

Electrocatalytic Sensing Using Novel Interfaces of Well-Ordered Hybrid Inorganic/Organic Monolayers

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Carbon electrodes which were modified with a monolayer of polyoxometallate ($P_2Mo_{18}O_{62}^{6-}$) or with a hybrid film of $P_2Mo_{18}O_{62}^{6-}$ and protonated 1,12 diaminododecane ($NH_2-(CH_2)_{12}-NH_2$), were used as substrates for the galvanostatic electrodeposition of highly dispersed platinum microparticles. For comparison, an unmodified (bare) carbon electrode was also considered. Significant differences in the morphology (dispersion and size of Pt deposits) were observed as a function of the pretreatment of the carbon substrate. Reactivity of the obtained electrocatalytic surfaces was probed by monitoring currents corresponding to the proton reduction and arsenic(III) oxidation. It was found that the respective voltammetric currents varied up to an order of magnitude despite the fact that, in all cases, equal amounts of Pt were deposited at the electrode surfaces. The electrocatalytic arsenic(III) oxidation current were correlated with the specific surface area of platinum particles deposited on the three types of electrodes studied. The existence of positively charged amino groups within the layer of polyoxometallate seems to have a profound effect on the distribution and morphology of platinum centers. Electrodeposition of metallic platinum in a form of submicro- or even nanoparticles is expected. Regardless the actual electrodeposition mechanism, the presence of positively charged amino groups from DAD is expected to have a profound effect on the final morphology of dispersed Pt. It is likely that platinum is produced in a form of submicro- or even nanoparticles. The ultimate goal is to prepare the ultrathin films self-assembled from polyoxometallate-based hybrid monolayers with catalytic metal submicrocenters that are dispersed, physically separated and exhibiting mutually activating metal-support interactions.

In the present work, we also 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. 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. 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. Details of the preparation and physicochemical, particularly electrochemical, properties of the produced films will be described. 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 coatings can be varied and tailored to practical needs. Our results also indicate that the incorporation of a polymeric backbone within the inorganic monolayer units significantly increase the stability of films. 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.

The intrinsic reactivity and electrocatalytic properties of these systems towards analytically important reactions like H_2O_2 or NO reduction should be enhanced by the introduction of precursors of noble metals like platinum or palladium into a multilayer built in a controlled manner by a new modification technique based on electrostatic interactions between the layers. The subsequent electrochemical treatment of the multilayer will produce highly dispersed metal particles attached to the electrode surface. The synergistic effect between the polyoxometallate and the noble metal (e.g. Pt) should provide enhanced catalytic efficiencies. In particular, this phenomenon should lead to the improved amperometric detection of small concentrations of H_2O_2 , which in turn is a key step for the development of various types of biosensors, since they are based on the use of H_2O_2 -producing enzymes.