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Communications

Entrapment of Polypyrrole Chains between MoS_2 Layers via an in Situ Oxidative Polymerization Encapsulation Reaction

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Recently, the general class of nanocomposite organic/inorganic materials, mixed at the molecular level, has been receiving considerable research interest. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The organic polymers can be saturated or conjugated, while the inorganic components can be three-dimensional framework systems such as zeolites,[1] two-dimensional layered materials such as clays[2,3] and metal oxides[4,5] and even one-dimensional materials such as $(Mo_3Se_3^-)_n$ chains.[6] In principle, nanocomposite organic/inorganic materials may exhibit a variety of unique properties arising from the combination of the organic and inorganic component.[7,8] Recently, we have shown that single-layer MoS_2 can encapsulate a variety of polymers to produce novel electrically conductive polymer/MoS_2 nanocomposites.[9,10] The methodology we have described is general and suitable for intercalation of very large MW polymers provided these polymers are soluble. Intractable materials, however, present a limitation to this approach. For example, the interesting but intractable conjugated polymers polypyrrole and polythiophene are not suitable in this case. Although insertion of these two polymers into several layered hosts has been demonstrated by in situ intercalative redox polymerization, it proceeds only if the hosts are good oxidants as is the case for FeOCl[11] and V_2O_5 xerogel.[12] We report here a new modification in the in situ intercalative polymerization reaction which, for the first time, allows the intercalation of polypyrrole into MoS_2.

The $(ppy)_{0.24}MoS_2$ (ppy = polypyrrole) was prepared by oxidizing an aqueous solution of single MoS_2 layers and pyrrole with $FeCl_3$.[13] The latter was added dropwise to the solution of the mixture and caused two important events to occur at the same time, polymerization of the pyrrole followed by coprecipitation of the MoS_2 layers. This results in a new lamellar nanocomposite material that is made of metal dichalcogenide layers and chains of polypyrrole. What is surprising about this process is the deposition of a single-phase material as opposed to a phase-separated material composed of a mixture of bulk polypyrrole and restacked MoS_2. The following evidence supports this conclusion. First, the X-ray powder diffraction patterns show an interlayer expansion of ∼4.5 Å which is consistent with a monolayer of polypyrrole in the gallery space; see Figure 1. A similar expansion was found for the polyaniline intercalated material.[9,14] Second, elemental analysis is consistent with computer models that predict a maximum possible stoichiometry of $(ppy)_{0.30}MoS_2$.[15] Third, the infrared spectra of the $(ppy)_{0.24}MoS_2$ show the polymer stretching vibrations at energies higher than those found in bulk polypyrrole, prepared under the same experimental conditions minus the MoS_2 layers. The average blue-shift for most peaks is ∼10

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(13) An amount of 0.20 g of $LiMoS_2$ (1.20 mmol) was exfoliated in 20 mL of H_2O. To this solution 0.016 g of pyrrole (0.24 mmol) dissolved in 5 mL of H_2O was added. The mixture was stirred in an ice bath for 15 min and to it an aqueous solution of 0.156 g (0.96 mmol) $FeCl_3$ was added dropwise. The reaction mixture was stirred in an ice bath for ∼24 h. The product was collected by filtration as black solid, washed with acetone, and dried in vacuum. Yield was quantitative. Anal. Calcd (%) for $(C_4H_3N)_{0.24}MoS_2$: C, 6.56%; H 0.41; N, 1.91. Found C, 6.59; H, 0.59; N, 1.31. Thermal gravimetric analysis (TGA) experiments are consistent with the proposed stoichiometry.

(14) The (PANI)MoS_2 was prepared by a different method in which a polymer solution was mixed with an aqueous solution of single MoS_2 layers.

(15) Assuming a monolayer of densely packed polypyrrole chains.

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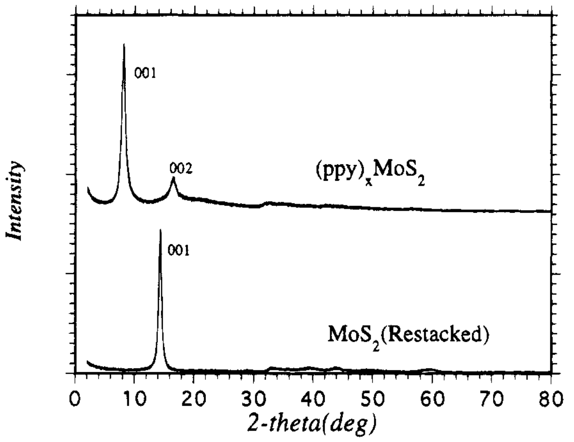

Figure 1. Typical X-ray powder diffraction patterns of (ppy)$_{0.24}$MoS$_2$ and restacked MoS$_2$.

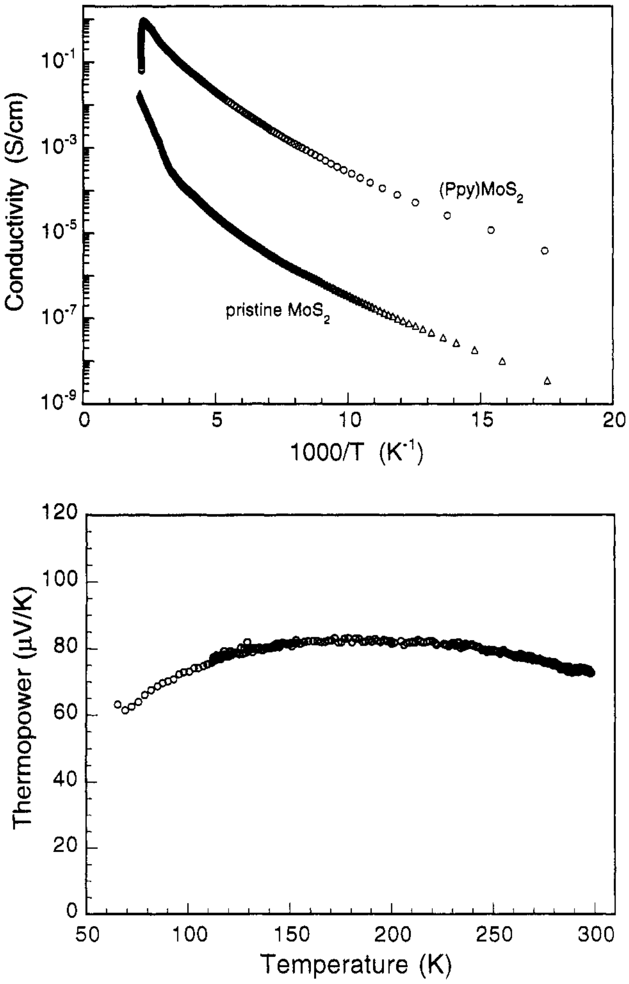

Figure 2. (A) Pressed pellet electrical conductivity data for (ppy)$_{0.24}$MoS$_2$ and pristine MoS$_2$. The dramatic change in direction at high temperatures is due to a metal-to-insulator transition associated with a structural transformation from octahedral to trigonal prismatic Mo centers. This transition is irreversible and is not observed upon cooling down from 200 °C. (B) Pressed pellet thermoelectric power data for (ppy)$_{0.24}$MoS$_2$.

cm^{-1}. This reflects the low molecular weight (MW) of the intercalated polymer and is consistent with previous work where the MW of in situ intercalated polymers is always found to be considerably smaller than that of corresponding bulk materials.[11,12] This is a consequence of polymer growth under kinetically restricted conditions. Since the polymer forms in the doped form, an important issue to be addressed here is what is the dopant anion in polypyrrole. This has not been simple to resolve. There are several possible candidates for counter ions in (ppy)$_y$MoS$_2$. These include FeCl$_4^-$, Cl$^-$, MoS$_2^{x-}$, and OH$^-$. Elemental analysis has shown that only trace levels of iron and chlorine exist in the material. It is possible that negatively charged MoS$_2^{x-}$ acts as the dopant, as is the case with FeOCl and V$_2$O$_5$, but this seems unlikely since these layers are known to completely oxidize to the neutral state upon exfoliation in air.[16] Such oxidation is even more likely in the present system because of the presence of Fe^{3+} ions in solution. A solvated hydroxide ion seems to be the most likely candidate but direct detection of these species in (ppy)$_{0.24}$MoS$_2$ is difficult.[17]

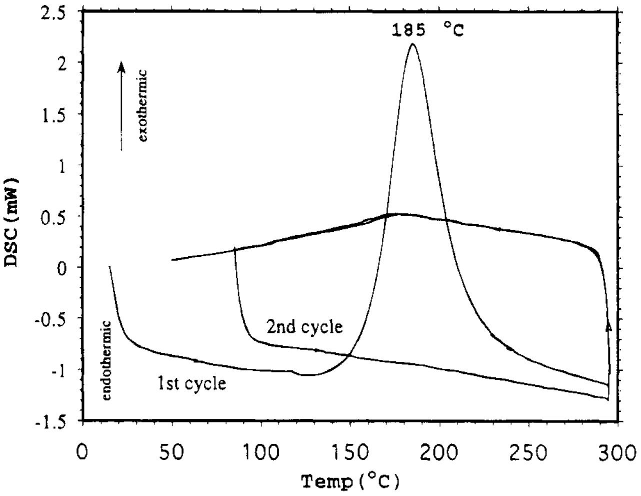

Figure 3. Differential scanning calorimetry trace of (ppy)$_{0.24}$MoS$_2$ showing the irreversible exothermic transformation from octahedral to trigonal prismatic Mo centers. The exothermic transition is clearly absent in the second heating cycle. Heating rate was 5 °C/min.

Variable-temperature electrical conductivity measurements for (ppy)$_x$MoS$_2$ indicate a considerably higher conductivity with respect to pristine MoS$_2$, as shown in Figure 2A. In the temperature range 50–300 K, the material exhibits weak, thermally activated behavior. The conductivity is similar in magnitude with that of the (PANI)MoS$_2$ consistent with the similar nature of the materials. The corresponding thermoelectric power measurements, however, show relatively large and positive Seebeck coefficient values which indicate a p-type conductor; see Figure 2B. The downward sloping thermoelectric power is consistent with a metallike charge transport, but the relatively large values suggest a deviation from an ideal metallic behavior.

As we explained earlier, the electronic structure of MoS$_2$, after it has been exfoliated and restacked, is changed because of a structural transition from a

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(16) Incomplete oxidation of MoS$_2^{x-}$ has been claimed in Li/PEO/MoS$_2$ systems but a full characterization of these materials has not been presented. In our hands the MoS$_2^{x-}$ appears to oxidize fully to the neutral state. Lemmon, J. P.; Lerner, M. M. *Chem. Mater.* **1994**, *6*, 207–210.

(17) The amount of hydroxide would be very small, about 0.024 mol/MoS$_2$ (assuming that ppy is doped at the 33% level per polymer formula unit). Under TGA conditions, the material loses ~2% of its weight between 50 and 160 °C which is due mostly to water possibly associated with, or originating from, OH$^-$ ions in the galleries. The polymer decomposes under oxygen flow at ~400 °C. We note that co-intercalation of hydroxide ions in MoS$_2$ has been claimed earlier: Gee, M. A.; Frindt, R. F.; Joensen, P.; Morrison, S. R. *Mater. Res. Bull.* **1986**, *21*, 543–549.

trigonal prismatic to an octahedrally coordinated metal.[10] In the latter the layers are similar to the 1T-MoS_2 which is metastable.[18] The MoS_2 layers in $(ppy)_{0.24}MoS_2$ are, therefore, prone to conversion to the 2H-MoS_2-like modification upon standing or with application of temperature or even pressure. Differential scanning calorimetry (DSC) studies on $(ppy)_{0.24}MoS_2$ show a well-defined strong exothermic transition at 185 °C (21 kJ/mol, see Figure 3), which is associated with conversion from the 1T to the 2H structural type. This is the highest conversion temperature of all (polymer)MoS_2 compounds reported thus far.[10] The structural conversion to the trigonal prismatic layers (i.e., 2H-MoS_2-type) is followed by a metal-to-insulator transition and a return to the low conductivity values of 2H-MoS_2; see Figure 2A.

The most important achievement described here is the encapsulation of an intractable, infusible polymer in a nonoxidizing host such as MoS_2. This is an advance from prior work where (a) an oxidizing host was required to produce polymer intercalation, (b) a soluble polymer was necessary for insertion into a nonoxidizing host, or (c) a monomer intercalation was required followed by a second step of polymerization. These approaches are not applicable to the MoS_2/polypyrrole, and by extension to the MoS_2/polythiophene systems. We have shown that with a suitable external oxidant it is now possible to in situ prepare and encapsulate conjugated polymers in nonoxidizing hosts. This development broadens further the field organic/inorganic nanocomposite materials as it accesses interesting new polymer/inorganic combinations for study and development.

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