

Structure and Reactivity of Organized Layers and Multilayers Based on Two-Dimensional Conducting Polymers and Polyoxometallates

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There is a need to produce highly functionalized, hybrid, conducting polymer based films of controlled architecture and thickness as well as to develop methods for their micro- and nanopatterning [1]. In the present work, we propose and develop the concept based on multiple formation of two-dimensional layers composed alternately of conducting polymers (such as polyaniline or polypyrrole) and polynuclear inorganic compounds (such as polyoxometallate of molybdenum or tungsten). In the procedure, a ca. monolayer of the inorganic heteropolyanion is first adsorbed onto the electrode surface [2,3]. By immersing the resulting self-assembled monolayer into a solution of organic monomer, a composite (hybrid) layer is formed due to the interaction between the adsorbed polyanion and the solution cationic species. In one of examples considered by us, the approach has also involved polymerization of surface confined anilinium ions that have been electrostatically attracted to a negatively charged monolayer of heteropolymolybdate on glassy carbon or gold surface. The actual polymerization step can be controlled both chemically or electrochemically. By repeated and alternated immersions (treatments) in the appropriate solution, the amount of material on the electrode surface can be increased systematically in a controlled fashion leading to stable three-dimensional multilayered assemblies. Further, incorporation of a polymeric backbone within the inorganic monolayer units significantly increase the stability of films. The formation, morphology, structural transformations and electrochemical properties of both two-dimensional conducting polymer nanostructures on self-assembled inorganic monolayers and multilayered systems are examined using cyclic voltammetry, potential step techniques, microgravimetry, FTIR spectroscopy, STM and scanning electrochemical microscope. The approach provides a novel concept of not only assembling conducting polymers and inorganic species into composite structures but also producing molecular systems capable of charge storage in bilayer type coatings as well as organized monolayer

and multilayer assemblies with specific electrocatalytic properties [5].

It is also noteworthy that electrooxidative polymerization of aniline itself can be facilitated by modification of electrode surfaces with inorganic polyoxometallate, namely with self-assembled monolayers of dodecamolybdophosphate, PMo12O40⁴⁻. But by introduction of positively charged protonated 1,12-diaminododecane, NH₂-(CH₂)₁₂-NH₂, into anionic PMo12O40⁴⁻ monolayer, its interfacial charge can be inverted and the access of anilinium monomers significantly blocked. Consequently, the selective deposition of polyaniline is feasible, and preferential growth of the polymer on electrode surfaces modified with polyoxometallate has been observed, whereas microcontact printed patterns of protonated 1,12-diaminododecane within dodecamolybdophosphate monolayer has largely inhibited electropolymerization of polyaniline. When compared to the recent attempts of production of micron-scale patterns of polyaniline on self-assembled monolayers on functionalized alkanethiols [5], our approach involves both interfacial acceleration and inhibition of electrochemical polymerization of PANI, and it offers complimentary selectivity criteria. Further research is in progress aiming at manufacturing of patterned conducting polymer structures at micrometer and submicrometer scales.

References [1] I. Turyan, D. Mandler, *J. Am. Chem. Soc.*, 120, 10733 (1998). [2] D. Ingersoll, P. J. Kulesza, L. R. Faulkner, *J. Electrochem. Soc.*, 141, 140 (1994). [3] Kuhn, F. C. Anson, *Langmuir*, 12, 5481 (1996). [4] D. Martel, A. Kuhn, P. J. Kulesza, M. T. Galkowski, M. A. Malik, *Electrochim. Acta*, 46, 4223 (2001). [5] N. Sayre, D. M. Collard, *J. Mater. Chem.*, 7, 909 (1997).