Master thesis proposal

Laboratoire PMC
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Title: Infrared surface plasmons for modifying electrochemical reactions

Keywords: Infrared surface plasmons, vibrational coupling, reaction landscape, electrochemistry

Scientific description:

Chemistry under ultraviolet or visible irradiation allows an easier formation of the transition chemical state by direct electron transition into a higher molecular level, thus increasing the reaction rate. In the last decade, a major breakthrough in this field was made when it was demonstrated that performing the chemical reaction in an optical cavity tuned to one of the vibration energies of the molecules along the reaction path, a modification of the reaction rate occurs. Since all molecules have absorption bands in the infrared range with specific vibration energies, this exciting and highly original development gave birth to a new field and offers a wide range of possibilities not only in manipulating a chemical reaction but also in providing more insight into reaction mechanisms.

In this internship work, we aim to apply these concepts to *electro*chemical reactions. For this purpose, we propose to design plasmonic electrodes absorbing in the infrared range to enhance the infrared electromagnetic field and induce large vibrational coupling of the molecules with the plasmon mode. This coupling will take place at the electrode surface where the electrochemical reaction takes place. In order to efficiently couple vibrational plasmon modes at a surface, we propose to use ultrathin Au films of two kinds: films formed from densely packed monolayers of Au nanoparticles and an array of Au antennas. The films may be grown electrochemically or by evaporation in vacuum using microfabrication techniques. They will be deposited on a Si prism or hemisphere for backside illumination of the electrode by a tunable infrared source. In both electrode configurations, the electrochemical cell design allows for normal electrochemical operation with no limitation due to ionic diffusion or electrolyte conductivity. The Au ultrathin films will be electrochemically covered by an ultrathin layer of catalyst (e.g. Ir, Pt, Cu) which will be chosen as a function of the studied electrochemical reaction (Ir for oxygen evolution reaction, Pt and Cu for CO_2 reduction). These two electrochemical reactions are important for energy and CO_2 conversion. For the oxygen evolution reaction, we will focus on the OH and H_2O vibration modes and study how the vibrational coupling might influence the reaction rate. For the CO_2 reduction, we will be interested in the reaction products and focus on the CO vibration modes.

This work is inter-disciplinary and relies on experimental competencies from the fields of electrochemistry (sample preparation and electrochemical characterizations), analytical chemistry (infrared spectroscopy) and optics (plasmonic, vibrational coupling). It will benefit from the collaboration between a physics group and a chemistry group of the multidisciplinary PMC laboratory.

Techniques/methods in use: plasmonic sample preparation, infrared spectroscopy coupled to infrared lasers, atomic force microscopy, electrochemical measurements
Applicant skills: background in optics and physical chemistry, instrumentation
Industrial partnership: N
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Possibility for a Doctoral thesis: Y (ANR project)