

A MULTIRESPONSE APPROACH TO THE STUDY OF ELECTROCHEMICAL PROCESSES IN NANOSTRUCTURED MATERIALS

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Design and development of new experimental set-ups combining arrays of techniques that provide information of different nature on processes/materials simultaneously, so-called multiresponse techniques, is crucial for an in-depth investigation of complex electrochemical processes occurring at the nanoscale. Aware of this fact, our group has devoted considerable effort to develop new multiresponse techniques of special relevance to the characterisation of nanostructured materials [1-4]. The aim of this communication is to review some of these techniques and to illustrate their versatility and usefulness for the study of different nanostructured materials with representative examples in which the chemical reaction at the nanoscale is electrochemically driven. That is, these techniques rely on applying an electrochemical perturbation to a system in order to induce a chemical reaction that will either produce a nanostructured material or alter the oxidation state/chemical form of the starting nanostructure. The array of techniques (spectrophotometric, gravimetric, scanning probe microscopy) coupled to the electrochemical cell enables us to follow simultaneously (not sequentially) the effect of the electrochemical perturbation on the morphology, reactivity, electrical and optical properties of the electroactive material.

Among them, Bidimensional Spectroelectrochemistry (Figure 1), a 3-response technique (one electrochemical and two spectroscopic ones) is a very powerful technique that has contributed significantly to elucidate the mechanism of electrosynthesis of conducting polymers and to investigate the electrochemical stability of the resulting polymer films [2]. It has also proven very useful to follow the electrochemically-controlled release of immobilized compounds from nanostructured composite films, along with the structural changes undergone by the host polymer matrix [3]. Furthermore, simultaneous acquisition of an additional signal, namely, the interfacial mass changes occurring during the electrochemical reaction (by joint Reflectance Spectroelectrochemistry and Electrochemical Quartz Crystal Microbalance measurements, Figure 2) enabled us to rationalize the differences noted in the potential-dependent reflectance of Au nanoparticle films in terms of dissimilar ion-binding strengths of the solution electrolyte anions [4].

Finally, some examples illustrating the power of Scanning Electrochemical Microscopy (and its combination with UV/Vis Reflectance Spectroscopy, Figure 3) to investigate the charge transport properties of ultrathin nanostructured films of different nature (gold nanoparticles, carbon nanotubes, conducting polymers, etc.) will be presented [5].

References:

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- [2] E. Muñoz, A. Colina, A. Heras, V. Ruiz, S. Palmero, J. López-Palacios, *Anal. Chim. Acta*, **573-574** (2006) 20.
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- [4] V. Ruiz, Á. Colina, M. A. Heras, J. López-Palacios, *Electrochem. Commun.*, **9** (2007) 255.
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Figures:

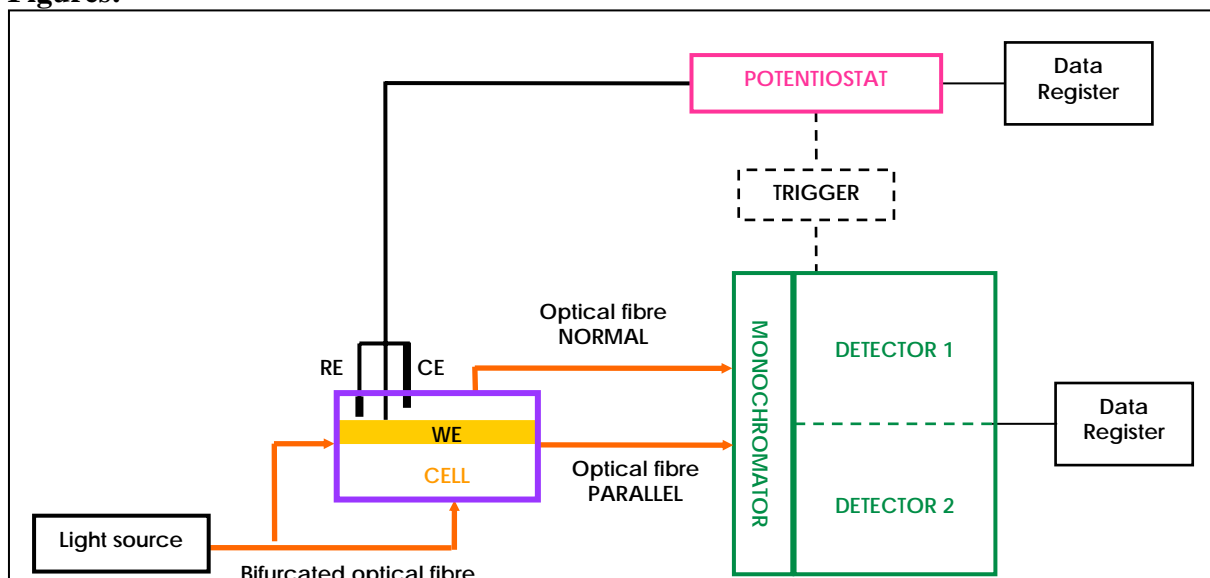


Figure 1: Schematic of the experimental set-up for bidimensional spectroelectrochemical measurements.

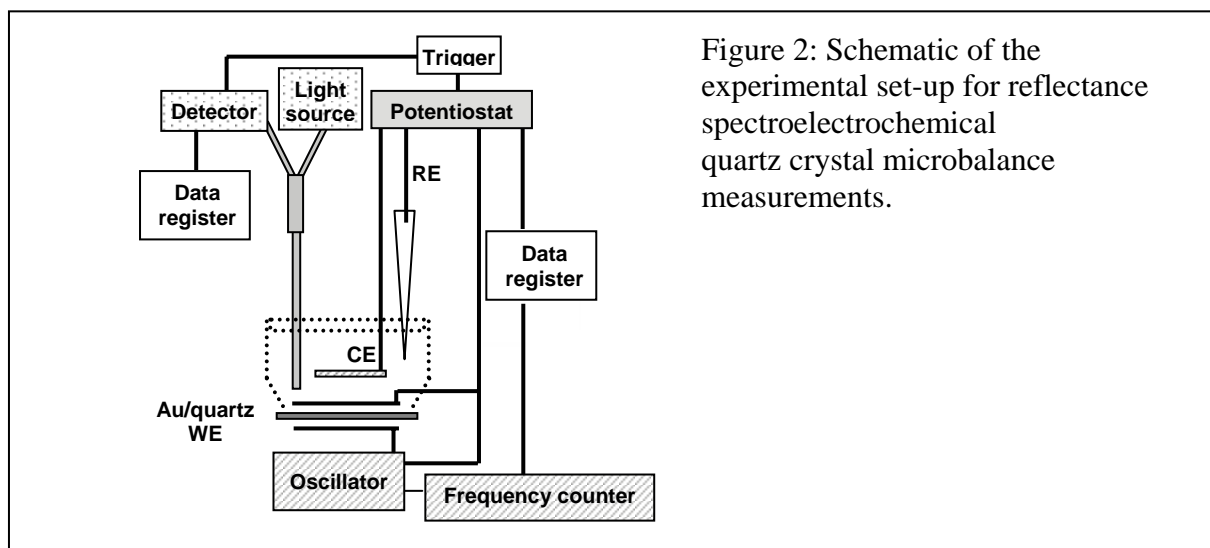


Figure 2: Schematic of the experimental set-up for reflectance spectroelectrochemical quartz crystal microbalance measurements.

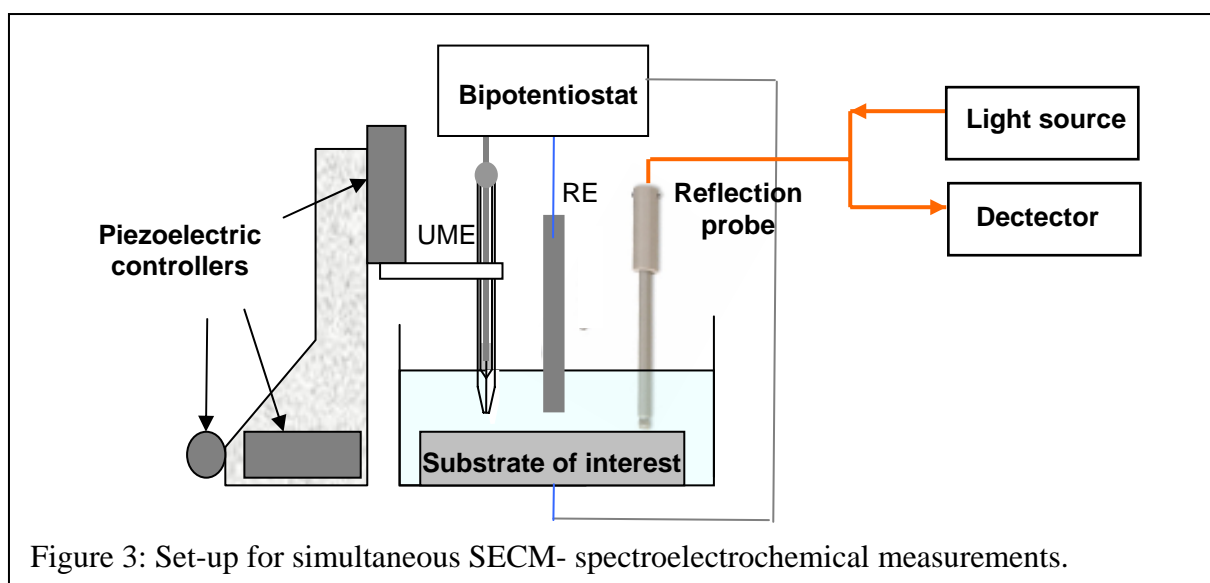


Figure 3: Set-up for simultaneous SECM- spectroelectrochemical measurements.