Chem. Mater. **1993**, *5*, 595–596

New Intercalation Compounds of Conjugated Polymers. Encapsulation of Polyaniline in MoS_2

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Received March 24, 1993

The insertion of conjugated polymers in layered host materials and other structurally organized environments is a topic of considerable interest because the resulting organic/inorganic nanostructures can possess novel electrical, structural, and mechanical properties.[1,2] Such systems can potentially show hybrid properties synergistically derived from both the host and the guest.[3] We have reported that the *redox intercalative polymerization* (RIP) of pyrrole, thiophene, and aniline to the corresponding conjugated polymers in $V_2O_5{\cdot}nH_2O$ and FeOCl produces well-ordered compounds with enhanced electrical properties.[4] This process works only with suitably oxidizing hosts and can be applied to other hosts to the extent that they can accept electrons at a low enough potential. Therefore, non-oxidizing hosts are not suitable for RIP. To broaden the scope of these new hybrid materials to other layered systems, we must use other synthetic methodologies for introducing polymers in non-oxidizing hosts. Here we report the encapsulation of polyaniline (PANI) in MoS_2, giving rise to a novel nanoscale molecular composite with unusual charge-transport properties.

Transition-metal dichalcogenides have been extensively investigated for their interesting electrical properties and their application as cathode materials for rechargeable high-energy-density lithium batteries.[5] MoS_2 is distinguished among the metal–dichalcogenides for not intercalating organic molecules such as pyridine, ammonia etc. As they are hard to reduce, intercalation into MoS_2 is possible only with highly reducing agents such as alkali metals.[6] Recently, however, MoS_2 was shown to disperse into single layers by reaction of Li_xMoS_2 with water.[7] Reprecipitation of the layers in the presence of small molecules gives intercalation compounds of MoS_2. We have exploited this important property and used single-layer MoS_2 in water and *N*-methylpyrrolidinone (NMP) solutions of PANI to produce a novel nanoscale composite material containing well-ordered alternating monolayers of PANI and MoS_2.[8] The addition of PANI solution to a suspension of single layers of MoS_2 causes flocculation during which the MoS_2 layers sandwich the PANI chains in a remarkably well-ordered fashion to produce a single-phase product. The synthesis of $(PANI)_{0.35}MoS_2$ (**I**) is represented in eqs 1 and 2.

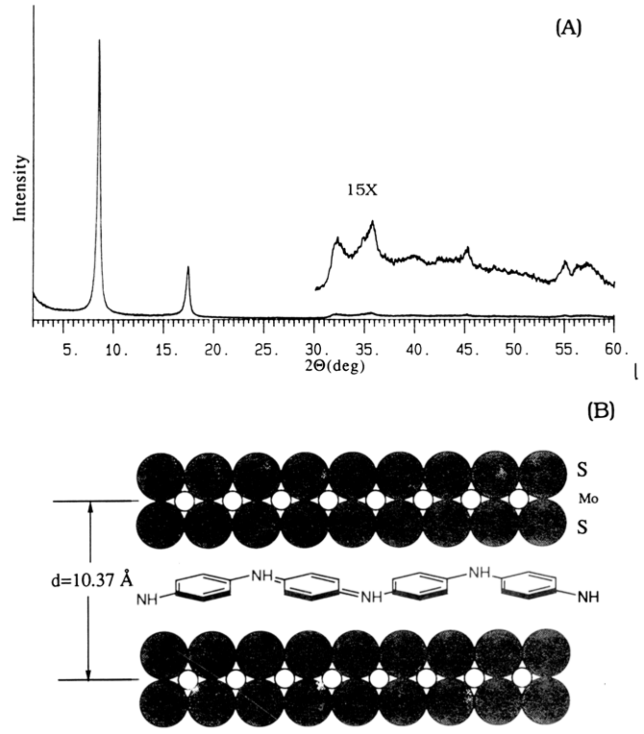

Figure 1. (A) X-ray powder diffraction pattern of $(PANI)_{0.35}MoS_2$. (B) Schematic representation of the lamellar arrangement of $(PANI)_{0.35}MoS_2$.

$$Li_xMoS_2 + xH_2O \rightarrow (MoS_2)_{\text{single layer}} + xLiOH + (x/2)H_2 \tag{1}$$

$$(MoS_2)_{\text{single layer}} + xPANI \rightarrow (PANI)_xMoS_2 \tag{2}$$

The black product shows a clean, sharp X-ray powder diffraction pattern, shown in Figure 1A, and an interlayer spacing of 10.37 Å. This represents an expansion of the MoS_2 layers by 4.2 Å, in good agreement with what is expected for a monolayer of PANI lying flat in the van der Waals gap. A schematic structure of this material is shown in Figure 1B. The stoichiometry $(PANI)_{0.35}MoS_2$ was determined by elemental analytical data and thermal gravimetric analysis measurements. No evidence for co-intercalation of solvent was found. The material is

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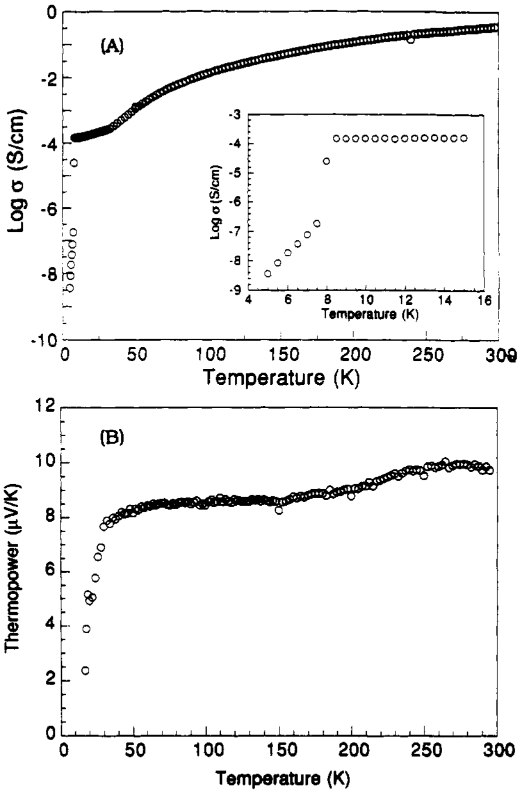

Figure 2. (A) Four-probe variable-temperature electrical conductivity of a polycrystalline pellet of $(PANI)_{0.35}MoS_2$. (B) Variable-temperature thermoelectric power of a polycrystalline pellet of $(PANI)_{0.35}MoS_2$. The inset in A shows an expanded view of the low-temperature data to highlight the metal-to-insulator transition.

thermally stable under nitrogen up to 260 °C and in oxygen up to 230 °C. PANI was characterized by FTIR spectroscopy after extraction from the metal–dichalcogenide framework using hot, concentrated H_2SO_4.[9]

The charge-transport properties of **I** were explored by four-probe electrical conductivity and thermoelectric power measurements of pressed pellet samples in the temperature range 5–300 K. $(PANI)_{0.35}MoS_2$ is highly conductive at room temperature, reaching values of 0.4 S/cm, which ranks among the highest reported for polymer/host nanocomposites. Conductivity measurements show weak, thermally activated transport behavior for temperatures above 50 K; see Figure 2A. Corresponding thermoelectric power data show a p-type, metallic behavior, as indicated by the small magnitude, positive Seebeck coefficient; see Figure 2B. A remarkable feature of both the thermopower and especially the conductivity data is an abrupt transition in transport behavior at low temperature. Between 8 and 9 K the conductivity of this sample changes by 3 orders of magnitude. Below this reversible transition the sample displays very strongly temperature dependent behavior, with the conductivity changing by an additional factor of 100 between 5 and 8 K. The inset of Figure 2A shows an expanded view of the region 4–16 K where this reversible transition occurs. The transition region was measured with both increasing and decreasing temperature, and the data show excellent agreement. As seen in Figure 2B, the thermoelectric power changes drastically near 30 K, with weak variation in thermopower at higher temperatures but with rapidly varying response below this point. These data have not been corrected for the contribution of the Au sample leads because that process has reduced accuracy below 50 K, and therefore corrected data would preclude showing the transition region. For temperatures less than ~13 K, the sample resistance increased to values such that accurate thermoelectric power measurements could not be taken and this provides further evidence of a transition to an insulating state in this material. It is important to note that different pressed pellets of this material were used for the two transport measurements, and it is believed that this may account for the variations in the apparent transition temperature. Magnetic susceptibility measurements confirm the metallic nature of $(PANI)MoS_2$, showing a well-behaved, temperature-independent Pauli-like paramagnetism in the 20–300 K region. The metal-to-insulator transition is also indicated here by a sudden change to Curie–Weiss paramagnetism below ~12 K. These results reveal an intriguing new instability in that neither PANI nor MoS_2 shows such a metal to insulator transition alone. This unique behavior is under further study at this time.

The metallic character of $(PANI)_xMoS_2$ is explained by considering the structure of MoS_2 in this material. Pristine semiconducting 2H-MoS_2 undergoes a structural transformation upon intercalation with lithium in which the coordination of the Mo^{3+} atom becomes octahedral from trigonal prismatic.[10] 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.[10b] Recently, Schöllhorn reported the preparation of the metastable 1T-MoS_2 which was proposed to contain octahedral Mo^{4+} centers.[11] This phase was shown to be metallic, by its Pauli paramagnetism, and themopower measurements. We believe that the restacked MoS_2 layers in $(PANI)_xMoS_2$ and those in 1T-MoS_2 are isostructural and thus have similar electronic properties. However, no metal-to-insulator transition was reported for 1T-MoS_2. Preliminary charge-transport data on plain restacked MoS_2 show similar electrical properties for this material confirming the arguments presented above.[12]

In summary, the exfoliation/reprecipitation property of MoS_2 can be exploited to produce a novel molecular nanocomposite lamellar material containing polyaniline. This approach is expected to be general and should apply to other soluble conjugated polymers such as poly(alkylthiophenes), polypyrroles, and even polyacetylenes.[12] Since conductive additives (e.g., graphite, carbon black) are often used in Li/MoS_2 rechargeable batteries to improve electrical access of the entire cathode material, the high conductivity of polymer/MoS_2 molecular composites reported here may give them an advantage as battery electrodes.

Acknowledgment. Financial support from the National Science Foundation (DMR-8917805) is gratefully acknowledged. M.G.K. is an A. P. Sloan Foundation Fellow 1991–1993. At Northwestern University this work made use of Central Facilities supported by NSF through the Materials Research Center (DMR-9190521).

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(9) Fourier transform infrared (FTIR) spectroscopy of these intercalated dichalcogenides show weak peaks that can be attributed to PANI. Although a considerable amount of polymer exists in the material, the weak intensities of the PANI vibration peaks is due to the highly conductive nature which reflects infrared radiation.

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