

In 1972 Fujishima and Honda published the first significant breakthrough converting light into chemical energy. They reported the electrochemical photolysis of water assisted by a semiconductor under UV-A radiation<sup>i</sup>. However as of today, despite all the scientific advances it remains a significant challenge to construct a device capable of producing solar fuels, such as hydrogen, at a scale and cost-effective capable of competing with fossil fuels. The US Department of Energy declared that the price of hydrogen must be below \$3.3 kg<sup>-1</sup> (including production, delivery and dispensing) in order to compete with gasoline for passenger vehicles. Most developments are based on large band gap semiconductors' (> 3 eV), such as TiO<sub>2</sub>. The TiO<sub>2</sub> compound is the most commonly used photo-catalyst for the conversion of solar radiation into chemical bonds. While being very effective catalytic material, TiO<sub>2</sub> requires excitation in the UV-regime due to its wide band gap energy (ca. 3.2 eV). The common strategy for improving visible light absorption is via structural modification/doping aimed at diminishing the TiO<sub>2</sub> band gap energy. For this reason, TiO<sub>2</sub> is doped with 3d or light elements like N, C or S able to shift conduction or valence band edges and consequently lower the band gap energy. While the doping of TiO<sub>2</sub> provides increased visible light absorption, in many cases, this counteracts with the reduction or in extreme cases destruction of materials catalytic performance.

The project aims at studying TiO<sub>2</sub> surface/bulk electronic structure modified by carbon, nitrogen and sulfur doping. We will employ a methodology developed by us that combine resonant X-ray emission spectroscopy and theoretical approaches to determine lowest occupied and highest unoccupied Ti electronic states. Application of X-rays for this project is crucial in order to probe the electronic structure of Ti-site in a real catalytic environment, i.e., under reducing or oxidative atmospheres and at different operating temperatures. The in-situ X-ray spectroscopy will be used to disentangle the effects of doping not only on bulk Ti-electronic structure but also more importantly on Ti surface states. This knowledge is necessary to understand why the doping-induced effect of increased visible light absorption, in many cases does not translate to improved material's catalytic activity. Since the chemical efficiency is determined by number of surface states available for reactions, effects of doping on the surface electronic structure have to be thus determined. Disentangling surface and bulk contributions will allow for deep insight understanding of photo-catalytic properties of doped-TiO<sub>2</sub> and in consequence may help in future development of chemical or pharmaceutical applications.

<sup>i</sup> A. Fujishima, K. Honda, Nature 238 (1972) 37.