## Abstract #2302, 224th ECS Meeting, © 2013 The Electrochemical Society New developments in electrophoretic nanotechnology.

## I. Zhitomirsky

## Department of Materials Science and Engineering McMaster University

## 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7

Despite the impressive progress achieved in the electrophoretic deposition of various nanomaterials, there is a need for simple and versatile methods for the efficient dispersion, charging and deposition of inorganic nanoparticles, carbon nanotubes, graphene and composites. A critical property of a dispersant is its adsorption on the particle surface. Therefore, there is a need in the development of charged dispersing agents with strong interfacial adhesion. A new bioinspired approach emerges from the mechanism of mussel adhesion to metal and mineral surfaces in underwater environment. The adhesion mechanism is related to the catecholic functionalities of natural biopolymers and their ability to form interfacial chemisorption complexes. The investigation of the biomimetic adhesion resulted in the development of new approach to the dispersion of inorganic nanoparticles using the organic/inorganic surface adhesion mechanisms.

Aromatic molecules from catechol, gallic acid, salicylic acid and chromotropic acid families were investigated as charging additives for the electrophoretic deposition of oxide nanoparticles. The deposition yield has been studied as a function of the additive concentration. The adsorption mechanism was investigated using Fourier transform infrared spectroscopy, UV-Vis spectroscopy, quartz crystal microbalance method and other techniques. The results obtained for the monoaromatic and polyaromatic molecules with different functional groups were analyzed and compared. The adjacent OH groups, as well as adjacent OH and COOH groups bonded to the aromatic rings of the aromatic molecules were beneficial for adsorption of the molecules on oxide particles. The adsorption mechanisms involved the interaction of COOH groups and OH groups of the organic molecules with metal ions on the particle surfaces and complexation. Gallic acid was shown to be an effective charging additive, which provided stabilization of oxide nanoparticles in the suspensions and enabled their anodic deposition. It was shown that composite oxide films of controlled composition can be obtained using gallic acid as a co-dispersing agent for different oxides. As an extension of these investigations, the adsorption of polyaromatic molecules from catechol and salicylic acid families on oxide nanoparticles has been studied. Fourier transform infrared spectroscopy data showed that the adsorption mechanism is related to the complexation of adjacent OH and COOH groups bonded to the aromatic ring. Polyaromatic molecules, such as pyrocatechol violet, calcon carboxylic acid, aluminon were utilized for the fabrication of composite films, containing nanoparticles of different oxide semiconductors.

An important finding was the possibility of cathodic and anodic deposition of polyaromatic molecules, which formed dense films or fibrous nanostructures. The discovery of novel dispersing agents with film forming properties allowed efficient deposition and co-deposition of various inorganic materials. The co-deposition of  $TiO_2$ with organic dyes has created opportunities in the dye sensitization of the materials prepared by electrophoretic deposition. Moreover, it was found that the adsorption of dopamine, gallic acid and other charged molecules from the catechol family resulted in the changes of optical properties of  $TiO_2$  nanoparticles.

The organic molecules from the catechol family and related phenolic molecules were investigated for the surface modification of oxide nanoparticles for application in advanced photovoltaic devices and sensors. The polyaromatic dispersants showed strong adsorption on carbon nanotubes and graphene. The adsorption mechanism is attributed to  $\pi$ - $\pi$  interactions. It was found that efficient dispersion and deposition of pristine carbon nanotubes and graphene can be achieved at low dispersant concentrations. The new dispersant molecules can be used for the dispersion of different types of materials, such as oxide nanoparticles, carbon nanotubes and graphene using different adsorption mechanisms. These results paved the way for the fabrication of metal oxide carbon nanotube, metal oxide - graphene and carbon nanotube-graphene nanocomposites. The fundamental deposition mechanisms were investigated and discussed. New approach was used for electrophoretic co-deposition of MnO<sub>2</sub> nanoparticles and carbon nanotubes for the fabrication electrochemical of electrodes for supercapacitors. The incorporation of carbon nanotubes in the composite films resulted in improved electronic conductivity and high specific capacitance. Significant improvement in capacitive behavior of carbon nanotubegraphene nanocomposites was achieved by the use of new dispersing agents.

The anionic dispersing agents were also investigated for the fabrication of composite polypyrrole - metal oxidecarbon nanotube films. In this approach the anionic molecules provided charge compensation during electropolymerization of pyrrole, and enabled efficient dispersion of oxide nanoparticles and carbon nanotubes and their electrophoretic incorporation into the polypyrrole films. It was found that the additives have another beneficient effect, which is related to their adsorption on the stainless steel substrates. The adsorption of the additives provided passivation of the substrates, enabled efficient charge transfer during electropolymerization and the formation of adherent films on stainless steel substrates.

The composite films prepared by electrophoretic deposition are promising materials for photovoltaic, energy storage and sensor applications. We developed a library of additives suitable for efficient dispersion and electrophoretic deposition of various nanomaterials.