic performances and electrochemical properties [7]. It is good to know that particle size and morphology of nanostructures depend on their synthesis method. A variation of possible routes including hydrothermal method [8, 9], simple template-free solution method [10] and co-precipitation method [11] have been applied to obtain different types of copper vanadates. Herein, we develop the precipitation method to provide $\text{Cu}_3\text{V}_2\text{O}_8$ nanocrystals. The precipitation method is a suitable synthesis process for preparation of many inorganic powders. This method is simple, convenient and cost effective synthetic procedure and provides an effective way to the synthesis of uniform nanocrystals. In this method, crystallization is performed at low temperature and design of reaction condition is very flexible. To optimize the $\text{Cu}_3\text{V}_2\text{O}_8$ size, morphology and ultimate properties, ligand shell was chosen. The ligand shell is a molecular monolayer encapsulating the core. In the case of organic species, ligands have a functional head group and one or more hydrocarbon tails that both elements play a role in the control of nucleation and growth [12]. Beside the well-known surfactants, recently our team have focused on the effect of ligands containing hard atoms (N, O) as well as bulky aromatic groups on the properties of obtained products [13–17]. In this work, the effect of different Schiff base ligands as capping agents on morphology, size and uniformity of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles were studied. Schiff base ligands containing four hard binding sites (N and O), are capable of stabilizing transition metal centers very well. These kinds of molecules are of concern in preventing crystal growth of

particular surface planes, or limiting the size of crystals in the synthesis of nanoparticles [18]. Herein, the $\text{Cu}_3\text{V}_2\text{O}_8$ nanostructures were synthesized with different Schiff base ligands via in-situ precipitation method using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 as copper and vanadium source, respectively. The effects of various parameters such as different Schiff base ligands and calcination temperatures on the size, morphology and uniformity of products were also investigated. Moreover, degradation of Methylene Blue (MB) was carried out to study the photocatalytic activity of $\text{Cu}_3\text{V}_2\text{O}_8$ nanostructures under UV and visible light irradiation.

2. Experimental

2.1. Materials and Physical Measurements

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, NH_4VO_3 , acetyl acetone (acac), ammonia, ethylenediamine (en), propylenediamine (pn), butylenediamine (bn), 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 $\text{K}\alpha$ 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. Optical analyses were performed using a V-670 UV–Vis–NIR Spectrophotometer (Jasco). The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.2. In-situ synthesis of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles

Synthesis of N,N'-ethylenebis(acetylacetone iminato)dianion (acacen) Schiff base was based on acetyl acetone (acac) and ethylenediamine at a molar ratio of 2:1. Acac and en was diluted in methanol and ethylenediamine was added to an acac solution under stirring at room temperature. Other amines were used for

preparing Schiff base ligands according this instruction. The used different amines for synthesizing of Schiff base were shown in Scheme.1. 0.5 g of CuSO₄·5H₂O was dissolved into deionized water and was added to Schiff base solution. 0.156 g of NH₄VO₃ with a molar ratio of Cu:V = 3:2 was dissolved into another deionized water at 80 °C. After that, the NH₄VO₃ solution was added slowly to the complex solution of Cu-Schiff base under stirring and the mixture were stirred for about 2 hours. The molar ratios of starting materials are listed in Table 1. The final products were collected by centrifugation, washed with deionized water and ethanol several times. The as-obtained products were dried at 80 under vacuum for 2 h, then calcined at different temperatures for 2 hours. Schematic of formation of Cu₃V₂O₈ nanoparticles is depicted in Scheme. 2. The different reaction conditions are listed in Table 2.

2.4. Photocatalytic measurements

The photocatalytic activity of Cu₃V₂O₈ nanoparticles was tested by using MB solution. The degradation reaction was carried out in a quartz photocatalytic reactor. The photocatalytic degradation was carried out with 5×10^{-5} M of MB solution containing 0.05 g of nanostructures. This mixture was aerated for 30 min to reach adsorption equilibrium. Then, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV and visible sources of 400 W Osram lamps. The quartz vessel and light sources were placed inside a black box equipped with a fan to prevent UV leakage. The experiments were performed at room temperature. 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:

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

Where A₀ and A_t are the absorbance value of solution at 0 and t min, respectively.

3. Results and discussion

Fig. 1 show the XRD patterns of the precursor before and after calcination at different temperatures. The XRD pattern of the precursor before calcination in Fig. 1(a) confirmed the formation of $\text{Cu}_3\text{V}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$ with the monoclinic structure [JCPDS Card No. 26-1119] and Copper acetyl acetate by-product [JCPDS Card No. 11-0800]. Fig. 1(b-e) show the XRD patterns of samples calcined at 450, 550, 650 and 750°C, respectively. Fig. 1(b) shows the XRD pattern of $\text{Cu}_3\text{V}_2\text{O}_8$ sample calcined at 450°C with two different phases including monoclinic [JCPDS Card No. 74-1503] and triclinic [JCPDS Card No. 49-0689]. Fig 1(c-e) show the XRD patterns of samples calcined at 550, 650 and 750°C, respectively. All diffraction peaks can be well indexed to $\text{Cu}_3\text{V}_2\text{O}_8$ triclinic [JCPDS Card No. 49-0689] and fingerite structural Copper Vanadium Oxide ($\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$) [JCPDS Card No.38-0378]. It was revealed that the same products were obtained while their crystallinity and average crystallite diameter were different. According to XRD patterns, the crystallite diameter (D_c) of Copper Vanadium Oxide nanostructures was obtained using the Scherrer equation [20]: $D = K\lambda/\beta\cos\theta$; 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. Results of crystalline diameter of products are shown at Table 2. To understand the influence of different amines and calcination temperatures on the morphology and particle size of Copper Vanadium Oxide nanostructures, several experiments were carried out, and the products obtained at different stages were investigated using the SEM techniques. Fig. 2(a-l) show SEM images of Copper Vanadium Oxide nanostructures prepared using different types of amines (sample Nos. 1-6), respectively. In Fig. 2(a,b) are shown that nanostructures prepared with NH_3 as a monodentate amine are consisting of agglomerated nanoparticles. The average particle size of this sample is estimated to be from 46 to 320 nm. Fig. 2(c-h) show copper vanadium oxide nanostructures prepared using en, pn and bn as bidentate amines, respectively. As shown in Fig. 2(c-h), by increasing the carbon chain length of amines, particles size are decreased. Bn is an optimum amine for this experiment because nanoparticles have appropriate size and uniformity. By changing amine from bidentate to tridentate (TETA)

and four-dentate (TEPA), agglomeration were observed. Particles size of samples obtained from SEM images are shown at Table 1. The effect of calcination temperatures on surface morphology and size of the obtained products is shown in Fig. 3. In Fig. 3(a-f) are shown the SEM images of obtained samples at calcination temperatures of 550, 650 and 750 °C, respectively. The copper vanadium oxide calcined at 450 °C is shown in Fig. 2(g, h). By increasing the calcination temperature from 450 to 750°C, the agglomeration are observed, although all of the samples have very small nanoparticles around 5 nm. However optimum calcination temperature for these experiments is 450°C because in this temperature nanoparticles have suitable size and uniformity, also this temperature is cheap economically. The shape and size of Copper Vanadium Oxide nanoparticles prepared in presence of the acacbn Schiff base ligand as capping agent were elucidated by TEM images. Fig. 4 shows the TEM image of sample No. 4 which contains nanoparticles with the average size from 7 to 32 nm. EDS analysis measurement was employed to investigate the chemical composition and purity of as-synthesized Copper Vanadium Oxide nanoparticles. EDS spectrum (Fig. 5) revealed the presence of Cu, V and O in this sample. Fig. 6 shows FT-IR spectra of the as-synthesized samples in the range of 400–4000 cm⁻¹. FT-IR spectra of the nanoparticles prepared before (sample No.10) and after (sample No. 4) calcination are shown in Fig. 6(a, b), respectively. The absorption from 3000 to 3600 cm⁻¹ can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1628 cm⁻¹ is due to the bending vibration of water molecules. The bands at around 2920 cm⁻¹ are assigned to the antisymmetric and symmetric C-H stretching vibrations of hydrocarbon moiety [21] that after calcination, intensity of peaks are decreased. From the FT-IR results, it can be concluded that probably a small amount of ligand is attached to the surface of nanoparticles which may have an effective role in preventing nanoparticles agglomeration. In addition, the adsorption peaks centered around 1116 cm⁻¹ could be related to the absorptions of CO₂ molecules from the atmosphere in Fig. 6 (a, b). According to the previous reports, the IR bands at 963, 760 and 528 cm⁻¹ in Fig. 6(a) are assigned to the vibrations of VO₄³⁻ [22, 23]. In Fig. 6(b), the band around 454 cm⁻¹ in the FT-IR

spectrum belongs to the **stretching** mode of the inorganic Cu-O. The vibration bands in the range of 936-454 cm^{-1} are attributed to tetrahedral VO_4 and octahedral CuO_6 vibration modes in the network. The remaining peaks in the range of 910-1600 cm^{-1} can be attributed to $\text{Cu}(\text{acac})_2$ complex that has remained in the product [24]. The absorption **spectrum** of $\text{Cu}_3\text{V}_2\text{O}_8$ **nanoparticle is** shown in Fig. 7. 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 [25]. The energy gaps of the samples have been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ to the energy axis (Fig. 7b) [26-28]. The E_g value is calculated 2.1 eV for the $\text{Cu}_3\text{V}_2\text{O}_8$ sample (sample No. 4). Hysteresis loop and magnetic property of $\text{Cu}_3\text{V}_2\text{O}_8$ nanostructure (sample No. 4) **has** been shown in Fig. 8. It can be found that no saturation of the magnetization as a function of the field is observed up to the maximum applied magnetic field. The hysteresis loop of the $\text{Cu}_3\text{V}_2\text{O}_8$ as-synthesized displays a weak ferromagnetic property at room temperature. Behavior of $\text{Cu}_3\text{V}_2\text{O}_8$ **nanoparticles were** changed from paramagnetic to ferromagnetic at field of 1800 Oe. The as-prepared sample shows a twofold behavior, ferromagnetic behavior in low fields and paramagnetic behavior in up fields. The coercivity (H_c) of as-synthesized $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles is about 32.37 emu/g. In this work, the photocatalytic activity of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticle (sample No. 4) **was** studied by photooxidation of **MB** under UV and visible light irradiations. The obtained results are shown in Fig. 9. As shown in Fig. 9, the **MB** degradation percentage of nanostructures increased rapidly after the Osram lamp turned on. According to photocatalytic calculations, the **MB** degradation was about 79 and 36 % after 135 and 180 min under UV and visible light irradiation by $\text{Cu}_3\text{V}_2\text{O}_8$

nanoparticles, respectively. These results indicated that Cu₃V₂O₈ nanoparticles are **desirable** for photocatalytic applications and UV light showed better photocatalyst activity at shorter time. The possible mechanism of the photocatalytic degradation of cationic dye can be summarized as follows:

The heterogeneous photocatalytic processes involve many stages, such as diffusion, adsorption and reaction. Appropriate distribution of the **pores** is **useful for** diffusion of reactants and products, which favors the photocatalytic reaction. In this work, the modified photocatalytic activity may be attributed to convenient distribution of the **pores**, numerous hydroxyl **contents** and high separation rate of photoinduced charge carriers [29].

4. Conclusions

In summary, Cu₃V₂O₈ nanostructures have been successfully synthesized using a new facile **in-situ** precipitation route. To the best of our knowledge, it is the first time that Cu₃V₂O₈ nanostructures are prepared by different Schiff base **ligands** with **in-situ** method. The effects of preparation parameters such as **different calcination temperatures** and amines **type** on the morphology and particle size of products were studied. Nanostructures were characterized using SEM, TEM, XRD, UV-vis and FT-IR techniques. The photocatalytic behavior of nanoparticles was evaluated using the degradation of a **MB** aqueous solution under UV and visible light irradiation. The results show that Cu₃V₂O₈ nanostructures are promising materials with excellent performance in photocatalytic applications for degradation of organic pollution under UV irradiation. The magnetic properties of the as-synthesized products were also studied.

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Table 1. Molar **ratios** of starting materials.

Cu:V:acac:Amine	Amine
3:2:6:6	NH ₃
3:2:6:3	en
3:2:6:3	pn
3:2:6:3	bn
3:2:6:3	TETA
3:2:6:3	TEPA

Table 2. Reaction conditions for Copper Vanadium Oxide nanostructures.

Sample No	Type of amine	Calcination temperature	Crystalline size (XRD)/nm	Particle size (SEM)/nm
1	ammonia	450 °C	-	40-340
2	Ethylenediamine	450 °C	-	40-520
3	propylenediamine	450 °C	-	35-210
4	butylenediamine	450 °C	27	20-200
5	triethylenetetramine	450 °C	-	50-750
6	tetraethylenepentamine	450 °C	-	50-650
7	butylenediamine	550 °C	26	60-350
8	butylenediamine	650 °C	45	100-250
9	butylenediamine	750 °C	78	20-150
10	butylenediamine	-	49	-

Figure Captions:

Fig. 1. XRD patterns of the $\text{Cu}_3\text{V}_2\text{O}_8$ samples: (a) before calcination and calcined at b) 450, c) 550, d) 650 and e) 750 °C.

Fig. 2. SEM images of the Copper Vanadium Oxide samples with different amines: (a,b) NH_3 , (c,d) en, (e,f) pn, (g,h) bn, (i,j) TETA and (k,l) TEPA.

Fig. 3. SEM images of the Copper Vanadium Oxide samples with different calcination temperatures: a) 550 °C, c) 650 °C and e) 750 °C.

Fig. 4. TEM image of the Copper Vanadium Oxide sample (sample No. 4).

Fig. 5. EDS pattern of the Copper Vanadium Oxide sample (sample No. 4).

Fig. 6. FT-IR spectra of the as synthesized the Copper Vanadium Oxide a) sample No. 4, b) sample No. 10.

Fig. 7. (a) UV–vis spectrum and (b) plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ of sample No.4.

Fig. 8. Magnetization versus applied magnetic field at room temperature for the $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles (sample No. 4).

Fig. 9. Photocatalytic MO degradation of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles under UV and visible irradiations.

Scheme 1. Different amines used for synthesizing of Schiff base ligand.

Scheme 2. Schematic depiction for the preparation of $\text{Cu}_3\text{V}_2\text{O}_8$ nanoparticles.

Scheme 1.

Scheme 2.

Fig 1.

Fig 2.

Fig 3.

Fig 4.

Fig 5.

Fig 6.

Fig. 7.

Fig 8.

Fig 9.

Graphical Abstract