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High Electronic Conductivity Molybdenum Disulfide-Dialkylamine Nanocomposites

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Electronic and conformational properties of organic species confined in low-dimensional inorganic matrixes have deserved increasing interest during the past decade,[1,2] especially because of their potential use as new materials. Our interest is mainly centered in intercalation compounds with special transport properties in which two clearly identifiable phases—an inorganic rigid phase and a mobile bidimensional one constituted by an organic component—are compatible at a nanoscale level,[3,4] being thus classified as nanocomposites.[5] Now we describe a novel series of secondary amine−MoS_2 nanocomposites with conductivities as high as 10^{-1} S cm^{-1}. An analysis of observed intercalation features applying the geometrical criteria is also attempted.

The intercalation of nitrogen donors into layered matrixes, especially titanium and tantalum dichalcogenides, has been widely studied.[6−8] That marked indeed the beginning of this chemistry in the 1970s.[8] Contrastingly, the chemistry of molybdenum dichalcogenides remains, apparently due to synthetic difficulties, practically absent. However, the discovery of new synthesis methods based on the exfoliation of the pristine MoS_2[9] has led in the past few years to the description of numerous organic donors−MoS_2 intercalates.[3,4,10−12] Nevertheless, reports on the intercalation of amines into MoS_2 are still scarce. Indeed, the unique examples we know are the intercalation of alkylammonium cations[13] and of 1,10-phenantroline.[14] In the latter, however, the intercalated species appears to be not the amine but its ammonium cation.

Secondary amines react with exfoliated MoS_2, leading to layered solids $Li_{0.1}MoS_2(HNR_2)_y$[15] (Figure 1). Although the products always retain about 0.1 mol Li, the organic-to-inorganic ratio, *y*, depends on the amine. X-ray powder diffraction patterns displaying clearly 00*l* reflections show that the products are pure phases (Figure 2b). The increase of the MoS_2 interlaminar distances (Table 1) also depends on the nature of the amine. Careful washing of the products with *n*-hexane guarantees that the amine is strongly retained by MoS_2. Thermal analysis (Figure 2a) corroborates the stability of the intercalate as well as the composition of the products.[15] Any presence of water in isolated intercalates was never detected. As a result of high absorption of the matrix, FTIR spectra are relatively poor. However, absorptions in the range 3500−3300 cm^{-1}, assignable to the N−H stretching, as well as the lack of the NH^+ bending modes in the range 1635−1380 cm^{-1}, assignable to alkylammonium compounds,[16,17] agree more with the presence of free amine than with the corresponding ammonium ions.

Galvanostatic polarization experiments using electron-blocking electrodes[18] (Figure 3) show that these amine−MoS_2 nanocomposites are mixed electronic−ionic conductors and that the polarization curves follow the typical relationships deduced for these kind of compounds:[19−21]

$$U = (4U_\infty/\pi^{3/2})(t/\tau)^{1/2} \qquad \text{for } t \le \tau/2 \tag{1}$$

$$U = U_\infty - (8U_\infty/\pi^2)e^{(-t/\tau)} \qquad \text{for } t \ge \tau/2 \tag{2}$$

where U and U_∞ are the polarization potential at $t = t$ and $t = \infty$ respectively and τ the characteristic relative time. Inserts in Figure 3 show the agreement of data with these equations for the nanocomposite $Li_{0.1}MoS_2$-

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(15) The products were obtained by treating a dry *n*-hexane suspension of single layer MoS_2 with an equivalent amount of the amine. Products were carefully washed with dry hexane and dried under vacuum. Single layer MoS_2 was obtained from exfoliation of $LiMoS_2$ in an ultrasound bath during 30 min at room temperature. $LiMoS_2$ was prepared by a 48-h treatment of MoS_2 (Aldrich) with 1.6 M *n*-butyllithium in *n*-hexane (Aldrich). All intermediates were washed, dried, and characterized separately. Reactions and products manipulations were carried out under argon atmosphere. Molar weight and elemental analysis exp (calcd): $Li_{0.1}MoS_2(C_4H_{11}N)_{0.42}$, 191.35: C 10.67 (10.86), H 2.13 (2.48), N 3.94 (3.16); $Li_{0.1}MoS_2(C_8H_{19}N)_{0.19}$, 185.25: C 10.06 (9.88), H 2.28 (1.95), N 1.50 (1.44); $Li_{0.1}MoS_2$-$(C_{10}H_{19}N)_{0.11}$, 178: C 7.66 (7.41), H 1.68 (1.42), N 0.91 (0.86); $Li_{0.1}$-$MoS_2(C_9H_{11}N)_{0.21}$, 190.15: C 11.79 (11.91), H 2.32 (2.09), N 1.55 (1.54); $Li_{0.1}MoS_2(C_{12}H_{23}N)_{0.21}$, 198.77: C 14.91 (15.21), H 2.73 2.43, N 1.47 (1.47).

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Figure 1. Transmission electron microscopy micrography of the intercalation product of dipentylamine into molybdenum disulfide, $Li_{0.1}MoS_2\{(C_5H_{11})_2NH)\}_{0.11}$. The dark lines are the layers separated by about 10 Å in agreement with the *d* spacing observed by XRD.

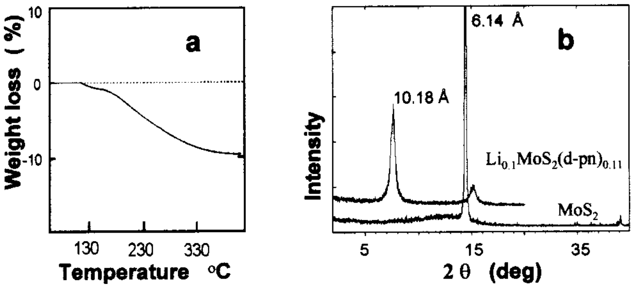

Figure 2. (a) Thermal analysis of $Li_{0.1}MoS_2$(d-pn)$_{0.11}$ and (b) powder X-ray diffraction patterns of $Li_{0.1}MoS_2$(d-pn)$_{0.11}$ and MoS_2 (Cu Kα radiation).

Table 1. Composition and Lattice Expansion of Molybdenum Disulfide–Dialkylamine Nanocomposites, $Li_{0.1}MoS_2(HNR_2)_y$

amine HNR_2	guest/host *y* (mol/mol)	lattice expansion Δ*c* (Å)
diethylamine (d-eth)	0.42	3.74
dibutylamine (d-but)	0.19	3.90
dipentylamine (d-pn)	0.11	4.04
N-isopropylcyclohexylamine (i-pr-c-hex)	0.21	4.26
dicyclohexylamine (d-c-hex)	0.21	4.45

(di-but)$_{0.19}$. Electronic conductivity to ionic conductivity ratio σ_e/σ_i for this compound is ~4 × 10^4. There had been no evidence of the actual lithium oxidation state in these compounds until now. However, because of electron pair donor capability of used amines, the main entity responsible for the ionic conductivity contribution is probably the Li^+ species.

Electrical conductivity obtained with compacted polycrystalline samples[22] (Table 2) are interestingly large.

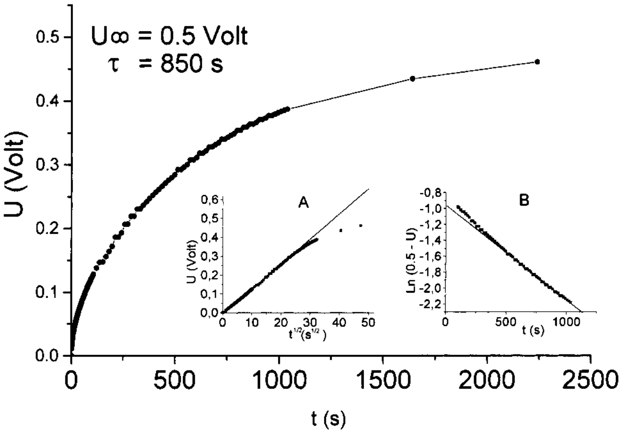

Figure 3. Galvanostatic polarization curve of $Li_{0.1}MoS_2$(di-but)$_{0.19}$ with electron-blocking electrodes. Constant current density $i = 8$ μA cm^{-2}. In the inserts, linearization of the plot at $t \leq \tau/2$ (a) and $t \geq \tau/2$ (b), according to eqs 1 and 2, respectively.

Table 2. Electronic Conductivity in Molybdenum Disulfide–Dialkylamine Nanocomposites, $Li_{0.1}MoS_2(HNR_2)_y$

HNR_2·NHN	conductivity 25 °C σ (S/cm)	activation energy[a] $\Delta H^{\ddagger}$ (eV)	correlation coefficient
d-eth	0.251	0.064	0.9959
d-i-but	0.197	0.052	0.9820
d-c-hex	0.038	0.143	0.9988
MoS_2	2.09 × 10^{-6}	0.597	0.9989

[a] $\sigma = A \exp -(\Delta H^{\circ\ddagger}/2RT)$.

It is known that the intercalation of organic guest as well as that of lithium enhances the electron transport in MoS_2.[23] However, features observed in the intercalation of amines are comparatively higher and, therefore, of great interest for the development of MoS_2-based conducting materials. Temperature dependence of the conductivity (Table 2) indicates a semiconductor behavior of the products. Relatively anomalous behavior of the dicyclohexyl derivative which also merges from structural analysis (vide infra) is being studied.

The comparison of the increase of the interlaminar distances associated to the topotactic intercalation of organic species into layered matrixes with the molecular geometry of the guest has been widely used for detecting the intercalation as well as for deducing, often with help of the intercalation ratios, the orientation of the guest in the interlaminar spaces.[24,25] The intercalation of metallocenes into MX_2 (M = Ti, Zr, Hf, Nb, Ta, Sn; X = S, Se) constitutes a still classical example.[26] There, such

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(18) Galvanostatic polarization experiments were carried out with compacted powder of the nanocomposites in the cell Li/0.5 M $LiClO_4$/sample/0.5 M $LiClO_4$/Li using a 0.5 M $LiClO_4$ solution in a 1:1 propylene carbonate–ethylencarbonate mixture as electron-blocking electrodes, with a constant current density of 8 μA cm^{-2} at 25 °C.

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(22) Electrical conductivity measurements were done by ac Complex Impedance Analysis with a PAR Model 6310 Electrochemical Impedance Analyzer. The samples were covered with gold to improve electrical contacts. Temperature was varied in the range 25–70 °C with a precision of ±0.2 °C while conductivity measurements were performed. All measurements were carried out under argon atmosphere.

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arguments lead to the conclusion that the metallocene molecules are oriented with its C_5 molecular axis parallel to dichalcogenide layers.[26] Moreover, composition and geometry of both MoS_2−naphthalene[27] and MoS_2−ruthenium arene complexes[28] intercalates have been also described using such criteria. The intercalation of secondary amines described here were also analyzed from a geometric point of view. With that purpose, we assume as a first approach (i) that the gas-phase amine molecular dimensions may be obtained from models considering both atomic van der Waals radii and optimized molecular configuration, and (ii) that, with regard to the guest in the intercalated state, it retains a configuration near to the most stable gas-phase configuration; it is arranged with their long axes parallel to the host layers; and it can rotate freely around its molecular axis. In Figure 4a, the experimental interlaminar distances are compared with those expected from calculated guest diameters.[29] Amine molecules appear to be consistently contracted in the intercalated state. An analogous although somewhat smaller volume decrease (~11%) is observed by comparing calculated gas-phase dimensions with those obtained from liquid-state densities.

Since observed interlaminar distance contraction could also arise from interstratification, it is convenient to contrast the maximal stoichiometries calculated considering both guest surfaces and available interlaminar surfaces (~8.6 Å^2 per MoS_2 unit),[14,27,28] with the observed intercalation ratios. Results are again paradoxical; experimental stoichiometries are much higher than the maximal calculated ones. However that is totally consistent with the interlaminar distances discussed above. Indeed, if for the calculations molecular amine dimensions reduced in a 25% are used, a reasonable agreement between calculated and experimental intercalation ratios is reached (Figure 4b).

Both electron density decrease and molecular rearrangements could be among the causes of observed guest size reduction. Partial guest−host charge transfer, reducing the electron density of the nitrogen lone pair orbital (HOMO), should certainly induce both van der Waals volume contraction and molecular geometry changes. Adaptation of the guest to a restricted space could not be excluded, specially by considering the small interconversion and activation energies associated to hydrocarbons isomerization. Studies directed to clarify the actual state of the confined amines are in progress.

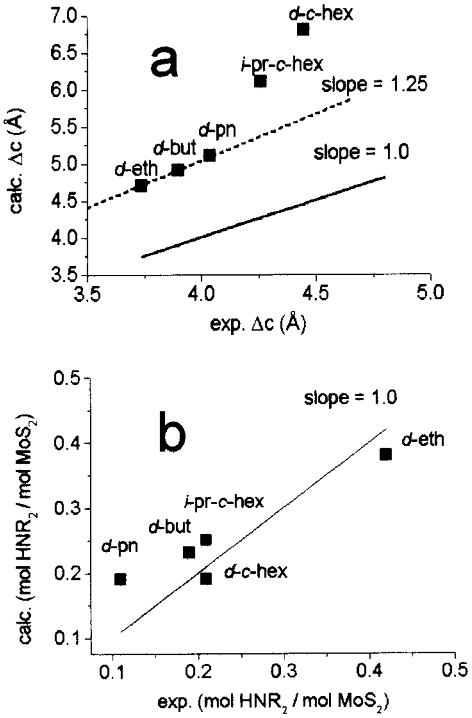

Figure 4. Geometrical model for the intercalation of dialkylamines into MoS_2: (a) Comparison of the experimental interlaminar distance increments with the amine molecular diameters calculated considering the van der Waals radii in the isolated molecule. Intercalated species appear to be contracted in ~25%. (b) Comparison of observed intercalation ratios (mole amine per mole MoS_2) with the values calculated from the molecular lengths and the molecular diameters corrected considering the contraction (25%) observed for the amines with linear substituents.

From the behavior of the new series of MoS_2 nanocomposites outlined above we can conclude that (i) intercalation induces guest volume contraction, (ii) amine contraction into MoS_2 goes beyond that in the liquid state, (iii) amine intercalation ratios nearly correspond to the formation of a compacted organic monolayer in the MoS_2 interlaminar spaces, and (iv) electronic changes associated with the nanocomposite formation lead to mixed ionic−electronic conductors displaying the highest electrical conductivity at room temperature observed until now for MoS_2 intercalates.

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