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SINGLE-LAYER MoS_2

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ABSTRACT

MoS_2 has been exfoliated into monolayers by intercalation with lithium followed by reaction with water. X-ray diffraction analysis has shown that the exfoliated MoS_2 in suspension is in the form of one-molecule-thick sheets. X-ray patterns from dried and re-stacked films of exfoliated MoS_2 indicate that the layers are randomly stacked. Exfoliated MoS_2 has been deposited on alumina particles in aqueous suspension, enabling recovery of dry exfoliated MoS_2 supported on alumina.

MATERIALS INDEX: molybdenum disulfide.

Introduction

For some time there has been a wide interest in two-dimensional systems from both a theoretical and experimental point of view. In this regard there has been considerable interest in the transition metal dichalcogenide layered compounds, a group of materials which are often considered to be two-dimensional because of the high anisotropy resulting from strong bonding within the layers and weak interlayer interactions (1). Additional interest in layered compounds arises from the fact that they can be intercalated with a variety of metals and compounds (2,3).

Exfoliation of the metallic layered compounds TaS_2 (4,5) and NbS_2 (5) by intercalation of hydrogen and water has been previously reported. We report here on the exfoliation of the semiconducting layered compound MoS_2 using a novel technique. We believe this is the first report on exfoliation of any semiconducting layered compound. In addition to the possibility of having practical applications, we believe that studies on single-layer MoS_2 and re-stacked MoS_2 can uniquely contribute to a general understanding of the layered compounds.

A single layer of MoS_2 consists of a sheet of Mo atoms sandwiched between two sheets of S atoms. In the most common naturally-occurring polytype, 2H-MoS_2, there are two layers per unit cell (1).

MoS_2 is well known as an active hydrodesulfurization catalyst, and numerous methods for the preparation of unsupported and supported MoS_2 have been described in the literature (6,7). In contrast to these techniques, which entail the synthesis of MoS_2 from other molybdenum compounds, the present contribution reports a method that uses bulk MoS_2 as the starting material. The method consists of exfoliation of MoS_2 in aqueous suspension, with or without alumina present, followed by flocculation or centrifuging and/or drying to obtain supported or unsupported materials.

The purposes of the present study were to prepare high surface area unsupported and supported MoS_2 by novel techniques, and to prepare MoS_2 with various proportions of basal plane and edge plane areas, so that further work (8) on active sites could be pursued. Our technique of exfoliation in aqueous suspension has also led to studies (9) on the inclusion of foreign species between the layers of re-stacked MoS_2.

We report here on X-ray diffraction studies of single-layer MoS_2 and compare our data to theoretical predictions. We believe that this is the first quantitative experimental work showing a single-layer diffraction pattern.

Methods

The starting material used in the reported studies was 2H-MoS_2 powder (-325 mesh) from Materials Research Corporation. The technique developed for the exfoliation of the MoS_2 is as follows. The MoS_2 was first soaked in a 1.6M solution of n-butyl lithium in hexane for a least 48 hours, in a dry box containing an argon atmosphere. This is known to intercalate the MoS_2 with lithium (10) to a mole fraction of at least $x = 1$. Following the intercalation of the MoS_2 by lithium, the MoS_2 was removed, washed repeatedly in hexane, dried, and sealed in a vial, still in the dry box under argon atmosphere. The vial was then removed from the dry box, immersed in water, and the cap removed from the vial. Upon contact with the water copious gas evolution followed and the MoS_2 powder formed a highly opaque suspension in the water. The suspension was ultrasonicated during the reaction to assist in the exfoliation.

It is assumed that the reaction between the water and the intercalated lithium forms hydrogen gas between the layers, and the expansion of this gas tends to separate the MoS_2 layers. As the reaction proceeds more deeply into each crystallite the layers become further separated. Eventually the layers become completely separated and remain suspended in the aqueous solution. The pH of the solution was moderately basic at this stage due to the presence of lithium hydroxide.

Although the results reported below refer to samples exfoliated in water, we have also exfoliated lithium-intercalated MoS_2 in methanol, ethanol, and isopropanol, as well as by rapid heating in vacuum to approximately 600C.

The as-received unexfoliated MoS_2, when suspended in water, settled out in times of the order of 10 minutes. MoS_2 exfoliated in water (at neutral to basic pH) remained in suspension for several days or more. Flocculation occurred rapidly (within one hour) when the pH was reduced to a value of 2 or less. With the addition of a surfactant, the particles remained in suspension for at least several months, requiring ultracentrifugation to clear the suspension.

Using no surfactant, it was found by experimentation that if exfoliation took place in the presence of a sufficient quantity of alumina powder, or if alumina powder was introduced following the exfoliation, the suspension would clear in a few minutes, implying deposition of the flakes of MoS_2 onto the alumina under conditions when it would not adhere to itself (flocculate). The deposition on alumina provided a method of removing the exfoliated MoS_2 from suspension without re-stacking by flocculation. Such "supported" samples were washed to remove lithium hydroxide, then dried. The amount of alumina (one micron diameter powder) necessary to clear a suspension of exfoliated MoS_2 was such that the total area of the alumina was approximately matched to half the total area of the MoS_2 (as calculated knowing the mass of MoS_2 and assuming single-layer dispersion). The suspension did not clear if insufficient alumina was present, indicating that the alumina particles became covered with monolayers of MoS_2 particles. Deposition of multilayers, if desired, was achieved at this point in the process by lowering the pH to cause flocculation. Numerous samples of alumina-supported MoS_2 were prepared; varying amounts of coverage were achieved using MoS_2 monolayers and multilayers. Typical proportions of MoS_2 to alumina were in the range 0.5% to 10% MoS_2 by mass. The characterization of these samples is reported elsewhere (8). We believe that the preparation of supported MoS_2 layers as described here is novel and will have important practical applications.

Results

Chemical analysis of dried exfoliated MoS_2 was carried out using a Perkin-Elmer model 595 scanning Auger microprobe (SAM) and a model ISI-DS 130 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer. Both forms of analysis showed that the ratio of Mo to S was unchanged (within approximately 5%) by exfoliation, indicating that the MoS_2 had not reacted to form other compounds. No new elements (e.g. lithium or oxygen) were detected after exfoliation. From the SAM results, oxygen, if present, comprised less than 0.5% of the surface regions of the samples analyzed. In contrast, analysis of MoS_2 exfoliated and re-stacked in the presence of suitable foreign species in solution did indeed show that foreign material can be included within the layers (9).

X-ray diffraction patterns were obtained with a Philips diffractometer using nickel-filtered Cu K-alpha radiation. The diffraction patterns for untreated 2H-MoS_2 (the starting material), for exfoliated MoS_2 in suspension, and for dried and re-stacked MoS_2 films are shown in Figure 1. In Figure 1(d), the pattern for exfoliated MoS_2 in suspension, the absence of the {002}, {103}, and {105} lines is strong evidence for monolayers. The suspension was a concentrated slurry obtained by centrifuging a more dilute suspension. In Figure 1(c), the pattern for a dried and re-stacked powder, the width of the {002} line indicates from the Scherrer formula (11) that the average correlation distance along the c-axis is approximately 8 layers. Random stacking is indicated by the asymmetric broadening of the {100} line (12) as well as by the near-absence of the {103} and {105} lines, and is consistent with calculations for interlayer rotation about the c-axis (13). Figure 1(b) is for a sample which was not ultrasonicated during exfoliation. In this case, the remaining presence of the {103} and {105} lines indicates that the layers had not completely separated, so that the resulting powder consisted of microcrystallites of MoS_2 with thicknesses of at least several layers.

Comparison of the data in Figure 1 with diffraction patterns calculated for crystallites of MoS_2 having thicknesses of 1,2, 3, and 4 molecular layers (13), shown in Figure 2, provides further demonstration of the small particle

thickness achieved. In particular, the striking agreement between Figure 1(d) and the calculated curve for one MoS_2 layer provides convincing evidence that Figure 1(d) is a single-layer diffraction pattern and that we have obtained totally exfoliated MoS_2. We have carried out single-layer calculations similar to those in Reference 13 and have determined that the shoulder on the {100} line at an angle 2θ of about 40 degrees is due to sulfur scattering. Our experimental results are consistent with the bulk S-S distance (sandwich height) of 3.17Å used for Figure 2.

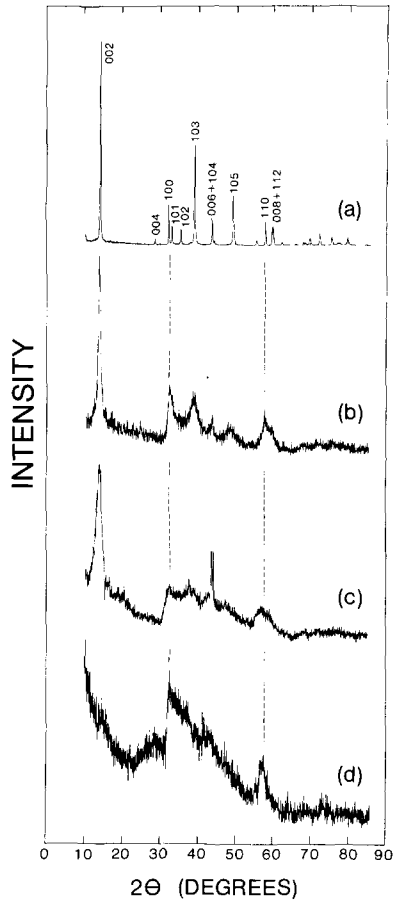

FIG. 1

X-ray diffraction patterns for (a) untreated MoS_2, (b) a dried film of partially exfoliated MoS_2, (c) a dried film of completely exfoliated MoS_2, and (d) completely exfoliated MoS_2 in suspension in water. The two sharp peaks in (c), midway between the {100} and {110} peaks, are not due to the sample.

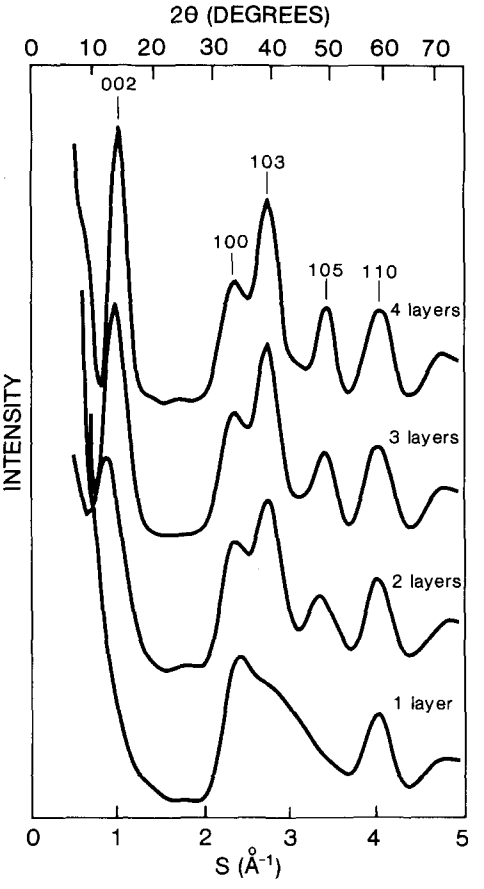

FIG. 2

Calculated X-ray diffraction patterns for microcrystallites of 2H-MoS_2. The number of layers varies from 1 to 4, with each layer containing 6x6 Mo atoms. [After Chien et al. (13)]

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