Title	Engineering Nanostructured Interfaces for Enhanced Electrochemiluminescence Response (Nano4ECL)

Proponent	Prof. Sara BONACCHI (PA)
Research Group	Molecular Electrochemistry and Nanosystems Group
Contact	web:
	email: sara.bonacchi@unipd.it
Co-Proponent	Dr. Alessandra Zanut (RTD-a)
Research Group	Analytical Chemistry
Contact	web:
	email: alessandra.zanut@unipd.it

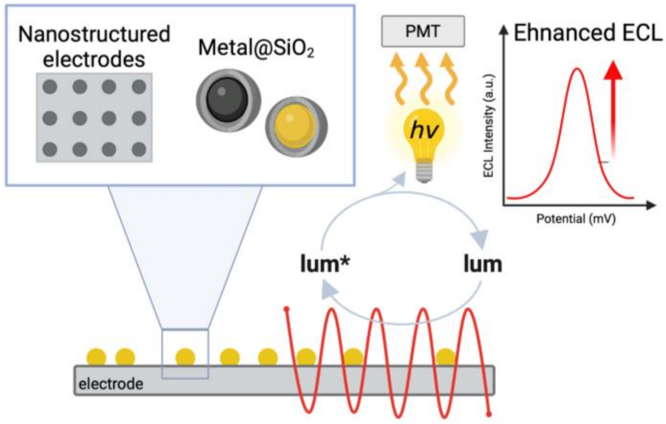
International Secondment	
PI	Professor Neso Sojic
Institute	Institut des Sciences Moléculaires, Analytical and Physical Electrochemistry Group
Place, country	University of Bordeaux, France
# months (min.3)	3 months

Project description (2 page max):

Since the emergence of nanotechnology, the miniaturization of materials to a scale where size-, shape-, surface- dependent effects operate has opened ambitious challenges not only from a technological perspective but also from a fundamental one. In this framework, the use of nanostructured electrodes is emerging as a pivotal strategy for increasing the luminescence efficiency within the electrogenerated chemiluminescence (ECL) approach[1]. In ECL spectroscopy, indeed, the emission of the light from a luminophore is primarily triggered by a heterogeneous electron transfer reaction between the electrode and the co-reactant[1,2]. Thus, electrodes nanoengineering offers plenty of opportunities to improve the optical signal towards highly sensitive analytical devices.
Lakowicz and co-workers[3] demonstrated the first example of enhanced electrochemical excitation of $Ru(bpy)_3^{2+}$ through a thin gold film on a glass electrode. This pioneered work led to the emergence of surface-enhanced electrochemiluminescence (SEECL), utilizing electrodes functionalized with colloidal metal nanoparticles (such as Au and Ag)[4] or nanoelectrode arrays[5,6]. These systems leverage plasmonic resonance effects and increased surface area to enhance electron transfer between the electrode and ECL reactants. Despite the potential for significant optical enhancements, practical and effective studies remain limited, likely due to the complex and partly unclear mechanisms underlying SEECL. While metal-enhanced fluorescence impacts the plasmonic electric field under optical excitation, resulting in enhanced emission intensity, ECL operates differently as it does not involve optical excitation[7].

In the **Nano4ECL** doctoral project, the **training-through-research** aims to integrate complementary approaches across synthetic nanostructures, electrochemistry, and photophysic to **go well beyond the state of the art** and provide the scientific community with insights into the mechanism controlling plasmon resonance with ECL generated light. To achieve this, a broad range of SEECL probes based on different metal nanostructures and luminophore/co-reactant couples will be synthesized and fully characterized.
This *iterative process will refine nanostructure design criteria* and identify optimal ECL-based devices in terms of brightness and stability. Additionally, to gain insight into the SEECL mechanism a **secondment** (at least 3

months) in the **Prof Sojic** (University of Bordeaux – France) who has a consolidated experience in the field of ECL microscopy, is planned. This collaboration will facilitate the acquisition of knowledge in mapping ECL chemical reactions on single nanoparticles, enhancing overall scientific research training.



Schematic of Nano4ECL PhD Project

The **Nano4ECL** project will involve:
(i) the synthesis and characterization of ***Silica/Shell - Metal/Core Nanoparticles*** *(Metal@SiO_2)* to modify electrode surfaces, enhancing the ECL signal via localized surface plasmon resonance (LSPR) effects;
(ii) the fabrication of ***nanostructured materials*** using top-down and high-throughput lithography techniques;
(iii) ***ECL analysis*** alongside optical and spectro-electrochemical investigations to thoroughly characterize the nanostructured materials, providing insights into SEECL mechanisms.
In particular, key parameters including the choice of *materials* (e.g., Ag, Au, etc.), the *size and shape* of nanostructures, and the distance between ECL emitters and plasmonic materials will be finely investigated. Special emphasis will also be placed on selecting organic fluorophores to optimize in order to maximize the *degree of overlapping* between the ECL activated emission and the plasmonic band of the nanostructures.

Nano4ECL is a ***truly interdisciplinary project*** combining synthetic ability, material sciences and, the state-of-the-art ECL studies to develop highly luminescent ECL platforms. The PhD candidate will receive *training in various experimental techniques* under the supervision of two experienced scientists with complementary skills i.e., Prof. Bonacchi (supervisor) who possesses a highly interdisciplinary scientific background spanning photochemistry, spectro-electrochemistry and, nanotechnology and Dr. Zanut (co-supervisor) who has extensive experience in ECL analysis and nanolithography. State-of-the-art electrochemical instrumentation available in the "Molecular Electrochemistry and Nanosystems group" host group will be regularly utilized, along with shared equipment within the host departments such as dynamic light scattering (DLS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). In addition, part of the activities will involve collaboration with Nanophoenix Srl, a startup located in Trieste, which provides access to instrumentation and facilities for high-throughput nanolithography.

Finally, the candidate will be a PhD student at the *prestigious Materials Science and Technology PhD school* within the framework of the Complex in Chemistry, *C2 - Dipartimento di Eccellenza Project* - Department of Chemical Sciences, DiSC - which it will allow the candidate to improve his/her scientific background attending international seminars, different courses, and activities.

References
[1] Nikolaou P, Valenti G, Paolucci F, *Electrochim Acta* **2021** 388:138586.
[2] Zanut A, Fiorani A, Canola S, et al., *Nature Communications* **2020** 11:1 11:1–9.
[3] J. Zhang, Z. Gryczynski, J. R. Lakowicz, *Chemical Physics Letters* **2004**, *393*, 483–487.
[4] S.Bonacchi, Genovese,G. Juris, R., Montalti, M., Prodi, L., Rampazzo, E., Zaccheroni N. Angew. Chemie Intern.Ed. 2011, 50, 4056–66.
[5] Cumba L, Pellegrin Y, Melinato F, Forster RJ, *Sensors and Actuators Reports* **2002** 4:100082.
[6] Heiderscheit TS, Oikawa S, Sanders S, et al, *Journal of Physical Chemistry Letters* **2021** 12:2516–2522.
[7] Wang D, Guo L, Huang R, et al, *Scientific Reports* **2015,** 5:1 5:1–7.