

Inclusion of Poly(aniline) into MoO₃

Rabin Bissessur,^a Donald C. DeGroot,^b Jon L. Schindler,^b Carl R. Kannewurf^b and Mercuri G. Kanatzidis*^a

^a Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824, USA

^b Department of Electrical Engineering and Computer Science, Northwestern University, Evanston, Illinois 60208, USA

Protonated emeraldine [poly(aniline)] has been encapsulated in MoO₃ by first inserting aniline into its lattice followed by successful polymerization with (NH₄)₂S₂O₈; the new material is characterized by X-ray diffraction, IR spectroscopy, scanning electron microscopy and charge transport measurements.

Intercalation of the prototype conjugated polymers poly(pyrrole), poly(aniline) (PANI) and poly(thiophene) has been achieved in layered FeOCl¹ and V₂O₅ xerogels.² Because of the highly oxidizing nature of these hosts, the monomers oxidatively insert into the gallery regions and polymerize, *i.e.* the monomers undergo *in situ* intercalative polymerization. Inclusion of conductive polymers into ordered lamellar structures is still not very common. We are, therefore, interested in developing new synthetic methodologies to incorporate conjugated polymers in a variety of 2D hosts, particularly ones that are not strongly oxidizing such as MoO₃. For instance, treatment of aniline with MoO₃ does not yield intercalated PANI but aniline-anilinium intercalation compounds.^{3,4} Therefore, alternative methods of insertion have to be devised. Our interest in this layered structure is twofold: its high crystallinity and its potential application as an electrode in lithium high energy density rechargeable batteries.⁵

Recently, intercalation of poly(*p*-phenylene vinylene), PPV, into MoO₃ was achieved in a series of steps.⁶ Mixed alkali hydrated bronzes of MoO₃ were first cation exchanged with the PPV precursor, poly(*p*-xylylene- α -dimethylsulfonium chloride), followed by heat treatment to yield (PPV)_xMoO₃. In this report we describe a different approach in which aniline is inserted in MoO₃ and then polymerized with (NH₄)₂S₂O₈, to obtain (PANI)_xMoO₃.

The insertion of aniline in MoO₃ forms (PhNH₃⁺)_x(PhNH₂)_yMoO₃, **I**, where $x + y = 0.4$.[†] Treatment of **I** with 2 equiv. of an aqueous 0.4 mol dm⁻³ solution of (NH₄)₂S₂O₈ yields (PANI)_{0.7}MoO₃, **II**, a black solid. The water used in the

[†] A detailed characterization of this material will be published elsewhere. In **I** the aniline-anilinium are arranged as bilayers (*d*-spacing 20.1 Å) with a coexisting second phase with *d*-spacing of 13.5 Å.

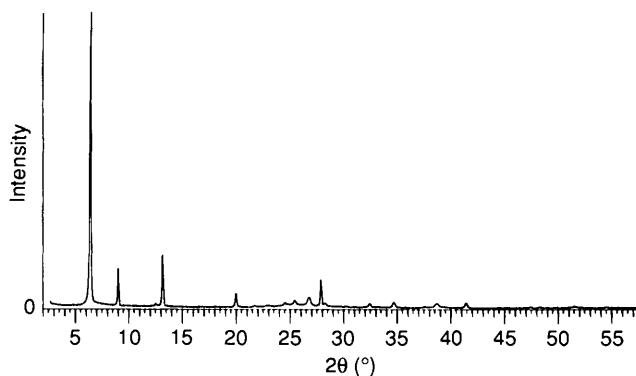


Fig. 1 X-Ray powder diffraction pattern of $(\text{PANI})_{0.7}\text{MoO}_3$

synthesis is cooled to 0°C prior to use.⁷ The higher polymer content in the product can be explained by the fact that SO_4^{2-} , formed during the oxidation process, is capable of partially dissolving the reduced MoO_3 layers, thereby increasing the polymer content.‡§

The X-ray diffraction pattern of **II**, see Fig. 1, reveals an interlayer spacing of 13.7 \AA and represents an expansion of 6.7 \AA which is consistent with having the aromatic rings of the polyaniline chains arranged roughly perpendicular to the MoO_3 sheets and similar to that reported for $(\text{PPV})_x\text{MoO}_3$. FTIR spectroscopy confirms the presence of the conductive form of poly(aniline) (*i.e.* emeraldine salt). It also confirms that the MoO_3 layers are still reduced, providing evidence that the polymer (positively charged) is trapped inside the negatively charged host. Here, the reduced layers are acting as 'dopant' anions. Poly(aniline) can be obtained by digesting the inorganic framework with aqueous hydroxide solution followed by treatment with 1 mol dm^{-3} HCl. FTIR of the extracted product is virtually identical to that of bulk emeraldine salt, see Fig. 2.

Additional evidence of PANI between the MoO_3 layers derives from scanning electron microscopy (SEM) which shows that the surface of the microcrystals of **II** are smooth and clean. No amorphous material is observed that could be attributed to an external poly(aniline)¶ phase. Hence, it is inferred that the polymer is inside the layered host in **II**.

Gel permeation chromatography (GPC) was performed on the PANI isolated from **II** and the data were compared with those of bulk chemically synthesized PANI.¶ The base form of the isolated polymer is soluble in *N*-methylpyrrolidinone (NMP). The GPC measurements of the polymer solution show two molecular weight bands, namely, a major (94%) fraction with $\bar{M}_n = 4850$ and $\bar{M}_w = 24\,200$, and a minor (6%) fraction $\bar{M}_n = 280$ and $\bar{M}_w = 294$. The latter corresponds to aniline trimer which did not undergo further chain elongation, a consequence of the restrictive habitat in which polymerization occurred. The molecular weight of the major fraction is only $\frac{1}{3}$ of that reported for bulk PANI ($\bar{M}_n = 7700$, $\bar{M}_w = 69\,000$) which is also explained by the constrained nature of the polymerization.

‡ Ideally $(\text{PANI})_{0.40}\text{MoO}_3$ should be obtained.

§ Control experiments in which aqueous $(\text{NH}_4)_2\text{SO}_4$ was stirred with $(\text{PANI})_{0.7}\text{MoO}_3$ and $(\text{AnH})^+\text{MoO}_3$ for several hours showed that MoO_3 dissolves partially. For example, $(\text{PANI})_{0.7}\text{MoO}_3$ becomes $(\text{PANI})_{1.0}\text{MoO}_3$.

¶ Bulk poly(aniline) itself, as observed under SEM, is shown to have a very featureless and amorphous character.

|| The \bar{M}_w measurements were performed using a Shimadzu LC-10A HPLC system coupled to a GPC column PLgel $5 \mu\text{m}$ mix which was held at 75°C . The eluent NMP contained 0.5 wt.% LiCl and the elution rate was 0.2 ml min^{-1} .

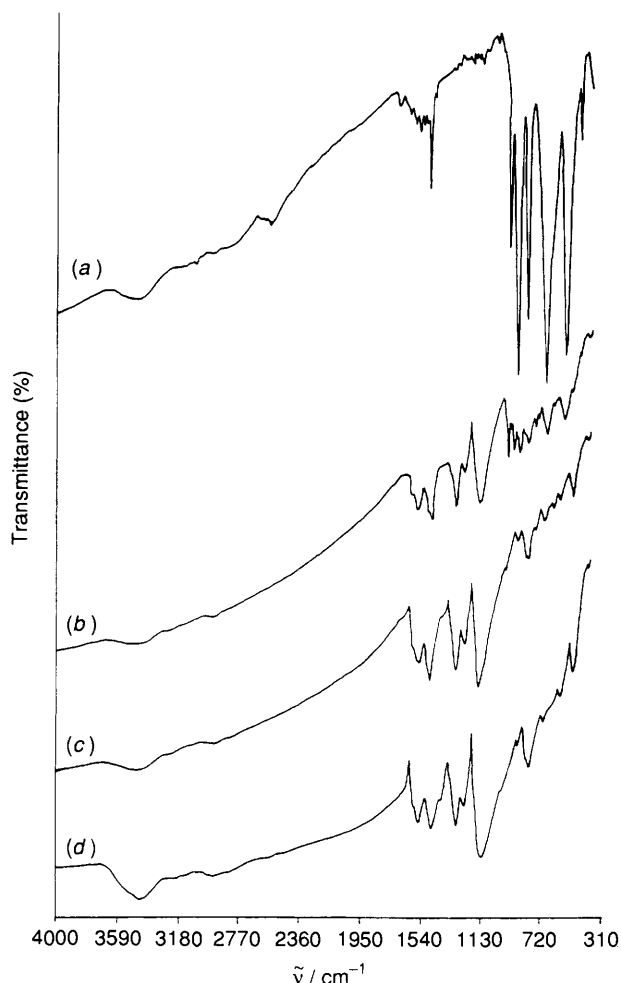


Fig. 2 FTIR spectra (KBr pellets) of (a) $(\text{PhNH}_3^+)_x(\text{PhNH}_2)_y\text{MoO}_3$, (b) $(\text{PANI})_{0.7}\text{MoO}_3$, (c) extracted poly(aniline) from $(\text{PANI})_{0.7}\text{MoO}_3$, (d) chemically synthesized poly(aniline) (salt form)

The possibility that PANI is on the surface of MoO_3 was further ruled out as follows. If some emeraldine salt were outside, it is reasonable to assume that either SO_4^{2-} or HSO_4^- [derived from $(\text{NH}_4)_2\text{S}_2\text{O}_8$] would be the dopant anions. Elemental analysis showed sulfur only at the impurity level. Treatment of an aqueous suspension of **II** with a 2 mol dm^{-3} aqueous solution of NaCl does not show Cl^- incorporation through $\text{SO}_4^{2-}/\text{Cl}^-$ exchange consistent with the absence of SO_4^{2-} . In contrast, when bulk $(\text{PANI})\text{HSO}_4$ samples are treated with aqueous solutions of 2 mol dm^{-3} NaCl or HCl, they do show complete $\text{SO}_4^{2-}/\text{Cl}^-$ exchange as expected.

The room temperature conductivity of **I** is $2 \times 10^{-6} \text{ S cm}^{-1}$. **II**, however, shows a dramatic increase in electrical conductivity by three orders of magnitude with a room temperature value of *ca.* 0.003 S cm^{-1} . This value is lower than that of bulk PANI and it is consistent with the intercalated model for PANI in a semiconducting host. Variable temperature measurements for polycrystalline pellets of **II** are shown in Fig. 3 and are characteristic of thermally activated transport. However, variable temperature thermoelectric power (TP) measurements show a more interesting behaviour. At 345 K, the Seebeck coefficient, *S*, is relatively small, about $+8.6 \mu\text{V K}^{-1}$ and decreases linearly with falling temperature to *ca.* $+4.6 \mu\text{V K}^{-1}$ at 235 K, the lowest temperature measured. The positive values of the thermopower and the positive slope of the curve implies that the composite material is intrinsically a p-type metallic conductor, suggesting that the observed thermally activated conductivity is due to grain boundaries between $(\text{PANI})_{0.7}\text{MoO}_3$ crystallites. Thus, the predominant charge carriers are holes, suggesting that the

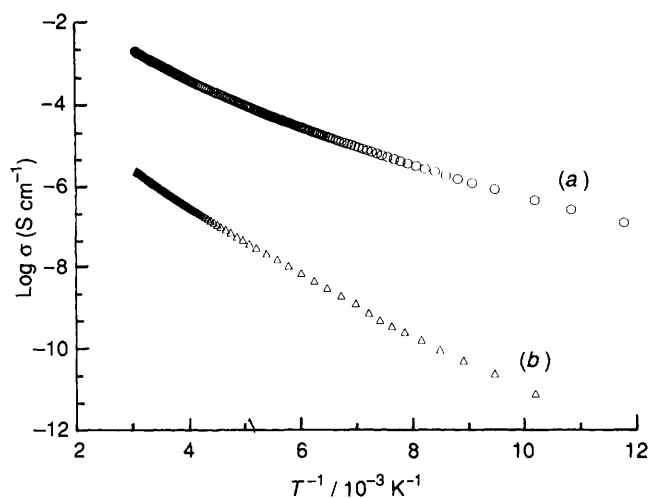


Fig. 3 Four-probe variable temperature electrical conductivity data of polycrystalline pellets of (a) $(\text{PANI})_{0.7}\text{MoO}_3$, (b) $(\text{PhNH}_3^+)_x(\text{PhNH}_2)_y\text{MoO}_3$

encapsulated polymer is playing a more important role, than the $(\text{MoO}_3)^{x-}$ layers, in charge transport.^{8**} Examples of polymerization of intercalated monomers in constrained environments include the oxidation of aniline in zeolite Y⁹ and the electrochemical polymerization of aniline absorbed into montmorillonite clay.¹⁰

We have shown that insertion of poly(aniline) is possible in MoO_3 , despite its inadequate oxidizing ability. This work further demonstrates that conductive polymers can still be intercalated in poorly oxidizing lamellar materials, using alternative routes. Thus, it opens new possibilities for the preparation of new nanocomposite organic-inorganic lamellar materials.

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** If the charge transport were predominantly through the MoO_3^{x-} layers, n-type conductivity would be expected.