

Coupling plasmonics and electrochemistry on gold nanoparticle-modified electrodes. Toward a new spectroelectrochemical approach of gold plasmonic tunability under electrochemical control

Vincent Wieczny,^a Stephania Rodríguez Muiña,^{a,b} Christophe Bonnet,^b Frédéric Chaput,^a
Michel Pellarin,^b Emmanuel Cottancin,^b Christophe Bucher^a and Frédéric Lerouge^a

^a *Laboratoire de Chimie – UMR 5182 – CNRS, ENS de Lyon, Université Lyon 1, Ecole Normale Supérieure de Lyon, France*

^b *Institut Lumière-Matière – UMR 5306 – CNRS, Université Lyon 1, Université Lyon 1, France*

vincent.wieczny@ens-lyon.fr

In the last few years, coupling gold plasmonic nanomaterials and electrochemistry contributed to the emergence of new applications upon electrochemical stimulation in the field of plasmon-induced phenomena such as molecular catalysis or sensing. (1) As an indirect effect, applying an electrochemical potential on gold plasmonic nanosystems results in a reversible tunability of their plasmonic signature. (2) However, the underlying mechanisms remain poorly investigated. Thereby, we developed multifunctional plasmonic transparent electrodes from gold nanoparticle suspensions (Figure), allowing spectroelectrochemical analyses. (3) Anisotropic gold nanostructures such as nanobipyramids and nanorods were considered together with nanospheres. Gold nanoparticles exhibit a specific and reversible potential-dependent plasmonic response in aqueous medium. Gold plasmons can be tuned on tenths of nanometers, without any change of geometry. A systematic correlation between spectroscopic and voltamperometric data resulted in a plasmonic hysteretic and stepped modulation in phase with the electrochemical gold activity (Figure). A methodological approach coupling spectroelectrochemical and XPS measurements with finite-element simulations confirmed a process controlled by successive gold oxidation/reduction steps at the nanoparticle surface, layer by layer. Spectroelectrochemical analyses on gold nanoparticles were successfully extended to detect low-concentrated metallic elements at their surface, such as silver, which open new perspectives, for instance, in the understanding of growth mechanism of gold nanoparticles.

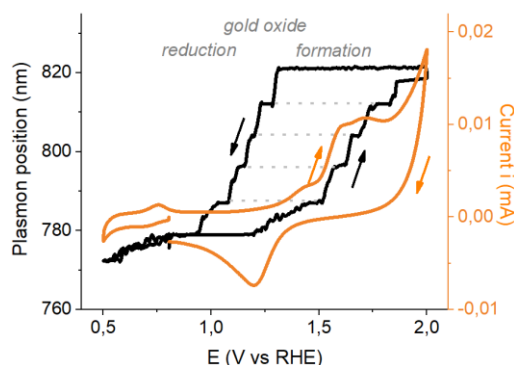
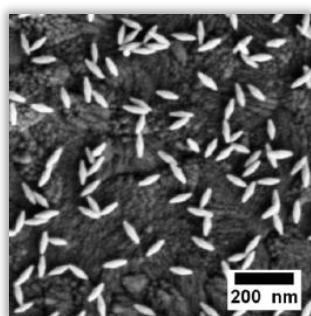


Figure. Electrochemically driven tunability of gold nanobipyramid (AuBP) plasmonic response

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Electrochemiluminescence Imaging of a Confined Enzymatic Reaction and Membrane Permeabilization of Giant Liposomes

Fatma Ben Trad,^a Bixente Carré,^a Vincent Wieczny,^a Jérôme Delacotte,^a Mathieu Morel,^a Manon Guille-Collignon,^a Stéphane Arbault,^b Frédéric Lemaître,^a Neso Sojic,^c Eric Labbé,^a Olivier Buriez^a

^a PASTEUR, Département de Chimie, Ecole Normale Supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France.

^b Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248 CNRS, F-33600 Pessac, France.

^c University of Bordeaux, CNRS, Bordeaux INP, ISM, UMR CNRS 5255, 33607 Pessac, France.

Various analytical approaches mainly based on fluorescence or/and electrochemical techniques have been developed to detect and analyze molecular fluxes across membranes [1]. In this context, we recently developed an original approach based on electrochemiluminescence (ECL) allowing imaging of liposome permeabilization processes triggered either by electroporation [2] or by an antimicrobial peptide [3]. The strategy consisted first in the encapsulation of ECL reagents ($[\text{Ru}(\text{bpy})_3]^{2+}$ and tripropylamine (TPrA) used as co-reactant) in sealed giant asymmetrical liposomes (100 μm in diameter) made of DOPG/DOPC phospholipids. Then, liposome permeabilization was triggered at the surface of a conductive and transparent ITO electrode, allowing the electrochemical oxidation of the content and the visualization of the leaking process. The simultaneous ECL, photoluminescent and amperometric monitoring provided information on the liposome shape during permeabilization, the assignment of the corresponding signals to a specific liposome, as well as the quantification of the TPrA released. This original approach was also recently successfully used to image a NADH-based enzymatic reaction confined within giant liposomes (Figure 1) [4]. This has also shown that NADH can be used instead of TPrA as a biologically compatible ECL co-reactant.

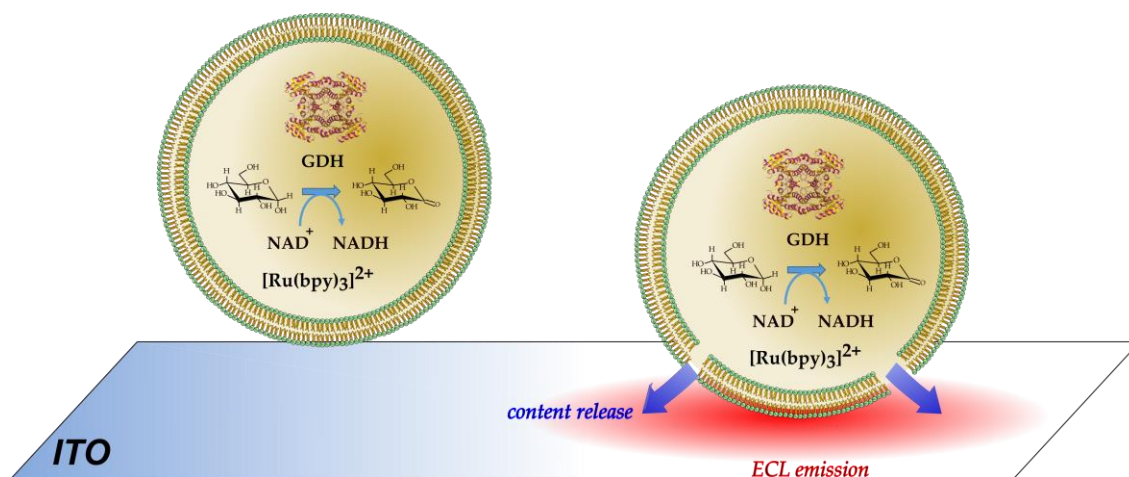


Figure 1. ECL imaging of the transient release by a liposome in which GDH catalyzes the oxidation of glucose concomitantly with the reduction of NAD^+ to NADH. ECL emission from the $[\text{Ru}(\text{bpy})_3]^{2+}$ luminophore occurs at the ITO electrode surface upon the opening of the liposome.

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Solar-assisted electrochemical CO₂ conversion on Silicon photocathodes decorated with bimetallic nanocatalysts

E. Torralba, H. Chaliyawala, K. Bah, C. Cachet-Vivier and S. Bastide

Institute de Chimie et Matériaux Paris-Est, 2-8 rue Henri-Ducloux, 94320 Thiais, France

E-mail : encarnacion.torralba-penalver@cnrs.fr

The continuous increase in atmospheric CO₂ emissions from the massive use of fossil fuels is responsible for global warming and related environmental problems. Reducing these emissions is therefore a major challenge for our societies at the heart of international climate policy. At ICMPE, we aim to develop innovative materials for the photoelectrochemical reduction reaction of CO₂ (PEC-CO₂RR), a promising technology that enables the conversion of CO₂ into high-energy molecules (e.g. CH₄), also known as solar fuels. It uses semiconductors as photoactive platforms and solar radiation as renewable energy input [1]. To scale up this technology, several key issues need to be addressed, including photoelectrode material and geometry, catalyst activity, selectivity and stability, and reactor design.

In this communication, we will present some of our recent results on the synthesis of M_xCu_{100-x} decorated Si photocathodes and their application to PEC-CO₂. Si is a photoelectrode material of choice due to its absorption in the Vis-NIR region and mature processing. Bimetallic catalysts allow tuning the activity and selectivity of electrocatalytic reactions by playing on the adsorption energy of key reaction intermediates. Despite its interest, very little work has been devoted to the PEC-CO₂RR on bimetallic-decorated Si supports and even less on 3D photoelectrodes [2]. The bimetallic systems selected are PdCu and AgCu, identified as promising catalysts for the CO₂RR [3,4]. As electrode geometries, flat Si and arrays of Si micropillars (SiMPs) are mainly considered. Finally, an original methodology based on metal-assisted chemical etching (MACE) is proposed as a synthesis procedure.

Physical characterizations (SEM-EDX, XPS and TEM) indicate that the chosen methodology allows precise control of the nanoparticle bimetallic composition and structure (e.g. Pd_xCu_{100-x} solid solution or phase-separated nanoparticles can be synthesized at will [5]). For the 3D electrodes, a homogeneous coverage over the whole length of the Si micropillars is achieved, highlighting the interest of the proposed method for high aspect ratio structures. J-V characteristics measured under CO₂ and under solar illumination show a photocurrent enhancement for SiMPs over flat Si due to lower reflectivity losses in the SiMPs array and the increased surface area in contact with the electrolyte. Long-term electrolysis coupled with stability tests show the synergy of the AgCu system to guide the selectivity towards high density energy products [6], but a significant disaggregation of the bimetallic nanoparticles as a result of the PEC-CO₂RR. Equivalent studies with the PdCu system are ongoing.

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Etude à l'échelle microscopique de l'électrofluorochromisme de dérivés tétrazines induit par résonance plasmonique

Baptiste MAILLOT¹, Ali DABBOUS¹, Jean-Frédéric AUDIBERT¹, Vitor BRASILIANSE¹ et Fabien MIOMANDRE¹

¹ENS Paris-Saclay, PPSM

4 avenue des sciences, 91190 Gif-sur-Yvette, France

E-mail : baptiste.maillot@ens-paris-saclay.fr

Les nanoparticules plasmoniques à base de métaux nobles possèdent d' uniques propriétés optiques, notamment une résonance plasmon localisée de surface dans le visible permettant la génération de porteurs de charge dits « chauds » par l'intermédiaire d'une excitation lumineuse. Les propriétés particulières de ces nanoparticules leur ouvrent de nombreuses applications dans des domaines très variés tels que l'imagerie, les capteurs, la photocatalyse ou encore le stockage d'énergie [1], [2].

Dans cette étude, des nanoparticules d'or plasmoniques sont électrodéposées sur des plaques d'ITO et des dérivés tétrazines (Figure 1.A) sont utilisés en tant que sonde électrofluorochrome pour étudier les effets photoélectrochimique induits par résonance plasmonique. Ces phénomènes sont étudiés grâce à une instrumentation dédiée constituée d'un microscope de fluorescence combiné avec un microscope électrochimique à balayage (SECM). Un laser focalisé sur la surface du substrat permet d'exciter la résonance plasmon des nanoparticules (Figure 1.B).

Deux dérivés tétrazines sont utilisés pour sonder les effets rédox en solution [3] ou directement sur la surface des nanoparticules via une monocouche greffée [4]. Dans les deux cas, les dérivés tétrazines ont permis d'attester de l'efficacité des trous créés par excitation plasmonique pour induire des réactions d'oxydation. Sous excitation plasmonique, le courant de la pointe du microscope électrochimique est modifié et l'intensité de fluorescence de la tétrazine est simultanément réduite (Figure 1.C) en accord avec un processus d'oxydation au niveau des nanoparticules. Les paramètres expérimentaux tels que le potentiel appliqué à la pointe du microscope électrochimique, la puissance du laser d'irradiation ou encore l'alignement entre la pointe et le laser ont été étudiés. Cette étude a permis de déterminer que le transfert de trous était le mécanisme dominant dans nos systèmes.

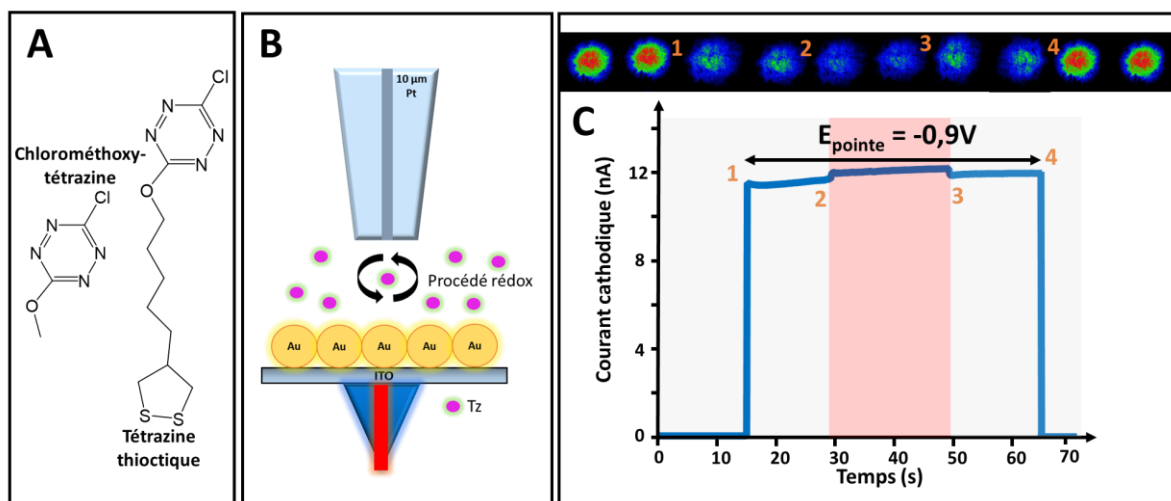


Figure 1 : A) Structure des tétrazines utilisées. B) Schéma du dispositif expérimental utilisé pour les mesures électrochimiques. C) Couplage entre signal électrochimique et signal de fluorescence lors de l'excitation plasmonique du substrat.

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Operando infrared spectroelectrochemistry reveals the existence of Fe-CO intermediates during CO₂ reduction to CO catalyzed by an Fe porphyrin

Aude Salamé,^a Michael Cheah,^b Julien Bonin,^a Marc Robert ^{a,c} and Elodie Anxolabéhère-Mallart ^a

^a Université Paris Cité, CNRS, Laboratoire d'Electrochimie Moléculaire, Paris, France

^b Molecular Biomimetics, Department of Chemistry, Uppsala University, Uppsala, Sweden

^c Institut Universitaire de France (IUF), Paris, France

aude.salame@u-paris.fr

Iron porphyrins are a type of catalyst that can facilitate the electrochemical reduction of carbon dioxide (CO₂). These catalysts commonly produce carbon monoxide (CO) and hydrogen (H₂) as reduction products, with the selectivity depending on the porphyrin structure used. The direct production of CO from CO₂ and green electricity is a significant environmental concern and plays a key role in the development of a circular economy based on CO₂ recycling. Despite the established efficiency of these catalysts, there is a need to understand the reaction mechanism in order to optimize their activity and stability.

We focus on [(pTMA)Fe^{III}-Cl] porphyrin catalyst (**Fig. 1, left**), known to selectively convert CO₂ into CO.^{(1),(2)} Spectroelectrochemistry (SEC), is a powerful tool to elucidate this mechanism.^{(3),(4)} Our collaboration with Uppsala University resulted in the development of a unique high-pressure SEC cell which allowed us to carry out operando infrared SEC experiments under CO₂ atmosphere and to obtain Fe-CO signatures (**Fig. 2, right**). The precise assignment of these bands is enabled through thorough exploration with comparable experiments under CO atmosphere, allowing a detailed catalytic cycle to be established.

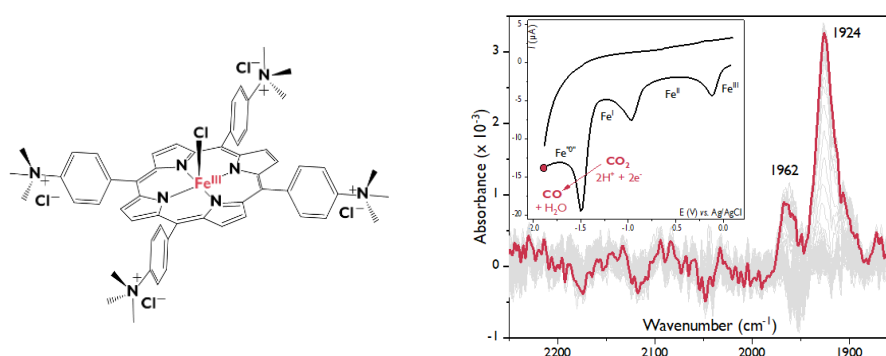


Figure 1. Left. Structure of [(pTMA)Fe^{III}-Cl]. Right. IR SEC spectrum obtained during CO₂ reduction to CO catalyzed by [(pTMA)Fe^{III}-Cl].

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Photoelectrocatalytic urea oxidation at silicon photoanodes

Joudi Dabboussi,^a Didier Floner,^a and Gabriel Loget^b

^a *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR6226, Rennes, F-35000, France.*

^b *University of Bordeaux, Bordeaux INP, ISM, UMR CNRS 5255, 33607 Pessac, France.*
Joudi.dabboussi@univ-rennes1.fr

Photoelectrochemical splitting of water into hydrogen (H₂) fuel is a sustainable way to meet energy demands without harming the environment. However, there are significant challenges associated with this approach. One such challenge is the low stability of narrow bandgap semiconductors, like Si when immersed in solution, and the requirement of interfacial catalytic layers that can impede light absorption. While coating the semiconductor with a catalyst layer can protect the electrode from deactivation, it may also reduce the flux of photons reaching the absorber, significantly reducing performance in a front-illumination configuration. Another challenge of electrochemical water splitting is the sluggish anodic half-reaction (oxygen evolution reaction, OER), which requires a considerable overpotential and yields a low-value product (O₂) already present in the air.

Replacing the OER with the thermodynamically more favorable urea oxidation reaction (UOR) offers the prospect of energy-saving H₂ production, along with urea-rich wastewater purification. In this presentation, we report the deposition of highly active and stable Ni-Mo-O (NMO) coatings (1) onto metal/insulator/semiconductor (MIS) *n*-Si/SiO_x/Ni junctions using a simple hydrothermal method.(2,4)These findings were completed by a complementary approach involving an electrolytic cell comprising efficient UOR and HER catalysts, connected to an external photovoltaic cell.

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Energy-storage smart windows based on the Zn/Prussian blue assembly

Renald Sangarane,^a Benoît Limoges,^a and Véronique Balland^a

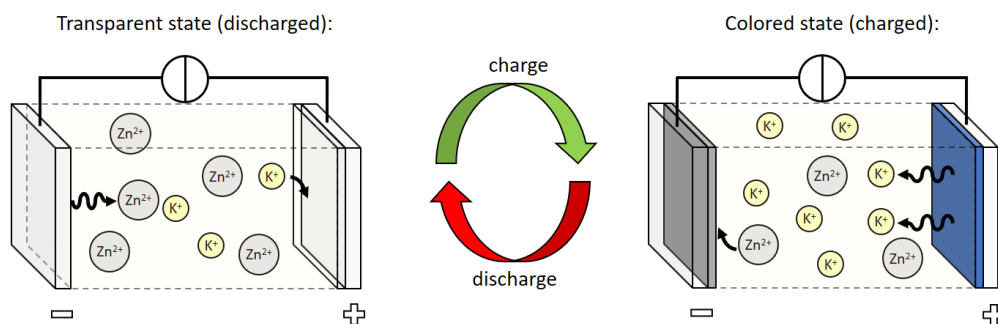
^a Université Paris Cité, Laboratoire d'Electrochimie Moléculaire
15, rue Jean-Antoine de Baïf, 75013 Paris, France
Email: renald.sangarane@u-paris.fr

Bifunctional smart windows, combining charge storage and electrochromism, are gaining interest in the field of energy self-sufficient buildings.⁽¹⁾ They offer an alternative to the current smart windows, so far predominantly based on electrochromic material such as metal oxides (*e.g.*, WO₃ and NiO_x), which also have the inconvenience to consume energy during their coloring/bleaching roundtrip. Thus, the use of bifunctional smart windows will permit improvement of the building's energy efficiency, by allowing the recovery of a large part of the energy stored upon charge.

In this context, we aim to develop bifunctional smart windows capable of coloring upon charge and relying on abundant and non-toxic materials. The choice of aqueous-based electrochromic devices exploiting the Zn²⁺/Zn couple at the negative electrode and the Prussian blue (PB)/Prussian white (PW) couple at the positive electrode fulfills these criteria, while delivering a reasonable voltage of ~1.2 V upon discharge.^{(2),(3)} In order to improve the device performances compared to the state-of-the-art regarding both energy density, optical contrast and scalability, our original approach consists of :

- (1) increasing the surface capacity by increasing the amount of PB film reversibly cycled. This was achieved by electrodepositing PB on high-surface area nanostructured transparent electrodes.
- (2) exploiting the electrochromic properties associated with reversible Zn electrodeposition at a transparent electrode, further enabling the face-to-face assembly of two electrochromic electrodes for greater optical contrast and optimized field lines, as depicted in Scheme 1.

In this presentation, we will discuss the preparation, construction and spectroelectrochemical characterization of various Zn/PB smart windows assemblies, as well as their performances.



Scheme 1. Bi-functional device combining reversible zinc electrodeposition at a transparent negative electrode and reversible cycling of Prussian blue at the positive electrode.

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