

## Monolayer and Multilayer Nanostructured Films of Ultra-Thin Conducting Polymers, Polynuclear Inorganic Compounds and Metal Nanoparticles

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During recent years, there has been growing activity in the area of fabrication and characterization of monomolecular (monolayer) and multilayered organized assemblies at solid surfaces that produce functionalized interfaces with well-defined composition, structure, thickness and catalytic reactivity. In this context, a substantial impetus is given to investigations of alkanothiols and their derivatives, which can be successfully employed to obtain dense robust monolayer coverages on gold. The self-assembly of ordered organic molecular arrays formed spontaneously as monolayers on solid surfaces or the sequential adsorption of oppositely charged polyelectrolytes are of particular interest to the advanced materials preparation. Attractiveness of the self-assembly includes the possibility of controlled formation of any number of layers of different composition on a large variety of substrates. For example, the formation of ultra-thin films and ordered or derivatized assemblies of conjugated polymers shall be mentioned. Also synthesis of nanoparticles and their organization into two-dimensional arrays and three-dimensional networks have prompted the increased interest due to potential applications in many areas including molecular and nanoelectronics, sensors, catalysis and electrocatalysis. Monolayers of alkanothiolates are capable of passivating gold nanoparticles and producing alkanothiolate monolayer protected clusters of gold. An important function of alkanothiolates is to separate the metal (Au) clusters to prevent their agglomeration (i.e. degradation or aging). Self-organization of such clusters into the network films of metal nanoparticles is feasible. Such films 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.

An important possibility arises from the adsorption or chemisorption of inorganic monolayers (templates) that permits formation of two-dimensional arrays and three-dimensional (layer-by-layer) domains on electrodes. Among rigid inorganic templates, polyoxometallates and metal hexacyanoferrates are particularly attractive because of their ability to adsorb irreversibly on solid surfaces. In particular, heteropolyacids of molybdenum and tungsten are characterized by reversible stepwise multielectron transfer reactions of importance to electrocatalysis, electrochromism, molecular electronics and sensing. We address here the formation of bilayer and multilayer films composed alternatively from monolayers of phosphododecamolybdate ( $\text{PMo}_{12}$ ) Keggin type anions and conducting polymer, mostly polyaniline (PANI) [1] but also polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) [2]. PANI is commonly studied due to its well-defined redox properties, good protonic conductivity, in addition to high electronic conductivity, and chemical stability in acid

media. PPy is often considered for many applications because it is stable and conductive in the broad range of media that include neutral and acid solutions. PEDOT has recently been recognized as exceptionally stable and conductive (in its doped state) organic polymer. The layer-by-layer procedure involves polymerization of surface confined monomer ions that have been electrostatically attracted to a negatively charged monolayer of heteropolymolybdate on glassy carbon. The polymerization step is completed electrochemically upon medium transfer to acid electrolyte. By repeated and alternate treatments in the appropriate solutions, the amount of material on the electrode surface can be increased in a controlled manner. The fact, that formal potentials of  $\text{PMo}_{12}$  redox processes lie in the potential range where polymer interlayers are conductive, produces a system capable of fast charge propagation. We extend the above layer-by-layer procedure towards preparation of cyanometallate (e.g. Prussian Blue or cobalt hexacyanoferrate) based nanostructured organic-inorganic hybrid films as well.

We also explore here the ability of polyoxometallate (phosphomolybdate) to undergo adsorption and form monolayers on metal (Pt) nanoparticles (ca. 7 nm) [3]. Nanoparticles of platinum and its alloys are characterized by high surface area to volume ratios and exhibit promising electrocatalytic properties towards fuels, namely the reduction of oxygen and the oxidation of hydrogen or methanol. But catalytic reactivity of alkanethiol-protected Pt, Au/Pt alloy, or alkyl isocyanide-derivatized and mercaptoaniline-functionalized platinum nanoparticles is rather limited. Much more promising for electrocatalysis are colloidal platinum nanoparticles prepared within the environment of mixed metal oxide nanostructures. Introduction of polymer matrices tends to improve such physical properties as dispersion, size and morphology of metal particles. Therefore, we fabricate polyoxometallate covered (protected) particles and link them together by ultra thin conducting polymer (polyaniline) bridges. The growth, surface morphology and electrochemical properties of our three-dimensional network films are examined using cyclic voltammetry, potential step techniques, FTIR spectroscopy and STM. The films produce interfaces with specific electrocatalytic properties towards reduction of nitrite, bromate, hydrogen peroxide, and oxygen.

### References

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