Reports

Inclusion Systems of Organic Molecules in Restacked Single-Layer Molybdenum Disulfide

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Novel materials have been obtained by restacking single-layer molybdenum disulfide (MoS_2) with organic molecules included between the layers. A large variety of organic molecules can be included between layers of MoS_2 and other transition-metal dichalcogenides. The films with the included organics are formed at the interface between an aqueous suspension of the MoS_2 and a water-immiscible organic liquid. The organic molecules are not necessarily electron donors. A highly oriented, conducting film of restacked MoS_2 containing ferrocene is presented as an example.

ORGANIC COMPLEXES OF THE METALLIC transition-metal dichalcogenides such as TaS_2 and NbS_2 (*1, 2*) can be obtained by intercalation techniques, although intercalation is restricted to organic molecules that are Lewis bases (electron donors) (*3*). However, semiconducting compounds such as MoS_2 and WS_2 have not been successfully intercalated with organics by direct reaction. The TaS_2 and NbS_2 compounds have been exfoliated into single layers (*4, 5*). Organic species have been included between the layers of such dichalcogenides and metal-phosphorus trichalcogenides MPS_3 in suspensions by ion-exchange reactions and flocculation (*4, 6–8*). In this report we describe a method for preparing a class of inclusion compounds of MoS_2 and other transition-metal dichalcogenides with organic substances that have been unavailable by conventional intercalation techniques. The organic substances are not necessarily electron donors as in the case of intercalation compounds.

A schematic diagram of the MX_2 single layer is shown in Fig. 1A. The bulk MX_2 is made up of such layers stacked in a particular order. We obtained single molecular layers of MoS_2 by exfoliation, where MoS_2 in the form of powder was first intercalated with lithium by soaking in *n*-butyllithium (*9*). Water was then added to the lithiated MoS_2 after the material was washed with hexane to remove excess *n*-butyllithium. The alkali metal between the layers is oxidized violently, and the rapid release of hydrogen gas separates the MoS_2 layers (*10*). The $Li_{0.1}(H_2O)_{0.6}MoS_2$ produced by Schöllhorn and Weiss (*11*) yields a *c* spacing of either 9.7 or 11.8 Å. No spacing corresponding to such hydrates of Li was observed with x-ray diffraction of our wet, restacked, single-layer suspensions after they were washed with water and centrifuged three to five times; thus there is no significant amount of Li in a well-washed single-layer suspension. In unwashed exfoliated MoS_2 suspensions the Li hydrate spacing was 11.8 Å. There is a distribution of lateral dimension of the single layers, a typical size being ~1000 Å.

The idealized version of the final structure of an inclusion compound is shown in Fig. 1B. Although the organic molecules are shown to be ordered, the situation in a real system could very well be different. As a representative system we discuss materials that can be prepared in the form of either thin films or powder by including ferrocene, a sandwich molecule of iron with two parallel cyclopentadienyl rings, between single layers of MoS_2.

Two interesting phenomena occur when a water-immiscible liquid (preferably an organic solvent) is added to the single-layer suspension in water and the mixture is shaken together in a glass container. First, a phase separation occurs in which the single layers leave the water and collect at the interface between the water and the immiscible liquid. With sufficient shaking, one can completely clear the suspension of MoS_2 with all single layers collected at the interface. Second, the collected layers at the horizontal interface, in most cases, spontaneously spread up the walls of the glass container.

Our model for the above phenomena is as follows. It is believed that the single layers in suspension are hydroxylated (Fig. 2A), as indicated by their negative charge (*10, 12*). The OH^- groups at edge sites are assumed to be more tightly bound than those at basal planes because the basal planes are inert compared with the edge planes (*13, 14*). Mixing with a water-immiscible organic liquid obviously modifies the suspended layers dramatically, as evidenced by their ready migration to the water-liquid interface. The attraction to the interface suggests that there are both polar and nonpolar regions on the layers at this stage. Shaking, which brings the nonpolar solvent into ready contact with the hydroxylated particles, probably induces displacement of the OH^- groups on the basal planes by the nonpolar molecules. Thus the basal regions become nonpolar while the edge regions remain polar (Fig. 2B). The modified platelets attain the lowest energy configuration at the water–organic liquid interface. The interface region can vary from one to many single layers in thickness, depending on the amount of single-layer material present in the original water suspension.

The spontaneous spreading of the collected material up the wall of the container is thought to be due to the electrostatic repulsion associated with the OH^- groups at the edge sites of the single layers. The film spreading can be described at a macroscopic level as a dramatic manifestation of the Marangoni effect (*15*), which involves the motion of surface fluids due to concentration, surface tension, or surface temperature gradients. In the familiar Langmuir-Blodgett technique, the geometry is entirely different in that only "head-tail"–like (polar-nonpolar) molecules are considered (*16*). In the case of MoS_2, macroscopic sheets of single molecular thickness with a different amphiphilicity are encountered.

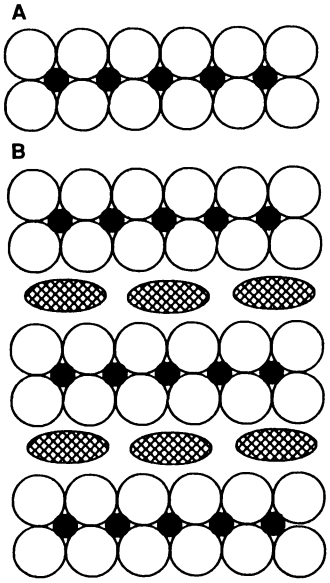

Fig. 1. (**A**) Schematic diagram of a single layer of MX_2 (M = Nb, Mo, or W and X = S or Se). Black circles represent the transition elements that are sandwiched between the chalcogen atoms represented by open circles. (**B**) Schematic diagram of an ideal organic inclusion compound of MX_2. The hatched oval shapes indicate organic molecules between the layers of MX_2.

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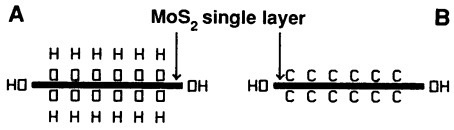

Fig. 2. Model proposed for (**A**) a single layer of MoS_2 and (**B**) a modified single layer of MoS_2 in the presence of organic molecules. A cross-sectional view of the single layers is shown, in which C represents an adsorbed organic molecule and OH represents an adsorbed hydroxyl group.

One can use the phase separation and the spreading phenomena for transferring films of organic-containing single layers of MoS_2 onto various substrates by dipping the substrates into the phase-separated, horizontal water–immiscible liquid interface. The resulting spread MoS_2 films are highly oriented with the basal surfaces of MoS_2 parallel to the substrate, as indicated by x-ray rocking curves. Generally, liquid molecules are trapped between the layers of MoS_2; molecules of volatile materials eventually desorb. One can obtain MoS_2 films devoid of foreign materials by baking them in an inert atmosphere. If a volatile solvent that is immiscible with water is used with some material dissolved in it, then one can obtain a film of MoS_2 with most likely a monolayer of that material included between the layers (*12, 17*). Alternately, one can simply pour off the liquids and dry the sample to make a powder.

As an example, a saturated solution of ferrocene, a solid at room temperature, was dissolved in a solvent such as carbon tetrachloride, benzene, or hexene and was used with a suspension of single-layer MoS_2 in water. Spread films obtained by dipping a wet glass substrate through the phase-separated MoS_2 were washed with the same solvent to remove excess ferrocene before they were analyzed by x-ray diffraction.

The x-ray diffractogram of a thin film prepared with carbon tetrachloride (Fig. 3A) shows sharp Bragg peaks that can be indexed as multiple (00ℓ) lines with an interlayer spacing of 11.8 Å. Only (00ℓ) peaks are present in this scan, indicating preferential orientation of the film. Only a single phase of material was seen in the x-ray diffraction, suggesting a homogeneous distribution of ferrocene in MoS_2. The powder diffraction patterns for the ferrocene-MoS_2 system showed that the *a* spacing of the MoS_2 is unchanged from the bulk value of 3.12 Å. Thin films of ferrocene-MoS_2, examined by electron diffraction, showed no discernible two-dimensional ordering of the ferrocene. The interlayer spacing of MoS_2 expanded by 5.6 Å (δc) with the inclusion of ferrocene. This δc value agrees closely with the size of the metallocene molecule (*18*). Similar expansions have been observed with other metallocene intercalated systems (*18–20*). Our diffraction data show that not more than a monolayer of ferrocene is included between the pairs of MoS_2 layers. The Fe/Mo ratios measured by x-ray fluorescence in a scanning electron microscope yielded an average ± SD of 5.4 ± 2.8% for ten samples, the maximum being 9.9%. This value is much less than the value of 25% observed for the metal ratio of chromocene and cobaltocene with intercalated TaS_2 and ZrS_2 systems (*2, 18*).

If we assume that ferrocene is distributed uniformly at Fe/Mo ≈ 10% (the observed maximum), then the average spacing between the molecules would be of the order of 10 Å, indicating a "pillared" structure similar to the situation observed with some clays (*21, 22*).

The x-ray diffractogram of the same sample as in Fig. 3A after heating in an argon atmosphere at 300°C for 30 min is shown in Fig. 3B. The diffractogram of unexfoliated MoS_2 powder is shown in Fig. 3C. Comparison of Fig. 3, B and C, shows that the bulk MoS_2 layer spacing is recovered upon heating with the removal of ferrocene. Bragg peaks corresponding to (00ℓ) reflections with ℓ = 1 to 3 are seen in Fig. 3B. The interlayer spacing of 6.2 Å obtained from these peaks is essentially the same as the value for unexfoliated MoS_2 (6.159 Å).

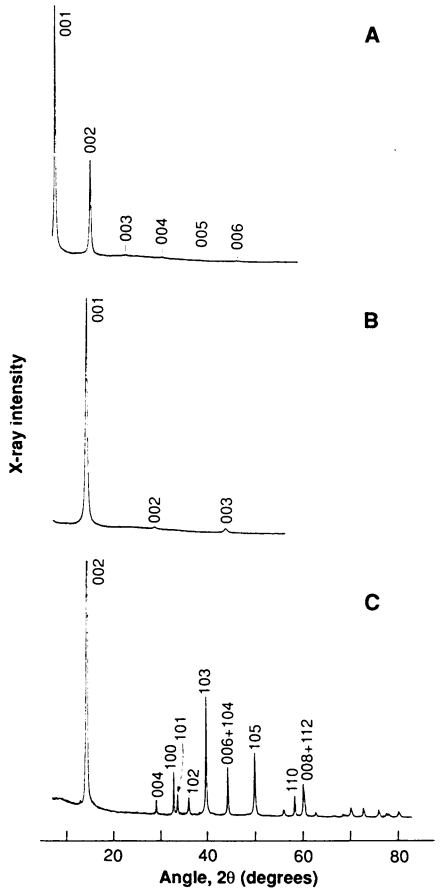

Fig. 3. X-ray diffractogram of (**A**) a film of ferrocene-MoS_2 obtained with a saturated solution of ferrocene in carbon tetrachloride and a suspension of single layers of MoS_2 in water; (**B**) the same film after the system was heated in argon at 300°C for 30 min; and (**C**) unexfoliated MoS_2 powder.

Table 1. Interlayer distances, obtained from x-ray diffraction, for MoS_2-organic systems.

System	Host interlayer distance, *c* (Å)	Host interlayer expansion, δc (Å)
MoS_2 (exfoliated and restacked)	6.2	
MoS_2–1-hexene	6.2	
MoS_2-benzene	6.2	
MoS_2–*n*-butyl alcohol	6.2	
MoS_2-dimethoxybenzene	9.6	3.4
MoS_2–*tert*-butylbenzene	9.6	3.4
MoS_2-heptane	10.1	3.9
MoS_2-styrene	11.5	5.3
MoS_2-polystyrene	12.3	6.1
MoS_2-ferrocene	11.8	5.6*
MoS_2-stearamide	56.8	50.6†

*δc for TaS_2-cobaltocene is 5.5 Å (*9*). †δc for TaS_2-stearamide is 51.0 Å (*1*).

Ferrocene between the layers of MoS_2 is stable at room temperature, as indicated by x-ray diffraction patterns obtained for a film left in room air for several months. However, experiments in which ferrocene-MoS_2 films were heated have shown that these films have a very low thermal stability, suggesting that bonding between the organometallic and the dichalcogenide is not very strong. This weak bonding is consistent with the electronic band structure of MoS_2, in which the filled dz^2 band inhibits electron transfer to the dichalcogenide (*2*). The relatively high ionization potential (6.88 eV) of ferrocene may also be relevant (*2*). Ferrocene intercalation is not mentioned in the literature to date.

We have used other organic molecules to form layer systems in MoS_2. Table 1 gives values of the interlayer spacing (*c*) and the expansion (δc) observed in other systems. Highly volatile liquids such as 1-hexene, benzene, and *n*-butyl alcohol as well as lower alkanes ($n < 7$) yield no *c* expansion, so we conclude that volatile organic molecules more readily leave the MoS_2 after the film transfer than less volatile organics.

The final layer expansion of these systems indicates that the organic molecules lie between the layers of MoS_2 with a preferred orientation, as suggested by the similarity of the layer expansion to the van der Waals dimension of the organic molecules. For example, in ferrocene the van der Waals diameter of the cyclopentadienyl ring is 5.6 Å, whereas the dimension perpendicular

to the two rings is 6.8 Å (*18*). The layer expansion of the MoS_2-ferrocene system is 5.6 Å (Table 1). Hence, the ferrocene molecules lie between the layers of MoS_2 with the planes of the cyclopentadienyl rings most probably perpendicular to the basal planes. In heptane and other higher alkanes, the van der Waals diameter perpendicular to the molecular axis is about 4 Å and the axial dimension is larger than 11.1 Å (*23*). The increase in c of systems of heptane (or higher alkanes, $n = 7$ to 12) with MoS_2 is 3.9 Å, so the molecular axis is probably parallel to the basal planes of the MoS_2.

In the new materials we have described, the included organic molecules need not be electron donors; thus a large class of exotic systems of transition-metal dichalcogenides containing polymers, organic dyes, liquid crystals, or organic semiconductors can be realized. It has recently been suggested (*24*) that the best candidates for new kinds of high-temperature superconductors are organic superconductors and inorganic layered compounds, particularly intercalated ones. In this context, this new class of restacked materials may provide an interesting combination of layered materials and organic superconductors.

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Toward Protein Tertiary Structure Recognition by Means of Associative Memory Hamiltonians

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The statistical mechanics of associative memories and spin glasses suggests ways to design Hamiltonians for protein folding. An associative memory Hamiltonian based on hydrophobicity patterns is shown to have a large capacity for recall and to be capable of recognizing tertiary structure for moderately variant sequences.

HOW THE SEQUENCE OF A PROTEIN determines its three-dimensional structure is a major unsolved question at the nexus of condensed matter physics, chemistry, and biology. It is widely (but not universally) believed that protein structure can be found by minimizing the free energy of the protein chain; numerous models using a reduced description of polymer conformation have been devised for estimating this free energy (*1*). These models give insight into the essential physics, but a systematic approach seems necessary to solve the structure prediction problem. One way to develop simplified models is to use inverse statistical mechanics: a great deal of information on protein structure is available, so that we ask, "Is there a way to infer a Hamiltonian that will give the known structures?"

The theory of associative memories as developed by Hopfield and others (*2, 3*) is an application of inverse statistical mechanics that draws upon analogies with spin systems and spin glasses. Many aspects of protein thermodynamics and dynamics have also been related to spin systems and their phase transitions (*4–7*). The oldest of these connections is the description of secondary structure formation that makes use of one-dimensional Ising models for helix-coil transitions (*5*). Researchers have used the direct connection to spin models to develop secondary structure prediction schemes (*8, 9*) based on associative memories. It is clear, however, that secondary structure is determined in part by influences distant in protein sequence and, therefore, it is appropriate to address the question of tertiary structure directly. Abstract statistical mechanical models have already been used to investigate aspects of tertiary structure formation with notions from spin glasses and associative memories (*7*). These studies have, however, not presented structural inference schemes. In this report, we propose a simple version of an associative memory Hamiltonian appropriate for predicting tertiary structure; the framework is easily extended. The applicability of the Hamiltonian to the recall of structures from a given database, and, to a modest extent, its ability to generalize from variant sequences are assessed.

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We describe tertiary structure by the α-carbon (Cα) coordinates of the protein. Sequence information is encoded in "charges," which are measures of hydrophobicity, size, electrical charge, and other amino acid properties. Folding is the arrangement of these charges into particular patterns. Our viewpoint is that folding is essentially crystallization in a finite system, thereby suggesting an analogy between proteins and associative memory spin systems that undergo phase transitions.

In spin associative memories, the interactions are given by the spin correlation function over the memory set (*2*). Similarly, the interaction potential for protein residues can be chosen as the "charge" density correlation function over the database. Thus the Hamiltonian in terms of the Cα coordinates is

$$H = -\sum_{i \neq j} \sum_{m,n} \sum_{\alpha} \lambda_{m,n}\, q_{m,i}\, q_{n,j}$$

$$q^{\alpha}_{m,i}\, q^{\alpha}_{n,j}\, \theta_{sw}(r_{ij} - r^{\alpha}_{ij})$$

where $\lambda_{m,n}$ is the weight of terms containing charges of the type m and n, $q_{m,i}$ is the mth charge of the ith residue of the protein to be folded, $q^{\alpha}_{m,i}$ is the corresponding charge for the αth protein in the memory database, θ_{sw} is a square-well function centered about zero, r_{ij} is the distance between the Cα's of residues i and j, and r^{α}_{ij} is the analogous quantity for the memory proteins.

This Hamiltonian is a function only of scalar distances and is therefore translationally and rotationally invariant. With a single memory, it may be used to determine structures consistent with distance constraints derived from nuclear magnetic resonance (NMR). The Hamiltonian's interactions are quite long range and capture the nonlocality of folding. Mean-field theories based on this Hamiltonian should be reasonably accurate. They suggest that recall should be essentially perfect for small databases. If the database is uncorrelated, then as the number of memo-