# Defects on $TiO_2$ surfaces*

Annabella Selloni
*Department of Chemistry,*
*Princeton University,*
*Princeton, New Jersey 08544*
*USA*

Defects strongly affect the physical and chemical properties of metal oxide surfaces. Here we discuss two types of defects commonly found on oxide surfaces, step edges and oxygen vacancies. We report first-principles calculations of the structure, energetics, and chemistry of step edges on the (101) surface of $TiO_2$ anatase, an important photocatalytic material. A procedure based on systematic calculations of related vicinal anatase $TiO_2$ surfaces has been used, which yields step edge energies with remarkable accuracy. Oxygen vacancies on $TiO_2$ surfaces are experimentally found to introduce localized $Ti^{3+}$ $3d^1$ states about 1 eV below the conduction band. These states are not removed when water is dissociatively adsorbed at the vacancy and hydroxyl groups are formed. Calculations based on pure DFT functionals have not been able to satisfactorily reproduce these findings. We show that a correct description of the localized defect states on the reduced and hydroxylated rutile $TiO_2$(110) surface is achieved only if proper geometry relaxation is accounted for using hybrid exchange functionals.

* Work in collaboration with Xue-Qing Gong, *Department of Chemistry, Princeton University;* Cristiana Di Valentin and Gianfranco Pacchioni, *Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca*; Ulrike Diebold, *Department of Physics, Tulane University.*