



**Gold 2018**

July 15-18, 2018 - Paris, France

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Ultrafast electrochemistry for molecular electronics onto gold electrodes

# Detecting Non-Trivial Phenomena Within Gold Break Junctions: Molecular Atropisomerization and Au-S Oligomerization.

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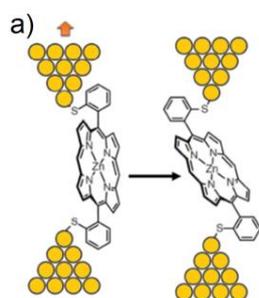
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We have employed the scanning tunneling microscope break-junction (BJ) technique to investigate the single-molecule conductance of a family of 5,15-diaryl porphyrins bearing thioacetyl (SAC) or methylsulfide (SMe) binding groups at the ortho position of the phenyl rings [1]. This attachment gives rise to *cis* and *trans* atropisomers, which can be chemically separated and which do not interconvert in solution under ambient conditions; even at 140 °C, isomerization takes several hours ( $\Delta H^\ddagger = 63 \text{ kJ mol}^{-1}$ ;  $\Delta S^\ddagger = -200 \text{ J mol}^{-1} \text{ K}^{-1}$  for SAC in  $\text{C}_2\text{Cl}_4\text{D}_2$ ). Stretching a single molecule junction of the *cis* isomer, however, does cause isomerization when the binding group is SAC (Fig.1a), but not SMe, which we show is due to the strength of the Au-S bond, and comparative weakness of the Au-SMe. The minimum-energy barrier to atropisomerization is lower than the strength of the Au-S and Au-Au bonds, but higher than the Au-SMe bond. The observed atropisomerization implies that the porphyrin ring adopts significantly non-planar conformations during stretching to achieve the transformation.

We then show that 'Au(RS)<sub>2</sub>' units play a significant role in thiol-terminated molecular junctions formed on gold [2]. We have studied a range of thiol-terminated compounds, and for all molecules we observe at least two groups of conductance plateaus. By a careful analysis of the length behavior of these plateaus, and comparison with SMe anchors, we demonstrate that the lower conductance groups correspond to the incorporation of Au(RS)<sub>2</sub> oligomeric units at the contacts. These can be found on the surface of gold nanoparticles (Fig.1b), but have not before been shown to exist in BJJs (Fig.1c-e). In these structures, gold atoms exist in the +1 oxidation state, and cause weaker molecule-electrode coupling. The results demonstrate the complex nature of thiol chemistry on gold, and moreover clarify the conductance of 1,4-benzenedithiol on gold. True Au-S-Ph-S-Au junctions have a relatively narrow conductance distribution, centered at a conductance of  $\log(G/G_0) = -1.7 (\pm 0.4)$ .

## Atropisomerization



## Au-S Oligomerization

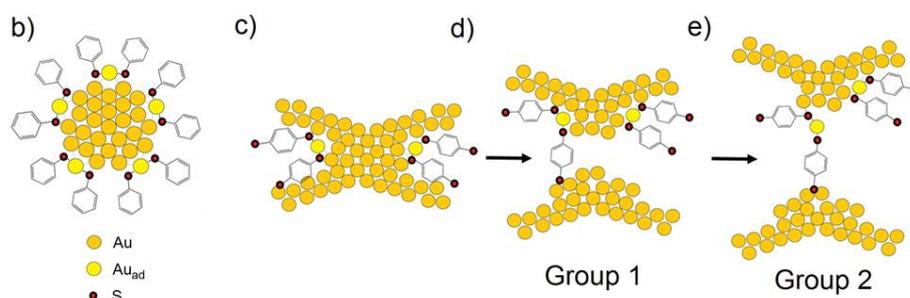


Figure 1. a) Mechanically-induced atropisomerization in a single porphyrin molecular junction. b) Representation of a thiolate-protected gold nanoparticle. c-e) Steps involved in Au-S oligomer formation at the Au electrode-molecule interface.

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# Controlling the electric charge of gold nanoplatelets on an insulator by field emission nc-AFM

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Flat metallic islands on an insulating substrate can be used as electron reservoirs to contact a molecule or a graphene nanoribbon in a planar geometry for molecular electronics applications. The challenge is then to stabilize the charge on a metallic nanocrystal for a time long enough to perform in-plane operations. Here, we report on the controlled charging of 2D Au nanocrystals deposited on a SiO<sub>2</sub> insulating substrate by electron field emission from the tip of an AFM in UHV environment. We image the platelets in the nc-AFM mode [1] and characterize their charge state by Kelvin Probe Force Microscopy (KPFM) (see figure 1) [2,3]. Our results demonstrate that the charge of these metallic islands can be precisely controlled by monitoring  $\Delta f(V)$  spectroscopy curves. The procedure works for both polarities, electrons being emitted by the tip or the substrate. As shown by an analytical model and complementary numerical simulations, the rise of the island's potential upon charging leads to a constant charging current and tip-island electric field [4]. Our measurements suggest that this method can be used to set the island's potential with a single-electron precision. This degree of control is achieved thanks to the increased stability and sensitivity provided by the UHV environment. The procedure is robust and opens the way to original experiments, such as establishing a bias at the extremities of a molecule connected between two islands or exploring locally the charge leaking mechanisms across an insulating layer.

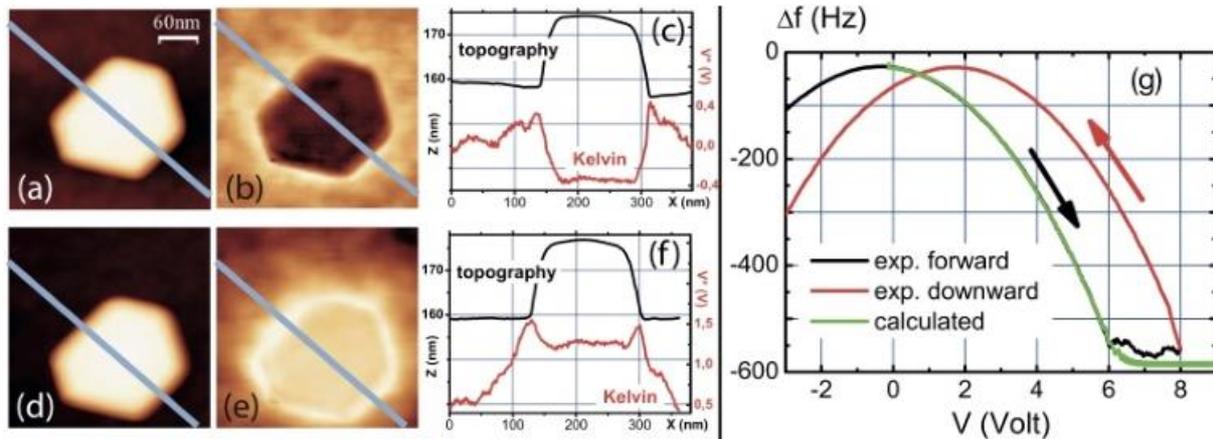


Figure 1. Topography and Kelvin potential image of an Au island on SiO<sub>2</sub> before (a, b) and after (d, e) charging. Profiles before (c) and after (f) charging. (g)  $\Delta f(V)$  curves measured on the Island showing the negative charging ( $\Delta f = -7\text{Hz}$ ,  $\Delta z = 2\text{nm}$ ). The black curves are recorded before the red ones. The green curves are simulated with a virtual AFM [4]

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# Nanoscale Opto-Electronic Device based on Single-Crystalline Gold Platelets

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Nanoscale opto-electronic devices have the potential for combining the high bandwidth of light with the integration density of modern-day microelectronics. Its applications demand a material that brings together high conductivity, easy processability and superior optical properties. Single-crystalline gold platelets show decreased optical damping compared to evaporated films<sup>1</sup> and allow electronic access through nanometer sized connectors.<sup>2</sup> Due to these advantages they allowed the experimental demonstration of integrated electrically driven optical antennas<sup>3</sup> based on inelastic electron tunneling (see Fig. 1a,b).

The combination of focused ion beam structuring of the single-crystal gold platelets and subsequent dielectrophoresis allows us to realize even more sophisticated structures, for example, complex antenna designs with tailored emission profiles. In another line of experiments, we have recently started to integrate electrically driven nano light sources into optical nanocircuits (see Fig. 1c). We will report the latest results of such efforts.

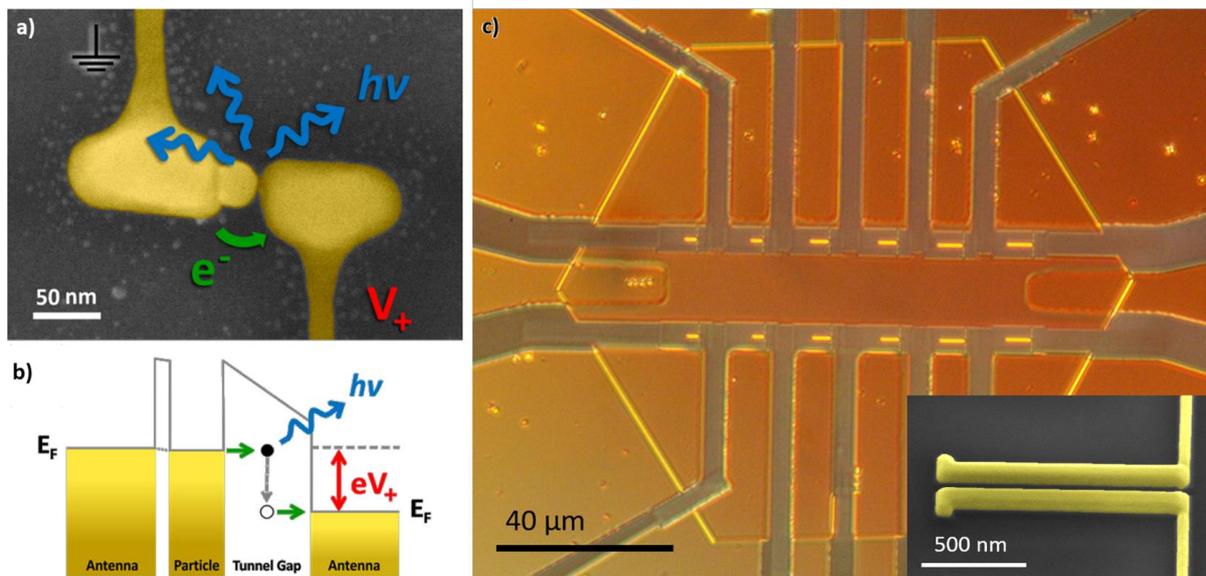


Figure 1. a) Scanning electron micrograph of an electrical connected optical antenna with a gold particle in the gap, creating a tunnel junction. b) Scheme of the inelastic tunneling process taking place between the particle and one antenna arm. c) Optical image of a gold platelet placed on an electrode structure. Subsequent focused ion-beam milling was used to create two rows of opto-electronic devices. Inset: Scanning electron micrograph of one of the devices.

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# Capturing electrochemical transformations by *in-situ* tip-enhanced Raman spectroscopy (TERS)

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Because of its powerful analytical capabilities, the analysis of electrochemical interfaces by *in situ* TERS will provide new insights in the understanding of the electron transfer with an unprecedented temporal and spatial resolution. Recent works have already demonstrated the possibility to carry out TERS experiments in liquids<sup>1</sup> and under electrochemical conditions (EC-tip-SERS).<sup>2</sup>

After the first STM-TERS imaging of an opaque sample in an organic liquid has been reported by our group in 2016,<sup>3</sup> we recently demonstrated the ability of a functionalized TERS tip to capture the electrochemical transformation of a molecular self-assembled monolayer: the tip acts as a single hot-spot Surface-Enhanced Raman Spectroscopy (SERS) platform. The proposed set-up (see Fig. 1) and protocol called electrochemical tip-SERS (EC tip-SERS) open new perspectives in the Raman characterization of redox architectures for molecular devices.<sup>4</sup>

This communication will describe in details this new approach together with our last developments on the imaging of electron transfers at the nanoscale by *in-situ* electrochemical TERS (EC-TERS).

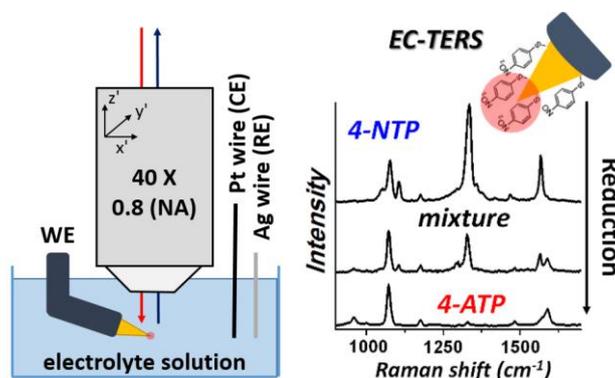


Figure 1. Setup and progressive reduction of an organic monolayer at a functionalized microelectrode monitored by EC tip-SERS.

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# From the Inert Insulator to the Active Electrocatalyst: Functionalization of h-BN and g-C<sub>3</sub>N<sub>4</sub> by Gold

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It is demonstrated that chemically inert and insulating hexagonal boron nitride (h-BN) nanosheets and corrugated carbon–nitrogen-based two-dimensional porous frameworks based on graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) supported on the inert gold surface can be functionalized by interaction with the gold support and become active electrocatalysts [1-6]. Two reactions of key importance for the development of a sustainable energy cycle - the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) are considered. It is shown theoretically that the corrugated g-C<sub>3</sub>N<sub>4</sub> / Au(111) heterojunctions and h-BN / Au(111) perimeter interfaces serve as active sites both for ORR and HER (see Figure 1). In the case of ORR such sites provide stabilization of oxygen and promote dissociation of OOH intermediate onto O and OH species, opening effective 4-electron pathway for oxygen reduction to water. In the case of HER our theoretical evaluations suggest that some of edge atoms of h-BN islands on Au(111) and g-C<sub>3</sub>N<sub>4</sub> / Au(111) heterojunctions provide energetically favored sites for adsorbed hydrogen. Further increase in catalytic activity of the considered systems can be achieved by decorating them by gold nanoparticles (Au-NP) which results in formation of the additional energetically favorable adsorption sites.

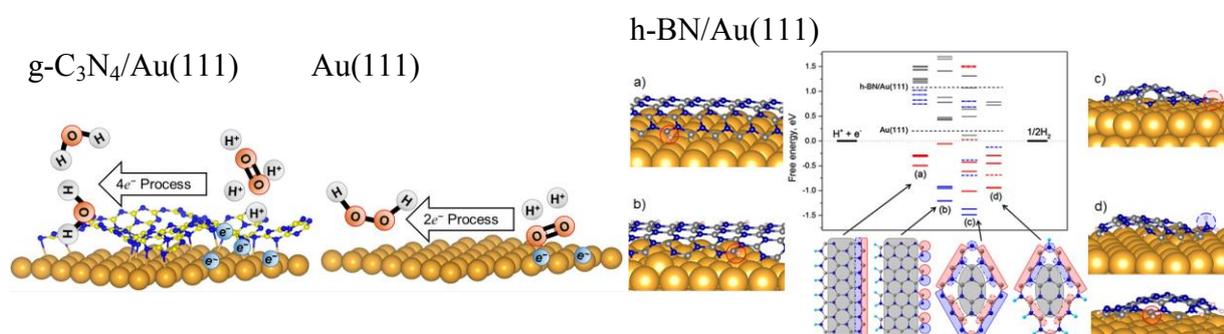


Figure 1. ORR catalyzed at the corrugated g-C<sub>3</sub>N<sub>4</sub> / Au(111) heterojunction (left) and pure Au(111) surface (middle); HER at the perimeter interfaces of h-BN islands on Au(111) (right).

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# Electrocatalysis of sized gold nanospheres

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Middle Ages artists used gold nanoparticles (AuNPs) for decorating glasses in multiple colours. This behavior of gold at nanoscale fascinated scientists and became an important research topic in various areas from physics to biotechnology. During the last 30 years, various investigations aimed at understanding the intrinsic relationship between the size, the morphology and the activity of nanoscale gold materials.

Recent studies on gold nanorods have shown that it is experimentally challenged but possible to study support-less gold nanoparticles<sup>1,2</sup>. In the present work, spherical gold nanoparticles (AuNSs) with a mean diameter from 4 to 15 nm were successfully synthesized and confirmed by transmission electron microscopy. The electrochemical investigations related to the surface of such nanoparticles clearly show the size dependent electrocatalytic activity for glucose oxidation. Moreover, this reaction seems to be controlled by diffusion process. Small AuNSs exhibited drastic increase of catalytic activity (Figure 1). This feature might result in the high specific area and reactivity of the surface electron induced by their small size. The study of the reaction mechanism was investigated by in situ Fourier transform infrared reflectance spectroscopy. Gluconolactone and gluconate were identified respectively as the intermediate and the final reaction products of the glucose electrooxidation.

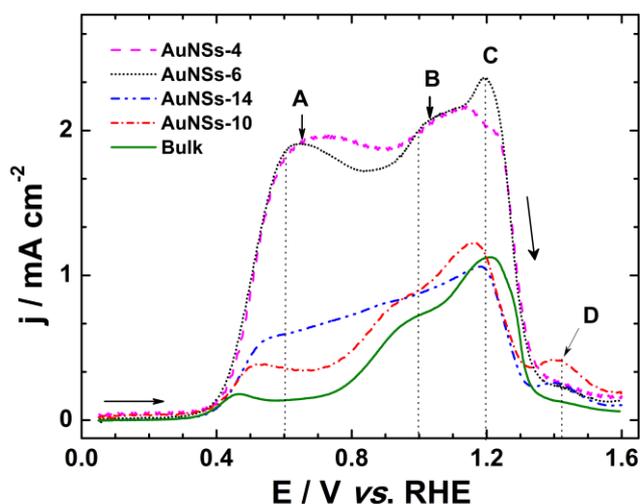


Figure 1. Linear sweep voltammograms of the gold bulk and the different AuNSs (size: 4, 6, 10 and 14 nm) electrodes in  $0.1 \text{ mol L}^{-1} \text{ NaOH} + 10 \text{ mmol L}^{-1} \text{ glucose}$ , recorded at  $20 \text{ mV s}^{-1}$  and at controlled temperature of  $20 \text{ }^\circ\text{C}$ .

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# Gold Nanorods vs. Octahedra: Electrochemical interaction with glucose

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The surprising properties revealed by gold nanoparticles (AuNPs) lead continuously to emerging applications over material science. These properties depend on the nanoparticles surface structure and morphology. Therefore the control of the size and the shape of nanoparticles mainly for gold becomes important for understanding the active site at the nanoparticles surface. In this work, single crystal, pentatwinned gold nanorods (noted respectively Au-SC-NRs, Au PTW-NRS) and gold octahedra (Au-Octa) exhibiting different facets were prepared<sup>1-3</sup>. Their physical characterizations revealed the presence of low and high Miller indices (Figure 1A). The electrochemical characterization in the supporting electrolyte show that the formation of oxide layer depends on the AuNPs surface morphology (Figure 1B). This feature was confirmed by the targeted adsorption of 4-mercaptobenzoic acid and the underpotential deposition of lead (UPD<sub>Pb</sub>) which is influenced by the crystallographic orientation, especially the low index facets. In the case of glucose electrooxidation carried in alkaline medium, the results clearly demonstrate the difference between the electrocatalytic activity induced by the high and the low index facets. High current densities were observed with Au-Octa, conversely to the behavior stated in the literature. This difference could be attributed to the presence of defects or low coordination sites.

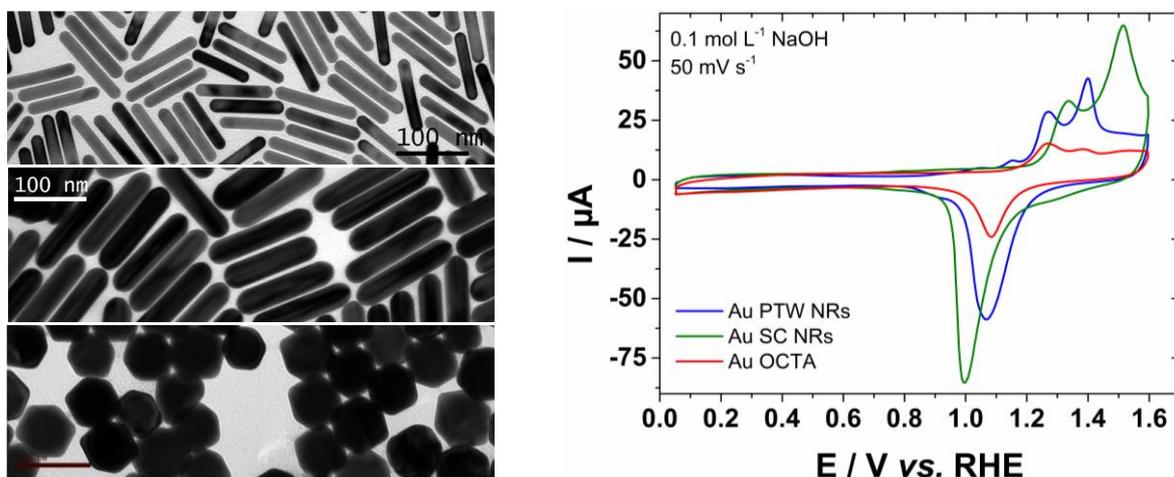


Figure 1. Left) Representative TEM images of single crystalline Au nanorods (top), pentawinned Au nanorods (middle) and Au octahedral (bottom) Right) Cyclic voltammograms of Au nanoparticles in alkaline media

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# When Halides Shape the Morphology and Electrocatalysis of Gold Nanoparticles Directly Grown onto Carbon Paper Electrodes

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During the last decade, several methods have emerged to engineer tunable metallic micro/nanostructures with specific sizes, shapes and hierarchies using nanoparticles (NPs) as elementary building blocks. The majority of the approaches occur physically separated from the electrodes, which are necessary for the final application. Thus, for their practical use in energy conversion, sensors or bioelectronic technologies, the implementation require further immobilization onto an electrode using various post-synthesis steps. Then, the support degradation and the loss of the binders lead to the aggregation and/or dissolution of NPs, which decreases significantly the overall performance. To address all these challenges, we recently developed a novel and versatile chemical method to grow anisotropic gold microstructures at the surface of carbon paper.<sup>[1]</sup> The success of the approach for in situ growth relies on a tight control of the reaction time together with the use of halide anions as effective tools. It was observed that halides play a crucial role in the morphology, leading to either complex flower-like rough surfaces (exhibiting high catalytic activity) in the presence of Br<sup>-</sup> or featureless smooth surfaces (exhibiting low catalytic activity) in the presence of I<sup>-</sup> (Fig. 1). To date, this first proof of concept that Au particles can be directly grown onto large surface (5 cm × 5 cm) of conducting electrodes by means of a chemical reduction method yielded significant electrocatalysis. For glucose electrooxidation, the use of Br<sup>-</sup> as regulator enables obtaining a record peak current density close to 10 milliamps per square centimeter of gold, which is higher than the conventional chemically synthesized AuNPs by an order of magnitude. Moreover, a designed glucose fuel cell has an outstanding open-circuit voltage (OCV) of 1.0 V and delivers a maximum power of 3.1 mW cm<sup>-2</sup> (at high cell voltage of 0.7 V without any fuel circulation at room temperature with metal loading of ~0.3 mg cm<sup>-2</sup>), which surpasses the relevant reported data as well as the commercial PtRu/C anode (1.4 mW cm<sup>-2</sup> at 0.5 V, OCV of 0.9 V using a high metal loading of 3 mg cm<sup>-2</sup>). The findings represent a decisive advance for the elaboration of structures with tunable size, morphology, and catalytic properties. These remarkable results greatly enhance our knowledge, add new strategies and pave new elegant approaches for the successful fabrication of low-cost, highly active and durable electrodes.

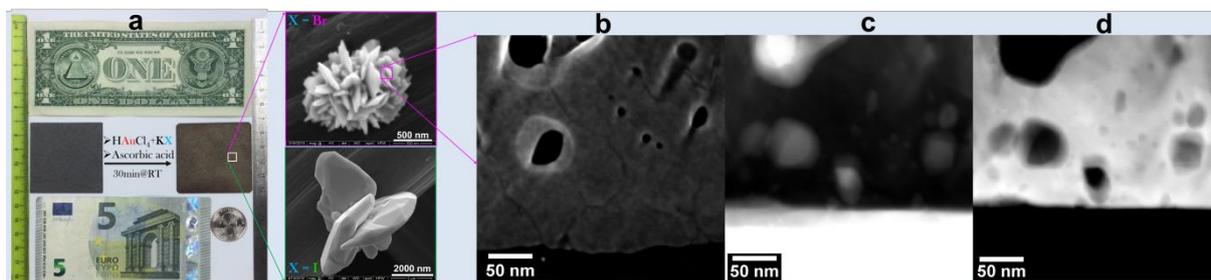


Figure 1. (a) Sketch illustrating the direct growth of metallic gold particles on carbon paper electrode (5 cm × 5 cm). Features of a particle (in the presence of bromide as regulator), sample prepared by focused ion beam dual beam microscope: (a) secondary electron (SE) tomography, (b) bright-field STEM image, (d) HAADF-STEM image

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# Enzymatic O<sub>2</sub> reduction and H<sub>2</sub> oxidation on gold surfaces: probing functional enzyme immobilization by electrochemistry, SPR and PMIRRAS

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Identification and production to purity of redox enzymes from various microorganisms living in very different environments have allowed to envision many of these biomolecules as catalysts in biosensors, bioreactors or bioenergy devices. Among these, one new generation of enzymatic fuel cells is based on very specific enzymes for H<sub>2</sub> oxidation and O<sub>2</sub> reduction, hydrogenase and bilirubin oxidase (BOD) respectively, in replacement of rare and expensive platinum metal, providing a fully sustainable fuel cell. Great improvement has been made during the recent years in the performance of H<sub>2</sub>/O<sub>2</sub> enzymatic fuel cells [1]. Actually, the resolution of the crystal structures of the enzymes has allowed to determine some of the molecular factors affecting the electron transfer rate at the electrochemical interface. Especially, the intramolecular and intermolecular electron pathways identification permitted to point out surface zones on the enzyme involved in the recognition with the electrode. The accordingly functionalization of host carbon nanostructures lead to currents reported to the mass of enzymes very close to the objective fixed for the platinum-based electrodes [2]. Despite these progresses, two remaining limitations severely limit the large scale development of the biodevices. The first one is the electrical wiring of the enzyme. It was in particular recently shown that less than 10% of the enzymes are in electrical contact with the carbon structure [2]. This issue implies the control of the oriented immobilization of the enzyme to enhance the electron transfer rate and optimize the charge of enzyme at the electrode. The second one is the stability of the bioelectrodes. Beyond the research in the biodiversity of more stable enzymes, there is a need to decipher between the various origins for such instability, protein leaching, reorientation, reconfiguration, denaturation..., then to be able to propose a remediation process.

In this work we present how we have addressed the issues of enzyme wiring and bioelectrode stability by adsorbing both hydrogenases and BODs from different origins on thiol-based Self-Assembled-Monolayers (SAM) on gold electrodes [3]. SAMs carrying different surface charge and hydrophobicity are used to tune the interaction with the enzymes. pH and applied potentials are especially studied as factors affecting both the surface of the enzymes and that of the electrode. Coupling first electrochemistry to PMIRRAS, we show that the orientation of the enzymes can be controlled either by hydrophobicity of the SAM for a membrane bound hydrogenase, or by electrostatic interactions for BODs of different origins. We further demonstrate that the controlled orientation also controls the type of electron transfer at the electrode, switching from a direct process to a mediated process. Coupling then electrochemistry to SPR, we establish the correlation between the continuous decrease in the electrocatalytic current to the leaching of the protein or to a switch in the protein orientation. We finally discuss whether the molecular basis obtained on SAMs can be extended to conductive materials such as carbon nanotubes which are mostly required to enhance the biofuel cell performance [4].

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# Ultrafast electrochemistry for molecular electronics onto gold electrodes

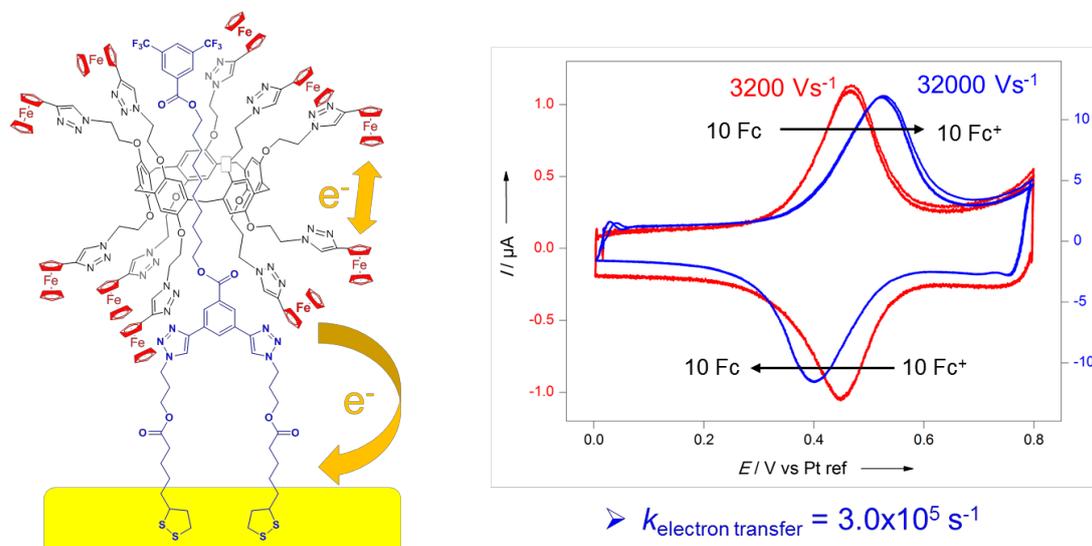
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The miniaturization of electronic devices is the most important challenge that needs to be tackled in the development of information technology. In this context, molecular systems offer an easy access to a large variety of building blocks with defined sizes, shapes, chemical and electronic properties. Ultimately, molecular electronics could also capitalize on the unique properties offered by supramolecular assemblies in order to generate novel, heretofore unrealized, electronic functions. There are a lot of ways to interrogate the communication within molecular and supramolecular systems. Electrochemistry (and more specifically cyclic voltammetry) presents a very interesting approach since it allows a direct visualization of the electron fluxes. However, for potential applications electron transfer need to be extremely fast, and the electrochemical kinetic window needs to be properly tuned<sup>1</sup>. To this respect, we will present the interest of using micrometric gold electrodes and a home-built potentiostat to reach nanosecond time scales.

Two types of molecular systems will be presented. The first ones are molecular wires bearing a single redox entity. The second ones are giant rotaxanes into which electron hopping between different entities may also play a major role<sup>2</sup>. These molecules always incorporate an anchor to drive adsorption onto gold electrodes (Figure 1).



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