Assemblies of Porphyrin Layers on ITO and Deposition of Polyaniline on Porphyrin Layered ITO

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Since the first report of high energy conversion efficiencies for dye sensitized TiO_2 solar cell, a great deal of work was devoted to understand the interfacial electron transfer phenomena and to increase the cell performance.[1] In order to increase the cell efficiency, systematic piling-up of photon harvesting dye molecules on the surface of semiconductor, such as multilayer sensitization, was proposed.[2] The multilayer structure of certain molecule forms a hole or column that can be occupied by an electro active guest molecule and the resulting composite might facilitate electron transfer.[3]

Polyaniline is a conducting polymer that has been widely studied for the electronic and optical application.[4] Polyaniline has five basic structures (leucoemeraldine, protoemeraldine, emeraldine, nigrraniline, pernigraniline) with different oxidation states, which are chemically and electrochemically switchable. This unique property of polyaniline can be utilized in electron transfer process, serving as either electron acceptor (hole acceptance),[1] or electron donor (hole injection)[5] depending on the relative positions of redox potential of exited dye molecule and polyaniline.

In this work, we report the procedure for assemblies of porphyrin multilayer as dyes on ITO (indium-thin oxide) and electropolymerization of aniline as conductive material inside porphyrin building blocks. Porphyrin units are assembled layer-by-layer by zirconium phosphonate (ZrP) linkage and polyaniline is electrochemically packed inside the porous films.

Experimental Section

Materials. Tetrabutylammonium perchlorate (TBAP) was purified by recrystallization from CH_2Cl_2, dried under vacuum and stored in a vacuum desiccator. Aniline (Aldrich) was freshly distilled before use and all solvents were dried and stored under nitrogen. Porphyrin, **1**, was prepared by Lindsey synthesis strategy.[6] Indium-tin oxide (ITO: Delta Technologies, Ltd., 10 Ω/square) plates were cleaned by a 15 minute-immersion in a heated aqueous solution of ethanolamine (Aldrich, 20%), then rinsed several times in deionized water (Milli Q) and dried under a stream of nitrogen. UV-visible absorption spectra were measured on a


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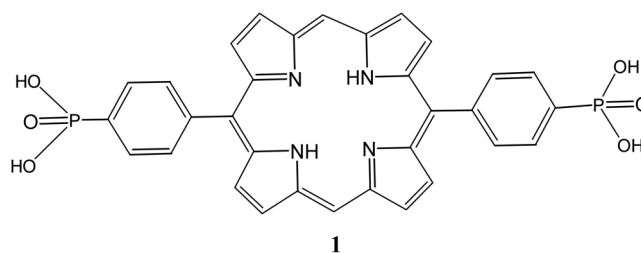
HP8452A spectrophotometer.

ZrP-assembled porphyrin films. The porphyrin layers were built on ITO as described in Literature.[7-9] Briefly, ITO platforms were cut to 0.8×3 cm and cleaned for 30 minutes in a piranha solution ($H_2SO_4 : H_2O_2 = 3 : 1$), then rinsed with deionized water and oven dried. ITO was phosphorylated in an 1 : 1 solution of 2,4,6-collidine (20 mM) and $POCl_3$ (20 mM) in acetonitrile for 30 minutes. The phosphorylated ITO surface was coordinated by tetravalent zirconium by an overnight soak in a 25 mM $ZrOCl_2$ aqueous solution. The platforms were rinsed and dried with N_2 stream, then soaked in phosphorylated porphyrin solution (0.01 mM in DMSO) overnight. Additional ZrP-porphyrin layers were assembled via successive treatment with 25 mM $ZrOCl_2$ and 0.01 mM porphyrin.

Electrochemistry. Experiments were performed in CH_2Cl_2 with 0.2 M TBAP (tetrabutylammonium perchlorate) as the supporting electrolyte using three electrodes arrangement with silver wire as a reference electrode, platinum foil as a counter electrode and ITO platform as a working electrode. Cyclic voltammograms were obtained at 100 mV/s with Bioanalytical Systems CV-27 potentiostat in 1 mM aniline. Solutions were degassed for 10 min with nitrogen.

Results and Discussion

ZrP-assembled porphyrin films. The best build-up of porphyrin layers are achieved when ITO plate is well dried with N_2 stream after each layer of Zr(IV) incorporation. Failure to dry the films gradually causes a hydrolytic decomposition of porphyrin in a DMSO solution and contaminates the solution. Molecule **1** is a highly absorbing ($\varepsilon_{402} = 2.5 \times 10^5 \, M^{-1} cm^{-1}$) chromophore. Polarized absorbance measure-
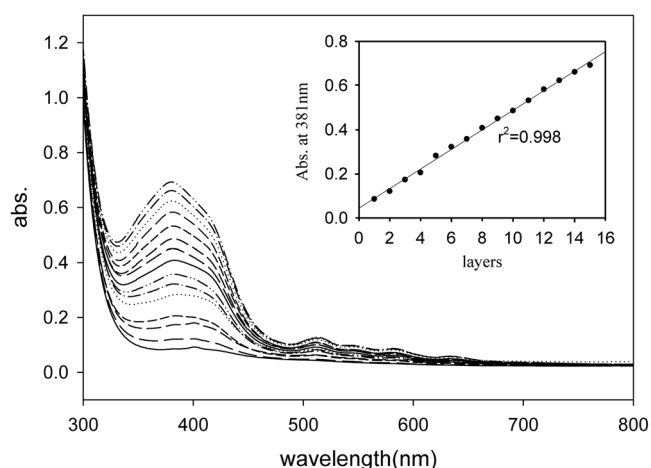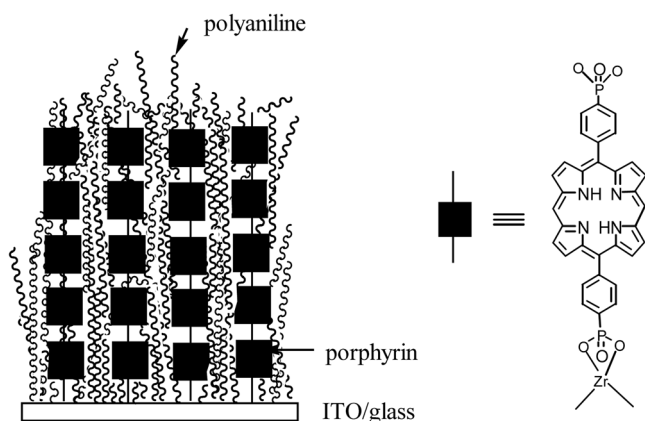
Figure 1. UV-Vis spectra of 15 layers of porphyrin on ITO. Inset: absorbance at 381 nm *vs.* porphyrin layers.

ments showed that the film-based porphyrins are oriented normal to the ITO surface.[7]

Upon assembling **1** on ITO surface via ZrP linkage, the porphyrin's Soret absorption band is broadened and split (Fig. 1). The broadening of the Soret band is characteristic of exitonic interactions arising from "edge-on-edge" porphyrin aggregate formation.[10] The intensity of absorbance at 381nm is plotted against the number of layers in inset. The linearity is well achieved with an average absorbance increase of 0.04 a.u. per layer. Since the films assemble on both sides of a platform, the absorbance increase per layer in one side is 0.02 a.u.. Due to the broadening of the Soret band, the intercept is not zero. The films are stable as long as it is stored in the dark under vacuum.

Electrochemical deposition of polyaniline on porphyrin layered ITO. To deposit a polyaniline on porphyrin layered ITO, electrochemical polymerization is applied. Schematic representation of the highly idealized porphyrin/polyaniline composite is given in Figure 2. As the ZrP-porphyrin building blocks are not stable in the acidic aqueous media which is a general condition for aniline polymerization,[11] non-aqueous solvent such as CH_2Cl_2 was chosen. Before the deposition of polyaniline on the

porphyrin layered ITO electrode, it is necessary to test the stability of the porphyrin assemblies under the potential range for aniline polymerization conditions. The porphyrin layered ITO plate was swept between 0-1.2 V under the same conditions for electropolymerization without aniline. Porphyrin film did not show redox wave, as expected. UV-Vis spectrum (not shown here) of porphyrin films does not change after 20 scans in this potential range, indicating that the films are inert under this experimental condition. The CH_2Cl_2 solution phase in which the porphyrin layered ITO was dipped, was tested by UV-Vis spectroscopy in order to check whether the porphyrin layers are partially destructed and porphyrin monomers were dissolved in CH_2Cl_2. UV-Vis spectrum showed no absorbance corresponding to porphyrin molecules. An independent study on the electrochemical assessment of porosity by the redox-active probe molecules was conducted with three layers of porphyrin in the range of potential, 0-1.2 V, referring that the film did not undergo destruction in this potential range.[7]

Oxidative electropolymerization in aniline-containing solutions was done with porphyrin-layered ITO electrode at a linearly cycling potential between 0.0 and +1.2 V. As is the characteristic of nonpassivating electropolymerization, the polymer film remains electroactive at the polymerization potential so that the oxidation and reduction envelopes grow

Figure 2. Highly idealized porphyrin/polyaniline composite.
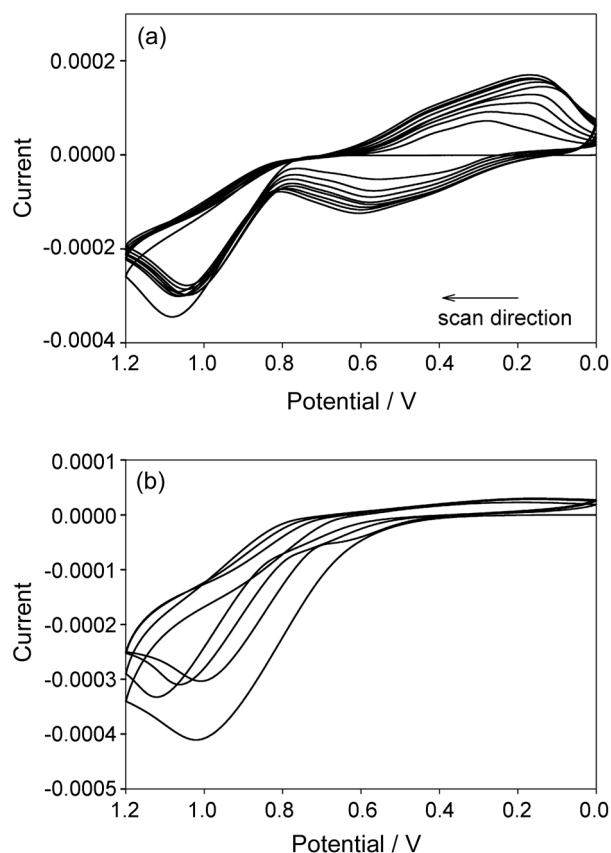
Figure 3. Cyclic voltammograms showing the growth of polyaniline films in 0.2 M TBAP, 1 mM aniline in CH_2Cl_2, scan rate 100 mV/s. (a) polyaniline on bare ITO. (b) polyaniline on porphyrin layered ITO.
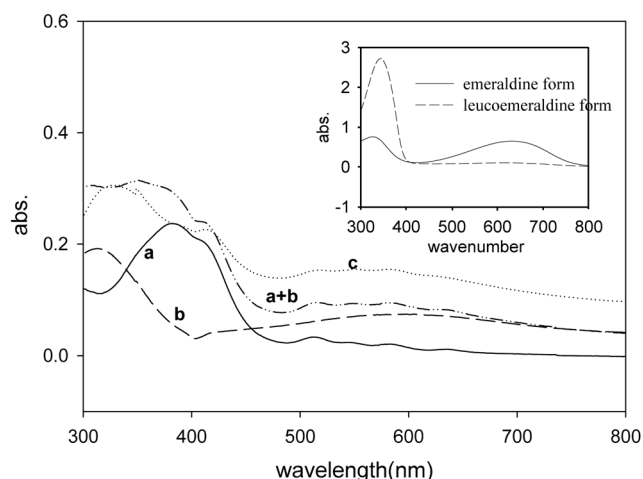
Figure 4. UV-Vis spectra for thin film on ITO obtained based on: (a) 5 layers of porphyrin, (b) polyaniline on bare ITO (50 scan), (c) polyaniline on porphyrin layered ITO. Also shown is the sum of spectra (a) and (b). Inset: UV-Vis spectra for polyaniline in emeraldine and leucoemeraldine form.

with each successive potential cycle in the Figure 3a. Similar CV patterns were reported in oxidative polymerization of aniline in acetonitrile.[12] For a comparison, polyaniline films obtained in aqueous acidic conditions show the oxidation at 0.16 V and 0.8 V and reduction at 0.20 V and 0.75 V.[13] Figure 3b shows the polymerization of aniline on the porphyrin layered ITO. The scan cycle related to the polyaniline hights was determined according to the literature, so that polyaniline was grown as high as the porphyrin layer.[7] (However, the exact estimation of polyaniline heights could not be made, as the RMS surface roughness ranged several tens of nanometer.) Excessively overcoated polyaniline is not desirable, as an excess deposition of polyaniline may interfere with the photoinduced electron transfer of porphyrin/polyaniline composite.

Voltammograms between 0.0 V and 0.5 V have no apparent redox peaks. It seems that the reversible redox process of polyaniline films in this potential range is influenced by the presence of porphyrin films that can limit an electron transport.[14,15] However, the oxidation of polyaniline films (oxidation from emeraldine to pernigraniline) is observed at *ca*. 1.0 V in a very similar pattern to Figure 3a referring that polyaniline is deposited on the porphyrin layered ITO plate.

UV-Vis spectra give more concrete information on the formation of porphyrin/polyaniline composite. Figure 4 shows UV-Vis spectra for thin films obtained from a) 5 layers of porphyrin, b) electropolymerized polyaniline, c) 5 layers porphyrin followed by polyaniline deposition. Also shown is the sum of spectra a) and b). The inset in Figure 4 shows the UV-Vis spectra of a pure leucoemeraldine and emeraldine form of polyaniline. The broad absorbance at *ca*. 600 nm in b) is characteristic for emeraldine form (partially

oxidized form). The intensity of this broad band is, however, weaker than that of the band at *ca*. 320 nm, indicating that oxidation from leucoemeraldine to emeraldine form is in progress. The polymer takes at first leucoemeraldine form, because the scan potential ends at 0 V, then the polymer is slowly oxidized to a stable emeraldine form upon exposure to air.[16] The enhanced intensity in the range of 500-800 nm in c), compared to the sum of a) and b), can be due to the contribution of the further transformation leucoemeraline form to emeraldine.

In conclusion, layer-by-layer assembled porphyrin films form a porous building block, the pores then can be filled with conductive polymer to give electroactive multicomponents material.

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