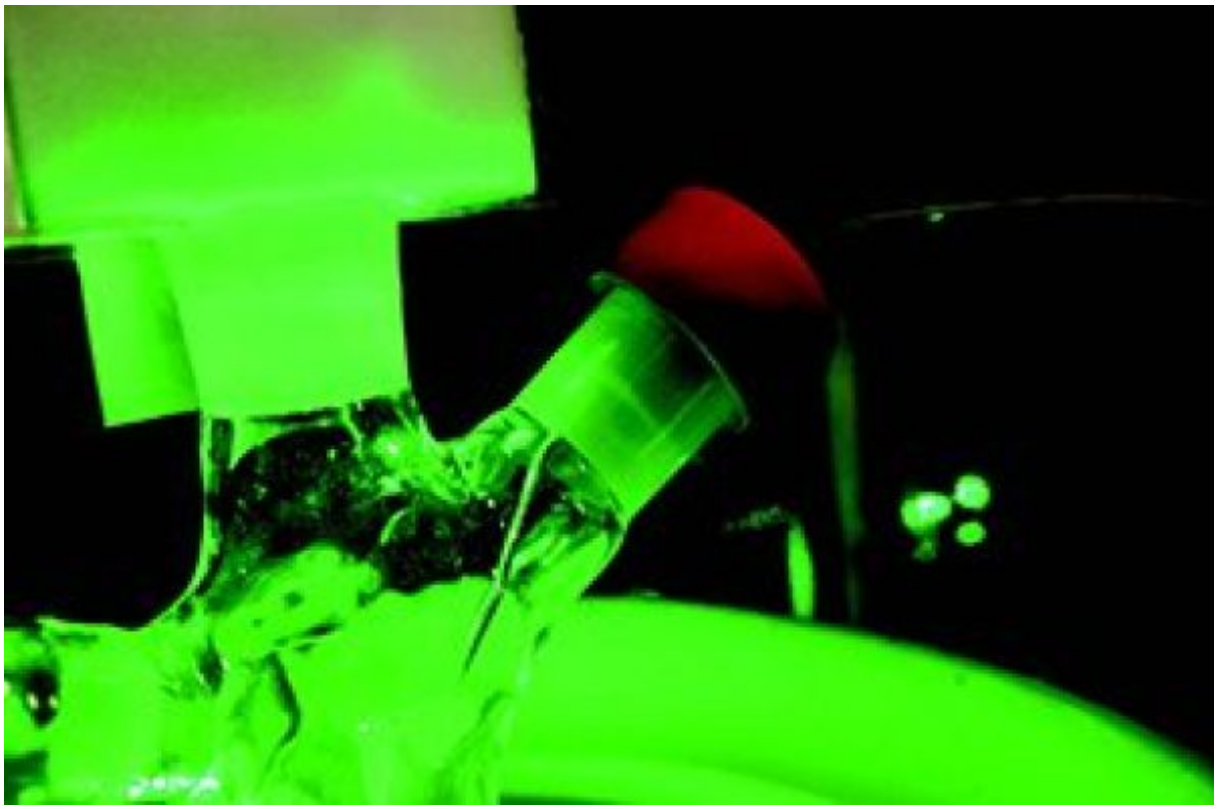

PhD THESIS DEFENSE: Discerning between thermal and electronic effects in plasmonenhanced organic reactions

IVAN BORDACCHINI

October 30, 2020

11:00

ICFO Auditorium and Online (Teams)

Since the pioneering work of Fujishima and Honda on titanium dioxide, TiO2, for the electrochemical photolysis of water under ultraviolet (UV) irradiation, semiconductor-based photocatalysis and photovoltaics have become a rapidly growing field of investigation. However, UV light accounts for only 4% of the solar spectrum, whereas the visible light represents 42% of the total solar radiation. Therefore, the scientific community focused their efforts on the optimization and extension of the absorption spectrum of semiconductor-based materials to the visible region of the solar spectrum. Well-established techniques include doping of the semiconductor or the deposition of a different element or

substance on the surface of the material.
Since 2004, the deposition of plasmonic nanoparticles (NPs) on semiconductors emerged as a possible solution to generate energetic electrons capable of driving reactions under visible irradiation. Since then, numerous contributions have been published in the field of plasmon-enhanced photocatalysis with relevant applications in water splitting, organic synthesis, and photovoltaics.
In the field of heterogeneous photocatalysis, plasmon-generated energetic electrons were widely accepted as responsible for the observed catalytic effect of plasmonic NPs. Recently, several scientific contributions have questioned the actual mechanism triggering plasmon-enhanced reactions, hypothesising that thermal effects are instead the predominant factor that influences the activity of a plasmonic catalyst.
In this work, we aimed at differentiating between the thermal and electronic effects of plasmonic NPs in a test reaction-the reductive coupling of nitrobenzene to azobenzene-under irradiation with 532 nm and/or 875 nm lasers. Moreover, we also aimed at developing a methodology that could be easily replicated in other laboratories and used as a benchmark test for plasmon-enhanced reactions run in solution.
We optimized the size and shape of AuNPs plasmonic catalysts to obtain materials with different absorption in the visible and near-infrared (NIR) region to tune the electronic and thermal effects of the catalyst. The activity of the synthesised catalysts for the test reaction was compared with the activity of the Gold World Council reference catalyst type A.
Characterization of the synthesised Au/TiO2 catalyst with diffuse reflectance measurements evidenced that the presence of small amounts of AuNPs did not modify the band gap position of the support, hence suggesting that, under visible light irradiation, the catalysis occurred on the surface of the AuNPs. The determination of the enthalpy of activation for each step of the reaction showed that the second step of the reaction was strongly influenced by the 532 nm laser irradiation. Indeed, our calculations demonstrated an energy difference between the illuminated and the dark reactions in the first step of reaction of 1,1kal mol-1 whereas the one for the second step was 1,1kal mol-1.
We further analysed the results of designed experiments running the test reaction in the presence of two catalysts differing by the shapes of the AuNPs and under different laser sources and irradiances. The results were processed to obtain predictive phenomenological models for the intermediate and the product of the reaction, azoxybenzene and azobenzene, respectively.
The obtained models allowed to confirm that the investigated reaction was triggered by electronic effects and that the contribution of thermal effects, generated by the electron-phonon decay of elongated AuNPs, was not significantly influencing the reaction outcome.

Due to recommendations in place to contribute containing the spreading of COVID-19, th

defence will be carried out semi presencial with a maximum of 66 Icfonians in t
e Auditorium, and partly remotely via MS Teams. This is the link to follow the Thesis Defe
se online: Join Microsoft Teams Meeting

If you are interested in attending in person, please address your request to mery.gil@icfo.eu by Wednesday October 28.

Friday October 30, 11:00, MsTeams - Auditorium

Thesis Advisor: Prof Dr Romain Quidant

Hosted by: HRE

Ivan Bordacchini's Thesi Cover