

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

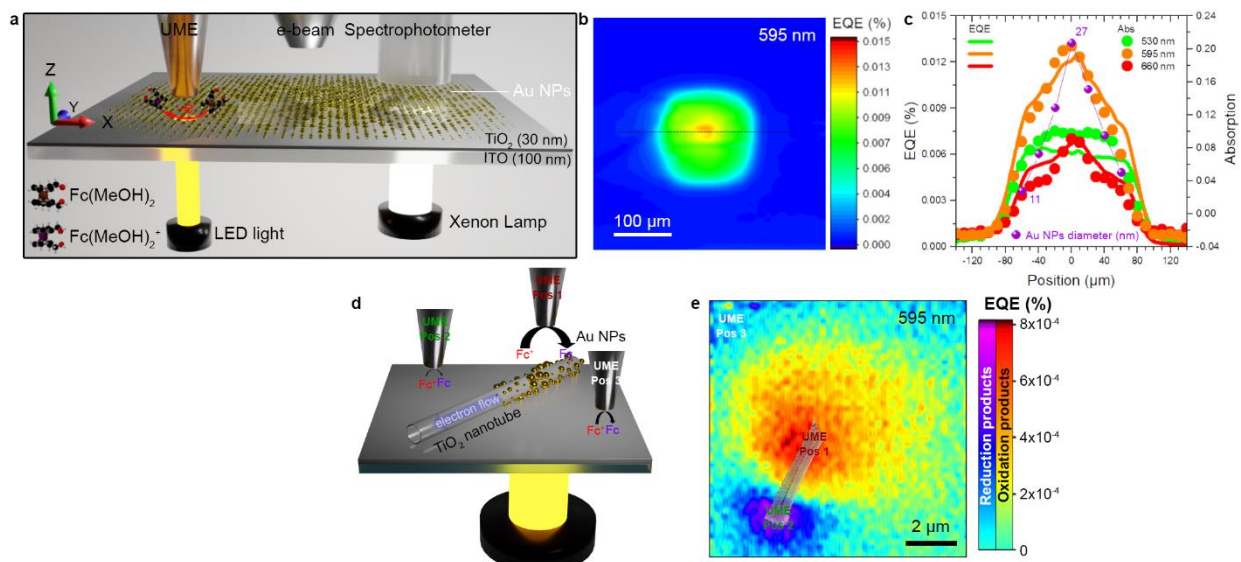
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Plasmonic photocatalysis received soaring interest due to the possibility of using plasmonic effects to enhance reactions rates or activate non-trivial reaction pathways [1]. Under light irradiation, surface plasmons (SPs) decay by generating non-thermal (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).



**Fig. 1** (a) Representation depicting the scanning techniques used to investigate the morphological, optical and photochemical properties of plasmonic planar Au/TiO<sub>2</sub> systems. (b) External quantum yield (EQE) map at 595 nm for planar Au/TiO<sub>2</sub>. (c) EQE (left axis, solid lines) along with absorption (right axis, filled circles) for the same line scan position in (b) at different wavelengths overlaid by the mean diameter of the Au NPs within the array (purple spheres). (d) Scheme of the investigation of a single TiO<sub>2</sub> nanotube partially covered by Au NPs. (e) EQE map at 595 nm for a single TiO<sub>2</sub> nanotube partially covered by Au NPs. The overlaid SEM image in (e) represents the investigate nanostructure.

The presented results are set up on a reference model including Au NPs deposited on a semiconductor/charge collector substrate formed by a TiO<sub>2</sub>/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 TiO<sub>2</sub> nanotube decorated with a gradient of Au NPs (Fig. 1.d,e).

## References

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