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Simple Precipitation Synthesis of Pure $Cu_3V_2O_8$ Nanoparticles and Investigation of their Optical Properties

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Abstract

Copper vanadate nanostructures were prepared via ex-situ precipitation approach in presence of Schiff-base ligand (N,N′-buthylenebis(acetylacetone iminato)dianion = acacbn) as a new capping agent. The effect of different Cu sources and pH on the size, morphology and size distribution of copper vanadate nanostructures was investigated. The as-prepared products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectrum, Electron Dispersive X-ray spectroscopy (EDX) and ultraviolet– visible (UV–Vis) spectroscopy. The optical properties of different samples were compared.

1. Introduction

The nanomaterials have received significant 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, $Cu_3V_2O_8$ with crystal structure of porous that consisted of Cu-O octahedra and V-O tetrahedra has been studied as a material with good optical properties. 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, pure $Cu_3V_2O_8$ nanoparticles were synthesized by ex-situ precipitation method in presence of Schiff base ligand as a new capping agent.

2. Experimental procedure

$CuSO_4.5H_2O$, NH_4VO_3, acacbn 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. 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).

In the in-situ precipitation method, 0.5 g of $CuSO_4.5H_2O$ was dissolved into deionized water. 0.156 g of NH_4VO_3 with a molar ratio of Cu:V = 3:2 was dissolved into another deionized water at 80 ˚C. After that, the NH_4VO_3 solution was added slowly to the complex solution of Cu under stirring and the mixture was stirred. In the ex-situ precipitation method, acacbn Schiff base ligand with Cu:acacbn=1:1 molar ratio was added to Cu-V solution. The as-obtained products were dried at 100 ˚C under vacuum for 2 h, then calcined at 450 ˚C for 5 hours. The different reaction conditions are listed in Table 1.

3. Results and discussion

In order to confirm the crystal phase and purity of the products, XRD analyse was carried out. XRD pattern of the product prepared using ex-situ precipitation approach is shown in Fig. 1. In Fig. 1, all of the reflection peaks can be attributed to the monoclinic phase $Cu_3V_2O_8$ (JCPDS card No. 74-1503).

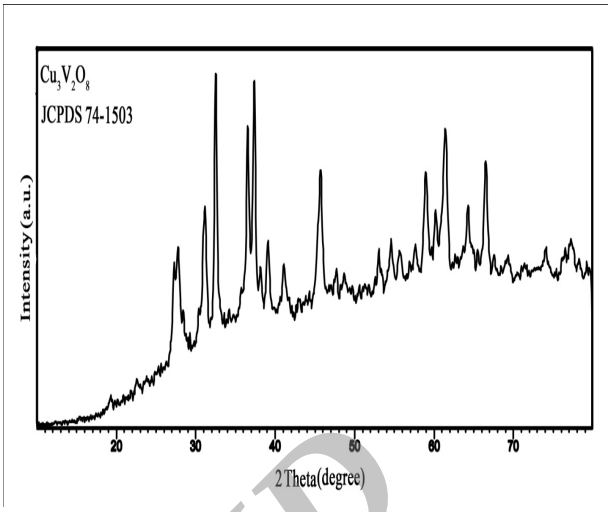

Fig. 1. XRD pattern of as- synthesized sample (sample No. 4).

Table 1. Preparation conditions for the synthesis of nanostructures with ex-situ precipitation method.

Sample No.	Copper source	pH	Size(SEM)
1	$Cu(NO_3)_2.3H_2O$	8	105.3
2	$Cu(CH_3COO)_2.H_2O$	8	71.79
3	$CuSO_4.5H_2O$	4	122.5
4	$CuSO_4.5H_2O$	8	55
5	$CuSO_4.5H_2O$	10	107.3

Fig.2 (a) and (b) are the typical SEM micrograph of the amorphous $Cu_3V_2O_8$ powder prepared using $Cu(NO_3)_2.3H_2O$ and $Cu(CH_3COO)_2.H_2O$, respectively. It can be found that the samples contains agglomerated nano-particles.

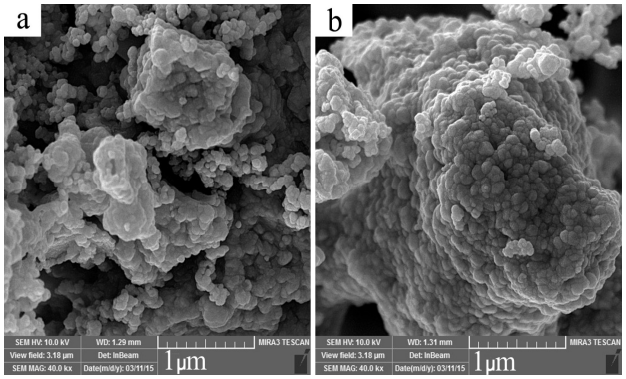

Fig. 2. SEM images of $Cu_3V_2O_8$ prepared using (a) $Cu(NO_3)_2.3H_2O$ and (b) TEM micrograph and (b) $Cu(CH_3COO)_2.H_2O$.

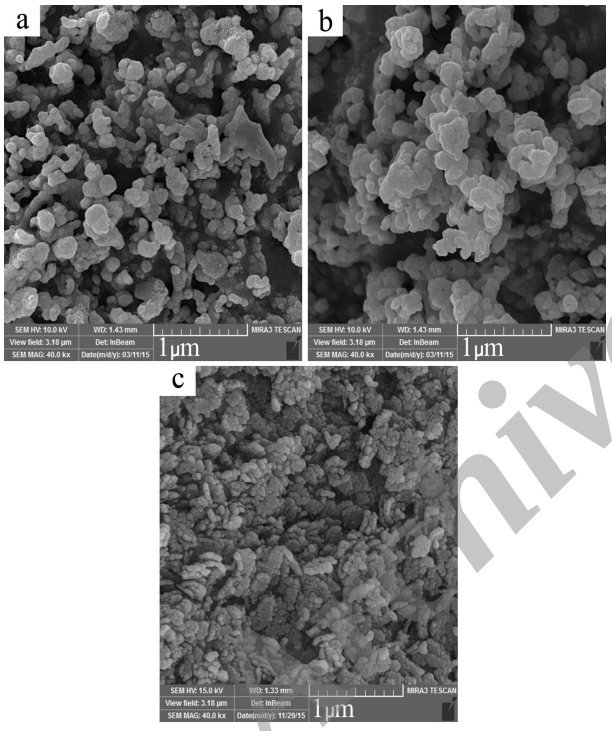

Fig. 3. SEM images of of $Cu_3V_2O_8$ prepared at different pH (a) 10, (b) 4 and (c) 8.

Fig 3(a-c) show SEM images of of $Cu_3V_2O_8$ nanostructures prepared at different pH. As-prepared nanostructures at acidic and basic solution are agglomerated. Optimum pH for synthesis of fine and uniform of $Cu_3V_2O_8$ nanoparticles is 8.

FT-IR spectrum of the copper vanadium oxide nanoparticle prepared by ex-situ precipitation method in presence of acacbn Schiff base ligand is shown in Fig. 4. The absorption around 3400 cm^{-1} can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water. The absorption around 1620 cm^{-1} is due to the bending vibration of water molecules. The bands at around 2920 cm^{-1} are assigned to the asymmetric and symmetric C-H stretching vibrations of hydrocarbon moiety. According to the previous reports, the IR bands around 880, 770 and 690 cm^{-1} are assigned to the vibrations of VO_4^{3-}. The band around 420 cm^{-1} 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 VO4 and octahedral CuO6 vibration modes in the network.

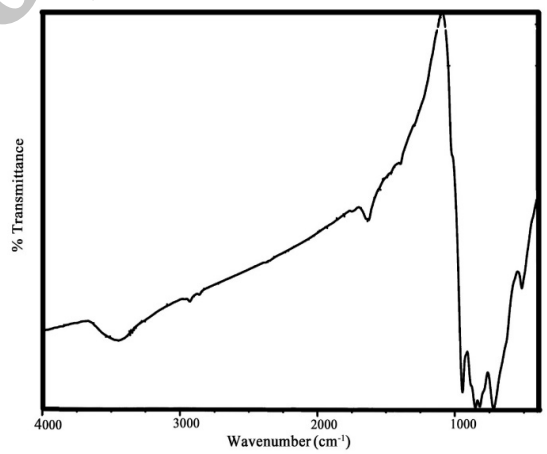

Fig. 4. FT-IR spectrum of $Cu_3V_2O_8$ prepared in optimum condition (sample No. 4).

EDS analysis measurement was employed to investigate the chemical composition and purity of as-synthesized $Cu_3V_2O_8$ nanoparticles. EDS spectrum (Fig. 5) revealed the presence of Cu, V and O in copper vanadium oxide nanoparticle synthesized by ex-situ precipitation.

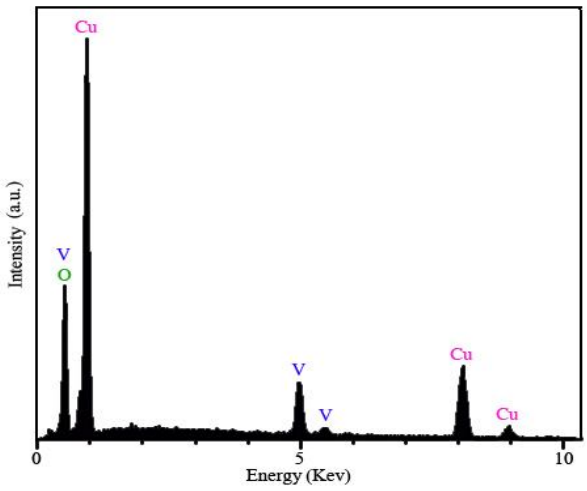

Fig. 5. EDS pattern of copper vanadium nanostructure (sample No.4).

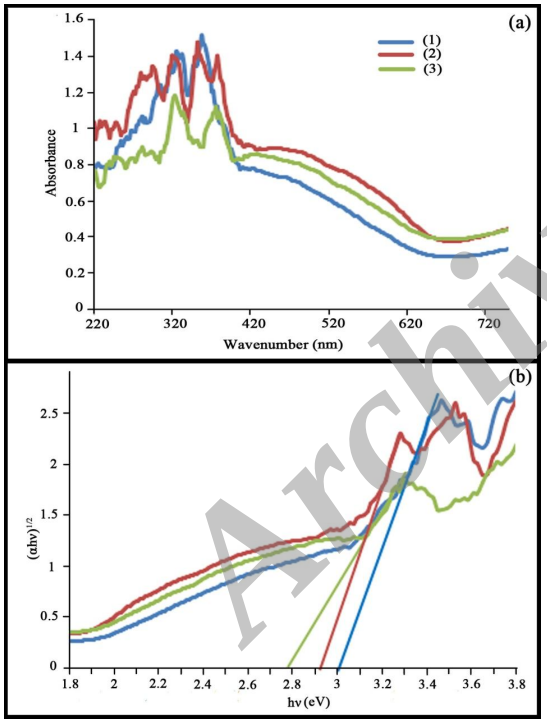

Fig. 6. (a) UV-Vis diffuse absorption spectra of the $Cu_3V_2O_8$ nanoparticles prepared (1) sample No. 4, (2) sample No. 2 and (3) sample No. 5. (b) the inset shows corresponding linear portion of the plots of $(\alpha h\nu)^{1/2}$ against (hv).

The absorption spectra of Copper Vanadium Oxide nanoparticles prepared by ex-situ precipitation are shown in Fig. 7a. The energy gaps of the samples have been determined by extrapolating the linear portion of the plots of $(ah\nu)^{1/2}$ against hν to the energy axis (Fig. 7b). The E_g value is calculated 3 (sample No. 4), 2.92 (sample No. 2) and 2.78 eV (sample No. 5) for the copper vanadium oxide nanoparticles.

4. Conclusion

$Cu_3V_2O_8$ nanostructures were prepared via ex-situ precipitation approach in presence of Schiff-base ligand acacbn as a new capping agent. The effect of different Cu sources and pH on the size, morphology and size distribution of copper vanadate nanostructures was investigated. The as-prepared products were characterized using XRD, SEM, FT-IR, EDX and UV–Vis spectroscopy. The optical properties of different samples were compared.

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