Diatom Frustules as a Biomineralised Scaffold for the Growth of Molybdenum Disulfide Nanosheets

Edward A. Lewis,a David J. Lewis,a,b,∗ Aleksander A. Tedstone,b Georgia Kime,c Simon Hammersley,d Philip Dawson,c David J. Binks,c Paul O’Briena,b,∗ and Sarah J. Haigh,a,∗

a School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.
b School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.
c Photon Science Institute, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

We report the use of diatom frustules as scaffolds for the growth of molybdenum disulfide nanosheets. The frustules were impregnated with a single source molecular precursor complex which is converted to MoS2 by solventless thermolysis. Randomly oriented few-layer thick MoS2 nanosheets are found to coat both the exterior surface and internal pores of the scaffold.

Nature displays exquisite control of phase and morphology during biomineralisation and the resulting mineralised structures have been found to possess attractive functional properties, particularly in the area of photonics.4,14 Consequently there is considerable scientific interest in replicating the intricate architectures found in nature,9 as well as enhancing the intrinsic properties of biomineralised structures11 by decoration with inorganic nanostructures.10−13

Diatoms are marine-dwelling eukaryotic unicellular algae,15 which produce biomineralised silica exoskeletons known as frustules. Diatom frustules comprise the majority of the biosilica found in oceans,14 and bulk quantities of the fossilised shells are recovered by dredging. This material is known as diatomaceous-earth (DE). It is widely available and inexpensive and finds use in a number of products including toothpaste and as a laboratory filter aid (under the trade name Celite™). Additionally, the intricate hierarchical nanostructures found in diatom frustules have attracted considerable interest for nanotechnology applications.15−16 Diatom frustules have the highest strength-to-weight ratio of all reported natural biomaterials,77 their periodic nanoscale pores result in both high surface areas and unique photonic properties which enhance light uptake.16−18 In the living diatom this aids photosynthesis but the functional structures persist in the deceased organisms’ biomineral shell.15−18,19

Biosilica is an inert insulator which provides an ideal scaffold or template for functional materials.13−15,20−22 By introducing semiconducting materials into the biomineralised architecture it is potentially possible to exploit the frustules’ photonic properties for light harvesting or its large surface area for sensing and catalytic applications.5,16,20 For example, diatom frustules coated with TiO2 have been incorporated into dye sensitised solar cells, where the devices’ enhanced performance was attributed to improved light scattering by the diatoms.9 A surface sol-gel process has been used to coat diatom frustules with a ~50 nm thick layer of SnO2; the resulting structures were used as NO gas detectors.20 Bao et al. have reported the conversion of the insulating silica of diatom frustules to semiconducting silicon by magnesiothermic reduction,33 after which the photocatalytic properties of the resulting structures was enhanced by subsequent deposition of CdS on the frustule’s surface.39 However, to-date, there have been no reports of the functionalization of biomineralised structure with twodimensional (2D) semiconductor materials.

Molybdenum disulfide (MoS2) is a layered transition metal dichalcogenide which can be isolated as monolayer or few-layer thick sheets.24−25 Unlike the archetypal 2D material graphene,26 2D MoS2 sheets have a thickness dependent bandgap57 and the material has attracted attention for electronic,27 optoelectronic,18,29 catalytic,30 and tribological applications.31 Numerous routes to 2D MoS2 nanosheets have been developed, including micromechanical exfoliation,32 ultrasonic exfoliation,33−34 shear exfoliation,35 chemical vapour deposition,36 and hot-injection synthesis.37,38 We have recently explored single source molecular precursors for the synthesis of MoS2;37−39 MoS2 sheets were produced by the hot-injection of Mo4O6S2(S2COEt)2 into oleylamine and these were combined with graphene to produce supercapacitor electrodes.37 Similarly tetrakis(diethylthiocarbamato)molybdenum(IV) (MoL4)39−41 has been used to produce thin films of
MoS₂ doped with transition metals using aerosol-assisted chemical vapour deposition (AACVD).⁵⁹

The air stability and solution processability of MoL₄, combined with its clean decomposition, make MoL₄ an attractive precursor to MoS₂. It seems feasible that the precursor’s high solubility in organic solvents could be exploited to coat a wide range of substrates or templates with the precursor which can then be converted to MoS₂. In this paper we demonstrate such an approach to MoS₂ decoration, using DE as a scaffold on which to grow few-layer MoS₂ nanosheets. We call these hybrid structures DE-MoS₂. In the final composite material we find that the diatom exoskeleton is thoroughly clad with MoS₂ nanosheets. The approach circumvents the need for assembly of a microporous scaffold and exploits nature’s ability to fabricate complex hierarchical structures which are expensive or impossible to produce using existing nanofabrication techniques.⁶⁰ The simple method outlined here allows the assembly of nanosheet layers on micro-patterned substrates of high surface area without the need for surface modification or linking agents.⁶¹,⁶²

In this approach, DE is immersed in a tetrahydrofuran solution of MoL₄ precursor, the majority of the solvent is then filtered off, leaving DE stained with the molybdenum(IV) complex. The resulting DE-MoL₄ powder is allowed to dry completely before annealing at 450 °C under an inert atmosphere. Annealing results in the molecular precursor’s decomposition, most likely through a β elimination reaction involving a cyclic intermediate,⁶³ to give DE-MoS₂ (full experimental details and a discussion of decomposition mechanism can be found in the SI). Analysis of DE-MoS₂ by Raman spectroscopy (Fig. 1) showed the formation of MoS₂, with the appearance of two strong peaks centred at 382 and 408 cm⁻¹ which are assigned to the E₂g and A₁g optical phonon modes. These features were not seen in either the unreacted MoL₄ precursor or in the DE-MoL₄ material before heat treatment. The Raman spectra suggest that the average thickness of MoS₂ sheets is >4 layers (see SI). X-ray diffraction (XRD) also confirms the conversion of the precursor to crystalline MoS₂, after heating at 450 °C for 30 minutes, as shown by the complete disappearance of the characteristic precursor peaks and the appearance of broad peaks corresponding to the MoS₂{002}, {100}, and {110} planes (see SI).

The micro- and nano-scale morphology of DE-MoS₂ was investigated by scanning electron microscope (SEM) imaging. Secondary electron (SE) SEM images revealed the nearly uniform presence of flake-like structures on the frustules’ surfaces (Fig. 2). There is also evidence that some of the pores of the diatom are infilled with similar material (Fig. 2d). Backscattered electron (BSE) SEM images show that the flakes observed in SE images are comprised of a higher atomic number material than the surrounding frustule, which is predominantly comprised of SiO₂ (Fig. 2d-e). Measurement of the surface bound flakes visible in the SEM images reveals them to have a mean diameter of 132 ± 29 nm (see SI).

Aberration corrected scanning transmission electron microscope (STEM) imaging was used to investigate the atomic structure of the MoS₂ flakes (Fig. 3). The flake-like structures observed in the SEM images are comprised of hundreds of smaller MoS₂ nanosheets. The sheets appear randomly oriented; within the same flake some sheets are side-on while others are found with their (001) basal plane parallel to the support (Fig. 3 c-d).

Lateral nanosheet dimensions and thicknesses can be estimated based on measurement of side-on sheets,⁶⁴ and we have determined an average lateral sheet size of 8.0 ± 3.9 nm and thicknesses ranging from monolayer to no more than 6-layers (see SI). Fourier transforms taken from atomic resolution
α-faces are c-separated. The flake is oriented with the lines the shape of the frustule, c-separated. It could be treated x-separated. α-option, good electron mobility, 37, 39. A periodic pattern of high intensity associated with Si α-nature, α-separation. α-protonic intensity regions is observed in the Mo and S maps, lower signal intensity is observed in the whole of the area where the Si was found, albeit at lower signal intensity. A periodic pattern of high intensity regions is observed in the Mo and S maps, these MoS rich regions correspond to pores in the frustule surface, confirming that the precursor is able to impregnate pores, leading to MoS decoration of both the interior and exterior surfaces of the diatom. Higher magnification EDX spectrum imaging was performed in the STEM: using a fragmented piece of frustule it was possible to map Mo, S, and Si distributions across a single pore edge (Fig. 4 e). A peak in the Mo and S X-ray counts before the onset of Si counts confirms that the interior of the pore is coated with MoS. In the example shown, the MoS layer coating the interior of the pore is ~50 nm thick (Fig. 4 f). Both thermogravimetric analysis and inductively coupled atomic emission spectroscopy suggest MoS loading of ~1 wt. %. Quantification of the EDX spectrum image for which the elemental maps are shown in Fig. 4 a-d, suggests a higher loading of ~2 wt. % MoS. However, this latter figure should be treated with caution: Celite™ contains a broad range of diatom architectures, most likely with different surface area to volume ratios, and the complex geometry of structures prevents accurate X-ray absorption correction.

The approach demonstrated here provides a promising route to new MoS based heterogeneous catalysts. The hierarchical nano- and micro-structure of the DE-MoS material produced is promising for catalytic applications, where a high surface area is desirable. In addition, these randomly oriented nanosheets, display an exceptionally large number of edge sites and this is known to improve catalytic activity in the hydrogen evolution reaction amongst others. In addition to electrochemical energy storage and conversion applications, it is also conceivable that the synthesis route developed here could be used to produce biosensors. Importantly, the synthesis approach presented here, which uses simple heating of a dry powder, may prove easier to scale than hot-injection methods. The resulting MoS structures are free from organic ligands, such as oleylamine, which would otherwise need to be removed prior to use in catalysis or energy storage applications.

UV-visible and photoluminescence (PL) spectroscopy of the samples are described in the Supporting Information, and demonstrate how the optical properties of the frustules can be controlled by the addition of the MoS nanosheets. The unique photonic properties of diatom frustules, in combination with the broadband absorption, good electron mobility, and tuneable band gap of MoS (ranging from 1.2eV in the bulk to 1.8eV in monolayers), could also be exploited in optoelectronic devices.

![Figure 3](image1.png)

**Figure 3.** HAADF STEM images. (a) MoS nanosheets covering a silica pore in a frustule fragment. (b-d) MoS nanosheets extracted from DE-MoS. (b) shows a typical structure comprised of smaller randomly oriented flakes, (c) shows and atomic resolution image of a region of where the flake is oriented with the (001) basal plane orthogonal to the electron beam, a fourier transform is inset to highlight the periodic lattice structure, (d) is a higher magnification image of the region indicated by the dashed box in (c) with an atomic overlay, showing positions of Mo atoms (red) and S atoms (green). Images typically show a high level of polycrystallinity supporting the observation from STEM images that the MoS structures grown on frustule surfaces are comprised of multiple small flakes (further STEM images are available in SI). Atomic resolution imaging of the flakes shows the expected hexagonal 2H-MoS crystal structure. 37 39 Energy dispersive X-ray (EDX) spectrum imaging in the SEM was used to confirm the elemental distributions of Mo (Lα, 2.29 eV and Kα, 17.4 eV), S (Kα, 2.31 eV) and Si (Kα, 1.74 eV) on the surface of DE-MoS (Fig. 4 a-d). The strong Si elemental signal outlines the shape of the frustule, showing clearly where the boundary of the silica structure lies. The deconvoluted signals from Mo and S were found to be co-localised and covered the whole of the area where the Si was found, albeit at lower signal intensity. A periodic pattern of high intensity regions is observed in the Mo and S maps, these MoS rich regions correspond to pores in the frustule surface, confirming that the precursor is able to impregnate pores, leading to MoS decoration of both the interior and exterior surfaces of the diatom. Higher magnification EDX spectrum imaging was performed in the STEM: using a fragmented piece of frustule it was possible to map Mo, S, and Si distributions across a single pore edge (Fig. 4 e). A peak in the Mo and S X-ray counts before the onset of Si counts confirms that the interior of the pore is coated with MoS. In the example shown, the MoS layer coating the interior of the pore is ~50 nm thick (Fig. 4 f). Both thermogravimetric analysis and inductively coupled atomic emission spectroscopy suggest MoS loading of ~1 wt. %. Quantification of the EDX spectrum image for which the elemental maps are shown in Fig. 4 a-d, suggests a higher loading of ~2 wt. % MoS. However, this latter figure should be treated with caution: Celite™ contains a broad range of diatom architectures, most likely with different surface area to volume ratios, and the complex geometry of structures prevents accurate X-ray absorption correction.

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![Figure 4](image2.png)

**Figure 4.** (a-d) SEM EDX spectrum imaging of MoS decorated frustule, (a) shows the SE electron image and (b), (c), and (d) show the corresponding maps of Si Kα, S Kα, and Mo Lα X-ray counts. (e-f) STEM EDX spectrum imaging of frustule pore, (e) shows maps of Si Kα, S Kα, and Mo Lα X-ray counts. (f) EDX spectrum line scan of Si Kα, S Kα, and Mo Lα X-ray emission taken from the region indicated by the arrow in (e), dotted vertical lines mark the onset of significant intensity associated with Si Kα and Mo Lα X-ray emission.
With over one hundred thousand known species of diatoms, and the potential for further genetic manipulation, a rich variety of frustule morphologies are available to explore. Furthermore, this approach could easily be adapted to other metal sulphides by changing the precursor chemistry. Single source precursor chemistry has previously been shown to allow control over the morphology of nanocrystal products, and combining multiple precursors offers a simple route to doped or alloyed nanostructures. This experimental flexibility provides enormous potential for control over both scaffold geometry and nanocrystal morphology and composition, which should allow extensive tuning of the resulting system’s properties and performance.

In conclusion, we have demonstrated the synthesis of MoS$_2$ nanosheets on diatom frustule scaffolds by solventless thermolysis of a single source precursor bound to the frustule’s surface. MoS$_2$ is found to coat both the external surface and internal pores of the frustules. It grows as aggregates of small (~8 nm), randomly oriented, nanosheets with thicknesses of less than 6 atomic layers. The use of the biominalised scaffold allows hierarchical microporous structures to be produced with relatively few synthetic steps. The simple molecular precursor chemistry employed in this work potentially offers a robust and versatile route to the decoration of a wide range of complex structures with MoS$_2$ nanosheets. This approach is potentially scalable and has advantages over established methods due to the absence of surface capping ligands.

ASSOCIATED CONTENT
Supporting Information: experimental details, XRD, PL, size analysis, further STEM and EDX data.

Corresponding Author
Sarah.Haigh@manchester.ac.uk
Paul.o'brien@manchester.ac.uk
david.lewis-4@manchester.ac.uk

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REFERENCES


