

Investigating the chemical oxidative polymerization of 1,8 - dihydroxynaphthalene using a correlative in-situ approach

Dr Nivedita Sudheer^{1,2}, Kevin Ziegler³, Emmanuel Maisonhute⁴, Vincent Ball³, Cédric Boissière⁵, Tom Ferte², Dris Ihiwakrim², Clement Sanchez^{1,5}, Ovidiu Ersen²

¹Collège de France, Paris, France, ²Institut de physique et chimie des Matériaux de Strasbourg (IPCMS), Strasbourg, France, ³Institut national de la santé et de la recherche médicale (INSERM), Strasbourg, France, ⁴Laboratoire Interfaces et Systèmes Electrochimiques (LISE), Paris, France, ⁵Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), Paris, France

Melanins, ubiquitous natural pigments found across various life forms, possess diverse biological functions such as camouflage and radioprotection. Notably, allomelanins derived from 1,8 - dihydroxynaphthalene (1,8-DHN) in Ascomycetes demonstrate robustness, offering protection against hostile environments. Despite their structural complexity and insolubility in solvents, allomelanins exhibit unique physical and chemical properties, including broadband visible-light absorption, free radical characteristics, water-dependent conductivity, and redox behavior, albeit their exact structure remains incompletely defined[1], [2]. Thin films derived using chemical oxidative polymerization from physiologically active chemicals such as polyphenols have been studied to exhibit remarkable versatility across diverse substrates[3], [4], [5]. This study presents an in-depth investigation utilizing in-situ correlative microscopy and surface electrochemical methodologies to scrutinize thin films formed via the oxidative polymerization of 1,8-DHN molecules in aqueous electrolytes.

The study showcases the electrodeposition of 1,8 DHN onto gold electrodes and glassy carbon electrodes through cyclic voltammetry under in-situ liquid TEM using a miniaturized electrochemical cell. The resulting films demonstrate adjustable thickness and swelling properties, modulated by varying the potential sweep rate (20mV/s, 200mV/s and 1000mV/s). Analysis of the films' surface characteristics is conducted through Raman-coupled electrochemical spectroscopy and in-situ ellipsometry, complemented by cyclic voltammetry to explore their electrochemical behavior. Additionally, employing in-situ TEM provides insights at the nanoscale, in direct space into the electrochemical mechanisms occurring during the film formation.

Through the application of in-situ liquid TEM using an electrochemical cell, the real-time mechanism of thin film formation during electrodeposition has been elucidated, marking a significant advancement in the field. A proposed mechanism for the oxidative polymerization of 1,8 DHN is supported by Raman-coupled electrochemical spectroscopy, indicating dimer formation during the initial stages. Additionally, concurrent analysis with in-situ ellipsometry has allowed for the simultaneous investigation of the relationship between film thickness, scan rates, and optical properties, while quasi-in-situ impedance spectroscopy has provided insights into the electrical and conducting properties of these polymers in relation to the sweep rates. Notably, these films exhibit inherent antioxidant properties with antioxidant components distributed throughout the films' structure within a restricted energy range of -1 V to +1 V versus Ag/AgCl.

From a material point of view, this correlative study which includes in-situ liquid TEM analyses highlights the considerable potential of employing mild electrochemical conditions to fabricate electropolymerized thin films via the Chimie-Douce mechanism utilizing fundamental organic constituents. Moreover, combining several in-situ techniques including electrochemical TEM, Raman coupled electrochemical spectroscopy, and ellipsometry, we bring new insights into chemical oxidative polymerization at different scales and more

generally a structural evolution during electrochemical phenomena. Given their insolubility in commonly used solvents and favorable mechanical properties, these films hold promise as protective coatings. Moreover, their electroactive and antioxidant properties render them highly suitable for a wide range of applications, including environmental remediation, biomedicine, and catalysis.

Graphic:

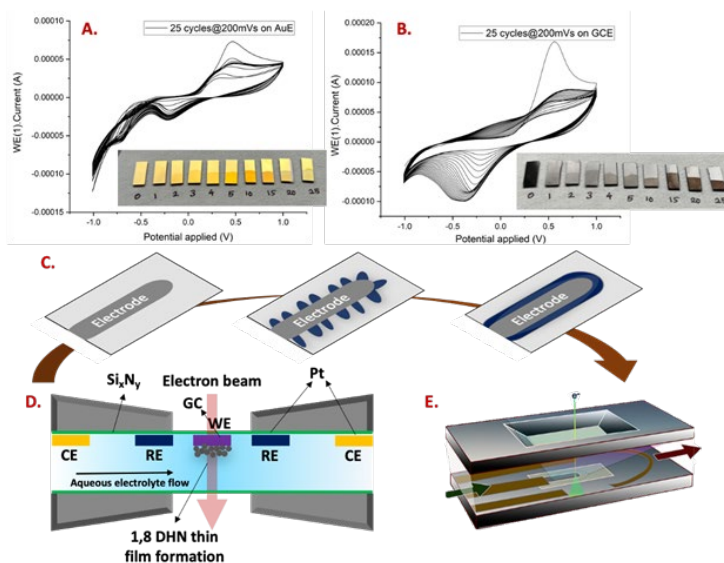


Figure 1. The figure illustrates the chemical oxidative polymerization and deposition of 1,8 DHN on the WE (Au and glassy carbon) which will be characterized using complimentary cyclic voltammetry techniques. (A) Cyclic voltammogram of 1,8 DHN at 25 cycles in 200mV/s on Au electrodes and the gradual formation of thin films with the number of cycles observed in the picture, (B) Cyclic voltammogram of 1,8 DHN at 25 cycles in 200mV/s on glassy carbon electrodes and the gradual formation of thin films with the number of cycles observed in the picture, (C) Illustration of formation of thin films on the working electrodes, (D) Transversal schematic view of the assembled cell. WE, CE and RE are the working, counter and pseudo-reference electrodes, respectively. GC is the glassy carbon current collector in the WE. (E) Side schematic view of an assembled cell.

Keywords:

In-situ-liquid TEM, Raman-coupled electrochemical spectroscopy

Reference:

1. Cecchini, M. M., Reale, S., Manini, P., d’Ischia, M. & De Angelis, F. Modeling Fungal Melanin Buildup: Biomimetic Polymerization of 1,8-Dihydroxynaphthalene Mapped by Mass Spectrometry. *Chemistry – A European Journal* 23, 8092–8098 (2017).
2. Lino, V. & Manini, P. Dihydroxynaphthalene-Based Allomelanins: A Source of Inspiration for Innovative Technological Materials. *ACS Omega* 7, 15308–15314 (2022).
3. Myers, R. E. Chemical oxidative polymerization as a synthetic route to electrically conducting polypyrroles. *J Electron Mater* 15, 61–69 (1986).
4. Gospodinova, N. & Terlemezyan, L. Conducting polymers prepared by oxidative polymerization: polyaniline. *Prog Polym Sci* 23, 1443–1484 (1998).
5. Higashimura, H. & Kobayashi, S. Oxidative Polymerization. in *Encyclopedia of Polymer Science and Technology* 1–37 (Wiley, 2016). doi:10.1002/0471440264.pst226.pub2.