

Encapsulation of Polymers into MoS₂ and Metal to Insulator Transition in Metastable MoS₂

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A general approach for the encapsulation of a variety of saturated polymers between the layers of MoS₂ giving electrically conductive lamellar compounds is reported.

Recently, the area of composite organic/inorganic polymeric materials, mixed at the molecular level, has been receiving considerable research interest. The organic polymers can be saturated or conjugated, while the inorganic components can be three-dimensional (3-D) systems such as zeolites,¹ 2-D layered materials such as clays² and metal oxides,³ and even 1-D materials such as (Mo₃Se₃⁻)_n chains.⁴ In principle, such systems may exhibit a variety of unique properties arising from the combination of the organic and inorganic components.⁵ For example, recently researchers from Toyota prepared new molecular-scale nanocomposites made from saturated polymers (Nylon-6 and other plastics) intercalated in clay layers.⁶ These products show extraordinary mechanical strength far greater than that attainable or expected by simply mixing the two components. Along similar lines, we chose MoS₂ as the inorganic component for intercalation with a series of saturated polymers and we present here preliminary results on materials obtained from such studies.

Recently, MoS₂ was shown to disperse into single layers by reaction of Li_xMoS₂ with water.⁷ Reprecipitation of the layers in the presence of small molecules results in intercalation compounds.⁸ We have exploited this property and used single layer MoS₂ in water and polymer solutions to produce novel polymer/MoS₂ nanocomposites. MoS₂ is attractive for investigation because it is readily available (it occurs naturally) and is already an important material with several practical applica-

tions, such as hydrodesulfurization (HDS),⁹ solid lubrication¹⁰ and rechargeable batteries.¹¹ A previous report described the polymerization of styrene in the galleries of MoS₂ to yield relatively low molecular mass polystyrene.¹² The approach reported here involves the direct intercalation of polymers and is not limited by the ability to polymerize a monomer after it has been inserted in MoS₂. Even if such polymerization can be initiated, the molecular mass of the polymer will be low and in some cases by-products could also be generated which have to be dealt with. Thus, the methodology described here is general and a very large molecular mass can potentially be intercalated.

Treatment of MoS₂ with 3 equiv. of BuⁿLi in hexanes under inert atmosphere yields LiMoS₂.¹³ Reaction of LiMoS₂ with water accompanied by sonication, results in a suspension of single layers of MoS₂. Addition of a polymer solution to the suspension causes flocculation during which the MoS₂ layers sandwich the polymer chains in a remarkably well-ordered manner; eqns. (1), (2) and (3) represent the general synthesis of (polymer)_xMoS₂.

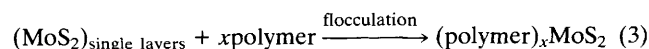
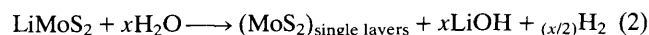
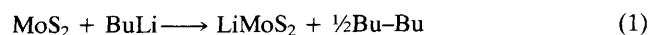


Table 1 Summary of results obtained from the encapsulation of various polymers in MoS₂

Intercalate	Polymer (M_r)	d -Spacing/Å	Expansion of layers/Å	Solvent	Room temp. cond. (S cm ⁻¹)	Thermal stability under O ₂ /°C	Thermal stability under N ₂ /°C
(PEO) _{0.92} MoS ₂	100 000	16.3	10.1	H ₂ O	0.1	225	284
(PEO) _{1.0} MoS ₂	5 000 000	14.5	8.3	H ₂ O	0.02	220	269
(PPG) _{0.5} MoS ₂	1 000	15.4	9.2	H ₂ O	0.2	200	250
(PVP) _{0.76} MoS ₂	10 000	21.1	14.9	H ₂ O	0.003	240	270
(MCell) _{0.26} MoS ₂	63 000	20.4	14.2	H ₂ O	0.0004	210	225
(PEI) _{0.83} MoS ₂	55 000	10.2	4.0	H ₂ O	0.005	248	253
(Nylon-6) _{3.6} MoS ₂	10 000	17.5	11.3	Hot CF ₃ CH ₂ OH	<10 ⁻⁶	277	320
[(-CH ₂) _n] _{3.0} MoS ₂	Ultra high	10.3	4.1	Hot decalin	<10 ⁻⁶	274	425

We intercalated poly(vinylpyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(propylene glycol) (PPG), methyl cellulose (MCell) and poly(ethylenimine) (PEI) by adding solutions in H₂O, MeOH or MeOH-H₂O-mixture to an aqueous suspension of single layers of MoS₂.[†] Using the non-miscible solvent decalin we also intercalated polyethylene of ultra-high molecular mass into MoS₂. Furthermore, we introduced the nylon-6 into MoS₂ using CF₃CH₂OH as a solvent for the polymer. All products were thoroughly washed with the appropriate solvent to remove any separate polymer phase.

X-Ray powder diffraction patterns show that all polymer intercalates have layered structures as suggested by the intense (001) reflections and indicate well-defined mono- or bi-layers of polymers in the gallery space (Fig. 1). The d -spacings, interlayer expansions and other properties for all intercalates are tabulated in Table 1. The largest MoS₂ layer separations were obtained from PVP and MCell.

The charge transport properties of these materials were determined by four-probe electrical conductivity measurements of pressed pellets. The room temperature conductivity values are listed in Table 1. Variable temperature electrical conductivity measurements for (PEO)_xMoS₂ (M_r of polymer: 100 000) indicate a surprisingly high conductivity, as shown in Fig. 2(a). In the temperature range 50–300 K, the material exhibits weak, thermally activated behaviour. 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. A marked feature in both the conductivity and the thermopower data is an abrupt, well-defined transition at ca. 14–15 K, see Fig. 2. Below 14 K, the conductivity decreases by six orders of magnitude while the thermopower suddenly discontinues its upward slope and drops to negative values. This type of behaviour is not typical for a normal metal. However, a similar anomalous decrease in conductivity at low temperatures has been reported for certain layered metallic dichalcogenide phases when doped with metal ions, e.g. 1T-Ti_{0.085}Ta_{0.915}S₂, 1T-Nb_{0.15}Ta_{0.85}S₂, 1T-Hf_{0.085}Ta_{0.915}S₂.¹⁵ The metal to insulator transition in these systems has been attributed to a charge density wave (CDW); a coupled periodic distortion of the conduction electron density with respect to the crystal lattice.¹⁶ Even though, the nature of the transition in our system is not well understood at the moment, we believe that a similar CDW effect might be operative at low

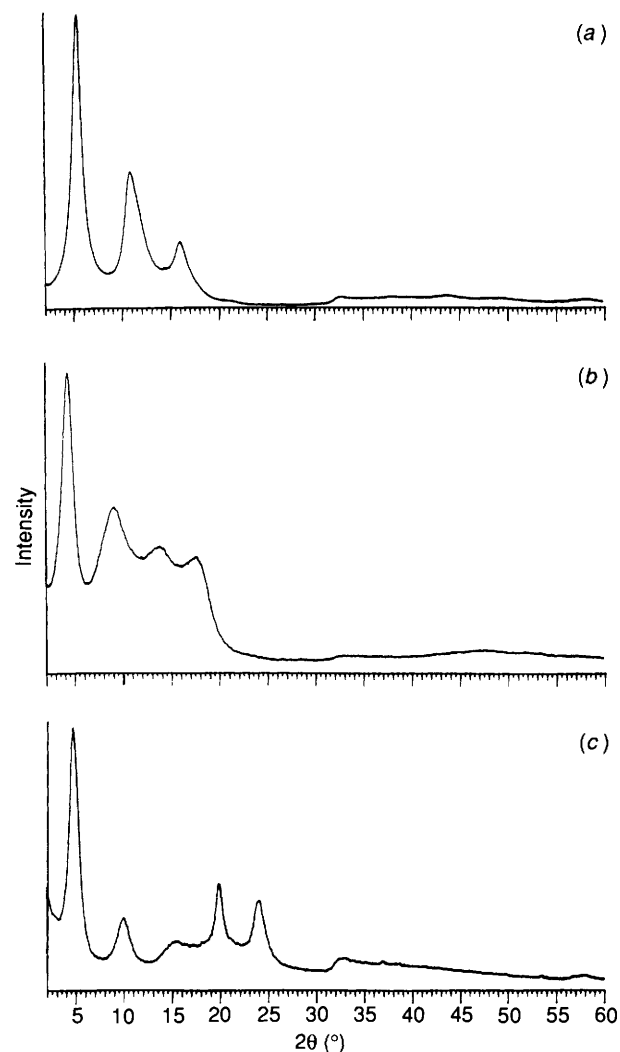


Fig. 1 XRD patterns of (a) (PEO)_{0.92}MoS₂, M_r of PEO = 100 000, (b) (MCell)_{0.26}MoS₂ and (c) (nylon-6)_{3.6}MoS₂

temperature (<14 K), creating an electronic instability. The metallic character of the material is confirmed by the magnetic susceptibility data, which show a well-behaved temperature independent Pauli-like behaviour in the 50–300 K, temperature range.

The metallic character of (PEO)_xMoS₂ is explained by considering the structure of MoS₂ in this material. Pristine 2H-MoS₂ undergoes a structural transformation upon interca-

[†] Contrary to the report of earlier workers,⁸ we found that this particular technique does not necessarily require the use of a water-immiscible liquid system. We have also successfully been able to intercalate neutral polyaniline dissolved in *N*-methylpyrrolidone (a water-miscible solvent), when added to an aqueous suspension of single molecular MoS₂ layers.¹⁴

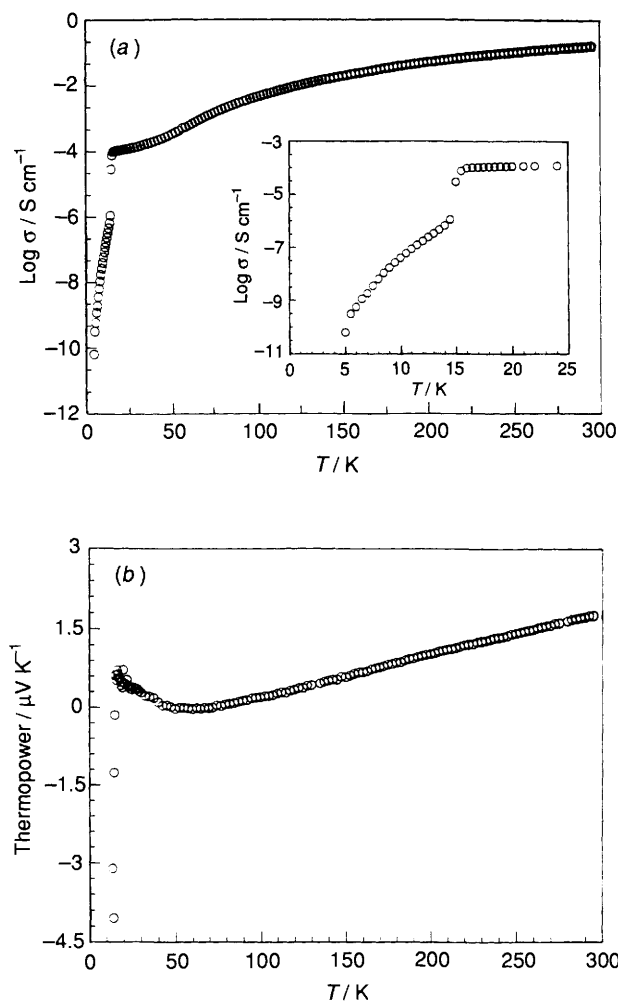


Fig. 2 (a): Four-probe variable temperature electrical conductivity data for polycrystalline pellets of $(\text{PEO})_{0.92}\text{MoS}_2$. The inset graph shows an expanded view of the low temperature data to highlight the metal to insulator transition. (b) Variable thermopower data of $(\text{PEO})_{0.92}\text{MoS}_2$ [M_r of PEO = 100 000]. The data were corrected for the contribution of the Au contacts employed during the measurements.

lation with lithium in which the coordination of the Mo^{3+} atom becomes octahedral from trigonal prismatic.¹⁷ The band diagram of 2H- MoS_2 indicates that it is a semiconductor.¹⁸ In 2H- MoS_2 each layer will be referred to as D_{3h} - MoS_2 . 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.^{17b} In this material each layer will be referred to as O_h - MoS_2 . Fig. 3 shows qualitative band structure diagrams associated with the D_{3h} - MoS_2 and O_h - MoS_2 layers. The trigonal prismatic modification develops a band gap between the filled d_{z^2} and empty $d_{x^2-y^2,xy}$ band. In the octahedral modification the degenerate $d_{xy,yz,xz}$ orbitals form a single band populated by two electrons producing a metallic system.¹⁹ Recently, Wypych and Schöllhorn reported the preparation of the metastable 1T- MoS_2 which was proposed to contain O_h - MoS_2 layers.²⁰ This phase was shown to be metallic, by its Pauli paramagnetism, and thermopower measurements. Differential scanning calorimetry (DSC) studies on our restacked O_h - MoS_2 layers show that the layers transform to the more stable D_{3h} form at ca. 100 °C, by observation of an exotherm at that particular temperature.

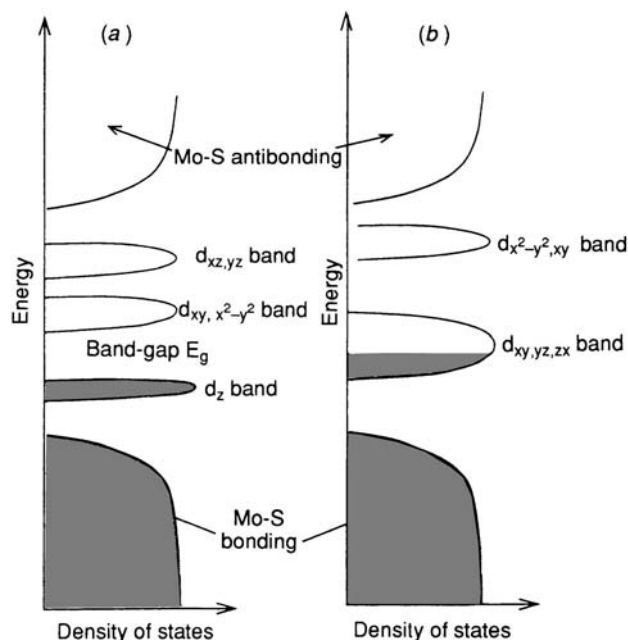


Fig. 3 (a): Qualitative band diagram of the D_{3h} - MoS_2 slab. (b) Qualitative band diagram of the O_h - MoS_2 . Shaded bands are filled. Adapted from refs. 18 and 19.

This is in good agreement with Schöllhorn's 1T- MoS_2 , which was reported to show an exothermic transition at ca. 95 °C. It appears that the material produced by restacking the dispersed MoS_2 layers and 1T- MoS_2 are one and the same product. Interestingly, the conversion temperature varies depending on the polymer involved and the associated d-interlayer spacing. The $(\text{PVP})_{0.76}\text{MoS}_2$ shows the highest conversion temperature (T_c ca. 177 °C) while plain restacked MoS_2 the lowest (T_c ca. 94 °C).

Upon aging, metallic 1T- MoS_2 reverts to the more stable semiconductive 2H-phase.^{17b} This is consistent with our observations that an aged $(\text{PEO})_x\text{MoS}_2$ sample shows three orders of magnitude lower conductivity. However, the transformation from O_h to D_{3h} is very slow and seems to take months to complete at room temperature. On the other hand, an increase in temperature, greatly accelerated this transformation. This is reflected in the observed low conductivities of $(\text{nylon-6})_{3.6}\text{MoS}_2$ and $(\text{polyethylene})_{3.0}\text{MoS}_2$ which were synthesized by refluxing the respective reaction mixtures.

The high electrical conductivities of $(\text{PEO})_x\text{MoS}_2$ and $(\text{PPG})_x\text{MoS}_2$ with respective room temperature values of 0.1 and 0.2 S cm^{-1} , are among the highest reported among polymer/host nanocomposites.³ 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 electrolyte²¹ and second, the high conductivity of the layers should not necessitate the addition of conductive additives (e.g. graphite, carbon black). The exfoliation/reprecipitation property of MoS_2 has been exploited to produce novel nanocomposites lamellar materials. This process appears to be general and should apply to a large variety of other soluble polymers including conductive polymers via soluble precursor routes such as poly(*p*-phenylene vinylene) and poly(*p*-phenylene).²²

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