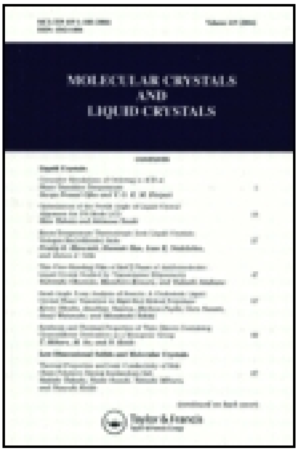

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Structure-Property Relationships in Molybdenum Disulfide Intercalates

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Structure-Property Relationships in Molybdenum Disulfide Intercalates

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The effects of host-guest and guest-guest interactions on the structure and electric cinductivity of the products of the intercalation of electron pair donors as poly(ethylene oxyde), short chain (n= 2-5) secondary amines, and long chain (n=12-18) amines into molybdenum disulfide are discussed. Although in most of the intercalates MoS_2 presents an octahedral conformation, induced principally by a host–guest charge transfer, in those with long chain amines predominate the hydrophobic intermolecular interactions bearing to products with different structural and transport properties.

Keywords Intercalation compounds; Molibdenum disulfide; Organic-inorganic nanocomposites.

INTRODUCTION

Most prominent properties of transition metal dichalcogenides are related to the lamellar nature of these compounds[1]. Mechanical, electrical, photochemical and chemical properties as well as their applications represent anisotropic phenomena related to the distinct nature of the chemical bonding in and between the layers[2]. Redox processes, causing a modification of the electronic structure of the layers, as well as chemical modification of the interlaminar space should lead to changes useful for the regulation of their properties.

Our attention has been focussed principally on the intercalation chemistry of molybdenum disulfide[3-9], specifically on the regulation of its properties by the intercalation of lithium and/or electron pair donor species. In this paper results related with the effects of the host-guest and guest-guest interactions on the structure and transport properties of the products are discussed.

EXPERIMENTAL

General procedure for the intercalation of amines or PEO into MoS_2: One equivalent of the guest is added to a suspension of exfoliated MoS_2 prepared by treating Li_xMoS_2 (x=0.9-1.2) with deionized, disaired water. The suspension is stirred during 24 h at room temperature and the solid product separated, washed, dried under vacuum, and stored under argon atmosphere. Products are characterized by elemental analysis, powder X-ray diffraction, and electrical conductivity.

RESULTS AND DISCUSSION

The stable form of MoS_2 under normal conditions, a layered structure with the molybdenum atoms surrounded in a trigonal prismatic way by sulfur atoms, differs from that in the intercalated derivatives in which an octahedral coordination at molybdenum atom is observed[3]. Both theoretical and experimental evidences indicate that for a d^2 electron configuration as in Mo(IV), a trigonal prismatic ligand arrangement is indeed the most favorable[3]. For a d^3 one, however, an octahedral ligand arrangement is preferred. From such a point of view, trigonal prismatic-octahedral phase transition is certainly favored by increasing negative charge in the MoS_2 layer, being phase change and intercalation synenergetically cooperative processes. Moreover, electron band perturbation associated to such a phase change suggests a notorious increase of the electrical conductivity of the products, a feature that could be used for detecting such a process.

The best known example of intercalation induced phase change for MoS_2 is the intercalation of lithium, where for insertion ratios beyond about 0.15 mol Li per mol MoS_2, the octahedral phase is stabilized[10].

For electron pair donors, MoS_2 also shows an octahedral configuration, even in absence of a great amount of co-intercalated lithium[6-9]. Stabilization in this case arises not only from the electron transfer from the guest but also from specific interactions of the guest in the interlaminar spaces. Figure 1 illuatrates how in the intercalation of poly(ethylene oxide), PEO, into MoS_2[6] two different pure phases may be stabilized. In a neutral medium with low lithium concentration, the compound $Li_{0.1}MoS_2(PEO)_{0.5}$ is formed. There lithium appears to be stabilized by interactions with both the host layer and the ether functions of PEO. In a basic medium containing a relatively high lithium amount, interactions PEO-lithium are strong enough to stabilize an structure in which a tetrahedral coordination of lithium ions by PEO in the interlaminar space occurs. Such structures are stable even though a relatively modest guest-host charge transfer, like that corresponding to a 10% of co-intercalated lithium, occurs. A similar behavior is observed for the intercalation of secondary amines into MoS_2[6]. Thus, in the products of the intercalation of aliphatic secondary amines (diethyl, dibutyl and dipentyl amines) $Li_{0.1}MoS_2(HNR_2)_y$ (y =0.11-0.42), the interlaminar distances are in the range 3.7-4.4 Å, being practically independent on the size of the amine molecules. Furthermore, the electrical conductivities of these intercalates are in the range 0.038-0.25 Scm^{-1}.

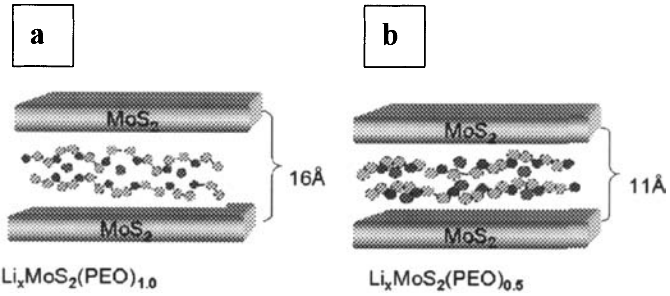

FIGURE 1 Intercalation of poly(ethylene oxide) into MoS_2.
(a) $Li_{0.1}MoS_2(PEO)_{0.5}$; (b) $Li_{0.1}MoS_2(PEO)_{1.0}$

TABLE 1 Interlaminar distances in the intercalation of the long chain amines into MoS_2.

Compound*	Interlaminar distance (Å)
$MoS_2\,(DDA)_{2.7}$	36.23 Å
$MoS_2\,(HDA)_{2.1}$	52.64 Å
$MoS_2\,(ODA)_{2.1}$	48.95 Å

*(DDA):dodecylamine;(HDA):hexadecylamine;(ODA):octadecylamine.

The behavior of the long chain amine-MoS_2 intercalates contrasts with that already described for short chain secondary amines derivatives. Interlaminar distances are rather very large and strongly depend on the size of the amine hydrocarbon chain (Table 1). Moreover, the electrical conductivity of these compounds is so low that it could not be measured ($\sigma<10^{-10}$ Scm^{-1}). Contrarily to the intercalation of donors commented above, stabilization of the products does not need the presence of residual lithium ($c_{Li}<0.01$). As illustrated in Figure 2, contrarily to the secondary amines, hydrocarbon chains are oriented perpendicularly to the MoS_2 layers. This situation is clearly different from those for the electron pair donors discussed above. Since practically no lithium is necessary for stabilizing the product, charge transfer appears to be not important in this case. The stability of the products depends entirely on hydrophobic intermolecular interactions of the guest in the interlaminar phase.

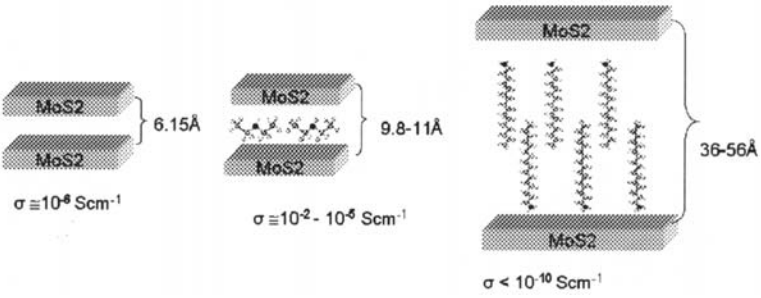

FIGURE 2. Intercalation of amines into MoS_2

CONCLUSIONS

Results discussed above show that the structural as well as other properties of intercalation compounds may be regulated by a carefully selection of both host and guest species. For the stabilization of intercalated species both, host-guest charge transfers and the interactions occurring in the interlaminar phase, are important. The contribution of the interactions occurring in the interlaminar phase may be sometimes determinant for the properties of the products. Thus for long chain amine molecules, the importance of host-guest charge transfer in the formation of the intercalates may be strongly reduced, permitting the formations of products with properties similar to those of the pristine host.

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