Metal nanoparticles supported on TiO$_2$ for photocatalysis: from nucleation to gas exposure

**Description du projet:** Titanium dioxide (TiO$_2$) is one of the most studied oxide material due to its extraordinary properties in various field, in particular photocatalysis. One of the main challenge is to improve the photoresponse of TiO$_2$ in the visible range in order to increase its photocatalytic activity when exposed to solar light. This has been recently achived by depositing noble metal nanoparticles having surface plasmon band, and particularly Au. Growth and nucleation of metal nanoparticles on the rutile polymorph r-TiO$_2$ have been widely studied. However, much less work has been devoted to the anatase a-TiO$_2$ polymorph, in spite of its much better photocatalytic activity. The purpose of the thesis is to follow the nucleation and growth of noble metal nanoparticles (Au, Cu) on a-TiO$_2$(101) surface, their stability upon gas exposure (O$_2$) and their photocatalytic activity for ethanol oxidation. Alcohol oxidation reactions are of great importance for producing carbonyl compounds used as versatile intermediates for the synthesis of fine chemicals.

The first part of the thesis will be devoted to the role of the surface defects on the nucleation. For r-TiO$_2$(110), we have precisely determined the influence of the different surface defects (oxygen vacancies, TiO$_x$ clusters) on the nucleation of Au and Cu [1]. On a-TiO$_2$(101) sub-surface oxygen vacancies are the most common defects. They can be brought at the surface by applying an electric field between the sample surface and the tip of a Scanning Tunnelling Microscopy (STM). The objective of this part is to use this phenomenon in order to vary the density of defects and determine how this density controls the nucleation rate of metal nanoparticles.

The second part of the thesis will be devoted to the stability of the particles towards heating and oxygen exposure. We have shown that Cu/r-TiO$_2$(110) nanoparticles dissociate upon O$_2$ exposure, but can be stabilized by adding a few percent of Au [2]. The comparison with a-TiO$_2$(101) will be very interesting since it will help understanding how the sintering of the particles depends on the structure of the substrate.

Eventually, the catalytic properties of the system will be tested for the oxidation of ethanol. Gas phase reactivity will be measured in the presence of UV-visible irradiation. The objective is to determine how the reactivity depends on the structural and electronic properties of the particles previously determined.

Experiments will be performed at INSP by in-situ STM, Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and mass spectrometry. They will take advantage of the use of an environmental-STM developed for *operando* studies under ambient gas pressure. They will be completed by synchrotron-based surface X-ray diffraction and photoemission experiments.


**Connaissances et compétences requises :** Knowledge of surface science basics, taste for experimental physics