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Journal Name

ARTICLE

A Simple Electrochemical Route to Metallic Phase Trilayer MoS₂: evaluation as Electrocatalysts and Supercapacitors

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ABSTRACT—The development of simple, scalable and reproducible technique for the synthesis of two dimensional MoS₂ nanosheets is of paramount importance in the field of catalysis and energy storage devices. Current routes to produce MoS₂ nanosheets in reasonable quantities involve either use solution exfoliation of bulk MoS₂ or the intercalation of organo-lithium into bulk MoS₂ which then subsequently exfoliated by immersing it in water. The former process produces semiconducting 2H-MoS₂ nanoplatelets with smaller lateral flake size whereas the latter process produces highly conducting metallic (1T) phase monolayer MoS₂. 1T-MoS₂ nanosheets have high catalytic activity for hydrogen evolution reaction (HER) and are efficient electrode materials for supercapacitor when compared to the 2H phase. However, the feasibility of producing 1T-MoS₂ by organolithium intercalation is undermined by the long reaction time (2–3 days) and by its pyrophoric nature. We report a simple, bench-top electrochemical process to produce exfoliated metallic phase MoS₂ within two hours. By using an inert Li salt (LiClO₄) as a source of lithium and a Pt counter electrode, an electrochemically lithium intercalated MoS₂ electrode was obtained which was subsequently exfoliated by immersing in water. Characterization of the exfoliated product using a variety of methods confirmed the formation of the 1T-phase. Remarkably, flake thickness measurement using atomic force microscopy and high-resolution transmission electron microscopy revealed that the majority of the nanosheets are trilayers. The 1T-MoS₂ nanosheets showed enhanced electrocatalytic activity towards hydrogen evolution compared to 2H-MoS₂ and are efficient materials for supercapacitor applications. Coin cells constructed from a 1T-MoS₂-graphene composite achieved a volumetric capacitance of over 560 F cm^{−3} in an aqueous system and 250 F cm^{−3} in a non-aqueous electrolyte with capacity retention of over 90 % after 5,000 cycles. This process is readily scalable and should ultimately support production of metallic MoS₂ for various applications. It can also be extended for producing 2H-MoS₂ nanosheets by heating the exfoliated 1T phase.

1. Introduction. The evolution of a more sustainable, environmentally benign energy supply is a key for future development and economic growth. There is an urgent need for energy storage and conversion devices (ESCs) that would be available in quantities, and at a cost, that is competitive with fossil fuels. Typical ESCs include solar cells, fuel cells, water electrolyzers, supercapacitors and rechargeable batteries. Widespread adoption of these technologies is currently hindered by several factors including performance, material stability and cost.¹ At the heart of these issues are the properties of the nanostructured materials employed in such devices.² The successful development of new nanostructured materials in this regard would represent a key step forward in ESCs technology. Recently, two-dimensional materials such as graphene and MoS₂ have shown great promise in ESCs applications because of their high surface area and properties that are distinct from their bulk counterparts.^{3,4}

Layered molybdenum disulfide exhibits two possible phases, the naturally occurring semiconducting phase (2H-MoS₂), and a non-naturally occurring metallic state (1T-MoS₂) that can be prepared by intercalation chemistry.⁵ The 2H phase is semiconducting with a direct bandgap of ~1.9 eV for monolayer sheets.⁶ The 1T phase though is metallic with a conductivity up to 10⁷ times higher than the 2H phase.⁷ Metallic phase MoS₂ nanosheets are very attractive for a number of electrochemical applications including as supercapacitor electrodes, as catalysts for hydrogen evolution and in dye-sensitised solar cells.^{7–11} For example, Chhowalla *et al.* recently demonstrated that the gravimetric capacitance of chemically exfoliated 1T-MoS₂ in aqueous electrolyte was 20 times higher than that of the 2H phase.⁷ The ability of 1T-MoS₂ to intercalate various ions, coupled with its high electrical conductivity and hydrophilicity, were suggested as reasons for this good performance.⁷ In the case of the hydrogen evolution reaction (HER), unlike the 2H-MoS₂ where the basal plane is catalytically inert towards HER, the basal plane of 1T-MoS₂ was found to be the main active site for HER resulting in a significant enhancement in the overall catalytic activity.^{9,12} The development of a simple and efficient route for synthesizing this material therefore is key to harnessing its potential. To this end, a few synthetic methods have been reported to produce 1T-MoS₂ including top-down (chemical exfoliation) and bottom-up (hydrothermal synthesis) approaches.^{11,13,14}

The most common method for producing 1T-MoS₂ nanosheets involves organolithium intercalation between the layers of bulk

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† Electronic Supplementary Information (ESI) available: [high resolution TEM image, SEM image and XRD of 1T-MoS₂ and 1T-MoS₂/graphene, cyclic voltammograms of 1T-MoS₂/graphene in 6.0 M KOH (aq) and 1.0 M [TEA][BF₄] in PC, Table on energy and power density of 1T-MoS₂/graphene and video showing MoS₂ exfoliation]. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

MoS₂.^{8,13-16} This process starts first by reacting butyllithium with MoS₂ to produce Li_xMoS₂.^{13,16} Then, the resulting Li intercalated bulk MoS₂ is immersed in water and sonicated to exfoliate it down to monolayer to few layer thick MoS₂ nanosheets with dimensions typically of submicron lateral size.^{15,17,18} Whilst this method is attractive due its high yield of monolayer MoS₂ sheets, it also has some major drawbacks; the process requires a long lithiation time (2-3 days) under reflux (100 °C) conditions.¹³⁻¹⁹ Furthermore, organolithium compounds are highly pyrophoric so must be handled away from oxygen and moisture, restricting the reaction to a glove box.²⁰ In an attempt to simplify the synthetic procedure, some groups proposed a bottom-up approach using a hydrothermal process.^{11,21} According to their reports, this method can produce stable 1T-MoS₂ in large quantities with a high concentration of metallic phase. This process, however, produces thicker MoS₂ nanoplatelets and smaller flakes (~100 nm).¹¹ Recently, Zhang *et al.* developed an electrochemical lithiation method for the synthesis of 1T-MoS₂.¹⁰ They prepared MoS₂ electrodes by mixing the powder with carbon black (10 %) as a conducting additive and polyvinylidene fluoride (PVDF) as a binder (10 %), and then inserted it into a battery cell within an Ar-filled glove box using metallic lithium as a source of Li.^{10,22} This method proved to be advantageous in terms of controlling the degree of lithium insertion as well as shortening the experimental time scale from days (as in chemical intercalation) to hours. Nonetheless, the use of metallic lithium restricts the intercalation process to controlled, inert atmosphere conditions. The battery-type electrochemical cell setup also presents challenges in terms of scale up.¹⁸ Furthermore, the conducting additive contaminated the exfoliated flakes and may have introduced side reactions during electrolysis.¹⁸

Herein, we report a simple and cost effective bench top experiment which eliminates the use of potentially explosive materials (such as metallic Li or organolithium compounds). MoS₂ pellets (or MoS₂ crystals) were used to demonstrate the principle of our approach. The pellet was made by pressing MoS₂ powder without any conducting additives or polymer binder. Lithium salt was used as a source of Li and inert Pt mesh was used as a counter electrode so that the experiment can be carried out under ambient conditions without the need for a glove box. Electrochemical intercalation of Li⁺ was conducted at a constant potential using 1.0 M LiClO₄ in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) in an open beaker under a N₂ atmosphere. As the intercalated MoS₂ was immersed in water, an instantaneous exfoliation was observed (see Video in supporting document). Characterisation of the exfoliated product was done using X-ray photoelectron spectroscopy, Raman spectroscopy and UV-visible absorption spectroscopy. This confirmed the formation of the 1T-phase with a concentration of 60 %. Significantly, atomic force microscopy (AFM) and Raman spectroscopy indicated that the majority of the flakes were trilayer in thickness. Finally, we show that the as-prepared material could be used as an efficient electrocatalyst for the hydrogen evolution reaction (HER) and as an electrode material for high performing coin cell supercapacitors.

2. RESULTS AND DISCUSSION

Cyclic voltammetry was used to determine the potential at which Li⁺ intercalation occurs into a MoS₂ pellet: Figure 1 shows the cyclic voltammogram (CV) recorded at the MoS₂ electrode in 0.1 M LiClO₄ in DMC/EC mixture under N₂ atmosphere. When the potential of

the electrode was scanned in a negative direction, a cathodic current started to flow at approximately -3.0 V vs. Ag wire, and a broad peak was observed between -4.5 to -5.0 V. This process was due to the insertion of Li⁺ into the MoS₂.^{23,24} In the return sweep, a broad anodic peak was seen at 1.0 V due to the de-intercalation of Li⁺ (Equation 1). The shape of the CV reported here is similar to that reported in the literature except that the peak-to-peak separation of the Li⁺ intercalation and de-intercalation is wider.²⁵ This could be due to the differing geometry of the electrochemical cell (and scan rate) since we utilised a three electrode cell where the working and counter electrodes were separated by a few centimetres. In contrast, most studies used a two electrode cell in a battery-type (coin cell) configuration which then minimizes the voltage drop.^{24,26} As shown in Figure 1, the formal potential of lithium intercalation/de-intercalation on a Ag wire pseudo reference scale is about -3.0 V whereas Chang *et al.* reported a formal potential of ~1.75 V for the same reaction on a Li⁺/Li scale.²⁴ This shows that the Ag wire reference electrode is at least -4.75 V negative of Li⁺/Li. Based on the CV result, -4.5 V (vs. Ag) was chosen for electrochemical insertion of Li⁺ into MoS₂ since at this potential the insertion of Li⁺ into MoS₂ occurs at diffusion controlled rate. It has been shown that the stability of Li_x[MoS₂] (where x is in the range of 0 ≤ x ≤ 1) strongly depends on the applied potential during electrolysis.²⁶⁻²⁹ At extreme negative potentials (<1.1 V vs. Li⁺/Li), below -6.0 V vs Ag wire, decomposition of Li_x[MoS₂] into Mo nanoparticles occurs, and conversion to Li₂S is the more favoured reaction.²⁶

Figure 1. Cyclic voltammograms recorded at MoS₂ electrode (MoS₂ pellet) in 0.1 M LiClO₄ in EC:DMC (1:1) under N₂ atmosphere. The potential was swept between 3.0 and -6.5 V at 30 mV s⁻¹.

Furthermore, excessive lithiation also leads to the decomposition reaction.³⁰ We wish to note that, on the scale of our reference electrode, an applied potential between -4.0 and -5.0 V vs. Ag wire did not result in any notable conversion reaction (see characterisation data below). Electrolysis was carried out for various time periods of 1 h, 2 h, 4 h and 6 h and the optimum electrolysis time was found to be 2 h. At longer electrolysis time (> 2 h), electrodeposition of Li⁺ onto MoS₂ occurs even if the MoS₂ electrode was made porous (mixing MoS₂ powder with PVDF and annealing at 450 °C under an Ar atmosphere) to facilitate Li-ion diffusivity. The optimum intercalation/exfoliation condition was obtained when thinner (~1.0-1.5 mm thickness) MoS₂ pellets were used and when no binder was added to the MoS₂ powder. The MoS₂ electrode showed slight expansion but not exfoliation during

Li^+ intercalation process whereas in solvents like dimethyl sulfoxide; an instantaneous detachment of MoS_2 electrode was observed before sufficient Li^+ intercalation occurred. The success of DMC/EC solvent system arises from the formation of solid electrolyte interface which prevents solvent co-intercalation.²⁶ The Li^+ intercalated MoS_2 ($\text{Li}_x[\text{MoS}_2]$) pellet was then immersed into deoxygenated, deionised water and sonicated for 30 min. During this process, a significant amount of gas evolution was noted due to the reaction between water and lithium which forms lithium hydroxide and hydrogen gas between the layers of MoS_2 (Equation 2 and see video in SI). The pressure of evolving hydrogen gas, catalysed by the MoS_2 , causes the exfoliation of the material.³¹

2.1 Characterization of the Exfoliated Product. Raman spectroscopy readily provides information on the phase of MoS_2 and the thickness of the MoS_2 flakes. The 2H and 1T phase can easily be distinguished since each phase has different symmetry structures.³¹ Figure 2 shows the comparison between the Raman spectra of the raw MoS_2 powder and the material after exfoliation by electrochemical intercalation of Li^+ . Two prominent Raman bands were observed in the bulk powder at 381.9 cm^{-1} and 407.4 cm^{-1} due to the in-plane vibration (E_{2g}^1) and the out-of-plane (A_{1g}) vibration respectively.³² After exfoliation, a series of extra Raman signatures emerged at 155 cm^{-1} (J_1), 227 cm^{-1} (J_2) and 330.5 cm^{-1} (J_3) in addition to the E_{2g}^1 (382.2 cm^{-1}) and A_{1g} (405.3 cm^{-1}). These bands are the characteristic features for the formation of the 1T phase.^{15,33} The formation of the 1T-phase in significant concentrations was also more evident by the major decrease in the intensity of the E_{2g}^1 peak after exfoliation.³³ Calandra suggested that J_1 was due to the in-plane shearing mode of one side of the MoS_2 chain relative to the other, J_2 corresponds to the shifts of the S-atom layers with respect to the Mo atoms and J_3 was due to the stretching of one side of the zig-zag chain relative to the other with a slightly out-of-plane component.³⁴ The peak shape and position of E_{2g}^1 and A_{1g} was also changed after exfoliation (Figure 2B). For example, the half width at half maximum of A_{1g} increased from 4.5 cm^{-1} in bulk MoS_2 to 9.5 cm^{-1} after exfoliation and the peak separation between E_{2g}^1 and A_{1g} decreased from 26 cm^{-1} in bulk MoS_2 , to 23.1 cm^{-1} in exfoliated samples. It has been reported in literature that the Raman spectrum of mechanically exfoliated MoS_2 crystals exhibits a peak separation of ~ 20 , ~ 22 and $\sim 23 \text{ cm}^{-1}$ respectively for monolayer, bilayer and trilayer MoS_2 nanosheets respectively.^{32,35} Based on this calibration data, the thickness of our exfoliated samples is therefore estimated to be trilayer.

The thickness of the exfoliated samples was further characterised by AFM and Figure 3A shows the typical tapping mode AFM image of the exfoliated MoS_2 flakes that were obtained from a MoS_2 pellet. Statistical analysis of 150 MoS_2 flakes revealed that the majority of the lateral flake sizes vary between 300 nm and 500 nm. However, it is possible to get lateral sizes over $2 \mu\text{m}$ if the starting MoS_2 material is a natural MoS_2 crystallite (Figure 3B and 3C), and this observation also the case when the flakes obtained from the two source were analysed by transmission electron microscopy (Figure S1).

Figure 2 (A) and (B) Raman spectra of electrochemically exfoliated MoS_2 by intercalation of Li^+ . The electrochemical intercalation was performed at -4.5 V vs Ag wire from a solution containing 1.0 M LiClO_4 in DMC/EC. The sample for Raman analysis was prepared by drop coating the dispersion of MoS_2 on to Si/SiO_2 wafer which was then dried in air at room temperature

Remarkably the majority ($>95\%$) of the flake thicknesses displayed the same topographic height of 4.5 nm regardless of the source of MoS_2 used for exfoliation (MoS_2 powder or crystalline). Previous works showed that the measured flake thicknesses for solution/chemically exfoliated MoS_2 deposited on Si/SiO_2 varied between 1.1 and 1.9 nm for monolayer and $\sim 5 \text{ nm}$ for trilayer nanosheets.^{15,36} The deviations from their theoretical thickness (0.615 nm for monolayer) were attributed to the presence of adventitious adsorbates, trapped or adsorbed water molecules and flake-substrate equilibrium separation.^{15,35} In the case of 1T phase in particular, the excess negative charge formed due to the electron donation from lithium is stabilised by adsorption of water molecules on both sides of the nanosheets which then increases the overall thickness of the flake.^{11,17} The presence of adsorbed water layers on 1T- MoS_2 is supported using powder X-ray diffraction data which shows a diffraction peak at $2\theta \approx 8^\circ$ that was not present in bulk MoS_2 (Figure S2) and the corresponding d-spacing is 1.1 nm . Previous work attributed this process to the adsorption of bilayer water molecules between the adjacent layers of MoS_2 nanosheets.¹⁷ A broad diffraction peak also seen at 14.5° (002) with interlayer distance of 6.1 nm , and no other peaks were observed unlike in bulk MoS_2 . We should also note that a few flakes showed a

ARTICLE

Journal Name

thickness of 1.5 nm which are probably monolayer MoS₂ (Figure 3D pink line). The thickness of a monolayer of water molecules

Figure 3 AFM images of MoS₂ flakes that were obtained by electrochemical intercalation of Li⁺ at -4.5 V vs Ag wire for 2 h in 1.0 M LiClO₄ in DMC/EC. The samples were prepared by spray coating Si/SiO₂ wafer from dilute dispersion of 1T-MoS₂ (A) obtained from MoS₂ pellet and (B) and (C) obtained from MoS₂ natural crystal. (D), (E) and (F) show the corresponding thickness of the selected flakes for (A), (B) and (C) respectively

Figure 4. (A) TEM image of MoS₂ flakes that were obtained by electrochemical intercalation of Li⁺ at -4.5 V vs Ag wire for 2 h in 1.0 M LiClO₄ in DMC/EC (B) high resolution TEM image collected in bright field (left) and dark field (right) showing predominately trilayer MoS₂ nanosheets and (C) the diffraction pattern obtained from trilayer MoS₂ flake.

was estimated as 0.26 nm¹⁷. Therefore, the thickness of a monolayer of MoS₂ covered with a bilayer of water molecules would equal 1.14 nm – similar to the interlayer spacing measured using XRD. The flake thickness and its diffraction pattern was also analysed by high resolution TEM. The majority of the flakes analysed formed trilayer MoS₂ nanosheets although there are some monolayer, bilayer, and multilayers (≥ 4) structures (see Figure 4B and Figure S3). It is interesting to note that the interlayer spacing of the nanosheets was consistently between 1.1 nm and 1.3 nm in agreement with XRD and AFM analysis. The diffraction pattern of the trilayer nanosheets also shows the typical crystalline hexagonal MoS₂ structure which is similar to the diffraction pattern reported for chemically exfoliated 1T-MoS₂.³⁷ Analysis of our Raman data in conjunction with AFM thickness measurement and TEM flake layers analysis strongly suggests that the majority of the flakes are trilayer. It has been widely acknowledged that the chemical intercalation of MoS₂ with butyllithium in stoichiometric amounts usually produces monolayer MoS₂.^{15,31} The fact that we obtained trilayer MoS₂ sheets demonstrated that the intercalation of Li⁺ is at a less than stoichiometric ratio. One of the interesting aspects of electrochemical intercalation over chemical intercalation is that we can determine the amount of lithium inserted during electrolysis. The number of moles of Li⁺ transferred was obtained by measuring the charge passed during electrolysis; this was then related to the number of moles of MoS₂ used for intercalation to calculate the value of x in Li _{x} MoS₂. We obtained $x = 0.75$ which confirms the sub-stoichiometric intercalation of Li⁺, and that the preferential exfoliation of MoS₂ to trilayer might be due to a staged intercalation process. Recent work by Fan *et al.* also showed that the chemical intercalation of butyllithium in sub-stoichiometry into MoS₂ produces trilayer nanosheets, and the authors attributed this to the formation of stage 3 Li intercalation where each Li inserts between three layers of MoS₂.³⁶

Figure 5 shows the UV-Visible absorption spectra of 1T-MoS₂ and 2H-MoS₂ dispersion (diluted in isopropanol). It is known that

the 2H phase is semiconducting and therefore exhibits characteristic excitonic peaks that are related to its band gap. The dispersion obtained from the 2H phase showed two notable excitons at 604 nm and 667 nm that were associated with the direct-gap transition due to the energy split from valence band and spin-orbit coupling.^{38,39} After exfoliation, the two excitonic peaks (A and B) disappeared due to the phase transition from the semiconducting to metallic MoS₂; this observation is consistent with previous reports.^{10,15} The difference in optical properties is also more evident when examining the colour of the respective phase dispersions where the 2H phase is dark yellow while the 1T-MoS₂ is dark grey.

Figure 5 Optical absorption spectrum of MoS₂ dispersion in water and isopropanol (1:1) mixture. The inset picture shows the dispersion of electrochemically exfoliated MoS₂ by Li intercalation and solution exfoliated by sonication

It has been shown that the complete phase transformation from 2H to 1T has never been realised using lithium intercalation

Figure 6 (A) High-resolution XPS spectrum of bulk MoS_2 in the Mo 3d region, (B) High-resolution XPS spectrum of bulk MoS_2 in the S 2p region, (C) High-resolution XPS spectrum of electrochemically exfoliated MoS_2 by intercalation of Li^+ in the Mo 3d region and (D) High-resolution XPS spectrum of electrochemically exfoliated MoS_2 by intercalation of Li^+ in the S 2p region. All peak positions were charge-corrected by setting the binding energy of the C 1s signal to 284.5 eV. The samples for XPS were prepared by filtering the dispersions onto a PVDF membrane

Figure 7 High angle annular dark-field scanning transmission electron microscopy of electrochemically exfoliated MoS_2 showing (A) 2H phase collected from multilayer region, (B) 1T phase from monolayer MoS_2 and (C) 1T' phase from MoS_2 . The yellow balls and red lines in inset of (C) indicate the zigzag chain of 1T' superlattice.

and often the resulting structures contain a portion of both 2H and 1T phases.^{15,40} XPS was used to quantify the fraction of each phase by the deconvolution of the high resolution spectra of the Mo3d and S2p peaks and Figure 6 shows the XPS spectra of the bulk and exfoliated MoS₂. The Mo 3d spectra of bulk 2H-MoS₂ displayed a doublet with peaks at 229.2 eV and 232.4 eV that correspond to Mo⁴⁺3d_{5/2} and Mo⁴⁺3d_{3/2}, respectively. After exfoliation, a new pair of peaks emerged, in addition to the known doublet peak of Mo⁴⁺ for 2H-MoS₂, that are shifted to lower binding energies by ~0.8 eV with respect to the 2H phase. Similarly, the S2p doublet also displayed a new pair of peaks at a lower binding energy of 161.5 eV (S2p_{3/2}) and 162.7 eV (S2p_{1/2}). These new pairs of peaks were due to the formation of the 1T phase.^{15,40} Deconvolution of the Mo 3d and S 2p regions indicates that the concentration of 1T phase in the nanosheets is 60%. The concentration of the 1T phase using chemical exfoliation yields between 60 to 70 %, which is in close agreement with our exfoliation method.^{7,41}

The structural change from the 2H to 1T phase is attributed to the electron donation from lithium into the conduction band of MoS₂.^{31,40} The unoccupied (4d) conduction band states in the Mo cations of the MoS₂ are lower in energy than the occupied valence electron states of lithium atoms.^{26,40} Electron transfer from lithium atoms to the unoccupied 4d orbitals occurs easily upon intercalation so that the resulting MoS₂ structure assumes a metallic nature. It has been suggested that the content of Li within the MoS₂ structures determines the most favourable phase of molybdenum disulphide. For example, when $x \leq 0.1$ (as in Li_xMoS₂ structure) the intercalation proceeds without disruption of the 2H phase. However, as the concentration of Li increases above $x=0.1$ within the 2H-MoS₂ lattice, the distorted octahedral structure becomes more stable.⁴²

The analysis of the XPS data showed that the exfoliated samples contained both the 2H and 1T-MoS₂ structures. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted on the exfoliated samples to gain further insight into the atomic structure. Figure 7 shows the high resolution HAADF STEM images of electrochemically exfoliated MoS₂ nanosheets. As expected the analysed flakes comprised of regions of 2H phase, the 1T phase and the distorted 1T phase (1T') which is in agreement with chemically exfoliated 1T-MoS₂.³⁷ It has been suggested that the electron transfer from lithium into MoS₂, during intercalation, leads to structural destabilization from the ideal 1T structure.^{31,37} The Mo atoms undergo structural distortion, reducing the inter-atomic spacing which results in the formation of a characteristic zig-zag pattern (inset of Figure 7C).

2.2 Electrochemical Application of the Exfoliated 1T-MoS₂

2.2.1 Hydrogen Evolution Reaction at 1T-MoS₂. To date, Pt-based materials are the most efficient and durable electrocatalysts for electrochemical H₂ generation.⁴³ Since Pt is scarce and expensive, intense research efforts have been made by the scientific community to find alternative, cheaper electrocatalysts. Transition metal dichalcogenides in general and molybdenum disulphide in particular, have recently emerged as a promising class of materials for HER electrocatalysis.^{44,45} Experimental and computational results indicated that the metallic edge (sulfide-terminated Mo-edge) structures of 2H-MoS₂ crystals are the active site for HER while its basal plane remains inert towards HER

because of its poor electrical conductivity.⁴⁶ Although intense studies focused on surface structure engineering of 2H-MoS₂ to increase the percentage of active edge sites,⁴⁷⁻⁴⁹ the overall performance of 2H-MoS₂ is still limited by inefficient charge transfer and poor electrical transport between the active sites and the basal plane.

The electrocatalytic activity of our electrochemically exfoliated 1T-MoS₂ towards HER was assessed using linear sweep voltammetry and electrochemical impedance spectroscopy using a three electrode configuration in deoxygenated 0.5 M H₂SO₄ (aq). The electrodes were prepared by drop-coating a suspension of 1T-MoS₂ onto glassy carbon electrodes to a mass loading of 12 μg cm⁻². Figure 8A shows the polarisation curve obtained at Pt, 2H-MoS₂ and 1T-MoS₂ electrocatalysts. In each case the current densities are normalized to the geometric area of each electrode and the data was corrected for *iR* (ohmic) drop. The 2H phase displayed an overpotential (η) of ~ 0.25 V and reasonable current density (10 mA cm⁻²) was only seen when η exceeded 0.35 V. The low catalytic activity for HER is presumably due to the small proportion of the active edge sites as well as poor electrical transport between the active site and the basal plane. In particular, for 2D 2H-MoS₂ nanosheets, the portion of the inert basal plane is significantly larger than its edge site; this then leads to the low HER electrocatalytic current. However, the 1T phase exhibited low η of 0.13 V with substantial improvement in electrocatalytic current density (for example, 50 mA cm⁻² recorded at η = 0.23 V), this observation correlates well with previously reported data.^{8,9} Voiry *et al.*⁹ have studied the HER using the chemically exfoliated 1T-MoS₂ electrocatalyst, and observed an HER overpotential of approximately 0.25 V at a current density of ~30 mA cm⁻². Their work also suggested that, unlike 2H-MoS₂ where the basal plane is catalytically inert towards HER, the basal plane of 1T-MoS₂ is the main active site for HER, which explains the high current density measured for the 1T-phase.⁹ The reactivity of the 1T phase basal plane has also been suggested by recent density functional theory work, which indicates that the basal plane at the surface sulfur sites acts as the binding site for the hydrogen atom.¹²

The measured Tafel slopes for Pt, 1T and 2H phase MoS₂ are 33, 49, and 109 mV decade⁻¹ (Figure 8B) respectively, these values are consistent with previous studies.^{8,9} The proposed general models^{50,51} for HER suggest that the Tafel plot should have a slope of 118 mV decade⁻¹ at 25 °C if the adsorption of hydrogen atoms (the Volmer step, Equation 3) is the rate-determining step:

The Volmer step may be followed by an electrochemical desorption step, or two adsorbed H atoms can combine and desorb:

where Equations 4 and 5 are the Heyrovsky and Tafel steps, respectively.

If the Heyrovsky or Tafel steps are rate determining, the Tafel slope should be about 40 mV decade⁻¹ and 30 mV decade⁻¹, respectively. Therefore, our data suggest that the rate of the HER at the 1T phase electrocatalyst is controlled by the Volmer–Heyrovsky step while at the 2H-phase the Volmer step is the rate determining. The electrocatalytic activity of the 1T and 2H phases were also further examined by electrochemical impedance spectroscopy at η = 0.25 V vs. RHE. Figure 8C shows the resulting Nyquist plots fitted to an

ARTICLE

Journal Name

equivalent circuit that contains solution resistance (R_s), a constant phase element (CPE) and a charge transfer resistance (R_{CT}) as shown

Figure 8 (A) polarization curve recorded in deoxygenated 0.5 M H₂SO₄ (aq) at indicated electrodes between 0.0 V to -0.4 V. (B) Tafel plot (log of current versus overpotential) generated from the polarisation curve shown in (A), (C) Nyquist plots obtained in deoxygenated 0.5 M H₂SO₄ (aq) at a 2H-MoS₂ and 1T-MoS₂ electrode in a three-electrode cell. The measurements were carried out at an oscillation amplitude of 5 mV in the frequency range 100 mHz to 100 KHz, at an applied potential of -0.25 V vs. RHE. The solid lines show the experimental data and the markers show theoretical fits generated using the equivalent circuit shown (inset).

in the inset of Figure 8C. The Nyquist plots show one semicircle due to the R_{CT} of HER. From the best fits of the data to the equivalent circuit, values for R_{CT} at each electrocatalyst were obtained. For the 2H phase the R_{CT} of HER was 320 Ω cm², this value decreased to 20 Ω cm² with the 1T phase. The trend in the R_{CT} values shows that charge transfer was significantly faster at the 1T-MoS₂ surface than at the 2H-MoS₂, which is consistent with the linear sweep voltammogram data.

2.2.2 Electrode Material for Supercapacitors. Chowalla *et al.* recently showed that the gravimetric capacitance of a cell constructed using chemically exfoliated 1T-MoS₂ was up to 20 times higher than a cell constructed using pure 2H-MoS₂.⁷ The enhancement in capacitance seen for the former cell was attributed to its high electrical conductivity, high hydrophilicity and its ability to intercalate various ions.⁷ Their work also showed that the cation intercalation process is the dominant charge storage mechanism at this novel electrode.⁷ We also tested the capacitance of our electrochemically exfoliated 1T-MoS₂ in symmetrical coin cells via the cyclic voltammetric (CV) and galvanostatic charge-discharge response. The CVs obtained using electrodes made from the 2H phase displayed a gravimetric capacitance of 6 F g⁻¹ whereas the 1T phase displayed a gravimetric capacitance of 102 F g⁻¹ at 10 mV s⁻¹ (Figure 9A) which are consistent with previous reports.^{7,52} The capacitance of the 1T phase was found to be strongly dependent on the potential scan rate: at 5 mV s⁻¹ the gravimetric capacitance was 114 F g⁻¹ and this value decreased almost by half, to 59 F g⁻¹, on increasing the scan rate to 100 mV s⁻¹ (Figure 9B). Similarly, the capacitance obtained from the charge-discharge curve also showed an analogous trend to the CV data where the capacitance decreased from 118 F g⁻¹ at 0.5 A g⁻¹ to 50 F g⁻¹ at 5 A g⁻¹. The decrease in capacitance upon increasing scan rate (ν) or discharge current might be associated with the effect of ion diffusion as well as with the resistivity of the electrode. In particular, when the charge storage mechanism involves ion intercalation, the effect of ion diffusion into layered MoS₂ structure becomes more pronounced. For example, the experimental time scale could be too short to intercalate ions into the layered structures at high ν which then accounts for the low capacitance. The internal resistance of the device also contributes to the decrease in capacitance. The effect of resistance is more apparent when examining the charge-discharge curve. As shown in Figure 9D, the discharge curve shows a significant voltage drop (>0.3 V) for the cell that was constructed using 1T-MoS₂. Therefore, increasing the conductivity of the electrode, by adding highly conductive graphene, is expected to enhance the capacitance at higher discharge currents. Herein, we fabricate a nanocomposite that consists of 1T-MoS₂ and solution exfoliated graphene (SEG) to alleviate these problems. The composite was made by mixing 1T-MoS₂ with SEG in a one to one concentration ratio and the SEM image of the membrane shows a randomly restacked layered structure (Figure 10E and 10F). The morphology of the composite material looks more interconnected porous and rougher surface than the individual components (Figure S4). Furthermore, the SEM image of pure graphene or MoS₂ shows an aggregated nanosheet. Figure 9E shows a representative Raman spectrum taken from the composite membrane. The spectrum shows the characteristic 1T-MoS₂ peaks and graphene peaks demonstrating that the two materials are uniformly mixed and distributed across the membrane. Moreover, the presence of graphene with 1T-MoS₂ in the composite did not induce a phase transition.

The electrodes made from the composite materials displayed typical capacitive behaviour with a nearly rectangular shape and the charge-discharge curve also displayed a symmetrical linear shape with voltage drop of less than 0.1 V (Figure 9A and 9C). Significantly, 1T-MoS₂/graphene electrode showed an enhanced gravimetric capacitance with little loss as the discharge current increased. For example, the composite material displayed a capacitance of 147 F g⁻¹ at 10 mV s⁻¹ and 120 F g⁻¹ at 100 mV s⁻¹ (Figure 9B). The enhanced capacitance in the composite material was probably due to the synergistic effect between 1T-MoS₂ and graphene where graphene enhances the overall conductivity of the

composite, reduces the re-aggregation of the sheets and partly contribute double layer capacitance while 1T-MoS₂ contribute pseudocapacitance through ion intercalation.⁵² Indeed, the nanocomposite dispersion showed stability without any substantial sedimentation over two month whilst the 1T-MoS₂ dispersion completely aggregated over the same period of time (Figure S6) which indicates that graphene plays a role in hindering the aggregation of MoS₂. This synergy was also evident when comparing the gravimetric capacitance of pure graphene which only produced 18 F g⁻¹ with that of the composite.

Figure 9 (A) Cyclic voltammograms recorded at 20 mV s⁻¹ in 6.0 M KOH (aq) using symmetrical coin cells constructed from indicated electrodes. (SEG denotes solution exfoliated graphene). The voltage was scanned between 0.0 V (initial potential) and 1.0 V, (B) Gravimetric capacitance as a function of scan rates at indicated electrodes, (C) Nyquist plots obtained using the coin cells at shown electrodes and the inset shows the Bode plot. The measurements were carried out at an amplitude of 5 mV in the frequency range of 100 mHz to 100 KHz at open circuit potential. (D) Charge-discharge curve obtained from indicated electrodes at 1.0 A g⁻¹, (E) Raman spectrum of composite membrane showing both the 1T-MoS₂ peaks (enlarged in inset, J₁, J₂, J₃, E_{2g} and A_{1g}) and graphene peaks (D, G and 2D bands). (F) Capacitance retention of 1T-MoS₂/SEG electrodes after 5,000 cycles in 6.0 M KOH (aq)

Figure 10 (A) Cyclic voltammograms recorded at 100 mV s⁻¹ in 1.0 M [TEA][BF₄] in acetonitrile and 1.0 M [TEA][BF₄] in propylene carbonate using symmetrical coin cells constructed from 1T-MoS₂/SEG electrodes. The voltage was scanned between 0.0 V (initial potential) and 2.7 V for acetonitrile and 0.0 V to 3.0 V for propylene carbonate, (B) galvanostatic charge-discharge curves obtained using 1.0 M [TEA][BF₄] in propylene carbonate at indicated currents, (C) Volumetric capacitance as a function of scan rates, (D) Capacitance retention of 1T-MoS₂/SEG electrodes after 5,000 cycles and (E) and (F) shows the cross sectional SEM image of the free standing 1T-MoS₂/SEG membrane

AC impedance spectroscopy was also carried out to further determine the electrochemical behaviour of each electrode. Nyquist and Bode plots were obtained at open circuit potential over the frequency range 10 mHz to 100 kHz are shown in Figure 9C. The Nyquist plot of the composite electrode displayed a nearly vertical curve with low series resistance of $0.4 \Omega \text{ cm}^2$ while the cell made from 1T-MoS₂ electrode showed a series resistance $1 \Omega \text{ cm}^2$ (Figure S5 for enlarged curve) and a transition from a linear looking feature to a classical Warburg impedance response occurred at a frequency of 2.6 Hz. These observations, together with the fact that the Bode phase angle is close to 90° at the composite electrode, meant that the cell is behaving close to an "ideal capacitor".

High volumetric capacitance is attractive for portable electronics and vehicles,⁵³ as such, we also assessed the volumetric capacitance of the cell constructed using our composite electrode. Volumetric capacitances of 560 F cm^{-3} at 10 mV s^{-1} and 458 F cm^{-3} at 100 mV s^{-1} were obtained. These values are higher than the volumetric capacitance achieved using the best performing carbon-based electrodes.^{54,55} Lin *et al.*⁵⁴ reported 490 F cm^{-3} in Li_2SO_4 (aq) with N-doped mesoporous few-layer carbon at 2 mV s^{-1} and Yang *et al.*⁵⁵ reported $\sim 250 \text{ F cm}^{-3}$ using restacked graphene sheets. Acerece *et al.* reported $\sim 450 \text{ F cm}^{-3}$ in KCl (aq) and 700 F cm^{-3} in H_2SO_4 (aq) using chemically exfoliated 1T-MoS₂, although it is likely that the values quoted are over-estimated due to parallel hydrogen evolution reactions that will occur under acidic conditions.⁷ Ghidui *et al.* reported 900 F cm^{-3} in H_2SO_4 (aq) at 2 mV s^{-1} using conducting and hydrophilic Ti_3C_2 electrodes.⁵⁶ While the gravimetric capacitance of our composite material is in the same range as for reduced graphene oxide-based electrodes,⁵⁷ the volumetric capacitance of our composite material is twice that of most carbon-based electrodes. Galvanostatic charge-discharge cycling of the composite material between 0.0 V to 0.8 V at 1 A g^{-1} for 5,000 cycles exhibited excellent stability with a capacitance retention of over 92 % (Figure 9F). Moreover, the serial resistance of the device did not increase by any notable amount after cycling. The small loss in capacitance indicates that there is no significant reversal of the material back to the 2H-phase. This is consistent with the XPS analysis of the cycled 1T-MoS₂ electrode reported by Chowalla *et al.*⁷, which showed the stability of the 1T-phase under potential cycling.

Finally, the composite electrode was tested using non-aqueous electrolytes to take advantage of their wide electrochemical window. Acetonitrile (AN) and propylene carbonate (PC) with tetraethylammonium tetrafluoroborate electrolyte were tested. As shown in Figure 10A, the AN-based electrolyte showed a potential window of $\sim 2.7 \text{ V}$ whilst the PC-based electrolyte showed an enhanced potential window of 3.0 V . Furthermore, examination of the CV and charge-discharge curve showed the composite electrode produced responses that are expected for capacitive behaviour. The volumetric capacitance of each electrolyte as a function of ν is shown in Figure 10C. Volumetric capacitances of 292 F cm^{-3} for AN and 247 F cm^{-3} for PC were obtained at 10 mV s^{-1} which are in close agreement with the ones obtained from charge-discharge at 0.5 A g^{-1} ; 287 F cm^{-3} for AN and 206 F cm^{-3} for PC. Furthermore, the composite electrode showed excellent stability in PC electrolytes with more than 96 % capacity retention after 5000 cycles while in AN the capacity retention was $\sim 90 \%$ (Figure 10D).

Energy and power densities as well as gravimetric and volumetric capacitance obtained at various discharge currents in each electrolyte are shown in Table S1. In general, the AN performed better than the PC electrolyte because of its lower viscosity, and associated lower solution resistance. In AN solutions, depending on the magnitude of discharge current, the energy densities varied between 0.08 Wh cm^{-3} and 0.28 Wh cm^{-3} with corresponding power densities between 1 W cm^{-3} and 18 W cm^{-3} , while in the PC electrolyte the corresponding values were between $0.06\text{--}0.25 \text{ Wh cm}^{-3}$ and $1.7\text{--}22 \text{ W cm}^{-3}$. The Ragone plot generated using AN electrolyte in comparison to other best performing materials is shown in Figure 11. The plot shows that the energy/power densities obtained at 1T-MoS₂/ graphene composite are much higher than that obtained at carbon-based electrodes⁵⁸⁻⁶⁰ and slightly higher than those reported for chemically exfoliated 1T-MoS₂ electrodes (Figure 11).⁷ This demonstrates that the 1T-MoS₂/ graphene composite are attractive electrode for portable supercapacitor devices.

Figure 11. Ragone plot obtained using best performing volumetric energy and power densities reported from various materials consisting of Li thin film battery,⁶¹ Li-ion battery,⁶¹ MXenes,⁶² graphene,^{61,63} core/shell nanowire WS₂,⁶⁴ 1T-MoS₂,⁷ and 1T-MoS₂/graphene composite.

In summary, a simple, scalable and rapid electrochemical method for preparation of metallic phase MoS₂ nanosheets has been developed. Our methods differ from previous work in that the use of pyrophoric materials (such as organolithium compounds or metallic Li) has been replaced with an inert Li salt and a Pt counter electrodes, which allowed the electrochemical intercalation process to be carried out with a benchtop setup. Characterisation of the exfoliated product using X-ray photoelectron spectroscopy, Raman spectroscopy and UV-visible absorption spectroscopy confirmed the formation of the 1T-phase with a concentration of $\sim 60 \%$. Importantly, this particular process can be used as a means for producing controlled trilayer MoS₂ nanosheets. As demonstrated here, the exfoliated metallic phase MoS₂ is a viable electrocatalyst for hydrogen evolution reaction and as an electrode material for supercapacitor. In particular, composite materials that were made from metallic phase MoS₂ and graphene sheets showed

an enhanced volumetric and gravimetric capacitance due to the synergistic coupling between individual components. The preparative route is cheap, simple, time efficient and should ultimately support the scalable production of metallic MoS₂ as well as other transition metal dichlogenides such as WS₂, MoSe₂ and WSe₂ for use in various applications. This method can also be extended for production of semi-conducting phase MoS₂ nanosheets if 1T-MoS₂ is treated by heat

3 Experimental Methods

3.1 Materials and Reagents. MoS₂ powder (99 %, ~6 µm), lithium perchlorate (99.99 %), anhydrous dimethyl carbonate (>99%) and ethylene carbonate (99%) were purchased from Sigma-Aldrich and used as received. MoS₂ natural crystals were obtained from Manchester Nanomaterials Ltd. U.K. Polytetrafluoroethylene was obtained from Omnipore membrane filters (JVWP01300) with a pore size of 0.2 µm and Polyvinylidene fluoride was obtained from Durapore® membrane filters (vvp01300, 0.1 µm). Millipore water (18.2 MΩ cm) was obtained from a Milli-Q water purification system.

3.2 Electrochemical Intercalation of Li⁺ into MoS₂: A MoS₂ pellet (Sigma, 99 % with an average particle size of 6 µm) or a MoS₂ natural crystal working electrode, a Pt mesh counter electrode and an Ag wire reference electrode were used for electrochemical measurements. The potential of an Ag wire was stable within a few mV over a 4 h period. The MoS₂ pellet (12 mm diameter) was made by hydraulic pressing of the powder (0.4-1.0 g) at 2.5 tons. Prior to performing electrolysis, N₂ gas was bubbled into the electrolyte for 30 min and during the electrochemical measurements an atmosphere of N₂ was maintained above the electrolyte. The electrolyte consists of 1 M LiClO₄ in a 1:1 v/v mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC). Electrochemical intercalation of Li⁺ was performed using chronoamperometry by applying a potential of -4.5 V vs Ag wire for 2 hr. The intercalated pellet was then rinsed with acetone and inserted immediately into deionised, deoxygenated water for exfoliation and followed by sonication for 30 mins. The resulting black suspension was added to a separating funnel and washed with n-hexane (50 mL) twice to extract any residual of organic impurities including the solid electrolyte interface. The concentrated black aqueous phase was collected and filtered using a PTFE membrane (0.2 µm pore size) and washed with 1 L of deionised water to remove excess lithium in the form of LiOH. The resulting washed powder was re-dispersed in deionised water and sonicated for 20 min, and then centrifuged at 1500 rpm for 30 min to remove any non-exfoliated material as sediment yielding a highly stable dispersion.

3.3 Solution phase exfoliation of MoS₂ to produce the 2H phase: For comparison, 2H phase MoS₂ was produced using the ultrasonic exfoliation route developed by Coleman *et al.*⁶⁵ 1.0 g of MoS₂ powder (Sigma, 99 % with average particle size of 6 µm) dissolved in 100 mL of water/isopropanol mixture (1:1 v/v) was placed in a 250 mL round bottom flask.⁶⁶ The mixture was then sonicated in a water bath sonicator (Elmasonic P70H) which operates at 37 kHz and 40 % amplitude for 12 h while cooling to maintain a stable temperature of 15 °C. The resulting suspension was centrifuged at 6000 rpm twice for 30 min to remove any unexfoliated material. A stable dispersion of the supernatant was obtained and characterisation of the resulting suspension revealed that the exfoliated MoS₂ was in the 2H-phase.

3.4 Solution phase exfoliation of graphite: In a similar way to the MoS₂, 2.0 g of graphite powder (sigma) was dissolved in 100 mL of water/isopropanol mixture (1:1 v/v) and sonicated for 18 h at 37 kHz and 40 % amplitude as previously method.⁶⁶ The resulting suspension was centrifuged at 6000 rpm twice for 30 min, and the supernatant collected for analysis.

3.5 Characterisation of the Exfoliated Product: Raman spectra were obtained using Renishaw inVia microscope with a 532 nm excitation laser operated at a low power of 0.274 mW with a 1800 l/mm grating and a 100× objective. The sample for Raman measurement was prepared by drop coating the dispersion of MoS₂ on to a Si/SiO₂ wafer which was then dried at room temperature. For AFM analysis the MoS₂ dispersion was spray coated onto a Si/SiO₂ substrate which was dried in a vacuum oven at 40 °C. SEM analysis was carried out using XL30 FEI Environmental scanning electron microscope or FEI Quanta 650 ESEM. Transmission electron microscopy and selected area electron diffraction (SAED) have been performed on FEI Talos at 200 kV. A FEI Titan 80-200 ChemiSTEM equipped with probe-side aberration correction and an X-FEG electron source was used for the aberration-corrected high-resolution scanning transmission electron microscope (HRSTEM) imaging. STEM experiments were performed using an acceleration voltage of 200 kV, a convergence angle of 21 mrad and a beam current of 90 pA. The inner and outer collection angles of the HAADF detector were 48 and 190 mrad, respectively. TEM and SAED data were also acquired on the FEI Titan microscope and the samples were prepared by drop casting the dispersion on holey carbon film (300 mesh Cu, Agar Scientific) or on ultra-thin carbon support film (300 mesh Cu, Agar Scientific) TEM grid. Powder X-ray diffraction analysis was performed on free standing 1T-MoS₂ membrane using Philips X'pert PRO diffractometer with Cu Kα radiation (λ = 0.154 nm) and operating at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al Kα X-ray source (E = 1486.6 eV, 10 mA emission), a hemispherical electron energy analyser and a multichannel plate and delay line detector (DLD). The samples for XPS were prepared by filtering MoS₂ dispersion on PVDF membrane. UV-visible spectroscopy measurements were taken using a model DH-2000-BAL (Ocean Optics).

3.6 Electrode Preparation for Hydrogen Evolution Reaction: Hydrogen evolution reaction measurements were performed using a three-electrode cell consisting of a 3 mm-diameter glassy carbon (GC) disk working electrode, an Ag|AgCl reference electrode, and a Pt counter electrode (area of 1.2 cm²). Before use, GC working electrodes were polished with aqueous 0.3 µm alumina (Buehler, Lake Bluff, IL) slurries on felt polishing pads and rinsed with deionized water. GC electrodes were modified with 10 µL of the MoS₂ dispersion (either 1T-MoS₂ or 2H-MoS₂) and then dried at room temperature in air. Cyclic voltammograms (CVs) were recorded in 1 M H₂SO₄ at 5 mV s⁻¹ which was deoxygenated prior to use by bubbling with N₂ for 30 min. A blanket of N₂ was maintained above the electrolyte during measurements. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 100 kHz to 100 mHz at an oscillation amplitude of 5 mV

and an applied potential of -0.45 V vs. Ag|AgCl. Impedance spectra were fitted to a Randles equivalent circuit model using Z-view software (Scribner Associates, Inc., Southern Pines, NC).

3.7 Electrode Preparation for Supercapacitor Testing: MoS₂ electrodes were prepared by filtering a known volume of the dispersions onto a pre-weighed PVDF filter using a syringe pump dispenser (New Era Pump Systems, Inc, NY). The MoS₂ membranes were then dried at room temperature in air. Coin cell assembly was prepared in standard CR2032 coin cell hardware with symmetrical active materials. The cells were assembled by stacking two symmetrical membranes back-to-back with the active material contacting the current collector.⁵² A few drops of the desired electrolyte (deoxygenated 6.0 M KOH (aq) or 1.0 M tetraethylammonium tetrafluoroborate ([TEA][BF₄]) in acetonitrile or propylene carbonate) was added to fill the electrode before the coin cell was sealed using a hydraulic crimping machine (MSK-160D). Coin cell assembly was carried out in an Ar-filled globe box for the case of organic electrolytes. Gravimetric capacitance, volumetric capacitance, energy and power density were calculated using the best practice methods established in literature.^{7,67}

3.8 1T-MoS₂-graphene composite formulation: Prior to mixing 1T-MoS₂ with solution exfoliated graphene (SEG), a stock solution of 1T-MoS₂ diluted with IPA to a concentration of 0.05 mg mL⁻¹. After words, 50 mL of it mixed with 50 mL of SEG (0.05 mg mL⁻¹) and sonicated for 20 min

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References

1. A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366-377.
2. Y. G. Guo, J. S. Hu and L. J. Wan, *Adv. Mater.*, 2008, **20**, 2878-2887.
3. F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff and V. Pellegrini, *Science*, 2015, **347**, 1246501.
4. X. Y. Zhang, L. L. Hou, A. Ciesielski and P. Samori, *Adv. Energy Mater.*, 2016, **6**, 21.
5. M. A. Py and R. R. Haering, *Can. J. Phys.*, 1983, **61**, 76-84.
6. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis, *Nat. Nanotechnol.*, 2011, **6**, 147-150.
7. M. Acerce, D. Voiry and M. Chhowalla, *Nat. Nanotechnol.*, 2015, **10**, 313-318.
8. M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. S. Li and S. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10274-10277.
9. D. Voiry, M. Salehi, R. Silva, T. Fujita, M. W. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nano Lett.*, 2013, **13**, 6222-6227.
10. C. Tan, W. Zhao, A. Chaturvedi, Z. Fei, Z. Zeng, J. Chen, Y. Huang, P. Ercius, Z. Luo, X. Qi, B. Chen, Z. Lai, B. Li, X. Zhang, J. Yang, Y. Zong, C. Jin, H. Zheng, C. Kloc and H. Zhang, *Small*, 2016, **12**, 1866-1874.
11. X. M. Geng, W. W. Sun, W. Wu, B. Chen, A. Al-Hilo, M. Benamara, H. L. Zhu, F. Watanabe, J. B. Cui and T. P. Chen, *Nat. Commun.*, 2016, **7**.
12. Q. Tang and D.-e. Jiang, *ACS Catal.*, 2016, **6**, 4953-4961.
13. P. Joensen, R. F. Frindt and S. R. Morrison, *Mater. Res. Bull.*, 1986, **21**, 457-461.
14. B. K. Miremedi and S. R. Morrison, *J. Catal.*, 1987, **103**, 334-345.
15. G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. W. Chen and M. Chhowalla, *Nano Lett.*, 2011, **11**, 5111-5116.
16. M. B. Dines, *Mater. Res. Bull.*, 1975, **10**, 287-291.
17. P. Joensen, E. D. Crozier, N. Alberding and R. F. Frindt, *J. Phys. C: Solid State Phys.*, 1987, **20**, 4043-4053.
18. J. Zheng, H. Zhang, S. H. Dong, Y. P. Liu, C. T. Nai, H. S. Shin, H. Y. Jeong, B. Liu and K. P. Loh, *Nat. Commun.*, 2014, **5**.
19. H. Zhang, *Acs Nano*, 2015, **9**, 9451-9469.
20. V. H. Gessner, C. Daschlein and C. Strohmann, *Chem. - Eur. J.*, 2009, **15**, 3320-3334.
21. Q. Liu, X. Li, Q. He, A. Khalil, D. Liu, T. Xiang, X. Wu and L. Song, *Small*, 2015, **11**, 5556-5564.
22. Z. Y. Zeng, T. Sun, J. X. Zhu, X. Huang, Z. Y. Yin, G. Lu, Z. X. Fan, Q. Y. Yan, H. H. Hng and H. Zhang, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 9052-9056.
23. L. Oakes, R. Carter, T. Hanken, A. P. Cohn, K. Share, B. Schmidt and C. L. Pint, *Nat. Commun.*, 2016, **7**, 11796.
24. K. Chang and W. X. Chen, *Acs Nano*, 2011, **5**, 4720-4728.
25. Y. Miki, D. Nakazato, H. Ikuta, T. Uchida and M. Wakihara, *J. Power Sources*, 1995, **54**, 508-510.
26. T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2014, **7**, 209-231.
27. G. Du, Z. Guo, S. Wang, R. Zeng, Z. Chen and H. Liu, *Chem. Commun.*, 2010, **46**, 1106-1108.
28. K. Chang and W. Chen, *ACS Nano*, 2011, **5**, 4720-4728.
29. J. Xiao, D. Choi, L. Cosimbescu, P. Koech, J. Liu and J. P. Lemmon, *Chem. Mater.*, 2010, **22**, 4522-4524.
30. Z. Y. Zeng, Z. Y. Yin, X. Huang, H. Li, Q. Y. He, G. Lu, F. Boey and H. Zhang, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 11093-11097.
31. D. Voiry, A. Mohite and M. Chhowalla, *Chem. Soc. Rev.*, 2015, **44**, 2702-2712.
32. C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *Acs Nano*, 2010, **4**, 2695-2700.
33. S. J. Sandoval, D. Yang, R. F. Frindt and J. C. Irwin, *Phys. Rev. B*, 1991, **44**, 3955-3962.
34. M. Calandra, *Phys. Rev. B*, 2013, **88**, 6.
35. M. Velicky, M. A. Bissett, C. R. Woods, P. S. Toth, T. Georgiou, I. A. Kinloch, K. S. Novoselov and R. A. W. Dryfe, *Nano Lett.*, 2016, **16**, 2023-2032.
36. X. B. Fan, P. T. Xu, Y. C. Li, D. K. Zhou, Y. F. Sun, M. A. T. Nguyen, M. Terrones and T. E. Mallouk, *J. Am. Chem. Soc.*, 2016, **138**, 5143-5149.
37. G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. W. Chen and M. Chhowalla, *Acs Nano*, 2012, **6**, 7311-7317.
38. J. P. Wilcoxon, P. P. Newcomer and G. A. Samara, *J. Appl. Phys. (Melville, NY, U. S.)*, 1997, **81**, 7934-7944.
39. Y. T. Liu, X. D. Zhu, Z. Q. Duan and X. M. Xie, *Chem. Commun.*, 2013, **49**, 10305-10307.
40. C. A. Papageorgopoulos and W. Jaegermann, *Surf. Sci.*, 1995, **338**, 83-93.

ARTICLE

Journal Name

41. R. Kappera, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite and M. Chhowalla, *Nat. Mater.*, 2014, **13**, 1128-1134.
42. C. M. Julien, *Mater. Sci. Eng., R*, 2003, **40**, 47-102.
43. M. Wang, L. Chen and L. C. Sun, *Energy Environ. Sci.*, 2012, **5**, 6763-6778.
44. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296-7299.
45. B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff and J. K. Nørskov, *J. Am. Chem. Soc.*, 2005, **127**, 5308-5309.
46. T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch and I. Chorkendorff, *Science*, 2007, **317**, 100-102.
47. J. Kibsgaard, Z. B. Chen, B. N. Reinecke and T. F. Jaramillo, *Nat. Mater.*, 2012, **11**, 963-969.
48. C. Tsai, F. Abild-Pedersen and J. K. Nørskov, *Nano Lett.*, 2014, **14**, 1381-1387.
49. Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong and H. J. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296-7299.
50. E. Navarro-Flores, Z. W. Chong and S. Omanovic, *J. Mol. Catal. A: Chem.*, 2005, **226**, 179-197.
51. B. Børresen, G. Hagen and R. Tunold, *Electrochim. Acta*, 2002, **47**, 1819-1827.
52. M. A. Bissett, I. A. Kinloch and R. A. W. Dryfe, *ACS Appl. Mater. Interfaces*, 2015, **7**, 17388-17398.
53. Y. Gogotsi and P. Simon, *Science*, 2011, **334**, 917-918.
54. T. Q. Lin, I. W. Chen, F. X. Liu, C. Y. Yang, H. Bi, F. F. Xu and F. Q. Huang, *Science*, 2015, **350**, 1508-1513.
55. X. W. Yang, C. Cheng, Y. F. Wang, L. Qiu and D. Li, *Science*, 2013, **341**, 534-537.
56. M. Ghidui, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi and M. W. Barsoum, *Nature*, 2014, **516**, 78-81.
57. M. D. Stoller, S. J. Park, Y. W. Zhu, J. H. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498-3502.
58. E. Raymundo-Pinero, M. Cadec and F. Beguin, *Adv. Funct. Mater.*, 2009, **19**, 1032-1039.
59. S. Murali, N. Quarles, L. L. Zhang, J. R. Potts, Z. Q. Tan, Y. L. Lu, Y. W. Zhu and R. S. Ruoff, *Nano Energy*, 2013, **2**, 764-768.
60. Z. Chen, J. Wen, C. Z. Yan, L. Rice, H. Sohn, M. Q. Shen, M. Cai, B. Dunn and Y. F. Lu, *Adv. Energy Mater.*, 2011, **1**, 551-556.
61. Z. S. Wu, K. Parvez, X. L. Feng and K. Mullen, *Nat. Commun.*, 2013, **4**, 2487.
62. M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum and Y. Gogotsi, *Science*, 2013, **341**, 1502-1505.
63. Y. Tao, X. Y. Xie, W. Lv, D. M. Tang, D. B. Kong, Z. H. Huang, H. Nishihara, T. Ishii, B. H. Li, D. Golberg, F. Y. Kang, T. Kyotani and Q. H. Yang, *Sci. Rep.*, 2013, **3**.
64. N. Choudhary, C. Li, H. S. Chung, J. Moore, J. Thomas and Y. Jung, *Acs Nano*, 2016, **10**, 10726-10735.
65. J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuvsen, D. W. McComb, P. D. Nellist and V. Nicolosi, *Science*, 2011, **331**, 568-571.
66. U. Halim, C. R. Zheng, Y. Chen, Z. Y. Lin, S. Jiang, R. Cheng, Y. Huang and X. F. Duan, *Nat. Commun.*, 2013, **4**, 7.

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