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## Covalent cross-linking of 2H-MoS<sub>2</sub> nanosheets

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Abstract: The combination of 2D materials opens a wide range of possibilities to create new generation structures with multiple applications. Covalently cross-linked approaches are a groundbreaking strategy for the formation of homo or heterostructures made by design. However, the covalent assembly of transition metal dichalcogenides flakes is relatively underexplored. Here, a simple covalent cross-linking method to build 2H-MoS<sub>2</sub>-MoS<sub>2</sub> homostructures is described, using commercially available bismaleimides. Theses assemblies are majoritarily connected vertically, basal plane to basal plane, creating specific molecular sized spaces between MoS<sub>2</sub> sheets. This straightforward approach, therefore, gives access to the controlled connection of sulfide-based 2D materials.

The stack of different 2D materials<sup>[1-6]</sup> is the root of the field of van der Waals heterostructures.[7] The most widespread method for the synthesis of heterostructures of bidimensional materials is the direct growth of one material on top of the other by chemical vapor deposition or van der Waals epitaxy. [8] Alternatively, one can manually stack one material on top of the other, using deterministic transfer methodologies. [9-14] These methods are limited to interfacing the 2D materials through van der Waals forces.

There are very few synthetic methods of building 2D-2D homo/heterostructures that allow for precise control of the distance and chemical nature of the interface between materials, which directly determines their electronic communication and is, therefore, crucial for function.[15, 16]

Covalently cross-linked structures are a very attractive strategy for the formation of homo/heterostructures made by design, with control over the size and chemical nature of the crosslinker.[15, 16] This type of approach has been explored for cross-linked homostructures of carbon nanotubes (1D-1D)[17-20] and graphene derivatives (2D-2D),[21-23] as well as mixed-dimensional heterostructures of fullerenes and graphene derivatives (0D-2D) [24-26] and carbon nanotubes and graphene oxide (1D-2D). [27,28] In comparison with the C-based nanomaterials, the covalent crosslinking of transition metal dichalcogenides (TMDCs) is relatively underexplored, most likely due to a less developed, even if quickly growing, toolbox of chemical reactions for the covalent modification of TMDCs.[29-36] Seminal work by C. N. Rao has described the covalent connection of MoS<sub>2</sub> with borocarbonitrides and C<sub>3</sub>N<sub>4</sub> with remarkable catalytic activity, [37, 38] and the formation of MoS<sub>2</sub>-MoS<sub>2</sub> homostructures through a two-step Sonogashira coupling reaction.[39]

Recently, we presented a "click" method for the covalent functionalization of 2H-MoS<sub>2</sub>, based on the presence of a soft nucleophile (the sulphur of MoS2 structure) which can attack the double bond of maleimide derivatives, resulting in the formation of a chemical C-S bond between the material and the organic moiety. [40, 41]

Here, we present the formation of covalently linked MoS<sub>2</sub>-MoS<sub>2</sub> homostructures in suspension, using the MoS2-maleimide "click" reaction. Few layer colloids of MoS2 were obtained through liquid phase exfoliation (LPE) in N-Methyl-2-pyrrolidone (NMP) using an ultrasonic probe (1h). The supernatant exfoliated material was separated from bulk through centrifugation (See SI, general procedures). The resulting 2H-polytype MoS<sub>2</sub> was characterized by UV-Vis, Raman spectroscopy and XRD.[41] The flakes showed a majority height profile below 12 nm (Figure S1) determined by AFM and a larger dimension of 374±125 nm on average, as determined by TEM measurements. To connect the MoS<sub>2</sub> flakes, the colloids were transferred to acetonitrile, then we added commercially available bis-maleimide 1, and the mixture was vigorously stirred overnight, to generate a covalently linked MoS2succ-succ-MoS<sub>2</sub> homostructure (Figure 1). The dispersion was filtered and washed several times using acetonitrile and isopropanol. The residues were checked by UV-Vis, confirming the total elimination of the physisorbed reagent after several washes (Figure S2). The resulting powder was dried and characterized exhaustively.

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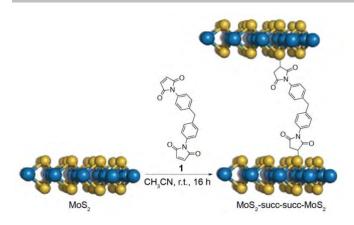


Figure 1. General scheme of the formation of  $\mbox{MoS}_2\mbox{-succ-succ-MoS}_2$  homostructure.

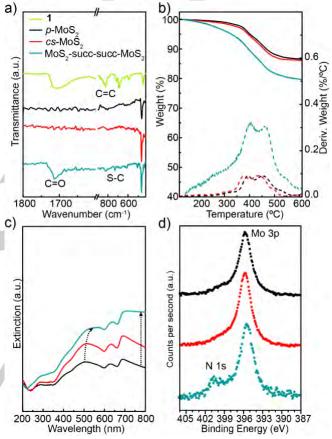
ATR-FTIR of the functionalized material (MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub>, blue trace in Figure 2a) revealed the presence of the vibrational mode of carbonyl stretch in the surface of MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub> (1715 cm<sup>-1</sup>), which is not present in either unreacted exfoliated material (*p*-MoS<sub>2</sub>) or in a control sample experiment (*cs*-MoS<sub>2</sub>), in which MoS<sub>2</sub> was subjected to the same reaction and purification process without the presence of 1 (black and red traces in Figure 2a, respectively). Moreover, we observe the disappearance of the sp<sup>2</sup> C-H bending of the alkene in 1 (821 cm<sup>-1</sup>, green trace in Figure 2a). Besides, a new band related by the generation of the C-S bond was observed at 729 cm<sup>-1</sup>, confirming the linking between the organic moiety and the surface of MoS<sub>2</sub>.<sup>[40]</sup>

Thermogravimetric analysis showed significant differences between the functionalized and control sample (Figure 2b). In the case of MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub>, derivative weight shows a new maximum between 210 and 320 °C, which we assign to the organic anchor; a second, slow, two-step decomposition between 350 °C and 550 °C is also observed and correlates well with the oxidation of MoS<sub>2</sub>. In addition, at 550 °C the differences in the thermal decomposition of the functionalized material against its unreacted exfoliated material is 6%. In comparison, cs-MoS2 did not show any difference with the exfoliated material (compare black and red traces in Figure 2b). TGA under N2 flow showed similar weight loss (Figure S3) with shifted variation in the thermal decomposition in the case of the homostructure MoS2-succ-succ-MoS<sub>2</sub>. XRD showed slight differences in the functionalization of the material (Figure S4). The XRD patterns of as-prepared exfoliated  $MoS_2$  and  $MoS_2$ -succ-succ- $MoS_2$ , are in good agreement with the standard data for MoS<sub>2</sub>.[42] No extra characteristic peaks from the organic moiety or the homostructure were detected, which may because of its relatively low diffraction intensity compared to that of MoS2. Resonant Raman spectroscopy measurements ( $\lambda_{exc}$  = 633 nm) showed clearly that the exfoliated material is few-layer 2H-MoS2 polytype, and remains as such after functionalization, with the characteristic E<sub>2g</sub>, A<sub>1g</sub>, and 2LA(M) modes. Besides, the relative intensity of the 2LA(M) mode of MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub> showed a decrease compared to the unreacted exfoliated material, which can be connected to an increase in number of layers/vertical size (Figure

The anchor of a chemical moiety onto the surface of MoS<sub>2</sub> with a bismaleimide functional group, allows the formation of vertical homostructures of MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub>. Such covalent cross-

linking involves a significant increase in particle size, which is clearly reflected as a significant increase on the scattering contribution observed in the extinction spectra, and a red shift on the excitonic peaks of  $MoS_2$ , in  $MoS_2$ -succ-succ- $MoS_2$  compared to  $p-MoS_2$  and  $cs-MoS_2$  (Figure 2c).<sup>[45]</sup>

Finally, XPS analysis showed the presence of N (1.9%), onto the surface of the functionalized material, while neither p-MoS $_2$  nor cs-MoS $_2$  showed detectable amounts of N (Figure 2d, Figure S6, Table S1). The relation with the modified sulphurs (4%) of the material would correspond to a 9% weight loss in TGA, see Eq. S1, which is in good agreement with our TGA data.



**Figure 2.** a) ATR-FTIR of bismaleimide **1** (green), unreacted exfoliated MoS $_2$  (black), MoS $_2$ -succ-succ-MoS $_2$  (blue) and control sample MoS $_2$  (red). b) TGA (air, 10 °C min $^1$ ) of  $p\text{-MoS}_2$ ,  $cs\text{-MoS}_2$  and MoS $_2$ -succ-succ-MoS $_2$  c) UV-VIS of unreacted exfoliated MoS $_2$  (black), MoS $_2$ -succ-succ-MoS $_2$  (blue) and control sample experiment (red). d) XPS core level of N 1s comparison between unreacted exfoliated MoS $_2$  (black), MoS $_2$ -succ-succ-MoS $_2$  (blue) and control sample experiment (red)

AFM analysis of hundreds of flakes of the different samples spin-coated from acetonitrile, showed a clear increase in the thickness of the flakes in the case of  $MoS_2$ -succ-succ- $MoS_2$  with respect to  $p\text{-}MoS_2$  (Figure 3a). However, the formation of the homostructure did not modify the lateral size of the sample significantly, indicating that a vertical cross-linking of  $MoS_2$  was the favored mode of reaction, in line with preferential functionalization of  $MoS_2$  basal planes. Remarkably, this thickness increase is observed only when the reaction is carried out with two maleimide anchor points that can react with the material, it was not observed in the reaction with other maleimides previously studied in our group or

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in the control sample experiment (Figure S7).  $^{[40,41]}$  In a closer look, AFM profiles of specific flakes of  $MoS_2$ -succ-succ- $MoS_2$  often showed a two-step profile, confirming the presence of two or more flakes connected vertically, while such pattern is rarely observed in p- $MoS_2$  (compare insets in Figure 3b and c).

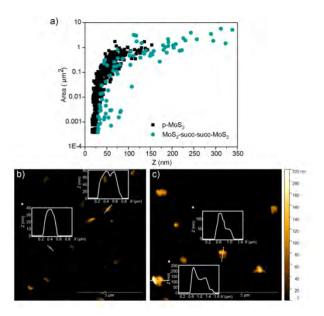
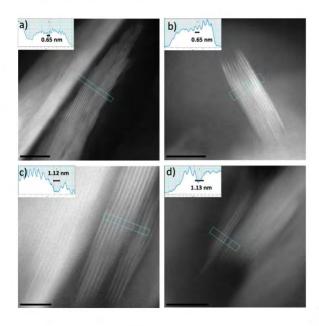


Figure 3. a) Scatter plot of area ( $\mu m^2$ ) vs height (nm) of unreacted exfoliated MoS<sub>2</sub> (black) and MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub> (blue), b) AFM images and height profiles of unreacted exfoliated MoS<sub>2</sub> and c) MoS<sub>2</sub>-succ-succ-MoS<sub>2</sub>.

A FEI Titan™ microscope working at an acceleration voltage of 300 kV was employed for the characterization of MoS<sub>2</sub> flakes through electron microscopy. A 10 µL suspension of the MoS<sub>2</sub> flakes dispersed in DMSO was drop-casted onto 200 square mesh copper holey carbon TEM grid and then dried overnight. Spherical aberration corrected HAADF-HRSTEM measurements are shown in Figure 4. Examination of the unreacted exfoliated and functionalized MoS2-succ-succ-MoS2 showed a variety of interlayer spacing. Thus, for the control sample a periodic interlayer spacing of 0.65 nm is consistently observed (Figure 4a). On the other hand, for the functionalized samples, we find both flakes that did not react and kept the original spacing (Figure 4b) and, frequently in other cases, a spacing around 1.1 nm can be observed between two flakes. Note that image contrast in HAADF-STEM is inversely correlated with the atomic mass, so the lighter elements in the organic fragment (C, H, N, O) are expected to appear dark when compared to the heavier Mo and S. These results correspond reasonably well to the estimated distance between two small fragments of MoS2 separated by 1 (1.3 nm, according to molecular mechanics calculations, see Figure S8). These results are one more clear indication of the covalent cross-linking MoS2 flakes (See Figure S9).



**Figure 4.** High-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images of  $MoS_2$  a) control experiment, b) isolated flake of functionalized  $MoS_2$  c) and d) cross-linked flakes of  $MoS_2$ -succ-succ- $MoS_2$ . Scale bar 5nm.

In summary, a simple methodology to covalently connect flakes of  $MoS_2$  for the generation of vertical  $MoS_2$ - $MoS_2$  homostructures was developed, using commercially available bismaleimide reagent. The new material showed an increase of the thickness of the nanosheets without significant changes in the lateral size as a reliable indicator of the vertical growth of the homostructure. We believe that this approach opens up many possibilities to connect other sulfide-based 2D materials through covalent bonds, with control of the interlayer distance, as a complementary approach to van der Waals homo/heterostructures. [46] Potential applications include the increase of conductivity or extinction coefficient or photoresponsivity of the active material in TMDC devices, while conserving the electronic properties of the monolayer material.

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There are no conflicts to declare.

**Keywords:** 2D materials • covalent homostructure •  $MoS_2$  • covalent functionalization

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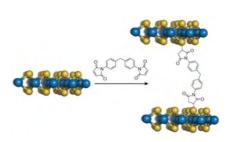
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#### **Entry for the Table of Contents**



The covalent combination of different flakes of 2D materials is relatively underexplored, in particular, in the case of transition metal dichalcogenides. This work reports a simple methodology of covalent cross-linking of MoS2 through bismaleimide reagent. The MoS2-MoS<sub>2</sub> homostructures show preferably a vertical connection, basal plane to basal plane of different flakes.

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