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The Covalent Functionalization of Few-layered MoTe₂ Thin Films with Iodonium Salts

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Abstract

Covalent functionalization of 2D materials provides a tailored approach towards tuning of their chemical, optical and electronic properties making the search for new ways to graft small molecules important. Herein, the reaction with (3,5-bis(trifluoromethyl)phenyl)iodonium salt is revealed as an effective strategy for functionalization of MoTe₂ thin films. Upon decomposition of the salt, the generated radicals graft covalently as aryl-(CF₃)₂ groups at the surface of both metallic (1T') and semiconducting (2H) polymorphs of MoTe₂. Remarkably, the reactivity of the salt is governed by the electronic structure of the given polymorph. While the functionalization of the metallic MoTe₂ occurs spontaneously, the semiconducting MoTe₂ requires activation by light. The reaction proceeds with the elimination of oxide from the original films yielding the functionalized products that remain protected in ambient conditions, presenting a viable solution to the ageing of MoTe₂ in air.

Keywords: transition-metal dichalcogenides; 2D materials; covalent functionalization; iodonium salts; thin films; surface chemistry

Once a mere academic curiosity, atomically-thin, two-dimensional (2D) transition-metal dichalcogenides (TMDCs) have become an important class of materials capable of driving transformative changes to modern electronic and photonic networks,[1–3] catalytic systems,[4–6] sensing and biomedical applications.[7–9] 2D materials consist mainly of surfaces that dictate their physical properties.[1] Thus, controlling the surfaces offers exciting opportunities for future developments of 2D TMDCs as even minor changes to the surface states could have a major impact over their electronic structures.

Chemical modification is a promising method to deliver such changes to the surfaces. A number of reagents have been shown to be able to tether to TMDCs through covalent and non-covalent interactions.[10,11] For example, grafting of thiol-related compounds is a relatively well-explored method for the functionalization of MoS₂ which is an archetypal TMDC.[12–14] Iodomethane, iodoacetamide and diazonium salts are other common small molecules that have been used for functionalization of TMDCs due to their ability to form a strong bond with the chalcogen atom.[15–20] However, chemical functionalization of TMDCs with diazonium salts does not proceed easily even when carried out on powdered samples.[17,19] For example, chemical exfoliation with organolithium reagents is often required to make MoS₂ accessible for nucleophilic attack and successful functionalization. Also, small flake sizes in powders (for example, only functionalized flakes that passed a 200 nm membrane were studied)[17] has prevented unambiguous identification of whether the functionalization occurred on edges, defects or basal planes.

Remarkably, MoTe₂ (an atomically thin cousin of MoS₂) appears to be more prone to functionalization without the need for a pre-treatment by organolithium reagents. Flakes (although

of unspecified sizes) mechanically exfoliated from a single crystal of MoTe₂ have been reported to be passivated by diazonium chemistry,[20] although it is unclear whether a covalent bond was formed upon grafting. Still, the ability of MoTe₂ to withstand aggressive electrophiles, such as 4-nitrobenzenediazonium tetrafluoroborate, without dissolution is remarkable, given the previous reports on the degradation of MoTe₂ under ambient conditions.[10] This suggests that MoTe₂ is a promising target for the functionalization chemistry and more research is needed in this direction. Since both metallic and semiconducting polymorphs of MoTe₂ can be prepared as atomically-thin and continuous films[21–23] there are exciting opportunities for investigating the role of crystal structure of MoTe₂ on the reactivity with small molecules. The difference in reactivity between MoS₂ and MoTe₂ suggests that alternative reagents could be explored for surface functionalization as well. Work in this direction could lead to new hybrid 2D materials as well as answering the question of whether a strong bond between MoTe₂ and grafting agent is formed.

Iodonium salts (ISs) are particularly interesting targets because unlike the commonly used diazonium salts, they manifest lower reduction potentials and a wider range of substituent functional groups (aromatic, alkynyl, alkyl, heterocyclic) that could be used for altering the chemical properties of the underlying TMDCs.[24] In addition, ISs are less prone to spontaneous reduction, making them very interesting targets for advanced control over surface grafting.[25] Furthermore, there are many ISs that have fluorine-containing groups which could be used as markers for detection of whether the functionalization took place. For example, even minor quantities of F can be detected by XPS, making F-containing ISs well suited models for the mechanistic studies of reaction processes.[26] Finally, the ability of IS to be activated under stimuli (such as light,[27] plasmonic resonance,[28] chemical agents[29] and electric potential[30]) offers

a better control over the reaction processes. Therefore, it is rather surprising that ISs have not been applied for chemical functionalisation of TMDCs so far.

In this work, we demonstrate using MoTe₂ thin films that reaction with a symmetric bis(3,5-bis(trifluoromethyl)phenyl)iodonium salt results in surface functionalization of MoTe₂ with aryl-(CF₃)₂ groups as evidence by a comprehensive studies with Raman spectroscopy, XPS, AFM and WCA. Remarkably, the reactive ability of the salts depends on the nature of the polymorphic phase used. This suggests that the electronic structure of the underlying MoTe₂ polymorph plays an important role in facilitating the reaction. In addition, the reaction of MoTe₂ with the iodonium salt provides an effective way of protecting (the otherwise unstable) MoTe₂ films against oxidation in ambient.

Results

Synthesis and characterization of MoTe₂ films

Thin films of the monoclinic 1T'- and hexagonal 2H-MoTe₂ were prepared in a CVD reactor at 650 °C using FeTe₂ precursor as the source of tellurium similar to previous work.[22] According to Raman spectroscopy the resulting products were either single-phased 1T'-MoTe₂ or 2H-MoTe₂ (Supplementary Fig. S1, Supplementary Table S1A) depending on the seeding layer used. The films were intentionally handled in air and no attempts were made to protect them from the ambient environment, for example, by encapsulation or deposition of a protective layer. AFM measurements (Supplementary Fig. S2) confirmed the film thicknesses of 8.2±0.5 nm for 1T'-MoTe₂ (*ca.* 10 layers) and 9.4±0.5 nm (*ca.* 12 layers) for 2H-MoTe₂. XPS survey spectra (Supplementary Fig. S3) showed the presence of oxygen; while high-resolution XPS analysis of Mo 3d and Te 3d (Supplementary Fig. S4) showed the presence of oxidized states on the surface, typical for MoTe₂ films exposed to the ambient environment.[31]

Reaction of 1T'-MoTe₂ films with bis(3,5-bis(trifluoromethyl)phenyl)iodonium salt (IS-CF₃)

Iodonium salts (ISs) are modification agents serving as the source of aryl radicals after the homolytic cleavage of the carbon–iodine bond (Fig. 1).[27] In contrast to more widely explored aromatic diazonium salts, ISs may be advantageous due to the lower reduction potential, wider range of substituents, and broader range of stimuli that can be used for their activation.[24,32] As shown in Fig. 1, the carbon – iodine bond cleavage in ISs generates a radical that can attack the surface (which poses the question about the nature of the chemical bond created between MoTe₂ and aryl radicals), while the remaining fragment of the initial molecule is reduced to iodoarene that is not reactivated and can be easily removed by rinsing with solvent.

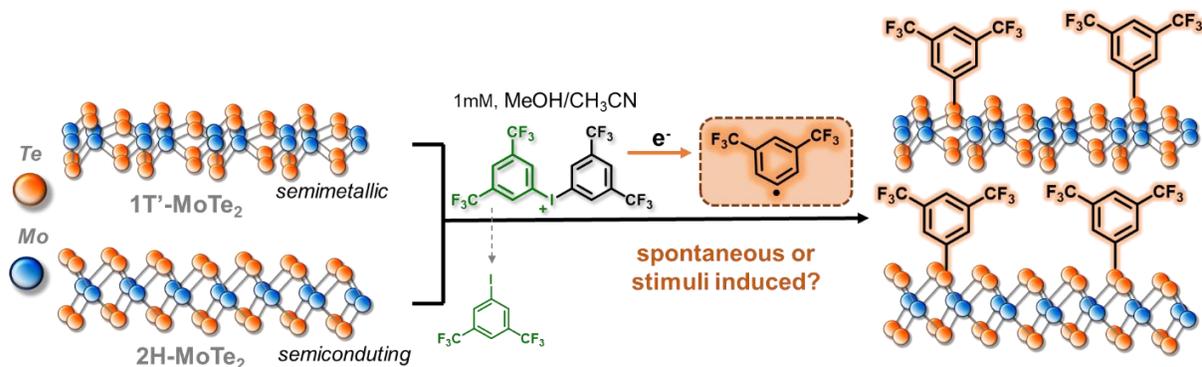


Figure 1. Schematic illustration of 1T'- and 2H-MoTe₂ functionalization using iodonium salts. ISs decompose *via* C-I bond homolysis with the formation of aryl radicals that graft to the surface. The remaining iodoarene is removed by washing with solvent

Bis(trifluoromethyl)phenyliodonium triflate (Supplementary Fig.S5) further denoted as **IS-CF₃**, was selected for the feasibility study of covalent functionalization of MoTe₂. After the reaction with the solvents was excluded (Supplementary Fig. S6-7), the 1T'-MoTe₂ film was immersed in a 1 mM solution of **IS-CF₃** in MeOH:CH₃CN for 1 hour, repeatedly washed with degassed MeOH:CH₃CN, and finally dried under an argon flow. The initial analysis by Raman spectroscopy of the product (denoted as 1T'-MoTe₂-CF₃) showed a blue shift of the A_{1g} peak by 3±1 cm⁻¹ suggesting the functionalization took place (Fig. 2A , Supplementary Fig. S8 and Supplementary Table S1A). A similar shift of the A_{1g} mode, that represents out-of-plane vibrations, was previously observed in other chalcogenides (for example, upon reaction with electron-withdrawing molecules)[33,34] and can be explained by the difference in Ch – C and Ch – Mo (Ch = S, Se, Te) bond strengths.[35] On the other hand, the E¹_{2g} in-plane mode remains unaffected in terms of position and intensity (Supplementary Table S1A). E¹_{2g} is highly sensitive to interlayer interactions and because it remains unaffected, damage of the film after functionalization can be excluded.[35]. Therefore, we conclude that grafting of aryl groups proceeds only to the top layer of MoTe₂ film.

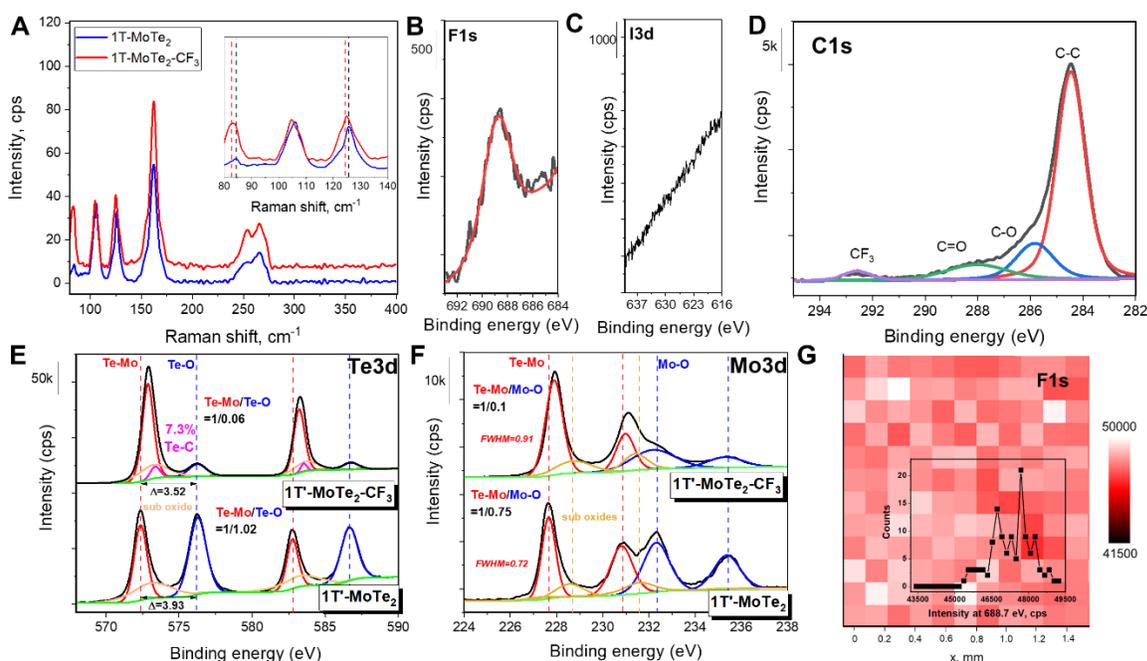


Figure 2. The characterization of 1T'-MoTe₂ films before and after the treatment with bis(trifluoromethyl)phenyliodonium salt. The 633 nm Raman spectra of the film before (red solid line) and after (blue solid line) (A); High resolution XPS spectra corresponding to F 1s (B), I 3d (C), C 1s (D), Te3d (E) and Mo 3d regions (F). The XPS mapping of F 1s peak over the area of 1.5 × 1.6 mm². The insert shows distribution of intensities of the peaks from the F 1s mapping (G).

XPS allows the detection of even minute amounts of fluorine,[26] and thus **IS-CF₃** is an excellent functionalization marker due to the presence of CF₃ groups (Supplementary Fig. S9). In addition, the F-peak at ≈690 eV in the survey XPS spectrum (Supplementary Fig. S10A) is well resolved and does not overlap with other peaks, for example, from MoTe₂ or the Si / SiO₂ substrate. According to the high-resolution spectrum the appearance of F1s peak at 688.7 eV (with 1.7 at. % concentration) confirmed that the surface grafting with F-containing groups took place (Fig. 2B). The simple sorption of the salt on the surface or between MoTe₂ layers can be excluded because

of the absence of the I 3d peak expected at BE = 622.9 and 634.4 eV suggesting that decomposition of the salt followed by functionalization of the surface took place (Fig. 2C). In addition, the position of the peak at 292.6 eV in the high-resolution C 1s spectrum corresponds to the position of carbon in the CF₃ moiety (Fig. 2D). Finally, XPS mapping collected by scanning 121 points over the area of 1.5 × 1.6 mm² confirmed the lateral distribution of fluorine across the surface (Fig. 2G). The sum of the F1s signals obtained from the mapping experiments revealed a homogeneous distribution of fluorinated groups over the surface with the average spectrum centred at 688.7 eV and the intensities deviating only marginally (<4 %) from the average signal of 46335 ± 1726.8 cps (Supplementary Fig. S10B). The prolongation of functionalization time could lead the increased content of F up to 4 at. % after 2.5 hours of reaction (Fig. S10C). Based on the evidences collected so far we hypothesize that surface functionalization by 3,5-(trifluoromethyl)phenyl groups (further denoted as Ar-(CF₃)₂ for brevity) took place in a kinetically controlled manner. In addition, significant changes observed in the high-resolution Mo 3d and Te 3d XPS spectra before and after the reaction with **IS-CF₃** seem to confirm the hypothesis. First, there is a substantial decrease in the intensity of the peaks associated with Mo – O and Te – O bonds. This is evident from the change in the relative ratio of the peak intensities marked as Te-Mo/Te-O that changed from 1/1.02 to 1/0.06 (Fig. 2E). At the same time, the intensity ratio of Mo-Te/Mo-O peaks decreased from 1/0.75 to 1/0.10 respectively (Fig. 2F). Secondly, the positions of Te 3d and Mo 3d peaks shifted by 0.4 eV and 0.15 eV, respectively (Supplementary Table S2). Thirdly, the full-width-at-half-maximum (FWHM) of Te 3d_{5/2} and Mo 3d_{5/2} peaks increased from 1.07 to 1.3 (Fig. 2E) and from 0.72 to 0.91, respectively (Fig. 2F). Similar peak shifts and broadening were observed in the Mo 3d XPS spectra of 1T-MoS₂ powders functionalized with aryl-iodides and diazonium salts.[4,16–18]

Covalent functionalization could in principle proceed through the formation of O-C (from Mo-O and Te-O), Te-C and Mo-C bonds. The significant reduction in the intensities of Mo-O and Te-O probably excludes the formation of bonding with surface oxygen; otherwise, the functionalization would proceed without elimination of the oxide layer. The stronger shift of Te-Mo peaks by 0.40 eV *versus* Mo-Te peaks that shift by only 0.15 eV after the reaction with **IS-CF₃** suggests that Te is the more probable binding site for the functional moieties. In addition, the analogy with the functionalization chemistry of MoS₂, where the covalent bond is formed between chalcogen and carbon (rather than molybdenum and carbon), suggests that Te is a more likely binding site for covalent bond.[4,18] Furthermore, the broadening of Te 3d_{5/2} peaks at 572.8 eV with the FWHM increasing from 1.07 to 1.3 suggests the presence of an additional component. This component is probably similar to the appearance of a prominent shoulder peak (ascribed to formation of covalent bond) in S 2p spectra of the functionalized MoS₂. [4,18] Therefore, we deconvoluted the broadening of Mo-Te peak in the high-resolution Te 3d spectra of 1T'-MoTe₂-CF₃ into two components at BE = 573.37±0.05 and 583.53±0.05 eV (Fig. 2E). We ascribed the second component (pink trace in Fig. 2E) to C-Te species. It was also possible to extract the information about the level of the functionalization in a similar fashion as it was carried previously for MoS₂.¹⁸ The relative degree of the covalent functionalization (calculated by dividing the peak area associated with this C-Te component to the total area of Te 3d_{5/2} peak) was found to be 7.3 %.

In addition, the thickness of the organic layer at the surface could be estimated from the Te 3d peak intensities using a method proposed previously with the relevant calculations given in the Supplementary Note 1.[36] Based on the observed attenuation of Te 3d spectra, the calculations revealed that Ar-(CF₃)₂ groups cover the surface with a density of 4.8×10¹⁴ molecules cm⁻² while the thickness of the layer was found to be 1.3±0.8 nm. These values are the same order of

magnitude as those achieved on graphene functionalised with IS using an electrochemical process.[37] Considering the size of the Ar-(CF₃)₂ moieties 0.6±0.2 nm, we can conclude that the formation of close to a monolayer coating is achieved.[28] The results are also close, for example, to previously observed coverages on gold surfaces.[38]

To validate this assessment, we performed an AFM analysis across a 3×3 μm² area on 1T'-MoTe₂ before and after functionalization. The results showed a marginal increase in arithmetic deviations in surface roughness (R_a) from 0.73±0.1 to 0.93±0.1 nm that we attributed to the formation of a smooth thin organic layer (Supplementary Fig. S11). Remarkably, there is also a negligible change from 8.2±0.5 to 8.5±0.5 nm in the thickness of the film before and after reaction (Supplementary Fig. S11), again suggesting the formation of close to a monolayer film of grafted Ar-(CF₃)₂ moieties.

Given the thickness of 1,3-bis(trifluoromethyl)phenyl monolayer of just ≈0.6±0.2 nm such as small value,[27] indirect experimental methods could be carried out to determine the presence of a fluorinated aryl layer also.

If the functionalisation takes place, it will lead to changes in the surface properties, for example, increased hydrophobicity due to the presence of CF₃ groups. The water contact angle (WCA) measurements showed that there was an increase in WCA from 76 ± 2.1° (similar to previously published results)[9] on the pristine film to 90±2.5° after the reaction. The increase in WCA suggests the presence of hydrophobic fluorine-containing groups on the surface (Supplementary Fig. S12A) and further confirms that the grafting of functional groups takes place.

The functionalization of metallic MoTe₂ is expected to alter the electronic structure of 1T' as electron extraction or injection depends on the dopant's / modification agent's electronegativity.[16,35] In the case of **IS-CF₃** it should lead to a *p*-type behaviour due to the

electron-withdrawing character of the CF_3 groups. Accordingly, the UV-vis measurements were carried out on $1\text{T}'\text{-MoTe}_2$ films on quartz substrates before and after functionalization. From the Tauc plots there is a change in properties of the films from initially metallic to a narrow bandgap semiconductor with $E_g \approx 0.3$ eV (Supplementary Fig. S12B).

Finally, we tested aromatic diazonium salts (ADSs) as a control modification agent for MoTe_2 thin films (Supplementary Note 2). Despite ADSs being reported as modification agents for MoTe_2 flakes obtained by mechanical exfoliation from a single crystal[20] we found that ADSs appear to be unsuitable agents for functionalisation of the MoTe_2 films. According to Raman and XPS results (Supplementary Fig. S13) the $1\text{T}'\text{-MoTe}_2$ film disintegrated after immersion into diazonium salt solution because no signals associated with MoTe_2 were detected by Raman and XPS Mo 3d and Te 3d spectroscopy. Therefore, the successful functionalization of $1\text{T}'\text{-MoTe}_2$ by **IS-CF₃** described above presents a more controllable route because it does not seem to compromise the integrity of the film.

Light-induced Reaction of 2H-MoTe_2 films with bis(3,5-bis(trifluoromethyl)phenyl)iodonium salt

Inspired by the successful spontaneous functionalization of $1\text{T}'\text{-MoTe}_2$ films by **IS-CF₃**, identical experiments were carried on 2H-MoTe_2 . As before, a fully characterized 2H-MoTe_2 film was immersed in 1 mM solution of **IS-CF₃** in $\text{MeOH}:\text{CH}_3\text{CN}$ for 1 hour, repeatedly washed with dry $\text{MeOH}:\text{CH}_3\text{CN}$ and finally dried under an argon flow. However, the XPS survey spectrum of the resulting film showed the presence of 0.3 at. % of iodine along with 0.9 at. % of fluorine (Supplementary Fig. S14) which suggests the sorption of the salt instead of covalent functionalization as was the case for $1\text{T}'\text{-MoTe}_2$. I3d signal is still observed on 2H-MoTe_2 after extensive washing (identical experimental procedure as for $1\text{T}'\text{-MoTe}_2$) confirming stronger

interaction of **IS-CF₃** with the formation of surface complex. Notably, the high-resolution I 3d spectrum (Supplementary Fig. S14) obtained after reaction between 2H-MoTe₂ and **IS-CF₃** displays two peaks unlike the I 3d spectrum of pristine **IS-CF₃** powder (Supplementary Fig. S9). This suggests a formation of a surface complex due to an electrostatic interaction with the surface.[9] However, an additional assessment by WCA method, showed (within the experimental error of 2-3°) that there is no substantial wettability change (Supplementary Fig. S15). Therefore, we concluded that the **IS-CF₃** molecules are physically adsorbed at the surface.

However, the low reactivity of **IS-CF₃** towards 2H-MoTe₂ is expected because the activation of ISs commonly proceeds through the cleavage of the C-I bond (Fig. 1). To cleave the bond an additional stimulus (such as applied potential or exposure to light) is required before surface grafting even takes place.[24,26,28,29,39] Light is a mild stimuli and it is often used in surface modification.[27,40] Therefore, we hypothesized that semiconducting 2H-MoTe₂ with a band gap of $E_g \approx 1.1$ eV would generate high-energy state electron-hole pairs upon illumination with photon energy higher than the E_g (Supplementary Fig. S16). The presence of the pairs could provide a pathway for the excitation of the surface complexes with the formation of dissociative states.[26,41]

To test this hypothesis, we performed the reaction of 2H-MoTe₂ with **IS-CF₃** under illumination of an LED with 780 nm wavelength (1.6 eV). The XPS analysis of the sample revealed the disappearance of I 3d peaks (Fig. 3A) while the F-content (from F 1s XPS) was detected at 2.1 at. % (Fig. 3B, Supplementary Fig. S17). The peak in C 1s spectra associated with CF₃ groups at 292.38 eV was also observed (Fig. 3C). Therefore, we concluded that the photon energy of 780 nm was sufficient for the photoexcitation of electrons in semiconducting 2H-MoTe₂ to initiate the

decomposition of **IS-CF₃**. Experiments under illumination with a lower energy light source were also carried out as described in Supplementary Note 3 and Supplementary Fig. S18.

The 633 and 523 nm Raman spectra on the functionalized film revealed that the positions and intensities of E_{12g} peaks remained unchanged (Fig. 3D, Supplementary Fig. S19, Supplementary Table S1B). However, there is a blue shift of 3 ± 1 cm⁻¹ for A_{1g} vibration modes after the LED driven reaction with **IS-CF₃**.^[35] In addition, the XPS data shows that Te-Mo peaks shift by 0.40 eV (Mo-Te shifts only by 0.15 eV) compared to the pristine film (Fig. 3E). There is also a broadening of the Te 3d peaks after the reaction (FWHM increased from 1.1 to 1.3) suggesting the appearance of a new component in the same way as described above for the functionalised 1T'-MoTe₂ films. Thus, the grafting of Ar-(CF₃)₂ groups in 2H-MoTe₂ probably proceeds through Te sites with the formation of a covalent Te-C bond (Fig. 3E). The degree of covalent functionalization (functional groups per Te), calculated based on the peak area underneath of this C-Te component relative to the total area of Te 3d, was found to be higher than for 1T'-MoTe₂ 11.8 %.

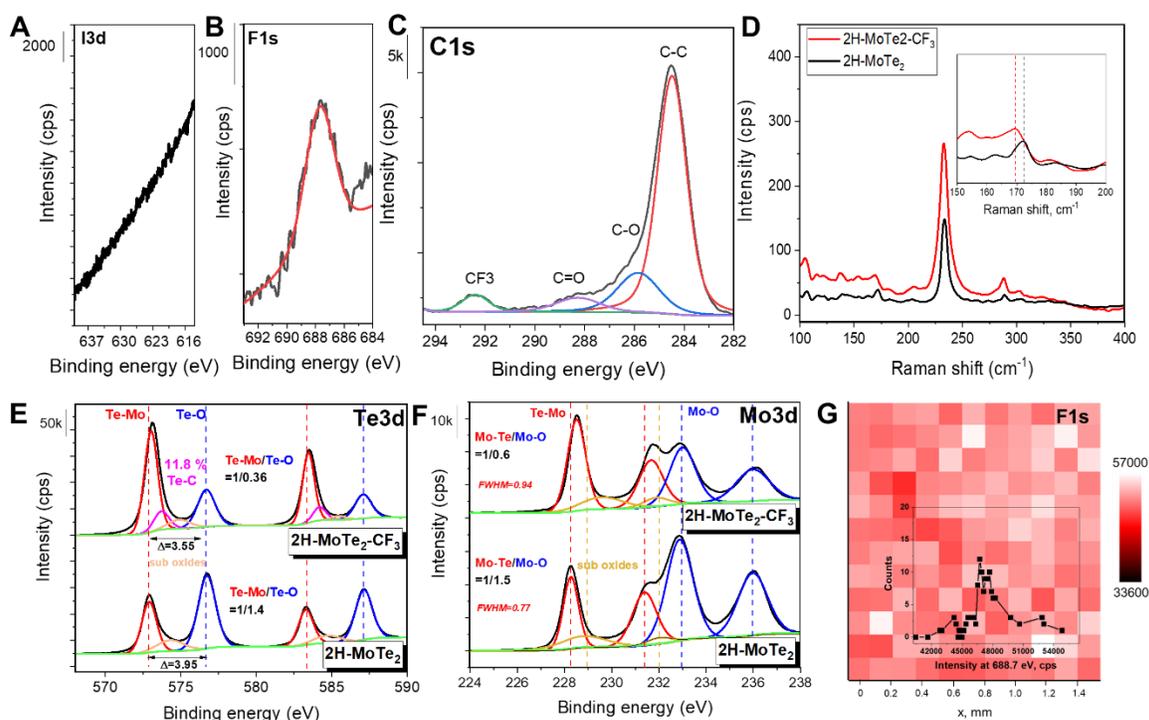


Figure 3. Surface chemical composition of 2H-MoTe₂ before and after spontaneous treatment with IS-CF₃. High resolution XPS spectra of I 3d (A), F 1s (B), C 1s (C), Te 3d (E) and Mo 3d (F); Raman spectra of 2H-MoTe₂ and 2H-MoTe₂-IS-CF₃ (D); The XPS mapping of F 1s peak over the area of 1.5 × 1.6 mm². The insert shows distribution of intensities from XPS F1s mapping (G)

However, even though the intensities of the peaks associated with Te-O / Mo-O bonds in high resolution Mo 3d and Te 3d XPS spectra are significantly suppressed in the functionalized 2H-MoTe₂ film (Fig. 3E,F) they are more pronounced than in case of the functionalized 1T'-MoTe₂ film (Fig. 2E,F). This indicates a higher oxygen content in the functionalized 2H-MoTe₂ films compared to the functionalized 1T'-MoTe₂ films. This may explain that, in comparison with the functionalized 1T'-MoTe₂ films, the reaction of IS-CF₃ with 2H-MoTe₂ led to a less homogeneous distribution of the organic layer according to the XPS mapping. The mapping showed the broader

distribution of intensities of F 1s peak across the scanned area (Fig. 3G, Supplementary Fig. S19B) with the average spectrum centred at 688.7 eV and the intensities deviating moderately (<6.6 %) from the average signal of 46655.2 ± 3111.3 cps. We hypothesize that upon light illumination of 2H-MoTe₂, the same reaction with **IS-CF₃** as for 1T-MoTe₂ takes place: selective C-I bond cleavage followed by the covalent functionalization of 2H-MoTe₂ over Te-sites by generated aryl radicals. However, due to the more pronounced peaks associated with Te-O / Mo-O the attachment of Ar-(CF₃)₂ groups may proceed through the O-sites as well. This could be explained by the fact that upon intense light illumination more active organic radicals are generated that may have propensity to react with the oxidized layer.[42]

The AFM measurements showed that in comparison with 1T'-phase there is a larger increase in surface roughness upon functionalization as well. The increase of R_a values from 0.69 ± 0.1 nm (before, Supplementary Fig. S20A) to 1.2 ± 0.1 nm (after, Supplementary Fig. S20B) suggests that there might be locations of the film with different degrees of functionalization. Also, the difference between the film's thickness (1.6 ± 0.5 nm, Supplementary Fig. S20C) before and after functionalization is larger according to AFM data and XPS (2.1 ± 0.8 nm, Supplementary Note 1) suggesting a thicker (or possibly more inhomogeneous) organic ad-layer on 2H-MoTe₂ films compared with 1T'-MoTe₂. Therefore, we can't exclude the possibility of formation of bilayer structure on 2H-MoTe₂ film. Although 3,5-bis(trifluoromethyl)phenyl groups provide the steric hindrance for the multilayer growth, the 4th position in the aromatic ring is still available for further attack under additional stimuli (Fig. S20D) as was shown for diazonium functionalization [43].

Still, as shown by WCA studies (Supplementary Fig. S21A), the surface of the functionalized 2H-MoTe₂ is hydrophobic (WCA increased from 70° to 95°). Such hydrophobic behaviour confirms

the functionalization with a conformation of molecules orthogonal to the surface. The UV-Vis spectroscopy and corresponding Tauc plots (Supplementary Fig. S21B), suggest that the semiconducting properties[3,44] of 2H-MoTe₂ are preserved with only a minor bandgap change from $E_g = 1.12$ eV to $E_g = 1.13$ eV after functionalization.

The formation of an Ar-(CF₃)₂ layer in both 1T'- and 2H-phases provides exciting opportunities for resolving the long-standing challenge of oxidation of MoTe₂ (and some 2D materials in general) in ambient conditions.[45,46] The protection strategies for MoTe₂ thin films from air exposure commonly rely on encapsulation by boron nitride[47] and graphene.[23] The growth of protective layer of Al₂O₃ has been also reported.[48] The simplicity of the covalent functionalization is a promising strategy because it proceeds through the removal of the oxide layer and therefore, it could be applied on films previously exposed to the ambient.

The stability of MoTe₂ films functionalized by IS-CF₃

The impact that the reaction with **IS-CF₃** had on the films' stability towards ambient conditions was investigated by exposing the as-prepared and functionalized films to moist air and direct sunlight for 336 hours. As mentioned above, as-prepared 1T'-MoTe₂ and 2H-films were handled in air and had a significant amount of surface oxides even before the stability experiments. However, from the comparison of the high-resolution Mo 3d and Te 3d XPS spectra, the degradation of the non-functionalized films continued after exposure to the ambient. In the non-functionalized 2H-MoTe₂ the intensity ratio between Mo-Te/Mo-O peaks changed from 1/1.5 to 1/5.3 and for Te-Mo/Te-O from 1/1.5 to 1/8.3, revealing that continuous surface oxidation, especially on tellurium sites, takes place over time (Fig. 4A). Similar ratios were registered for 1T'-MoTe₂ films as well (Fig. 4B). The films experienced a significant degradation in line with

previous reports showing the rapid degradation of MoTe₂ films in ambient conditions.[46] It has been also reported that the Mo-Te-O layer growth does not seem to stop but proceeds (although slowly) to complete degradation of the film. This may be less of an issue with few-layered films studied in this work, but it would certainly present a significant challenge for mono- or bi-layer MoTe₂ films that are important in technological applications.

However, as evident from the high-resolution Te 3d and Mo 3d spectra recorded on functionalized 1T'- and 2H-MoTe₂ films before and after the 336 hours of the stability experiment, the Mo-Te / Mo-O and Te-Mo / Te-O peak ratios remain constant (Fig. 4A,B). We hypothesize that the stability of functionalized MoTe₂ is explained by the covalent attachment of Ar-(CF₃)₂ groups over Te-sites and the hydrophobic nature of CF₃ groups that repel moisture. Hence, the reaction with **IS-CF₃** provides a simple and efficient way for protecting films from the ambient conditions, broadening the possibilities for future applications of MoTe₂.

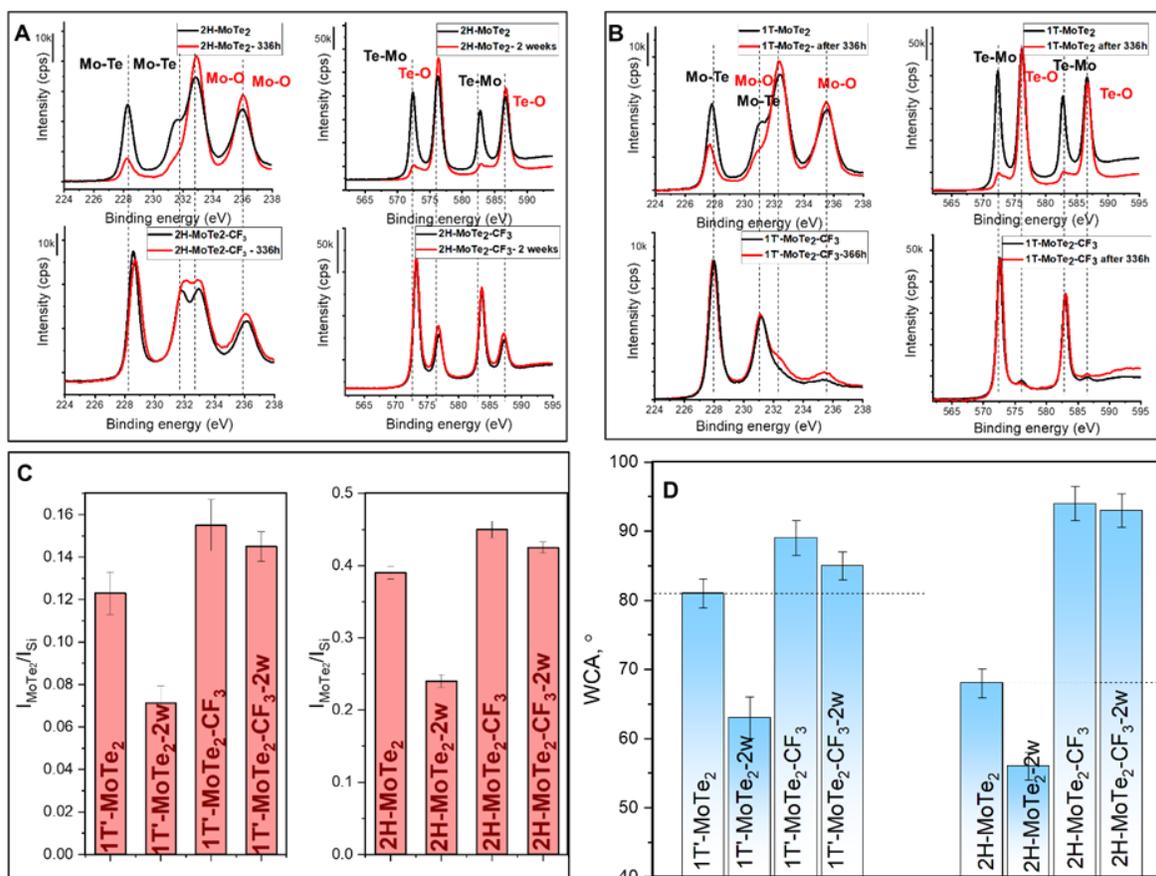


Figure 4. Protective properties of functionalized MoTe₂-CF₃ compared to pristine MoTe₂.—High resolution XPS spectra from Mo 3d and Te 3d regions for 2H /1T'-MoTe₂ and 2H /1T'-MoTe₂ -CF₃ (A, B); Comparison of characteristic Raman peak ratios $I_{\text{MoTe}_2}/I_{\text{Si}}$ after 336 h in air (C) and WCA measurement data (D).

Remarkably, despite XPS points out continuous oxidation, the as-made, non-functionalized films still show the characteristic peaks of 1T'-MoTe₂ or 2H-MoTe₂ in the Raman spectra (Supplementary Fig. S22). This suggests that, unlike XPS, Raman spectroscopy provides only qualitative assessment of the films and does not detect oxide phases. However, the change in characteristic Raman peak intensities at 125.7 cm⁻¹ (1T'-MoTe₂) and 230.1 cm⁻¹ (2H-MoTe₂)

relative to the intensity of the silicon peak at 520.1 cm^{-1} can be used to monitor the degradation with time (Supplementary Fig. S22). While in non-functionalized MoTe_2 films the relative intensity ratios reduced by half after 336 hours of exposure to ambient conditions, in the functionalized MoTe_2 they remained constant (Fig. 4C).

Finally, while the WCA measured on pristine, non-functionalized 1T'- and 2H- MoTe_2 after 336 hours of stability measurements decreased, the WCA of the functionalized film remains unchanged in line with the hydrophobic nature of the surface due to the attachment of $\text{Ar}-(\text{CF}_3)_2$ groups (Fig. 4D). Interestingly, the damaging effect of moisture is visually evident from the appearance of the 2H- MoTe_2 surface after WCA measurements: traces from water drops with lighter colours are well-visible (Supplementary Fig. S23). The XPS analysis from the regions demonstrated the increased oxidation of the surface (Supplementary Fig. S24). In contrast to pristine 2H- MoTe_2 , the surface of functionalized 2H- MoTe_2 remains the same after contact with water suggesting protection against moisture is achieved due to a lower interaction with water molecules. Overall, the experiments provided convincing evidences that covalent functionalization with $\text{Ar}-(\text{CF}_3)_2$ took place and further mechanistic insights into the process are needed. Alternative methods of protection against oxidation such as BN, Al_2O_3 etc [47,48] are quite expensive and challenging to perform. In contrast to them, developed functionalization procedure are accessible in terms of equipment and chemicals. However, the observed changes in the electronic structure of MoTe_2 films (Fig. S12 and S21) after functionalization should be considered as well.

Mechanistic insight into MoTe_2 functionalization using ISs

The functionalization of various surfaces by ISs has been described as occurring *via* a two-step process.[28–30,39] Firstly, the cleavage of C–I bond takes place after interaction with the substrate, often with additional stimuli (electric potential, light, plasmon). The bond cleavage leads

In addition, we utilized the common radical scavenger (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), which was added equimolarly together with **IS-CF₃** during the reaction. TEMPO can quench the generated aryl radicals. That means if the reaction takes place over radical formation then the presence of TEMPO would prevent the functionalization of the surface by entrapping of the reactive species (Supplementary Fig. S26A). In line with this assessment, in the presence of TEMPO, the high-resolution F 1s is absent from the XPS spectrum (Supplementary Fig. S26B). Similarly, the peak related to CF₃ is absent from the C 1s spectrum (Supplementary Fig. S26C). This suggests that aryl radical generated during the reaction process were trapped by TEMPO and thus, prevented them from reacting with the MoTe₂ surface. These collective results confirm the radical nature of the MoTe₂ functionalization process.

The detailed study of the interaction of metallic 1T'-MoTe₂ and semiconducting 2H-MoTe₂ with **IS-CF₃** revealed different reactivity of the polymorphs with the generated radical, which can be explained by the difference in electronic structure. From the electronic point of view, the 1T'-phase is a metal with a significant number of delocalized electrons available for metallic transport behavior.[50] Therefore, the absence of band gap enables the transfer of electrons to the **IS-CF₃** molecule that trigger the generation of radicals resulting in spontaneous grafting of Ar-(CF₃)₂ as shown in Fig. 5A. However, for semiconducting 2H-MoTe₂ to generate electron transfer light illumination is required as there is no spontaneous electron transfer to IS. Therefore, **IS-CF₃** forms a charge-transfer complex at the 2H-MoTe₂ surface (Fig. 5B). The surface complex enables the cleavage of C-I bond accelerated by electron transfer due to the energy provided by illumination with a photon energy larger than the 2H-MoTe₂ energy bandgap.[41] Similar reactivity patterns were proposed for MoS₂ [13] and single-walled carbon nanotubes, where the metallic CNTs were found more reactive towards diazonium salts than semiconducting ones.[51] The specificity for

stimuli offers exciting directions for adapting the strategy to other TMDCs, where reactivity may be dictated by electronic structure. Moreover, laser illumination opens perspectives for selective functionalization reversal as previously shown for the case of graphene with diazonium salts.[52]

Conclusions

In conclusion, we provide the first example of successful covalent functionalization of MoTe₂ by a symmetrical iodonium salt. A detailed XPS study shows that functional 3,5-bis(trifluoromethyl)phenyl groups are grafted directly onto the surface suggesting the formation of covalent Te-C bonds. The utility of **IS-CF₃** as a reagent demonstrates that the grafting of the organic layer prevents atomically thin films of MoTe₂ from further oxidation. This is evidenced by the lack of noticeable changes in WCA, Raman and XPS spectra over the period of at least 2 weeks confirming the protecting function of 3,5-bis(trifluoromethyl)phenyl groups. Thus, the proposed method offers a practical solution to a long-standing challenge associated with the spontaneous oxidation of MoTe₂.

A strong impact on the future direction in device fabrication as well as finding (and preserving) new electronic states in exotic (but unstable in ambient) 2D materials could be anticipated. Moreover, as the reactivity of **IS-CF₃** depends on the electronic structure of the 1T'-MoTe₂ and 2H-MoTe₂ polymorphs, the reported functionalization strategy may open new ways for a targeted functionalization of 2D materials. For example, **IS-CF₃** reacts spontaneously through C-I bond cleavage with the metallic 1T'-MoTe₂. In contrast, the semiconducting 2H-MoTe₂ forms a surface complex with **IS-CF₃** which decomposes under light exposure with a photon energy larger than the band gap of 2H-MoTe₂. This could potentially provide a platform for the precise modification of thin films, for example, by the attenuation of homojunctions between two polymorphic MoTe₂ phases.

Finally, functionalization with iodonium salts opens new directions in the selective tuning of the chemical properties of MoTe₂, for example, by changing the nature of the substitution groups in the grafted aryl molecule or aliphatic/heterocyclic groups. This could be then extended to TMDCs and other 2D materials, where reactivity is dictated by the electronic states, providing exciting opportunities for their fundamental science and applications.

Methods

300 nm SiO₂/Si (100) (Inseto) substrates (10×10 mm²) were first cleaned by sonication in acetone for 10 min, followed by sonication in isopropyl alcohol for a further 10 min before being dried under a stream of nitrogen gas. Molybdenum (99.95%) precursor films were deposited on to the cleaned 300 nm SiO₂/Si substrates via electron beam physical vapour deposition using a Plassys MEB550s. Deposition occurred under a vacuum of 1×10⁻⁶ mbar at a rate of 0.07 nm s⁻¹, with the electron beam gun emission current at 220 mA. Molybdenum trioxide precursor films were deposited on to the cleaned 300 nm SiO₂/Si substrates by thermal evaporation of MoO₃ pellets (99.99%, Pi-Kem) in a Plassys MEB400 under a vacuum of 2×10⁻⁶ mbar at a rate of 0.2 nm s⁻¹. The precursor films were then converted into 2H- and 1T'-MoTe₂ by CVD with the nature of the precursor layer dictating the phase of MoTe₂ as described in previously published work.[22] The substrate with precursor layer was placed in the hot zone of a horizontal Lenton tube furnace with the FeTe₂ source (30 mg) positioned 7 cm upstream. The dwell temperature of the source and substrate were set at 630 and 650 °C, respectively. The dwell temperatures were reached at a ramp rate of 5 °C/min with dwell time of 4 hours before cooling naturally to room temperature. Throughout the deposition process a carrier gas of 5% H₂/Ar was flowed through the CVD chamber at a rate of 300 sccm. Before beginning the deposition process the chamber was evacuated

to a pressure of 1×10^{-2} mbar and subsequently refilled with the carrier gas, this was repeated for a total of three cycles to ensure an oxygen free environment for the deposition.

Methanol (MeOH) and acetonitrile (MeCN) were purchased from Sigma-Aldrich and degassed by freeze– pump – thaw (3 cycles) followed by purging the solvent with Ar for at least 30 min. MoTe₂ films were immersed in 5 ml of freshly prepared 1mM bis(3,5-bis(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate or 3,5-bis(trifluoromethyl)benzenediazonium tosylate (see Supplementary information for synthesis) solutions in MeOH/CH₃CN (1/1 vv) and kept for 1 hour without stirring. After, samples were removed and washed by immersion in MeOH for 45 minutes 3 times and dried under Ar flow. For experiment under LED irradiation MoTe₂ films were immersed in 5 ml of freshly prepared 1mM bis(3,5-bis(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate or 3,5-bis(trifluoromethyl)benzenediazonium tosylate in a petri dish and coated with transparent glass cover. They were irradiated by LED sources (1050nm, 50 mW Thorlab product number M1050L4 or 780 nm, 800 mW, (Thorlab product number M780LP1) from 1 cm distance for 1 hour and washed by immersion in MeOH for 45 minutes 3 times and dried under Ar flow.

X-ray photoelectron spectroscopy (XPS) was performed on S-Probe Monochromatized XPS spectrometer (Thermo-scientific XPS NEXSA) with AlK α x-ray (1486.6 eV) monochromatic source (take off angle: $\theta=90^\circ$; voltage and power of the source 10 kV, 200 W. A flood gun was used for compensation of charging effects. The XPS survey spectra were collected with a pass energy $E_p = 157.7$ eV and energy steps $E_s = 0.22$ eV, the high-resolution spectra with $E_p = 107.5$ eV and $E_s = 0.1$ eV. The XPS spectra were analyzed using Avantage software. High resolution envelopes were fitted using Smart baseline method.

Raman spectroscopy was performed using a Thermo Scientific iXR Raman Spectrometer with a 532 nm laser set at 1 mW with an acquisition time of 40 seconds per scan. The Raman spectra obtained under 633 nm laser excitation were recorded in the backscattering geometry in a confocal Raman microscope (NT-MDT Spectral Instruments, Russia), with the laser beam focused on the sample with a 100x objective. Thirty spectra were averaged at 1 second per spectrum.

Atomic force microscopy was performed in the semi-contact mode using a scanning probe microscope (NT-MDT, The Netherlands). The images were background subtracted and used for roughness and film thickness determination at the same MoTe₂/SiO₂ location before and after functionalization. The reported film thicknesses are the means of at least 5 values obtained from three scratches, and the uncertainty is the standard deviation of the mean value.

The water contact angle (WCA) was evaluated using a Drop Shape Analyzer – DSA25 (Kruss, Germany) at 10 positions (drop volume - 2 µL) at room temperature. The sessile drop method in air was used during WCA measurements. The measurements were processed using the software package ADVANCE (Kruss, Germany).

The Agilent Technologies 1290 Infinity II series HPLC system was used for chromatography measurements using a column Zorbax Eclipse Plus C18 column (50 mm × 2.1 mm, 1.8 µm, Agilent, USA) at 40°C temperature with a flow rate of 0.3 ml min⁻¹ and isocratic consisting of mobile phase acetonitrile (A) and 0.1% trifluoroacetic acid in water (B) at the ratio 1:1. Injection volume was 10 µL and temperature with autosampler temperature 10°C.

For the tandem mass spectrometric (MS/MS) analysis, an Agilent 6470 Triple Quadrupole LC/MS spectrometer (QQQ) (Agilent Technologies, USA) equipped with an electrospray ionization source (ESI) operating in positive mode was used. The operating parameters were the following:

drying gas (nitrogen), temperature 350°C with a flow rate of 8 L min⁻¹, nebulizer gas (nitrogen) 40 psi, capillary voltage 3500 V. The MS/MS detector was run in the multiple reaction monitoring (MRM) mode. The optimal parameters of MRM analysis were mass transitions 341→75, fragmentor voltage 135V and collision energy (CE) 35 eV.

The UV–Vis spectra were measured using Spectrometer Lambda 25 (Perkin-Elmer) in 200–1100 nm wavelength range using MoTe₂ film prepared on quartz substrates.

Author Contributions

OG, AYG and PP conceived and managed the experiments. OG designed the experiments and carried them out with the help of NS and ES. OG analysed and plotted the data. RR carried out AFM measurements and Raman. AI carried out LC-MS experiments. OG and AYG wrote the manuscript. JF designed and carried out CVD experiments. All authors have contributed to writing of the manuscript and have given approval to the final version of the manuscript.

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Data availability

The raw data required to reproduce these findings are available on request to corresponding authors.

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