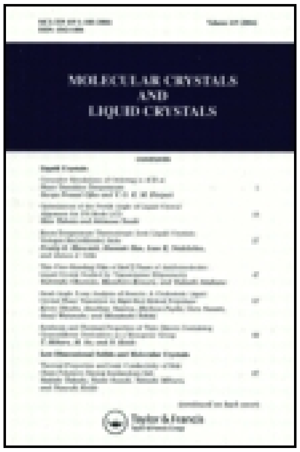

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Photochemical Processes on Oxide Surfaces. A Diffuse Reflectance Laser Flash Photolysis Study

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PHOTOCHEMICAL PROCESSES ON OXIDE SURFACES. A DIFFUSE REFLECTANCE LASER FLASH PHOTOLYSIS STUDY.

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Abstract The diffuse reflectance laser flash photolysis experiments which elucidate the excited state behavior of a thiazine dye on the surfaces of SiO_2, Al_2O_3 and TiO_2 are described. The permanent degradation of the dye observed on the TiO_2 surface has been explained on the basis of a direct electron-transfer quenching of excited states by TiO_2.

INTRODUCTION

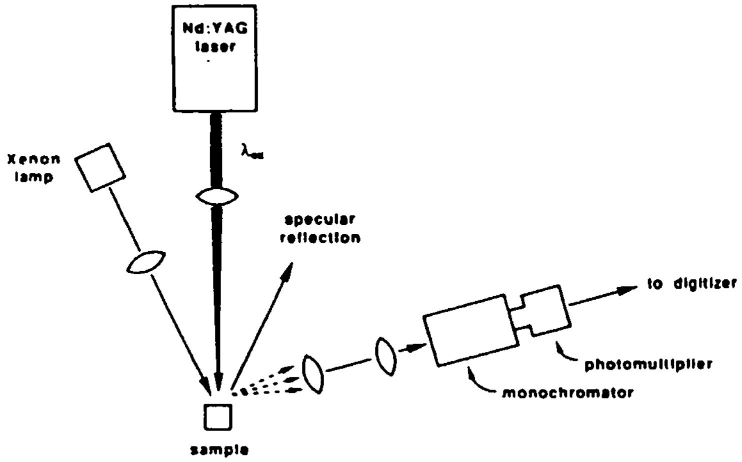
Our continuing interest in the photophysics and photochemistry of molecules adsorbed onto the surfaces of submicron-sized inorganic particles[1-5] has led us to study the excited state behavior of dyes on oxide surfaces such as SiO_2, Al_2O_3 and TiO_2. Such support materials can be classified into two categories: (i) inorganic supports such as SiO_2 or Al_2O_3 which provide an ordered two-dimensional environment for effecting and controlling photochemical processes more efficiently than can be attained in homogeneous solutions; and (ii) semiconductor supports such as TiO_2 or ZnO, which directly participate in the photochemical processes either by absorbing the incident photon and transferring charge to an adsorbed molecule or by quenching the excited state of the adsorbed molecule.

There have been a number of studies that employed fluorescence emission as a probe for investigating the radiative and nonradiative processes of organic dyes and inorganic complexes on oxide surfaces.[6-8] We have now investigated excited state behavior of an organic dye, thionine, on the surfaces of SiO_2, Al_2O_3 and TiO_2 using diffuse reflectance laser flash photolysis. This technique has been found useful in investigating spectroscopic and kinetic properties of the transients generated upon laser pulse excitation of opaque solid samples in the form of powders and films.[9-12]

EXPERIMENTAL

Anatase TiO_2 powder (surface area 50 m^2/g, particle diameter 30 nm) was obtained from Degussa Corp. (P-25). Silica powder (200-425 mesh, 60 Å) and alumina (neutral, ~ 150 mesh, 58 Å) were obtained from Aldrich. The dye was adsorbed onto these support materials by dispersing the particles in acetonitrile and adding a known amount of the dye solution. The suspension was stirred for two hours and filtered. The samples were dried in an oven at 65 °C for 24 hours.

The diffuse reflectance absorption spectra of thionine adsorbed on oxide particles were recorded with a Cary 219 spectrophotometer with a diffuse reflectance attachment (Harrick Scientific). Time-resolved diffuse reflectance laser flash photolysis experiments were carried out in a vacuum-tight 10 x 10 x 40 mm^3 rectangular quartz cell. The dried samples were evacuated for 3-5 hours. The 532 nm laser pulse (10 mJ, pulse width 6 ns) from a Quanta Ray DCR-1 Nd:YAG laser system was used for the excitation of the sample. A 1000 W xenon lamp was used as the monitoring source. The diffusely reflected monitoring light from the sample was detected with photomultiplier, the output of which was fed to a Tektronix 7912AD digitizer. The schematic diagram of the experimental setup is shown in Scheme I, the details of which will be described elsewhere.[13]



Scheme I. Schematic diagram of the diffuse reflectance laser flash photolysis setup.

RESULTS AND DISCUSSION

Absorption and Emission Characteristics

The absorption spectra of thionine (TH^+) adsorbed on SiO_2, Al_2O_3 and TiO_2 are shown in Figure 1. TH^+ on silica exhibits an absorption maximum at 605 nm which is similar to the absorption characteristics of the monomeric dye in polar solvents. However in the case of Al_2O_3 and TiO_2 the absorption band (530-550 nm) due to dye aggregation dominates the absorption spectrum. The absorption due to monomeric dye appears only as a shoulder at ~ 600 nm. It is interesting that

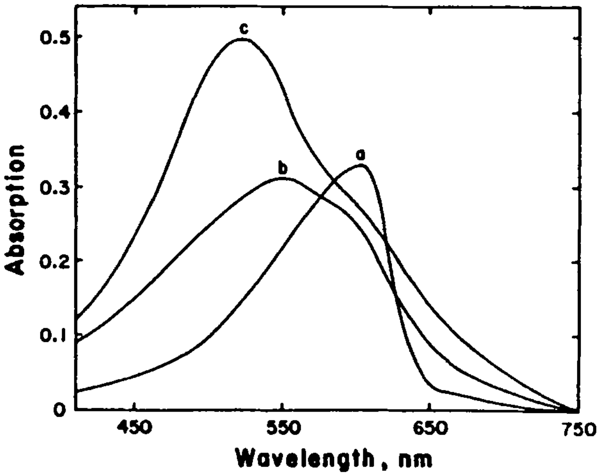


Figure 1 Diffuse reflectance ground state absorption spectra of thionine on (a) silica, (b) Al_2O_3 and (c) TiO_2 particles. The surface coverage of the dye in each case was 0.4 mg/g support.

even at submonolayer coverages, both TiO_2 and Al_2O_3 promote aggregation of the dye on its surface. These observations are very similar to our recent study[14] of anthracene-2-sulfonate on alumina coated silica particles in which dimerization of anthracene-2-sulfonate was observed even when fewer than 1% of available adsorption sites were occupied.

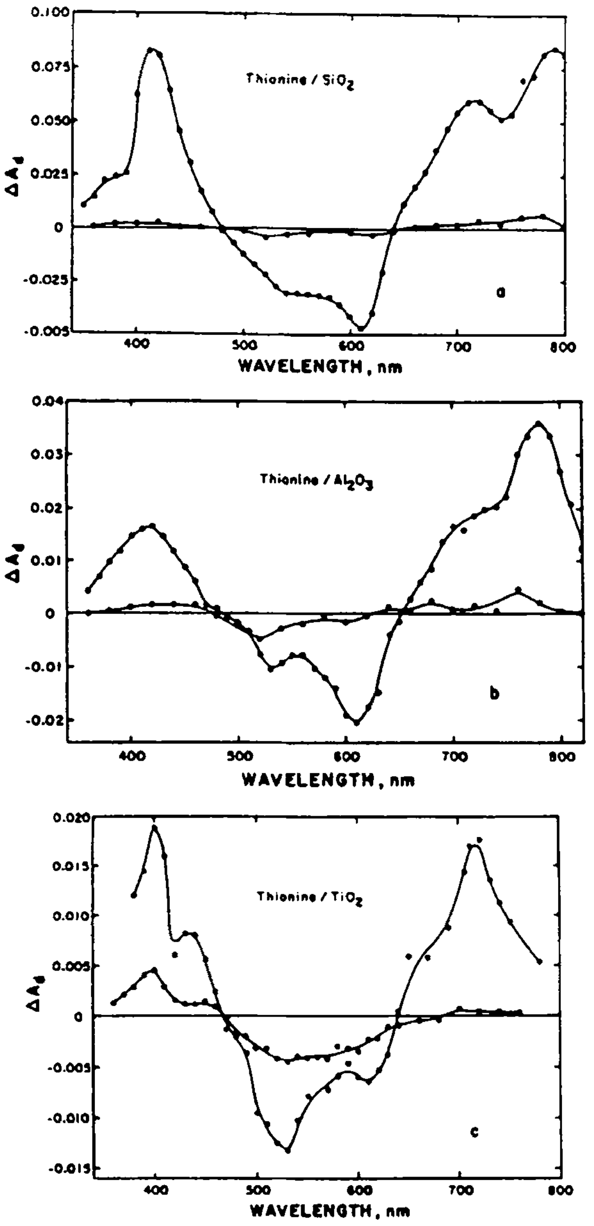


Figure 2 Transient absorption spectra recorded immediately after 532 nm laser pulse excitation of thionine adsorbed on (a) silica, (b) Al_2O_3 and (c) TiO_2 surfaces (0.4 mg/g support): (●) degassed and (o) O_2-saturated samples.

Laser Flash Photolysis

The transient absorption spectra recorded upon 532-nm laser pulse excitation of thionine adsorbed on various support materials are shown in Figure 2. The effect of oxygen on the transient is demonstrated by comparing the absorption spectra recorded under degassed and oxygenated conditions. The transient absorption of TH^+/SiO_2 TH^+/Al_2O_3 samples which show absorption maxima at 410 and 780 nm arises as a result of triplet excited state of thionine on these oxide supports.

$$TH^+ \xrightarrow{h\nu} {}^1TH^{+*} \longrightarrow {}^3TH^{+*} \qquad (1)$$

The bleaching maximum at 605 nm further supports the contention that the formation of transient corresponds to the depletion of monomeric dye. The lifetime of ${}^3TH^{+*}$ on SiO_2 and Al_2O_3 was ~ 200 μs. Such a long lifetime of triplet excited state is commonly observed on oxide supports.[6] The triplet dye was found to be very sensitive to the presence of oxygen. As can be seen from figure 2a and 2b, the oxygen-saturated samples exhibited very small transient absorption which is below the limit of spectral resolution. At low laser intensities the degassed samples exhibited a complete recovery of the dye. This shows that the dye do not undergo net photochemical changes on the surface of SiO_2 and Al_2O_3. However at higher laser intensities, biphotonic photoionization could lead to some irreversible changes in the dye.

A different photochemical behavior of TH^+ was seen on the surface of TiO_2. Transient absorption maxima were seen at 400, 440 and 720 nm. Along with triplet thionine, the semioxidized thionine and trapped electron also contribute to the transient absorption. As established earlier,[2,3,5] we attribute this to the charge injection from excited thionine into the conduction band of TiO_2.

$${}^1TH^{+*} \text{ (or } {}^3TH^{+*}) + TiO_2 \longrightarrow TH^{2+} + TiO_2\text{ (e)} \qquad (2)$$

The broad absorption in the near-infrared region which is sensitive to oxygen is attributed to the trapped electron at the TiO_2 surface.[2,5,15] A considerable absorption in the region of 400 nm was retained even when the TH^+/TiO_2 sample was saturated with oxygen. The semioxidized thionine, TH^{2+}, has an absorption maximum at 470 nm in acetonitrile.[16] The broad bleaching observed in these samples and the interaction with surface hydroxyl groups could blue-shift the transient absorption maximum. It is also interesting to note that the bleaching maximum observed at 530 and 610 nm indicates participation of monomeric and aggregated forms of thionine in the photochemical process. The bleaching recovery traces indicated that nearly 90% of the dye underwent permanent degradation on the TiO_2 surface.

Steady-State Photolysis

If indeed, charge injection from excited dye into the TiO_2 particle is a major pathway for the photochemical degradation, it should also be possible to monitor it via steady-state photolysis. The absorption spectra of TH^+/TiO_2 sample recorded after irradiation with the visible light (> 400 nm from a 250 W Halogen lamp) are shown in Figure 5. Nearly 80% of the TH^+ degraded as a result of its exposure to the visible light. Other photochemical processes such as excited state annihilation or reaction with oxygen could also lead to the dye degradation, but their contribution is considered to be very small.

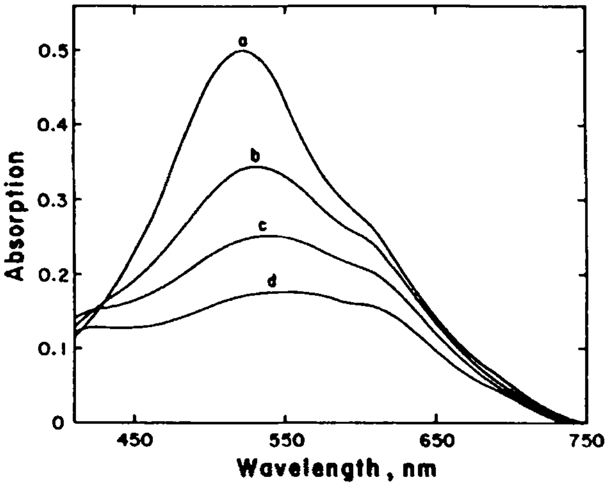


Figure 3 Photodegradation of thionine on TiO_2 surface as monitored by the diffuse reflectance ground-state absorption spectra of TH^+/TiO_2 sample at different irradiation (> 400 nm) periods: (a) 0, (b) 15, (c) 45 and (d) 105 min.

Less than 5% of thionine underwent degradation on SiO_2 and Al_2O_3 surface when photolyzed under similar conditions.

The semiconductor properties of TiO_2 promote the photochemical process described by reaction (2) and lead to permanent dye degradation. These observations highlight the importance of photochemical studies on solid surfaces for improving the efficiency of photosensitization in photography and xerography, and understanding the mechanism of dye degradation in paints.

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