

Bottom-up microwave-assisted preparation of poly(methacrylic acid)-MoS₂ hybrid material

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Abstract

The bottom-up preparation and in-situ functionalization of MoS₂ with poly(methacrylic acid) (PMAA), was accomplished. For the realization of the PMAA-MoS₂ hybrid material a facile yet fast protocol based on the thermal decomposition of ammonium tetrathiomolybdate, as source for Mo and S, under microwave irradiation and in the presence of PMAA was employed. The PMAA-MoS₂ was characterized by complementary spectroscopic, thermal and electron microscopy imaging techniques. Moreover, meaningful information about the dispersibility, the nature of the colloidal dispersion and the solution properties of the hybrid material were acquired by dynamic light scattering assays.

Keywords: transition metal dichalcogenides, polymers, functionalization, hybrids, characterisation

1. Introduction

Transition metal dichalcogenides (TMDs) have drawn significant attention due to their novel structural characteristics and fascinating properties [1-3]. Notably, MoS₂ as the most studied analogue of TMDs, is considered potentially suitable in energy-related applications [4-7] as well as in photo- and electro-catalysis [8, 9]. In general, TMDs are stacks of atom-thick transition metal layers sandwiched by chalcogen layers, weakly interacting by van der Waals forces. In a typical example, MoS₂ can be exfoliated from the bulk with the aid of sonication in liquid media. Diverse exfoliation conditions employed, based on wet media as well as the presence or not of intercalant species, have led to the preferential and/or dominant acquisition of different polytypes, semiconducting [10] or metallic [11, 12] of few-layered TMDs. However, progress and full exploitation of the novel characteristics of TMDs is hampered by solubility issues, which prevent handling and manipulation in organic solvents. The way out to the latter handicap is chemical functionalization of TMDs, providing new opportunities for fabricating devices from thin-films. In this frame, a straightforward approach for acquiring modified MoS₂ with enhanced solubility is via covalent

functionalization of exfoliated MoS₂ with 1,2-dithiolanes [13]. The latter approach allowed the easy realization of innovative hybrid materials with interesting photophysical [14] and electrocatalytic [15] properties. Other strategies employed for the functionalization of TMDs involve reactions with organoiodides [16], diazonium salts [17], thiols [18-21] and coordination [22] of surface sulfur atoms with metal carboxylates. Moreover, in-situ polymerization of exfoliated MoS₂ with poly(acrylic acid) and poly(acrylamide) was performed and the hybrid materials obtained used to fabricate self-assembled layer-by-layer films [23].

Beyond those top-down approaches, involving exfoliation from the bulk and functionalization of TMDs, the corresponding bottom-up route has largely remained undeveloped. Although, thermal or hydrothermal decomposition of inorganic and/or organometallic species employed as precursors for the metal and chalcogen atoms of TMDs has been reported [24, 25], the applicability of the approach for the realization of functional TMDs has yet to be fully accomplished.

Herein, a simple, facile yet fast protocol for the bottom-up preparation and in-situ functionalization of MoS₂ with poly(methacrylic acid), abbreviated as PMAA, is reported. The PMAA is a polyelectrolyte, carrying a large number of

electron-rich ionizable groups, thereby facilitating dissolution of the modified MoS₂ in aqueous media, while at the same time providing anchor points for complexation with the electron-deficient molybdenum atoms of MoS₂.

2. Experimental section

2.1 General

Chemicals, reagents, and solvents were purchased from Sigma-Aldrich and used as received. PMAA (MW=30,000) homopolymer was synthesized by hydrolysis of poly(tert-butylmethacrylate) homopolymer prepared by anionic polymerization. Raman measurements were performed with a Renishaw confocal spectrometer at 633 nm. An ALV GmbH system was used for the dynamic light scattering measurements, with an ALV/CGS-3 compact goniometer, an ALV 5000/EPP multi- τ digital correlator with 288 channels and an ALV/LSE-5003 light scattering electronics unit for stepper motor drive and limit switch control. JDS Uniphase 22 mW He-Ne laser (λ =632.8nm) was utilized as a light source. The temperature of the measurement cell was controlled through a Polyscience 9102A12E bath circulator. The average of five measurements was taken at each angle. Cumulant methods and CONTIN software were utilized for the correlation function analysis. Toluene was the calibration standard. For DLS measurements four solubilization protocols were utilized for the light scattering studies of MoS₂ and PMAA-MoS₂. The first protocol (Protocol A) includes the direct solubilization in distilled water, regulated in pH 3, 7 and 10. The second (Protocol B) includes the direct solubilization in methanol and the third (Protocol C) includes the direct solubilization in DMF, while the fourth includes the direct solubilization in 1,4-dioxane. All samples were sonicated for 30 minutes before use. Mid-IR spectra in the region of 550-4000 cm⁻¹ were taken with an FTIR spectrometer (Equinox 55, Bruker Optics) equipped with a single reflection diamond ATR accessory (Dura-Samp1IR II by SensIR Technologies). Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500 TGA Analyzer in the temperature range of 30-900°C at a heating rate of 10 °C/min in an inert atmosphere. Microwave synthesis was undertaken in 10 mL vials using a CEM Discover SP Microwave System with an Activent technology. During the synthesis, the microwave system was operated in a dynamic mode where the power was automatically adjusted to maintain the set temperature. TEM images were taken at room temperature using a JEOL JEM-2100F, operated at an acceleration voltage of 80 keV under a pressure of 10⁻⁵ Pa. The obtained samples were sonicated in 3 mL hexane for 1 minute using an ultrasonic bath sonicator (Nanoruptor, NR-350, Cosmo Bio Co. Ltd), and 10 drops of the dispersion solution were deposited onto carbon-coated copper grids. TEM images were recorded on a Gatan MSC

794 1 k×1 k CCD camera with a typical exposure time of 0.3 s.

2.2 Preparation of PMAA-MoS₂

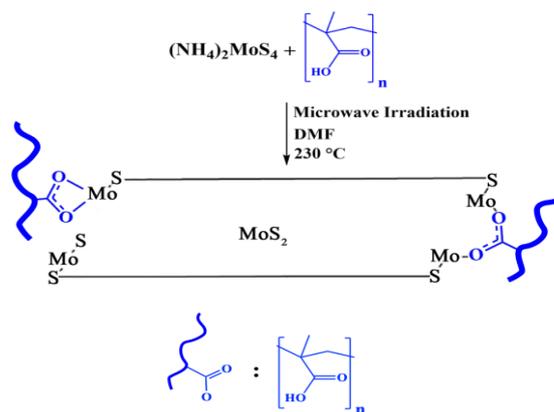
The hybrid was synthesized by microwave irradiation. Briefly, 10 mg of (NH₄)₂MoS₄ in 3 mL DMF sonicated for 30 minutes. Then, 30 mg of PMAA were added and the mixture underwent microwave treatment for 2 hours at 230 °C. After that period, the reaction mixture was filtered over PTFE filter (pore size 0.2 μ m) to obtain PMAA-MoS₂ as solid which was extensively washed with DMF and methanol.

2.3 Dispersibility studies

Distilled water in pH 3, 7 and 10, methanol, DMF and 1,4-dioxane were utilized for the solubilization/dispersibility studies of MoS₂ and PMAA-MoS₂ hybrid material, using the same protocols as above. All samples were sonicated for 30 minutes before use.

3. Results

The fabrication of MoS₂ was accomplished upon thermal decomposition of ammonium tetrathiomolybdate [26] under microwave irradiation conditions, as green and effective means. Instantaneously in a one-pot reaction, incorporation of PMAA in the reaction mixture allowed the realization of the PMAA-MoS₂ hybrid material via complexation of the -COOH units of PMAA with the Mo atoms located at the edges of MoS₂, according to Scheme 1.



Scheme 1. Illustrative bottom-up microwave-assisted preparation of MoS₂ and in-situ functionalization with PMAA yielding the PMAA-MoS₂ hybrid material.

The so-formed PMAA-MoS₂, purified by filtration of the reaction mixture through a PTFE membrane (0.2 μ m pore size) and extensive washing with DMF and methanol until no PMAA was detected in the filtrate, gave stable ink-like dispersions in DMF (0.1 mg/mL), methanol, water and 1,4-

dioxane. The dispersibility of PMAA-MoS₂ in the various solvents during time is illustrated with digital images shown in Fig. 1. The solubility achieved for PMAA-MoS₂ is the first indirect evidence for the success of the preparation of PMAA-MoS₂ since unmodified MoS₂, prepared under the same reaction conditions, but in the absence of PMAA, is insoluble in those solvents. Markedly, PMAA-MoS₂ suspensions were found to be stable for several weeks, without observing any precipitation.

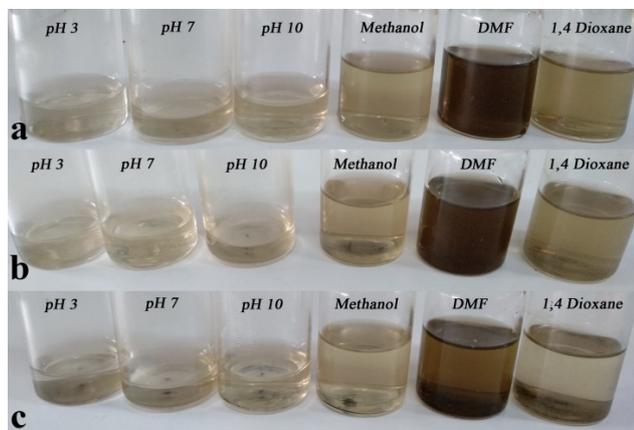


Fig. 1. Suspension of PMAA-MoS₂ (0.1 mg/mL) in water (pH 3, 7 and 10), methanol, DMF and 1,4-dioxane (from left to right, respectively), (a) immediately after sonication, and after (b) 4 hrs, and (c) 24 hrs of preparation.

Spectroscopic proof for PMAA-MoS₂ was delivered by vibrational spectroscopy. In the ATR-IR spectrum (Fig. 2a) the characteristic carbonyl vibration mode due to the -COOH unit of PMAA homopolymer appears at 1705 cm⁻¹. The corresponding band is found shifted to lower wavenumbers, at 1633 cm⁻¹, for PMAA-MoS₂, due to complexation with Mo. Similarly red-shifted were found bands owed to C-O-C in PMAA-MoS₂ at 1196 and 1102 cm⁻¹, as compared to those due to intact PMAA at 1263 and 1174 cm⁻¹ [27]. Furthermore, C-H stretching vibrations in PMAA-MoS₂ are evident at 2991 and 2928 cm⁻¹.

The Raman spectrum of PMAA-MoS₂, acquired under on-resonance conditions (λ_{exc} . 633 nm) is rich in features due to strong electron-phonon coupling interactions. Characteristic bands of MoS₂ at 373, 404 and 452 cm⁻¹ corresponding to the in-plane E_{2g}¹, out-of-plane A_{1g} and the 2LA(M) mode associated with disorder and defects, respectively, are evident (Fig. 2b). In addition, bands at lower frequency assigned as A_{1g}(M)-LA(M) at 184 cm⁻¹ and J₁, J₂ and J₃ at 150, 224 and 325 cm⁻¹ respectively, are identified. The latter J₁-J₃ phonon modes are fingerprints of the metallic polytype 1T-MoS₂ [28, 29].

Thermogravimetric analysis (TGA) of PMAA under nitrogen, showed 25 % mass loss at 200-250 °C denoting degradation of the carboxyl groups of PMAA (Fig. 2c), while

the remaining mass loss identified up to 450 °C depicts pyrolysis of the PMAA backbone [30]. In the case of PMAA-MoS₂, a slight mass loss was observed up to 200 °C due to entrapped solvents, while the 10 % mass loss registered at 200-300 °C implies degradation of -COOH units of PMAA. Finally, a 25 % mass loss at 300-450 °C depicts decomposition of the PMAA backbone. Then, the polymer loading is calculated to be one MAA per 307 MoS₂ units.

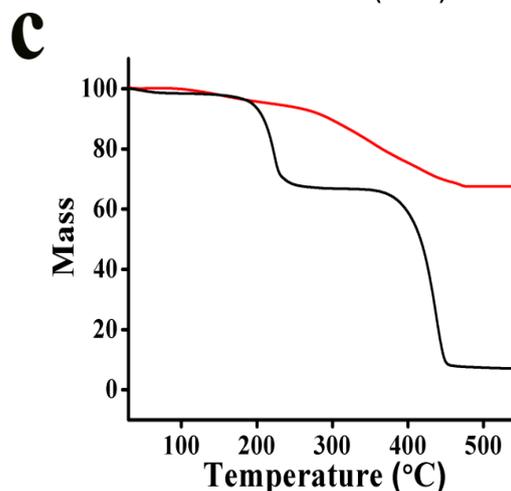
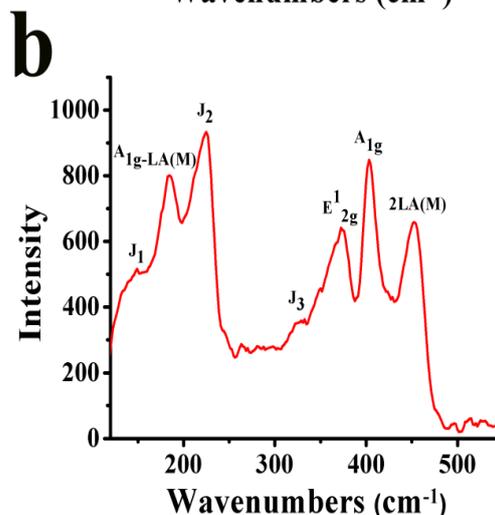
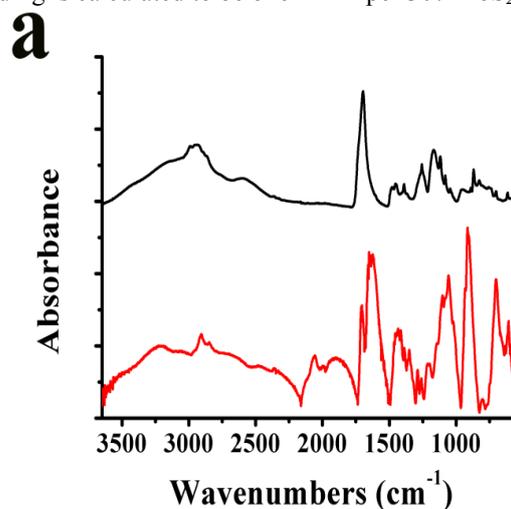


Fig. 2. (a) ATR-IR spectra for PMAA (black) and PMAA-MoS₂ (red). (b) Raman spectrum ($\lambda_{\text{exc.}}$ 633 nm) for PMAA-MoS₂. (c) Thermogravimetric analysis for PMAA-MoS₂ (red) and PMAA (black).

A typical transmission electron microscopy (TEM) image of the as-produced PMAA-MoS₂ is displayed in Fig. 3a, suggesting the existence of oligolayered structures. The interlayer distance of MoS₂ in PMAA-MoS₂ is found to be 0.62 ± 0.1 nm, which is in excellent agreement with that of MoS₂ bulk crystals. The highly crystalline nature of MoS₂ crystals with a lattice spacing of 0.31 nm, corresponding to the (004) atomic plane, was observed from high-resolution TEM image (inset Figure 3a), which is consistent with previous reports [4-7]. The energy dispersive X-ray (EDX) spectrum obtained from the corresponding area shows strong peaks due to C, Mo, O, and S atoms (Fig. 3b). The presence of Mo and S is attributed to the layered MoS₂, while that of C and O to the added PMAA. In the EDX spectrum, C and O are always detected with Mo and S, further verifying that the produced MoS₂ crystals are functionalized with PMAA.

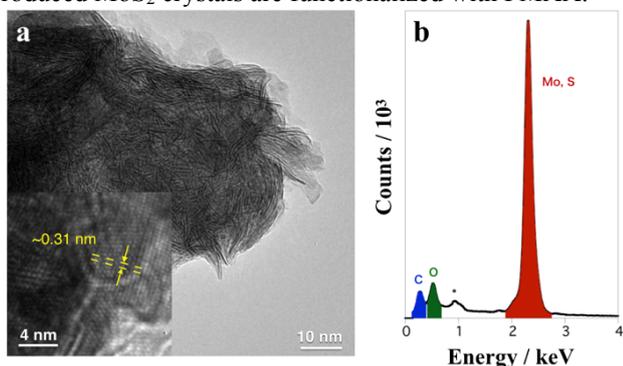
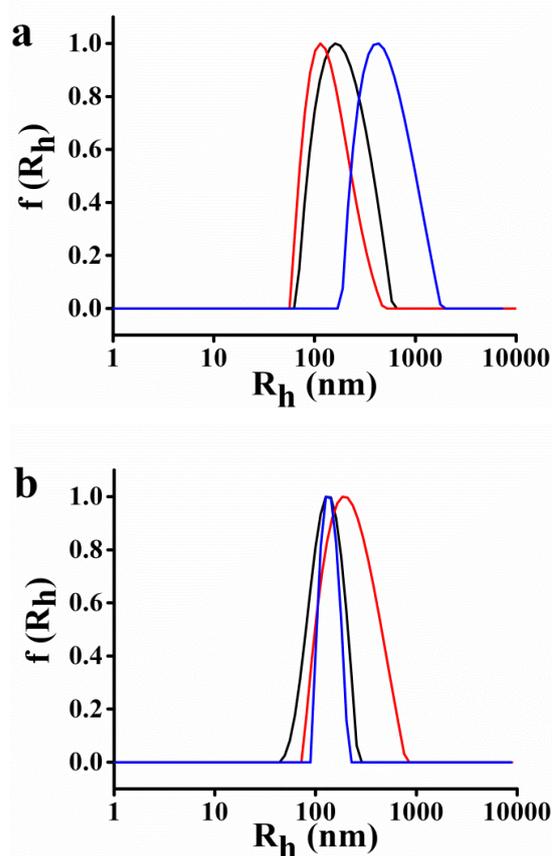


Fig. 3. (a) TEM and high-resolution TEM (inset) images, and (b) EDX spectrum of PMAA-MoS₂. The peak labeled with * is due to Cu of TEM grid.

In order to collect information about the dispersibility, the nature of the colloidal dispersion and the solution properties of PMAA-MoS₂, dynamic light scattering (DLS) measurements were undertaken in various good solvents for PMAA. Table 1 summarizes the effect of different solvents on R_h values of PMAA-MoS₂ in comparison with intact MoS₂. The DLS assays were performed in diluted samples to avoid absorbance phenomena and to diminish intra-hybrid interactions. CONTIN analysis of DLS correlation functions for PMAA-MoS₂ indicates an increase in R_h values with decreasing solvent polarity (Fig. 4a). In aqueous media (Fig. 4b), samples in pH 3 form larger aggregates, while increasing the pH results in decreasing the R_h and the polydispersity of the formed aggregates. The latter observations are due to the fact that the carboxyl groups of the PMAA are protonated at pH 3, and thus being less hydrophilic, contributing to a more aggregated state of

dispersion. Conversely, at pH 10 carboxyl groups are deprotonated, PMAA chains become negatively charged and thus being repelled by each other and forced to stretch.³¹ This leads to a better dispersed, more soluble and less aggregated, hybrid nanomaterial. On the other hand, DLS studies of intact MoS₂ could be accomplished only in DMF and methanol, since intact MoS₂ dispersions showed immediate precipitation in both 1,4-dioxane and water. CONTIN analysis of DLS correlation functions (Fig. 5) for MoS₂ shows that R_h decreases by increasing solvent's polarity, pointing to a better solubilization state of the nanomaterial. The results further support the preparation of PMAA-MoS₂ since solubility in solvents, especially in water, is possible only due to the presence of the PMAA component in the



hybrid structure.

Fig. 4. CONTIN analysis of DLS correlation functions for PMAA-MoS₂ hybrid material in (a) methanol (red), DMF (black), 1,4-dioxane (blue), and (b) in water at pH 3 (red), 7 (black) and 10 (blue).

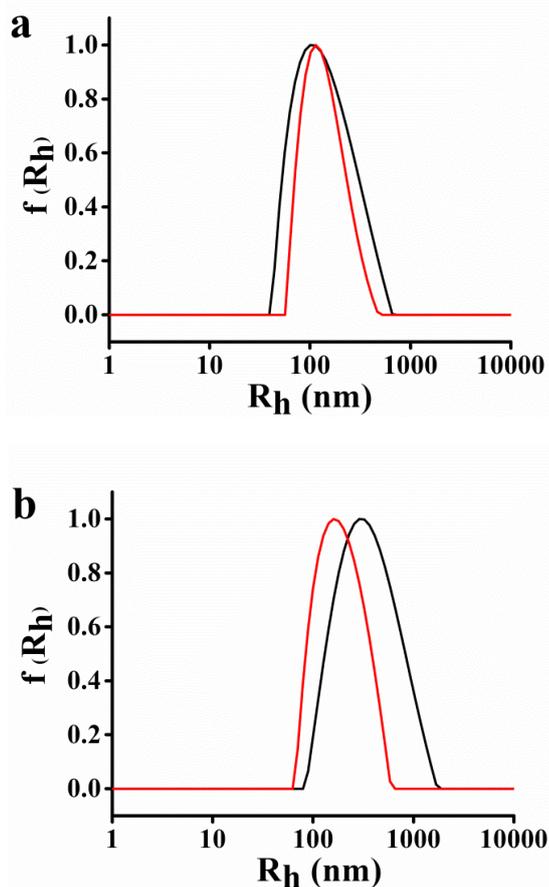


Fig. 5. CONTIN analysis of DLS correlation functions for MoS₂ (black) and PMAA-MoS₂ hybrid material (red) in (a) methanol and (b) DMF.

Table 1. R_h values for intact MoS₂ and PMAA-MoS₂ hybrid material determined by DLS.

Solvent	MoS ₂ R_h (nm)	PMAA-MoS ₂ R_h (nm)
H ₂ O (pH 3)	-	217
H ₂ O (pH 7)	-	128
H ₂ O (pH 10)	-	137
Methanol	134	133
DMF	307	172
1,4 Dioxane	-	500

4. Conclusions

In summary, a facile one-pot route for the bottom-up preparation of MoS₂, based on the microwave-assisted decomposition of ammonium tetrathiomolybdate, in-situ functionalized by PMAA was accomplished. The PMAA-

MoS₂ hybrid material was characterized by a gamut of techniques, based on IR and Raman spectroscopy, TGA and TEM imaging coupled with EDX, which proved the coexistence of the two species in the hybrid material. The presence of polymer in the hybrid material allowed solubility enhancement, mainly in DMF but also in methanol, 1,4-dioxane and water, permitting to perform DLS assays and study the solution properties of PMAA-MoS₂. By extension, the newly developed protocol can be applied for the preparation and modification of diverse transition metal dichalcogenides incorporating different polymeric species, by employing suitable inorganic precursors and macromolecules, opening new pathways for fast and easy preparation of modified TMDs.

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