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Single-Atom Sensitive Chemical and Structural STEM Characterisation of Two-Dimensional MoS_2 Nano-Catalysts

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The anisotropic, layered structure of graphite is encountered in a variety of complex compound materials such as the transition metal disulfides MS_2 (M=Mo, W). These compounds consist of S-M-S layers with covalent intralayer bonds and with a weak van der Waals interlayer interaction. Like graphene, such S-M-S layers have within the last two decades been found to form numerous of nanoscale polymorphs (including fullerene-like structures, nanotubes/wires and platelets), each with unique physico-chemical properties significantly different from the corresponding bulk materials [1]. Here, we focus on planar, single-layer MoS_2 nanoparticles, which is of broad, current interest as catalyst for the industrial oil refining, hydrogen evolution and photo-oxidation.

The chemical reactivity of the MoS_2 slabs is associated with their edges [2] and so detailed structural information about the edge structures is of the utmost importance to understand the nature of the catalytic active sites. Previously, unprecedented insight into the atomic structure of MoS_2 nanocatalysts prepared under ultra high-vacuum on planar model substrates have been obtained from scanning tunnelling microscopy (STM) and from density functional theory (DFT) calculations [2]. However, the information from the model systems is difficult to relate to the large-scale catalysts synthesis methods because the morphology and distribution of the catalytically important edge sites of the MoS_2 slabs are found to be sensitive to the preparation conditions, edge-attached promoter atoms, and interactions with support media [2]. Only with recent advances in high-resolution transmission electron microscopy, resulting in significantly improved contrast and sensitivity, has the atomic-resolution imaging of industrial-style MoS_2 nanocatalysts been made possible (fig. 1), resolving directly for the first time the individual basal planes viewed in (001) of MoS_2 particles supported on a few-layers-graphene flake [3].

We show here how pioneering work on atom-by-atom chemical analysis in annular dark field scanning transmission electron microscopy [4] can now be applied to these technologically relevant materials. The Mo and S sub-lattices are readily identified in monolayer particles from a single image, and the type, chemical make-out and detailed structure of the catalytically active particle edges are unambiguously determined: fig. 2. Furthermore, site-specific bonding arrangements and electronic structure details can be probed using atomically-resolved electron energy loss spectroscopy. Ensuring that the particles suffer no damage during the observations is key: lower microscope acceleration voltage and custom-developed distributed-dose techniques for EELS acquisition [5] are applied. Together with model STM studies and ab-initio DFT calculations, these results should help establish new, improved structure-functionality relationships in hydrodesulfurisation catalysts.

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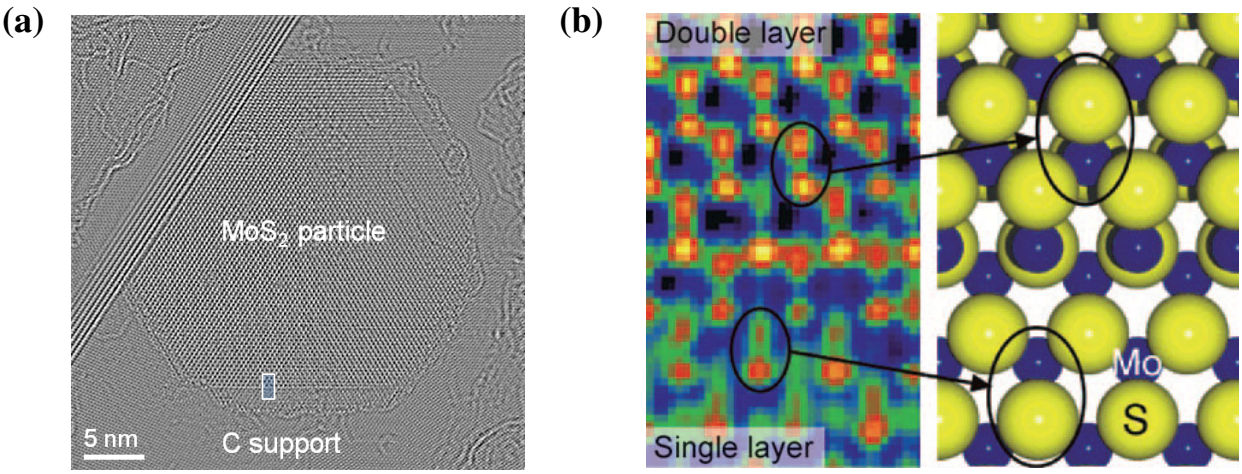

FIG. 1. *a)* Phase image obtained from the exit-wave reconstruction of a through-focal series of HRTEM images acquired at 80kV on the TEAM 0.5 microscope. The MoS_2 nano-catalyst particle is supported on a few layers of graphite. *b)* Close-up detail (false colours) of the region of the image shown in *(a)*, at the bottom of the particle, revealing the atomic arrangement of the lattice. A step from mono- to bi-layer illustrates the single atom sensitivity [3].

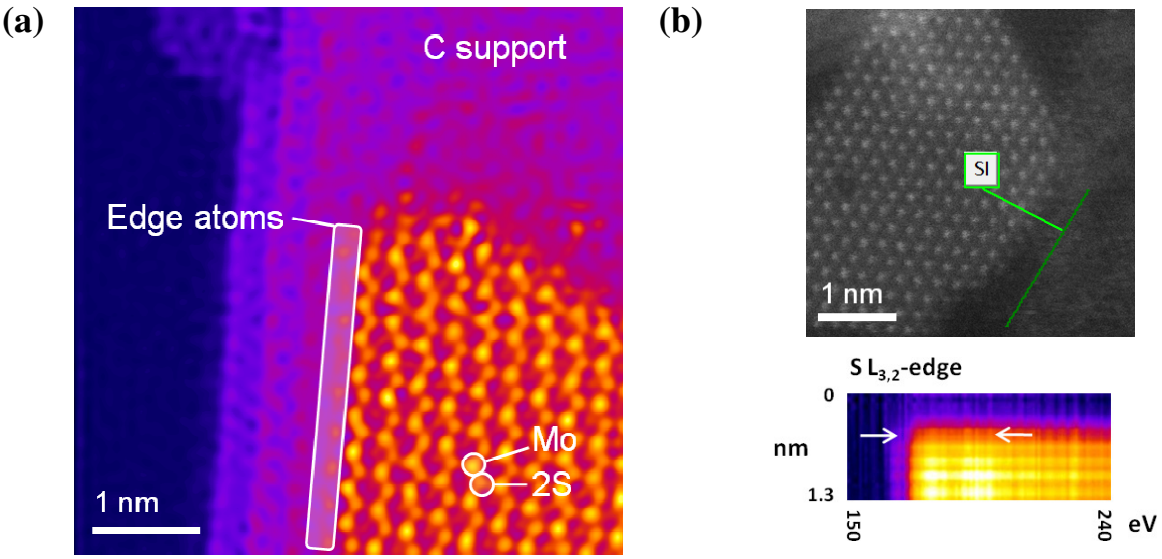

FIG. 2. *a)* HAADF image of a triangular monolayer MoS_2 particle, obtained at 60kV on a Nion UltraSTEM 100. The image was deconvoluted using a maximum entropy algorithm to minimise noise. *b)* Distributed dose EELS linescan (SMART acquisition [5]). The electron dose is distributed along the atomic planes, parallel to the particle edge as indicated on the HAADF survey image, but atomic resolution is retained in the EELS map.

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