Abstract #2460, 224th ECS Meeting, © 2013 The Electrochemical Society

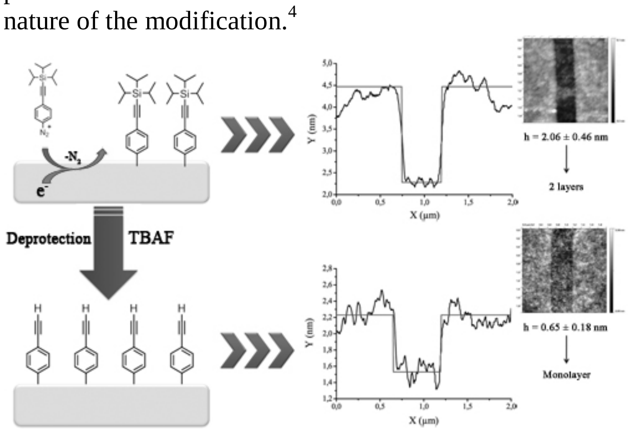
Nanostructured Monolayer Films Electrografted on Carbon Substrates. Application to the electrochemical preparation of surfaces with reversible photo-switchable properties.

Yann R. Leroux and Philippe Hapiot

Institut des Sciences Chimiques de Rennes, Université de Rennes 1, CNRS, UMR 6226 (Equipe MaCSE), Campus de Beaulieu, 35042 Rennes Cedex, France.

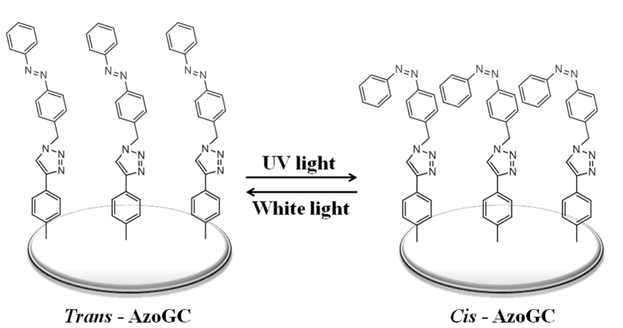
So-called "smart surfaces" meaning surfaces able to react to an external stimulus such as light are subject of numerous investigations.[1] We present a general strategy for preparing and studying such robust nanostructured monolayers on carbon materials that will display reversible photo-switchable properties. As an example, we focus on the preparation of azobenzene derivatives monolayer covalently bound to carbon substrates and presenting a controlled organization. Azobenzene derivatives were chosen, as they are simple to handle systems due to a relatively facile synthesis and the possibility of reversible photo-isomerization.[2]

Our method is based on the electrochemical reduction of a specific silyl-protected aryl diazonium salt followed by a deprotection step and a click chemistry coupling reaction.[3] The procedure leads to a robust modification of the surface where molecular entities are placed in a "frozen" structuration thanks to the covalent nature of the modification.[4]



Scheme 1. Electrografting and deprotection steps used for the preparation of the molecular platform.

Association with photoactive moieties like azobenzene, which are introduced by click chemistry on the prepared molecular platform, permits a reversible modulation of the surface permeability upon irradiation.



Scheme 2. Modulation of the monolayer porosity with light irradiation.

The photo-switchable properties of the surface are probed by electrochemistry (cyclic voltammetry) using different specific redox couples.[5] Analysis of the electrochemical data that were based on models of interacting diffusing pinholes[6] permits simple estimations of semi-quantitative parameters as the apparent free available surface and of their variations upon surface preparation or light-irradiation. Validity of such models will be rapidly discussed in the presentation.

More generally concerning "smart surfaces", UV-visible light irradiation provides an easy way to reversibly modulate the permeability in a monolayer film grafted onto carbon materials. Aryldiazonium electrochemistry[7] combined with click chemistry[3,4] is a versatile method to prepare such robust and dense nanostructured monolayer on carbon surfaces. This possibility is particularly interesting in the design of hierarchical nanostructured monolayer either in the layer preparation steps or for a modulation of a defined sensitive property. The same strategy could be considered for other immobilized chemical systems when similar photo-switchable properties are desired.

References

1 D. Ishikawa, E. Ito, M. Han, M. Hara, *Langmuir* **2013**, *29*, 4622 and references therein.
2 M. Irie, *Chem. Rev.* **2000**, *100*, 1683.
3 Y.R. Leroux, H. Fei, J.-M. Noël, C. Roux, P. Hapiot, *J. Am. Chem. Soc.* **2010**, *132*, 14039.
4 Y.R. Leroux, P. Hapiot, *Chem. Mater.* **2013**, *25*, 489.
5 S. Lhenry, Y. R. Leroux, P. Hapiot, *Anal. Chem.* **2012**, *84*, 7518.
6 C. Amatore, J.-M. Savéant, D. Tessier, *J. Electroanal. Chem.* **1983**, *147*, 39.
7 J. Pinson, F. Podvorica, *Chem. Soc. Rev*. **2005**, *34*, 429.