Preparation of Nanocomposites by Intercalation and in Situ Polymerization of Aniline in a Layered Transition Metal Oxide : Study of their Microstructural and Optical Properties

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ABSTRACT

Intercalation is a novel chemical route to synthesize nanosized materials within the interlayer spaces. In the present investigation conducting polyaniline (PANI) was intercalated in the interlamellar space of layered hydrated vanadyl phosphate, $VOPO_4.2H_2O$. The nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and high-resolution scanning electron microscopy. The amount of water decreases with the increase in PANI concentration. Plate like layered structures are observed for pristine $VOPO_4.2H_2O$ as wel as intercalated nanocomposites. Formation of the nanocomposites and interaction of PANI with vanadyl phosphate are observed in FTIR and UV absorption spectroscopy. The optical band gap of vanadyl phosphate is reduced due to intercalation of polyaniline.

Keywords : Redox Intercalation, Polymerization, Vanadyl Phosphate, Nanocomposite

I. INTRODUCTION

Layered Inorganic compounds are most attractive host systems to synthesize smart materials within the interlamellar spaces by intercalation method. Vanadyl phosphate ($VOPO_4-2H_2O$.) has been extensively studied for major applications [1-6] as inorganic ion exchangers, ionic conductors, capacitors and catalysis [7-8]. At ambient condition the hydrated crystalline structure which in turn the most stable phase comes out as $VOPO_4-2H_2O$. The crystalline structure of vanadyl phosphate, $VOPO_4-2H_2O$ consists of chains of distorted VO_6 octahedra connected by PO_4 tetrahedra [9-10]. One water molecule is coordinated with trans to an axial oxygen site of a VO_6 octahedron. The second water molecule resides in the van der Waals gap bonding with the PO_4 tetrahedron. A weak interlayer bonding like van der Waals forces assists in insertion of foreign molecules within the host matrix by the replacement of water molecules. The host compounds possess some distinctive physicochemical

property to accommodate guest species [12]. Inorganic solids such as FeOCl, V_2O_5 xerogel and $VOPO_4-2H_2O$ with open structure and high oxidative e property are very much suitable for redox intercalation [13-20]. The structure of pristine host is not modified due to insertion of guest species. The physical properties are strongly affected due to the synergetic effect of host and guest. Conducting polymers are extensively studied for their unique electronic properties [21]. The higher electrical conductivity of some polymers helps to prepare the conducting nanowire by intercalation. The V–P–O layers are electronically non-conducting. Intercalation of conducting polymers into the interlayer region represents a nanocomposite with alternate conducting and insulating layers. Very few reports on the synthesis and characterization of vanadyl compounds intercalated with conducting polyaniline (PANI) are available [18-23]. The electrical and optical properties of vanadyl phosphate– PANI nanocomposite has not yet been studied in detail. In the present study an attempt has been made

to synthesize PANI within the interlamellar space of hydrated vanadyl phosphate and to investigate its microstructural and optical properties.

II. MATERIALS AND METHOD

Vanadium (V) oxide, Phosphoric acid (H_3PO_4) and aniline are purchased from Sigma Aldrich (India).

Dihydrate vanadyl phosphate $VOPO_4$-$2H_2O$ was prepared by refluxing a mixture of V_2O_5 (24 g) and concentrated H_3PO_4 (136 ml) in a solution of distilled water (580 ml) for 16 h in air [22]. The product came out was separated by filtration in vacuum and washed several times with distilled water and ethanol. Yellow powder was obtained after drying in air. The nanocomposites in the present case were prepared as described elsewhere [23]. To prepare polyaniline intercalated$VOPO_4$-$2H_2O$ nanocomposites, 0.05 and 0.1 moldm^{-3} aniline in 50 ml dry ethanol were poured in 50 ml of dry ethanol containing 5 mmol $VOPO_4$-$2H_2O$. The solution was stirred by magnetic stirrer at room temperature for 24 h. The products were filtered in vacuum, washed with water and dry ethanol and dried in air at room temperature.

III. CHARACTERIZATION

The X-ray powder diffraction studies were carried out with Philips Diffractometer (PW 1710) in the range 2°–40° using Cu–K_α radiation. Elemental analysis (CHN) was done using Perkin Elmer-2400 Series-II CHN analyzer. Fourier transform infrared (FTIR) spectra were recorded from pressed KBr pellets using a Perkin–Elmer-1600 FTIR spectrometer. UV study was done using UV-2401PC (Shimadzu, Japan) spectrometer. Scanning electron microscopy (SEM) was done on a JEOL-JSM 35CF microscope operated at 20 KV. Samples were pelletized using hydraulic pressure (applied pressure5 ton).

IV. RESULTS AND DISCUSSION

Vanadium V^{5+} ions in $VOPO_4$-$2H_2O$ have empty 3dorbital. Electrons transfer within V–OH bonds associatedwith water molecules give rise to acidic dissociation of V–OH bond at water-vanadium oxygen interface. Aniline monomer is converted into anilinium cation $C_6H_5NH_3^+$ when comes in contact with acidic $VOPO_4$-$2H_2O$. This cation is inserted within the layers of vanadyl phosphate via proton exchange. It is polymerized into polyaniline by reducing vanadium ions [24,15]. The chemical compositions and the amount of water of two nanocomposites, $(PANI)_x VOPO_4$- nH_2O were determined by elemental carbon, hydrogen and nitrogen (CHN) analysis. The water and polymer contents in the nanocomposites are shown Table1

Table 1. Amount of monomer intercalated (y) and chemical compositions of $(PANI)_x$-VOP_4- nH_2O (value of x and n, calculated from CHN data.

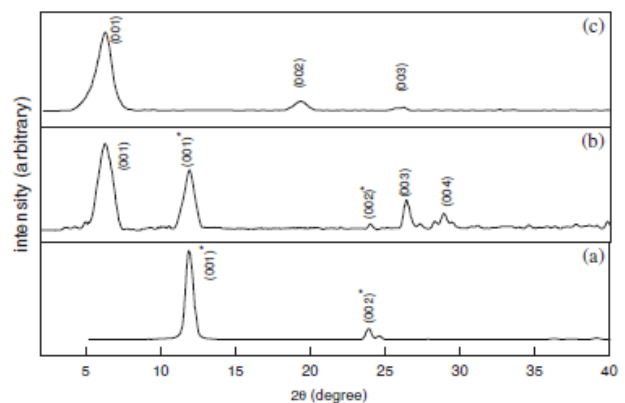| Sample	y (mol dm^{-3})	C (%)	H (%)	N (%)	x	n
P1	0.05	7.64	2.24	1.49	0.28	1.71
P2	0.1	9.98	2.49	1.93	0.42	1.44

Fig.1: X-ray diffraction pattern of (a) $VOPO_4$-$2H_2O$, (b) nanocompositeP1 and (c) nanocomposite P2.

The X-ray diffraction (XRD) patterns of crystalline $VOPO_4$-$2H_2O$, and intercalated nanocomposites are shown in Fig. 1. For all the nanocomposites the diffraction pattern show broad and low intensity peaks suggesting that the layered structure of the host was retained even after intercalation despite a decrease in crystallinity with respect to the host matrix. The first peak indicates (001) reflections. The first peak in Fig. 1(b) shifts to lower angle which corresponds to the lattice expansion from 7.64 Å to14.12 Å. For both the nanocomposites the lattice expansions are same. The $VOPO_4$-$2H_2O$ phase with d=7.64 Å is present in nanocomposite P1, which is completely absent in the maximum loading nanocomposite P2. As the molecular dimension of water is about 2.8 Å, the interlayer expansion of 6.48 Å is sufficient to accommodate PANI and water molecules.

The FTIR spectra of $VOPO_4$-$2H_2O$ and PANI intercalated nanocomposites are shown in Fig. 2. The absorption peaks as presented in Fig. 2(a) at 678, 940, 998 and1090 cm^{-1} are the characteristics of $VOPO_4$-$2H_2O$ [11-13].The bands at 998 and 940 cm^{-1} are assigned to the V–O stretching of the vanadyl group (V=O). The peak at 1090 cm^{-1}corresponds to P–O stretching vibration of the PO_4 tetrahedral group. The band at 678 cm^{-1} can be ascribed to V–O–P bending vibration. The band around 1606 cm^{-1} is due to H–O–H bending vibration of water molecule. A broad band between 3000 and 3600 cm^{-1} arises from O–H stretching of water.
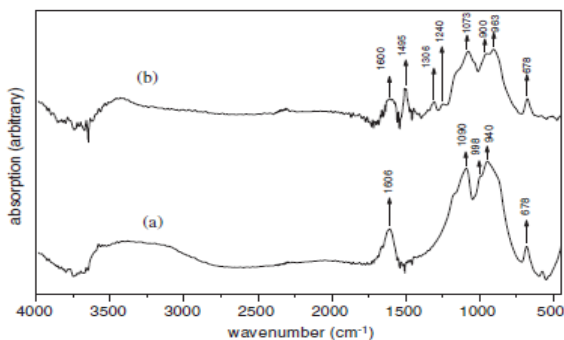
The FTIR spectrum of nanocomposite P2 as presented in Fig. 2(b) reveals the characteristics bands of PANI at 1240, 1306 and 1495 cm^{-1} [25-26]. The bands at1240, 1306 cm^{-1}originate from C–N stretching and1495 cm^{-1} is from the stretching vibration of C–C bond. The band at 678 cm^{-1} associated with V–O–P bond remains unchanged upon intercalation. After intercalation of PANI, the vibrational peaks of $VOPO_4$-$2H_2O$ shift from 940 and 998 cm^{-1} to 900 and 963 cm^{-1}, respectively. Both V=O and V–OH bonds become weak due to the appearance of IR peaks at lower wave numbers. These indicate the interaction of guest PANI within the host. These changes are attributed to the greater number of V^{4+}centers present in the nanocomposite. The peak at 1600 cm^{-1} becomes broader and a new sharp peak appears at 3644 cm^{-1} for water. The broad band between 3000 and 3600 cm^{-1} due to O–H stretching of water becomes narrower after intercalation of PANI.
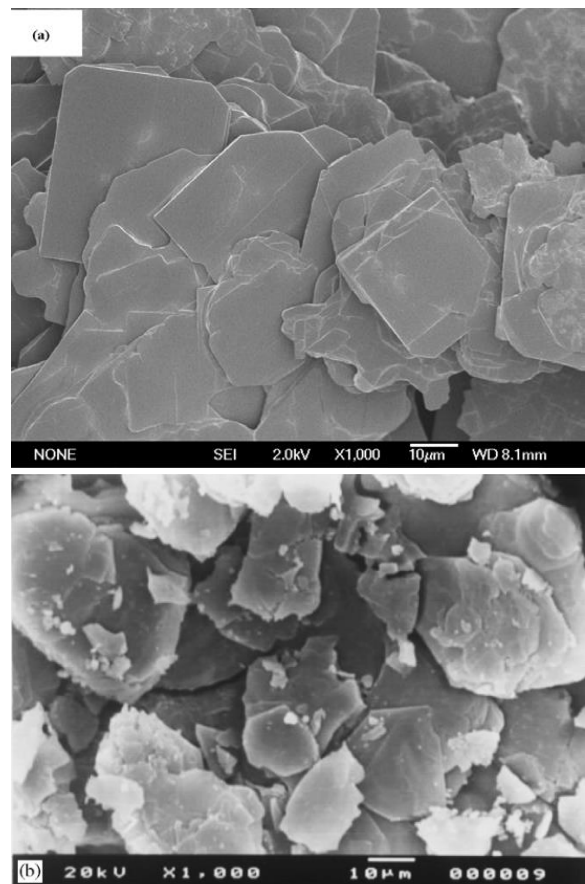

Fig. 2: Fourier Transform Infrared (FTIR) spectra of (a) $VOPO_4$-$2H_2O$ and (b) nanocomposite P2.

Fig. 3: Scanning electron micrograph (SEM) of (a) $VOPO_4$-$2H_2O$ and (b) nanocomposite P2.

SEM images of pristine host VOPO$_4$-2H$_2$O and nanocomposite (P2) are shown in Fig. 3(a) and (b). The nanocomposite reveals plate like morphology similar to that of VOPO$_4$-2H$_2$O. This result supports that the layered structure is preserved even after intercalation of PANI.
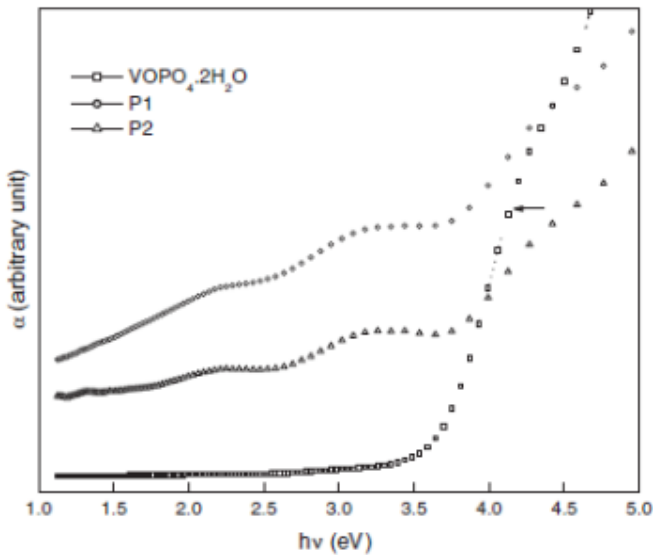

Fig. 4: UV–VIS spectra of VOPO$_4$-2H$_2$O and two nanocomposites samples P1 and P2.

The UV-vis spectra of VOPO$_4$-2H$_2$O and two nanocomposites (P1, P2) are shown in Fig. 4. The absorption spectrum of vanadyl phosphate shows a shoulder like structure around 4 eV as shown in Fig. 4. Three main features are found in P1 and P2 between 2 and 4 eV. The absorption coefficient a of the semiconductor can be described as [27]

$$\alpha h\nu = A(h\nu - E_g)^m \qquad (1)$$

where photon energy is hν, h being the plank constant and E_g is optical band gap. Fig. 5 shows the relation between $(\alpha h\nu)^2$ and hν for the nanocomposite P2.
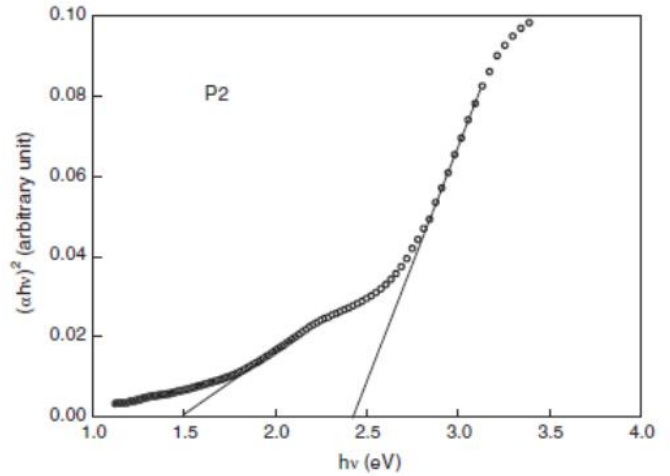

Fig. 5: $(\alpha h\nu)^2$ versus hν for the nanocomposite P2.

This gives two straight line portions and the extrapolation of these two lines at $(\alpha h\nu)^2 = 0$ yield the so-called optical band gaps. In the present situation m= 1/2, so the inter band transition is allowed direct. Absorption bands at 3.8 eV (325 nm) and 2.0 eV (625 nm) are found for π-π^* transitions of benzenoid and excitonic effect of quinoid rings of polyaniline emeraldine base. The estimated band gaps are 1.5 and 2.4 eV. These two band gaps are attributed to direct transitions from the highest and the second highest valence bands to the lower polaron band of protonated polyaniline [28-29]. The optical band gap of vanadyl phosphate calculated in a similar manner as shown in Fig. 5 is 4.0 eV. The valence and conduction bands of V$_2$O$_5$ are mainly oxygen p and vanadium d states [30,31]. The basic difference between V$_2$O$_5$ and VOPO$_4$ is that one vanadium is replaced by phosphorous atom. The absorption around 4.0 eV may originate from occupied p bands of oxygen and phosphorous to unoccupied d bands of vanadium. The calculated band gap in the nanocomposites reduce to 3.7 eV. The interlayer lattice parameter increases with intercalation of polyaniline. This may lead to decrease in band gap in vanadyl phosphate.

V. CONCLUSION

Conducting polyaniline was inserted in the mixed valent hydrated vanadyl phosphate, VOPO$_4$-2H$_2$O by

in situ redox intercalation method. The amount of water content decreases with the increase of polyaniline concentration in the composites.SEM indicates layered structures for both VOPO$_4$-2H$_2$O and intercalated nanocomposites. The protonation of the polymer and formation of nanocomposites is confirmed by XRD, UV absorption and FTIR spectra. The optical band gap in the nanocomposites decreases from 4.0 eV to 3.7 eV with increase in PANI concentration.

VI. REFERENCES

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