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Inclusion of Poly(tetramethyl-*p*-phenylenediamine dihydrochloride) into MoO$_3$: A Cooperative Formation Route to Construct a Polymer/MoO$_3$ Layered Structure

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In recent years molybdenum trioxide has attracted considerable attention due to its intercalation property and potential applications in the field of material chemistry.[1−6] Especially with the realized property enhancement originating from the incorporation of conducting polymers into a layered MoO$_3$ inorganic host, interest in polymer/MoO$_3$ nanocomposites remains high.[7−10] However, until now intercalation of these polymers into MoO$_3$ via in situ concurrent polymerization is still not feasible because MoO$_3$ is not a strong oxidizing agent.[7] The usual way to intercalate polymers is still to first pillar the MoO$_3$ inorganic layers apart and then insert the organic species by ion exchange. Thus only after a series of steps can the polymers be intercalated. Therefore, alternative simple and more effective methods of insertion have to be developed.

Our interest in this layered structure is in constructing layered polymer/MoO$_3$ via a cooperative route. That is to say, MoO$_3$ deposits together with polymerization of the organic monomers and thus polymers can be intercalated into MoO$_3$ layers at the same time. The polymer acts as a template, and MoO$_3$ acts as a host. In fact, since MoO$_3$ can be deposited as a hydrolysis product of $(NH_4)_6Mo_7O_{24}\cdot 7H_2O$ at acidified conditions,[11] the key step is to polymerize the organic monomers contemporarily. Meanwhile, as MoO$_3$ is not a strong oxidizing agent, TMPD (tetramethyl-*p*-phenylenediamine dihydrochloride) is chosen as the first tested object because TMPD can be oxidatively polymerized by oxygen in the air under ambient conditions. Its polymerization mechanism has been studied before.[12−14] The polymer consists of a highly resonating, meriquinone-like structure (Chart 1). The electron pair shown as two dots in the center of structure **1** may be said to belong alternatively to either N. Structure **1** is in resonance with another, with right and left sides exchanged.

In our experiment, inclusion of poly(TMPD) into MoO$_3$ was tried by mixing TMPD monomers with aqueous solution of ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 7H_2O$ at pH 1 (the mole ratio is 1:3). As soon as they were mixed, the solution turned yellow and then dark green. (The yellow color indicates TMPD intermediate radical and dark green is the color of TMPD polymers.)[13] Instantly a copious precipitate was deposited. Thus the formed precipitate was called compound **1**. For comparison, compound **2** was synthesized under otherwise identical conditions except that a nitrogen atmosphere was maintained. Auto-oxidation polymerization of TMPD was also carried out at ambient conditions under sunlight irradiation. Comparison between products of the three reactions will be discussed in the following part.

Figure 1 records UV spectra of TMPD during its auto-oxidation polymerization process. As can be seen, before irradiation, TMPD had no absorption at the visible-light region. Once placed under sunlight, three peaks at 521, 563, and 611 nm appeared in the visible-light region indicating that a highly conjugated system had been formed. As time went on, absorption at the three peaks strengthened meaning that the percentage of polymerized TMPD increased according to literature.[12] On the other hand, as can be seen from the insert, absorbency increase at 563 nm slowed after a period of time, indicating polymerization rate decreased. In other words, equilibrium between TMPD monomer and its polymers would be achieved after a period of time. Under this condition, polymerization of TMPD was not instant but was in fact step by step.

However, as described above, polymerization of TMPD was almost instant when ammonium molybdate was introduced. The composite was deposited as soon as the starting materials were mixed. And later it was shown to be a layered structure of poly(TMPD)/MoO$_3$. Figure 2 is an X-ray desorption (XRD) pattern of compound **1**, which is the reaction product of ammonium molybdenum and TMPD under ambient conditions, showing a layered structure. Four peaks are indexed as 001, 002, 003, and 004, which correspond to *d* values of 2.26, 1.13, 0.753, and 0.565 nm, respectively. The inorganic layer and organic TMPD polymer layer are arranged alternatively along the *c* axis. Furthermore it is confirmed by Raman spectrum and IR spectra that MoO$_3$ has been formed and acts as the inorganic framework of compound **1** (Figure 3). In its Raman spectrum, peaks at 991, 816, and 665 nm are observed indicative of MoO$_3$. The three peaks are ascribed to Mo═O, $Mo_2{-}O$ (one oxygen atom is shared by two molybdenum atoms), and $Mo_3{-}O$ (one oxygen atom is shared by three molybde-

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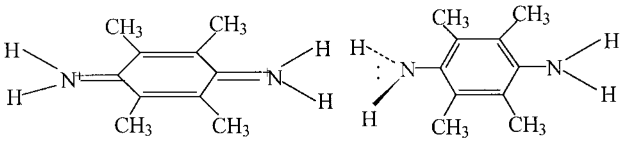
Chart 1. Structure of Poly(TMPD)



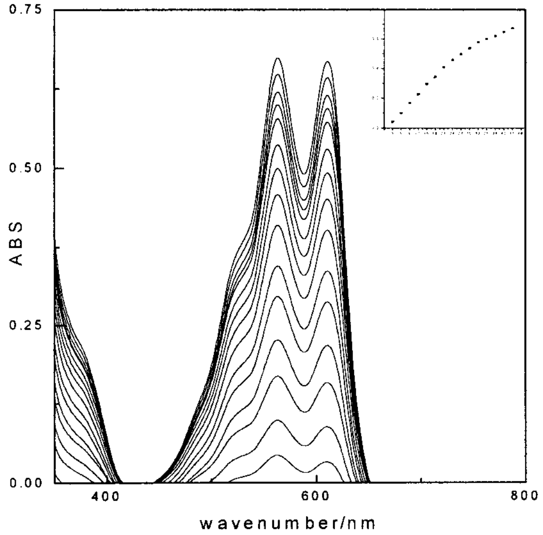


Figure 1. UV absorption spectrum of TMPD recorded under sunlight irradiation of 0, 3, 6, 9, ..., 45 min. The insert is an $A-t$ curve at 563 nm.

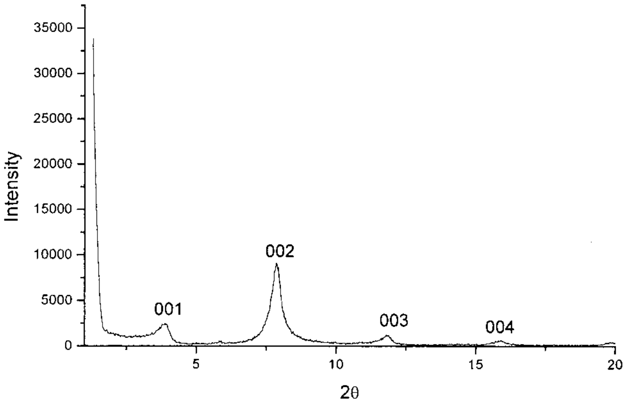


Figure 2. XRD pattern of compound **1**.

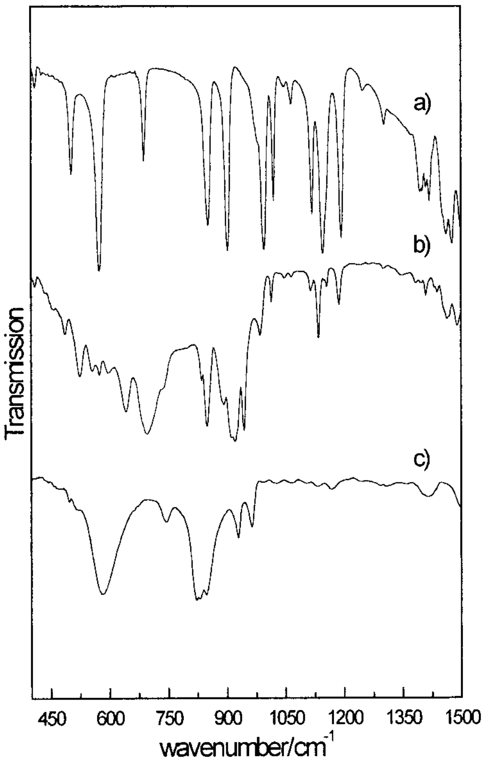


Figure 3. IR spectra of (a) TMPD, (b) compound **2**, and (c) compound **1**.

num atoms) vibrations, respectively.[15] IR spectra (Figure 3, curve c) show characteristic peaks of MoO_3 also. Meanwhile fine vibration peaks corresponding to TMPD monomer have disappeared as a result of polymerization. So far we can say a layered poly(TMPD)/MoO_3 structure has been constructed under ambient conditions.

As we can see during synthesis of the layered poly(TMPD)/MoO_3, polymerization of TMPD was almost instant and much faster than its "step-by-step" autooxidation polymerization. It is obvious that polymerization of TMPD has been greatly accelerated by the presence of MoO_3. It is proposed that MoO_3 has oxidized TMPD and thus accelerated its polymerization rate. Therefore, for comparison, compound **2** was synthesized from TMPD and ammonium molybdate under otherwise identical conditions except that the nitrogen atmosphere was kept. Compound **2** was proved to have no layered structure since no peaks appeared in the small angle region ($2\theta < 9°$) of its XRD pattern. The IR spectrum of compound **2** showed that fine vibration peaks of monomer TMPD were still retained (Figure 3, curve b) indicating MoO_3 had not oxidatively polymerized TMPD only by itself. As is seen, oxygen in the air played a crucial role during the polymerization process. MoO_3 cannot oxidize TMPD although it did promote the polymerization rate of TMPD. Its accelerating function can be explained by its characteristic intercalation property. In this experiment, MoO_3 layers deposited when ammonium molybdate was introduced to the acidified solution. On the other hand, TMPD monomer began to be oxidized and polymers came into being. Its polymerization was reversible.[14] Once MoO_3 layers were formed, these layers would entrap polymers between them and the polymers could act as a template along which the MoO_3 layers could grow on. At last a layered complex poly(TMPD)/MoO_3 was deposited. In this way polymerization of TMPD was made irreversible and accelerated. The polymerization was accelerated so much that it could go on simultaneously with formation of MoO_3. To our knowledge, this is a new route to construct a polymer/MoO_3 layered structure.

The TGA curve of compound **1** showed that no other components but lattice H_2O molecules were released before 300 °C with a weight loss of 3%. A sequential mass loss (20%) between 300 and 500 °C should correspond to combustion of TMPD from a composite with a stoichiometry of $[\text{poly(TMPD)}]_{0.23}MoO_3(H_2O)_{0.31}$.

In conclusion, the most important point during cooperative formation of polymer/MoO_3 is to ensure that polymerization can go on with deposition of MoO_3 synchronously. MoO_3 can entrap polymers and then accelerate the polymerization to a certain degree, as is shown in Scheme 1. It can be successfully achieved for

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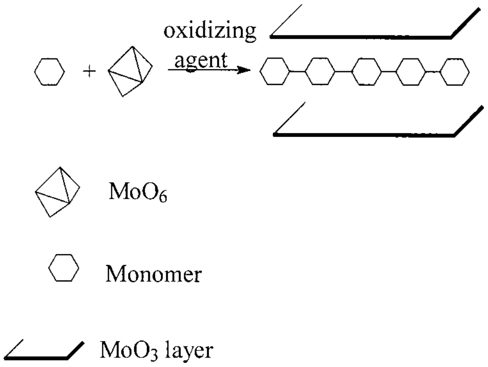
Scheme 1. Cooperative Formation Process of Polymer/MoO_3 Layered Structure



TMPD which can be easily oxidatively polymerized under ambient conditions. But for other monomers, such as aniline, external oxidizing agent should be introduced to help the polymerization. Once the polymerization is induced, cooperative formation of polymer/MoO_3 can be easily realized. Thus it opens new possibilities for the preparation of new nanocomposite organic−inorganic lamellar materials. In our research work, a conducting layered nanocomposite of poly(aniline)/MoO_3 has also been constructed via this cooperative method. Details of this work will be reported in future.

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