Mussel Inspired Preparation of MoS₂ based Polymer Nanocomposites: The Case of PolyPEGMA

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Abstract

In this work, we report a facile strategy to prepare PEGylated MoS₂ nanosheets through the combination of mussel inspired chemistry and Michael addition reaction. The MoS₂ nanosheets were obtained from lithium intercalation and exfoliation method. Meanwhile, the amino-contained poly((polyethylene glycol) methyl ether methacrylate) (PPEGMA) were obtained via chain transfer free radical polymerization using cysteamine hydrochloride as the chain transfer agents and PEGMA as the monomer. To introduce PPEGMA on MoS₂ nanosheets, polydopamine (PDA) thin films were first coated on the surface of MoS₂ nanosheets through self polymerization of dopamine as the ad-layers, which can react with amino-terminated PPEGMA through Michael addition reaction. The structure, morphology and chemical compositions of MoS₂ nanosheets and MoS₂-PDA-PPEGMA have been characterized by various characterization techniques. The results demonstrated that the amino-terminated PPEGMA can be successfully immobilized on MoS₂ nanosheets via PDA thin films as the ad-layers. More importantly, the strategy described in this work could also be utilized for surface immobilization of various polymers on many other materials and surfaces because of the universal adhesion of PDA and the good monomer applicability of chain transfer free radical polymerization. Taken together, we developed a facile and versatile method to fabricate multifunctional MoS₂ based polymer nanocomposites with designable properties and applications via combination of mussel inspired and chain transfer free radical polymerization. The resultant composites are expected to be potentially used for drug delivery and photothermal cancer treatment.

Key words: MoS₂ nanosheets, mussel inspired chemistry, PDA based polymer nanocomposites, chain transfer free radical polymerization

Introduction

Two-dimensional (2D) material, such as graphene, hexagonal boron nitrides and transition metal dichalcogenides (TMDs) have drawn a large amount of attention thanks to their unique optical, electrical, mechanical, thermodynamic properties and other excellent performance in recent years.[1-16] As the typical TMDs, molybdenum disulfide (MoS_2) has been extensively explored for different applications ranging from catalysis and electronics to biomedicine because of its special hexagonal system of layered structure.[17-27] As is known to all, MoS_2 is difficult to be dispersed in water due to its hydrophobic cleavage planes. In order to full harness the capabilities (e. g. cancer photothermal treatment or drug delivery), it is highly desirable to modify MoS_2 nanosheets with water soluble and biocompatible functional polymers or other components. For example, Liu et al, have demonstrated that MoS_2 nanosheets can be facilely surface modified with lipoic acid terminated polyethylene glycol (LA-PEG) relied on the ligand exchange between $\text{MoS}_2\text{-Fe}_3\text{O}_4$ nanocomposites and mercapto group of LA-PEG.[28] They demonstrated that the successful surface modification of water soluble and biocompatible polymers LA-PEG could obviously enhance the aqueous stability of MoS_2 nanocomposites, leading to excellent photothermal therapy effects under near-infrared laser irradiation. On the other hand, the surface modification of MoS_2 based nanomaterials with other thiol-contained compounds has also demonstrated by some other groups.[29-31] However, surface modification of MoS_2 based materials with synthetic polymers has rarely been demonstrated thus far.

Mussel inspired chemistry is an emerged surface modification method towards various materials and surfaces taken advantage of the universal and strong adhesion of polydopamine (PDA) coatings.[32-34] The PDA coatings could not only provide active sites for immobilization of initiators for surface initiated polymerization, but also could react with the compounds that contained special functional groups (e. g. $-\text{SH}$ and $-\text{NH}_2$) through Michael addition reaction.[35, 36] Based on the mussel inspired chemistry, a large number of functional materials and surfaces can be fabricated and showed great potential for different applications ranged from antibacterial, tissue engineering, and environmental adsorption, energy storage and. [33, 34, 37-48] As compared with other modification methods, mussel inspired chemistry has simple operation and mild reaction conditions. Taken advantage of above described features, mussel inspired chemistry should be useful for surface modification of MoS_2 nanosheets especially for fabrication of MoS_2 nanosheets based polymer nanocomposites.

In this contribution, we present a facile strategy for surface modification of MoS_2 nanosheets via combination of mussel inspired chemistry and chain transfer free radical polymerization. As shown in **Scheme 1**, amino terminated PPEGMA was synthesized via chain transfer free radical polymerization using cysteamine hydrochloride as the chain transfer agent and poly(ethylene lycol) monomethyl ether methacrylate (PEGMA) as monomer (**Step 1**). MoS_2 nanosheets

were obtained by chemical exfoliation methods using lithium intercalation based on [previous report](#).^[49] To prepare the MoS₂ nanosheets based polymer nanocomposites, PDA thin films were coated on the MoS₂ nanosheets through self polymerization of dopamine under weak alkaline solution. Then the synthetic polymers (PPEGMA) with amino end group were further immobilized on MoS₂-PDA nanocomposites via Michael addition reaction. The successful fabrication of final products (MoS₂-PDA-PPEGMA) was confirmed by a number of characterization techniques.

Scheme 1 The preparation of MoS₂-PDA-PPEGMA via mussel inspired chemistry. **Step 1** shows the synthesis of PPEGMA by free radical living polymerization using cysteamine hydrochloride as the chain transfer agent and poly(ethylene glycol) monomethyl ether methacrylate (PEGMA) as the monomer. **Step 2** shows the preparation of MoS₂ nanosheets and MoS₂ nanosheets based nanocomposites (MoS₂-PDA-PPEGMA) through Michael addition reaction between amino-terminated PPEGMA and MoS₂-PDA, which was simply obtained from surface coating MoS₂ nanosheets with PDA.

2. Experiment

2.1 Materials and characterization

Molybdenum (IV) sulphide (MoS₂, MW: 160.08 Da, 98%) powder was purchased from Heowns (Tianjin, China), dopamine hydrochloride (DA, MW: 198.64 Da, >98%) was purchased from Sangon Biotech, Tris-hydroxymethylaminomethane (Tris), Poly(ethylene glycol) methylethermethacrylate (PEGMA, MW: 950 Da, 98%), cysteamine hydrochloride, ammonium persulphate and n-butyllithium (1.6 M solution in hexanes) were obtained from Aladdin (Shanghai, China). Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 Spirit microscope operated at 120 kV to investigate the surface morphology of MoS₂ samples. The X-ray photoelectron (XPS)

spectra were recorded on a VGEscalab 220-IXL spectrometer using an Al K α X-ray source (1486.6 eV) to ascertain the major elements in MoS₂ samples and analyze the corresponding chemical bonds. The Fourier transform infrared (FT-IR) spectra were collected using a Nicolet 380 Fourier transform spectrometer instrument by transmission mode ranging from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹ to detect the characteristic functional group. TGA curves were recorded on a Q50 thermo gravimetric analyzer under N₂ flow and the samples were heated from 25 to 600 °C with the weight of 5-10 mg.

2.2 Synthesis of amino-contained PPEGMA

The amino-contained PPEGMA was prepared via free radical polymerization using cysteamine hydrochloride as CTA and PEGMA as monomer. In a typical experiment, PEGMA (40 mmol), cysteamine hydrochloride (1 mmol), ammonium persulphate (0.5 mmol) and deionized water (30 mL) were introduced in a polymerization bottle and purged by N₂ flow, and the reaction was carried out at 80 °C for 48 h. The crude product was purified by dialysis treatment for 48 h with frequent refreshing of water. The finally polymers were dried at 40 °C for 24 h.

2.3 Synthesis of MoS₂ nanosheets

MoS₂ nanosheets were obtained by a lithium intercalation and exfoliation method according to the previous literature.[49] In a typical experiment, 1.0 g MoS₂ powder was added into 10 mL of 1.6 M n-butyllithium solution in hexanes in a round-bottom flask with N₂ protect, and the reaction was carried out at room temperature (25 °C) for 48 h. After that, the mixture was filtered and washed with water to remove excess n-butyllithium, and the mixture was exfoliated by ultrasonic bath for 60 min. The obtained solid was separated by centrifuging at 6000 rpm for 10 min, and washed several times with water and ethanol, and dried at 40 °C for 12 h.

2.4 Synthesis of MoS₂-PDA

The method for preparation of MoS₂-PDA is similar with functionalization of other materials such as carbon nanotubes, silica nanoparticles *etc.*, which were reported from our previous works.[50-52] 300 mg MoS₂ nanosheets were dispersed in 100 mL 5 g/L dopamine solution. Then 1 mL of 1 M Tris buffer solution was added into the aforementioned solution and stirred at room temperature for 6 h. After this reaction, the product was separated by centrifuging at 6000 rpm for 10 min. Then wash with water and ethanol for several times and dried for further experiment.

2.5 Synthesis of MoS₂-PDA-PPEGMA

The MoS₂-PDA-PPEGMA was prepared by Michael addition reaction. 150 mg MoS₂-PDA was first dispersed in 100 mL of Tris buffer solution (10 mM, pH = 8.5), 300 mg PPEGMA was added into the reaction system, and this reaction was carried out at room temperature (25 °C) for 12 h. The final product was separated by centrifugation at 6000 rpm for 10 min, washed with water and ethanol for several times to remove the unreacted polymers and dried at 50 °C for 12 h.

3. Results and discussion

Fig. 1 The TEM images of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA.

In order to ascertain the successful synthesis of MoS₂-PDA-PEGMA, a series of characterization techniques have been employed, including TEM, XPS, FT-IR and TGA. The structure and morphology of these MoS₂ samples were observed via TEM. **Fig. 1** shows the TEM image of MoS₂ nanosheets (A), MoS₂-PDA (B) and MoS₂-PDA-PPEGMA (C). As compared with the raw MoS₂ nanosheets, the thickness of these sheets was obviously increased in the modified MoS₂ samples. The results clearly indicates that the successful modification of MoS₂ nanosheets by coating with PDA via mussel chemistry. However, TEM analysis cannot provide enough evidence for successful synthesis of MoS₂-PDA-PPEGMA.

Fig. 2 The FTIR spectra of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA.

Further characterizations were used to ascertain that the PDA thin films and PPEGMA were successfully coated on the surface of MoS₂ nanosheets. For example, the FT-IR spectra of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA are shown in **Fig. 2**. The new characteristic absorbance peak at about 3453 cm⁻¹ can be attributed to the O-H and N-H stretching vibration. Furthermore, the absorbance peaks located between 1400 and 1700 cm⁻¹ were also found in the spectrum of MoS₂-PDA, indicating that aromatic rings were existed in the sample of MoS₂-PDA. The above comparison implied that PDA have coated on MoS₂ nanosheets successfully. Expect from the N-H and O-H groups, some other absorbance bands at 1640 and 1100 cm⁻¹ were emerged in the sample of MoS₂-PDA-PPEGMA. These FT-IR signals can be ascribed to the stretching vibration of carbonyl groups and C-O, which evidenced that amino-terminated PPEGMA has linked onto MoS₂-PDA through Michael addition reaction. Therefore, we can conclude that MoS₂-PDA-PPEGMA nanocomposites can be successfully fabricated via combination of mussel inspired chemistry and Michael addition reaction.

Fig. 3 TGA curves of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA.

TGA was employed to provide further evidence for the stability of the samples and determine the amount of polymer on the surface of MoS₂. **Fig. 3** shows the TGA curves of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA. The raw MoS₂ nanosheets show very low weight loss (about 7.1 %) at temperature of 600 °C, indicating the excellent thermal stability of MoS₂ nanosheets. However, the weight of MoS₂-PDA and MoS₂-PDA-PPEGMA were significantly increased to 24.9% and 33.7%, respectively. The results suggest that the MoS₂ have been modified with PDA and PPEGMA, and the weight percentage of PDA and PPEGMA can be calculated to be about 17.8% and 26.6%, respectively.

Fig. 4 (A) XPS full scan spectrum range from 0 to 1200. (B) Mo3d, (C) S2p, (D) C1s (E) N1s and (F) O1s scan spectra of MoS₂ samples.

The chemical compositions of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA were examined by XPS. As shown in the survey scan XPS in **Fig. 4A**, the elements including Mo, S, C, N and O were found in MoS₂ samples. The more information of XPS spectra was shown in **Fig. 5B-F**. Compared with the unmodified MoS₂ nanosheets, the relative intensity of S2p and Mo3d signal at MoS₂-PDA and MoS₂-PDA-PPEGMA was decreased while the relative intensity of C1s signal was increased correspondingly. At the same time, a new peak between 398-404 eV relating to N1s was emerged in the samples of MoS₂-PDA and MoS₂-PDA-PPEGMA, indicating that PDA was successfully coated on the surface of MoS₂ nanosheets. Moreover, the relative intensity of N1s in the sample of MoS₂-PDA-PPEGMA was decreased as compared with MoS₂-PDA. On the contrary, the relative intensity of O1s was significantly increased in the samples of MoS₂-PDA and MoS₂-PDA-PPEGMA. These results clearly implied that PDA and PPEGMA have immobilized on MoS₂ nanosheets through self polymerization of dopamine and subsequent Michael addition reaction.

Table 1 Element contents (%) of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA based on XPS analysis.

Sample	Mo3d	S2p	C1s	N1s	O1s
MoS ₂	14.51	26.88	31.53	0	27.09
MoS ₂ -PDA	5.44	9.48	61.13	4.68	19.27
MoS ₂ -PDA-PPEGMA	3.84	7.50	64.57	1.49	22.60

Based on XPS analysis, the detailed atom percentages in MoS₂ samples were calculated and listed in **Table 1**. After coated with PDA, two element contents (%) (Mo and S) of MoS₂ were decreased obviously from 14.51% and 26.88% to 5.44% and 9.48%, respectively. Moreover, a new element (N) was found in the sample of MoS₂-PDA and MoS₂-PDA-PPEGMA, indicating that the successful coating MoS₂ with PDA. With the introduction of polymer, the percentage of C increases from 31.53% to 61.13 and 64.57% in the samples of MoS₂-PDA and MoS₂-PDA-PPEGMA, respectively.

Fig. 5 Dispersion of MoS₂ samples (Bottles from left to right are the samples of MoS₂, MoS₂-PDA and MoS₂-PDA-PPEGMA, respectively) in water in different time.

The dispersibility of MoS₂ samples has been investigated. As shown in **Fig. 5**, the MoS₂ nanosheets were precipitated rapidly within 5 min in water. The raw MoS₂ nanosheets were almost completely deposited after 2 h. The

precipitation was observed in the sample of MoS₂-PDA at the time point of 24 h, while MoS₂-PDA-PPEGMA still kept good dispersion. These results suggested that the method can be used for modification of MoS₂ and to improve the dispersibility of MoS₂ by the combination of mussel inspired chemistry and Michael addition reaction. It is well known that PEG is a biocompatible and water dispersible polymer, which has been extensively investigated for surface modification of different nanomaterials to improve their water stability and adjust their biological behavior *in vitro* and *in vivo*. [47, 53, 54] For example, we have demonstrated that ND can be effectively modified with PEG and polyPEGMA relied on the conjugation reaction and surface initiated ATRP. [53] On the other hand, surface modification of carbon nanotubes and graphene oxides has also demonstrated by Liu et al through noncovalent hydrophobic interaction. [55] However, the surface modification of MoS₂ nanosheets by polymers has attracted very little attention. [28] The surface modification of MoS₂ nanosheets with polymers through mussel inspired chemistry has not been reported thus far. In this work, we demonstrated for the first time that MoS₂ nanosheets can be facilely modified synthetic polymers via combination of mussel inspired chemistry and chain transfer free radical polymerization under rather mild experimental conditions, such as aqueous solution, air atmosphere and low temperature. More importantly, many other MoS₂ based polymer nanocomposites are expected to be fabricated through the similar method due to the universality of mussel inspired chemistry and monomer applicability of chain transfer living radical polymerization. Combined the photothermal conversion capability of MoS₂ and PDA and the desirable biological properties of PEG, these PEGylated MoS₂ nanosheets are expected to be promising for various biomedical applications such as intracellular delivery biological active agents and photothermal cancer treatment.

Conclusions

In this work, a facile method for synthesis of water soluble and biocompatible PEGylated MoS₂ nanosheets was developed by using mussel inspired chemistry and Michael addition reaction. A series of characterization techniques have been used to evidence the successful preparation of PEGylated MoS₂ nanocomposites. Considered the mild reaction and good adoptability of mussel inspired chemistry and chain transfer living radical polymerization, a large number of polymer nanocomposites with different compositions and functions can be fabricated based on the strategy developed in this work. Moreover, the method can also be used to design a large number of amino- and thiol-contained polymers to covalently link PDA for the surface modification of MoS₂ nanosheets and other materials, and used to some potential applications in various fields such as biomedicine, catalysis and so on.

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A facile and universal strategy has been developed for surface modification of MoS₂ nanosheets via combination of mussel inspired chemistry and chain transfer free radical polymerization