Interaction between tetrasulfophthalocyanines and colloidal titanium dioxide and photoelectric behavior on sensitized microporous TiO₂ electrodes

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The photosensitization of wide-band gap semiconductors using organic dyes is the subject of an
intensive investigation due to its importance for solar energy conversion[1]. However, the efficiency of such photovoltaic devices is rather low. The problems arise primarily from the relatively low absorbance of monolayer of dyes adsorbed on a smooth surface. Thick dyes layers tend to increase the electrical resistance of these films, so the overall light to electric conversion efficiency decreases. Recently, Gratzel and collaborators[2] described a dye-sensitized TiO$_2$ photoelectrochemical device using microporous TiO$_2$ electrode with a monolayer coating of ruthenium polypyridyl complex dye. Because of the high surface area of the TiO$_2$ film and the characteristic spectral properties of the dye, the device harvests a high proportion of incident light and has a solar-to-electric conversion efficiency of 7%—12% comparable to amorphous-silicon cells. However, the ruthenium dye they used absorbs light around the 500 nm region. The search for sensitizers that may harvest more energy available in the solar spectrum is of particular interest. Phthalocyanines possess intense absorption in the visible region and are stable toward heat and light so that they can be employed in the sensitization of semiconductor electrodes and particles. One of the important criteria for an efficient photosensitization is to adsorb the dyes on the semiconductor surface with an electrostatic or chemical interaction. In this note, we describe phthalocyanine and its gallium and titanium derivatives with a sulfonic group as the substituent that can interact with the TiO$_2$ surface and facilitate charge injection into the conduction band of the semiconductor. Interaction between the sensitizer and colloidal TiO$_2$ was probed with absorption and fluorometric spectroscopy. The apparent association constants for the association between colloidal TiO$_2$ and phthalocyanines were calculated. The photoelectric behavior of sensitized microporous TiO$_2$ electrode was studied, the photocurrent spectra were measured and the mechanistic aspects of the photosensitization process were studied.

1 Experimental

1.1 Materials

TiOTSPc and H$_2$TSPc were synthesized in our laboratory[3]. GaTSPc was provided by Prof. Wu Xing of Yangzhou Normal University. The crude product was purified and characterized by elemental analysis before use.

Preparation of ultrafine colloidal TiO$_2$[4]: The colloidal TiO$_2$ was prepared by hydrolysis of titanium (IV) isopropoxide, then subjected to dialysis to exclude traces of isopropanol. The pH of the solution was adjusted to 2.5 and the solution was diluted to 0.1 mol/L for spectroscopic measurements. The average particle size of the colloidal TiO$_2$ was determined to be 5 nm by TEM.

Electrode preparation: The microporous TiO$_2$ electrode was prepared according to the published method[4] and was about 20 μm thick with a specific surface area of 271. The TiO$_2$ electrode was immersed in 0.1 mol/L HCl solution for 20 min, then in a 2.0 × 10$^{-4}$ mol/L tetrasulfophthalocyanine aqueous solution for 24 h, resulting in deep blue coloration due to attached dye.

1.2 Methods

Absorption spectra were recorded with a Shimadzu UV-2201 spectrophotometer. Fluorescence spectra were measured by a Perkin-Elmer LS-5 spectrofluorometer equipped with a 3 600 data station with excitation wavelength 608 nm, excitation slit 5 nm. Relative fluorescence quantum yield was determined using ZnPc (Φ = 0.3)[5] as standard.

Photocurrent was measured by a potentiostat model CMBP-1. Monochromatic light was