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Preparation and characterization of polythiophene/molybdenum disulfide intercalation material

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ABSTRACT

Utilizing the solvothermal synthesis technique, lithium intercalated molybdenum disulfide Li_xMoS_2 was expediently obtained, which was allowed to react with water to the formation of single-molecule-layer suspension. The intercalation of polythiophene into MoS_2 was achieved by means of in situ polymerization of the intercalated monomers. The nanocomposite was characterized by X-ray powder diffraction, thermogravimertic analysis and differential scanning calorimetry. It was revealed that the intercalated polymer chain favors the monolayer arrangement with the thiophene rings lying parallel with the host layers. The optimum conditions were explored to prepare the single-phase product with a composition of $Li_{0.12}(PTP)_{0.54}MoS_2$. The nanocomposite exhibits enhanced electrical conductivity in the order of 10^{-2} S cm^{-1} at ambient temperature, resulted from the incorporation of the electronically conductive polythiophene between the semiconducting host layers and the coupling between the guest conjugated π-orbits and the host layers.

1. Introduction

Inorganic/organic hybrid materials, based on interactions between organic and inorganic components, have been greatly developed in the past decades [1–4]. The inorganic components include zeolite [5], layered structures [6–8] and sometimes one-dimensional polymers [9]; and the organic component could be small organic molecules [10], organometallics [11] or organic polymers [12,13]. The resultant hybrids may exhibit properties synergistically derived from the two components [14,15]. MoS_2 has a layered structure with interesting properties and practical applications, such as catalysts [16] and cathode materials [17]. It has a modulated structure containing S–Mo–S sandwich layers. Each molybdenum atom in the layers is coordinated by six S atoms in either a trigonal prismatic (for 2H-MoS_2) or octahedral (for 1T-MoS_2) arrangement by strong S–Mo bonds, while van der Waals bonds connect the nearest layers. Inserting guests into the host will modify the properties of MoS_2 and have interesting applications [12,18,19]. Due to their anisotropic optical and electrical properties, electrochemical and electrochromic behaviors, conjugated polymers such as polypyrrole [13], polyaniline [20] and oligothiophene [21] have been used as guests into the layered gallery of MoS_2 to form layered nanocomposites.

Generally, the synthetic methodology of a layered nanocomposite depends on the chemical and physical properties of the host inorganic materials and the guest organic polymers [22,23]. Recently, by exploiting the exfoliation and restacking properties of Li_xMoS_2 in water, different types of guest species have been included into MoS_2 [10–22]. It has been believed that the guest species needs to be soluble in some solvent system, whether miscible or immiscible with water [13]. To date, most of polymer/MoS_2 layered nanocomposites have been achieved through the direct insertion approach, where the polymers are first dispersed in water or organic solvent and then inserted into the MoS_2 layered structure [12,13,20,21,22]. Another synthetic approach involves insertion of monomer first, followed by treatment with an oxidant. Wang et al. employed this approach to prepare the polypyrrole/MoS_2 nanocomposite [24]. In this paper, this approach has been developed to prepare the intercalation of polythiophene into MoS_2. The as-prepared polythiophene/MoS_2 nanocomposites were characterized by X-ray diffraction, FTIR spectroscopy, TG/DSC analysis and electrical conductivity measurements.

2. Experimental

2.1. Preparation of Li_xMoS_2

2H molybdenum disulfide (Acros, 99.5%) and *n*-butyllithium (Aldrich, 2.2 M in hexane) were used as received. Distilled and deionized water was used in all preparations. Li_xMoS_2 was

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prepared by the solvothermal methodology, similar to the preparation procedure of Li_xWS_2 [25]. 0.5 g (3.125 mmol) MoS_2 was put into the autoclave and 12 ml 0.5 M solution of *n*-butyllithium in hexane was then added. The autoclave was tightly sealed and heated at 80 °C for 4 h. The product was filtered, washed with anhydrous hexane, and then dried in vacuum at room temperature. Lithium analysis of the product by both of titrating with a standardized HCl solution and atomic absorption spectrum gave a stoichiometry of $Li_{1.12}MoS_2$.

2.2. Exfoliation of MoS_2

Exfoliation of MoS_2 into single-molecule layers was achieved via the rapid hydrolysis and ultrasonication of Li_xMoS_2. In a typical reaction, 0.5 g Li_xMoS_2 was hydrolysed in 1000 ml water, and ultrasonicated at ambient temperature for 2 h to produce a colloidal suspension of single-molecule MoS_2 layers. The suspension was neutralized with dilute acid (1 M nitric acid).

2.3. Preparation of polythiophene/MoS_2 composite

Thiophene was purchased from Alfa Aesar and used without further purification. Typically, 1 g thiophene was dissolved in 50 ml *N*-methylformaminde (NMF)/water mixed solvent (1:1, v/v). The solution was then slowly dropped into the single-molecule-layer suspension under mechanical stirring. After 2 h, a solution containing 2 g $(NH_4)_2S_2O_8$ in 50 ml water was slowly added to the mixture. The mixture was modified to pH $\approx$ 4.5 by 1 M nitric acid, and then kept under constant stirring at the controlled temperature of 50 °C for 12 h to ensure completion of the intercalation reaction. The resultant black precipitate was separated by centrifugation at 4000 rpm, and then washed several times with *N*-methylformaminde and water to remove unreacted monomer and other soluble products. The product was dried under suction and then freeze-dried.

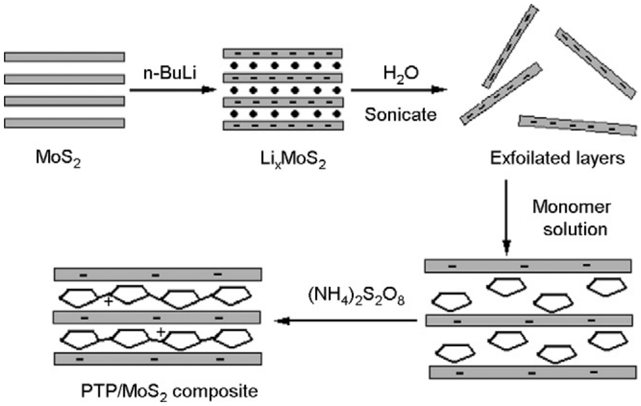
2.4. Characterization

The X-ray powder diffraction (XRD) patterns were recorded at ambient temperature on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) at 36 kV and 15 mA at a scanning rate of 0.2° at 2θ min^{-1} ranging from 2° to 60°. C, H and S analyses were performed on a PerkinElmer 2400 II element analyzer, Mo analysis was carried out on a PerkinElmer Optima 3300DV ICP spectrometer, and Li analysis was achieved on a PerkinElmer 1100B atomic absorption spectrophotometer. The simultaneous TG/DSC measurements were performed from ambient temperature to 750 °C in flowing air using a Shimadzu TGA-60H thermal analyzer. Electrical conductivities at room temperature were determined using a conventional four-probe method on pressed pellets in an inert atmosphere, where the pressed pellets with diameter of 13 mm were prepared under a pressure of 20 MPa.

3. Results and discussion

3.1. Preparation of PTP/MoS_2 composite

The synthetic technique used here for the layered nanocomposite of MoS_2 is shown in Scheme 1. Layered nanocomposites derived from two-dimensional MoS_2 host lattices resemble intercalation compounds. However, MoS_2 undergoes intercalation chemistry only with powerful reducing agents such as *n*-butyllithium [26]. A route to intercalated MoS_2 has been developed that entails initial intercalation with Li, followed by aqueous exfoliation, and subsequent restacking of single-layer MoS_2 [27].



Scheme 1. Preparation procedure for PTP/MoS_2 intercalation material.

Employing this single-layer dispersion technique, MoS_2 has been intercalated with a variety of compounds [10–13,20–24,26–28]. Typically, to enable lithium to thoroughly intercalate into MoS_2, MoS_2 powder was soaked in a hexane solution of *n*-butyllithium at room temperature for more than 2 days. Enlightened by the preparation of Li_xWS_2 [25], we have used the solvothermal synthesis technique to prepare Li_xMoS_2 to save the procedure time. As shown in Fig. 1, the Li concentration x is increased with elevating the intercalation temperature. It was observed that the Li concentration x in Li_xMoS_2 is more than one at the temperature of higher than 80 °C under the molar ratio of MoS_2:*n*-butyllithium was 1:1.92 under autogenous pressure with a fill factor of approximately 70% for 4 h. The solvothermal reaction at 80 °C gave $Li_{1.12}MoS_2$. The reaction can be described by Eq. (1), similar to the conventional synthesis [26].

$$MoS_2 + n\text{-BuLi} \rightarrow Li_xMoS_2 + 0.5\,C_8H_{18} \tag{1}$$

It was observed that the complete exfoliation was undertaken when the Li concentration x in Li_xMoS_2 is more than 0.9, and that partial exfoliation occurred when $x < 0.9$. Reaction of Li_xMoS_2 ($x > 0.9$) with water, together with the sonication process, resulted in the formation of a colloidal suspension of single-layer MoS_2, as shown by Eq. (2) [27]. After neutralized by dilute acid, the resulting suspension was observed to keep dispersed for several days. Adding into the colloidal suspension, thiophene first tended to the surface of single layers of MoS_2. Upon treatment with ammonium

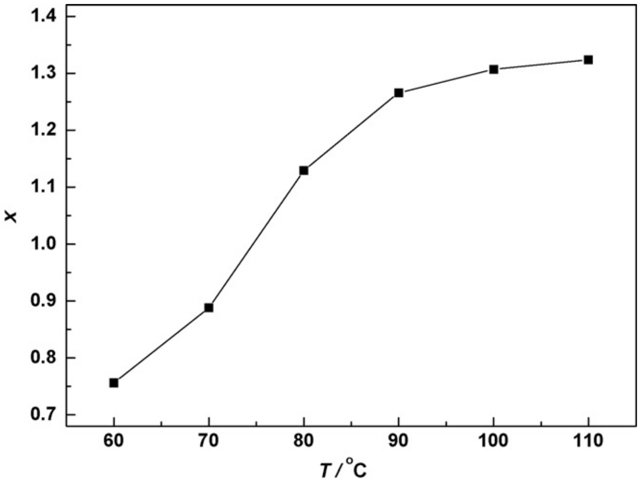


Fig. 1. The Li concentration x in Li_xWS_2 as a function of intercalation temperature.