

EXCITING CORNERS AND EDGES: NANOCHEMISTRY OF OXIDES

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We will consider the mechanisms of site-selective photo-stimulated chemical reactions and modification of oxide surfaces. Recent advances in Atomic Layer, Chemical Vapour, ballistic and other deposition techniques allow one to produce oxide nanoclusters and deposited ultra-thin films with unusual and interesting properties. The most technologically important systems include nanocrystalline thin films of so-called high-k oxides, such as HfO₂ and Hf silicates on silicon. Magnesia, alumina and silica nanoclusters and thin films on metal substrates have been studied for catalytic applications. Controlled manipulation of the physical and chemical properties of these nanostructured materials requires correlating their spectroscopic properties and reactivity with specific surface sites. One of the best studied wide-gap oxides remains MgO, which is widely used also as a substrate for metal cluster deposition and for growth many other materials. It has been demonstrated both experimentally and theoretically that one can selectively excite terrace, step and corner sites at MgO surfaces using well-defined photon energies [1]. Chemical Vapor Deposition in conjunction with subsequent thermal activation allows one to produce cubic MgO particles with average sizes in the range between 3 nm and 10 nm. Due to the dramatically enhanced concentration of corner and edge sites with distinct spectroscopic properties and reactivity, these particles represent a convenient model system for revealing physical and chemical properties of oxide nanostructures. In conjunction with theoretical modelling, they have been used for studying the surface topographic features, such as corners, kinks and edges [2]. These surface sites and their chemical reactivity have been characterized using a wide arsenal of optical, vibrational and electron spin resonance spectroscopies. Recently we combined selective photo excitation of the edge and corner sites at nanocluster surfaces with sequential exposure to H₂ atmosphere to achieve controlled modification of the electronic structure and chemical properties of MgO nanoclusters. On the basis of EPR data and theoretical modelling we identified a new type of a surface defects created as a result of photo-induced surface reactions at oxygen corners and describe their properties. The chemical modification of MgO nanocubes represents an example of electronic structure engineering where occupied as well as unoccupied electronic states appear in the band gap of MgO due to F(1), F(2) and (H⁺)(e⁻)(H⁺) centers. The concentration of these states can be regulated by the size and morphology of the MgO structures, the UV energy and fluence and by the concentration of

H[•] radicals available. This approach is expected to be generic for materials with strong OH⁻ bonds and can be used for modifying their properties.

Another powerful way of controlled surface modification is photo-desorption of surfaces. We will discuss and compare the mechanisms of photo-induced desorption of alkali halides and MgO. In a series of recent experimental and theoretical studies it has been demonstrated that photo-excitation of alkali halide surfaces with photons with specially tuned energies is accompanied by the hyper-thermal halide atoms desorption. The latter is induced by exciton decomposition at an alkali halide surface, which results in the formation of surface F centres and halogen atom desorption. Combining a sensitive detection technique and ab initio theoretical calculations we determined excitation energies of surface excitons in all alkali halides. It has been demonstrated that desorption produces single atom deep pits on these surfaces, which can be used e.g. for studying assembly or organic molecules.

Recently, the laser-induced desorption of oxygen atoms with hyperthermal velocities has been observed for the first time from thin MgO films. In contrast to alkali halides, magnesium atoms are also desorbed with hyperthermal velocities. To understand these results, we developed a two-step mechanism for oxygen and magnesium atom desorption from the MgO surface corners. The results of our calculations suggest that the first photon at *ca.* 3.5 - 4.5 eV creates a charge transfer exciton O⁻ ... Mg⁺. Similar excitons are formed at magnesium corners. However, the first excitation does not lead to desorption of neither oxygen nor magnesium ions. We demonstrate that surface excitons relax via radiative and non-radiative processes and predict the luminescence energies and barriers for thermal quenching. The exciton can be further excited at about 4.8 eV creating a bi-exciton, where the oxygen species becomes effectively neutral. The adiabatic potential energy surface for the second excited state is such that oxygen and magnesium atoms prefer to leave the surface with the maximum kinetic energy of several tenths on an eV. The results demonstrate the excitonic mechanism of desorption of low-coordinated sites at cubic oxide surfaces and open the way to sensitive chemical analysis and modification of these surfaces.

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[2] O. Diwald, M. Sterrer, E. Knözinger, P.V. Sushko, A.L. Shluger, *J. Chem. Phys.* 116 (2002) 1707.