

Synthesis and characterization of halo-substituted polyanilines/ VOPO_4 nanocomposites

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Abstract

We report on the synthesis and characterization of a series of halo-substituted polyanilines into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. Treatment of the corresponding monomers with the highly oxidizing host $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ resulted in *in situ* intercalation/polymerization. The resulting intercalated nanocomposites were characterized by powder X-ray diffraction, FTIR spectroscopy and thermogravimetric analysis.

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1. Introduction

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is a fascinating layered system that has been shown to undergo intercalation chemistry via several techniques such as acid/base [1], coordination [2], exfoliation/reconstruction [3], and *in situ* intercalation/polymerization [4]. The structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ can be described as consisting of VOPO_4 sheets which are made up of VO_6 octahedra and PO_4 tetrahedra linked through the corners. In addition, there is a water molecule bound to each of the vanadium centers, with interlamellar water hydrogen bonded to the coordinated water [5]. *In situ* intercalation/polymerization is a particularly exciting route for the insertion of electrically conductive polymers into the layered host system. This technique of intercalation is suitable for lamellar structures which are highly oxidizing, where simultaneous polymerization and intercalation of the monomers take place. To the best of our knowledge, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ [4] in addition to FeOCl [6] and $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ [7] are the only layered materials that are capable of undergoing *in situ* intercalation/polymerization when treated with molecules such as aniline and pyrrole. The insertion of conductive polymers such as polyaniline, polypyrrole and polythiophene into 2D constrained environments can lead to at least partially oriented polymer chains which can aid in elucidating the structure of these polymers [8]. The bulk polymers are completely amorphous and

are insoluble in common organic solvents rendering it virtually impossible to solve their structures by routine techniques such as solution NMR spectroscopy. In addition, growing single crystals of these materials are difficult. Therefore, sequestering the polymer chains in restricted environments such as the gallery space of lamellar host structures is a stepping stone towards gaining structural insight of these materials, which could in turn lead to a better understanding of their charge transport properties. The hybridization of layered compounds and conductive organic polymers have, indeed, been intensely investigated by several researchers [9].

In this article we have capitalized on the *in situ* intercalation/polymerization properties of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and we have been able to prepare novel intercalated materials of poly(3-fluoroaniline) (PFA), poly(3-chloroaniline) (PCA) and poly(3-bromoaniline) (PBA) into VOPO_4 . While the insertion of aniline into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ has been studied in detail there are few reports on the encapsulation of substituted anilines into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and so far these have been restricted to alkyl substituted anilines [10]. The intercalation of halo-substituted polyanilines into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ have not been reported in the past and we have therefore decided to focus our attention on the abovementioned halo-substituted anilines.

2. Experimental

2.1. Materials

3-Fluoroaniline (FA), 3-chloroaniline (CA), 3-bromoaniline (BA), vanadium pentoxide (V_2O_5) and concentrated phosphoric acid were purchased

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from Aldrich, and were used as received without any further purification.

2.2. Synthesis of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

The preparation was carried out by following the procedure described in Ref. [2]. To powdered V_2O_5 (24 g, 0.13 mol) was added an acidic solution prepared by adding 135 mL of conc. H_3PO_4 to 580 mL of H_2O . The reaction mixture was allowed to reflux in air for 31 h and then allowed to gradually cool down to room temperature. The yellowish precipitate obtained was then filtered under suction, washed with deionized water and allowed to dry under suction. By performing thermogravimetric analysis in air, the composition of the layered structure was determined to be $\text{VOPO}_4 \cdot 1.7\text{H}_2\text{O}$. Throughout the text we will refer to our layered system simply as $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

2.3. Synthesis of polymer- VOPO_4 intercalates

In a typical reaction, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (0.21 g, 1.1×10^{-3} mol) was suspended in 20 mL of 95% ethanol with the help of sonication. About 36 equiv. of the monomer (3-fluoroaniline, 3-chloroaniline, 3-bromoaniline) were then added to the suspension. The reaction mixture was allowed to reflux in air for 24 h and then cast onto a glass plate as a thin film.

2.4. Instrumentation

Infra-red spectroscopy was run on a Perkin-Elmer 1600 FTIR series instrument.

Powder X-ray diffraction (XRD) was run on a Bruker AXS D8 advance diffractometer equipped with a graphite monochromator, variable divergence slit, variable antiscatter slit and a scintillation detector. $\text{Cu}(\text{K}\alpha)$ radiation ($\lambda = 1.542 \text{ \AA}$) was utilized and the data collection was carried out at room temperature. Samples were pressed as pellets and run in air with a scan range of $2\text{--}60^\circ$. In order to minimize scattering from materials other than the samples in the XRD measurements, the pressed samples were placed on a zero background single crystal silicon substrate with the surface cut parallel to the (5 1 0) plane [Gem Dugout, PA].

Thermogravimetric analyses (TGA) were performed on a TA 500 instrument using a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

The identity of our synthesized layered structure was confirmed by powder X-ray diffraction (Fig. 1(b)). The interlayer spacing was found to be 7.29 \AA , which is in good agreement with

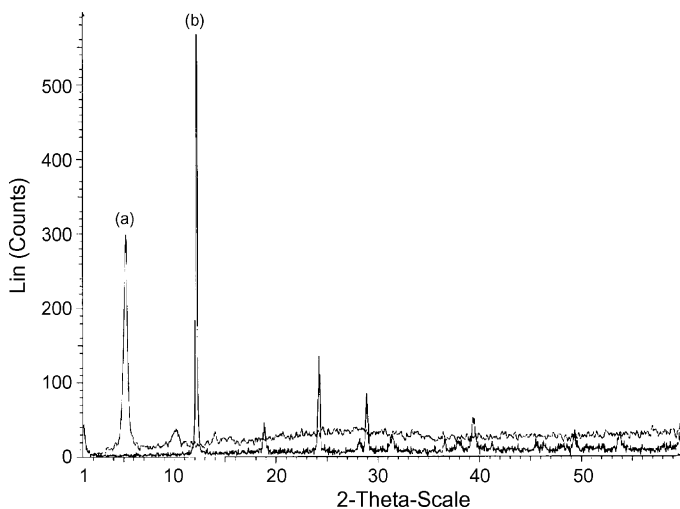


Fig. 1. XRD of (a) PCA/ VOPO_4 and (b) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

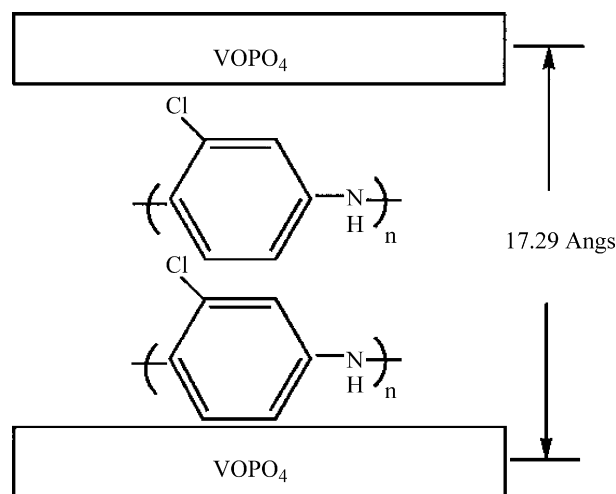


Fig. 2. Lamellar arrangement of PCA/ VOPO_4 .

the literature [11]. Upon treatment of the monomers with the yellow ethanolic suspension of the layered structure, an immediate color change to green and then black was observed, suggesting that a redox reaction occurred between the monomers and layered structure.

XRD on the isolated products confirmed that genuine intercalation compounds of the polymers into VOPO_4 have been formed. For instance, the powder pattern of PCA/ VOPO_4 system is illustrated in Fig. 1(a). The interlayer spacing of the material is 17.29 \AA and compared to VOPO_4 , which has a d_{value} of 4.16 \AA , an interlayer expansion of 13.13 \AA is noted. The intercalation reaction is driven by entropy, and therefore most of the interlamellar and coordinated water molecules in the layered structure are displaced by the incoming polymer. It is well documented in the literature that entropy is the major driving force when polymers are inserted into layered systems containing interlamellar water molecules. For example, the intercalation of polyanilines [12] and polypyrrole [13] into graphite oxide is driven by entropy.

For the case of PCA/ VOPO_4 the observed interlayer expansion of 13.13 \AA corresponds to a bilayer arrangement of the polymer sandwiched perpendicular to the VOPO_4 sheets as shown in Fig. 2. Such a bilayer arrangement has been proposed for other polymers intercalated into VOPO_4 , e.g. polyaniline- VOPO_4 system [10]. However, other structural arrangements are also possible, and further investigation will be required in the future. The XRD data are summarized in Table 1, and similar patterns are observed for the other intercalates. It is interesting to note that as the size of the halogen atom increases,

Table 1
Summary of X-ray data

Intercalate	Interlayer spacing (\AA)	Net expansion (\AA)	Proposed structural arrangement
VOPO_4	4.16	–	–
PFA/ VOPO_4	15.73	11.57	Bilayer
PCA/ VOPO_4	17.29	13.13	Bilayer
PBA/ VOPO_4	17.91	13.75	Bilayer

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