In Situ Insertion of Poly(aniline) into Molybdenum Oxide Layers

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A one-pot reaction design is proposed in this paper for synthesis of layered polymer/MoO_3 materials. The experimental results evidenced the availability of this design. By using acidified ammonium molybdate as precursor of the inorganic hosts and $FeCl_3$ as the oxidizing agent of aniline, layered PANI/MoO_3 has been obtained via a one-step coprecipitation route.

Insertions of conjugated polymers into layered inorganic hosts have been examined intensively over the past decade due to their potential applications in electronic and electric materials.[1–11] In situ insertions can be easily achieved if the hosts are strong oxidizing agents, such as FeOCl and V_2O_5 xerogels.[12,13] But for the inadequate oxidizing agents, for example, MoO_3 or MoO_3-like layers, in situ intercalative polymerization of organic monomers is still a challenge. Usually polymers are intercalated into MoO_3 layers via ion exchange and only after a series of steps these layered structures can be obtained.[14] In our research work, we become interested in in situ syntheses of layered polymer/molybdenum oxide composite, a potential electrode in rechargeable lithium batteries.[15] Our design is to fabricate this layered structure via a coprecipitation route. It has been known that ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot H_2O$ can be hydrolyzed into molybdic acid $(MoO_3\cdot nH_2O)$[16] readily, so the most important point to realize in situ syntheses of the composite is to polymerize the monomers contemporarily with the hydrolysis of ammonium molybdate. Therefore, deposition of molybdenum oxide and polymerization of the organic monomers can go synchronously. The polymer can be intercalated into the oxide layers and the oxide layers may grow along the polymer chain template at the same time. Thus the layered composite can be constructed in a cooperative formation way.

Here we report the in situ preparation of a layered PANI/molybdenum oxide by this method using $FeCl_3$ as an oxidizing agent, to promote oxidative polymerization of aniline.[18] 100 ml of an aqueous solution containing 1.00 ml of aniline (0.011 mol) was acidified to pH = 0.5, to which an aqueous solution containing 2.2864 g of $(NH_4)_6Mo_7O_{24}\cdot 7H_2O$ (0.002 mol) in 200 ml was added. 1.000 g of $FeCl_3$ (0.007 mol) in 100 ml was added almost instantly and copious precipitate was deposited. The precipitate was soon filtered, washed with deionized water several times and air-dried. Thus formed product was called compound **1**.

Figure 1a shows the XRD pattern of compound **1**. Three peaks are observed at $2\theta = 5.82°$, $11.34°$, and $17.42°$ corresponding to *d* spacing of 15.17 Å, 7.79 Å, and 5.09 Å, which can be indexed as 001, 002, and 003 diffraction, respectively. The pattern indicated that compound **1** has a layered structure and the interlayer spacing is 15.17 Å. This value reveals that the aromatic rings of the anilines are arranged nearly perpendicular to the molybdenum oxide sheets.[14]

For comparison, Figure 1 also shows XRD spectrum (Figure 1b) of aniline/MoO_3 layered hybrid obtained by direct coprecipitation of ammonium molybdate and aniline at acidified conditions (without $FeCl_3$). This XRD pattern has been indexed to be a triclinic system (parameters: $a = 14.76$ Å $b = 10.03$ Å $c = 7.98$ Å $\alpha = 85.14°$ $\beta = 105.23°$ $\gamma = 114.19°$). As can be seen, at the absence of $FeCl_3$, aniline itself doesn't template a regularly-packed aniline/MoO_3 layered structure. And only when $FeCl_3$ has been introduced as the oxidizing agent, aniline can be polymerized and the polymer chain template formation of a regularly-packed MoO_3/PANI layered structure.

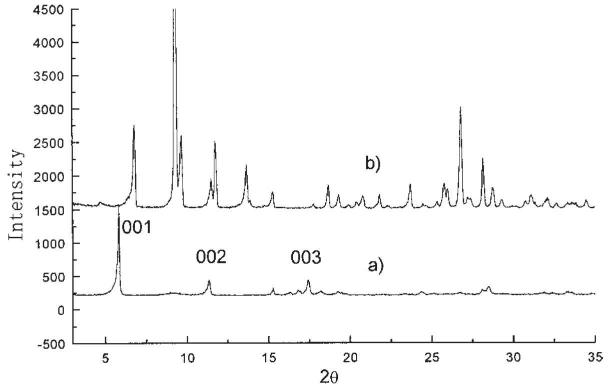

Figure 1. XRD patterns of a) layered PANI/MoO_3 (coprecipitation of MoO_3 and aniline at presence of $FeCl_3$); b) triclinic system of aniline/MoO_3 (coprecipitation of MoO_3 and aniline at absence of $FeCl_3$).

FTIR spectrum of compound **1** confirms the presence of the conductive form of poly(aniline) in the layered material (Figure 2b). A broad peak at $1120\,\mathrm{cm}^{-1}$ (δ(C–H), in plane bending of the *para*-substituted phenyl ring) as well as other peaks at $1613\,\mathrm{cm}^{-1}$ (ν(C=C), quinoid phenyl ring breathing mode), $1495\,\mathrm{cm}^{-1}$ (ν(C=C), benzenoid phenyl ring breathing mode), $1300\,\mathrm{cm}^{-1}$ (ν(C–N), quinoid-benzenoid-quinoid) and $1243\,\mathrm{cm}^{-1}$ (ν(C–N), aromatic) are all characteristic of a poly(aniline) in emeraldine salt form.[10] Poly(aniline) can be obtained by digesting the inorganic framework with an aqueous hydroxide solution followed by treatment with $1\,\mathrm{mol\cdot dm^{-3}}$ HCl. FTIR spectrum of the extracted product is virtually identical to that of emeraldine salt (Figure 2a).

The composition of this layered structure is decided by TGA analysis, which shows the weight loss process when the temperature increases from 30 °C to 550 °C. The first weight loss (20%, 30 °C to 300 °C.) is attributed to lattice H_2O molecules. A sequential mass loss (14.48%, 300 °C to 550 °C.) should correspond to combustion of PANI. And the residue (65.52%) is evidenced to be MoO_3 by XRD analysis. Thus the composite is calculated to have a stoichiometry of $[\mathrm{PANI}]_{0.35}MoO_3(H_2O)_{1.11}$. This is consistent with the elemental analysis result: N, 2.2%; C, 11.58%; H, 2.08%; Mo, 43.01%. It's noteworthy that Cl of 0.9% was also detected in the composition. It can be explained by the in

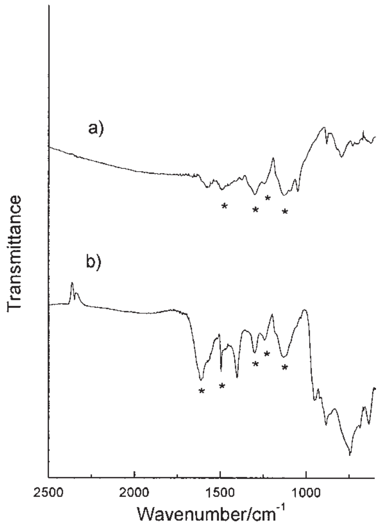

Figure 2. IR spectra of a) PANI extracted from the composite; b) PANI/molybdenum oxide composite. * peaks are from emeraldine salt.

conporation of Cl^- ion between the MoO_3 layers to balance the cationic charges carried by PANI emeraldine salt.

A variable-temperature conductivity plot of bulk **1** is shown in Figure 3. It shows a linear decrease in conductivity as a function of decreasing temperature, indicative of thermally activated electron transport. The variable-temperature conductivity of this material is consistent with other poly(aniline)/MoO_3 nanocomposite.[14,15] At the same time, the conductivity of compound **1** is substantially increased over that of pristine MoO_3 which is an insulator with a room-temperature conductivity of 5×10^{-11} S·cm^{-1}.[17]

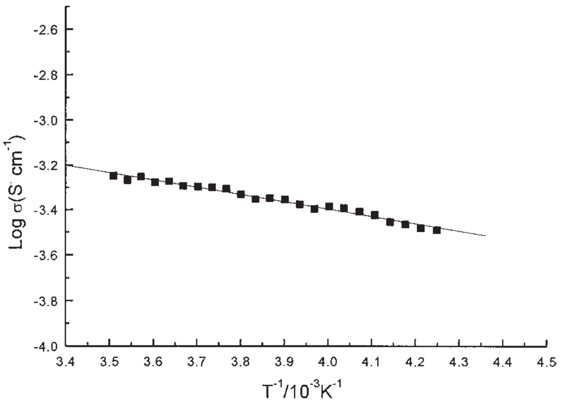

Figure 3. Four-probe variable temperature electrical conductivity data of compound **1** (bulk film).

In conclusion, in situ insertion of poly(aniline) into molybdenum oxide layers has been realized, despite the inadequate oxidizing ability of the inorganic hosts. XRD and IR results confirm the layered poly(aniline)/MoO_3 hybrid structure. This one-pot coprecipitation route opens new possibilities for the preparation of novel nanocomposite organic/inorganic layered materials.

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