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Probing the interaction between 2D materials and oligoglycine tectomers

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Abstract: Heterostructures of 2D materials using graphene and MoS2, have enabled both pivotal fundamental studies and unprecedented sensing properties. These heterosystems are intriguing when graphene and MoS2 are interfaced with 2D sheets that emulate biomolecules, such as amino-terminated oligoglycine self-assemblies (known as tectomers). The adsorption of tectomer sheets over graphene and MoS2 modulates the physicochemical properties through electronic charge migration and mechanical stress transfer. Here, we present a systematic study by Raman spectroscopy and tectomer-functionalised scanning probe microscopy to understand mechanical strain, charge transfer and binding affinity in tectomer/graphene and tectomer/MoS2 hybrid structures. Raman mapping reveals distinctive thickness dependence of tectomer-induced charge transfer to MoS2, showing p-doping on monolayer MoS2 and n-doping on multilayer MoS2. By contrast, graphene is n-doped by tectomer independently of layer number, as confirmed by X-ray photoelectron spectroscopy (XPS). The interfacial adhesion between the amino groups and 2D materials are further explored using tectomer-functionalised probe microscopy. It is demonstrated here that these probes have potential for chemically sensitive imaging of 2D materials, which will be useful for mapping chemically distinct domains of surfaces and the number of layers. The facile tectomer-coating approach described here is an attractive soft-chemistry strategy for high-density amine-functionalisation of AFM probes, therefore opening promising avenues for sensor applications.

Keywords: Heterostructure, 2D materials, peptide assemblies, adhesion force, strain, doping, Raman spectroscopy
**Introduction:**

There is significant research interest in exploring the modulation of mechanical and physicochemical properties when interfacing different two-dimensional (2D) materials. Such vertical heterostructures using graphene, transition metal dichalcogenides (such as MoS$_2$ and WS$_2$), and hexagonal boron nitride can exhibit electronic doping and strain phenomena as well as other synergies such as moiré superlattice which can improve device performance in myriads of applications.[1-10] Beyond conventional 2D materials, coupling these nanosheets with derivatives of biomolecules such as peptides and their assemblies can modulate the intrinsic physical properties of 2D materials and provide new functionalities as well as processing versatility. Thus, it enables the use of these nanosheets as the platform for chemical and biosensing applications in biomedicine, bioelectronics and micro-mechanical devices.[11-16]

Most of these sensor applications are based on non-covalent interactions at the interface between 2D material-based sensing layers and the biomolecules of interest that preserve the electrical properties and intrinsic strength of the 2D materials,[17] in contrast to defect-induced detection.[18] In graphene, sp$^2$ hybridised carbon atoms are arranged in a long-range $\pi$ conjugation acting as a semi-metal. During the physisorption of foreign species, these conjugated systems recognise subtle changes in electronic and physical characteristics. While chalcogenides such as MoS$_2$ have a trilayer configuration of S-Mo-S, they demonstrate thickness-dependent electronic and optical properties. Monolayer MoS$_2$ is a semiconductor ($E_g \approx 1.9$ eV) and is extremely sensitive towards physisorbed foreign molecules at its basal plane through electrostatic and van der Waals interactions.[19, 20] One of the general mechanisms of sensing foreign entities attached to the 2D sheets is to measure the shifting of Fermi level as a result of the induced n- or p-doping.[21] Several studies have demonstrated the ability of graphene- and MoS$_2$-based biosensors to detect DNA-protein complexes, nucleobases and amino acids.[21-23]

The influence of the interactions with biomolecular species on graphene and MoS$_2$ sheets can be envisioned in terms of locally induced mechanical strain ($\varepsilon$) and charge carrier density ($n$) compared to their pristine state. There are several detection techniques, namely fluorescence, colourimetry, electrochemiluminescence, etc., which have been implemented to detect the changes in the adsorbed system.[24, 25] Raman spectroscopic imaging is another powerful experimental technique to study the physicochemical interactions in graphene and MoS$_2$, which has been established as a promising non-destructive tool to evaluate the mechanical strain and carrier density.[26, 27] The Raman modes G (E'$_{2g}$) and 2D (A$_{1g}$) of graphene (MoS$_2$) are known to be associated with the change of interatomic distances and the redistribution of charge carriers.[28-30] The interactions of graphene and MoS$_2$ can also be visualised by measuring the interfacial adhesion, which is only indirectly probed by spectroscopic techniques,[31] and thus, a direct alternative would be atomic force microscopy (AFM) with the state-of-the-art concept of probe functionalisation.[32][33]

The complementary use of Raman mapping and scanning probing techniques is useful in gathering interfacial interaction between 2D materials and biomolecules such as oligopeptides. The advantage of using a peptide-based assembly to develop this sensing approach is that they emulate the diversity of a range of biological structures and functional groups such as DNA and amino acids.[34] Amino-terminated oligoglycine peptides consist of antennae of typically four to seven glycine units connected by alkyl linkers, C$_8$H$_{16}$-(CH$_2$-NH-Gly)$_n$$_2$. These oligopeptides self-assemble into sheet-like 2D structures (single-layered platelet thickness $\sim$5.6 nm) through cooperative hydrogen bonding between adjacent glycine units in neighbouring antennae. The oligoglycine assembly is pH-responsive, a unique
feature among 2D materials, that allows the controlled load and release of cargo as a function of pH.[34, 35] Additionally, surface amino groups in the tectomer provide remarkable adhesive properties that can be exploited to coat and provide new functions to a range of substrates by efficiently attaching a variety of molecules and nanoparticles. Previous research suggests tectomers can exhibit ambipolar charge transfer, and thus the significant areal doping when successfully interfaced with other 2D nanomaterials can be utilised for the fabrication of novel layered composite materials.[35, 36]

In the present work, we show that the binding affinities of the amine surface groups of tectomers with MoS$_2$ and graphene nanosheets lead to specific changes in charge carrier density and mechanical strain, which are monitored by Raman mapping. In addition, AFM probe functionalisation by wrapping tectomer around the tip apex provides spatially resolved information on interfacial interaction as well as quantitative measurement of critical adhesion force (pull-out) between tectomers and the 2D materials tested. Thus, it is demonstrated here that these probes have potential for chemically sensitive imaging of 2D materials, which will be useful for mapping chemically distinct domains of surfaces and the number of layers. The measured interfacial adhesion force values show a similar trend with binding energy (BE) shifts of N1s peaks in tectomers from X-ray photoelectron spectroscopy (XPS). The results reported here open attractive avenues for the use of amino-terminated oligopeptides in the development of future surface and chemical sensors as well as the fabrication of novel functional heterostructures with other 2D materials.

**Results and Discussion:**

AFM topography of tectomers deposited on MoS$_2$ and graphene on silica substrates are shown in Fig. 1a and b respectively. Chemical vapor deposition (CVD) grown MoS$_2$ is in the form of triangular monolayer island, while CVD grown graphene was transferred onto silica as a continuous single layer (1L) with bilayer (2L) islands. Over both surfaces, the thickness of the deposited tectomer sheets is 5.6 ± 0.5 nm, corresponding to a monolayer (Fig. S1).

![Fig. 1. Tectomer deposition on MoS$_2$ and graphene:](attachment:image.png) (a) AFM topography of tectomer sheets over CVD-grown MoS$_2$ on a silica substrate. (b) Tectomer sheet on CVD-grown graphene on a silica substrate. For both MoS$_2$ and graphene, the thickness of tectomer sheets is 5.6 ± 0.5 nm corresponding to a monolayer (Fig. S1).

The typical Raman spectra of bare 1L MoS$_2$ and tectomer-coated 1L MoS$_2$ are compared in Fig. 2a. The Raman bands for bare 1L MoS$_2$ corresponding to the in-plane vibrations ($E_{1g}$) and out-of-plane
vibrations ($\Gamma_{1g}$) of Mo and S atoms are located at approximately 385 cm$^{-1}$ and 405 cm$^{-1}$ respectively,[27, 38] where the Raman peak difference ($\Gamma_{1g}$ - $\Gamma_{13g}$) of $\sim$20 cm$^{-1}$ confirms that it is a monolayer.[39] Additional AFM images for the monolayer can be found in Fig. S2. Upon tectomer coating of MoS$_2$, the $\Gamma_{13g}$ mode downshifts while the $\Gamma_{1g}$ mode upshifts. To study this effect extensively, Raman mapping of bare 1L MoS$_2$ (Fig. 2b, c) and tectomer-coated 1L MoS$_2$ (Fig. 2d, e) are carried out by collecting spectral data within the same region, which can be used to extract strain ($\varepsilon$) and charge carrier density (n) in MoS$_2$ by a generalized linear transformation (Eq. 1):

$$
\begin{pmatrix}
\omega_1 \\
\omega_2
\end{pmatrix}
= \begin{pmatrix}
-2\gamma_1 \omega_1^0 & k_1 \\
-2\gamma_2 \omega_2^0 & k_2
\end{pmatrix}
\begin{pmatrix}
\varepsilon \\
n
\end{pmatrix}
$$

(1)

where $\gamma$ is the Grüneisen parameter, $k$ is the doping sensitivity, and $\omega^0$ is the absence of strain and doping frequency. The subscript 1 and 2 represents $\Gamma_{13g}$ and $\Gamma_{1g}$ mode where constant values are respectively $\gamma_{13g} = 0.086$, $\gamma_{1g} = 0.15$, $k_{13g} = -0.33 \times 10^{-13}$ cm$^{-1}$, and $k_{1g} = -2.22 \times 10^{-13}$ cm$^{-1}$.[30, 40] Using Eq. (1), a correlation plot of $\Gamma_{1g}$ against $\Gamma_{13g}$ (Fig. 2f) can be plotted with contour lines (marked as gray dashed lines) representing equal level of strain and carrier concentration. The point of intersection of the strain axis (in pink) and the doping axis (in brown) calculated as (384.9 ± 0.4 cm$^{-1}$, 405.0 ± 0.2 cm$^{-1}$) provides the average value of strain and doping of bare MoS$_2$. The distribution and the histogram of the data is illustrated in Fig. S3. Thus, the deviation from the intersection in the Raman modes represents the locally induced strain and doping due to the interaction with tectomer.

These results show that tectomer coating modifies the Raman shifts of $\Gamma_{13g}$ and $\Gamma_{1g}$ mode in 1L MoS$_2$ to (384.2 ± 0.3) cm$^{-1}$ and (405.8 ± 0.4) cm$^{-1}$ respectively, indicating a surface morphology change by mechanical stretching which induces a tensile strain increase of (0.11 ± 0.05) %, as well as a decrease in charge carrier density by (4.0 ± 1.8) x 10$^{12}$ cm$^{-2}$ (as indicated by the black arrow in Fig. 2f), i.e., p-doping to 1L MoS$_2$. The distribution of the above data can be found in the histogram in Fig. S3. On the other hand, the correlation plot used for multilayer (ML) MoS$_2$-tectomer system (Fig. 2g-i) is limited to a qualitative description as the layer number itself will have an influence on the peak positions (see Fig. S2 for the thickness distribution and Raman mapping of ML MoS$_2$). Nevertheless, the shift of the Raman modes of ML MoS$_2$ indicates n-doping and compressive strain induced by tectomer (black arrow in Fig. 2i). This clearly illustrates that the changes in MoS$_2$ carrier concentration imposed by tectomer decoration are layer dependent.
Fig. 2. Raman mapping characterization of tectomer-coated MoS$_2$: (a) Raman spectra of MoS$_2$ and tectomer-coated MoS$_2$ show E'$_{2g}$ and A$_{1g}$ MoS$_2$ bands. (b) The Raman map of E'$_{2g}$ and (c) A$_{1g}$ of the 1L MoS$_2$ region without tectomer. (d) The Raman map of E'$_{2g}$ and (e) A$_{1g}$ of the tectomer-covered 1L MoS$_2$. (f) Correlation plot of 1L MoS$_2$ region and tectomer-covered 1L MoS$_2$ region shows the effect of tectomer on MoS$_2$ for charge concentration (n) and strain (ε). (g) Raman map of E'$_{2g}$ and (h) A$_{1g}$ of the tectomer-covered ML MoS$_2$. Tectomer-coating (marked by a dashed circle) is located at the center of the MoS$_2$ flake. (i) Correlation plot of ML MoS$_2$ region and tectomer-covered ML MoS$_2$ region shows an increase of carrier concentration and compressive strain induced by tectomers on ML MoS$_2$.

As for graphene, the tectomer coating induces downshift of 6 cm$^{-1}$ and 2 cm$^{-1}$ of the G and 2D Raman modes respectively as illustrated in the typical Raman spectra (Fig. 3a), where the additional peak at
1654 cm\(^{-1}\) shows the presence of polyglycene II type crystalline structure that results from the oligoglycine self-assembly.[41] The effect of tectomer coating on modulating strain and doping in 1L graphene (see Fig. S2 for the thickness measurement by AFM) can also be calculated by the linear transformation in Eq. (1), where the subscript 1 and 2 are now replaced by G and 2D modes and the corresponding constants are \( \gamma_1 = 1.95 \), \( \gamma_2 = 3.15 \), \( k_1 = -1.407 \times 10^{-12} \) cm\(^{-1}\) and \( k_2 = -0.285 \times 10^{-12} \) cm\(^{-1}\).[26, 42] The resulting correlation plot in Fig. 3b shows the increase in electron concentration (less p-doping) of \((4.9 \pm 1.6) \times 10^{12} \) cm\(^{-2}\) in graphene induced by the tectomer decoration (see Fig. S3 for the distribution of data). Nevertheless, the strain in graphene layer does not alter significantly when interfaced with tectomer, and the whole system remains in compressive strain, which is typical for the graphene/silica interface.[43] Given the minimal strain exerted on 1L graphene upon tectomer coating, \( G_0 \) linearly varies with the absolute value of the Fermi level from the Dirac point \(|E_F|\) (Eq. 2):[44, 45]

\[
G_0 - 1580 = |E_F| \times 42 \text{ cm}^2 \text{ eV}^{-1}
\]  

A significant shift in \( E_F \) of \((290 \pm 90) \) meV can be calculated for graphene with adsorbed tectomer. These results reveal that tectomer sheets modify the electronic carrier concentration of 1L graphene (and, therefore, act as dopants) but do not induce mechanical strain. Also, 2L graphene has shown a similar response as its 1L counterpart (Fig. 3c), i.e., tectomer leads to an increase in carrier concentration (n-doping) in graphene without significant modulation of strain as indicated by the redshift in G and 2D peak positions.

**Fig. 3.** Raman analysis showing the effect of tectomer coating on strain and doping of 1L and ML graphene: (a) Raman spectra of graphene show the G and 2D Raman modes shifting as a result of tectomer deposition. (b) The correlation plot of bare 1L graphene and tectomer decorated graphene illustrates deconvoluted strain and doping. The arrow directions reveal the increase in carrier concentration with minimal alteration in straining. (c) Raman spectrum of 2L graphene showing downshift in G and 2D peak position after tectomer deposition.

XPS characterization reveals the interactions established by the amino groups on the tectomer surface with MoS\(_2\) or graphene by monitoring the changes in N1s XPS spectra of tectomer/ML MoS\(_2\) and tectomer/ML graphene. The identification of the N1s peak requires a comprehensive analysis of the spectra near the Mo3p\(_{3/2}\) peak centred at 395.2 eV as it overlaps the N1s region. In Fig. 4a, the peak at
399.6 eV corresponds to the nitrogen atoms in the oligoglycine antennae of tectomers. The 2.0 eV shift towards higher binding energy (BE) in the presence of MoS$_2$ (Fig. 4a, c) indicates the donation of electron density (n-doping) from tectomer amino surface groups towards ML MoS$_2$, which is consistent with Raman spectroscopy results. Fig. S3 shows S2p and Mo3d XPS spectra of pristine MoS$_2$ and tectomer/MoS$_2$ hybrids. The two identified doublets are characteristic of the S$^2-$ and Mo$^{4+}$ features presented in pristine MoS$_2$.[46] Interestingly, all peaks in the XPS spectra in Fig. S4 are shifted identically to higher BE ~0.3 eV in tectomer/MoS$_2$ hybrids with respect to pristine MoS$_2$, suggesting a change in the Fermi level associated with n-doping.[47, 48] On the other hand, for tectomer/ML graphene, N1s XPS spectra exhibit a 1.6 eV shift towards higher BE (Fig. 4a, d) that can be explained by charge transfer (n-type doping) of amino groups in tectomers into the $\pi$-system in graphene. Also, a shift of 1.6 eV in N1s XPS spectra was previously measured for other graphene-based material, such as carbon nanocones, where the donation of electrons from amino groups in tectomers to the $\pi$-system of carbon nanocones also occurs.[36] Further characterization of tectomer/MoS$_2$ and tectomer/graphene hybrids by TEM, SEM and EDX analysis are shown in Fig. S5 and S6. The effect of electrical doping from tectomer to ML MoS$_2$ and ML graphene can also be validated by I-V characterization as a function of different bias voltages (-2 to 2V), and at constant applied voltage (1V) as a function of time (s). A sharp distinction in the resistance trend has been observed for graphene (increasing) and MoS$_2$ (decreasing). Given graphene usually being p-type and MoS$_2$ being n-type, this suggests tectomer n-dope both ML graphene and ML MoS$_2$. These results corroborated Raman spectroscopy and XPS results which suggest n-doping of tectomer to both ML graphene and MoS$_2$ (see Supplementary Information Fig. S7 for details).
Fig. 4. XPS characterization of layered hybrids of tectomer/ML MoS$_2$ and tectomer/ML graphene: High resolution XPS spectra showing the N1s and Mo3p$_{3/2}$ core levels of (a) tectomers, (b) pristine MoS$_2$, (c) tectomer/MoS$_2$ and (d) tectomer/graphene.

Raman spectroscopy and XPS results indicate that tectomers interact differently with MoS$_2$ and graphene, leading to specific changes in charge carrier density, mechanical strain, and BE. This distinctive tectomer interaction towards 2D materials could be exploited in the development of tectomer-based surface recognition sensors. As a proof-of-concept, the interfacial interaction of tectomers with MoS$_2$ and graphene was characterised using tectomer-functionalised AFM probes, so routine adhesion force AFM measurements through force-distance spectroscopy provide the specified interfacial interaction between the surface amino terminated groups of tectomers and the scanned samples.[33, 49] Fig. 5a illustrates a pristine AFM tip with a radius of 70 nm, which increases to 250 nm upon tectomer coating (Fig. 5b, c). The schematic representation of functionalised probe microscopy over graphene and MoS$_2$ is shown in Fig. 5d. The interaction between bare Pt/Ir-coated Si probe apex towards tectomer sheets as a function of time, AFM images showing minimal adhesion affinity dependence on tectomer thickness, and a separate study on the mass of the tectomer deposited over the cantilever are included in Supplementary Information Fig. S8, S9 and S10, respectively.

Adhesion force measurements are performed using tectomer-functionalized AFM probes scanning over 1L MoS$_2$ and 1L graphene deposited on silica substrates as illustrated in Fig. 5e, f and Fig. 5g, h respectively. There is a significant contrast in the adhesion force maps measured for silica substrate, graphene and MoS$_2$ layers. The conversion of absolute adhesion force values into adhesive pressure[33] is attained by normalizing the adhesion force values from silica substrate at the same acquisition and introducing the adhesive pressure ratio between tectomer/2D materials and tectomer/silica. This normalisation provides measurements independent of the contact area between tip apex and the surface. The adhesive pressure values of tectomer-functionalised tip towards 1L graphene being nearly 25% higher than 1L MoS$_2$ (Fig. 5i) reveals its chemical selectivity towards surface carbon and sulphur atoms. Moreover, the tectomer-functionalised probe is sensitive to the number of layers for both graphene and MoS$_2$ and shows a clear distinction in adhesion force values with different layer(s) in the following order: 1L graphene > ML MoS$_2$ > 1L MoS$_2$ > 2L (folded) graphene > ML graphene (Fig. 5j, k). While the adhesion of tectomer/1L graphene is higher than that tectomer/1L MoS$_2$, the adhesion of graphene (MoS$_2$) decreases (increases) with layer number and eventually the adhesion of tectomer/ML graphene becomes lower than that of tectomer/ML MoS$_2$.

The overall distribution of the adhesive pressure values could be explained using the reference from XPS results. The higher BE shift of tectomer/ML MoS$_2$ than tectomer/ML graphene reveals stronger interaction of tectomer towards ML MoS$_2$. However, graphene/silica and MoS$_2$/silica system offer different layer-dependent electrostatic interaction due to variations in the densities of carrier types (i.e., p-type and n-type). The concentration of their respective charge carriers depends on the number of layers due to screening effect.[50, 51] Graphene is usually a p-doped system on silica substrate.[43, 52] Thus, 1L graphene is rich in hole carriers which gradually decrease with increasing the number of layers.[50] Given that amino-terminated tectomers are susceptible to donating electrons, the interfacial adhesion will be stronger for a more positively charged surface (such as 1L graphene/silica), than a less positively charged surface (2L graphene/silica). In contrast, the three-layered structure (S-Mo-S) in MoS$_2$ has a different interaction with silica substrate (typically n-doped).[52, 53] With increasing the number of MoS$_2$ layers, charge screening together with the effect of adsorbed airborne impurities (charge trapping centers, e.g. water molecules)[51] lead to less n-doping (more positive charges). Consequently, electron density donation from tectomer and hence the interfacial adhesion will be stronger for thicker MoS$_2$. 


It is worth noting that the AFM-based elastic indentation depth is lower for the multilayers for both graphene and MoS$_2$ (Fig. S11), and thus lower contact area between the functionalised probe apex and the 2D materials is expected. Therefore, the interaction between the functionalised probe and graphene or MoS$_2$ will be primarily influenced by the charge distribution at the surface rather than mechanical indentation. The trend of adhesion force values can be validated through a separate experiment (Fig. S12) where silicon wafer (covered with native oxide) is stimulated at different bias voltages (-2, 0, 2V) to monitor the electrostatic adhesion towards tectomer coated probe. It has been observed that negative bias voltage results in lower adhesion force value, which is gradually increasing with the positive bias. Thus, interfacial interaction between the amino-terminated functionalised probe with its counter surfaces is dominated by localised charge domains over the substrate.

Fig. 5. Interaction between tectomer-functionalised AFM probes and 2D materials: (a) SEM image of pristine AFM tip. Inset shows the encircled tip apex in high resolution, revealing a radius of 70 nm. (b) SEM image of tectomer-coated AFM tip apex and (c) the zoomed image shows the radius increases to 250 nm. (d) Schematic diagram of tectomer-coated AFM tip scanning on MoS$_2$ and graphene (Gr). (e, f) AFM morphology and adhesion force map of the tectomer-coated tip scanning over silica-MoS$_2$ and (g, h) silica-graphene. (i, j) Adhesive pressure ratio profile of silica-MoS$_2$, silica-graphene and graphene wrinkle. (k) The distribution of adhesive pressure ratio varies over different surfaces showing that the tectomer-coated AFM probe is sensitive to the number of layers.
Conclusion

2D material-based sensing is demonstrated using graphene and MoS₂ against amino-terminated oligoglycine. The versatile surface chemistry provided by the surface amino groups of tectomers enables the fabrication of novel heterostructures with other 2D nanomaterials, inducing changes in the mechanical strain and carrier density of the (semi)conducting materials. Functionalised probe microscopy in conjunction with Raman mapping and XPS reveals valuable insights into interfacial interactions. The different susceptibilities of tectomer to modulate the properties of 1L and ML MoS₂ is discussed towards strain and doping; p-doping and tension is observed for 1L MoS₂ and n-doping and compression for ML MoS₂. In contrast, graphene is always n-doped by the amine groups of tectomer sheet independently of the layer number. Interestingly, no additional strain has been observed in both 1L and 2L graphene from the tectomers which is useful to monitor the modulation of the Fermi level. It is also demonstrated that tectomer-functionalised AFM probes present the possibility of chemically sensitive imaging of 2D materials which will be useful for mapping chemically distinct domains of surfaces. The facile tectomer-coating approach described here is an attractive soft-chemistry strategy for high-density amine-functionalisation of AFM probes. These amine groups allow further functionalisation for molecular recognition imaging, therefore opening promising avenues for sensor applications.

Materials and methods

Preparation of MoS₂ and Graphene

The fabrication of MoS₂ crystals island over silica is comprehensively described in the literature.[54] A silicon wafer with a 90 nm silica oxide layer is spin coated by aqueous solution of NaMoO₃ (concentration 2 mg/mL). The coated wafer is placed in the furnace equipped with two different temperature settings, i.e., 750 °C with a rate of 10 °C/min and 230 °C. During the second stage of temperature treatment, the quartz crucible loaded with S (2 g) and treated for 15 minutes at the same temperature. Later the sample is removed from the furnace and allowed to cool at room temperature. Single layer CVD graphene over silica was purchased from Graphenea (Graphenea, Inc, Spain). The distribution of 1L graphene was monitored through Raman mapping. Mechanically exfoliated graphene was fabricated through scotch tape method and deposited over 90 nm thick silica.

Preparation of Tectomer

Biantennary oligoglycine peptide (C₆H₁₀(-(CH₂-NH-Gly)₂ 2HCl, purity > 95%) was supplied by PlasmaChem GmbH. Tectomers resulted from the self-assembly of oligoglycine solutions in ultrapure water (Siemens LaboStar Di/UV 2 system, resistivity: 18.2 MΩ cm at 25 °C) bath sonicated (100 W Branson 2510 bath sonicator) for 3 min.

Preparation of Tectomer/MoS₂ and Tectomer/Graphene Hybrids for XPS Characterisation

Liquid-phase exfoliated (LPE) MoS₂ dispersion in cyclopentanone (CPO) (0.45 mg·mL⁻¹) was prepared by a procedure that involves successive sonication of MoS₂ powder samples and centrifugation steps. Tectomers are poorly soluble in CPO; thus, solubilisation of tectomers in CPO and subsequent tectomer/MoS₂ hybrid formation were achieved by tectomer phase transfer from aqueous solution. CPO and H₂O form a two-phase system, where CPO is located in the upper layer due to its lower density. Thus, a 2 mg·mL⁻¹ oligoglycine aqueous solution was added 1:1 to a MoS₂ dispersion in CPO. The two-phase system consisting of MoS₂-containing CPO (upper phase) and tectomer solutions (lower phase) was vigorously shaken by hand and then led settle for 24 hours. Tectomer/MoS₂ hybrids were collected from the CPO upper phase and characterized by XPS.
A similar procedure was followed for graphene (from Aldrich ref#900561). Thus, a dispersion of graphene in CPO (2 mg·mL\(^{-1}\)) was prepared by sonication and then a 2 mg·mL\(^{-1}\) oligoglycine aqueous solution was added 1:1. The two-phase system was vigorously shaken by hand and then left for 24 hours. Tectomer/graphene hybrids collected from the aqueous lower phase was characterized by XPS.

**AFM and KPFM Measurements**

AFM characterization is performed by Bruker Dimension Icon with PF-QNM (PeakForce-Quantitative NanoMechanical) mode. Tectomer functionalized probe is made by dipping SCM-PIT tip into tectomer solution for 30 minutes. Multiple dip coatings have been performed to ensure complete coating of the probe. Adhesion is measured by the pull-out force in the force-distance curve when the tip leaves the surface. This force corresponds to the interaction between tectomer and the measured sample.

**Raman Spectroscopy**

Raman spectroscopy is carried out by Renishaw inVia™ confocal Raman microscope with 0.8 cm\(^{-1}\) spectral resolution and 532 nm laser (type: solid state, model: RL53250). 1800 mm\(^{-1}\) grating in 100x magnification and 5 mW laser power is used. The peak position and peak intensity are then evaluated by Lorentz fitting.

**Electron Microscopy Characterization**

Transmission electron microscopy (TEM, Tecnai F30, FEI) microscopes were used to characterize the structural features of tectomers and MoS\(_2\) platelets and their interaction in the hybrids. Samples for TEM imaging were prepared depositing a droplet of dispersions of the tested materials onto carbon-coated copper grids (previously treated in a UV-ozone chamber for 5 min). The samples were allowed to dry under ambient conditions after wicking away most of the solution.

Scanning electron microscopy (SEM) characterization was performed with an Inspect F50 field emission SEM microscope (FEI). Samples were coated with a 14 nm thick palladium layer by sputtering prior to SEM imaging. Energy dispersive X-ray spectroscopy (EDS) allowed us to allocate MoS\(_2\) nanosheets in tectomer/MoS\(_2\) hybrids.

**X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) was performed on drop-cast dispersions dried at room temperature on Al foil using an ESCA Plus Omicron spectrometer provided with a Mg anode (1253.6 eV) working at 225 W (15 mA, 15 kV). Binding energy (BE) positions were corrected by setting sp\(^3\) carbon at a binding energy (BE) = 284.8 eV. CASA software was used for the peak deconvolution and Shirley type baseline correction was applied.

**Graphene and MoS\(_2\) Chemiresistor**

The microscale electrical response for the interaction between the 2D materials and tectomer were carried out over interdigitated electrodes (IDEs). Mechanically exfoliated few layers of graphene and MoS\(_2\) are deposed over the IDEs gold electrodes. ME 2D materials are preferred over CVD based 2D materials due to their crystalline nature, mitigation of structural defects (such as grain boundaries in graphene), and unwanted organic residue appeared during wet transfer. Difference in the electrical response (\(A\)) has been measured in pre and post deposition of the tectomers through I-V curves as a function of different voltages (-2 to 2V) and as a function of time (s) to monitor the doping effect from tectomer.
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