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Enhanced quantum efficiency from a mosaic of two dimensional MoS₂ formed onto aminosilane functionalised substrates

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Developing scalable methods of growing two dimensional molybdenum disulphide (2D MoS₂) of strong optical properties, on any desired substrates, is a necessary step to move towards industrial uptake of this material for optical applications. In this study, Si/SiO₂ substrates were functionalised using self-assembled monolayers of three different aminosilanes with various number of amine groups and molecular lengths, as underlayers for enhancing the adherence of molybdenum precursor. The tetrahedral [MoS$_4$]$^{2-}$ anion groups from the molybdenum precursor were bonded on these silanised Si/SiO₂ substrates afterwards. The substrates were then treated with a combined thermolysis and sulphurisation step. The results showed that silanisation of the substrates using longest chains and largest number of amine groups provided a good foundation to grow quasi 2D MoS₂ made from adjacent flakes in a mosaic formation. Microscopic and spectroscopic investigations revealed that these quasi 2D MoS₂ formed using this long chain aminosilane resulted in flakes with lateral dimensions in micron and submicron ranges composed of adjoining MoS₂ pieces of 20 to 60 nm in lateral dimensions, dominantly made of 3 to 5 MoS₂ fundamental layers. The obtained quasi 2D MoS₂ shows a high internal quantum efficiency of 2.6% associated to the quantum confinement effect and high stoichiometry of the adjoining nanoflakes that form the structure of the sheets. The synthesis technique in this study is reliable, facile and offers a procedure to form large, scaleable and patternable quasi 2D MoS₂ sheets on various substrates with enhanced optical properties for practical applications.

Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs), and particularly 2D molybdenum disulphide (MoS₂), have attracted great attention in recent years, owing to their unique electronic and optical properties. 1-3

In comparison to its bulk counterpart, which has an indirect band gap of ~1.3 eV, 4 monolayered MoS₂ has a direct bandgap of ~1.9 eV. 4, 5 Photoluminescence (PL) emission inherited from this direct band gap, make monolayered MoS₂ suitable for many optical units. 6 The high on-off current ratio and good electronic performance exhibited by monolayered MoS₂ transistors suggest their promise in future electronic circuits, requiring low stand-by power attractive for the realisation of 2D optoelectronic devices. 6 To date, 2D MoS₂ has found numerous potentials in units including those incorporated in field-effect transistors (FETs), 7,10 catalysts, 11-16 energy storage, 17, 18 photodetectors, 19 gas separation membranes, 20 piezoelectric systems, 21 bio and gas sensors, 1, 22-26 and photovoltaics. 27 Therefore, synthesis of wafer scale 2D MoS₂ using facile and reliable approaches is essential for widespread application of this material in optical and electronic devices.

In nature, 2H phase of MoS₂ has a stratified crystal. Many top-down techniques such as micromechanical cleavage, 4, 7 liquid exfoliation, 28-31 and intercalation-assisted exfoliation, 32 have been used for obtaining atomically thin MoS₂ nanoflakes. However, such exfoliation methods are impractical for wafer processes in optical and electronic industries. The yield for mechanical cleavage methods is generally low. 33 Liquid exfoliation always results in laterally polydisperse samples. 28, 29 Many intercalation-assisted exfoliation processes involves the use of hazardous liquids such as butyllithium, which are very reactive and explosive reagents.

The bottom-up techniques are also widely investigated for growing large area MoS₂ thin sheets. They generally rely on the reactions of selected molybdenum-containing compounds on the surface of substrates, together with sulphurisation and
annealing steps. For instance, vacuum deposition of Mo, MoO2 microcrystals, molybdenum trioxide (MoO3), and MoCl5 powders, followed by sulphurisation processes have been demonstrated. These methods have shown promise in synthesising 2D MoS2 on substrates such as sapphire, while monolayer of MoS2 in triangular islands of tens of micrometres in lateral dimensions can be obtained. Many of these reactions normally tend to partially form MoS2 nanoparticles or nanorod structures during the synthesis and significant tunings are required.

To promote the formation of layered MoS2, it is common to make use of solution based precursors. These precursors are usually placed on the surface of the substrates using methods such as dip-coating and spin-coating. As one of the first demonstrations on these approaches, Liu et al. used a two-step thermolysis process to obtain few-layered MoS2 thin films. Molybdenum compound was first formed on the substrate and then converted into 2D MoS2 by annealing and sulphurisation steps. Although the technique leads to high quality MoS2 thin films, the dip-coating process is not compatible with conventional semiconductor manufacturing practices due to its unsuitability for many large-area applications. Spin-coating is likely to perform worse as it produces uneven thicknesses of the precursor on the wafer.

SiO2 covered substrates, such as SiO2/Si, are the most important of all wafers to form 2D MoS2 onto due to their fundamental significance in electronic and optical device industries. However, so far most of the reports on 2D MoS2 deposition on SiO2 have demonstrated lack of localised crystallinity for 2D material’s domains due to the relatively high surface roughness and amorphous nature of SiO2 covered substrates. This leads to reduced optical qualities. As such, devising a method that can result in large area 2D MoS2 with improved and enhanced optical properties, on SiO2/Si substrates is of great importance.

Many aspects should be considered in the synthesis of 2D MoS2 with high optical properties. One of the main issues is that 2D MoS2 has a naturally relatively low internal quantum efficiency which makes it difficult to incorporate in many practical applications in optics. The quantum yield for prototypical 2D MoS2 has been reported to be less than 1.0%, which results in low optical intensity of light emitting diodes based this material. Also this low quantum yield comes as an obstacle for many bio medical applications in which the readability of the optical signal defines the minimum detection limits. We have previously shown that it is possible to increase the quantum yield by reducing the lateral dimension of MoS2 nanoflakes in suspensions. Based on this past observation, we hypothesize that if 2D MoS2 laid on a substrate is made of small adjoining flakes, quantum yield will be enhanced. Creating 2D semiconductors from adjoining flakes may be disadvantageous for making electronic devices but can be of great benefit for developing enhanced optical unit.

One of the approaches that can be potentially used for preparing the surface of substrates for precursors is the use of silane compounds. Silanisation is one of the most used methods for the functionalisation of SiO2 surface.
However, the applicability of silanes has not been fully investigated in the deposition of 2D MoS₂ or any other TMDs. Specifically, we are curious to investigate whether the concept of quasi 2D MoS₂, with enhanced optical properties, can be realized using silane based growth. Therefore in this study, we demonstrate the formation of quasi 2D MoS₂, made of adjoining flakes, on silanised Si/SiO₂ substrates using a combined thermolysis and sulphurisation of the attached [MoS₄]²⁻ anion groups. Three different self-assembled monolayers of aminosilane groups of - (3-Aminopropyl)triethoxysilane (APTES), N-[3-(Trimethoxysilyl)propyl]ethylenediamine (EAPTSMS) and N₂-[3-(Trimethoxysilyl)propyl]dithylenetriamine (DETA) are used. These groups have different molecular lengths and amine groups on their backbones. It is shown that DETA, with a longer chain and larger number of the amine group, is the most successful of them in establishing larger size quasi 2D MoS₂ made of small flakes on Si/SiO₂ substrates. To assess the physicochemical properties of the synthesised quasi 2D MoS₂, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) as well as Raman and PL mapping are conducted. The samples are assessed for their optical properties by measuring the internal quantum efficiency and PL decay dynamics.

Results and discussions

Quasi 2D MoS₂ flakes were formed on Si/SiO₂ substrates via thermolysis and sulphurisation after the substrates are silanised using three different aminosilanes. Details are presented in the Methods section. In brief, the Si/SiO₂ substrates were cleaned and hydroxylated in a piranha solution. After that the wafers were immersed in freshly prepared APTES, AEAPTM S and DETA solutions in ethanol. Then the substrates were soaked in a solution-phase precursor of (NH₄)₂MoS₄ in dimethylformamide (DMF). In the following step, the samples were treated using a thermolysis and sulphurisation process. The synthesis process is illustrated in Scheme 1.

The interaction between amine groups of aminosilane and (NH₄)₂MoS₄ is described by:

\[
2 \text{(R-NH₃)}_2\text{MoS₄} \rightarrow 2 \text{(R-NH₃)MoS₄}+2\text{NH₃}\uparrow \quad (1)
\]

in which R is all the structure of aminosilane without one NH₂ functional group. The formula is based on the acid-base reaction between aminosilanes and (NH₄)₂MoS₄. Here, NH₃ as a weaker base can be released and was removed in the vacuum oven. This leads to a shift of the reaction equilibrium and tetrahedral [MoS₄]²⁻ anion group non-reversible interaction on the substrate. The same principle has been illustrated for the reaction of (NH₄)₂MoS₄ with ethylenediamine to obtain the diaminium salt.⁵¹

The control of surface wettability via functional groups plays an important role in study of the surface and ion exchange properties.⁵² As a result, water contact angle (WCA) measurements were conducted on the piranha treated and three different silanised Si/SiO₂ substrates. The piranha treated Si/SiO₂ substrate shows strong hydrophilicity (Fig. 1a), resulting in a WCA value of 23.5° ±0.8°. This is due to the appearance of OH group on the surface. After treated with the piranha solution, the cross-linked Si-O bond on SiO₂ surface were oxidised and hydroxylated by hydrogen peroxide (H₂O₂) and ammonium hydroxide (NH₄OH). After the silanisation, aminosilanes of APTES, AEAPTM S and DETA in this study, with their alkyl chains, ethoxyl and amine groups appear on the surface. In these cases, the WCA increased to 52.8° ± 0.5°, 58.3° ± 0.2° and 60.1° ± 0.8°, for APTES, AEAPTSMS and DETA, respectively (Fig. 1b-d). This corresponds to an increasingly higher WCA and reduction in the degree of hydrophilicity, indicating that the longer DETA chain resulted in a larger contact angle. The larger contact angle is likely to promote the precursor reaction on the surface of the substrate, which is beneficial for obtaining larger size quasi 2D MoS₂ flakes.

Silanisation process provides amine groups on Si/SiO₂ surface which facilitates the [MoS₄]²⁻ anion interaction. After the substrates were treated using thermolysis and sulphurisation, quasi 2D MoS₂ nanoflakes were formed. AFM was used for characterising the surface morphology and thickness of quasi 2D MoS₂. The topographic images and corresponding height profiles for the obtained flakes are presented in Fig. 2a-c.

As can be seen from Fig. 2a, the nanoflakes synthesised on APTES silanised substrates have lateral dimensions in the order of ~100 nm and are sparsely located on the substrate. Clear steps of ~3–4 nm (corresponding to ~4–6 monolayers of MoS₂ - thickness of monolayer MoS₂ is 0.65 nm) can be observed in typical nanoflakes. For the MoS₂ grown on an AEAPTSMS silanised substrate, larger flakes begin to appear. The lateral dimensions are increased to ~350 nm and thicknesses of the flakes are between 3 and 5 nm (Fig. 2b). From the AFM images, it is revealed that the DETA silanised substrate provides the best platform to grow the largest quasi 2D MoS₂ nanosheets. From the example presented in Fig. 2c, it is seen that the obtained nanoflakes had a thickness of ~2-3 nm, which corresponds to ~3 to 5 MoS₂ monolayers. DETA has more bonding sites which has larger number of -NH₂ groups. It was also shown that DETA makes the largest WCA. As a result, [MoS₄]²⁻ groups have more possible affinity sites and highest probability to come close and interact with the DETA silanised substrate (Scheme 1), compared to APTES and AEAPTSMS treated surfaces, leading to a larger dimension of quasi 2D MoS₂ nanoflakes. In our large samples, the surface roughness (σ) was measured using AFM. The surface roughness of the bare Si/SiO₂, DETA silanised, and MoS₂ grown on DETA silanised substrates were measured and compared with the background roughness. From the analysis, the root mean square (RMS) surface roughness for the DETA silanised sample and its background SiO₂/Si substrate was found to be ~400 and 130 pm, respectively, confirming that surface functionalization led to a jagged surface and possibly made of smaller adjoining connected flakes. The other important observation is the fact that jagged 2D MoS₂ formed on DETA silanised substrates are made of adjoining small flakes of ~30-50 nm (as an example Fig. 2d). The schematic map which presents the formation of this unique 2D structure is
shown in Fig. 2e. It seems that DETA molecules are assembled at different angles on the substrates. Different angles mean various heights for the MoS$_2$ growth points with reference to the substrate’s surface. This, in result, promotes the formation of jagged and adjoining 2D surfaces of MoS$_2$.

As in this study DETA produced the largest quasi 2D MoS$_2$ flakes, the optical and compositional analysis will be more comprehensively presented based on this self-assembled monolayer.

XPS was used for determining the chemical compositions and chemical states of the DETA monolayers and obtained quasi 2D MoS$_2$ sheets. Before we carried out studies on the $[\text{MoS}_4]^{2-}$ anion surface treated samples, as a control experiment, the DETA treated substrates were first investigated by XPS to ensure that all the expected elements of the aminosilane are on the surface. For the DETA silanised substrate, two peaks are seen in the N 1s spectra, one at 399 eV binding energy related to the C-N binding and the other at 407 eV due to the protonated amines (Fig. 3a). The deconvoluted C 1s spectrum shows two peaks with binding energy of 284.7 and 286 eV, which are ascribed to C-C and C-N bondings (Fig. 3b). The Si 2s has the same peak locations as a previous study (Fig. 3c). For the spectra of Si 2p (Fig. 3d), it shows two binding energies at 99.1 and 99.6 eV, corresponding to Si 2p$_{3/2}$ and Si 2p$_{1/2}$ from the bulk silicon wafer beneath the oxide layer.
signal appears at the binding energy of 100.9 eV is contributed by aminosilane (Si-O) on the silicon dioxide and the one at 102.2 eV is ascribed to silicon dioxide. 

For the DETA silanised substrates with the molybdenum precursor, the XPS results for Mo and S binding energies are shown in Fig. 4a and 4b. The deconvoluted Mo 3d spectrum shows that two Mo 3d peaks at 232.3 and 235.6 eV, corresponding to the 3d_3/2 and 3d_5/2 binding energies, respectively, characteristic for the Mo⁶⁺ state. The S 2s peak can be observed at 229.7 eV. From S 2p spectra, S 2p₁/₂ and S 2p₃/₂ are located at 168.5 and 163.2 eV (Fig. 4b). The XPS assessments provide good evidence that the DETA silanisation process has been a success.

After the substrates were treated with a combined thermolysis and sulphurisation, obtained quasi 2D MoS₂ flakes were observed to have lower binding energies for Mo 3d and S 2p peaks (Fig. 4c and d). It also exhibited two characteristic Mo 3d peaks at 229.1 and 232.2 eV, corresponding to the 3d_3/2 and 3d_5/2 binding energies for Mo⁴⁺. S 2s peak was found at 226.3 eV. The sulphur peak for the 2p orbital (Fig. 4b and d) is shifted from 163.2 to 162.3 eV (for 2p₃/₂) and from 168.5 to 163.8 eV (for 2p₁/₂). Decreases of binding energy for both Mo and S elements are due to the change of oxidation state of Mo from Mo⁶⁺ to Mo⁴⁺, which leads to a reduction of bonding strength between Mo and S. The XPS results confirm the Mo oxidation transition from +6 to +4, which means the transition from bonded [MoS₄]²⁻ anion groups to nearly perfect stoichiometric MoS₂ composition after the thermolysis and sulphurisation process.

The XPS results for MoS₂ grown on APTES and AEAPTMS silanised substrate were also confirmed to form MoS₂. The data are presented in the Supporting Information.

Energy dispersive X-ray (EDX) spectrum measurement was used for characterising the chemical composition of the synthesised MoS₂ nanosheets and the result is shown in Figure S3. Peaks associated with Mo and S are found at 2.29 and 2.3 keV in the spectrum. Quantitative analysis shows that the atomic ratio of S to Mo is approximately 2.1, which further confirms stoichiometric state of MoS₂.

Raman spectroscopy is also used for assessing the thickness and number of layers of the obtained quasi 2D MoS₂ flakes on DETA silanised Si/SiO₂ substrate. From Fig. 5a, the spectrum reveals that two characteristic Raman modes of MoS₂, E₁₁₁ and A₁₁₁, which represents the in-plane strain and out-of-plane modes (Fig. 5b). The frequency difference between E₁₁₁ and A₁₁₁ phonons has been shown as an indicator of the number of the layers in MoS₂. We observe the frequency difference of the E₁₁₁ and A₁₁₁ peaks in different sample areas to be around 23 to 26 cm⁻¹. The Raman spectra results indicate that 3 to 5 layers can be dominant in different regions of the synthesised flakes. This Raman spectroscopy results are also consistent with the AFM profiles. MoS₂ nanosheets synthesised in this method have a polycrystalline structure. This can be evidenced in a full range scan of Raman spectroscopy. From Figure S4, Raman spectra at 520 and 300 cm⁻¹ are contributed by Si/SiO₂ substrate. Two MoS₂ Raman modes are located at 407 and 384 cm⁻¹. Interestingly, there is an additional peak at 226 cm⁻¹ which is suggested to be a disordered-induced peak ascribed to MoS₂ due to first-order scattering of LA(M) phonons obtained from randomly oriented MoS₂. Besides this, AFM image in Figure 2 of the manuscript also shows that MoS₂ sheets are composed of adjoining small nanoflakes with different
orientations. This can further confirm that the synthesised MoS₂ nanosheets in this study have a polycrystalline nature.

X-ray diffraction (XRD) was also conducted for the as grown MoS₂ flakes and the result is presented in Figure 5S. From the XRD pattern, the typical planar MoS₂ peak at 14.5° which corresponds to (002) plane was not observed, confirming the polycrystalline nature of our quasi 2D MoS₂ sheets.

PL measurements: To investigate the optical properties of the quasi 2D MoS₂ flakes made of adjacent entities in a mosaic formation, PL mapping was performed. PL spectroscopy was also conducted to explore whether the formation of the small flakes cause any improvement in the PL signatures. Fig. 5c shows the PL intensity-integrated map and the average PL spectrum obtained from the region plotted in Fig. 5d.

Using the Fityk Software package (version 0.9.2), two Gaussian curves were estimated to fit the obtained PL spectrum. These two peaks are at 590 and 650 nm, which correspond to the energy of the B and A excitons in quasi 2D MoS₂. Blue shifting of the PL emission peak was observed compared to the previous report on 2D MoS₂ deposited on glass substrates. The shift can be due to the combination of two different effects. It may be due to the depression of A exciton in n-type doped MoS₂ by the Si/SiO₂ substrate, resulting in only A’ (trion) contributing to PL. Excitons are generated when photons, with sufficient energy, excite semiconductors like 2D MoS₂. These excitons are electron-hole pairs which are attracted to each other by coulomb forces. These forces become more prominent when the thickness of the thin film decreases. Therefore, nanoflakes with relatively small dimensions contribute to higher energy PL emission. The shift can also be due to the quantum confinement effect associated to the small dimensions of the adjacent flakes forming the main planes. This observation was also similarly seen in the liquid phase 2D MoS₂ with laterally polydispersed samples.

To compare the photodynamics of our synthesised quasi 2D MoS₂ with previous works, we assess the internal quantum efficiencies of the samples. The internal quantum efficiency η is obtained using the following equations:

\[ \eta_i = \frac{Bn^2}{G} \]  
\[ I_{PL} = \theta Bn^2 \]  
\[ G = \frac{0.4 \times P_{laser} \alpha}{A_{spot} h \nu} \]

Here B represents the radiative bimolecular coefficient, \( n \) is the photoexcited carrier concentration, and \( G \) is the steady state carrier generation/recombination rate, which is calculated using the experimental equation (4). In equation (3), \( \theta \) is a constant which can be determined based on the measurement parameters presented in ref 50 and \( I_{eq} \) is the integrated PL intensity. In equation (4), \( P_{laser} \), \( A_{spot} \), and \( h \nu \) are the laser power, excitation area, and excitation photon energy, respectively, and \( \alpha = 0.05 \) per layer.

Total lateral dimensions of quasi 2D MoS₂ planes sufficiently large to ensure the illumination of the entire nanosheet by the laser for the DETA silanised sample, allowing the determination of the quantum yield. The calculated internal quantum efficiency of our 3–5 layered sample is found to be 2.6%, which is possibly indicative of a highly stoichiometry sample. This is associated with theoretical mono layer efficiency of ~11%. Non-radiative recombination processes frequently occur at defect sites and thus the quantum yield can be utilised to assess the degree of stoichiometry. In comparison to our result, high quality mechanically exfoliated monolayer MoS₂ flakes feature an intrinsic internal quantum efficiency of 8.3% at room temperature for one layer. The highest observed internal quantum efficiency for monolayer MoS₂ has been reported to be above 95%. To achieve this high efficiency, Amani et al. designed a process to functionalise mechanically exfoliated flakes using the nonoxidising organic superacid bis(trifluoromethane) sulfonimide. This kind of superacid successfully inhibited defect-mediated nonradiative recombination processes, leading to the largely increased quantum efficiency.

The internal quantum efficiency obtained from ion intercalation-assisted exfoliated monolayer MoS₂ flakes has been reported to be 1.3%, which is less than that of our samples.

The enhancement of internal quantum efficiency may also be due to quantum confinement effects due to the formation of a mosaic of smaller flakes within the structure of quasi 2D MoS₂. It has been reported the quantum efficiency increases with decreasing of flake sizes, as smaller size of samples lead to fewer nonradioactive recombination. The idea has been extended to 2D flakes with small lateral dimensions, generating quantum confinement within thickness and across. As a result, the presence of small flakes may result from an increase of internal quantum efficiency. For our samples, as can be seen from Fig. 2c and d, the synthesised sheets have a mosaic structure, which is composed of adjoining small MoS₂ nanoflakes.

PL radiative decay of quasi 2D MoS₂ grown on three different silanised substrates was also measured in this study. Fitting of the data in Figure 5e, the mean excitonic recombination time for quasi 2D MoS₂ grown on APTES, AEAPTMS and DETA were determined to be 0.26, 0.43 and 0.70 ns. Considering that the DETA sample provides the longest recombination time, the assumption that it has the lowest defect and hence a relatively large internal quantum efficiency is confirmed.

All in all, the technique presented in this paper, when further perfected, can be potentially used as a replacement to CVD methods for the deposition of specific configurations of 2D MoS₂. Advantageously, the as grown layers can also take the shape of patterns on pre-silanised substrates. The method is also compatible with other liquid phase deposition techniques. This method can be transferrable to grow other TMD nanosheets. The reaction in this study is based on the interaction between amine groups of aminosilane and transition metal containing precursor in the form of ammonium salt. TMD nanosheets can be obtained via a combined thermolysis and sulphurisation of the transition metal precursor on silanised Si/SiO₂ substrate.

Materials and Methods
The Si-SiO₂ wafers (<100>), n-doped, 0-100 Ω cm, 300 nm-thick dry thermal grown silicon dioxide) were purchased from WRS Materials (San Jose, CA, USA). APTES, AEAPTMS and DETA were purchased from Sigma Aldrich. Ammonium tetrathiomolybdate ([NH₄]₂MoS₄) was ordered from Sigma. Toluene and Dimethylformamide (DMF) was purchased from Sigma. DI water was used throughout the experiment.

Surface functionalisation of Si/SiO₂ substrate with aminosilanes

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The Si-SiO2 wafers were cut into 10×10 mm² pieces. The substrates were sequentially cleaned with acetone and 2-propanol in an ultrasonic bath for 3 minutes, respectively, followed by rinsing with DI water and then dried with N2 flow. The substrate 300 nm SiO2 on Si (SiO2/Si) was first cleaned with a standard piranha solution (a mixture of 3:1 (v/v) 30% H2O2 and 27% NH4OH) at 70 °C for 30 min. The substrate was functionalised with APTES, AEAPTMS and DETA using the method reported previously. Briefly, self-assembled monolayers of aminosilanes on Si/SiO2 substrates with –NH2 functional groups were prepared by soaking the substrates in a 2% solution of APTES, AEAPTMS and DETA in ethanol for 30 mins. Upon their removal from the solution, the samples were washed thoroughly with ethanol and then blown dry with nitrogen.

**Surface attachment of the Mo containing ions on substrates**

0.15 g of high purity of (NH4)2MoS4 powder was added to 20 mL of DMF solvent to form a solution. The concentration was chosen based on the suggestion by Liu et al. The solution was sonicated in DMF solvent to form a solution. The concentration was chosen based on the suggestion by Liu et al. The solution was sonicated in DMF solvent to form a solution.

**Thermolysis process by annealing and sulphurisation**

After soaking, the substrates were immediately moved into a chemical vapour deposition (CVD) furnace in which the sulphur powder was placed in the colder zone at 300 °C and sample substrates were placed on the reaction zone of the quartz tube and kept at 450 °C. The forming gas was a static gas mixture of Ar and H2 (95:5, vol/vol).

**Characterisation of silanised substrate and grown MoS2 thin films**

AFM (Bruker Dimension Icon) in a tapping mode was used for assessing the thickness and topology of the flakes and images were analysed using Scan-assist® Software. Raman spectra were obtained using a confocal microscope system (WI Tec, alpha 300R) with a >100 objective (NA = 0.9) in an ambient condition. A 532 nm laser was used to excite samples which were placed on a piezo crystal-controlled scanning stage. XPS measurements were performed on a Thermo scientific K-Alpha VG-310F instrument using aluminium monochromated X-rays (20 kV, 15 mA) with the hemispherical energy analyser set at a pass energy of 20 eV for the peak scans. WCA measurements were conducted using an OCA 20 system (DataPhysics Instruments, GmbH, Germany) with an automatic dispenser. The height of the each drop was confirmed using a CCD camera prior to each measurement to ensure consistency in the drop volume. A 10 μL DI water droplet was dropped on the surface of the gel and the angle is measured using the circle fit. The PL volume. A 10 μL DI water droplet was dropped on the surface of the gel and the angle is measured using the circle fit. The PL

**Conclusions**

In summary, we demonstrated the synthesis of large-area quasi 2D MoS2 nanosheets, made of adjoining flakes, by the aminosilane functionalisation and subsequent thermolysis and sulphurisation of Si/SiO2 substrates. AFM results show that samples obtained from the DETA functionalisation provided the best foundation to grow relatively large quasi 2D MoS2 sheets. The characterisation of these thin sheets showed that lateral dimensions in the order of micron or submicron and dominant 3-5 layers were obtained, which are made of nanoflakes with the lateral dimensions in the order of 30 to 50 nm. The number of layers was also confirmed by Raman spectroscopy. The surface contact angle measurements showed that the lowest wettability belonged to DETA covered substrates. This observation together with the fact that DETA has the longest chain and larger number of amine groups on its chain were associated to the more efficient lateral growth of quasi 2D MoS2 sheets on SiO2 substrate. XPS confirmed the formation of highly stoichiometric 2D MoS2, which was also confirmed by PL decay assessments. The obtained quasi 2D MoS2 nanosheets sheets using DETA functionalised substrates had a high internal quantum efficiency and relatively long excitonic recombination time, which were associated to the quantum confinement effect in the mosaic of adjoining small nanoflakes and also the high stoichiometry of the 2D material.

This work presents a new approach for depositing quasi 2D MoS2 sheet with enhanced optical properties by an intermediate process of silanisation which is particularly compatible with oxide surfaces.

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