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Surface modification and drug delivery applications of MoS_2 nanosheets with polymers through the combination of mussel inspired chemistry and SET-LRP

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ABSTRACT

Mussel inspired chemistry is a promising surface modification tool, which has attracted great research attention for different applications owing to its universality and interest properties. In this work, a rather simple and efficient method for the surface modification of MoS_2 nanosheets with copolymers was achieved through the combination of mussel inspired chemistry and single-electron transfer living radical polymerization (SET-LRP) using 2-methacryloyloxyethyl phosphorylcholine (MPC) and itaconic acid (IA) as the monomers. The obtained MoS_2-PDA-poly(MPC-IA) nanocomposites were ascertained by a series of characterization techniques, such as nuclear magnetic resonance spectroscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy. Moreover, the MoS_2-PDA-poly(MPC-IA) nanocomposites showed enhanced dispersibility and great biocompatibility. The results implied that the MoS_2-PDA-poly(MPC-IA) nanocomposites showed great potential in the field of biomedical science. In this work, the drug loading capability and controlled drug release behavior towards CDDP have been investigated. The drug loading in MoS_2-PDA-poly(MPC-IA) composites is as high as 55.26%. All of these above results suggested that the combination of mussel inspired chemistry and SET-LRP is a facile and efficient strategy for fabrication of MoS_2 based polymer nanocomposites with great potential application in biomedical fields.

1. Introduction

Over the past several years, molybdenum disulphide (MoS_2) nanosheets as one of the most popular two-dimensional (2D) layered materials have received a great of attention of the scientists from material, chemistry and other fields due to its unique mechanical, electronic, catalytic and optical properties [1–12]. These unique two-dimensional nanosheets and their composites have been extensively exploited for catalysts, photothermal cancer ablation and drug delivery etc [1–9]. However, there are strong covalent bonding between the atom and each layer, and predominantly weak van der waals force between adjacent MoS_2 layers in the layered structure [13–15]. Therefore, the unmodified MoS_2 nanosheets are difficult to be dispersed in water and lack of functional groups, which will several hinder their applications especially in the biomedical fields. In order to solve these problems, many efforts have been made for surface modification of MoS_2 nanomaterials to improve their water dispersity, endow novel properties and enhance their performance [16–20]. In particular, surface modification of MoS_2 nanosheets with functional polymers should be one of the best choices to achieve these promising performances in biomedical applications. Nevertheless, the effective methods for surface modification of MoS_2 nanosheets with polymers are still scarcely developed thus far.

Mussel inspired chemistry is a simple and efficient method for surface modification of different inorganic and organic materials that was inspired by the composition of adhesive proteins and universal adhesion capability of mussel feet and has attracted increasing interest and been intensively explored for a wide range of applications [21–35]. It has been demonstrated that the dopamine and other catechol compounds can play the role of binding agents for coating the surface of a variety of organic and inorganic materials with thin adherent polymer films through self-polymerization under alkaline environment [21]. On the other hand, the thin polymer films can further react with some functional compounds like amino group terminated polymers through Michael additional

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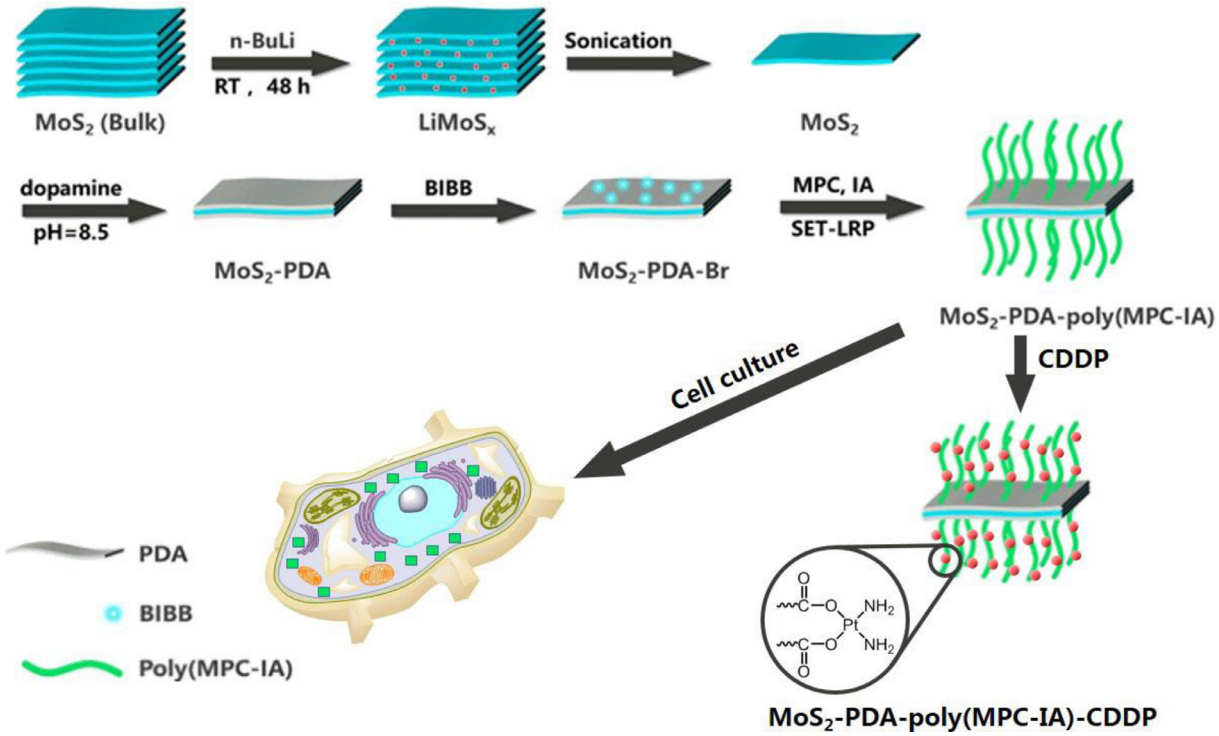

Scheme 1. The schematic procedure for preparation of MoS_2 nanosheets and MoS_2-PDA-poly(MPC-IA) polymer composites based on the combination of mussel inspired chemistry and SET-LRP.

reaction, and also can provide active sites for immobilization of initiators through esterification or amidation reaction [35]. Hence, the surface modification strategy is a rather simple and efficient method and could be expanded to the surface modification of other useful materials. Single electron transfer living radical polymerization (SET-LRP) is an efficient controlled radical polymerization method that relied on the Cu(0)/ligand as catalyst system and haloalkanes as initiator [36–47]. In comparison with other living radical polymerization including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) and nitroxide-mediated radical polymerization (NMP), the SET-LRP possess many advantages, such as ultrafast polymerization, air atmosphere, in various polymerization solvents, low polymerization temperature, small amount of catalyst, good monomer adoptability and narrow molecular weight distribution [48–56]. Therefore, SET-LRP has been regarded as one of the most attractive surface modification strategy for fabrication of multifunctional polymer composites. However, to the best of our knowledge, no reports have demonstrated the surface modification of MoS_2 nanosheets through the combination of mussel inspired chemistry and SET-LRP.

In this contribution, we demonstrated an efficient method for surface modification of MoS_2 nanosheets utilizing a combination of mussel inspired chemistry and surface-initiated SET-LRP. The synthetic route is shown in Scheme 1. To obtain the ultrathin MoS_2 nanosheets, the bulk MoS_2 powders have been successfully exfoliated by a lithium intercalation method based on the previous report [57]. Then the MoS_2 nanosheets were coated with PDA thin films through the self-polymerization of dopamine under alkaline environment. Due to the introduction of amino and hydroxyl groups, the PDA films modified MoS_2 nanosheets can be further reacted with 2-Bromoisobutyryl Bromide (BIBB) through the amidation and esterification reactions. The 2-methacryloyloxyethyl phosphorylcholine (MPC) molecule is usually used to synthesize highly hydrophilic polymer biomaterials because they possess excellent hemocompatibility and tissue compatibility. The MPC polymer shows great potential for applications in the fields of biomedical science, such as artificial organs, drug delivery and therapy, tissue engineering [58]. The synthetic Br-containing MoS_2-PDA nanocomposites can be further used for the surface initiated polymerization with MPC and itaconic acid (IA) using tris[2-(dimethylamino) ethyl] amine (Me_6TREN) as ligand and CuBr as the catalyst based on the SET-LRP technique. The obtained MoS_2-PDA-poly(MPC-IA) nanocomposites showed favorable disperibility in phosphate buffer saline (PBS) solution. Cisplatin (CDDP) is a widely used anti-cancer drug in the treatment of numerous tumors, such as ovarian, prostate, testicular, nasopharynx, esophagus cancer, head and neck, and lung cancers [59]. This work uses the CDDP loading and releasing as the model to evaluate the applications of MoS_2-PDA-poly(MPC-IA) nanocomposites in biomedicine fields. Due to the surface modification strategy described in this work is simple and effective, it can be expanded for other useful materials for biomedical applications, such as hydroxyapatite, polymer prussian blue and zeolitic imidazolate framework 90 [60–63].

2. Experiment section

2.1. Materials

Molybdenum (IV) sulphide (MoS_2, M_W: 160.08 Da, 98%) powder was purchased from Heowns (Tianjin, China), dopamine hydrochloride (DA, M_W: 198.64 Da, > 98%) was purchased from Sangon Biotech, tris-hydroxylmethylamiomethane (Tris), MPC (M_W: 295.27 Da, 98%), IA (M_W: 130.10 Da, 99%), BIBB (98%), tris(2-(dimethylamino)ethyl)amine (Me_6TREN) and CDDP (M_W: 300.05 Da) were purchased from Aladdin (Shanghai, China). All other reagents and solvents were obtained from Aladdin and used without further purification.