Watching electrochemistry with BALM optical microscopy

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K. Jaouen, S. Campidelli, B. Jousselme, V. Derycke, R. Cornut
LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay
CEA Saclay, 91191 Gif-sur-Yvette Cedex, France
kevin.jaouen@cea.fr

Backside Absorbing Layer Microscopy (BALM) is a new optical microscopy technique developed by D. Ausserré at IMMM, which uses absorbing anti-reflection layers to achieve extreme contrast at an interface. It combines a *sub*-nm vertical sensitivity comparable to the one of AFM with the versatility and real-time imaging capabilities of an optical microscope. Recently, we showed how this technique allows observing 2D materials and their chemical modification with unprecedented Z-resolution (1).

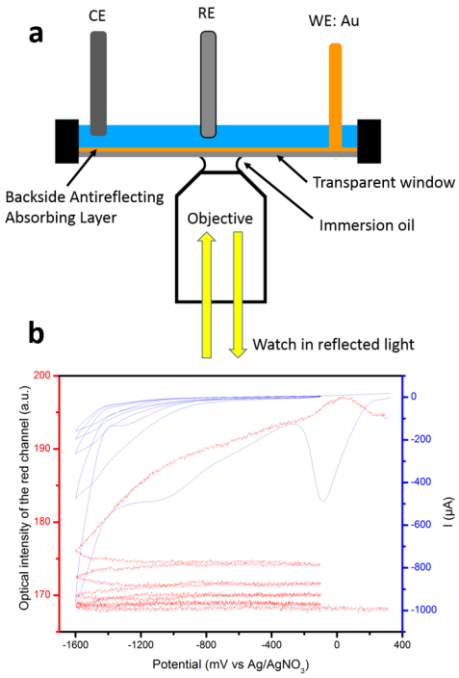

Fig.1. a) Schematic of BALM coupled to an electrochemistry set-up. b) Electro-grafting of nitrobenzene diazonium on gold (Blue line is the current response and red line is the optical intensity which is related to the layer thickness).

The BALM geometry (Fig. 1a) and its capability to image surfaces and nanomaterials in liquid are ideally suited to its coupling with electrochemistry. This optical technique is extremely sensitive to minute changes of refractive index therefore it allows following in real-time the deposition or the electro-grafting of molecules with a precision significantly below the monolayer thickness. This is exemplified in Fig. 1b for the electro-grafting of nitrobenzene diazonium salt on gold by cyclic voltammetry. The optical signal being directly proportional to the layer thickness in a large thickness range, the technique proves capable of monitoring layer growth with angstrom precision in the vertical direction.

More importantly, as a microscopy technique, it is also spatially resolved. As a simple example, Fig. 2 presents the *in situ* monitoring of the electrodeposition of copper by chronoamperometry respectively on gold (a) and on Graphene Oxide flakes (b).

In this communication, we will show how the coupling of BALM and electrochemistry allows addressing different classes of problems in electrochemistry by taking advantage of real-time imaging and high sensitivity.

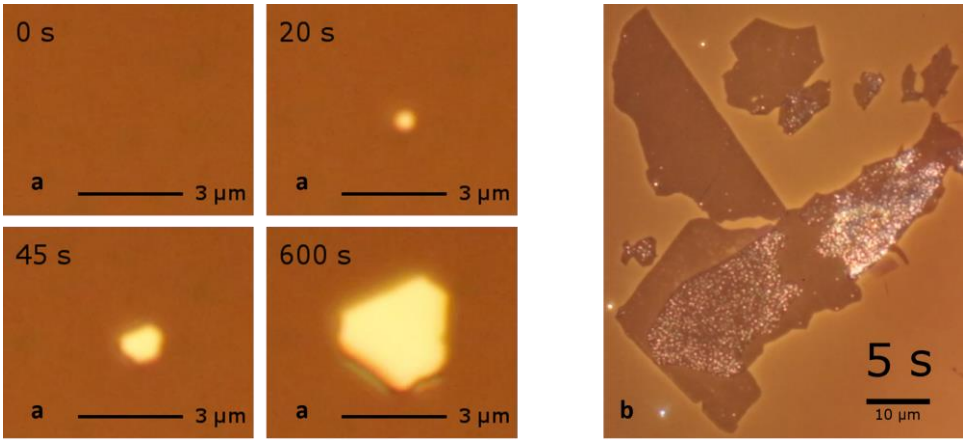

Fig.2. Short part of a BALM movie showing the in-situ electrodeposition of copper under chronoamperometry. a) on gold. Extracted from (1). b) on Graphene Oxide flakes

(1) Campidelli, S.; Abou Khachfe, R.; Jaouen, K.; Monteiller, J.; Amra, C.; Zerrad, M.; Cornut, R.; Derycke, V.; Ausserré, D., *Science Advances 3, e1601724 (2017).*