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Organic monolayer nanopatterning via interfacial solid-phase electrochemical oxidation

Jacob Sagiv
Weizmann Institute of Science, Israel

We report recent results of ongoing efforts devoted to the advancement of unconventional approaches to the *in-situ* functionalization of self-assembled OTS monolayers,1 which enable effective nondestructive chemical patterning of such inert monolayers on length scales from centimeters down to less than 10 nanometers. The developed methodology exploits novel electrochemical transformations confined at the interface between two solid materials, here the to-be-patterned OTS monolayer and a thin film coating that acts as a site-activated reagent/catalyst upon exposure to electrons.2 Site-targeted nanoscale exposure to electrons is achieved either by the use of a conductive AFM tip3 or a focused electron beam4. Our findings demonstrate the equivalence of the monolayer surface chemical transformations induced by the electrical AFM and the e-beam lithography approaches. Besides circumventing the need of *ex-situ* synthesis of functional monolayer components, this nondestructive electrochemical patterning methodology offers a number of unique features that allow realization of surface channels exhibiting unusual ionic and electronic transport5 along planned surface paths with precisely designed layouts that may reach centimetre lengths with widths down to less than 20 nm. Such channels represent a novel trype of inherently patternable single-layer functional material with tunable electrical properties.

Recent Publications

1. Monolayers assembled from n-octadecyltrichlorosilane (CH_3-(CH_2)17-$SiCl_3$) precursor molecules.
2. R. Maoz, D. Burshtain, H. Cohen, P. Nelson, J. Berson, A. Yoffe, J. Sagiv. Site-Targeted Interfacial Solid-Phase Chemistry: Surface Functionalization of Organic Monolayers via Chemical Transformations Locally Induced at the Boundary between Two Solids. *Angew. Chem. Int. Ed*. 2016, 55, 12366-12371.
3. R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv. "Constructive Nanolithography": Inert Monolayers as Patternable Templates for *in-situ* Nanofabrication of Metal-Semiconductor-Organic Surface Structures – A Generic Approach. *Adv. Mater*. 2000, 12, 725-731.
4. R.Maoz, J. Berson, D. Burshtain, P. Nelson, A. Zinger, O. Bitton, J. Sagiv. Interfacial Electron Beam Lithography: Chemical Monolayer Nanopatterning via Electron Beam-Induced Interfacial Solid-Phase Oxidation. *ACS Nano*, DOI: 10.1021/acsnano.8b03416.
5. J. Berson, D. Burshtain, A. Zeira, A. Yoffe, R. Maoz, J. Sagiv. Single-Layer Ionic Conduction on Carboxyl-Terminated Silane Monolayers Patterned by Constructive Lithography. *Nature Mater*. 2015, 14, 613-621.

Biography

Jacob Sagiv is a Professor in the Weizmann Institute Department of Materials and Interfaces. He received the BSc in Chemistry and Physics from the Hebrew University of Jerusalem, and PhD (1975) from the Weizmann Institute. As postdoctoral fellow (1975-1978, with Prof. Hans Kuhn) at Max Planck Institute for Biophysical Chemistry, Göttingen, J. Sagiv pioneered the modern research area of monolayer self assembly (*J. Chem. Phys*. 1978, 69, 1836-1847; *J. Am. Chem. Soc*. 1980, 102, 92-98). The term "self-assembling monolayer" was coined in 1983 (*New Scientist* 1983, 98, 20) with reference to the advancement by Sagiv group at WIS of the concept of chemically controlled layer-by-layer self-assembly (*J. Am. Chem. Soc.* 1983, 105, 674-676). The nondestructive chemical patterning of highly ordered self-assembled mono- and multilayers and special applications based on such purpose-designed synthetic structures have been central topics of Sagiv group's research at WIS. The 2005 Prize for Excellence of the Israel Chemical Society, "*for pioneering contributions to modern surface science by developing the self-assembly method of ordered arrays of molecules on surfaces*." The 2010 Kolthoff Prize in Chemistry, awarded by the Technion - Israel Institute of Technology. The 2015 Prize for Excellence in Research of the Israel Vacuum Society.