Local in situ chemical mapping of hot carrier-driven catalysis with plasmonic nanosystems

Olivier Henrotte and Alberto Naldoni

1. Czech Advanced Technology and Research Institute, Regional Centre of Advanced Technologies and Materials Department, Palacký University Olomouc, Šlechtitelů 27, Olomouc 78371, Czech Republic
2. Department of Chemistry and NIS Centre, University of Turin, Turin 10125, Italy
E-mail: olivier.henrotte@upol.cz

Plasmonic photocatalysis received soaring interest due to the possibility of using plasmonic effects to enhance reactions rates or activate non-trivial reaction pathways [1]. Under light irradiation, surface plasmons (SPs) decay by generating non-thermal (hot) electron-hole pairs having enough energy to drive chemical reactions. Many research efforts revealed the importance to investigate the nanostructure/molecule interactions at the nanoscale to unravel the lush applicability provided from plasmon-driven photocatalysis [2-4]. Nevertheless, a methodology unlocking the local in situ mapping of chemicals produced through plasmon-driven reactions is still absent.

Herein, we present an original methodology to scan locally the material morphology, optical properties and in situ photoactivity applied on plasmonic nanostructures (Fig. 1.a). Scanning electrochemical microscopy (SECM) enables 2D quantitative mapping of plasmon-driven reaction products. The collected data coupled with diffusion model allow to compute external quantum efficiency (EQE) maps (Fig. 1.b). The methodology elucidates structure-activity relationships at the origin of the plasmonic activity (Fig. 1.c).

The presented results are set up on a reference model including Au NPs deposited on a semiconductor/charge collector substrate formed by a TiO2/ITO substrate, which is already well-referenced in the literature [5]. Ultimately, we aim to shed light on the correlation between the system properties (e.g. size, shape, composition, interface and embedding media) and its activity at the nanoscale as illustrated through the study of a single TiO2 nanotube decorated with a gradient of Au NPs (Fig. 1.d,e).

References