

A two-dimensional transition metal dichalcogenide film and method of forming the same

Technical Field

- 5 The present invention relates to an improved transition metal dichalcogenide film and a method of forming thereof.

Background

- Two-dimensional interlayer spacing-expanded transition metal dichalcogenides (TMDCs) are promising nanomaterials for electrochemical energy applications.
- 10 Conventional interlayer spacing-expanded TMDCs are prepared by two-step processes, which take days and form materials that are unstable due to the uncontrollable kinetics for interlayer expansion that will lead to exfoliation into single layer. Some post-growth intercalation processes make use of highly unstable and flammable intermediates, which are dangerous and unsuitable for industrial purposes. Typical TMDCs formed from such
- 15 processes are in the form of powders, nanosheets or flakes, which causes decrease in ion diffusion pathway and loss in optical transmission due to aggregation/re-stacking of powders. The uniform layered structures are easily lost, leading to unstable electrochemical reactions, which consequently causes property variation in devices.

- Thus, there is a need for an improved intercalated transition metal dichalcogenide film
- 20 and method of forming the same.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved intercalated transition metal dichalcogenide film and method of forming the same.

- According to a first aspect, the present invention provides a continuous intercalated two-
- 25 dimensional transition metal dichalcogenide film, comprising a plurality of layers intercalated with alkali metal.

According to a particular aspect, the film may have an average lateral size of  $> 50 \mu\text{m}$ .

- According to a particular aspect, the interlayer spacing between each of the plurality of layers is greater than that of a layered non-intercalated transition metal dichalcogenide
- 30 film with the same transition metal and dichalcogenide.

According to a particular aspect, the film may have a sheet resistance of 0.5-20 k $\Omega$ /sq. The film may have a charge density of 1-25 mC/m<sup>2</sup>.

According to a particular aspect, the film may be provided on a substrate. The substrate may be transparent. The substrate may be a conductor.

- 5 According to a particular aspect, the film may switch between a reflective state and a transparent state upon switching a voltage bias.

According to a second aspect, there is provided a method of forming a continuous intercalated two-dimensional transition metal dichalcogenide film comprising a plurality of layers intercalated with alkali metal, the method comprising:

- 10           -       applying a composition comprising an alkali metal and transition metal to a surface of a substrate;
- heating the substrate; and
- exposing the substrate to an asymmetric gas flow comprising a chalcogen gas.

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The heating the substrate may be at a temperature of 300-700 °C.

According to a particular aspect, the heating the substrate and the exposing the substrate may be simultaneous.

- 20 The heating the substrate may be for 2-4 hours. The exposing the substrate may be for 2-4 hours.

According to a particular aspect, the method may further comprise heating a chalcogen source to form the chalcogen gas. The heating a chalcogen source may be at a temperature of 110-250 °C.

- 25 According to a particular aspect, the asymmetric gas flow may further comprise a reducing gas and a carrier gas.

According to a particular aspect, the method may further comprise applying the composition to the surface of the substrate prior to the providing.

The formed film may have an average lateral size of > 50  $\mu$ m.

#### Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic diagram of the space-confined configuration inside a furnace for preparing interlayer spacing-expanded molybdenum disulfide (i-MoS<sub>2</sub>), with the opening side of a one-end opened quartz tube facing the flow stream of N<sub>2</sub>/H<sub>2</sub> gases;

Figure 2 shows examples of annealing profiles of the substrate and sulphur source;

Figure 3 shows (a) a schematic diagram of the cross-sectional structure of i-MoS<sub>2</sub> with sodium intercalates; (b) photograph of transparent i-MoS<sub>2</sub> grown on fluorine-doped tin oxide on glass, with spots 1-5 identified for cross-sectional TEM imaging; (c) optical transmission data of i-MoS<sub>2</sub> film; (d)-(h) the cross-sectional TEM images (scale bar of 5 nm) measured from different areas (spots 1-5 from Figure 3(b)) of the i-MoS<sub>2</sub> film;

Figure 4 shows (a) cross-sectional HRTEM image of the i-MoS<sub>2</sub> with expanded interlayer spacing; (b) interlayer spacing of i-MoS<sub>2</sub> along the continuous line in Figure 4(a); (c) EDX analysis showing the Na intercalates within i-MoS<sub>2</sub> on TEM copper grid;

Figure 5 shows high resolution TEM image of i-MoS<sub>2</sub>;

Figure 6 shows Raman spectrum of i-MoS<sub>2</sub>;

Figure 7 shows (a) comparison in sheet resistance between i-MoS<sub>2</sub> and MoS<sub>2</sub> prepared by the prior art methods; (b) charge density of i-MoS<sub>2</sub> and MoS<sub>2</sub> grown on FTO substrate evaluated under CV measurement in electrolyte of 0.12 M NaCl/ MeOH; (c) charge-discharge behaviour of i-MoS<sub>2</sub> in DMSO-based electrolyte containing 500 mM LiCl; and

Figure 8 shows optical reflectance of an REM device with i-MoS<sub>2</sub> counter electrode, upon switching under different bias: -3.0 V (Ag mirror formation) and + 1.6 V (Ag mirror dissolution).

#### Detailed Description

As explained above, there is a need for an improved intercalated transition metal dichalcogenide film and method of forming the same.

In general terms, the present invention provides a continuous two-dimensional layered transition metal dichalcogenide film, comprising a plurality of intercalated layers with alkali metal. The film may have a well-defined layered structure with uniform and controlled intercalation over a larger area. The uniform intercalation over a large area  
5 advantageously allows improved ion storage in electrochemical devices, and the intercalated layered structure advantageously provides large-area and intimate electrode-electrolyte contact surface, enabling fast interfacial charge transfer. This allows for further applications of the film to electrochemical devices.

According to a first aspect, the present invention provides a continuous intercalated two-  
10 dimensional transition metal dichalcogenide film, comprising a plurality of layers intercalated with alkali metal.

For the purposes of the present invention, the use of the singular includes the plural unless specifically stated otherwise. It should be noted that, as used in the specification and the appended claims, the singular forms "a", "an" and "the" include plural referents  
15 unless the context clearly dictates otherwise. Further, the use of the term "including", "comprising", and "having" as well as other forms, such as "include", "comprise", "have" are not considered limiting.

For the purposes of the present invention, references to a continuous film refers to a film which is uniform and homogeneous with well-connected grains, rather than in the form  
20 of isolated flakes or isolated sheets.

For the purposes of the present invention, references to lateral size refers to the measurement of at least one side, other than thickness, of a film.

The continuous film has a scalable lateral size and well-connected grains. The continuous film may advantageously increase ion diffusion pathways and maintain  
25 optical transmission, thereby allowing it to be used in various electrochemical applications.

The continuous intercalated two-dimensional transition metal dichalcogenide film may comprise a plurality of layers intercalated with alkali metal. The film may have any suitable number of two-dimensional transition metal dichalcogenide layers. The film may  
30 have any suitable thickness. For example, the film may comprise 2-40 layers. In particular, the film may comprise 5-35 layers, 10-30 layers, 15-25 layers. Even more in

particular, the film may comprise 7-15 layers. For example, the film may have a thickness of < 30 nm. In particular, the film may have a thickness of < 25 nm, < 20 nm, < 15 nm, < 10 nm. Even more in particular, the film may have a thickness of < 10 nm.

The transition metal comprised in the two-dimensional transition metal dichalcogenide may be any suitable transition metal. For example, the transition metal may be molybdenum, tungsten. In particular, the transition metal may be molybdenum. The chalcogen comprised in the two-dimensional transition metal dichalcogenide may be any suitable chalcogen. For example, the chalcogen may be sulphur, selenium, tellurium, or any combination thereof. In particular, the chalcogen may be sulphur.

The two-dimensional transition metal dichalcogenide may be molybdenum disulphide ( $\text{MoS}_2$ ), tungsten disulphide ( $\text{WS}_2$ ), molybdenum diselenide ( $\text{MoSe}_2$ ), tungsten diselenide ( $\text{WSe}_2$ ), molybdenum ditelluride ( $\text{MoTe}_2$ ), tungsten ditelluride ( $\text{WTe}_2$ ). In particular, the two-dimensional transition metal dichalcogenide may be molybdenum disulphide ( $\text{MoS}_2$ ). According to a particular aspect, the two-dimensional transition metal dichalcogenide may be molybdenum disulphide ( $\text{MoS}_2$ ) in 1T phase with a structure of one sheet of a layer of S-Mo-S per unit cell in a trigonal crystal system.

The alkali metal may be any suitable alkali metal for intercalation within the plurality of layers. For example, the alkali metal may be lithium, sodium, potassium. In particular, the alkali metal may be sodium. The degree of intercalation may be adjusted by tuning the ratio in a precursor. The precursor may have a general formula of  $\text{X}_2\text{YO}_4:\text{YO}_3$ , where X represents the alkali metal and Y represents the transition metal. For example, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be increased to increase the degree of intercalation. An increase in proportion of alkali metal intercalates may weaken the interlayer interaction and interlayer coupling, and may thereby lead to a transition metal dichalcogenide film with increased interlayer spacing. For example, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be  $x:(1-x)$ , where  $x \leq 1$ . In particular, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be 1:1, 1:9, 2:8, 3:7, 4:6, 6:4, 7:3, 8:2, 9:1. Even more in particular, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be 1:1.

The continuous intercalated two-dimensional transition metal dichalcogenide film may have an average lateral size of > 50  $\mu\text{m}$ . For example, the film may have an average lateral size of > 50  $\mu\text{m}$ , > 55  $\mu\text{m}$ , > 60  $\mu\text{m}$ , > 65  $\mu\text{m}$ , > 70  $\mu\text{m}$ , > 75  $\mu\text{m}$ , > 80  $\mu\text{m}$ , > 85  $\mu\text{m}$ , > 90  $\mu\text{m}$ , > 95  $\mu\text{m}$ , > 100  $\mu\text{m}$ , > 1000  $\mu\text{m}$ , > 2000  $\mu\text{m}$ , > 3000  $\mu\text{m}$ , > 4000  $\mu\text{m}$ , > 5000  $\mu\text{m}$ , > 6000  $\mu\text{m}$ , > 7000  $\mu\text{m}$ , > 8000  $\mu\text{m}$ , > 9000  $\mu\text{m}$ , > 10,000  $\mu\text{m}$ , > 15,000  $\mu\text{m}$ , >

20,000  $\mu\text{m}$ , > 25,000  $\mu\text{m}$ , > 30,000  $\mu\text{m}$ , > 35,000  $\mu\text{m}$ , > 40,000  $\mu\text{m}$ , > 45,000  $\mu\text{m}$ , > 50,000  $\mu\text{m}$ . The lateral size of the film may be limited only by the area on which a precursor was applied on a surface of the substrate that the film was grown on, and as such, there is advantageously high scalability in the lateral size of the film.

- 5 According to a particular aspect, the interlayer spacing between each of the plurality of layers of the film may be greater than that of a layered non-intercalated transition metal dichalcogenide film with the same transition metal and dichalcogenide. For example, the plurality of layers may comprise molybdenum disulphide ( $\text{MoS}_2$ ) layers intercalated with an alkali metal, and the interlayer spacing between each of the plurality of layers may be greater than that of a layered non-intercalated molybdenum disulphide ( $\text{MoS}_2$ ). In particular, the interlayer spacing between each of the plurality of layers may be > 0.61 nm, which is greater than that of a layered non-intercalated molybdenum disulphide ( $\text{MoS}_2$ ). Even more in particular, the interlayer spacing between each of the plurality of layers may be  $\geq 0.65$  nm,  $\geq 0.66$  nm,  $\geq 0.67$  nm,  $\geq 0.68$  nm,  $\geq 0.69$  nm,  $\geq 0.70$  nm,  $\geq 0.71$  nm,  $\geq 0.72$  nm,  $\geq 0.73$  nm,  $\geq 0.74$  nm,  $\geq 0.75$  nm,  $\geq 0.76$  nm,  $\geq 0.77$  nm.

For example, the plurality of layers may comprise tungsten disulphide ( $\text{WS}_2$ ), molybdenum diselenide ( $\text{MoSe}_2$ ), tungsten diselenide ( $\text{WSe}_2$ ), molybdenum ditelluride ( $\text{MoTe}_2$ ), tungsten ditelluride ( $\text{WTe}_2$ ) intercalated with an alkali metal, and the interlayer spacing between each of the plurality of layers may be greater than that of a layered non-intercalated tungsten disulphide ( $\text{WS}_2$ ), molybdenum diselenide ( $\text{MoSe}_2$ ), tungsten diselenide ( $\text{WSe}_2$ ), molybdenum ditelluride ( $\text{MoTe}_2$ ), tungsten ditelluride ( $\text{WTe}_2$ ), respectively. In particular, the interlayer spacing between each of the plurality of layers may be 0.65-0.77 nm, 0.66-0.76 nm, 0.67-0.75 nm, 0.68-0.74 nm, 0.69-0.73 nm, 0.70-0.72 nm.

- 25 According to a particular aspect, the film may have a sheet resistance of 0.5-20  $\text{k}\Omega/\text{sq}$ . For example, the film may have a sheet resistance of 1-19  $\text{k}\Omega/\text{sq}$ , 2-18  $\text{k}\Omega/\text{sq}$ , 3-17  $\text{k}\Omega/\text{sq}$ , 4-16  $\text{k}\Omega/\text{sq}$ , 5-15  $\text{k}\Omega/\text{sq}$ , 6-14  $\text{k}\Omega/\text{sq}$ , 7-13  $\text{k}\Omega/\text{sq}$ , 8-12  $\text{k}\Omega/\text{sq}$ , 9-11  $\text{k}\Omega/\text{sq}$ . In particular, the film may have a sheet resistance of 1-10  $\text{k}\Omega/\text{sq}$ .

According to a particular aspect, the film may have a charge density of 1-25  $\text{mC}/\text{m}^2$ . For example, the film may have a charge density of 2-24  $\text{mC}/\text{m}^2$ , 3-23  $\text{mC}/\text{m}^2$ , 4-22  $\text{mC}/\text{m}^2$ , 5-21  $\text{mC}/\text{m}^2$ , 6-20  $\text{mC}/\text{m}^2$ , 7-19  $\text{mC}/\text{m}^2$ , 8-18  $\text{mC}/\text{m}^2$ , 9-17  $\text{mC}/\text{m}^2$ , 10-16  $\text{mC}/\text{m}^2$ , 11-15  $\text{mC}/\text{m}^2$ , 12-14  $\text{mC}/\text{m}^2$ . In particular, the film may have a charge density of 6-20  $\text{mC}/\text{m}^2$ .

The film therefore advantageously has significantly improved charge storage behaviour in terms of greater charge density, leading to improved electrochemical performance. The film also acts as a stable host to offer wide open diffusion channels for electrochemically cycled guest ions, which can alleviate host-guest interactions and  
5 facilitate stable long-term charge-discharge.

According to a particular aspect, the film may be provided on a substrate. The substrate may be any suitable substrate to enable the film to grow. In particular, the substrate may be transparent. For the purposes of the present invention, references to transparent refers to optical transparency that allows visible light to pass through. In particular, the  
10 substrate may have a wide bandgap with energy value greater than those of visible light, such that photons with energies below the bandgap value are not absorbed by the substrate and visible light passes through.

The substrate may be a conductor. For the purposes of the present invention, references to conductor refers to any material that allows the flow of charge in one or more  
15 directions. The film may be grown such that the plurality of layers are parallel to the transparent conductor. In this way, the film may advantageously be used as an ion storage layer for transparent electronics, to form a transparent electrochemical device when integrated with another transparent electrode and electrolyte, including but not limited to reversible electrochemical mirrors, transparent batteries, etc.

20 For example, the substrate may comprise a transparent conducting oxide, a transparent conducting polymer, graphene, metal grids and metallic nanowires. In particular, the substrate may comprise fluorine tin oxide, indium tin oxide, sapphire, aluminium zinc oxide, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), poly(4,4-dioctyl  
25 cyclopentadithiophene), graphene, reduced graphene oxide, silver grids and silver nanowires.

According to a particular aspect, the film may switch between a reflective state and a transparent state upon switching a voltage bias. For example, the film may be in a reflective state, having > 80 % reflectance at 650 nm when a negative voltage is applied.  
30 The film may be in a transparent state, having < 10 % reflectance at 650 nm when a positive voltage is applied. The film may have a change in optical reflectance between the reflective state and the transparent state of > 70%. The film may therefore be

incorporated as a counter electrode in a reversible electrochemical mirror, with advantageously high capability in balancing the charges required for the electrochemical reactions happening during device switching, and high charge storage behaviour.

According to a second aspect, there is provided a method of forming a continuous  
5 intercalated two-dimensional transition metal dichalcogenide film comprising a plurality of layers intercalated with alkali metal, the method comprising:

- applying a composition comprising an alkali metal and transition metal to a surface of a substrate;
- heating the substrate; and
- 10 - exposing the substrate to an asymmetric gas flow comprising a chalcogen gas.

The applying may be by any suitable method. For example, the applying may be by coating. In particular, the applying may be by spin coating, dip coating, spray pyrolysis,  
15 inkjet printing, brush coating, doctor blading, screen printing.

The substrate may be as described above. The present method advantageously enables the growth of continuous intercalated two-dimensional transition metal dichalcogenide films with controllable thickness, directly on a substrate that can be used for the fabrication of electronic devices, without post-treatment. This eliminates the use of  
20 conventional intermediates typically used for post-growth intercalation processes, which are highly unstable and flammable.

The method is also highly scalable, with growth area of the film being determined by the area on which the composition is applied on the surface of the substrate. The method also enables the film to be grown on a transparent conductor, thus allowing the film to  
25 be used in a variety of applications requiring transparent electronics.

The composition may comprise any suitable precursor for forming the film. For example, the composition may comprise a salt of an alkali metal cation and transition metal oxyanion, and a transition metal oxide. The alkali metal and the transition metal may be as described above.

30 According to a particular aspect, the precursor comprised in the composition may have a general formula of  $X_2YO_4:YO_3$ , where X represents the alkali metal and Y represents

the transition metal. In particular, the precursor may comprise  $\text{Na}_2\text{MoO}_4\text{:MoO}_3$ ,  $\text{Na}_2\text{WO}_4\text{:WO}_3$ ,  $\text{K}_2\text{MoO}_4\text{:MoO}_3$ ,  $\text{K}_2\text{WO}_4\text{:WO}_3$ ,  $\text{Li}_2\text{MoO}_4\text{:MoO}_3$ ,  $\text{Li}_2\text{WO}_4\text{:WO}_3$ . The ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be any suitable ratio. For example, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be  $x\text{:}(1-x)$ , where  $x \leq 1$ . In particular, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be 1:1, 1:9, 2:8, 3:7, 4:6, 5 6:4, 7:3, 8:2, 9:1. Even more in particular, the ratio of  $\text{X}_2\text{YO}_4$  to  $\text{YO}_3$  may be 1:1.

The asymmetric gas flow may be produced by any suitable means. For example, the asymmetric gas flow may be produced by having a space-enclosed environment. In particular, the substrate may be placed in a first container having one open end, and the first container may be placed in a second container having more than one open end. The 10 first and second container may each be a tube, and the configuration may be a tube-in-tube configuration. The substrate may be exposed to a flowing gas stream facing the open end of the first container. In this way, the asymmetric gas flow comprising a chalcogen gas is confined and advantageously allows for steady growth of the film.

According to a particular aspect, the heating the substrate may be at a temperature of 15 300-700 °C. In particular, the heating the substrate may be at a temperature of 350-650 °C, 400-600 °C, 450-550 °C, 400-500 °C. Even more in particular, the heating the substrate may be at a temperature of 450-550 °C.

According to a particular aspect, the heating the substrate and the exposing the substrate may be simultaneous. The heating the substrate may be for 2-4 hours. The exposing the 20 substrate may be for 2-4 hours. In particular, the heating the substrate may be for 2.5-3.5 hours, 2-3 hours. In particular, the exposing the substrate may be for 2.5-3.5 hours, 2-3 hours. The combination of the temperature and time parameters may lead to annealing of the film. Thus, the present method advantageously requires only a low growth temperature and short growth time, thereby allowing the plurality of layers to be 25 integrated with complementary metal-oxide-semiconductor (CMOS) technology at back-end-of-line (BEOL).

According to a particular aspect, the method may further comprise heating a chalcogen source to form the chalcogen gas. The heating the chalcogen source may be at any suitable temperature to form the chalcogen gas. For example, the heating a chalcogen 30 source may be at a temperature of 110-250 °C. In particular, the heating a chalcogen source may be at a temperature of 175-225 °C.

The asymmetric gas flow may further comprise a reducing gas and a carrier gas. The reducing gas may be any suitable reducing gas to reduce the composition. For example, the reducing gas may comprise hydrogen. The carrier gas may be any suitable gas for carrying the gas flow. For example, the carrier gas may comprise an inert gas. In particular, the carrier gas may comprise nitrogen, helium, argon. The reducing gas and the carrier gas may be in any suitable ratio. For example, the ratio of the reducing gas and the carrier gas may be 40:60 to 5:95. In particular, the ratio of the reducing gas and the carrier gas may be 40:60, 35:65, 30:70, 25:75, 20:80, 15:85, 10:90, 5:95. Even more in particular, the ratio of the reducing gas and the carrier gas may be 5:95.

The formed film may have an average lateral size of  $> 50 \mu\text{m}$ . For example, the formed film may have an average lateral size of  $> 50 \mu\text{m}$ ,  $> 55 \mu\text{m}$ ,  $> 60 \mu\text{m}$ ,  $> 65 \mu\text{m}$ ,  $> 70 \mu\text{m}$ ,  $> 75 \mu\text{m}$ ,  $> 80 \mu\text{m}$ ,  $> 85 \mu\text{m}$ ,  $> 90 \mu\text{m}$ ,  $> 95 \mu\text{m}$ ,  $> 100 \mu\text{m}$ ,  $> 1000 \mu\text{m}$ ,  $> 2000 \mu\text{m}$ ,  $> 3000 \mu\text{m}$ ,  $> 4000 \mu\text{m}$ ,  $> 5000 \mu\text{m}$ ,  $> 6000 \mu\text{m}$ ,  $> 7000 \mu\text{m}$ ,  $> 8000 \mu\text{m}$ ,  $> 9000 \mu\text{m}$ ,  $> 10,000 \mu\text{m}$ ,  $> 15,000 \mu\text{m}$ ,  $> 20,000 \mu\text{m}$ ,  $> 25,000 \mu\text{m}$ ,  $> 30,000 \mu\text{m}$ ,  $> 35,000 \mu\text{m}$ ,  $> 40,000 \mu\text{m}$ ,  $> 45,000 \mu\text{m}$ ,  $> 50,000 \mu\text{m}$ . The lateral size of the film may be limited only by the area on which a precursor was applied on a surface of the substrate that the film was grown on, and as such, there is advantageously high scalability in the lateral size of the film.

Having now generally described the invention, the same will be more readily understood through reference to the following example which is provided by way of illustration, and is not intended to be limiting.

### Example

#### Materials and methods

##### *Synthesis of i-TMDC*

A fluorine-doped tin oxide (FTO) substrate was coated with a 10 nm thick coating of a binary composition of alkali metal molybdate/tungstate and transition metal oxide ( $\text{Na}_2\text{MoO}_4\text{:MoO}_3$ ) via spin coating.

The  $\text{Na}_2\text{MoO}_4\text{:MoO}_3$  coated FTO was placed in a one-end opened quartz tube (Figure 1). Thereafter, the one-end opened quartz tube was transferred into a double-end opened quartz tube inside a CVD furnace (Figure 1) filled with steady flow of  $\text{N}_2/\text{H}_2$  gases

at a volume ratio of 95:5, with the opening side of the one-end opened quartz tube facing the flow stream of  $N_2/H_2$  gases, and purged for at least 3 hours.

The substrate was subject to sulfurization at an elevated temperature of 500 °C, with sulphur precursor gas applied to form i-MoS<sub>2</sub>, wherein sulphur powder was heated at 200 °C under the flow stream of  $N_2/H_2$  gases. The sulphur vapour was diluted by the  $N_2$  carrier gas and the concentration of sulphur was regulated with mass flow controller of 150 sccm. The tube-in-tube configuration generated a space-enclosed environment, where the trapped sulphur gas inside the inner tube confined the asymmetric gas flow for steady growth of i-TMDCs. The annealing profiles are shown in Figure 2.

#### 10 Characterization

An FEI Titan 80/300 Scanning/TEM (200 kV) and FEI Tecnai F20 with fast Fourier transform measurements were used for imaging high-resolution TEM images and STEM-EDX analysis.

The i-MoS<sub>2</sub> was transferred onto the 200-mesh TEM Cu grid using poly(methyl methacrylate) (PMMA 950 in anisole, A5, KAYAKU Advanced Materials, Inc.). The focused ion beam technique was employed to prepare a lamella, used for obtaining a cross-sectional image of i-MoS<sub>2</sub> film.

#### Results and discussion

##### 20 *High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) analysis*

Figure 3 (a) shows a schematic diagram of the cross-sectional structure of i-MoS<sub>2</sub> with sodium intercalates. As seen from Figures 3(b) and 3(c), the scalable growth of optically transparent i-MoS<sub>2</sub> has been demonstrated on a FTO substrate. The substrate size was 25 mm x 25 mm. The well-defined layered structure of i-MoS<sub>2</sub> with increased interlayer spacing (0.73 nm) was confirmed by the cross-sectional TEM images measured from random spots (spots 1 to 5 in Figures 3(d) to 3(h)).

Table 1 shows a comparison of lateral sizes of films formed using prior art preparation methods, and the present method.

| Preparation conditions of interlayer spacing-expanded MoS <sub>2</sub> (i-MoS <sub>2</sub> )                                 |                                                                                                                                |                  | Lateral size of i-MoS <sub>2</sub> (μm) | References                                                                  |
|------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|------------------|-----------------------------------------|-----------------------------------------------------------------------------|
| Synthesis methods                                                                                                            | Follow-up procedures                                                                                                           | Preparation time |                                         |                                                                             |
| Bulk MoS <sub>2</sub> crystals soaked into aprotic solvents containing lithium and ammonia                                   | Washed with hexane; stored in aprotic solvents                                                                                 | > 1 day          | < 2                                     | US10309027B2                                                                |
| Exfoliation of bulk MoS <sub>2</sub> crystals in n-butyllithium in hexane and restacking of exfoliated sheets via filtration | Washed with hexane; sonicated in water for 1 h followed by washing; dispersed in water for storage or restacked via filtration | 2 days           | 0.3-0.8                                 | M. Acerce et. al., <i>Nat. Nanotechnol.</i> , 2015, 10, 313–318.            |
| Exfoliation of bulk MoS <sub>2</sub> crystals in n-butyllithium in hexane                                                    | Washed with hexane; sonicated in DI water for 6 h/1 h; centrifuged                                                             | 3 days           | 0.05-0.7                                | M. Acerce et. al., <i>Nature</i> , 2017, 549, 370–373                       |
| Exfoliation of bulk MoS <sub>2</sub> crystals in n-butyllithium in hexane                                                    | Washed with hexane; sonicated in water for 1 h and centrifuged several times; dispersed in water for storage                   | 2 days           | 0.5-1                                   | H. Huang et. al., <i>Nano Energy</i> , 2016, 26, 172–179                    |
| Exfoliation of bulk MoS <sub>2</sub> crystals in n-butyllithium in hexane                                                    | Washed with hexane; sonicating in water for 5 min; centrifuged                                                                 | > 1 day          | 0.3                                     | X. Fan et. al., <i>Nano Lett.</i> , 2015, 15, 5956–5960                     |
| Exfoliation of bulk MoS <sub>2</sub> crystals in lithium borohydrate under heating at 300°C                                  | Immersed in water; sonicated for 1 h; centrifuged                                                                              | 3 days           | 0.2-1                                   | D. Voiry et. al., <i>Nano Lett.</i> , 2013, 13, 6222–6227                   |
| Hydrothermal method                                                                                                          | Nil                                                                                                                            | 1 day            | 10000                                   | F. Z. Wang et. al., <i>Scientific Reports</i> 6, 31092 (2016)               |
| CVD method under single-tube configuration using transition metal precursor                                                  | Fabricate an electrochemical device for n-butyl-lithium exposure                                                               | ~ 1 day          | 5-30                                    | D. Voiry et. al., <i>Nat. Mater.</i> , 2016, 15, 1003–1009                  |
| Evaporation of alkali metal on MoS <sub>2</sub> flakes inside high vacuum chamber containing hydrogen                        | Nil                                                                                                                            | ~ 3 hours        | 5-50                                    | Sherman J. R. Tan et. al., <i>J. Am. Chem. Soc.</i> 2017, 139, 6, 2504–2511 |

|                                                                                                                                                                                                             |     |           |       |                                                    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|-----------|-------|----------------------------------------------------|
| Electrochemical intercalation with MoS <sub>2</sub> crystals in LiPF <sub>6</sub> , NaPF <sub>6</sub> , KPF <sub>6</sub> in EC/DEC for Li <sup>+</sup> , Na <sup>+</sup> , and K <sup>+</sup> intercalation | Nil | ~ 3 hours | ~ 5   | J. Zhang et. al., <i>Nat. Comm.</i> 9, 5289 (2018) |
| Sulfurization in space-enclosed environment using precursors consisted of alkali metal molybdate and transition metal oxide                                                                                 | Nil | ~3 hours  | 25000 | This work                                          |

Table 1: Comparison of lateral sizes of films

The growth of i-MoS<sub>2</sub> film occurred at a much higher concentration of the precursor sources inside the one-end opened quartz tube by confining the outward diffusion of the heated precursors. The i-TMDCs film grown using this method was highly uniform and continuous (Figure 3 and Table 1) with expanded interlayered spacing (0.73 nm), as shown in Figures 4(a) and 4(b), which is larger than that of conventional MoS<sub>2</sub> film (0.62 nm).

As seen in Figure 4(c), EDX analysis confirmed the presence of Na intercalates inside i-MoS<sub>2</sub> on TEM copper grid.

High resolution TEM image (scale bar 2 nm) showed the presence of 1T phase of MoS<sub>2</sub>, which is the typical behaviour of interlayer spacing-expanded MoS<sub>2</sub> with intercalation (Figure 5).

Raman Spectroscopy

As seen in Figure 6, the Raman spectrum of i-MoS<sub>2</sub> showed characteristics unique to the Na-intercalated MoS<sub>2</sub>, which consisted of multiple peaks located at Raman mode of 158, 218, 334, 383 and 410 cm<sup>-1</sup>, corresponding to the J<sub>1</sub>, J<sub>2</sub>, J<sub>3</sub>, E<sub>2g</sub> and A<sub>1g</sub> peaks, respectively.

Sheet resistance, charge density, and ion storage

Sheet resistance of the synthesised i-MoS<sub>2</sub> was at least two orders of magnitude lower than that of pristine MoS<sub>2</sub> (i. e. pure MoS<sub>2</sub> without intercalants) synthesised by conventional growth methods (Figure 7(a)).

In particular, i-MoS<sub>2</sub> had demonstrated significant improvement in charge storage behaviour, in terms of its high charge density. Figure 7(b) shows the relatively high charge density of i-MoS<sub>2</sub> (about 12 mC/cm<sup>2</sup>, which is nearly two times higher than that of prior art MoS<sub>2</sub> with only about 6.3 mC/cm<sup>2</sup>), suggesting that i-MoS<sub>2</sub> has improved electrochemical performance compared to conventional MoS<sub>2</sub> based electrode.

In addition, i-MoS<sub>2</sub> acted as a stable host to offer open diffusion channels for the electrochemically cycled guest ions, which alleviates host–guest interactions and thus facilitate ion diffusion and a stable long-term charge-discharge test. Efficient ion storage behaviour in i-MoS<sub>2</sub> film was further demonstrated based on the charge-discharge test of i-MoS<sub>2</sub> in DMSO-based electrolyte containing 500 mM LiCl (Figure 7(c)).

Reversible electrochemical mirror (REM) devices

The i-MoS<sub>2</sub> material was applied as an electrode in a reversible electrochemical mirror (REM) device, which showed better device performance (high-contrast light reflection) than literature results (Table 2).

| Device structure                                                                 | Reflection property R (%) @ 650nm |                            |        | Refs.                                                                                             |
|----------------------------------------------------------------------------------|-----------------------------------|----------------------------|--------|---------------------------------------------------------------------------------------------------|
|                                                                                  | R (%) under mirror state          | R (%) under bleached state | ΔR (%) |                                                                                                   |
| TCO / DMSO containing CuCl <sub>2</sub> , LiClO <sub>4</sub> , KI and PVA / TCO  | 62                                | 8                          | 54     | A. L. Eh et. al., <i>J. Mater. Chem. C</i> , vol. 5, pp. 6547-6554, 2017                          |
| TCO / DMSO containing AgNO <sub>3</sub> , LiBr and CuCl <sub>2</sub> / TCO       | 52                                | 22                         | 30     | C. Sung et. al., <i>Adv. Mater. Technol.</i> vol. 5, pp. 2000367, 2020                            |
| TCO / DMSO containing AgNO <sub>3</sub> , TBABr, CuCl <sub>2</sub> and PVB / TCO | 49                                | 6                          | 43     | R. Kimura et. al., <i>Solar Energy Materials &amp; Solar Cells</i> , vol. 177, pp. 128–133, 2018. |
| TCO / MeOH containing AgNO <sub>3</sub> and NaCl/ MoS <sub>2</sub> / TCO         | 86.5                              | 15.5                       | 71     | This work                                                                                         |

Table 2: Performance comparison of REM devices

The REM device is an electrochromic application that rely on the electrodeposition and dissolution of a silver (Ag) metal layer to achieve spectrum control. The two-electrode REM device was constructed by sandwiching the Ag ions based liquid electrolyte between the MoS<sub>2</sub> counter electrode and the indium tin oxide (ITO) working electrode.

- 5 By modulating the potential across the two electrodes, the reflective Ag metal with a thickness of about a few tens of nanometer would be either formed on the ITO working electrode or dissolved into the electrolyte, and thus the REM device becomes reflective-transparent switchable. The charges released/consumed during the oxidation/reduction reactions occurring on the working electrode must be compensated effectively by those  
10 involved in the reduction/oxidation reactions happening on the counter electrode.

As shown in Table 2 and Figure 8, the wide dynamic control in the light reflectance (86.5 % and 15.5 %, in the mirror and bleached states, at wavelength of 650 nm, respectively) was measured upon switching the Ag-based REM device with i-MoS<sub>2</sub> counter electrode between -3.0 V and +1.6 V. The i-MoS<sub>2</sub> counter electrode having high charge storage  
15 behaviour is the ideal ion storage layer in REM, considering it can balance the charges required for the electrochemical reactions happening during the device switching.

The large optical modulation in the light reflectance ( $\Delta R$  of about 71 % as shown in Figure 8) and lower power consumption (about 24 W/m<sup>2</sup>) suggests that an REM device with i-MoS<sub>2</sub> counter electrode can meet energy-saving requirements.

20

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A continuous intercalated two-dimensional transition metal dichalcogenide film, comprising a plurality of layers intercalated with alkali metal.
2. The film according to claim 1, wherein the film has an average lateral size of > 50  
5  $\mu\text{m}$ .
3. The film according to claim 1 or 2, wherein interlayer spacing between each of the plurality of layers is greater than that of a layered non-intercalated transition metal dichalcogenide film with the same transition metal and dichalcogenide.
4. The film according to any preceding claim, wherein the film has a sheet resistance  
10 of 0.5-20  $\text{k}\Omega/\text{sq}$ .
5. The film according to any preceding claim, wherein the film has a charge density of 1-25  $\text{mC}/\text{m}^2$ .
6. The film according to any preceding claim, wherein the film is provided on a substrate.
- 15 7. The film according to claim 6, wherein the substrate is transparent.
8. The film according to claim 6 or 7, wherein the substrate is a conductor.
9. The film according to claim 8, wherein the film switches between a reflective state and a transparent state upon switching a voltage bias.
10. A method of forming a continuous intercalated two-dimensional transition metal  
20 dichalcogenide film comprising a plurality of layers intercalated with alkali metal, the method comprising:
  - applying a composition comprising an alkali metal and transition metal to a surface of a substrate;
  - heating the substrate; and
  - 25 - exposing the substrate to an asymmetric gas flow comprising a chalcogen gas.
11. The method according to claim 10, wherein the heating the substrate is at a temperature of 300-700  $^{\circ}\text{C}$ .

12. The method according to claim 10 or 11, wherein the heating the substrate and the exposing the substrate is simultaneous.

13. The method according to any of claims 10-12, wherein the heating the substrate is for 2-4 hours.

5 14. The method according to any of claims 10-13, wherein the exposing the substrate is for 2-4 hours.

15. The method according to any of claims 10-14, further comprising heating a chalcogen source to form the chalcogen gas.

10 16. The method according to claim 15, wherein the heating a chalcogen source is at a temperature of 110-250 °C.

17. The method according to any of claims 10-16, wherein the asymmetric gas flow further comprises a reducing gas and a carrier gas.

18. The method according to any of claims 10-17, wherein the formed film has an average lateral size of > 50 μm.