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**Formation of Monodisperse (WO<sub>3</sub>)<sub>3</sub> Clusters on TiO<sub>2</sub>(110)\*\***

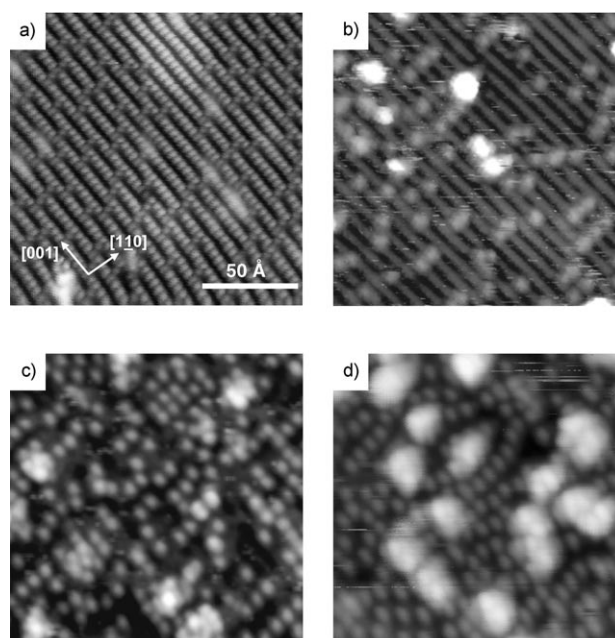
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The preparation and characterization of small clusters on supporting surfaces remains a significant challenge for nanoscience in general and, in particular, for systems used in surface science as catalysis models.<sup>[1–4]</sup> In the case of metals, clusters of specific size can display dramatically different catalytic properties.<sup>[5–7]</sup> Owing to the high mobility of metals and their tendency to cluster, the preparation methods of mass-selected clusters have been restricted exclusively to soft-landing of gas-phase mass-selected charged species.<sup>[8]</sup> To date, no studies have been reported on mass-selected supported oxide clusters. The preparation techniques that lead to formation of supported oxides have been restricted to metal evaporation in an oxidizing environment and/or postoxidation of evaporated metals both on metal<sup>[9–14]</sup> and metal oxide

substrates.<sup>[15–18]</sup> In all cases, clusters with a distribution of sizes were reported.

Here, we focus our attention on tungsten trioxide, an early transition-metal oxide (TMO) that represents a particularly important class of catalytically active oxides. TMO clusters, and in particular vanadium oxide clusters, have received significant attention in model catalytic studies and have been prepared on such substrates as Pd(111),<sup>[12]</sup> Rh(111),<sup>[11,12]</sup> TiO<sub>2</sub>(110),<sup>[16]</sup> Al<sub>2</sub>O<sub>3</sub>/NiAl(110),<sup>[17,18]</sup> and SiO<sub>2</sub>/Mo(112).<sup>[17]</sup> On Rh(111), a disattachment and diffusion of cyclic V<sub>6</sub>O<sub>12</sub> clusters from two-dimensional vanadium oxide islands was observed, demonstrating that large, cyclic oxide cluster structures can be stable on surfaces.<sup>[11,12]</sup> In this study, we employed a qualitatively different deposition approach, which involved direct sublimation of tungsten trioxide, and prepared monodisperse WO<sub>3</sub> clusters on TiO<sub>2</sub>(110). On the basis of atomically resolved imaging, X-ray photoelectron spectroscopy (XPS), mass balance of deposited WO<sub>3</sub>, and supporting theoretical calculations, we conclude that the clusters are cyclic (WO<sub>3</sub>)<sub>3</sub>. To our knowledge, this is the first successful attempt to form monodisperse oxide clusters supported on another oxide. As such, this system shows great promise as an ideal platform for reactivity studies on well-defined supported model TMO catalysts.

The empty-state scanning tunneling microscopy (STM) image of a clean TiO<sub>2</sub>(110) (1×1) surface is shown in Figure 1a. The bright features along the [001] direction correspond to topographically low-lying pentacoordinated Ti<sup>IV</sup> ions, and the dark rows correspond to topographically high-lying bridge-bonded oxygen (BBO) ions.<sup>[19]</sup> The bright spots between Ti<sup>IV</sup> rows are BBO vacancies (typically 8–14 %) generated from thermally induced TiO<sub>2</sub> bulk reduction.



**Figure 1.** STM images (150×150 Å<sup>2</sup>) of a) clean TiO<sub>2</sub>(110) (1×1) and b–d) TiO<sub>2</sub>(110) with different coverages of WO<sub>3</sub>: b) 0.7×10<sup>14</sup>, c) 3.5×10<sup>14</sup>, and d) 5.0×10<sup>14</sup> WO<sub>3</sub> cm<sup>−2</sup>. All images (empty states) were taken with a sample bias of +1.5 V and a current of 0.1 nA.

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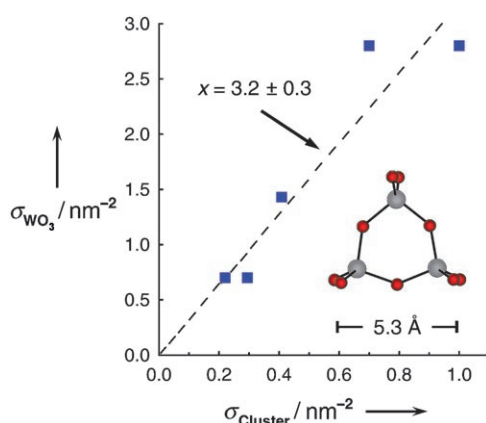
Figure 1b–d show STM images after deposition of  $\text{WO}_3$  at 300 K followed by 10 min of annealing at 600 K. The images clearly exhibit bright features related to deposited  $\text{WO}_3$ . Our attempts to image the as-deposited  $\text{WO}_3$  yielded poorly defined, amorphous-like images (not shown). Clearly, the annealing at 600 K results in the formation of well-defined, monodisperse  $\text{WO}_3$  clusters. From XPS data (not shown), the oxidation state of W remains as +6 upon heating to 600 K.

At low coverage of  $\text{WO}_3$  ( $0.7 \times 10^{14} \text{ WO}_3 \text{ cm}^{-2}$  in Figure 1b), the images show only isolated clusters that are identical in size. While a small fraction ( $\approx 1/5$ ) are centered on the BBO rows, most clusters are centered on the  $\text{Ti}^{\text{IV}}$  rows. As a result of insufficient STM resolution, we were unable to determine whether the latter clusters are centered on top of the  $\text{Ti}^{\text{IV}}$  sites or bridged between them. We speculate that the clusters centered on the BBO rows are located at positions where there were BBO vacancies initially.

At intermediate coverage of  $\text{WO}_3$  ( $3.5 \times 10^{14} \text{ WO}_3 \text{ cm}^{-2}$  in Figure 1c), the majority of the clusters are centered on the  $\text{Ti}^{\text{IV}}$  rows, a small fraction are centered on BBO rows, and some larger three-dimensional aggregates appear. Line scans along the [001] direction over the cluster maxima (not shown) give an apparent cluster height of approximately 1.5 Å and diameter of about 6 Å. Additionally, spatial distribution analysis of the nanoclusters along the [001] direction shows that they never occupy two neighboring  $\text{Ti}^{\text{IV}}$  sites. This arrangement is most likely the result of steric repulsions due to the large cluster size. From this observation, we conclude that the maximum cluster density in the first layer is half the density of  $\text{Ti}^{\text{IV}}$  sites, that is,  $2.6 \times 10^{14} \text{ cm}^{-2}$ .

A further increase in the  $\text{WO}_3$  coverage (Figure 1d,  $5.0 \times 10^{14} \text{ WO}_3 \text{ cm}^{-2}$ ) results primarily in an increased number of larger 3D clusters. The smaller, monodisperse clusters directly in contact with  $\text{TiO}_2(110)$  are also resolved in the image.

Having established that for low doses the clusters are monodisperse (STM) and composed of  $\text{WO}_3$  (XPS), we could determine the number of  $\text{WO}_3$  units in each cluster by correlating (Figure 2) the number of clusters per unit area (from STM) with the areal mass density (from quartz crystal



**Figure 2.** Areal mass density of deposited  $\text{WO}_3$  ( $\sigma_{\text{WO}_3}$ ) from QCM studies as a function of the number density of tungsten trioxide clusters ( $\sigma_{\text{cluster}}$ ) from STM studies. The slope ( $x = 3.2 \pm 0.3$ ) confirms that the clusters are trimers ( $(\text{WO}_3)_3$ ). The inset indicates the cyclic structure and observed size of gas-phase  $(\text{WO}_3)_3$  trimers.

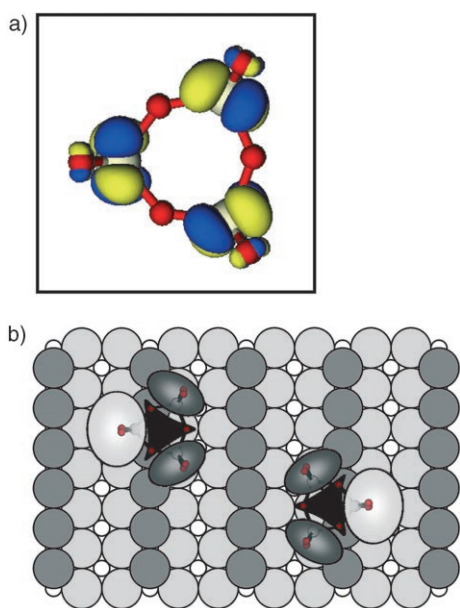
microbalance, QCM). Within experimental error the slope is three, which is indicative of trimers,  $(\text{WO}_3)_3$ . Note that mass spectrometry studies of vacuum-sublimed  $\text{WO}_3$  reveal that the dominant gas-phase product of  $\text{WO}_3$  sublimation is  $(\text{WO}_3)_3$ .<sup>[20,21]</sup>

In this context, the structure of gas-phase  $(\text{WO}_3)_3$  is known from photoelectron spectroscopy (PES) and density functional theory (DFT) calculations.<sup>[20,21]</sup> The gas-phase  $(\text{WO}_3)_3$  trimer is cyclic with  $D_{3h}$  symmetry<sup>[20]</sup> (its structure is shown schematically in the inset of Figure 2). The calculated diameter of 5.3 Å<sup>[20]</sup> is consistent with STM data and indicates that two  $\text{Ti}^{\text{IV}}$  sites are required to accommodate one cluster. Additional STM data strengthen the evidence favoring the cyclic  $(\text{WO}_3)_3$  trimers on  $\text{TiO}_2(110)$ . In a number of cases, presumably when the STM tip was very sharp, we observed signal contrast within the  $(\text{WO}_3)_3$  clusters. An example is shown in Figure 3, in which clusters exhibit a dark triangular feature with one corner aligned with a  $\text{Ti}^{\text{IV}}$  row and the opposite side tilted with equal probability to the left or right away from the  $\text{Ti}^{\text{IV}}$  row where the cluster is centered. This observation confirms that this structure is not an STM artifact.



**Figure 3.** High-resolution STM image ( $70 \times 70 \text{ Å}^2$ ) exhibiting strong trigonal intensity contrast within each  $(\text{WO}_3)_3$  cluster. One of the corners aligns with a  $\text{Ti}^{\text{IV}}$  row and the opposite side is tilted with equal probability to the left or right away from this row.

To explain the contrast within the clusters we turn to DFT calculations of isolated  $(\text{WO}_3)_3$ , as detailed in Reference [20]. A schematic view of the expected acceptor orbitals on the  $D_{3h}$   $(\text{WO}_3)_3$  cluster is shown in Figure 4a. All the empty states in  $(\text{WO}_3)_3$  are W 5d-based, in-plane or out-of-plane molecular orbitals. As the out-of-plane orbitals are expected to have better overlap with states from the STM tip, they should constitute primarily the accepting (imaged) orbitals. The orbital shown in Figure 4a represents one of such out-of-plane 5d orbitals. The bright features with a dark triangular center observed in the high-resolution STM image (Figure 3) resemble the symmetry of the accepting molecular orbitals of the  $(\text{WO}_3)_3$  trimer (Figure 4a).



**Figure 4.** a) One of the empty low-lying out-of-plane molecular orbitals of  $(\text{WO}_3)_3$ <sup>[20]</sup> expected to be the accepting states in the high-resolution STM images of  $(\text{WO}_3)_3$ . b) Schematic view of the  $\text{TiO}_2(110)$  surface (small white circles:  $\text{Ti}^{\text{IV}}$ ; light gray circles: bridge-bonded oxygen; dark gray circles: second-layer oxygen) with two cyclic  $(\text{WO}_3)_3$  clusters. The orientation of the top cluster is identical with that shown in part (a). Both clusters have the plane of the rings tilted with two tungsten atoms pointing into the  $\text{Ti}^{\text{IV}}$  row and the third tungsten atom tilted up and pointing towards the neighboring BBO row (one to the left and the other to the right). This tilt results in a different brightness above the three tungsten atoms of the ring, with the top one being significantly brighter than the other two.

To further illustrate the qualitative agreement between the out-of-plane empty states of isolated  $(\text{WO}_3)_3$  clusters (Figure 4a) and the high-resolution empty-state STM image (Figure 3), we show a schematic view of the  $\text{TiO}_2(110)$  surface with two  $(\text{WO}_3)_3$  clusters bound along the  $\text{Ti}^{\text{IV}}$  row. The clusters have the plane of the rings tilted away from the surface normal with two tungsten atoms pointing into the  $\text{Ti}^{\text{IV}}$  row and the third tungsten atom tilted towards the neighboring BBO row (one to the left and the other to the right), as observed in the STM images (Figure 3). This tilt results in a different brightness above the three tungsten atoms of the ring, with the tungsten atom toward the BBO row being significantly brighter than the other two. The structure that emerges involves bonding between neighboring cationic  $\text{Ti}^{\text{IV}}$  and terminal oxygen atoms on adjacent W atoms of the trimer. The tilt to the left or right is likely due to an attractive interaction between the BBO row of the substrate with the third  $\text{W}^{\text{VI}}$  ion of the trimer.

In conclusion, we have synthesized monodisperse oxide clusters supported on  $\text{TiO}_2(110)$  by using direct thermal evaporation of  $\text{WO}_3$ . On the basis of results from STM, XPS, and mass balance of deposited  $\text{WO}_3$ , we conclude that the clusters are cyclic  $(\text{WO}_3)_3$ . This conclusion is further supported by prior mass spectrometric, photoelectron spectroscopy, and density functional theory studies of tungsten trioxide gas-phase species.<sup>[20–22]</sup> The apparent similarity

between the supported and free  $(\text{WO}_3)_3$  clusters suggests stability and robustness, which may prove important for their use as model catalysts.

### Experimental Section

STM experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with an Omicron variable-temperature scanning tunneling microscope as well as apparatus for Auger electron spectroscopy and quadrupole mass spectrometry. The  $\text{TiO}_2(110)$  rutile single crystal ( $10 \times 5 \times 1 \text{ mm}^3$ , Princeton Scientific) was mounted on a standard Omicron single-plate tantalum holder and heated radiatively with a tungsten filament heater located behind the sample plate. The temperature dependence of the sample on heater power was calibrated in a separate experiment by using a  $\text{TiO}_2(110)$  crystal with a chromel–alumel thermocouple glued directly to the crystal surface. Well-ordered  $\text{TiO}_2(110)$  surfaces were prepared by using repeated cycles of Ar ion sputtering and UHV annealing at 900 K. All STM images (empty states) were taken at room temperature under tunneling conditions typical for  $\text{TiO}_2(110)$  imaging (+1.0–1.7 V, 0.1–0.2 nA). Prior to use, commercial STM tips (Tungsten, Custom Probe Unlimited) were cleaned by means of Ar sputtering and UHV annealing.

$\text{WO}_3$  was deposited by direct sublimation of  $\text{WO}_3$  powder (99.95%, Aldrich) onto  $\text{TiO}_2(110)$  at 300 K using a high-temperature effusion cell (CreaTec). The deposition flux ( $0.2\text{--}1.4 \text{ ngs}^{-1} \text{ cm}^{-2}$ ) was monitored with a quartz crystal microbalance (Inficon). The composition and oxidation state of evaporated tungsten oxide were determined in separate experiments conducted in a second UHV system equipped with an identical deposition setup, XPS apparatus, and other surface analytical tools described previously.<sup>[23]</sup> The W 4f XPS spectra (not shown) demonstrate that the tungsten in the deposited tungsten oxide is exclusively in the +6 oxidation state. Additionally, the W/O ratio in the W 4f and O 1s XPS peaks from the thicker films ( $\approx 50$  monolayers) is 1:3. From these data, we conclude, in agreement with prior mass spectrometric studies,<sup>[22]</sup> that only  $(\text{WO}_3)_x$  is sublimed.<sup>[21]</sup>

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