Spectral Sensitization of ZnO by Phthalocyanine and/or Porphyrin Molecules Attached by Electrochemical Self- Assembly

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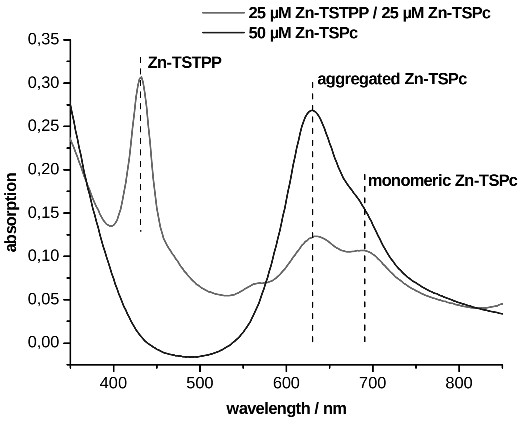
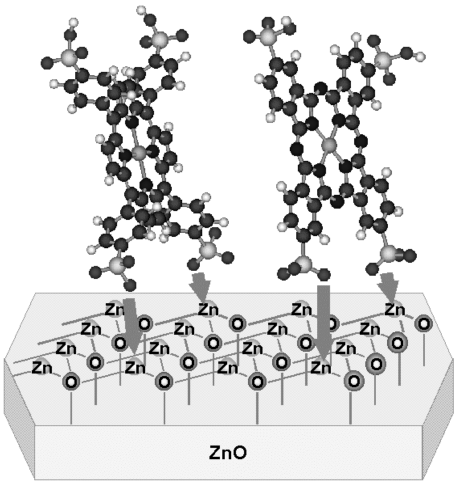
Composite thin films of nanoparticulate ZnO sensitized with different organic dye molecules were prepared in a one step electrodeposition from aqueous mixed solutions of zinc chloride or -nitrate and water- soluble dye molecules. Such electrochemical self- assembly has turned out to be an excellent method for the construction of well- controlled inorganic/ organic hybrid films with prospective use as photo- electrodes in dye- sensitized solar cells [1,2]. Crystalline ZnO was obtained in almost all cases, but the morphology of the films was strongly influenced by the condition of film growth and the specifics of different dyes. The films were characterized by UV/Vis-spectroscopy, X-ray diffraction, atomic force microscopy and by their photoelectrochemical activity. The orientation of the crystallites relative to the substrate electrode turned out to be dependent on preferential adsorption of the dyes on the different ZnO surfaces.

The present contribution is focused on the use of tetrasulfonated porphyrins and phthalocyanines as structure- directing agents during film growth and, subsequently, as sensitizers. Aside from their close similarity to each other (18 π- electron macrocyclic system), these molecules are interesting to study because of the technical relevance of phthalocyanines and the biological significance of porphyrins.



In composite electrodes of tetrasulfonated phthalocyanines (TSPc) and ZnO deposited by electrochemical self- assembly a strong difference was seen in the photoelectrochemical efficiency when either monomeric or aggregated forms of dyes were present [3,4]. The problem of a generally low efficiency of aggregates could be overcome by the use of tetrasulfonated tetraphenyl porphyrines (TSTPP) since the phenyl groups break the stiffness of the molecule and thereby hinders the formation of aggregates. These molecules were also adsorbed during growth of ZnO and the photoelectrochemical studies showed that they also worked as sensitizers for ZnO. The kinetic feasibility of the charge transfer to a redox electrolyte at the surface of these films was investigated by photocurrent transients. Further, it was possible to co- deposit both organic dyes, TSPc and TSTPP simultaneously, together with ZnO. The presence of monomeric vs. aggregated forms of the dyes in these films was investigated based on UV/Vis- spectra. The photoelectrical characteristics of these electrodes were studied under simultaneous, parallel activity of both dyes, but also independently.



For this purpose, photocurrent transients were measured in the ms- range. A mixture of acetonitrile and ethylenecarbonate (1:4 by volume) dissolving 0.5M KI was used as the redox electrolyte. White light from a 1000 W arc lamp with an intensity of 250mW cm^{-2} was used. To allow light absorption by either all, only some, or individual absorbing components (ZnO, TSTPP, TSPc), a combination of a UV cutoff filter and evaporated films of the two classes of pigments (unsubstituted TPP and Pc) were used to provide the highest possible selectivity at a maintained high light intensity.

Films with either one of the two classes of dyes or also both classes of dyes present simultaneously worked as photoelectrodes. Aside from adding the individual contributions of both dyes to the overall sensitized photocurrent in a given film, however, interactions of the different dye molecules played a decisive role. These interactions were detected when the characteristics of films with only one dye were compared to those films with both dyes adsorbed to ZnO. In particular the initial response to a light flash showed interesting differences.

In the present study, simultaneous adsorption of different dye molecules could be proven to yield electrodes of crystalline ZnO that can be sensitized by both dyes. This method opens an interesting option to include panchromaticity in dye- sensitized oxide electrodes at still only one step of preparation.

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