Large-Area Electrodeposition of Ultra-Thin MoS$_2$ on Graphene for 2D Material Heterostructure Photodetectors

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Abstract

Heterostructures involving transition metal dichalcogenides and other two-dimensional materials such as graphene have a strong potential to be the fundamental building block of many electronic and opto-electronic applications. The integration and scalable fabrication of such heterostructures is of essence in unleashing the potential of such technologies. For the first time, we demonstrate the growth of films as thin as a bilayer MoS$_2$ on monolayer graphene via non-aqueous electrodeposition. Through methods such as scanning electron microscopy, atomic force microscopy, Raman spectroscopy, energy and wavelength dispersive X-ray spectrosopies and X-ray photoelectron spectroscopy, we show that this deposition method can produce large-area MoS$_2$ films with high quality and uniformity over graphene. We reveal the potential of these heterostructures through demonstrating the operation of the structure as a prototype photodetector. These results pave the way towards developing the electrodeposition method for the large-scale growth of heterostructures consisting of varying 2D materials for many applications.

Keywords: Electrodeposition, non-aqueous, transition metal dichalcogenides, molybdenum disulfide, MoS$_2$, graphene, heterostructure, photodetector

Introduction

Transition metal dichalcogenide (TMDC) two-dimensional (2D) materials such as molybdenum disulfide (MoS$_2$) are being investigated to make ultrasparsitive photodetectors, high on/off ratio transistors and sensitive sensors that exceed the performance of their counterparts made from other materials. In addition, mechanical measurements of monolayer MoS$_2$ have shown that it is 30 times stronger than steel and can be deformed by up to 11%, making it one of the strongest semiconductor materials for applications in flexible and wearable electronics. Heterostructures based on 2D materials offer the platform to enable new technologies and exciting scientific discoveries due to the unique properties of their atomic layer constituents. Specifically, 2D material heterostructure photodetectors based on stacking TMDC on graphene have been shown to have high speed, responsivity and gain. Such devices have been integrated on silicon photonic circuits and bare Si substrates. Heterostructure devices involving MoS$_2$ as their core material commonly use graphene for their electrical contacts, due to the latter’s exceptional electrical conductivity for high performance electronics and its optical transparency for emerging optoelectronic technologies. The scalability of graphene has largely been overcome through the development of chemical vapour deposition (CVD) and wet transfer methods, enabling wafer scale graphene to be routinely producible. However, a major obstacle that hinders the development of MoS$_2$ based heterostructures is its low scalability. Therefore, developing improved methods for depositing MoS$_2$ on graphene is an immediate and essential goal that remains to be achieved before such heterostructures can make any impact on the (opto-) electronics industry.

Several methods have been developed to produce MoS$_2$ such as mechanical, liquid and chemical exfoliation, chemical vapour deposition, plasma sputtering, solution based thermal decomposition and pulsed laser deposition. However, each of these methods has certain limitations that prevent it from producing large, uniform and continuous monolayers with a high yield, high throughput, low cost and controllable atomic layer thickness. An alternative method that has rarely been investigated for the deposition of 2D materials is the electrochemical deposition method. Atomic layers are deposited through this bottom up method by applying an electric potential via an electrode in a solution containing the precursor of the material to be deposited. Site selective material growth in the nanometre scale can be achieved by patterning the electrodes and/or coating the electrodes with a patterned non-conductive layer such as SiO$_2$. In comparison to the aforementioned methods for depositing MoS$_2$, electrodeposition is potentially capable of producing wafer-scale continuous films of 2D materials rapidly and with high throughput for reasonably low costs. In addition, a unique advantage of electrodeposition is that it is not a line-of-sight deposition method and can be utilised to conformally coat complex three dimensional structures including patterned structures of high aspect ratios. This method also offers the prospect for integrating 3D shaped graphene nanosheets with other 2D materials to make van der Waals hybrids for superior performance and promising applications in various energy fields. Furthermore, unlike deposition by plasma sputtering techniques which are carried out in harsh environments that can potentially damage existing materials on the substrate such as graphene, electrodeposition does not affect the quality of the existing materials and can be performed at room temperature and pressure.

A few works have previously attempted to electrodeposited bulk MoS$_2$ using an aqueous solution over glassy carbon, polytetrafluoroethylene and conductive glass. However, building 2D heterostructures for device applications requires that the deposition be done over other 2D materials such as graphene, a common electrical bottom contact material for device structures. One report has previously showed the simultaneous deposition of thick MoS$_3$ and MoS$_2$ films on graphene via galvanostatic two-electrode aqueous deposition. The films were then converted to MoS$_2$ by an annealing step. However, the main disadvantage of the galvanostatic deposition method is that it does not allow controllability over the electrodes’ potentials, which becomes essential in the deposition of 2D material monolayers. In addition, the electrochemical potential window is limited in aqueous solution to ca. 1.3 V by electrolysis of water. This limitation causes hydrolysis of the precursor, and oxidation or hydrolysis of the deposited material. This limits the uses of the aqueous electrodeposition method to depositing only materials that reduce at moderate potentials. MoS$_2$ is an electrocatalyst for hydrogen evolution, hence the deposition of MoS$_2$ will facilitate evolution of H$_2$ and the solution at the electrode will become basic, further complicating the process. Electrodeposition in non-
aqueous solvents using a three-electrode electrodeposition setup is an alternative to overcome these limitations. We have recently reported the successful electrodeposition of several materials such as GeSbTe, BiTe and HgTe on TiN via non-aqueous solutions.23,36-38 These materials are technologically important and have great applications in phase change memory, thermoelectric and infrared detection devices. The growth of these materials was achieved by non-aqueous electrodeposition in nano and macro structures using in-house prepared precursors. A commercially available and commonly used precursor for depositing MoS₂ via thermal decomposition and electrodeposition is [NH₄]₂[MoS₄]. However, this precursor is not compatible with non-aqueous solvents such as dichloromethane (CH₂Cl₂) or acetonitrile (CH₃CN).

In this work, we show for the first time that the electrodeposition method can produce ultra-thin MoS₂ films using a graphene electrode. To the best of our knowledge, this work presents the thinnest and most uniform MoS₂ film ever produced via the electrodeposition method. We are demonstrating the electrodeposition of MoS₂ over graphene using tetrabutylammonium tetraithiomolybdate [N⁴Bu₄]₂[MoS₄] as a single source precursor that is compatible with CH₂Cl₂ and makes a better replacement to the more common [NH₄]₂[MoS₄] precursor for non-aqueous electrodeposition. Using a variety of characterisation techniques, we showed that the MoS₂ electrodeposited is of high quality, which allowed to demonstrate a proof of principle photodetector based on a MoS₂/graphene heterostructure.

**Electrodeposition of MoS₂**

Graphene monolayer was grown by CVD on a copper foil. The graphene was spin coated with poly methyl methacrylate (PMMA) and wet transferred onto the target Si substrate by wet etching the copper foil and slowly scooping/fishing the floating PMMA/graphene film with the substrate, see Figure S1 in the supplementary information. The PMMA layer was later dissolved in acetone and rinsed off with isopropyl alcohol (IPA). To improve the electrical contact a Cr (10 nm)/Au (190 nm) layer was thermally evaporated on part of the graphene film away from the electrodeposition area. [N⁴Bu₄]₂[MoS₄] was synthesised in-house to function as a single source precursor that can deliver both Mo and S, and has excellent solubility in CH₂Cl₂ compared to [NH₄]₂[MoS₄].39 [N⁴Bu₄]Cl was used as the supporting electrolyte and trimethylammonium chloride (CH₃)₃NHCl was...
used as the proton source in the electrodeposition solution. The electrodeposition process, including the electrolyte preparation was carried out inside a glovebox equipped with a nitrogen recirculating system to maintain the O₂ and H₂O levels below 10 ppm. The deposition was performed inside a three-electrode reactor setup that employs a Pt gauze as a counter electrode and an Ag/AgCl (0.1 M [NBut]Cl in CH₂Cl₂) reference electrode as shown in Figure 1 (a). The CH₂Cl₂ used in this work was previously dried and degassed by refluxing with CaH₂ before distillation to minimise its water content. The moisture content was measured by Karl-Fischer titration to be ca. 18 ppm.

Cyclic voltammetry (CV) scans were carried out to study the electrochemical behaviour of the electrolyte with the graphene working electrode. The electrolyte and background CV scans were performed on two different graphene coated substrates on separate days, using a newly prepared electrolyte each time, see Figure 1 (b). A cycle includes sweeping the voltage from 0 to -2.0 V, -2.0 to 1.0 V and 1.0 to 0 V. The indicative arrows on the observed current curves show the direction of the sweep. The CV scans show a clear dip in the current at around -0.6 V which can be clearly observed in the magnification inset of the figure. This dip was confirmed to be caused by the electroreduction of [MoS₄]²⁻ ions to MoS₂. We confirmed the deposition of material at this potential by polarising the graphene electrode at -0.8 V for 30 minutes which resulted in a thin film uniformly covering the electrode. The CV scan on graphene is compared to that on TiN in supplementary Figure S2.

The electrodeposition of MoS₂ is achieved by fixing the potential applied to the working electrode at -0.8 V and varying the deposition time to control the thickness of the deposited material. During the electrodeposition process, the substrate is placed inside a sealed container to ensure that MoS₂ is deposited within a predefined 4 mm circular area to prevent materials from depositing at the sides and back of the substrate. This also ensures that the measured current from the deposition process relates to that from the electrodeposition of MoS₂ as much as possible. We expect this approach to be easily scalable to large wafer scales with a larger reactor setup and large-area graphene. After the deposition, the sample is rinsed with pure CH₂Cl₂ and left to dry inside the glove box. Figure 1 (c) shows a photograph of an as-deposited large-area MoS₂ films with a thickness of 5.8 nm following a 90 s deposition, demonstrating a large colour contrast with the graphene only area. Figure 1 (d) depicts a microscope image of the deposited MoS₂ film, showing the uniform colour of the MoS₂ film to give an indication of the uniformity and continuity of the deposited material at the millimetre scale. The damage on the graphene at the border with the MoS₂ film is caused by the reactor’s o-ring which seals other areas of the substrate from being exposed to the electrolyte solution.

The as-deposited MoS₂ is amorphous, hence an annealing step was introduced in the process to crystallise the film. The sample annealing was done inside a tube furnace initially at 100 °C for 10 minutes followed by a 500 °C for two hours in a sulfur environment.

**Material characterisation**

A scanning electron microscopy (SEM) image of the deposited film is shown in Figure 2 (a). The image shows a continuous MoS₂ film next to an intentionally made scratch to expose the SiO₂ substrate. Energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy (WDX) were used to confirm the deposition of MoS₂ on the graphene and to measure its atomic ratios. The EDX shows the presence of only C, O, Si,
Mo and S, that are expected to come from graphene, PMMA residue, the SiO$_2$ substrate and the film. This indicates that the electrodeposition is a clean method that can deposit high purity 2D materials. Other elements that are present in the electrolyte such as chlorine were not found in the deposit. Due to the spectral overlap between the Mo-L$_a$ (2.293 keV) and the S-K$_x$ (2.307 keV) X-ray emission lines, WDX was used to resolve the Mo and S spectra and calculate the film’s material composition, as shown in the inset of Figure 2 (b). The S/Mo ratio was measured to be $2 \pm 0.1$. In both measurements, a commercial MoS$_2$ crystal was used as a calibration standard to calibrate the tools. The measurements were repeated after annealing and a negligible change was found in the S/Mo ratio.

Atomic force microscopy was used to measure the thickness of the electrodeposited MoS$_2$ after annealing. Figure 2 (c) and its magnified view (d) shows the height profile of a film deposited for 90 s between two crossing scratches. Figure 2 (e) and its magnified view (f) show the height profiles of a film deposited for 10 s. The AFM height profiles for the two attempts show total thicknesses of ~6.8 nm and ~3.2 nm, respectively. The AFM measurements on graphene show that the graphene has a thickness of ~1.0 nm as shown in supplementary Figure S1. As a result, the deposited MoS$_2$ film thicknesses on graphene were ~5.8 and ~2.2 nm, respectively. Hence, the thinnest sample is indicated by AFM to contain a bilayer to trilayer MoS$_2$ film. The small particles at the top of the film shown in Figure 2 (f) may also indicate that there is a “uniform” bilayer layer and a partially grown third layer that is stopped at an intermediate seeding state. The supplementary Figure S3 shows an AFM image of a 10 min deposited film with a thickness of 18 nm. AFM characterisation of these films has shown that they have significantly better film continuity and uniformity than any other electrodeposited MoS$_2$ films from previous works.$^{30-34,40}$

Raman spectroscopy is a common method used to characterise TMDC materials. In this work, the presence of MoS$_2$ on the substrate, its thickness and degree of crystallinity were investigated by measuring the Raman scattering of a 532 nm laser at room temperature in ambient environment. Light excitation and collection were implemented through a 50x objective to reduce the measurement area to ~1 $\mu$m$^2$. Raman measurements of MoS$_2$ primarily report the study of the E$_{2g}^1$ and A$_{1g}$ scattering peaks. It has been established by several studies that the separation between the two peaks is strongly dependent on the number of stacked MoS$_2$ layers, up to “bulk” films.$^{41-45}$ The separation was found to increase as the number of layers is increased, and vice versa. The blue shift in the A$_{1g}$ peak with increasing the number of layers is commonly attributed to higher atomic vibration force constants caused by interlayer Van der Waals forces. The relatively smaller red shift in the E$_{2g}^1$ peaks, on the other hand, is attributed to stacking-induced structural changes or long-range Coulombic interlayer interactions in multilayer MoS$_2$. In this work, several electrodeposited films were studied with Raman spectroscopy. Figure 3 (a) shows the Raman spectra obtained from three annealed films with different thicknesses and a fourth spectrum from an unannealed film. The electrodeposited MoS$_2$ films did not show any Raman signature before annealing, indicating that the as-deposited material is amorphous and that the annealing step is required to crystallise the deposit. The separation between the two Raman peaks for MoS$_2$: were found to reduce when the film thickness determined by AFM is reduced as expected, matching the results from literature. The 18 nm thick film showed a peak separation of 24.5 cm$^{-1}$, this separation is conventionally abbreviated by “bulk” MoS$_2$, indicating that the material is more than ten monolayers thick. The thinner film characterised in Figure 2 (c) showed a peak separation of 23.5 cm$^{-1}$, indicating a grown film of “few-layer” MoS$_2$. A series of scans across a large film area can be found in supplementary Figure S4, showing a strong overlap between the peaks. The thinnest film, characterised in Figure 2 (e) showed a peak separation of 22.2 cm$^{-1}$, indicating a bilayer MoS$_2$ film. The full width half maxima (FWHM) of the A$_{1g}$ and E$_{2g}^1$ peaks were also found to decrease with decreasing the number of layers, a feature that is indicative of higher level of crystallinity. Figure 3 (b) shows four Raman spectra of bare and MoS$_2$ coated graphene, before and after annealing. The intensity ratio of the 2D and G peaks, I$_{2D}$/I$_G$, following the electrodeposition process was found to be ~3.7, indicating a high quality graphene monolayer. This means that the electrodeposition process has little effect on the crystallinity of graphene. A very small peak around the defect related D band around 1350 cm$^{-1}$ was found with a small increase in the Raman shift for the 2D and G peaks, which may be attributed to graphene doping.$^{46}$ However, the I$_{2D}$/I$_G$ ratio was reduced to ~1.0 and ~0.9 after annealing for graphene only and graphene/MoS$_2$ areas, respectively. The hump near the defect band, and the
Figure 4. XPS spectroscopy measurements of the Mo 3d (a) and S 2p (b) energy ranges before and after (c and d) annealing. The graphs show the clear improvement in the material crystallinity after annealing as abbreviated by the sharper and more intense emission peaks. Further increase in the Raman shift for the 2D and G peaks is most likely due to sulfur induced hole doping and compressive stress in graphene.\(^\text{47}\) It is expected that lowering the annealing temperature, time and sulfur level in the chamber will reduce graphene doping. It is worth to emphasise that the quality of graphene reported here, which had undergone an electrodeposition process, remains significantly better than those that had undergone a plasma sputtering process from previous reports.\(^\text{25-29}\)

X-ray photoelectron spectroscopy (XPS) measurements were performed to study the chemical environments and composition of the Mo and S atoms in the films before and after annealing. Figure 4 shows the Mo 3d (a and c) and S 2p (b and d) region spectra for the exact same area of a sample before and after annealing. The Mo 3d spectra can be resolved primarily into a doublet at 228.9 and 232.0 eV, corresponding to the Mo\(^{4+}\) 3d_{5/2} and 3d_{3/2}, respectively. The S 2s peak can also be found at 226.2 eV in the same spectra. No evidence of Mo\(^{6+}\) was detected before annealing. After annealing, the Mo\(^{4+}\) 3d peaks were found to become sharper and more intense. The reduction in the full width half maximum after annealing is an indication of increased crystal order in the material.\(^\text{48}\) Figure 4 (c) also shows a very small peak at 235.3 eV which may be related to a Mo\(^{6+}\) 3d_{3/2} oxidation peak. The two S 2p emission peaks at 161.7 and 162.9 eV corresponding to S 2p_{3/2} and 2p_{1/2}, respectively, evolved to become much more intense and prominent after annealing as shown in Figure 4 (b and d). This was also accompanied by a great reduction in the FWHM, which may also be attributed to the increased crystal order of the material. In addition, two extra peaks were found at 163.8 and 164.8 eV that are believed to correspond to bridging S\(^2-\) and/or apical S\(^2-\) ligands, as shown in Figure 4 (d). In addition, a very small peak, probably corresponding to [SO_{4}^{2-}], was observed at around 169 eV. All the XPS results are consistent with the previously reported measurements in the literature.\(^\text{54,48-50}\) The S/Mo composition ratio of the film was also quantified via XPS to be 2.0 ± 0.1 following annealing and a short ion etch of the top few atomic layers. A wide energy range XPS scan can be found in Figure S5 in the supplementary information. The wide scan shows significantly lower oxygen content in the film compared to that from,\(^\text{60}\) which is expected to arise due to the presence of oxygen in aqueous electrolytes.

2D material heterostructures for photodetection

In this work, the photoreponse of a large-area electrodeposited MoS_2 layer on graphene was tested at room temperature and ambient air using a 532 nm laser source with ~1 mW power, see Figure 5 (a). Two electrical probes were placed on the MoS_2 layer and the Au back contact to act as the positive and negative terminals of the device, respectively. The positive probe directly contacted a 25 nm thick MoS_2/graphene layer without the use of a contact pad because the latter could short the electrical path to the underlying graphene layer through cracks or voids in the MoS_2 film. A voltage sweep between -1 and 1 V was applied to
Figure 5 (a) A schematic illustration of the electrodeposited MoS$_2$/graphene heterostructure photodetector. The device has a MoS$_2$ film thickness of ~25 nm contacted via graphene using a Cr/Au electrode of 10/190 nm thickness and excited with a 532 nm laser with P ~1 mW. (b) IV characterisation of the device showing a clear current increase with illumination (red line) compared to that without illumination (black line). (c) photo-illumination cycles showing the switching of induced photocurrent with the switching of a laser source.

The device to characterise its electrical response in the dark and under illumination as shown in Figure 5 (b). The IV characteristics of the device have shown a Schottky behaviour with up to an order of magnitude change in current between -1 and 1 V, which presumably arises at the MoS$_2$/graphene junction. Under illumination, the photocurrent (red line) was found to increase by three-fold compared to that for the dark current (blue line) at positive voltage biases. On the other hand, the photocurrent was found to be only marginally larger than the dark current at negative voltage biases. Figure 5 (c) presents the photocurrent induced via a 1 mW laser using a voltage bias of 1 V between the two contacts as a function of the laser switching time.

The photoresponsivity of the device can be calculated using the following equation:

$$\text{Photoresponsivity} = \frac{I_{ph}}{P_{laser}}$$

Where $I_{ph}$ is the photoinduced current which can be found by subtracting the device current under illumination from that in the dark ($I_{dark}$), and P is the incident laser power. In this work this was calculated at $V = 1$ V to be approximately $2 \times 10^{-5}$ A W$^{-1}$. This responsivity figure is smaller than previously reported due to the large area separation between the top and bottom area contacts and because the laser spot was directed to the film without the use of a focusing objective lens.

Conclusions

We reported the successful growth of large-scale and continuous polycrystalline bilayer MoS$_2$ on graphene via non-aqueous electrodeposition. We used an in-house synthesised precursor that is designed to be compatible with dichloromethane CH$_2$Cl$_2$ for non-aqueous electrodeposition. The electrochemical behaviour of the precursor was investigated via cyclic voltammetry studies and a reduction potential around -0.6 V was found to be suitable for the electrodeposition of MoS$_2$. The material’s purity and compositional ratio were measured via energy and wavelength dispersive X-ray spectroscopies, and the S/Mo ratio was found to be $2.0 \pm 0.1$. AFM, Raman and XPS measurements were used to measure the thickness of the MoS$_2$ film and characterise its evolution after annealing. We found that an annealing step is required to improve the crystallinity of the film following electrodeposition. Raman spectroscopy confirmed that the thinnest MoS$_2$ consisted of a bilayer and that the electrodeposition method can preserve the quality of the graphene electrode for future TMDC/graphene heterostructures in contrast to other methods such as plasma sputtering. The MoS$_2$/graphene heterostructure was subsequently tested for photodetection application and the electrodeposited film has shown a clear photoresponse indicating the material’s high quality and the method’s potential for future (opto-) electronic applications.
Electrodeposition is a cost-effective, simple, and flexible method that has great potential to be scaled to wafer sizes to enable the deposition of several layers of different 2D materials for heterostructure devices. This is in contrast with more commonly used methods such as CVD and mechanical exfoliation. Other materials that are likely to be feasible to grow via electrodeposition on graphene include WS₂, MoSe₂, WSe₂, MoTe₂, WTe₂, etc. The non-aqueous electrolyte also allows a larger electrochemical potential window providing a more flexible foundation to future incorporation of dopants, and heterostructure growth of different 2D semiconductors. This paves the way towards making the electrodeposition method a key method in the manufacturing of 2D material heterostructure devices for applications in flexible light emitters, photodetectors, transistors, sensors and batteries as examples.

Author contributions
YJN proposed the idea and coordinated the project; ST and PNB worked on the electrodeposition experiments; SR and NK worked on the graphene growth and transfer; DES, VG, ALH and GR worked on the precursor preparation; YJN, NA and CHDG worked on the material characterisation. YJN wrote the manuscript with contributions from all authors.

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