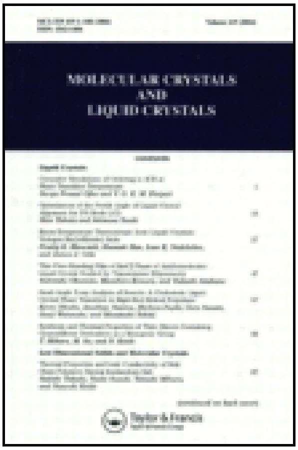

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Nanoscale Composites Formed by Encapsulation of Polymers in MoS_2. From Conjugated Polymers to Plastics. Detection of Metal to Insulator Transition.

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Abstract Polyaniline, poly(ethylene oxide), poly(propylene glycol), poly(vinylpyrrolidinone), methyl cellulose, polyethylenimine, polyethylene, and Nylon-6, were encapsulated into MoS_2. Electrical conductivity and thermoelectric power measurements of pressed pellets of $(PEO)_{0.92}MoS_2$ and $(Polyaniline)_{0.35}MoS_2$ show p-type metallic behavior. Below 14 K and 9 K respectively both show a metal to insulator transition. The thermal stability of these materials is reported.

Introduction

This work is part of a larger program in our laboratories aimed at synthesizing and exploring the properties of composite organic/inorganic polymeric materials[1]. The polymers can either be saturated or conjugated. In principle, such systems may exhibit a variety of unique properties arising from the combination of the organic and inorganic components. For example, recently researchers from Toyota prepared new molecular-scale nanocomposites made from saturated polymers (Nylon-6 and other plastics) intercalated in clay layers[2]. These products were claimed to be tougher than what is attainable by merely mixing the two components. We chose MoS_2 as the inorganic component because, in addition to being layered, it is also a semiconductor and thus, the resulting products may exhibit interesting electrical properties. Recently, MoS_2 was shown to disperse into monolayers upon contact of Li_xMoS_2 with excess water[3]. Flocculation of the layers in the presence of small molecules results in intercalation compounds[4]. We have exploited this property and used single layer MoS_2 in water and polymer solutions to produce novel polymer/MoS_2 lamellar nanocomposites.

Results and Discussion

Sonicating $LiMoS_2$ in water results in a suspension of single layers of MoS_2[3,5].

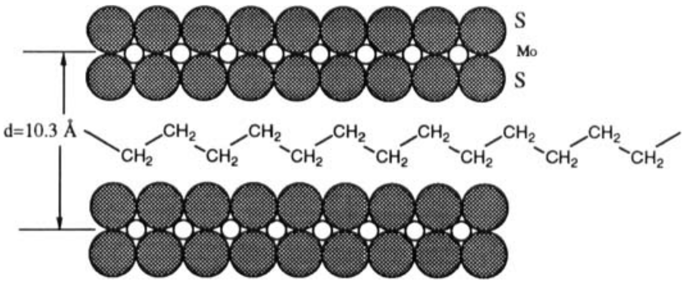
Addition of a polymer solution to the suspension causes flocculation during which the MoS_2 layers sandwich the polymer chains in a remarkably well-ordered manner. The general synthesis of $(polymer)_xMoS_2$ is shown below.

$$LiMoS_2 + xH_2O \longrightarrow (MoS_2)_{\text{single layers}} + xLiOH + (X/2)H_2$$

$$(MoS_2)_{\text{single layers}} + x\text{polymer} \xrightarrow{\text{flocculation}} (\text{polymer})_xMoS_2$$

We intercalated poly(vinylpyrrolidinone), poly(ethylene oxide), poly(propylene glycol), methyl cellulose, and poly(ethylenimine) by adding solutions of H_2O, MeOH or MeOH/H_2O mixture to an aqueous suspension of single layers of MoS_2. We have also successfully encapsulated neutral polyaniline dissolved in N-methylpyrrolidinone (a water miscible solvent), when added to an aqueous suspension of single molecular MoS_2 layers[6]. Contrary to the initial report which describes small molecule encapsulation[4], we found that this particular technique does not necessarily require the use of a water-immiscible liquid (two-phase) system. In addition, using the non-miscible solvent decalin ultra-high molecular weight polyethylene can be inserted into MoS_2. We also introduced Nylon-6 into MoS_2 using CF_3CH_2OH as a solvent.

X-ray powder diffraction patterns show that all polymer intercalates have layered structures as suggested by the intense (001) reflections, and indicate the formation of well-defined mono-or bilayers of polymers in the gallery space, see figure 1. The d-spacings, interlayer expansions and other properties for the intercalates are shown in Table 1. The largest MoS_2 layer separations were obtained from poly(vinyl pyrrolidinone) and methyl cellulose. A schematic representation of the generic structure of these materials is shown below.



Schematic representation of the structure of $(polymer)_xMoS_2$.

Interestingly, two different molecular weights of PEO give two different phases as judged by the different interlayer spacings observed. Although the origin of this is not clear, it is reasonable to assume that it reflects differences in polymer chain packing and perhaps conformation in the intralamellar space. The magnitude of the observed expansion, 8.3Å and 10.1 Å, for the high and low MW respectively, is consistent with a bilayer or multilayer of extended chains or a monolayer of chains in the coil conformation. Of course other reasonable possibilities cannot be excluded. Further experimentation is needed to distinguish between the various possibilities.

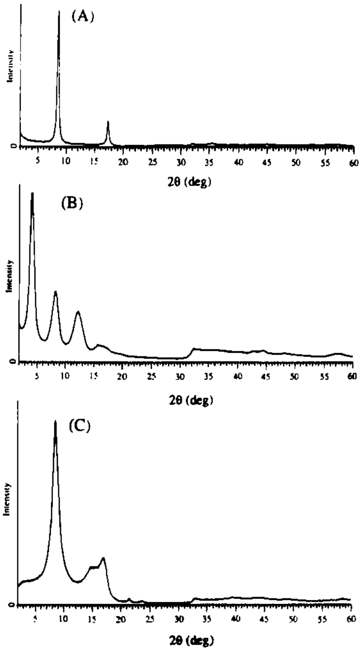


Figure 1. X- ray powder diffraction patterns of (A) $(PANI)_{0.35}MoS_2$
(B) $(PVP)_{0.76}MoS_2$
(C) $\{(-CH_2-)_n\}_{3.0}MoS_2$.

Table 1. Comparison of Some Properties of the $(Polymer)_xMoS_2$ Intercalates.

Intercalate	d-spacing (Å)	Layer Expans. (Å)	RT cond. (S/cm)	Thermal Stability (in N_2)
$(PEO)_{0.92}MoS_2$*	16.3	10.1	0.10	284
$(PEO)_{1.0}MoS_2$**	14.5	8.3	0.02	270
$(PPG)_{0.5}MoS_2$	15.4	9.2	0.20	250
$(PVP)_{0.76}MoS_2$	21.1	14.9	0.003	270
$(MCel)_{0.26}MoS_2$	20.4	14.2	0.0004	225
$(PEI)_{0.83}MoS_2$	10.2	4.0	0.005	253
$(Nylon\text{-}6)_{3.6}MoS_2$	17.5	11.3	$<10^{-6}$	320
$\{(-CH_2-)_n\}_{3.0}MoS_2$	10.3	4.1	$<10^{-6}$	425
$(PANI)_{0.35}MoS_2$	10.4	4.2	0.4	260

* MW=100000; ** MW=5000000
Abbreviations: poly(ethylene oxide), PEO; poly(propylene glycol), PPG; poly(vinylpyrrolidinone), PVP; methyl cellulose, MCel; polyethylenimine, PEI.

Preliminary charge transport studies of these materials, particularly four-probe electrical conductivity and thermoelectric power, were carried out on pressed pellets. The room temperature conductivity values are given in Table 1. Variable temperature electrical conductivity measurements for $(PEO)_xMoS_2$ (MW of polymer:100,000) indicate a surprisingly high conductivity. The data are shown in Figure 2. In the temperature range

50-300 K, the material exhibits weak, thermally activated behavior. The corresponding thermoelectric power measurements, however, indicate that the material is a p-type metallic conductor, as observed by the very small and positive Seebeck coefficient, Figure 3. A marked feature in both the conductivity and the thermopower data is an abrupt, well-defined transition at ~ 14 -15 K. Below 14 K, the conductivity decreases by 6 orders of magnitude while the thermopower suddenly discontinues its upward slope and drops to negative values. Interestingly, (PANI)$_x$MoS$_2$ shows a similar transition at 9K. This type of behavior is not typical for normal metals. However, similar anomalous decrease in conductivity at low temperatures has been reported for certain layered metallic dichalcogenide phases when doped with metal ions[7]. The metal to insulator transition in these systems has been attributed to a charge density wave (CDW)[8]. It appears that a similar CDW effect associated with an electronic instability might be operative at low temperature.

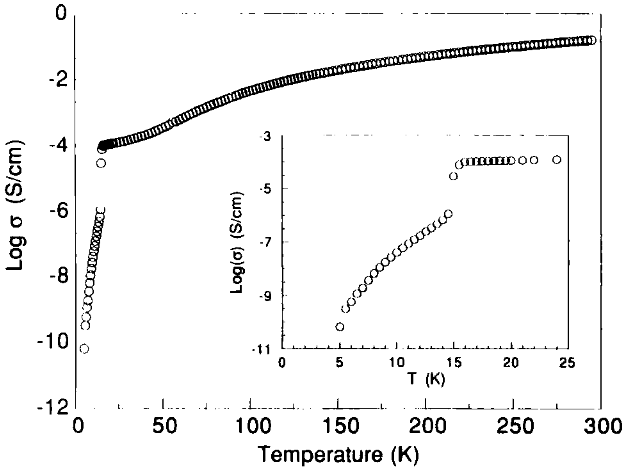


Figure 2. Four-probe variable temperature electrical conductivity data for polycrystalline pellet of (PEO)$_{0.92}$MoS$_2$. The metal to insulator transition is shown in more detail in the inset graph.

The metallic character of the intercalates can be explained by considering the structure of MoS$_2$ in these materials. Upon intercalation with lithium, 2H-MoS$_2$ undergoes a structural transformation in which the coordination of the resulting Mo^{3+} atom becomes octahedral from trigonal prismatic[9]. Upon reaction of LiMoS$_2$ with water, single MoS$_2$ layers form by rapid oxidation which leaves the Mo^{4+} atom trapped in an octahedral coordination, thereby stabilizing a metastable structure for an MoS$_2$ layer. Qualitative band structure diagrams for this configuration show that 2H-MoS$_2$ develops a band gap between the filled d_{z^2} band and empty $d_{x^2-y^2,xy}$ band, while the octahedral modification results in a partially populated band yielding a metallic state[10], see Figure 4.

The octahedral form is metastable and converts readily to the 2H-MoS_2 form. For example, differential scanning calorimetry (DSC) studies of restacked MoS_2 layers show that they transform to the more stable 2H-MoS_2 at ~100 °C, by observation of an exotherm at that particular temperature. Interestingly, the conversion temperature varies depending on the polymer involved and the associated d-interlayer spacing. The $(PVP)_{0.76}MoS_2$ shows the highest conversion temperature (T_c~177 °C) while plain restacked MoS_2 the lowest (T_c~94 °C).

The metallic MoS_2 slowly reverts to the more stable semiconductive 2H-phase upon standing at room temperature over the period of several months. This is consistent with our observations that old samples of $(PEO)_xMoS_2$ show much lower conductivity. The aforementioned structural transformation is responsible for the low conductivities found for $(Nylon\text{-}6)_{3.6}MoS_2$ and $\{(CH_2)_n\}_{3.0}MoS_2$ since they were prepared at higher temperatures.

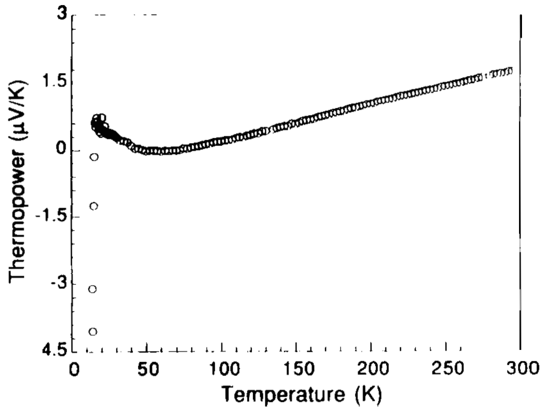


Figure 3. Variable temperature thermopower data of $(PEO)_{0.92}MoS_2$ [MW of PEO=100,000]. The data were corrected for the Au contacts.

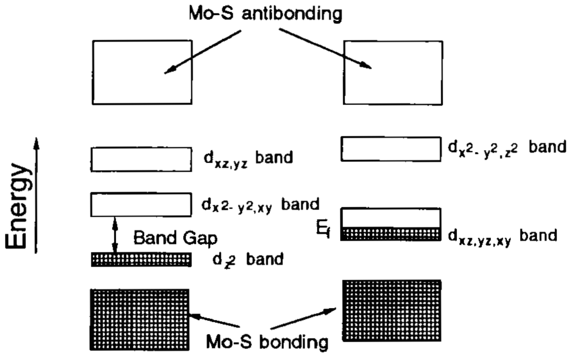


Figure 4 (A): Qualitative band diagram for a 2H-MoS_2 layer. (B) Qualitative band diagram for a MoS_2 layer in the octahedral modification. Shaded bands are filled.

Concluding Remarks

The exfoliation/reprecipitation property of MoS_2 appears to provide a general avenue by which a large variety of soluble polymers including conductive polymers can be introduced in the intralamellar space of MoS_2 and other related dichalcogenide compounds, such as those of metals from group 4 and 5[11]. This approach involves the direct intercalation of polymers and is not limited by the ability to polymerize a monomer after it has been inserted in MoS_2. These materials can offer two advantages as cathodes in solid state high energy density lithium batteries. First, the encapsulated polymers when complexed with Li would provide the desired solid electrolyte and second, the high conductivity of the layers should not necessitate the addition of conductive additives (e.g. graphite, carbon black).

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