Structure and Reactivity of Network Films Composed of Nanostructured Polyoxometallates, Conducting Polymers and Metal Particles

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There has been growing interest in the fabrication of organized monomolecular (monolayer) and multilayered assemblies at solid surfaces that produce functionalized interfaces with well-defined composition, structure, reactivity and thickness. In this context, a substantial impetus is given to investigations of alkanothiols and their derivatives which can be successfully employed to obtain monolayer coverages on gold. An interesting alternative originates from the possibility of self-assembling inorganic monolayers on electrode surfaces. Inorganic (e.g. polyoxometallate) templates as design elements in nanocomposites at electrode surfaces provide potentially better stability, and they undergo reversible stepwise multielectron transfer reactions of importance to such technologies as electrocatalysis, electrochromism, molecular electronics and sensing. Heteropolyacids of molybdenum and tungsten are particularly attractive because of their ability to adsorb irreversibly on carbon and metal surfaces and to form structured films. We pursue here the concept based on multiple formation of two-dimensional arrays and three-dimensional networks composed alternately of a conducting polymer, such as polyaniline or polypyrrole, and a polyoxometallate of molybdenum or tungsten. In the procedure, a monolayer of the inorganic heteropolyanion is first adsorbed on a metal or carbon surface. By immersing the resulting self-assembled polyoxometallate nanostructure into a solution of organic monomer, a composite (hybrid) ultrathin layer is formed due to the interaction between the adsorbed polyanion and the solution cationic species. It is noteworthy that the electrostatic attachment does not freeze the orientation of the monomer but it leaves it a sufficient degree of freedom necessary for polymerization process. The actual polymerization step can be controlled both chemically, by choosing a polyoxometallate with sufficiently oxidative potential, or electrochemically by applying sufficiently positive potential to the system upon medium transfer to electrolyte. 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. Consequently, the thickness, composition, and physicochemical properties of the resulting three-dimensional networks can be varied and tailored to practical needs [1].

During recent years, it has also been established, that dense robust monolayers of alkanothiolates are capable of passivating gold nanoparticles and to produce alkanothiolate monolayer protected clusters or nanoparticles of gold [2]. They combine bulk and molecular properties within a nanometer scale material that is expected to yield novel and promising size-dependent electronic, optical and chemical properties. In the present work, we explore the ability of polyoxometallates to form self-assembled monolayers on metal nanoparticles and fabricate platinum (ca. 7-10 nm) nanoparticles (clusters) covered (protected) with polyoxometallate (phosphotungstate, phosphomolybdate) monolayers. Further, we can link them together by conducting polymer (polyaniline, polypyrrole) bridges to form network polymer films on glassy carbon, platinum and gold electrodes including gold-coated quartz crystals. The formation, morphology, structural transformations and electrochemical properties of the three-dimensional network films are examined using cyclic voltammetry, potential step techniques, microgravimmetry, FTIR spectroscopy, STM and scanning electrochemical microscope. From functional point of view, our preliminary results show that the approach is fairly general. Further, it 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.

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