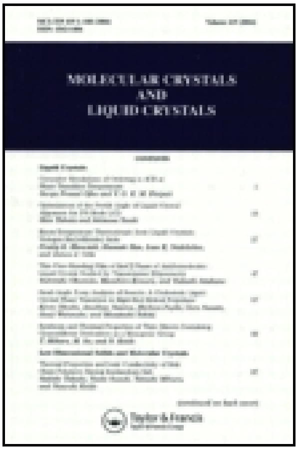

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Restacked $WS_2(PEO)_{1.4}$ Nanocomposites

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Restacked $WS_2(PEO)_{1.4}$ Nanocomposites

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WS_2/PEO (poly-ethylene oxide, $-CH_2CH_2O-$) nanocomposites were prepared by direct flocculation when single layer WS_2 in suspension in water was mixed with a PEO aqueous solution. As with earlier work on similar systems using MoS_2, the resultant composite material is a remarkably well-ordered polymer-intercalated tungsten disulfide. The powder x-ray diffraction patterns contain (hk0) peaks of the two-dimensional type and (00l) peaks of the three-dimensional type. No mixed (hkl) peaks are observed. The diffraction clearly shows that the system is turbostratically restacked with the WS_2 layers parallel to each other with an expanded interlayer spacing due to the insertion of PEO, but random in translation along the layers and in rotation about the normal to the layers. The host WS_2 layers have a strongly distorted octahedral structure with a $2a_0$ superlattice and an expanded a-spacing.

Very highly oriented $WS_2(PEO)_{1.4}$ thin films have been formed on glass substrates. We found that the interlayer spacing of $WS_2(PEO)_{1.4}$ is extremely sensitive to humidity. As the relative humidity at room temperature increases from 0% to 100%, the c-spacing reversibly changes from 14.6 Å to 20.2 Å due to absorption of water. Conductivity measurements have also been carried out on the highly oriented thin films.

Keywords: tungsten disulfide; polymer intercalation; X-ray diffraction

1. Introduction

Transition metal dichalcogenides (TMD) are often considered to be quasi-two-dimensional, since these materials have highly anisotropic physical properties resulting from the layer structure, with a strong bonding within the layers and weak interlayer interaction[1]. Tungsten disulfide and molybdenum disulfide are such structures where each layer is a sulfur-metal-sulfur sandwich which is bound to adjacent layers by weak van der Waals forces. Within a layer of such compounds, the metal atom can be coordinated by six chalcogen atoms in either an octahedral or trigonal prismatic arrangement. In the case of WS_2 or MoS_2, only the trigonal prismatic coordination of the metal atom is found in the natural material.

A remarkable property of layer compounds is that single molecular layers of TMD such as MoS_2 and WS_2 can be formed in suspension in water by exfoliation[2,3]. The exfoliated material has a thickness of only one molecular layer, typically about 4 Å, and a lateral size of up to a micron. The single layers are suspended in an aqueous solution and provide a perfect system for study of physical and chemical properties of two-dimensional (2-D) material. Furthermore, single-molecular-layers of TMD can be restacked in many ways, and this opens up a new approach for the synthesis of new materials[4,5]. For example, organic/inorganic included compounds can be formed by adsorbing various atoms or molecules on the host TMD layers before restacking.

In some earlier work, MoS_2/polymer nanocomposites were formed and some unique properties explored[4]. In this paper, we present the preparation and the detailed structure of the $WS_2(PEO)_{1.4}$ nanocomposite and discuss its sensitivity to humidity. Although MoS_2 and WS_2 have the same structure and similar properties, tungsten (atomic number 74) has more electrons than molybdenum (atomic number 42). This is a big advantage for x-ray diffraction studies.

2. Experimental Results

The preparation technique for single molecular layers of tungsten disulfide in water suspension includes two basic steps: Li intercalation forming Li_xWS_2 and exfoliation of the Li-intercalated compound to single molecular layers of WS_2 in a water suspension. The starting material is WS_2 powder with a particle size of 3 microns. For Lithium intercalation[3], the powder is soaked in a solution of butyl lithium in hexane for 18 hours at a temperature of 100 °C. The intercalation procedure is carried out in an Argon atmosphere glove box since the butyl lithium solution in hexane reacts with moisture and air. The Lithium interaction of butyl lithium with WS_2 or MoS_2 results in formation of octane and Li_xWS_2, where $x \geq 1$. On adding distilled water to Li_xWS_2 powder, copious gas evolution occurs and a highly opaque WS_2 suspension is formed. The reaction between water and the intercalated lithium forms lithium hydroxide and hydrogen gas, separating the WS_2 layers. At this point, a water-bilayer phase of WS_2 is obtained, as evidenced by a very-well defined and increased c-spacing of 11.8 Å from X-ray diffraction. To obtain single layer WS_2 in water suspension, the material was washed in distilled water and centrifuged at least five times. This procedure reduces the lithium concentration in the solution (pH~7) and finally breaks the water-bilayer WS_2 into single layer WS_2.

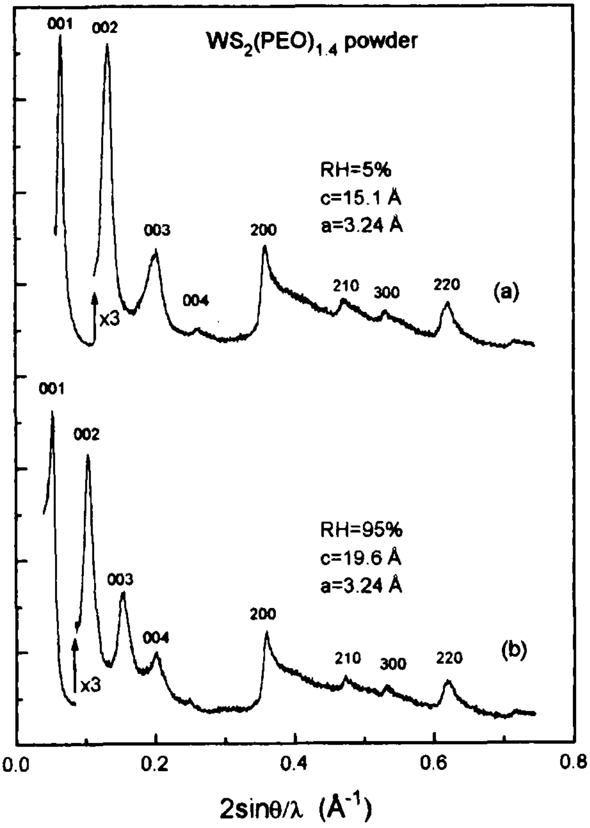

Fig. 1. X-ray diffraction patterns of $WS_2(PEO)_{1.4}$ nanocomposite powders exposed to 20°C air for (a) RH=5% and c-spacing 15.1 Å, (b) RH=95% and c=spacing 19.6 Å

The $WS_2(PEO)_{1.4}$ studied was prepared by direct flocculation of WS_2 single layers in a concentrated PEO aqueous solution. We mixed 20 ml of PEO solution (concentration: 150 mg/ml) 15 ml of WS_2 single layers in water (concentration: 20 mg/ml). The mixture was stirred for 10 minutes to complete the flocculation. Then the flocculated material was washed in distilled water and centrifuged twice to get rid of excess PEO. Finally the wet slurry was dried and ground to form $WS_2(\text{-}CH_2CH_2O\text{-})_{1.4}$ powder. The molecular ratio of ethylene-oxide unit to WS_2 was obtained by thermo-gravimetric analysis, where the $WS_2(PEO)_{1.4}$ sample was heated up to 500°C in Argon and the weight loss due to the decomposition of the polymer monitored. The average molecular weight of the PEO used was 100,000.

The X-ray diffraction pattern of $WS_2(PEO)_{1.4}$ powder is shown in Fig. 1(a). It contains two sets of peaks: the (hk0) peaks and (00l) peaks. No mixed (hkl) peaks are observed. The (hk0) peaks are of the 2-dimensional type with a strong asymmetric line shape, clearly seen in the (200) peak, with a rapid increase on the low angle side and slow decrease on the high angle side. The (00l) peaks are of the 3-dimensional type, with a symmetric line shape. This feature clearly demonstrates that the system is turbostratically restacked, i.e., the WS_2 layers are parallel to each other at the same interlayer spacing, but random in translation parallel to the layers and in rotation about the normal to the layers[6]. The c-spacing is well-defined and expanded to 15.1 Å, an increase by 9.0 Å from the original 2H-WS_2 value. The 9 Å space between the WS_2 layers is sufficient to accommodate two polymer chains.

It should be noted that single layers of WS_2 or MoS_2 are different from their bulk counterparts of 2H-WS_2 or 2H-MoS_2. They have a different structure and different physical properties. Single molecular layer WS_2 (and MoS_2) has a structure in which the W atoms are octahedrally coordinated, in contrast to the trigonal prismatic coordination of W atoms in bulk 2H- (or 3R-)WS_2. The octahedral coordination of single layer WS_2 is strongly distorted, with $2a_0$ superlattice and an expanded a-spacing. The similarity of the (hk0) peaks in Fig. 1 for $WS_2(PEO)_{1.4}$ powder to that for isolated WS_2 single layers[3] clearly demonstrates that the WS_2 in the $WS_2(PEO)_{1.4}$ nanocomposite maintains the distorted octahedral structure of the single layers. This layer distortion results in metallic behavior[3], rather than the semiconducting properties found in trigonal prismatic WS_2.

Thin oriented $WS_2(PEO)_{1.4}$ films can be formed by spin-coating the highly concentrated $WS_2(PEO)_{1.4}$ water suspension onto a glass substrate. Fig. 2(a) shows the X-ray diffraction peaks for a dried $WS_2(PEO)_{1.4}$ thin film. Only (00l) peaks are observed, indicating that the $WS_2(PEO)_{1.4}$ film is highly oriented with the basal plane of WS_2 layers parallel to the substrate. X-ray rocking curves show that the WS_2 layers in $WS_2(PEO)_{1.4}$ films are parallel to the substrate surface within ± 5 degrees.

An interesting feature of $WS_2(PEO)_{1.4}$ anocomposites is that they are extremely sensitive to humidity. As the relative humidity (RH) at room temperature increases from 0% to 100%, the c-spacing reversibly changes from 14.6 Å to 20.2 Å due to absorption of water. This difference of 5.6 Å is the same as the measured interlayer expansion due to a water bilayer in MoS_2[2]. Our X-ray studies show no humidity effects for the in-plane structure of the host WS_2 layers.

We attribute the increase in c-spacing to the absorption of water molecules between WS_2 layers, likely a monolayer of water on the WS_2 layer surfaces. We

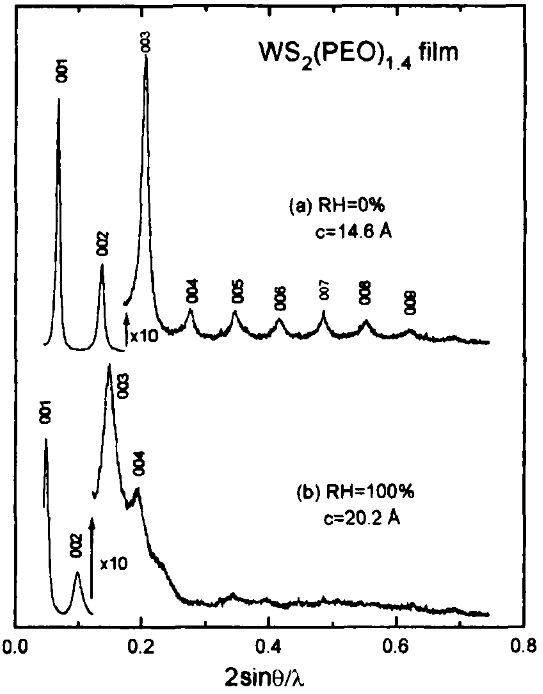

Fig. 2. X-ray diffraction patterns of a $WS_2(PEO)_{1.4}$ oriented film at 20°C for (a) RH=0% and (b) RH=100%. The c-spacing increases from 14.6 Å to 20.2 Å.

have measured the weight increase in $WS_2(PEO)_{1.4}$ on exposure to water. In comparison with completely dry air, the weight increases by 17.2% as the material exposed to air of RH = 100%, corresponding to $WS_2(PEO)_{1.4}(H_2O)_{3.2}$.

Up to the 9-th order of (00*l*) peaks is observed in $WS_2(PEO)_{1.4}$ shown in Fig. 2(a), indicating the variation of interlayer spacing is moderate. We found that more (00*l*) peaks can be observed with a relative humidity of 30 %, as shown in Fig. 3. Here the c-spacing is 16.5 Å. Seventeen orders of (00*l*) peaks are present in Fig. 3, showing that the $WS_2(PEO)_{1.4}$ is remarkably well-ordered along the stacking axis.

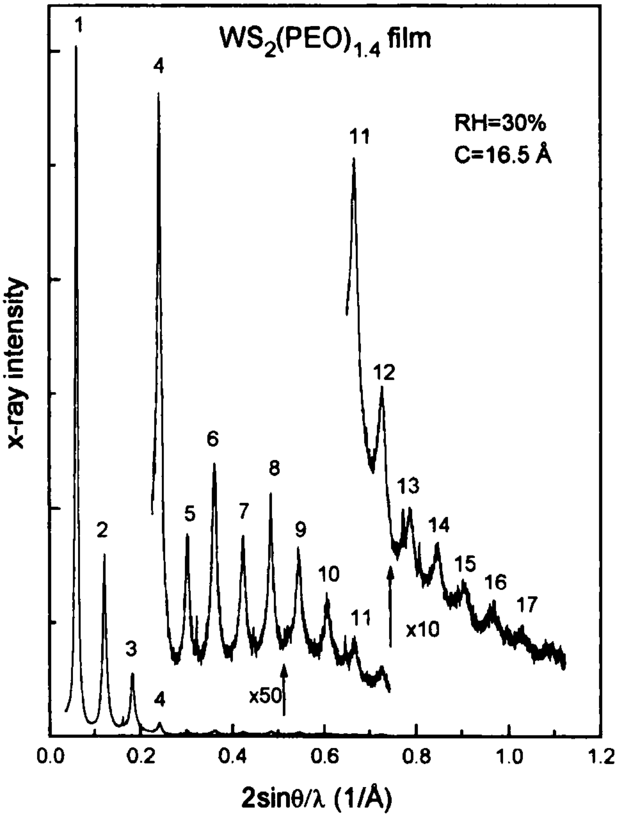

Fig. 3. X-ray diffraction patterns of a $WS_2(PEO)_{1.4}$ oriented film measured at 20°C with RH=30%.

It is well-known that the thermal fluctuation (or constant variation) of atom planes about their equilibrium position will reduce the intensity of the high order peaks. With thermal fluctuation the diffracted intensity of Bragg peaks decreases with increasing scattering angle according to the exponential Debye-Waller factor[7],

$$I = I_0 \exp(-2B\sin^2\theta/\lambda^2),$$

where I_0 is the scattering intensity for a zero-fluctuation system, and B is the temperature factor, which is given by

$$B=8\pi^2\langle u^2\rangle.$$

The $\langle u^2\rangle$ is the mean-square atomic plane fluctuation from the equilibrium position. For inorganic crystals, B is normally between 2.0 and 3.5 Å^2. For an organic solid, B can be well beyond 10. Fig. 4 is a plot of the scattering intensity (log scale) versus $S^2=(2\sin\theta/\lambda)^2$ for all seventeen (00*l*) peaks shown in Fig. 3. The peak intensity has been corrected for the active sample area, Lorentz and polarization factor, atomic scattering factor and structure factor. The structure factor was calculated using the WS_2 contribution only. A straight line is obtained over a range of two and half orders of scattering intensity. From the line slope in Fig. 4, we obtain B=11.5 and a root-mean-square atomic plane fluctuation of 0.4 Å, about 2.5 % of the c-spacing of 16.5 Å. This confirms that $WS_2(PEO)_{1.4}$ is remarkably well-ordered. Measurements at different temperatures are required to determine the relative contributions to the line intensity of thermal and constant variations in layer spacing.

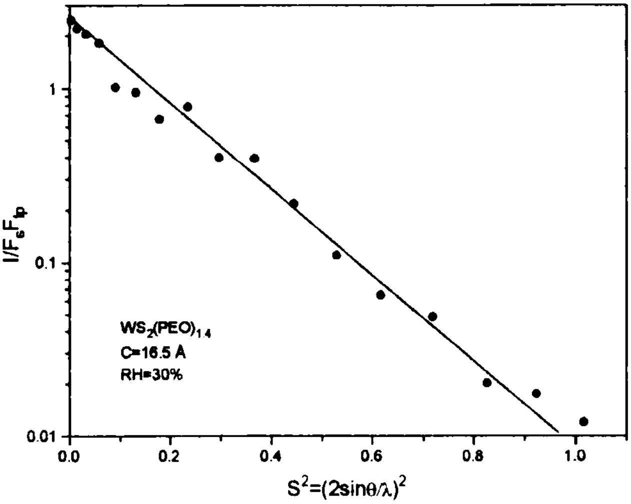

Fig. 4. A plot of scattering intensity versus the square of scattering vector for all (00*l*) peaks shown in Fig. 3.

The resistivity of $WS_2(PEO)_{1.4}$ changes with humidity. Fig. 5 shows the resistance response of an oriented $WS_2(PEO)_{1.4}$ thin film to varying humidity by alternately passing dry air (RH = 0%) and wet air (RH = 90 %) into the sample chamber. The thickness of the film is about 50 microns. The resistance of the sample increases dramatically by a factor of 12 as the relative humidity at room temperature increases from 0% to 95%, and the resistive response to humidity is reversible. The response time is well below one minute.

We have found the $WS_2(PEO)_{1.4}$ nanocomposite to be highly stable. We have monitored samples for over a year, and find no significant change in layer spacing, sample resistance or response to humidity changes.

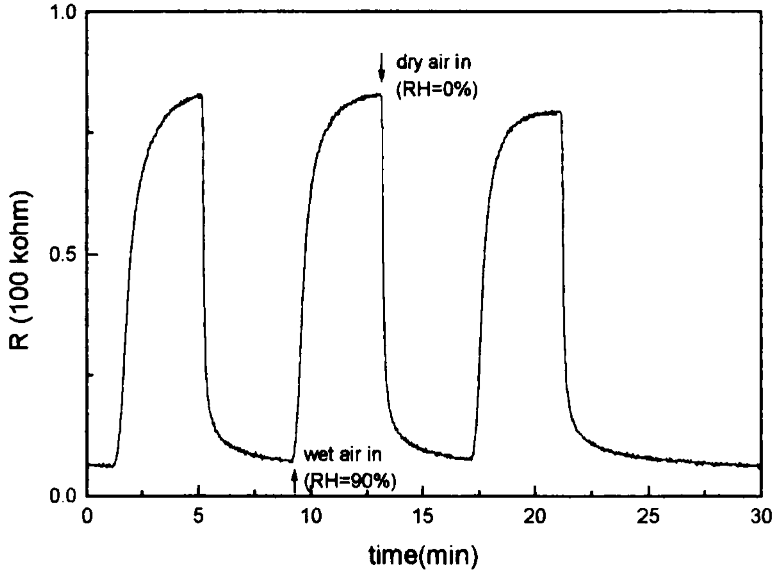

Fig. 5. The reversible response of electrical resistivity of a $WS_2(PEO)_{1.4}$ film to relative humidity, cycling between dry air at RH=0% and wet air at RH=90%.

3. Discussion

We have shown that a WS_2/PEO nanocomposite can be formed and that the WS_2 stacking is turbostratic. The separation between WS_2 layers is remarkably uniform and is sufficient to accommodate two polymer chains.

A turbostratically stacked system is like a pile of randomly stacked cards. Strictly speaking, it does not have periodicity in c-direction. It is, however, very-well ordered in the c-direction in such a way that the material has the same interlayer spacing. Our X-ray studies on $WS_2(PEO)_{1.4}$ clearly show that the material is remarkably ordered in this sense, with a fluctuation in interlayer spacing of 2.5 percent. This fluctuation arises from a combination of thermal motion and structural static fluctuations in the c-spacing. In $WS_2(PEO)_{1.4}$ nanocomposites, the polymer is unlikely to be ordered between WS_2 layers, so that some static fluctuation in the interlayer spacing is expected. We speculate that each PEO chain is in a random configuration between WS_2 layers and that the random crossover points of the PEO chains provide the pillars that separate the WS_2 layers. On the other hand, the weak force between WS_2 layers will enhance thermal fluctuations. A temperature dependent measurement is needed in order to distinguish static fluctuations from thermal fluctuations.

The molecular ratio of the absorbed H_2O to WS_2 in the nanocomposite exposed to wet air can be as high as 3.2 to 1 (as compared to 2 to 1 for a water bilayer in MoS_2[2]). The amount of water absorbed in the material shows that the physical absorption of water is a bulk effect. The fact that poly-ethylene oxide is a water soluble polymer likely enhances the absorption of water in the material.

Layered compounds in general are extremely electrically anisotropic materials with high conductivity along the layer planes, and low conductivity perpendicular to the layer planes. The dramatic increase in resistance of $WS_2(PEO)_{1.4}$ films on exposure to wet air is correlated with the increase of interlayer spacing. An increase in resistance of a material on exposure to water is unusual. The simplest explanation is geometrical and we speculate that the increase in interlayer spacing increases the c-axis resistivity and disconnects some of the conduction paths between the WS_2 layers and hence causes the measured increase in the resistivity of the films.

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