Polyoxometallates as Inorganic Templates for Nanostructured Bilayers and Multilayers of Two-Dimensional Conducting Polymers

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There is an interest in fabrication of highly functionalized, hybrid, conducting polymer based films of controlled architecture and thickness as well as to develop methods for their micro- and nanopatterning. 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 heteropolymolybdate and heteropolytungstate). In the procedure, a ca. monolayer of the inorganic heteropolyanion is first adsorbed onto the electrode surface. By immersing the resulting self-assembled monolayer into a solution of organic monomer, a hybrid bilayer 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 heteropoly-molybdate on glassy carbon or gold surface. The actual polymerization step can be controlled both chemically and electrochemically. By repeated and alternated immersions in the appropriate solutions, the amount of material on the electrode surface can be increased systematically in a controlled fashion leading to stable multilayered assemblies. Consequently, physicochemical properties of the resulting coatings can be varied and tailored to practical needs. The formation, morphology and electrochemical properties of the nanostructered hybrid films are examined using cyclic voltammetry, potential step techniques, microgravimmetry, FTIR spectroscopy, STM and scanning electrochemical microscope. The approach provides a novel concept of not only assembling conducting polymers and inorganic species into composite nanostructures but also producing systems capable of effective and controlled charge transport and storage or electrocatalytic reactivity in organized monolayer and multilayer assemblies.