# Real Space Observation of Peroxide-like Dimers on a Sodium Tungsten Bronze Surface by Scanning Tunnelling Microscopy

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Oxygen dimers on the (2 × 1) reconstructed surface of $Na_{0.65}WO_3(001)$ have been observed by scanning tunnelling microscopy, with an O–O separation (2.2 Å) that is significantly less than twice the ionic radius of the oxide ion (2.8 Å).

The sodium tungsten bronzes are prototype metallic oxides adopting a cubic perovskite-like structure based on corner sharing $WO_6$ octahedra.[1] Along the [001] direction one finds alternating planes with stoichiometry $Na_xO$, $WO_2$, $Na_xO$ *etc.* and it is possible to envisage termination of the (001) surface in either type of plane. Cleaved or low-temperature annealed surfaces of tungsten bronzes exhibit a (2 × 1) superstructure in low energy electron diffraction which is generally attributed to sodium ordering in a somewhat sodium depleted $Na_{0.5}O$ surface layer.[2,3] However, there is growing evidence from techniques such as photoemission and high-resolution electron energy loss spectroscopy that oxidation of alkali metals adsorbed on metals[4,5] or oxides[6] may lead to the formation of surface peroxide species. This is hardly surprising given the stability of bulk peroxide phases for the Group 1 elements other than Li. The question naturally arises as to whether peroxide species may also form on the surface of ternary oxides containing alkali metals. In the present communication we apply the technique of scanning tunnelling microscopy to characterise the (2 × 1) surface structure of $Na_{0.65}WO_3$. Dimeric oxygen species are observed on the surface with an O–O separation of only 2.2 Å. This is less than twice the ionic radius usually assigned to $O^{2-}$ (2 × 1.4 Å = 2.8 Å) and suggests that there must be incipient bonding between the oxygen ions to produce peroxide-like surface species.

A high quality 1 × 1 $cm^2$ (001) oriented slice of a single crystal of $Na_{0.65}WO_3$ was used in the present investigation. Growth and characterisation of the crystal have been described in detail elsewhere.[7] *Ex situ* surface preparation involved polishing with progressively finer diamond pastes down to 1 μm, followed by ultrasonic rinsing in distilled water. STM experiments were carried out in an ion and turbomolecular pumped UHV system (base pressure $8 \times 10^{-11}$ mbar) equipped with an OMICRON STM microscope stage, OMICRON rearview LEED optics and CSA analyser and twin-anode X-ray source for XPS measurements. The sample was mounted on an Mo plate and held in position with strips of Ta foil spot-welded to the sample plate. The crystal surface was cleaned by annealing in UHV at elevated temperatures for periods typically of the order of 15 hours, heating being effected by radiative emission from a tungsten filament immediately behind the crystal plate. A chromel alumel thermocouple measured the temperature of the sample support plate. Microscope tips were prepared from 0.25 mm diameter polycrystalline tungsten wire as described previously.[8] The piezo drives in the microscope were calibrated from atomically resolved STM images of Si(111) (7 × 7) and Ni(110) (1 × 1).

Surfaces were cleaned in the UHV conditions of the microscope by annealing at elevated temperatures. Preparation of surfaces showing a well-defined (2 × 1) reconstruction required a delicate optimisation of conditions to ensure surface cleanliness, without subjecting the crystal to temperatures much above 650 °C: this results in loss of surface oxygen and formation of a ($\sqrt{2} \times \sqrt{2}$)R45° reconstruction.[7] Extended annealing at 600 °C produced surfaces with minimal levels of

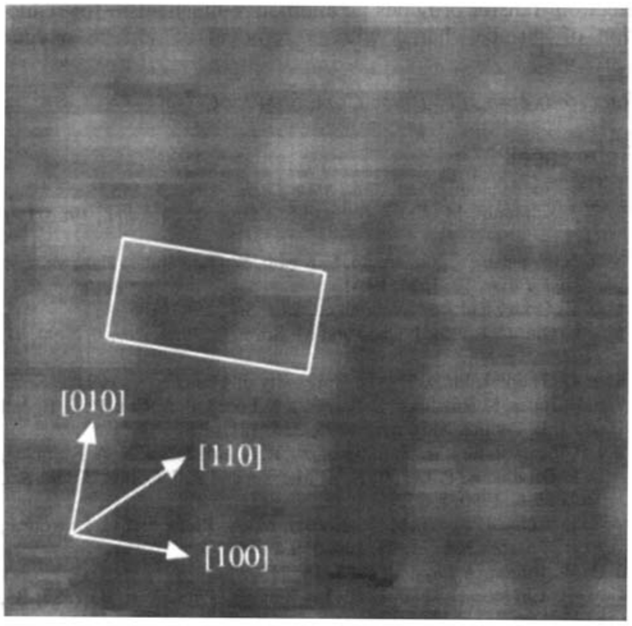

**Fig. 1** High-resolution 23 Å × 23 Å STM image of $Na_{0.65}WO_3(001)$ (2 × 1) taken at 1 nA tunnel current and +0.4 V sample bias (empty state image). Whereas the unreconstructed (001) surface would show a square array of topographic maxima, the image clearly shows a doubling of the periodicity along the [100] direction.

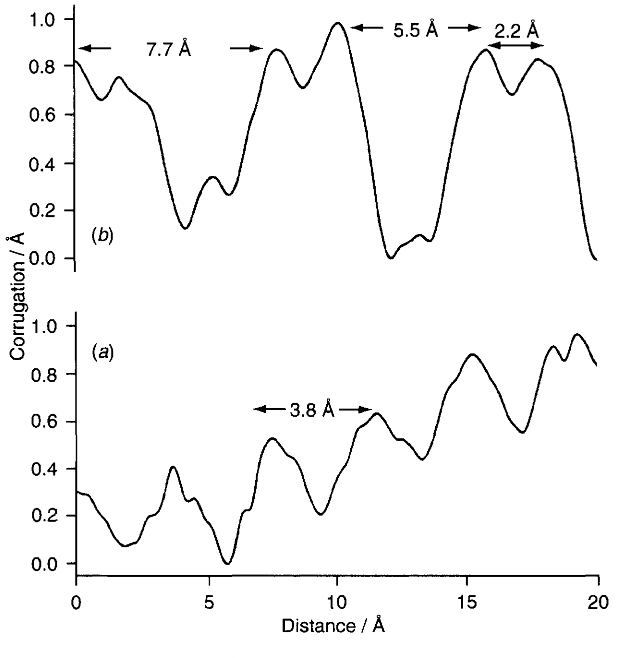

**Fig. 2** Corrugation profiles from image of Fig. 1. (*a*) Along [010] direction through ends of dimers. The average periodicity of 3.8 Å is close to the bulk lattice parameter of 3.839 Å. (*b*) Along [100] direction. The average periodicity is now 7.7 Å, with alternating separations of 2.2 and 5.5 Å between maxima.

surface carbon or other contaminants showing tolerably sharp LEED patterns with spots at ($m + 1/2$, $n$) and ($m$, $n + 1/2$), where $m$ and $n$ are integers, but with no spots at ($m + 1/2$, $n + 1/2$). This indicates that the surface should be dominated by atomically ordered terraces with orthogonal domains of (2 × 1) and (1 × 2) periodicity.

STM showed that the (2 × 1) surface still contained areas where atomic ordering was far from perfect. Boundaries between orthogonal (1 × 2) and (2 × 1) domains were also observed in many images, as well as areas showing higher-order reconstructions such as (2 × 2). However, the focus of the present communication is on details of the structure within the (2 × 1) domains. Fig. 1 shows a typical high-resolution image taken at +0.4 V sample bias and 1 nA tunnel current. Instead of the square array of topographic maxima expected for the unreconstructed (001) termination of a cubic perovskite-like material, the image clearly shows a doubling of periodicity along the [100] direction due to dimerisation of topographic maxima: corrugation profiles along the [100] direction reveal a dimer separation of only 2.2 Å, as compared with a unit-cell parameter of order 3.8 Å (Fig. 2). In addition the images contain topographic intensity between the dimer rows. The STM images of the present work show very much more pronounced anisotropy than those obtained by Rohrer and coworkers[9] from a $Na_{0.85}WO_3$ (001) surface prepared by cleavage in air followed by UHV annealing. The (2 × 1) periodicity in this earlier study was attributed to relaxation of oxygen ions in a $WO_2$ surface plane towards an ordered arrangement of Na ions in a subsurface $Na_{0.5}O$ layer.

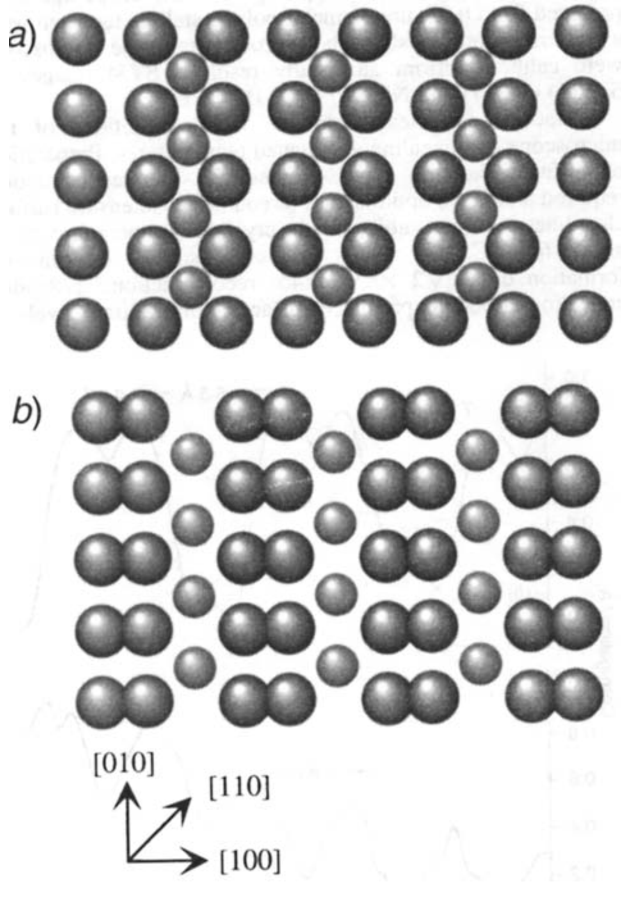

**Fig. 3** Schematic representation of $Na_{0.5}O$ plane on $Na_xWO_3(001)$. The ions are assigned the ionic radii tabulated by Shannon and Prewitt. Large ions are $O^{2-}$: small ions are $Na^+$. (*a*) Unrelaxed structure derived from bulk lattice parameter. (*b*) Relaxed surface structure deduced from STM image. The $O^{2-}$ ions are seen to overlap.

However, the lateral relaxation found in the present work is so extreme that there is no obvious way of reconciling the ionic packing in the $WO_2$ planes with the dimerisation evident from the STM images. We must therefore deduce that the images represent $Na_{0.5}O$ surface planes in which oxygen ions are displaced by 0.8 Å along the [100] direction, as shown schematically in Fig. 3, to double the surface periodicity. In this model the intensity between the dimer rows is attributed to ordered $Na^+$ ions. The density of states at the Fermi energy in $Na_{0.65}WO_3$ is localised mainly on the W ions, which one would thus expect to image in STM. However, band calculations by Bullett[10] and Christensen and Mackintosh[11] on hypothetical $NaWO_3$ indicate that there is significant mixing between O and W states at the Fermi energy giving the bulk electronic states around 20% O 2p atomic character. Moreover the mixing increases on moving up the conduction band into empty states. It is not therefore unreasonable to assign the maxima in the STM images to protruding O ions, as in the case of the $c(2 \times 2)$ reconstruction.[7] However, a problem with this model is that the O–O separation (2.2 Å) is less than twice the conventional ionic radius of $O^{2-}$ ($2 \times 1.4$ Å $= 2.8$ Å). An $(O^{2-})_2$ dimer has a formal valence electron configuration $\sigma_g{}^2\pi_u{}^4\pi_g{}^4\sigma_u{}^2$. The close approach of two $O^{2-}$ ions will raise the energy of the upper antibonding $\sigma_u$ orbital and if this level moves above the Fermi level there must be transfer of electron density out of this orbital. Note that this dimerisation will further enhance the oxygen partial density of states at the Fermi level. In the limit of complete transfer the electron configuration becomes $\sigma_g{}^2\pi_u{}^4\pi_g{}^4$ and the surface dimer is a peroxide species $O_2{}^{2-}$. However the bond length in true peroxides such as $Na_2O_2$ (1.49 Å) is much shorter than in the STM images so that we refer to the species as being peroxide-like, in the sense that there is only partial electron transfer out of the $\sigma_u$ orbital. A simple model for the driving force for the electron transfer out of the surface ionic plane can be developed with reference to the $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction which is formed by annealing at higher temperature.[7] Here we have argued that the large surface energy associated with the full formal ionic charge of 2− on an O layer outside a 2+ $WO_2$ layer is reduced by removal of half the surface $O^{2-}$ ions to generate the reconstruction. Dimerisation and electron transfer provides an alternative mechanism for reduction of surface charge without removal of surface oxygen ions.

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