

VISTA Seminar

Seminar 60

November 22, 2023

**10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT London / 4:00 pm –
5:30 pm CET Paris / 11 pm CST Beijing**

TOC:

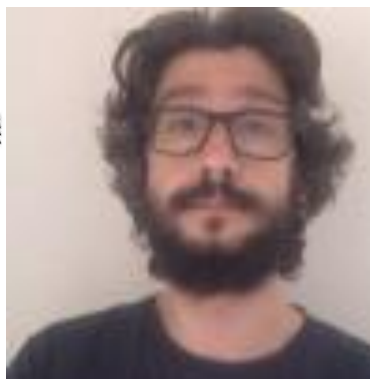
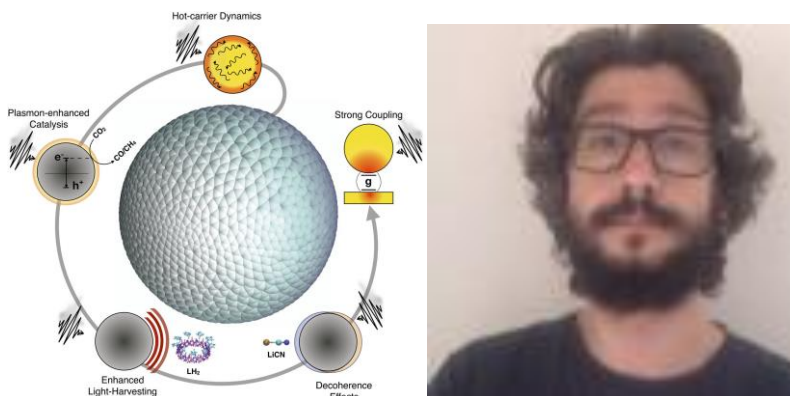
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Recent advances in modelling plasmon-assisted electron dynamics

Emanuele Coccia

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Italy

Email: ecoccia@units.it



Molecular nanoplasmonics [1] exploits collective electron excitations in metal nanostructures to enhance and control properties of molecules under the influence of light. Different theoretical communities contributed to this interdisciplinary research field over the last years, with the aim to interpret and predict the physico-chemical phenomena occurring at the molecular- and nanoscale. In particular, the fast and ultrafast electronic response of the composite system, i.e., molecule+nanostructure, is a key aspect allowing one to understand experimental findings. Here I will present two recent applications, based on time-resolved methods, which emerged as ideal tools to study the photoinduced plasmon-assisted electron dynamics in molecule+nanostructure systems [2]. Plasmonic-driven photocatalysis may lead to reaction selectivity that cannot be otherwise easily achieved. A fundamental role is played by hot carriers, i.e. electrons and holes generated upon plasmonic decay within the metal nanostructure that can interact with molecular species. In the case of carbon dioxide reduction, it was experimentally shown [3] how in presence of a rhodium nanocube the photo-induced process selectively produces methane against carbon monoxide as opposed to the thermal reaction pathway. By means of a state-of-the-art multiscale modelling approach going beyond density functional theory description, we show that selectivity in this prototypical reaction is due to hole injection from the rhodium nanoparticle to the reaction intermediate CHO, that enhances the reactivity [4]. The second example is about giant enhancement of electronic circular dichroism signal of chiral molecules (methyloxirane and [4]helicene), driven by plasmonic effects [5]: such an enhancement is rationalized in terms of plasmonic field, gap between plasmon and molecular excitation, and favorable coupling with pulse polarization.

References:

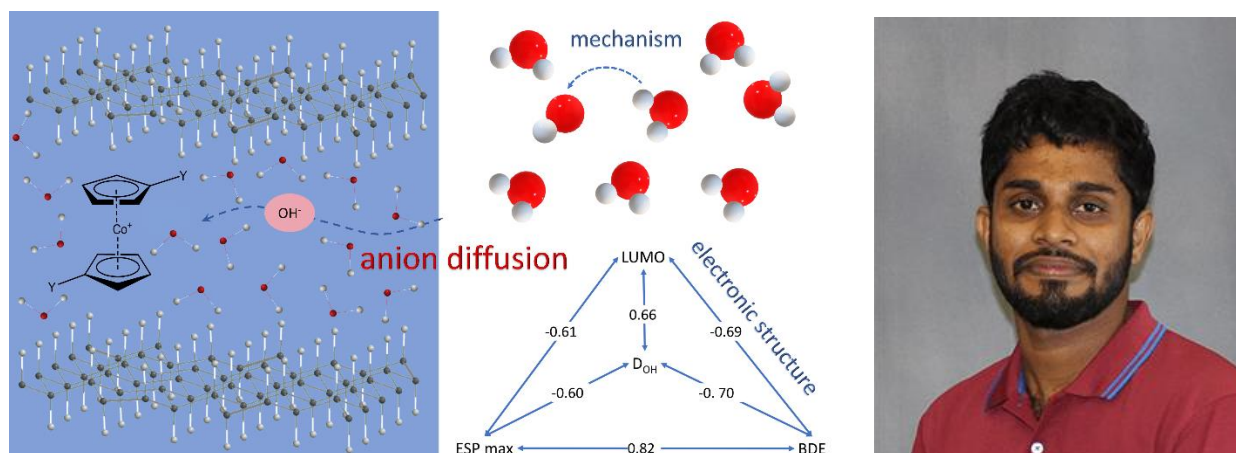
- [1] A. Lauchner *et al.*, *Nano Lett.*, **15**, 6208 (2015)
- [2] E. Coccia, J. Fregoni, C. A. Guido, M. Marsili, S. Pipolo and S. Corni, *J. Chem. Phys.*, **153**, 200901 (2020)
- [3] X. Zhang, X. Li, D. Zhang, N. Su, W. Yang and H. Everitt, *Nat. Commun.*, **8**, 14542 (2017)
- [4] G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and E. Coccia, submitted
- [5] L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and E. Coccia, submitted

Theoretical Examination of the Hydroxide Transport in Cobaltocenium-Containing Polyelectrolytes

Sachith Wickramasinghe

University of South Carolina, SC, USA

Email: sachith@email.sc.edu



Polymers incorporating cobaltocenium groups have received attention as promising components of anion-exchange membranes (AEMs), exhibiting a good balance of chemical stability and high ionic conductivity. In this work, we analyze the hydroxide diffusion in the presence of cobaltocenium cations in an aqueous environment based on the molecular dynamics of model systems confined in one dimension to mimic the AEM channels. In order to describe the proton hopping mechanism, the forces are obtained from the electronic structure computed at the density-functional tight-binding level. We find that the hydroxide diffusion depends on the channel size, modulation of the electrostatic interactions by the solvation shell, and its rearrangement ability. Hydroxide diffusion proceeds via both the vehicular and structural diffusion mechanisms with the latter playing a larger role at low diffusion coefficients. The highest diffusion coefficient is observed under moderate water densities (around half the density of liquid water) when there are enough water molecules to form the solvation shell, reducing the electrostatic interaction between ions, yet there is enough space for the water rearrangements during the proton hopping. The effects of cobaltocenium separation, orientation, chemical modifications, and the role of nuclear quantum effects are also discussed.¹

References

- 1) DOI: 10.1021/acs.jpcc.3c04118

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 60

Time: Nov 22, 2023 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting

<https://buffalo.zoom.us/j/93146691375?pwd=Q1pPQUNPT010a29xcHILNlAyazZlZz09>

Meeting ID: 931 4669 1375

Passcode: 906368