



How does metallophthalocyanine molecule catalyze redox reaction at a supramolecular level?

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Abstract – Recently, we showed that incorporation of nanoparticles in supramolecular layer-by-layer (LbL) films containing metallophthalocyanines (MTsPc) enhanced the Faradaic currents for the redox processes. Also, MTsPc one needs a supramolecular environment to be persuaded of a maximum catalytic effect. This only occurred effectively for MTsPc in LbL films owing to the high rates of charge transfer, which points to the importance of supramolecular effects to the charge transport mechanism. Here, we show experimental evidences of the pathway of the redox reaction involving MTsPc at a supramolecular level. Furthermore, we will demonstrate for the first time that the unusual synergistic effects from combining nanoparticles and MTsPc in the same system, tuning on its electrochemical properties for applications in sensors.

Motivation for studying phthalocyanine arises from its biocompatibility and high solubility in physiological media, in addition to the possible tuning of its optical and dielectric properties and varied applications in sensors and catalysts [1,2]. With regard to electrocatalysis, attempts have been made to optimize the electrochemical properties of supramolecular structures based on metallophthalocyanines (MTsPc) and metalloporphyrins (MPc). Higher catalytic activity was measured with MTsPc, in comparison to MPc, mainly because of the possible incorporation of withdrawal groups to the phthalocyanine ligand (Pc), which increases the potential of the metal center and TsPc ligand. For example, in layer-by-layer (LbL) films comprising polyallylamine hydrochloride (PAH) alternated with nickel tetrasulfonated phthalocyanine (NiTsPc) via electrostatic interaction between $-\text{NH}^{3+}$ (PAH) and $-\text{SO}^{3-}$ (NiTsPc) groups, a second redox process was observed for the metallic center [1,3-5]. This only occurred effectively for NiTsPc in LbL films owing to the high rates of charge transfer, which points to the importance of supramolecular effects to the charge transport mechanism [4,5].

Here, we focus on the production of new classes of nanomaterials, whose properties are varied significantly by the interplay among their constituents at electrode surface. As example, we incorporate gold nanoparticles (AuNP) in the polymeric matrix of poly(allylamine hydrochloride) (PAH) to enhance the charge transport properties of phthalocyanine molecules in nanostructured films. The strategy was to investigate the electrocatalytic properties toward oxidation of hydrogen peroxide in multilayers films and verify the importance of adding AuNPs. Also, we use LbL technique in order to assemble CoTsPc and PAH in a hybrid supramolecular systems. We used electronic spectroscopy and cyclic voltammetry to study the PAH/CoTsPc multilayers growth and the cysteine amino acid catalytic oxidation. It is shows truly understand that the CoTsPc catalyze oxidation of cysteine based firstly on $\text{CoTsPc(II)} \rightarrow \text{CoTsPc(III)} + e^-$ electrochemical reaction. Furthermore, PAH/CoTsPc showed high electrochemical stability and worthwhile to mention is the remarkable influence of supramolecular arrangement on the final redox properties of the system

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