Fabrication and atomic structure of size-selected, layered MoS$_2$ clusters for catalysis

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Well defined MoS$_2$ nanoparticles having a layered structure and abundant edges would be of considerable interest for applications including photocatalysis. We report the atomic structure of MoS$_2$ size-selected clusters with mass in a range all the way from 50 to ~2000 MoS$_2$ units. The clusters were prepared by magnetron sputtering and gas condensation prior to size selection and soft landing on carbon supports. Aberration-corrected scanning transmission electron microscopy (STEM) in high-angle annular dark-field (HAADF) mode reveals a layered structure and Mo–Mo spacing similar to the bulk material. The mean number of layers in these lamellar clusters increases from one to three with increasing mass, consistent with density functional theory calculations of the balance between edge energies and interlayer binding. The intense renewal of interest in the layered compound MoS$_2$ reflects the abundance of potential applications of what are now called “2D materials”, such as the transition metal dichalcogenides, and the different properties emerging in the few layer regime. For example, the monolayer of MoS$_2$ presents a direct, blue-shifted band gap compared with the indirect gap of the bulk material, suggesting possible applications in optoelectronics. At the same time chemically synthesised MoS$_2$ nanoparticles show promise as a cheap alternative to precious metals in catalysis, e.g., for the hydrogen evolution reaction, and also seem to exhibit a size-dependent band gap. However, molybdenum sulphide nanostructures may present different stoichiometries (e.g. Mo$_2$S$_3$, ref. 8) and different atomic structures (e.g. fullerenes). Of special interest for photocatalysis would be nanoparticles with the layered structure characteristic of bulk MoS$_2$ crystals and an abundance of edges where catalysis, electrocatalysis and/or photocatalysis are likely to take place.

Such structures have previously been fabricated in solution and as supported nanostructures by sulfidation of molybdenum. These methods have yielded excellent studies of the catalytic activity of MoS$_2$ nanoparticles and the crystal structure of platelets, however size-control is limited. Determination of size-dependent catalysis in these structures is lacking a method of depositing a large amount of size-controlled clusters, appropriate for both vacuum characterisation and electrochemical measurements.

In this Letter we report the controlled (gas-phase) synthesis, deposition and atomic structure of few-layer MoS$_2$ clusters of exactly this type, over a very wide mass range running from 50 to 1936 MoS$_2$ sub-units (±3%), while a theoretical model based on first-principles calculations helps to explain the number of layers observed in the clusters as a function of their mass.

Results and discussion

The MoS$_2$ clusters were created in a cluster beam source in exactly the same way as the elemental metallic alloy clusters we have reported previously. The ionised clusters so formed were mass-selected with a high transmission, lateral time-of-flight mass filter, prior to deposition onto standard amorphous carbon microscopy supports at selected kinetic energy (<2 eV per MoS$_2$ sub-unit, corresponding to the soft landing regime). X-ray photoelectron spectroscopy (XPS) of deposited multilayer cluster films (after storage and transport through the ambient) gave a stoichiometry Mo : S of 1 : 1.6 ± 0.1, not far from that of the MoS$_2$ target. We envisage that a degree of oxygen attack depletes the sulphur content of the clusters somewhat during ambient exposure (see also below). The selected masses were chosen in the range from 8000 to 309 760 amu, which we designate for convenience according to the corresponding number of MoS$_2$ sub-units, e.g., 16 000 amu = (MoS$_2$)$_{100}$.

Fig. 1(a) is to set out to demonstrate the successful production and sizing of deposited, mass-selected MoS$_2$ clusters. Shown are the measured HAADF-STEM cluster intensity distributions of four illustrative cluster samples, (MoS$_2$)$_{50}$, (MoS$_2$)$_{100}$, (MoS$_2$)$_{150}$, (MoS$_2$)$_{200}$, and a reference Au$_{309}$ cluster.
array used as a “mass balance”. The distinct size fractions are clearly seen. Note that the distributions are broader \( (I_{\text{max}}/\Delta I \sim 4) \) than the set mass-resolution of the cluster mass filter (18) because of the inevitable broadening associated with the STEM intensity measurements (due to substrate thickness variations for example). The 200 keV electron beam also causes knock-on damage to the clusters over time, this is noticeable from the absence of sulphur atoms in the images as the beam transfers enough energy to make the sulphur atoms mobile.

Fig. 1(b) and 1(c) illustrate the atomic structure of the deposited MoS\(_2\) clusters obtained from high resolution HAADF-STEM imaging (lateral resolution \( \sim 0.1 \) nm) consistent with its lamellar trigonal-prismatic coordination in the bulk (space group: \( P6_3/mmc \)). Shown in Fig. 1(b) is one \((\text{MoS}_2)_{500}\) cluster, with the shape of an irregular hexagon and very distinct lateral hexagonal atomic structure corresponding to the high atomic number Mo atoms which dominate the high angle imaging regime. A fast Fourier transform (FFT) of the cluster image (not shown) yields diffraction spots corresponding to the \( (100) \) reflection at \( 0.27 \pm 0.02 \) nm, which matches well with the value in bulk MoS\(_2\) of \( 0.2726 \pm 0.0003 \) nm. That the cluster consists of more than one layer is evident from the higher STEM intensity in the centre of the cluster as well as the projected area observed, which implies a mean height of \( 3.7 \pm 0.8 \) layers in this case. While most clusters adopt this geometry (layers parallel to the support), in a few cases clusters are observed side-on, as Fig. 1(c) illustrates; such images, as in this case of an \((\text{MoS}_2)_{650}\) cluster, establish a lamellar structure with observed interlayer spacing (here \( 0.69 \pm 0.07 \) nm) consistent with that of bulk MoS\(_2\) (0.615 nm). We have several other examples of side-on and slanted orientation, possibly caused by defects in the carbon support, and numerous examples confirming the in-plane hexagonal Mo–Mo structure. Note that these proofs of a cluster atomic structure associated with bulk stoichiometric MoS\(_2\) suggest that sulphur loss between cluster preparation and STEM imaging is either negligible or at least largely confined to the cluster edges.

A three-dimensional representation of a set of three (apparently four) \((\text{MoS}_2)_{500}\) clusters in the high resolution HAADF-STEM is shown in Fig. 2(a). We say three not four because (on the basis of intensity measurements) the two fragments at the top left of the image arise from one cluster which has fragmented on landing. The atomic columns corresponding to the Mo atoms in the clusters are readily apparent in each case. A line profile (Fig. 2(b)) of the same image shows the consistent step changes in HAADF intensity indicative of multiple layers. The cluster in the bottom right of Fig. 2(a) has a maximum height of four atomic layers and a projected area of \( 11.4 \pm 1.4 \) \( \text{nm}^2 \),
together corresponding to $543 \pm 67$ MoS$_2$ units (compared with the size-selected value of $500 \pm 15$). The cluster nearest the centre in Fig. 2(a) has a larger projected area ($13.7 \pm 1.7$ nm$^2$) than the one in the bottom right and is correspondingly less high (maximum height 3 layers); again these values correspond to approximately 500 MoS$_2$ units ($489 \pm 60$ to be exact). Thus the STEM measurements of the mass-selected MoS$_2$ clusters, in this example $(\text{MoS}_2)_{500}$, confirm that the size after deposition matches the size selected in the gas phase and furthermore demonstrate that the cluster structure corresponds to a few, finite layers of the bulk MoS$_2$ layered structure.

The measured projected areas of the same clusters, allow us to obtain the number of layers the clusters contain as a function of the cluster mass (equivalent number of MoS$_2$ units) independent of STEM intensity (layers $= \text{(cluster size)} \times \text{(unit cell area)}$). The results of this analysis, across a cluster size range from 50 to 1936 MoS$_2$ units and including analysis of approximately 50 clusters of each size, are shown in Fig. 2(c). We find that the number of layers increases monotonically from between one and two layers at small size to saturate at approximately three layers by a size of $\sim$500 units, where it remains up to size 2000 units. Note that the number of layers is not the same as the maximum height discussed in connection with Fig. 2(b); by number of layers in Fig. 2(c) we refer to the equivalent number of complete layers with size equal to the footprint (projected area) of the cluster. Since not

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**Fig. 2** MoS$_2$ layer structures measured by integrated HAADF intensity. (a) Dark-field image of $(\text{MoS}_2)_{500}$ clusters. (b) HAADF intensity line profile of region in (a) shows step changes in cluster height (layers marked as a guide). (c) Calculated number of layers for cluster sizes 50–1936 ($\pm 3\%$), based on measured cluster area and known selected size. The theoretically predicted number of layers from Fig. 3(b) is plotted in green for comparison.
all layers will be as large as the footprint, the actual number of “incomplete” layers (the maximum height) will be larger. The large variation in measured area is partly due to electron beam damage to the fragile clusters, especially the periphery, and likely combined with real variation in the number of layers due to the similarity in free energy of these states (Fig. 3(b)). The average fractional number of layers in Fig. 2(c) shows that we do indeed have a mixture of clusters with a different number of layers. From a technological point of view these results are particularly promising, since they indicate that the number of layers always lies in the few layer regime where interesting properties may be anticipated, while the equivalent number of layers may also be controlled by the cluster size in the regime below 500 MoS$_2$ units. Future studies will be needed to establish whether the number of layers can be selected, for a given cluster mass, by varying the sputtering and condensation conditions in the source.

One of the outstanding questions emerging from this systematic body of experimental work is why the number of MoS$_2$ layers depends on cluster size in the way that it does (Fig. 2(c)). We may imagine that – for a given mass – there is a balance between the edge energy (which will be smallest for a single large layer) and the stabilising effect of interlayer interactions in a stack of MoS$_2$ layers. To set this notion on a firm footing, we evaluate theoretically the energy required to construct the cluster with respect to the energy of the same number of MoS$_2$ units in an infinite monolayer sheet:

$$E = N_L 3n\sigma(\mu_S) + \frac{N_{MoS2}}{N_L} E_{vdW}(N_L)$$

(1)

where $N_L$ is the number of layers in the flake, and $n$ is the edge length of the flake (expressed as the number of edge MoS$_2$ units). These are related to the number of MoS$_2$ units in the system $N_{MoS2}$ by

$$\frac{N_{MoS2}}{N_L} = \frac{n(n+1)}{2}.$$

(2)

$E_{vdW}$ is the van der Waals binding energy and $\sigma(\mu_S)$ the edge energy which depends on sulphur chemical potential $\mu_S$ (and thereby on edge reconstruction type, since the edges are individually non-stochiometric). The energy-terms, $E_{vdW}$ and $\sigma(\mu_S)$, are evaluated using first-principles density-functional theory (DFT) calculations. The edge energies can be computed by considering triangular structures of increasing size, such as shown in Fig. 3(a), and fitting the total energy to eqn (1). Our calculated edge energies are identical to those reported in ref. 24. Still, a problem remains in choosing the edge energy (or S chemical potential) that matches the experimental conditions. The lowest edge energy at realistic values of $\mu_S$ is 0.65 eV; it is larger for other edge reconstructions and when the conditions correspond to an S deficit. For $E_{vdW}$ we take the value calculated by a highly accurate post-DFT random phase approximation method, giving $-0.18$ eV per MoS$_2$ unit for a pair of layers.

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The energy as a function of the number of MoS$_2$ units, either arranged in a single layer or when divided among
different numbers of layers, is shown in Fig. 3(b) for the case of $\sigma = 0.65$ eV. The monolayer is energetically favourable for $N_{\text{MoS}_2} < 140$, the bilayer for $N_{\text{MoS}_2} < 790$ and the trilayer up to 2300 units. Although the trend is in good agreement with the experiments shown in Fig. 2(c), the calculations tend to give a somewhat smaller absolute number of layers. Moreover, the calculated results were obtained with the lowest edge energy, whereas for other edge reconstructions the energy is higher. In addition, in the experiments some of the flakes appear dendritic, meaning that they consist of the edges exhibiting various reconstructions. The evolution of the expected number of layers as a function of MoS$_2$ units with various edge energies is shown in Fig. 3(c). The steps correspond to the numbers of MoS$_2$ units at which the curves shown in Fig. 3(b) for $\sigma = 0.65$ eV intersect, that is the system with a larger number of layers becomes energetically more favorable. With increasing edge energy the number of layers tends to be closer to one, suggesting that an additional mechanism plays a role giving rise to an increase in the number of layers.

The explanation may lie in either (i) presence of defects that increase the binding energy between the layers or in (ii) kinetic factors – the smaller flakes attach to each other during their flight in the condensation chamber. Our calculations indicated that introduction of S vacancies does not alter the interlayer binding energy. For adatoms/interstitial atoms, the binding energy increases for Mo interstitials and decreases for S interstitials. Since we cannot estimate the number of interstitial atoms in our flakes from the STEM images, it is difficult to quantify this effect. On the other hand, whenever flake attachment occurs, the total binding energy for these flake sizes will be of the order of tens of eV and thus subsequent exfoliation is highly unlikely. Therefore we believe that the latter is the dominant mechanism giving rise to the increased average number of layers. Overall, our theoretical results are in a reasonable agreement with the experiments and suggest that the experimental conditions can be tuned to control the number of layers in the growing clusters.

Conclusions

To summarize, we have demonstrated that small, size-selected, lamellar MoS$_2$ nanoparticles with abundant edges can be prepared in a cluster beam source. Characterization of the clusters by aberration-corrected scanning transmission electron microscopy reveals that the clusters have the layered structure, of the bulk crystal and good crystallinity. The mean number of layers in these lamellar clusters varies from one to three with increasing mass. This finding is rationalized using a theoretical model based on first principles calculations of the balance between edge energies and interlayer binding. Layered systems with a high number of catalytically active edge sites are of considerable interest in e.g. the hydrogen evolution reaction. Our approach is easily scalable and the clusters can readily be landed onto different substrates, so the method of nanofabrication demonstrated may represent an important step towards controllable preparation of size-selected nanoclusters of layered materials for applications in catalysis.

Methods

The MoS$_2$ clusters were created in a cluster beam source$^{16,17}$ from bulk hot-pressed MoS$_2$ targets by DC magnetron sputtering (45 W) and gas condensation (0.6 mbar). The ionised clusters so formed were mass-selected with a high transmission, lateral time-of-flight mass filter,$^{22}$ prior to deposition onto standard amorphous carbon electron microscopy supports at selected kinetic energy (~2 eV per MoS$_2$ sub-unit, corresponding to the soft landing regime$^{23,24}$). Typical cluster beam currents at the support were 30 pA, with nominal mass resolution ($M/\Delta M$) of 18. Deposition of a sub-monolayer coverage of the clusters on each TEM grid took about 2 minutes. The atomic structure of the clusters was revealed by HAADF-STEM imaging with a JEOL 2100F electron microscope running at 200 keV with a field emission gun and spherical aberration-corrected probe beam.

Spin-polarized DFT calculations were carried out using plane-wave projector-augmented wave formalism, as implemented in the VASP package$^{35,36}$ and adopting the Perdew-Burke-Ernzerhof exchange-correlation functional.$^{37}$

Funding sources

EPSRC, the Birmingham Science City project and Academy of Finland.

Acknowledgements

We acknowledge financial support from the EPSRC. The STEM instrument employed in this research was obtained through the Birmingham Science City project “Creating and Characterising Next Generation Advanced Materials”, supported by Advantage West Midlands (AWM) and part-funded by the European Regional Development Fund (ERDF). We further acknowledge financial support from the Academy of Finland through Project No. 263416 and Centre of Excellence Programme (2012-2017) under Project No. 251748. We also thank CSC Finland for generous grants of computer time.

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