Synthesis of Lateral Size-Controlled Monolayer 1H-MoS$_2$@Oleylamine as Supercapacitor Electrodes.

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ABSTRACT: A new wet chemistry approach, based on the hot-injection–thermolysis decomposition of the single-source precursor [Mo$_2$O$_4$S$_6$(S$_2$COEt)$_2$] in oleylamine, is described for the production of nanodimensional 1H-MoS$_2$@oleylamine. High quality freestanding MoS$_2$ nanosheets capped with oleylamine have been prepared and subjected to detailed compositional analyses for the first time. The selection of the appropriate reaction temperatures (200–325 °C) in the simple yet robust procedure allows control of the lateral nanosheet dimensions which range from 4.5 to 11.5 nm, as 1H-MoS$_2$@oleylamine entities which maintain a consistent chemical composition (MoS$_2$@oleylamine$_{0.28-0.33}$). This work provides the first example of atomic resolution STEM imaging of these fine-scale nanosheet materials, providing new insights into their morphology and demonstrating that those freestanding MoS$_2$ nanosheets are pure, highly crystalline, randomly oriented monolayers. The 1H-MoS$_2$@oleylamine samples were analyzed by attenuated total reflectance FT-infrared spectroscopy (ATR-FTIR), transmission electron microscope (TEM) imaging, aberration corrected scanning transmission electron microscope (STEM) imaging, energy dispersive X-ray (EDX) spectrum imaging, powder X-ray diffractometry (p-XRD), thermogravimetric analysis (TGA), and Raman spectroscopy. Composite materials of the as-synthesized MoS$_2$ nanosheets and exfoliated graphene were then used to construct coin-cell supercapacitor electrodes with a specific capacitance of 50 mF/cm$^2$, demonstrating its utility as an energy storage material.

INTRODUCTION

Since the discovery of graphene in 2004,$^{1,2}$ two-dimensional materials of atomic thickness have captivated the research community, owing to their unique physical and electronic properties, a result of quantum confinement within their highly anisotropic structures. With the unique physical properties and potential applications of graphene as inspiration,$^{3-9}$ a family of 2D nanosheets produced from transition metal dichalcogenides (2D-TMDs) have also been extensively investigated. These materials have a similar structure to that of graphene. Due to the rich diversity of electronic, optical, thermal, mechanical, and reactivity profiles, 2D-TMDs such as MoS$_2$ and WS$_2$ have found a variety of applications in many fields of research.$^{10-22}$

In addition, nanoscale 2D-TMD nanosheets have been envisaged to have potential in small molecule sensing units, battery technology, and supercapacitors. Supercapacitors in particular are an ideal technology to exploit the beneficial properties of 2D nanosheets, with graphene already shown to be ideal due to its high specific surface area, high conductivity, as well as mechanical durability.$^{23-26}$ Supercapacitors work through a combination of charge storage mechanisms: Electrochemical double-layer capacitors (EDLC) work through the accumulation of electrolyte ions at the electrode–electrolyte interface, whereas pseudocapacitors store charge through surface mediated redox reactions.$^{27}$ 2D-TMD nanosheets, such as MoS$_2$ have received much less attention than graphene for electrochemical energy storage but are a promising material to increase the energy density of devices, particularly in combination with graphene.$^{28-37}$ Recently it was demonstrated that the metallic 1T-MoS$_2$ phase can act as a highly efficient supercapacitor electrode material due to its conductivity combined with ion intercalation pseudocapacitance.$^{38}$ 2H-MoS$_2$ is known to be a semiconductor with its indirect band gap changing depending on the number of layers from 2 to bulk.$^{39}$ Monolayer MoS$_2$ (1H-MoS$_2$), however, is a direct gap semiconductor, with a band gap of 1.85 eV. This makes their conductivity relatively lower than that in the metallic phase.

Herein we discuss a novel method to produce high purity 1H-MoS$_2$@oleylamine by the hot-injection thermolysis of a single-source precursor. Our work has shown that the dimensions of nanosheets within 1H-MoS$_2$@oleylamine can be restricted to the nanometer-scale by control of injection temperature, allowing for control of the active edge-density for future catalysis applications. These MoS$_2$ nanosheets were then used to form supercapacitor electrodes, demonstrating the
excellent performance possible from highly controlled lateral dimensions and thicknesses.

**Experimental Section**

**Methods.** Elemental analyses were performed using a Thermo Scientific Flash 2000 organic elemental analyzer by the microanalytical laboratory at the University of Manchester. Thermogravimetric analysis measurements were carried out by a Seiko SSC/S2000 model under a heating rate of 10 °C min⁻¹ in both nitrogen and atmospheric conditions. Raman spectra were acquired on a Renshaw 1000 system, with a solid state (50 mW) S145.6 nm laser (operating at 10% power). The laser beam was focused onto the samples by a 50x objective lens. The scattered signal was detected by an air cooled charge coupled device (CCD) detector. Approximately 5 mg of the 1H-MoS2@oleylamine dispersed in toluene was drop cast onto a glass substrate for p-XRD studies, performed on a Bruker AXS D8-Advance diffractometer, using Cu Kα radiation. The thin film samples were mounted flat and scanned over the range 10−80°. FTIR spectra were obtained with a Thermo Fisher Nicolet iS5 spectrometer equipped with an ATR cell. Samples for transmission electron microscope (TEM) imaging were prepared from dilute 1H-MoS2@oleylamine dispersions in toluene (which were sonicated for 5 min) by drop casting onto holey carbon support films which were then washed with toluene and air-dried. Bright field images and selected-area electron diffraction (SAED) patterns were obtained using a Philips CM20 TEM equipped with a LaB₆ electron source and operated at 200 kV. Scanning transmission electron microscope (STEM) and energy dispersive X-ray (EDX) analysis was performed in a probe-side aberration corrected FEI Titan G2 80−200 ChemiSTEM microscope equipped at 200 kV equipped with the Super-X EDX detector with a total collection solid angle of 0.7 sr. For annular dark-field (ADF) imaging a probe current of ~75 pA, convergence angle of 21 mrad, and a detector inner angle of 28 mrad were used. EDX spectrum images were acquired with the sample at 0° tilt and with all four of the ChemiSTEM silicon drift detectors (SDDs) turned on. STEM images were recorded in FEI TITAN software, and EDX data was recorded and analyzed using Bruker Esprit; quantification of EDX spectra was performed using the Cliff−Lorimer method [using the S K-series (2.31 keV) and Mo K-series (17.48 keV)] and adsorption correction [assuming the flocculate has a density of bulk MoS2 (5.06 g/cm³) and thickness of 150 nm].

**Synthesis of [Mo₂O₄(S₂CNEt₂)₂]**

The procedure used was modified from that described in the literature. In a dry nitrogen environment, a slow stream of H₂S was bubbled through a solution of [Mo₂O₄(S₂CNEt₂)₂] (5.6 g, 7.7 mmol) in dry chloroform (250 mL) for 2 h. The solution was sealed in the H₂S-rich environment and stirred overnight. After careful removal of volatile gases, the solvent was evaporated by vacuum leaving a dark brown powder. The yellow products were removed from the solids by acetone extraction (2 × 100 mL) and filtered to give an orange powder. The powder was washed with acetone (2 × 50 mL) and dried in a vacuum to give pure [Mo₂O₂S₂(S₂CNEt₂)₂] as an orange powder (3.0 g, 5.6 mmol, 73%).

**Graphene Nanosheets by Hot-Injection−Thermolysis.** In a typical synthesis, a 200 mg solution of [Mo₂O₂S₂(S₂CNEt₂)₂] in oleylamine (5 mL) was rapidly added to hot oleylamine (25 mL; reaction temperatures from 200 to 325 °C) under stirring. The solution turned a black color, and drops in reaction temperatures of 10–38 °C were observed; the reaction was kept at the lower temperature after addition. Aliquots of 9 mL were taken at regular intervals and added to methanol (35 mL), resulting in a flocculant-like precipitate. The black precipitate was separated by centrifugation (4000 rpm for 20 min) and the supernatant removed. The precipitate was washed by repeated dispersion into 30 mL of methanol and centrifuged before 1H-MoS2@oleylamine was finally dried in a vacuum for 16 h.

**Electrochemistry.** Graphene dispersions were produced by solution ultrasonication using previously reported methods. Briefly, graphite flakes were dispersed in N-methyl-2-pyrrolidone (10 mg/mL) and bath sonicated for 12 h before centrifuging to remove any unexfoliated material. MoS₂ dispersions were produced by first removing the oleylamine by thermal annealing (500 °C, in N₂); the resulting material was dispersed in NMP and combined with the graphene dispersion in a 1:1 ratio by weight. The concentrations for the MoS₂−NMP and graphene−NMP dispersions were determined by UV−vis. Films of the MoS₂ and graphene composite were synthesized by first diluting the NMP dispersions in isopropanol (IPA) by a factor of 20 followed by filtering through PVDF filters with 0.1 μm pore size. A number of active materials used on each membrane was ~1 mg (1 mg/cm²). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) were performed using a PGSTAT302N potentiostat (Metrohm Autolab, The Netherlands). All electrochemical measurements were performed in a sealed symmetrical coin cell (CR2032) using an aqueous electrolyte (1 M Na₂SO₄). The membranes were stacked back-to-back within the coin cell with the active material making direct contact with the current collector. EIS was performed at a frequency range of 0.1 Hz to 100 kHz with a 10 mV (RMS) perturbation and 0 V dc bias. Specific capacitance was calculated using the established best practice methods.

**Results and Discussion**

A number of molybdenum-based complexes that contain either xanthate or dithiocarbamate ligands were surveyed to find the best candidates as precursors in these reactions. The complexes studied were [Mo₂O₃(S₂CNEt₂)₂], [Mo₂O₃(S₂COEt)₂], [Mo₂O₃(S₂COEt)₃], [Mo₂O₃(S₂COEt)₄], and [Mo₂S₄(S₂COEt)₃]. The complex [Mo₂O₃(S₂COEt)₄] was deemed the best precursor for the production of 1H-MoS2@oleylamine due to its lower decomposition temperature and gives cleaner products; the details of the studies that led to this conclusion can be found in the Supporting Information.

1H-MoS2@oleylamine samples were prepared by the decomposition of [Mo₂O₃(S₂COEt)₃] in oleylamine via a hot-injection−thermolysis method. Reactions were carried out at temperatures ranging from 200 to 325 °C to produce black materials. Aliquots were taken at regular intervals and the reaction products isolated, by repeated ethanol washing and centrifugation steps. Upon injection, decomposition of the precursor occurs rapidly; there was no evidence of unreacted [Mo₂O₃(S₂COEt)₃] within the products or the supernatants, even with the short reaction times used at most temperatures (e.g., 3 min at 250 °C). The only exception was 3 min at the lowest temperature studied (200 °C; sample 1). The supernatant in this case contained a small amount of the unreacted precursor, giving it a brown hue. In methanolic suspensions, all 1H-MoS2@oleylamine samples consisted of black flocculates. Once isolated and dried most of the products were obtained as brittle solids, although we found that a significant increase in both the reaction time and temperature led to the isolation of greasier materials (i.e., 16, 19, and 20; see Table 1).

TEM analysis shows that all of the 1H-MoS2@oleylamine products consist of small MoS₂ nanosheets which form highly disordered, aggregated structures. These flocculates typically have lateral dimensions from hundreds to thousands of nanometers and are commonly found to both adhere to and mold around the carbon film on lacy carbon TEM grids (Figure S3). On performing high resolution TEM imaging of the flocculates (Figure 1a,b), it is clear that the MoS₂ nanosheets are randomly oriented within an oleylamine matrix, with the strongest phase contrast observed for nanosheets with their basal planes oriented parallel to the incident electron beam. The nature of the oleylamine interaction was further probed by (ATR) FTIR spectroscopy (details in the
The dimensions of the MoS$_2$ nanosheets within each of the 1H-MoS$_2$@oleylamine samples were estimated by statistical analysis of the basal plane dimensions observed for side-on monolayer nanosheets seen in the TEM images (sample size in each study: N = 40). This analysis revealed that the lateral sizes of the nanosheets can be controlled by the selection of reaction temperature (Table 1 and Figure 2a). The low temperature reactions at 200 °C and 250 °C produced MoS$_2$ nanosheets within the 1H-MoS$_2$@oleylamine with an approximate lateral size of 4.5–5 nm, whereas the gradual increase of the reaction temperature above 250 °C promoted the growth of larger nanosheets of up to an average of ca. 11.5 nm at 325 °C. These observations suggest that a nonclassical crystal growth mechanism is prevalent in the formation of the MoS$_2$ nanosheets. In all cases, the deviation of the nanosheets measured never exceeds ±15% of the mean nanosheet length, showing a significantly increased level of control in the growth of the nanoscale-MoS$_2$ monolayers, compared to other known processes where little-to-no control is observed. Nanosheet sizes appear to be unaffected by the reaction times employed; a survey of the aliquots obtained from the same hot-injection reactions at 3 and 20 min intervals showed no significant size variations, suggesting that in all samples the nanosheet growth process is complete in under 3 min.

A probe-side aberration corrected STEM was used to perform high resolution annular dark field (ADF) imaging of the flocculate structure for sample 19 (synthesized at 325 °C for 12 min). The atomic resolution ADF images in Figure 2e,f support the microstructures seen in the TEM images, showing structures composed of large numbers of randomly oriented MoS$_2$ nanosheets.

Figure 1. TEM images of the 1H-MoS$_2$@oleylamine flocculates give evidence for the presence of monolayer MoS$_2$ nanosheets. The variation of the average nanosheet dimension from the reactions carried out at (a) 200 °C (sample 3; average size of 4.78 ± 0.78 nm) and (b) 325 °C (sample 19; average size of 11.29 ± 1.26 nm). The inserted images represent the SAED patterns, supporting the identification of the 1H-crystallites.

Supporting Information, confirming the capping ligands are chemisorbed onto the surface of the 1H-MoS$_2$ nanosheets.)

Table 1. Summary of All of the Available Data for the 1H-MoS$_2$@Oleylamine Samples Produced by Hot-Injection—Thermolysis

| sample | reaction temp (°C) and time (min) | appearance | purity (%) | MoS$_2$@oleylamine ratio$^a$ | av nanosheet size$^b$ (nm) | Raman band separation (cm$^{-1}$) |
|--------|----------------------------------|------------|------------|-----------------------------|---------------------------|-------------------------------|
| 1      | 200 °C, 3 min                    | dry        | 71.5       | MoS$_2$-oleylamine$_{0.29}$ | 4.80 ± 0.65               | 24.4                          |
| 2      | 200 °C, 6 min                    | dry        | 69.6       | MoS$_2$-oleylamine$_{0.31}$ | 4.51 ± 0.61               | 24.3                          |
| 3      | 200 °C, 12 min                   | dry        | 71.1       | MoS$_2$-oleylamine$_{0.21}$ | 4.78 ± 0.78               | 24.0                          |
| 4      | 200 °C, 20 min                   | dry        | 68.3       | MoS$_2$-oleylamine$_{0.30}$ | 5.24 ± 0.83               | 24.3                          |
| 5      | 250 °C, 3 min                    | dry        | 69.9       | MoS$_2$-oleylamine$_{0.31}$ | 4.62 ± 0.65               | 24.0                          |
| 6      | 250 °C, 6 min                    | dry        | 68.7       | MoS$_2$-oleylamine$_{0.29}$ | 4.63 ± 0.52               | 24.0                          |
| 7      | 250 °C, 12 min                   | dry        | 68.0       | MoS$_2$-oleylamine$_{0.28}$ | 4.69 ± 0.68               | 23.9                          |
| 8      | 250 °C, 20 min                   | dry        | 70.0       | MoS$_2$-oleylamine$_{0.24}$ | 5.07 ± 1.04               | 24.1                          |
| 9      | 275 °C, 3 min                    | dry        | 73.3       | MoS$_2$-oleylamine$_{0.24}$ | 7.14 ± 0.97               | 23.5                          |
| 10     | 275 °C, 6 min                    | dry        | 71.5       | MoS$_2$-oleylamine$_{0.29}$ | 6.88 ± 1.06               | 23.2                          |
| 11     | 275 °C, 12 min                   | dry        | 72.5       | MoS$_2$-oleylamine$_{0.31}$ | 6.98 ± 0.77               | 23.3                          |
| 12     | 275 °C, 20 min                   | dry        | 73.9       | MoS$_2$-oleylamine$_{0.31}$ | 6.95 ± 0.92               | 23.2                          |
| 13     | 300 °C, 3 min                    | dry        | 68.8       | MoS$_2$-oleylamine$_{0.23}$ | 8.78 ± 1.23               | 22.6                          |
| 14     | 300 °C, 6 min                    | dry        | 73.0       | MoS$_2$-oleylamine$_{0.31}$ | 8.61 ± 1.29               | 22.6                          |
| 15     | 300 °C, 12 min                   | dry        | 73.8       | MoS$_2$-oleylamine$_{0.33}$ | 8.93 ± 1.09               | 22.7                          |
| 16     | 300 °C, 20 min                   | greasy     | 71.1       | MoS$_2$-oleylamine$_{1.20}$ | 8.97 ± 1.64               | 23.0                          |
| 17     | 325 °C, 3 min                    | dry        | 76.4       | MoS$_2$-oleylamine$_{1.23}$ | 11.47 ± 1.56              | 22.1                          |
| 18     | 325 °C, 6 min                    | dry        | 76.6       | MoS$_2$-oleylamine$_{0.32}$ | 11.02 ± 1.43              | 22.0                          |
| 19     | 325 °C, 12 min                   | greasy     | 36.5       | MoS$_2$-oleylamine$_{1.47}$ | 11.29 ± 1.26              | 22.3                          |
| 20     | 325 °C, 20 min                   | greasy     | 23.6       | MoS$_2$-oleylamine$_{1.45}$ | 10.85 ± 1.28              | 22.5                          |

$^a$Determined by TGA. $^b$Determined by the size analysis in TEM.
expected for bi- and multilayer structures. It is therefore believed that the flocculates are composed exclusively of monolayer MoS₂ nanosheets; multilayer flakes either are extremely rare or entirely absent from these samples. This observation is consistent with the TEM selected-area electron diffraction (SAED) and p-XRD patterns, which both display highly broadened bands for the (100) and (110) crystal planes of MoS₂, indicative of a 1H-phase (in addition to a broadened signal at approximately 20° for the reflections of the glass substrate in the p-XRD spectra; Figures 1d,e and 2b).

The SAED pattern also highlights the highly polycrystalline nature of the MoS₂@oleylamine, as no clear spots corresponding to the (100) and (110) planes of MoS₂ are observed, only highly diffused bands. There were no discernible bands corresponding to the (002) reflection at ca. 14° from either diffraction experiment. In ADF STEM images of sample 19, occasional flakes were favorably oriented with their basal planes normal to the optic axis allowing them to be imaged with atomic resolution. Even within relatively small scan areas (for example the 25 × 25 nm² area of sample 19 shown in Figure 3), Fourier transforms (FTs) of the atomic resolution images revealed ring-like patterns characteristic of a polycrystalline material (with ring radius corresponding to the 0.27 nm d-spacing of the {100} planes), as opposed to the distinct spot patterns present when imaging individual isolated nanocrystals. Closer inspection of the images shows small nanosheets randomly oriented with respect to their neighbors and often overlapping one another. The lateral dimensions of the sheets seen in these images (ca. 11 nm) are consistent with the sizes determined from TEM imaging.

STEM was also used to perform energy dispersive X-ray (EDX) spectrum imaging on flocculates, allowing chemical composition to be probed with nanometer resolution. Figure 4 shows a spectrum image of a typical region of flocculate from sample 19. The resulting elemental maps reveal homogeneous distributions of Mo and S. It should be noted that the S Kα (2.31 keV) and Mo Kα (2.29 keV) peaks overlap making deconvolution on a pixel by pixel basis challenging. The summed EDX spectra suggest that the MoS₂ is pure, with all other elements seen in the spectrum associated with the TEM support (C, Si, O, Cu). Quantification of the spectra supports the expected 1:2 Mo:S stoichiometry. The only detected Raman peaks in all samples were those of the LA(M), E₂g, and A₁g bands of MoS₂ (at ca. 225, 380, and 405 cm⁻¹, respectively); no other identifiable signals were observed in the 200–1000 cm⁻¹ range. This supports the expected decomposition mechanism of such xanthate-bearing complexes to MoS₂, even in the presence of oxo-groups (Scheme S1). Raman spectroscopy of large MoS₂ nanosheets (lateral dimensions >100 nm) is regularly used to estimate nanosheet thicknesses of these materials, as the A₁g and E₂g bands are known to exhibit a well-defined dependence on layer thickness. However, Raman analysis of 1H-MoS₂@oleylamine does not show the expected peak separation of 18 cm⁻¹ for single-layer MoS₂; instead showing band separations which depend upon the lateral sizes of nanosheets in the 1H-MoS₂@oleylamine (Figure 2d,e and Table 1). The peak separation from the samples obtained at 200 and 250 °C (average nanosheet size measured by TEM ~ 4.8 nm) was approximately 24 cm⁻¹. This separation narrowed upon increasing reaction temperature, falling to...
To confirm both the purities and the compositions of the products, the dried 1H-MoS2@oleylamine samples were subjected to TGA (10 °C/min, up to 600 °C in 1 atm air; an example thermogram is shown in Figure S4). All the thermograms obtained display the same three stages of decomposition, previously described by Altavilla et al.44 and discussed in more detail in the Supporting Information. We were able to approximate both the purities and the component ratios within the 1H-MoS2@oleylamine from the data obtained, showing that most of the samples attained give reasonable purities (ca. 70%, the impurities consisting of sulfur adatoms and physisorbed oleylamine) and MoS2/chemisorbed oleylamine ratios of MoS2/oleylamine (thus significantly lowering the purities of the products to a MoS2 content as low as 24%) as demonstrated by samples 16, 19, and 20; the excess impurities probably contribute to the oily appearances of the products.

To demonstrate the applicability of this material for use in electrochemical energy storage applications, symmetrical coin-cell type (CR2032) supercapacitors were constructed using a composite of the 1H-MoS2@oleylamine (flake size approximately 8 nm) combined with graphene as a conductive additive to overcome the inherent resistivity of the semiconducting MoS2 flakes, and analyzed using best practice methods.55 Previous studies53 found that coin-cell supercapacitors constructed from a composite of liquid-exfoliated MoS2/graphene showed significantly improved supercapacitance than equivalent cells containing either of the 2D-materials. Therefore, MoS2@oleylamine/graphene composites are considered for our coin-cell devices as it is also thought that the composite would give similar synergetic effects in its supercapacitance. The oleylamine was removed from the MoS2 first by thermal annealing (500 °C; XRD and Raman spectroscopy of the annealed MoS2 materials are shown in Figure S5); the resulting crystals were redispersed in an organic solvent (N-methyl-2-pyrrolidone, NMP) and combined with a graphene dispersion, also prepared by liquid-exfoliation, in a 1:1 (w/w) ratio. This method of graphene production is known to produce large amounts of few layer flakes (1–5 layers) with lateral dimensions of 1–5 μm.41 This composite dispersion was then filtered through a polyvinylidene fluoride (PVDF) filter to form a supported membrane without the need of any of the additional polymeric binders that are typically used.44 The mass of active material was approximately 1 mg (mass loading of 1 mg/cm2) which produces a mechanically flexible and stable thin film with a thickness of several micrometers. Due to the low mass loadings used and the thickness of the film, we report the capacitances as a function of area (mF/cm2). These composite membranes were then stacked together in a symmetrical coin-cell arrangement, as demonstrated previously for ultrasonication exfoliated MoS2.53

Figure 5 and Figure S6 show schematically the design of the coin cell as well as a photograph of the MoS2/composite membrane and electrochemical response of the membrane using an aqueous electrolyte (1 M Na2SO4). The use of a pH neutral electrolyte is to avoid unwanted side-reactions such as hydrogen evolution and oxygen reduction that can occur due to the highly catalytic nature of MoS2. In the optical microscope image (Figure 5a) we can see that several larger graphite flakes are still visible, and with further optimization of the exfoliation it is expected that the capacitance values could be further

ca. 22 cm–1 for samples prepared at 325 °C (average nanosheet size measured by TEM ~ 11.3 nm). The expansion of the A1g to E2g band separation, as a consequence of the lateral dimensions of single-layer nanosheets being ≤100 nm, is thought to occur due to the quantum confinement of the crystal structure within the 2D plane. This phenomenon has previously been observed in both MoS2 nanosheets and fullerene-like nanoparticles.62
improved. In Figure 5b the cyclic voltammetry (CV) at differing scan rates is shown.

At low scan rates the CV curves exhibit the expected “square” shape of an ideal electrochemical double-layer capacitor (EDLC) with no discernible pseudocapacitance peaks; however, as the scan rate increases the curves deviate from the ideal shape, and this indicates a change in the charge storage mechanism to surface mediated ion adsorption.28,29,31,55 The transition in charge storage mechanism is also reflected in the rapid decrease in the measured specific capacitance with increasing scan rate or current density. At low scan rates (current densities) the relatively slow ion adsorption is able to dominate the capacitance, but as the charge/discharge speed is increased only the much faster but lower magnitude double-layer capacitance occurs. This has been seen for many TMDC-based supercapacitors in the literature and is important when considering future applications.32,53,56,57 Figure 5c shows the galvanostatic discharge curves for the cell with increasing current densities, along with the calculated specific capacitance as a function of current density. The gravimetric capacitance at this current density is calculated to be 46 F/g. The full charge−discharge curves as well as the Coulombic efficiency are shown in the Supporting Information (Figure S8).

The increase in capacitance over previously reported values is attributed to the small MoS2 flake dimensions used in this synthesis method compared to solution exfoliated material, whose dimensions range from several hundred nanometers to micrometers.58 The small flake dimensions lead to a maximum in the available surface area, providing a high density of highly reactive edge sites which can increase the available sites for ion adsorption on the surface.59 In combination with the small lateral dimensions, the synthesized MoS2 nanosheets are exclusively monolayer, as discussed previously. Despite some restacking that will occur during filtration, the monolayer nature of the flakes will maximize the available surface area and provide a maximum specific capacitance per unit area when compared to thicker less well-defined material. The decrease in Csp with increasing current density indicates that the charge storage mechanism of the MoS2/graphene composite is not purely a double-layer effect due to the internal resistance of the membrane. This is in agreement with the measured impedance response of the cell (see Supporting Information) at high frequencies. The calculated energy and power densities (Ragone plot) for the composite cell are also shown in the Supporting Information (Figure S9) and compare favorably with similar thin-layer-based systems. However, by further optimization of the ratio of graphene to MoS2 it may be possible to maximize the power density while still maintaining the high energy density that the MoS2 composite provides.

CONCLUSIONS

We have developed a one-pot synthetic route, based on hot-injection−thermolysis, for the production of pure, high quality MoS2 nanosheets capped by oleylamine. Nanometer-scale control over the lateral dimensions of 1H-MoS2 nanosheets (ranging from 4.5 to 11.5 nm) has been achieved by modulation of the reaction temperature (between 200 to 325 °C) while maintaining consistent levels of purity and oleylamine capping. In addition, the first atomic resolution STEM imaging of this class of materials gives new insights into the structure of MoS2 within the oleylamine matrix. Specifically, we have shown that monolayer, highly crystalline, and randomly oriented nanosheets were formed. The high purity of monolayer sheets, combined with small flakes size, was demonstrated to be ideal for energy storage applications such as supercapacitors. The calculated specific capacitance (of up to 50 mF/cm2) was significantly larger than that previously reported from ultrasonication prepared MoS2, and can be maximized through further optimization. These results indicate that composites of well-defined and thoroughly characterized 2D materials, such as MoS2 and graphene, show increasing promise for wide-scale electrochemical energy storage applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04476.

Information regarding precursor selection studies, further characterization of the MoS2@oleylamine produced, equations to determine MoS2@oleylamine composition, and electrochemical impedance spectroscopy (PDF)
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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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