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ENHANCEMENT OF SOLAR PHOTOCATALYTIC DETOXIFICATION BY ADSORPTION OF PORPHYRINS ONTO TiO_2*

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ABSTRACT

Titanium dioxide (TiO_2) is a photocatalyst for solar detoxification of water containing organic contaminants such as solvents, PCB's, dioxins, pesticides, and dyes. Unfortunately, the ultraviolet (UV) energy used by TiO_2 (λ<400 nm) only comprises about 4% of the solar spectrum. One way of enhancing the efficiency of solar detoxification technologies is to utilize a larger portion of the solar spectrum to initiate the TiO_2-catalyzed detoxification chemistry. Metalloporphyrins strongly absorb visible and near infrared radiation. By utilization of a process called photosensitization, adsorption of these dyes onto TiO_2 can enable a much broader portion of the solar spectrum to be used. Photosensitization relies upon the ability of the dye molecule to absorb more of the solar energy than bare TiO_2 and to interact electronically with the TiO_2 surface in such a way as to initiate TiO_2-based redox photochemistry using the dye-absorbed energy.

Using visible light, we have investigated Ni(II) uroporphyrin (NiUroP), Sn(IV)Cl_2 uroporphyrin (SnUroP) and Sn(IV)Cl_2 tetrakis(*p*-carboxyphenyl)porphyrin (SnTCPP) as possible enhancers of destruction of a model organic toxic compound, salicylic acid (SA), by means of photosensitization of colloidal TiO_2 particles. All three porphyrins are found to adsorb reversibly onto the colloidal suspension of TiO_2 powder upon variation of pH. Adsorption of these porphyrins results in the induced colloidal stability of fine TiO_2 particles in a pH range where the colloid is not normally formed. While NiUroP on TiO_2 does not show any enhancement of photodestruction of salicylic acid, the adsorption of SnUroP increases the destruction rate compared to that of the bare TiO_2 surface. The enhancement of destruction is presumably due either (1) to injection of electrons from the reduced Sn porphyrins into the conduction band of TiO_2, (2) to reduction of porphyrin by conduction band electrons, or (3) to photosensitization involving the production of reactive species such as singlet O_2. The effect of ambient oxygen on the observed photolability of the Sn porphyrins and the contribution of oxygen species to enhancement of photodetoxification was investigated. SnTCPP does not photodecompose upon illumination either in the presence or absence of TiO_2, but neither does it bind to the TiO_2 surface at pH 6. At pH 4.5, SnTCPP is fully adsorbed onto TiO_2 but it also photodecomposes at this pH. We are trying to stabilize photodegradable porphyrins, such as SnUroP, by modifying them with suitable substituent groups at the periphery of the porphyrin moiety.

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