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Sodium alginate-assisted exfoliation of MoS_2 and its reinforcement in polymer nanocomposites

Dandan Xuan, Yifeng Zhou*, Wangyan Nie, Pengpeng Chen*

College of Chemistry & Chemical Engineering, Anhui University, Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Hefei 230601, China

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ABSTRACT

In this work, molybdenum disulfide (MoS_2) nanosheets were facilely prepared by direct exfoliation of MoS_2 in aqueous media with the assistance of sodium alginate (SA). Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectra results showed that the raw MoS_2 was successfully exfoliated into few-layer MoS_2 nanosheets (SA-MoS_2). FTIR and thermal gravimetric analysis (TGA) investigations showed that the obtained MoS_2 nanosheets were modified by SA after exfoliation and improved dispersion in water were achieved. The obtained SA-MoS_2 nanosheets were employed to reinforce the water-soluble polymer SA. No obvious macroscopic phase separation could be found from the SA/SA-MoS_2 films. Dynamic mechanical analysis (DMA) results showed that almost 9 times enhancement for the storage modulus of SA was achieved with the incorporation of only 0.5 wt% of SA-MoS_2, and the thermal stability of SA was also found improved with the addition of SA-MoS_2 according to the thermal gravimetric analysis TGA results.

1. Introduction

Due to the excellent anisotropic physical properties, ultra-thin structure, and quantum size effects (Guo, Duan, Zhou, & Zhu, 2014; Kisku & Swain, 2012; Layek & Nandi, 2013; Young, Kinloch, Gong, & Novoselov, 2012), graphene has been drawing great attentions to serve as nanofillers in polymer composites. However, the electrical conductivity of graphene based polymer nanocomposites restricts their use in some electrical and electronic applications such as transmission lines, power electronics and capacitors. Similar to graphene, MoS_2 has a layered structure that hexagonal Mo layers are sandwiched between two hexagonal S layers (Huang, Chen et al., 2013; Zhang, Wu, Guo, & Lou, 2012). The MoS_2 nanosheets have interesting optical and electrical properties (Coleman et al., 2011) which have been capitalized in many research fields such as photochemistry, materials science (Zhou, Liu, Wen, Hu, & Gui, 2014), nanoelectronics (Sanchez et al., 2006) and catalysis (Radisavljevic, Radenovic, Brivio, Giacometti, & Kis, 2011; Shi et al., 2012; Yang et al., 2013; Zhiyuan et al., 2011). Same to graphene, MoS_2 nanosheets also possess excellent mechanical properties and high storage modulus. But different from graphene, the MoS_2 nanosheets are nonconductive which is quite beneficial as a reinforcer for polymer nanocomposites in some special fields. Recently, a general trend has emerged for using MoS_2 modified polymer, such as MoS_2/PVA nanocomposites (Jiang et al., 2014) and MoS_2/chitosan nanocomposites (Feng et al., 2014). The polymer nanocomposites prepared with MoS_2 showed enhanced mechanical properties in varying degrees compared to the neat polymers, suggesting the promising potential as a nanofiller of MoS_2 nanosheets. Importantly, those MoS_2 reinforced polymers preserved their electrical insulation well.

MoS_2 nanosheets can be prepared through several different ways such as mechanical exfoliation (Splendiani et al., 2010), chemical vapor deposition (CVD) on substrates (Jeon et al., 2015), chemical exfoliation through intercalation (Chou et al., 2013; Luo et al., 2014), etc. Mechanical exfoliation is an effective method to prepare few-layers MoS_2 nanosheets. Novoselov et al. used the method to prepare nanosheets from various bulk materials to single layer (Novoselov et al., 2005). However, the yield is low and the method is time consuming. CVD has been used to synthesize high quality MoS_2 nanosheets in a controllable manner with different compositions. Lee et al. used MoO_3 and S as the precursors to prepare MoS_2 nanosheets under the condition of heating (Lee et al., 2012). But the method is not easy to scale-up. Chemical exfoliation is a simple method to prepare few-layers MoS_2 nanosheets. The mostly used chemical exfoliation method involves lithium inter-

* Corresponding authors.
E-mail addresses: yifengzhou@126.com (Y. Zhou), chenpp@ahu.edu.cn (P. Chen).

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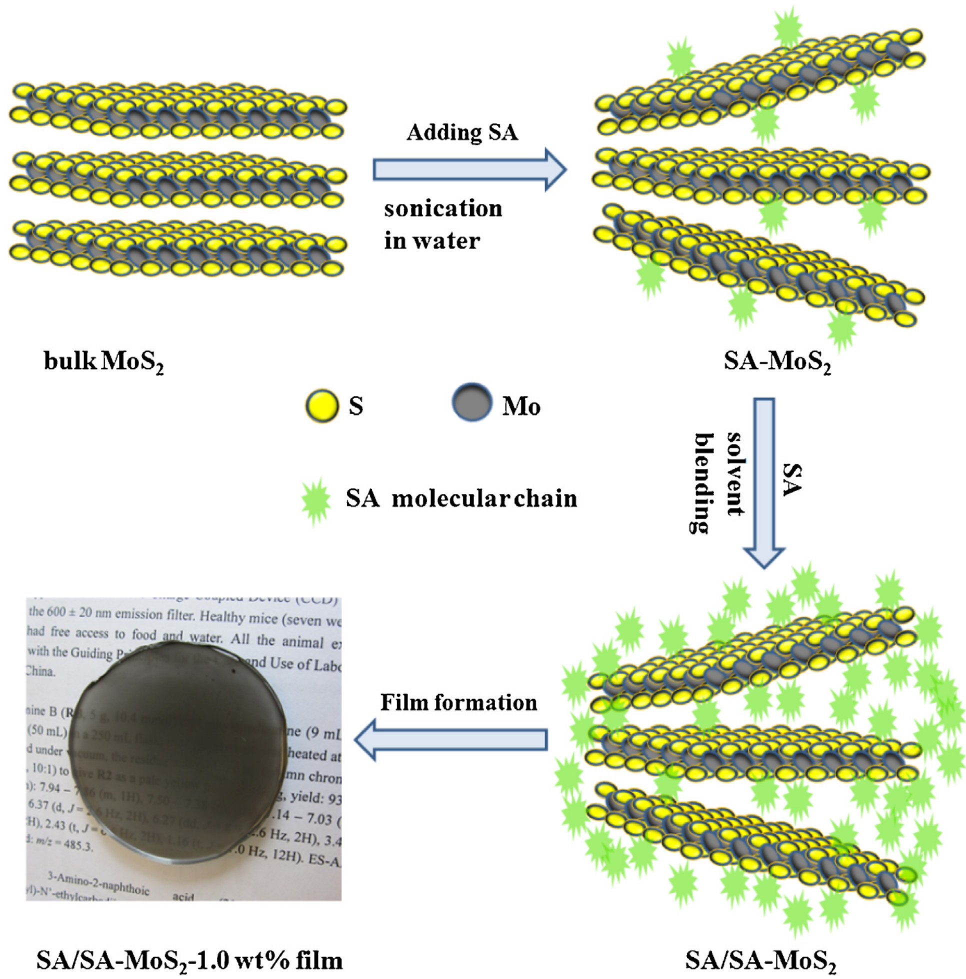

Scheme 1. Illustration of the preparation process of the SA/SA-MoS_2 nanocomposites.

calation using n-butyllithium (n-BuLi) as a lithiation agent, which was invented by Joensen (Ashori, 2014; Gee, Frindt, Joensen, & Morrison, 1986), etc. One disadvantage about this method is the lithium intercalation rate is low and often needs more than 40 h and a high temperature to prepare MoS_2 nanosheets (Ashori, 2014; Tang & Alavi, 2011).

Recently, the liquid-phase exfoliation of MoS_2 assisted with green polymer attracted many attentions. Because it not only can produce the well-stripped nanosheets, but also graft some hydrophilic polymer chains at the same time, which can facilitate introducing into many water soluble polymers and achieved homogeneously dispersion in them (O'Neill, Khan, & Coleman, 2012). For example, by taking alkali lignin as a surfactant, Lu et al. directly exfoliated MoS_2 into single-layer and few-layer nanosheets, which possessed abundant hydrophilic groups on its surface (Liu, Zhao et al., 2015; Liu, Zhou et al., 2015). SA is a natural polysaccharide derived from brown sea algae, which is a linear polyanionic copolymer composed of (1–4)-linked-D-mannuronic acid (M) and guluronic acid (G) residues (Pawar & Edgar, 2012; Yang, Xie, & He, 2011). As a hydrophilic biopolymer with −COOH and −OH in each unit, SA is favorable for its intercalation into MoS_2 layers. Besides, SA was demonstrated as a dispersing agent and stabilizer for graphene oxide in aqueous solution (Nie et al., 2015). Furthermore, SA possesses many advantages including sustainability, chemical flexibility, human and eco-friendliness. However, as a polymer material, neat SA displays some unsatisfactory properties such as weak mechanical strength, low thermal stability and loss of structural integrity, which limits its applications in many fields (Rani, Mishra, & Sen, 2013). Compositing with nanofillers was proved to be an efficient way to enhance SA (Wan, Chen, Xiong, Guo, & Luo, 2014).

In this article, hydrophilic polymer SA was employed to assisting exfoliates MoS_2 in aqueous media. Morphology and structure characterizations showed that the MoS_2 was successfully exfoliated and functionalized at the same time. Taking SA as a model water soluble polymer, the prepared SA-MoS_2 was employed to reinforce SA (Scheme 1). DMA results showed that the storage modulus of SA/SA-MoS_2 was almost 9 times higher compared to neat SA. The thermal stability of SA was found improved as well.

2. Experimental section

2.1. Materials

MoS_2 (99% purity) was purchased from Sigma-Aldrich Chemicals Inc (USA). Sodium alginate (SA) was purchased from Adamas-beta (China) and used without further purification.

2.2. Exfoliation of MoS_2

The preparation of the MoS_2 dispersion was described as follows: 1 g SA was dissolved in 100 mL deionized water at 50 °C in glass vial with stirring to prepare SA aqueous solution for 2 h. Then, 0.1 g MoS_2 powder was put into the solution upon ultra-