

STUDY OF STRUCTURAL AND OPTICAL PROPERTIES OF V_2O_5/SiO_2 NANOCOMPOSITES



Physics

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ABSTRACT

Binary oxide nanocomposites consisting nanoparticles of vanadium pentoxide (V_2O_5) and silica (SiO_2) were prepared by coprecipitation technique using metallic chlorides as precursors. Subsequently composites were annealed at 200, 300 and 700°C for 2h. The sample were structurally characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Ultraviolet visible spectroscopy (UV-Vis). The effects of thermal treatment on the structural and Optical properties of nanocomposites were investigated. The size of the nanoparticulate increases with increase in annealing temperature. The λ_{max} of nanocomposite (annealed at 700°C for 2h) are higher than that of bulk V_2O_5 and the direct and indirect band gap decreases from room temperature to 700°C. The realization of the adjustable particle sizes and the controllable optical properties makes the applicability of the V_2O_5/SiO_2 nanocomposite more versatile.

INTRODUCTION

Among the profuse nanostructure of metal oxides, Vanadium have several oxidation states and generally forms a variety of oxides, such as VO_2 , V_2O_5 , V_2O_3 , V_6O_{13} etc. among these oxides vanadium pentoxide (V_2O_5), is of great importance because of its potential applications to catalysts [1], chemical sensors [2], field effect transistors [3], electrochemical and photochromism devices [4,5]. The orthorhombic layered structure of V_2O_5 and high surface-to-volume ratio at nano dimensions promises a high ionic storage capacity for energy storage applications where as high surface activity of V_2O_5 (1D) structures promises other applications, such as field emitters [6], transistors [6,7], chemical sensors [9-11] etc. In addition, V_2O_5 with a direct optical bandgap at visible-light region ($E_g = 2.2$ to 2.7 eV) [6,7-10] also inspires the studies of optoelectronic applications such as photodetection [6,11], optical waveguide [12], and high speed photoelectric switch [13-14]. Many synthetic approaches have been employed to prepare V_2O_5 nanocrystals [11-15], the nanocrystals produced usually have a strong tendency to aggregate, which makes it very difficult to exploit the physico-chemical property. The dispersion of nanoparticles in an inorganic, polymer, vitreous, amorphous matrix is an important method to avoid particle agglomeration and control of particle size [16]. In addition such nanocomposites may have many advantages from technological point of view, allowing to improve catalytic [17], optic [18] and mechanical properties [19-20] of the material. Coprecipitation process has been proved to be an efficient method to prepare ultra-fine particles dispersed in different matrices [21-23]. Using this method a control over the surface morphology, structure, texture and chemical composition can be attained by carefully monitoring the preparation parameters [24]. In this work nanocomposites of V_2O_5 dispersed in a silica matrix were prepared by coprecipitation method. The XRD, FTIR, and UV-Vis studies of the prepared samples were carried out. Special attention is given to the correlation between the structure and optical properties of vanadium pentoxide embedded in silica matrix.

EXPERIMENT:

Synthesis of V_2O_5/SiO_2 nanosuspension: Firstly suspension of SiO_2 was prepared by adding 50ml 0.3M SiO_2 (AR grade; Aldrich 99.99%) aqueous solution in 50ml 0.6M NaOH (Aldrich 99.99%) containing 0.3M V_2O_5 (AR grade; Aldrich 99.99%) using method given in literature [25], which gave to $Na_2SiO_3 + V_2O_5$; this solution when mixed with 50ml 0.6M HCl, gave grayish white precipitate of V_2O_5/SiO_2 in suspension form. This suspension so obtained was stirred at a constant speed of 6000 rpm for 3h at temperature of 50°C; and then washed many time with deionized water to remove NaCl completely from the suspension. The resultant solution was then filtered and

washed many times and then the filtrate was dried at 85°C in a vacuum oven at a pressure of 98mm Hg for 3h. The dried sample was ground to very fine powder. These fine powdered samples were then heated at 300° and 700°C separately for two hours using a programmable furnace (KSL 1600X, MTL). It was noticed that the color of the doped samples was glassy steel gray due to the presence of vanadium. The powder form of the prepared samples was obtained by pestle and mortar.

Characterization of sample

Complementary methods were used to characterize annealed samples. In order to determine the crystallite size and lattice constant, XRD patterns of samples were recorded by using a Philips X-ray powder diffractometer PW/1710 having GIXRD geometry; with Ni filter, using monochromatic $CuK\alpha$ radiation of wavelength 1.5418Å at 50KV and 40mA. The divergence of scanning beam on the source slide was controlled with the help of 0.15mm slit. The specimen were scanned in the range 20° to 80°. Fourier transform infrared spectrometer has been used to study the IR properties of prepared sample in the Mid-IR range, 4000-400 cm^{-1} using Perkin-Elmer instrument. Absorption spectra of the samples were studied with the help of Lambda 750 (Perkin Elmer) spectrophotometer in the wavelength range of 200–800 nm.

XRD:

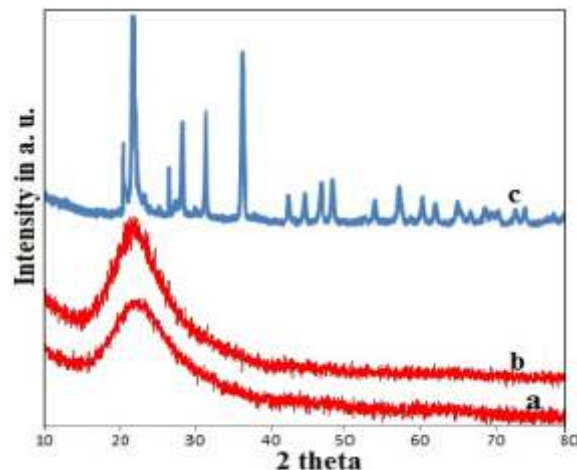


Figure 1: XRD pattern of V_2O_5/SiO_2 powder for (a) as-prepared, (b) at 300°C, (c) at 700°C

XRD is used for determining the presence of crystalline phases. The XRD pattern of the prepared samples is shown in figure 1. The samples were scanned from 2θ to 80° . Fig1 (a) and (b) shows the XRD patterns of the as-prepared and heat treated samples at 300°C . A hump around 230 revealed amorphous phase of SiO_2 . Figure 1(c) show diffractogram of powder heat treated at 700°C . The pattern shows peaks at 2θ 20.290° (0 0 1), 25.550° (0 2 1), 26.152° (1 1 0), 31.030° (0 4 0), 42.027° (0 1 2), 44.410° (0 5 1), 46.923° (1 5 0), 48.826° (1 0 2), 54.700° (1 3 2), 56.270° (2 1 1), 60.020° (0 7 1), 61.106° (2 1), 65.094° (2 4 1), 66.029° (0 2 3), 68.339° (2 1 2), 69.632° (1 0 3), 70.177° (1 1 3), 72.283° (2 6 0), 77.672° (0 9 1), 79.506° (1 9 0). These peaks are readily indexed for V_2O_5 [JCPDS file 850601]. The mean crystalline size for each sample was calculated using the Debye Scherrer eq. $D_c = k\lambda/\beta\cos\theta$, Where β is the breadth of observed diffraction line at its half intensity maximum, k is the shape factor which usually takes a value of about 0.9 and λ is the wavelength of x-ray source used in XRD. The particle sizes of the powdered sample were obtained from Scherrer's formula, and were found in the range of 28 to 40nm. The evaluated lattice parameters were $a = 3.564\text{nm}$, $b = 11.519\text{nm}$ and $c = 4.373\text{nm}$, which are congruent with JCPDS file 850601.

FTIR:-

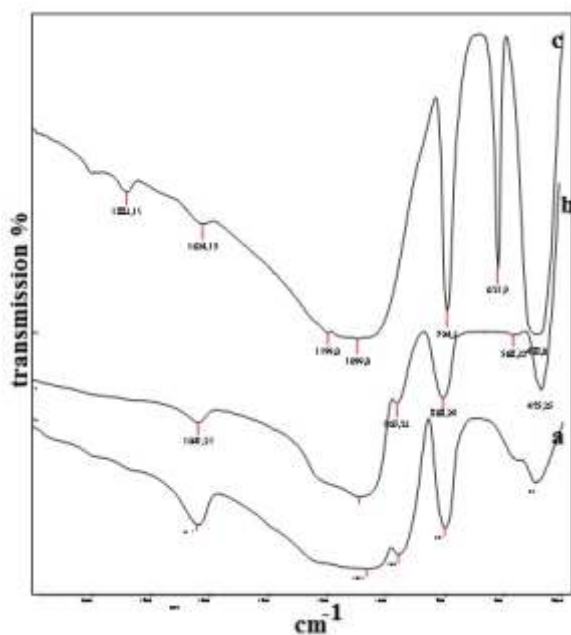


Figure 2: FTIR spectra of $\text{V}_2\text{O}_5/\text{SiO}_2$ powder for (a) as-prepared, (b) at 300°C , (c) at 700°C

An FTIR spectrum of the prepared samples is shown in Figure 2. The spectra of as-prepared sample (Fig 2(a)) indicate strong absorption bands at 475, 568, 808, 965, 1091 cm^{-1} which may be assigned to Si-O-Si symmetric bond stretching vibration, vibration mode of ring structure of SiO_2 tetrahedra, TO mode of Si-O-Si asymmetric bond stretching vibration and bending vibration modes of H-O-H absorbed in silica respectively. The characteristic absorption at 1091, 808, 475 cm^{-1} indicates the formation of silica network. The absorption band of silanol group due to stretching of Si-OH bond (965 cm^{-1}) is however, gradually weakens and disappears with thermal treatment (fig. 2(b)) indicate the phase transformation of V_2O_5 and SiO_2 . This reveals that the network structure of short-range order tetrahedral SiO_4 was destroyed and became more disordered. The absence of crystalline V_2O_5 is confirmed, because the corresponding band at 1020 cm^{-1} is never observed, while absorption at 960–990 cm^{-1} confirms the formation of polyvanadic species, of low nuclearity, also at low vanadium charge [26]. The original SiO_2 support shows an intense band of absorption at 3747 cm^{-1} corresponding to isolated silanol groups Si-OH [27,28]. After heat treatment at 300°C the band corresponding to Si-O-Si vibrations becomes narrow and shifts to 1067, 958 and 802 cm^{-1} for

Si, and After heat treatment at 700°C the band corresponding to Si-O-Si vibrations becomes narrow and shifts to 1099, 794 and 458 cm^{-1} for Si. This behavior is typical of the silica reduction process with heat treatment. FTIR spectra of sample at 300°C shown in Fig.(2b). For polycrystalline pellets of V_2O_5 the peak at 802 cm^{-1} and 958 cm^{-1} transferred to 1099 cm^{-1} at 700°C . FTIR spectra of sample at 700°C is shown in Fig.(2c). The sample at 700°C shows main features of V_2O_5 spectrum, however not all bands of typical crystalline V_2O_5 were developed.

UV-Vis (UV-Visible);

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The absorption spectra of the prepared samples dispersed in ethanol. The band gap energy of samples has been calculated using the relation between the incident photon energy ($h\nu$) and the absorption coefficient (α) which is given by the equation: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where A is a constant and E_g is the band gap energy of the material and the exponent n depends on the type of transition [29]. Direct band gap of the samples (using $n = 1/2$) were calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis at $\alpha = 0$. The band gap of the samples calculated from the straight part of the optical absorption spectra. The band gap of sample decreases from room temperature to 700°C (fig.3)

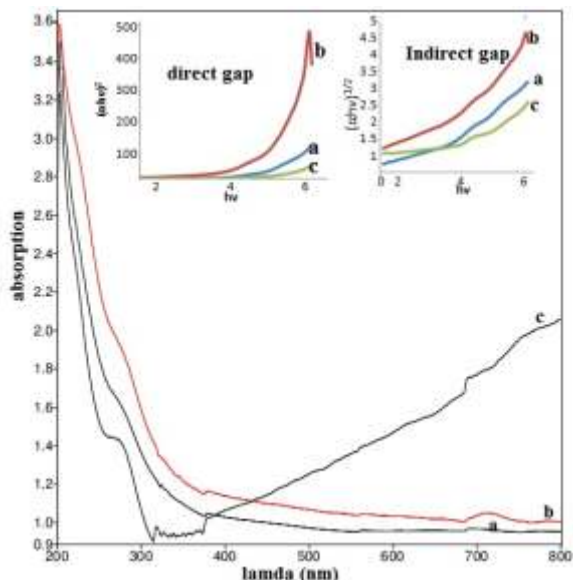


Figure 3: UV-vis spectra of $\text{V}_2\text{O}_5/\text{SiO}_2$ powder for (a) as-prepared, (b) at 300°C , (c) at 700°C

CONCLUSIONS

The coprecipitation method was adopted in this work to prepare $\text{V}_2\text{O}_5/\text{SiO}_2$ composites. The analytical, spectroscopic and chemical results show that during the synthesis process an exchange mechanism takes place. After heat treatment the solid structure is rearranged conducting to the formation of V_2O_5 species mixed in the SiO_2 network. It can be concluded that V_2O_5 supported silica will possess a high specific surface area available for the adsorption and decomposition process. The use of silica support with large surface area and high porosity makes the applicability of the $\text{V}_2\text{O}_5/\text{SiO}_2$ nanocomposite more versatile. It is worth to say that SiO_2 employed as supports because they are chemically inert, transparent to the UV radiation and also have high specific surface area.

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