

PECULARITIES OF ELECTRONIC INTERACTION OF POLAR AND NON-POLAR ORGANIC FLUORESCENT PROBES IN THE MIXED TITANIA-SILICA COMPOSITIONS

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Abstract

Spectral characteristics of polar – push-pull stilbene (St) and nonpolar pyrene (Py) molecules on the silica and silica-titania surfaces have been studied by the methods of steady-state and momentary spectrofluorimetry. Photochemistry of Py molecules in microheterogeneous media titania-silica colloids is controlled at presence of cyclodextrine. Change of the spectral position of the fluorescence maxima of stilbenes and lifetimes of stilbenes correlated with the change of local polarity around the adsorbed species due to competitive adsorption of water molecules from air and removing of adsorbed stilbenes to places with lower polarity. Stilbenes fluorescence is quenched effectively and this quenching is attributed to electron injection from excited stilbene to titania.

The utilization of semiconductor particulate systems as a reactive heterogeneous media has been and remains very popular in carrying out photochemical transformations of organic and inorganic compounds [1-8]. Nanosized titania catalysts exhibit unique and efficient reactivity for various photocatalytic reactions in which many organic substrates have been shown to be oxidatively (in some cases reductively) degraded and ultimately mineralized completely under UV irradiation [9-13]. Mixed silica - titania compositions are also of significant technological importance. The method of arrested precipitation known as sol-gel process [14] can be employed to prepare small semiconductor particles (SP) in porous silica medium [15]. Mixed oxide composite materials can often be more efficient photocatalysts than pure substances. In the case of silica-titania systems, the increase in photocatalytic efficiency has been attributed to the improved adsorption and concentration of the reactants near the active sites [16, 17].

The properties of titania-silica binaries are strongly dependent on their chemical composition, homogeneity and texture, which depend on synthesis conditions. The electronic spectra of luminescent molecules to detect local chemical and structural peculiarities of the solids has been extensively studied [18-22]. Fluorescent organic dyes, e.g. oxazines, erythrosin B, eosin, Ru(bpy)₃²⁺ and derivatives have been widely used as luminescent probes as well in the sensitization of large band semiconductors as TiO₂ due to their strong visible adsorption and ability to interact with semiconductor surfaces [23-25]. However, less is known about the application of push-pull stilbenes as luminescent probes. Donor-acceptor substituted stilbenes, called push-pull-stilbenes, were studied with respect to charge separation in excited state, as the dipole moment

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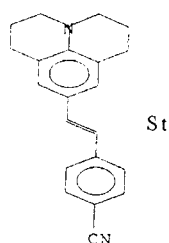
strongly increases [26-28]. Highly emissive TICT state of the stilbenes in polar solvents has a large dipole moment. Application of donor-acceptor substituted stilbenes on the surface of Ti-contained compositions is underlined, as it should provide the sensibilization of heterogeneous photocatalysts to the near ultraviolet and visible light. Adsorbed stilbenes in heterogeneous media seem to be the new interesting photochemical systems with the variation of fluorescence properties.

In this study, we deal with the preparation of highly transparent $\text{TiO}_2/\text{SiO}_2$ (0.1 - 10 wt % of titania) colloids, films and powders using the sol-gel method and the characterisation of these systems by means of fluorescence spectra of adsorbed luminescent probes: non-polar pyrene (Py), and high polar donor-acceptor substituted push-pull stilbene *E*-9-(4-Cyanostyryl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-*i,j*]quinoline, $\text{C}_{21}\text{H}_{20}\text{N}_2$ (St). Monomer fluorescence of Py in mixed titania-silica colloids contained β -cyclodextrin has been studied. Electronic interactions between adsorbed species Py, St and Ti-doped silica matrices have been studied by the methods of steady-state and momentary spectrofluorimetry. SiO_2 powder was used as reference compound for the luminescence study of adsorbed fluorophores.

Experimental

Py was introduced into the colloids from ethanol solution or as a CD inclusion complex. Mixed silica-titania colloids (1, 3, 5 % of titania) were produced by the acid hydrolysis of tetraisopropoxyorthotitanate embedded in a stable colloid silica sol. On the preparation of $\text{TiO}_2/\text{SiO}_2$ system, an alkoxide process was used (Ti/Si-1). Titanium tetraisopropoxide (TPOT) is subjected to condensation reaction with previously hydrolysed tetraalkoxysilane (TEOS) together with ethanol, filtered deionized water and HCl (catalyst). TEOS was prehydrolyzed with ethanol and water for 2 hours at 70 °C, under continuous stirring. The prehydrolyzed TEOS was cooled to room temperature. The mixture was stirred overnight at room temperature before dip-coating procedure. Thin films consisted of 1 to 2 consecutive layers, and the total thickness was approximately 200-350 nm. Silica Merk 100 modified with TiO_2 was used for the comparative studies (Ti/Si-2) [28]. The resulting silica-titania solid after heating at 500° C is contained with amorphous phase of titania as determined by X-ray powder diffraction. The crystallinity of Ti/Si coatings was identified by X-ray diffraction (XRD) method employing CuK_α radiation. The thickness of the films was observed using electron microscopy-profilometry method. Spectroscopic analysis of adsorbed molecules was performed using a Hitachi U3000 spectrophotometer. Emission and excitation spectra were studied for the vacuummed and opened in air samples to compare the effect of oxygen quenching and water vapour addition on the arbitrary intensity and lifetimes of adsorbed species. Fluorescence and excitation spectra of adsorbed molecules were registered with a Elmer LS 50B fluorimeter. Lifetimes of the adsorbed stilbenes were also registered. The apparatus and deconvolution procedure, based on the method of single photon counting, was described elsewhere [27].

For the structures of stilbene see Scheme 1:



Results and discussion

Adsorption capability of silica and Ti/Si samples in powder form with respect to the fluorophores is on the average 10^{-5} - 10^{-6} mol/g or from 10 to 1 % from monolayer coverage. High polar push-pull stilbene is easily adsorbed onto the OH-groups of SiO_2 and Ti/Si surfaces due to hydrogen-bond interaction. In contrast to the powder surface absorbability, only small amount of molecules are confined on the films surfaces due to their low porosity and small specific surface area. Increasing the Ti content within Ti/Si systems results an decrease in the intensity of the photoluminescence spectra. These finding indicate that adsorbed molecules make contact with titanium ions located on the surface.

Fluorescence spectra and decay traces of pyrene within CD/Ti/Si colloids

In the presence of CD, pyrene fluorescence intensity is high enough in the mixed Ti/Si sol to indicate that pyrene trapped in sol-gel glass is protected by CD against the quenching action of Ti ions. The intensity ratio, I_3/I_1 , of the third vibronic band to that of the 0-0 band of pyrene fluorescence, which was used as a measure of the polarity of the medium surrounding pyrene [19], changes from 0.81 on pure silica gel to 0.866 in ethanol, 1.11 in Py/CD/silica/water sol, 1.085 in Py/CD/silica/3%Ti/water sol, and to 1.42 in CD/ethanol/water solution. These results indicate that pyrene molecules are distributed between CD cavities and the bulk polar phase (silica or ethanol-water). Py emission is quenched completely when does not include in the CD cavity (Fig. 1, 1). It is interesting to note that there is no pyrene excimer emission in the colloid systems, despite the fact that pyrene molecule formed excimers when dissolved in hexane solution or being adsorbed on silica surface under the using concentrations. The absence of excimer emission indicates strong adsorption of pyrene molecules on the surface of colloid particles and a lack of diffusion in a life time of excited state of pyrene.

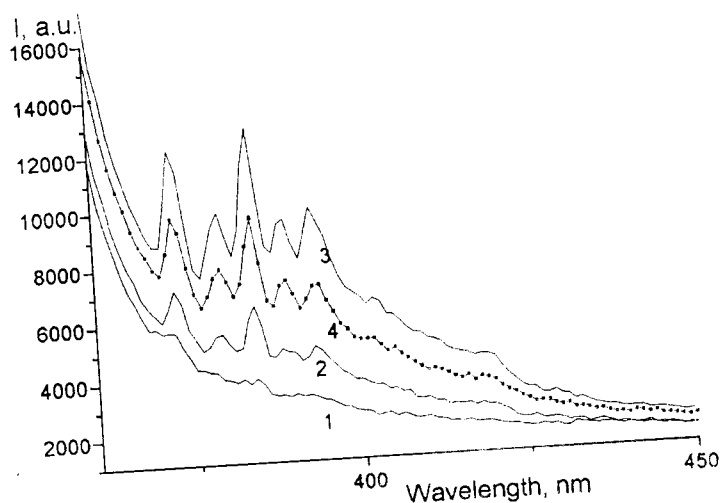


Fig. 1. Py fluorescence spectra in Ti/Si colloids: 1-1% Ti in Py/Ti/Si; 2- 1% Ti; 3-3% Ti, 4- 5% Ti in Py/Cd/Ti/Si.

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Fluorescence decay curves of pyrene within mixed Ti/Si colloids correlate with titania content, suggesting that electron injection from excited state of pyrene to titanium ions or titania small particles does take place. Life time and quenching behavior of excited pyrene changed when CD is present in the colloid systems suggesting protection of solubilized pyrene molecules within CD cavities against of titanium ions. In parallel with the solubilization, part of pyrene molecules is localized out of CD cavities undergoing the quenching process and decrease of life time of excited state.

Fluorescence of Py both monomer and excimer is suppressed in presence of Ti within silica powders (Ti/Si-1 and Ti/Si-2) and totally quenched on the TiO_2 surface. The fluorescence emission quenching should be attributed to electron transfer from the excited state of pyrene to the titania particles with the appearance of blue color of Ti^{3+} ions. Effect of titania on the Ti/Si-1 film surfaces is much less than it is on the Ti/Si-2 (Fig 2). The excimer fluorescence is clearly indicated as broad structureless band with the maximum 480 nm for the film contained 1wt % of titania, spectrum 3, when Py was introduced on the stage of mutual hydrolysis of TEOS and TPOT. The favourable conditions for the molecules approach each other occurred on the stage of sol-gel transfer in the confined space of the gel. Low sensitivity of the fluorescence of adsorbed Py to the presence of Ti ions within Ti/Si-1 suggests that atomic mixing between titania and silica occurs in the sol-gel produced films and titanium ions are not accessible for the immediate contact with Py molecule on the surface. In the case of Ti/Si-2, small titania crystalline particles are initially formed and composed as individual sites on the surface or within the pores of silica and are accessible for the adsorbed Py at this concentration range. Fluorescence spectra of adsorbed St also are indicative to the method of preparation and correspondingly surface chemistry of Ti/Si compositions.

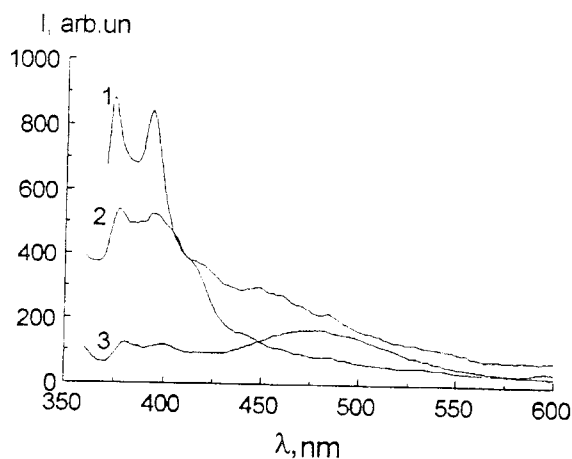


Fig.2. Fluorescence spectra of pyrene molecules on the Ti/Si films surfaces:

1 - 0.5% Ti, 2 - 3% Ti, 3 - 1% Ti, Py is captured in the film by co-precipitation.

Stilbene

Fluorescence spectra of adsorbed stilbene also are indicative to the method of preparation and correspondingly surface chemistry of Ti/Si compositions.

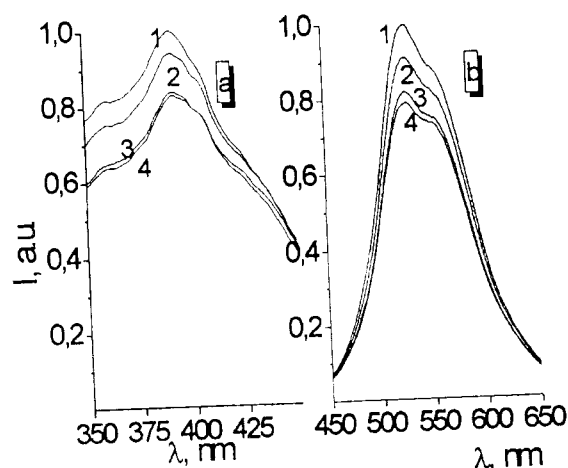


Fig. 3. Excitation (a) and fluorescence (b) spectra of St on SiO_2 under vacuum conditions at temperatures ($^{\circ}\text{C}$): 20 (1), 40 (2), 60 (3) and 80 (4).

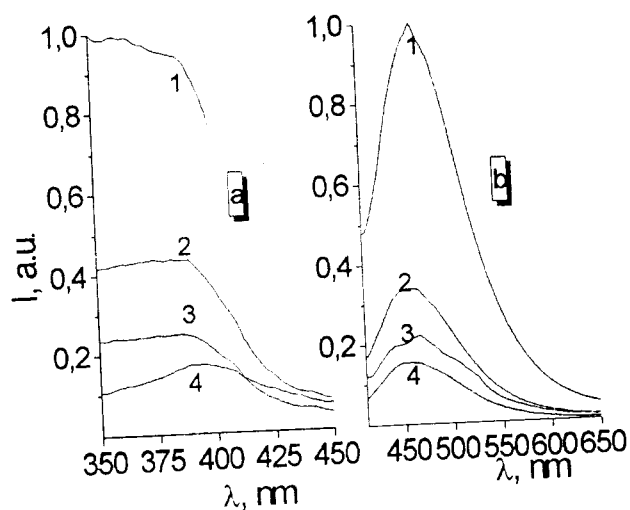


Fig. 4. Excitation (a) and fluorescence (b) spectra of St on SiO_2 under air conditions at temperatures ($^{\circ}\text{C}$): 20 (1), 40 (2), 60 (3) and 80 (4).

Fluorescence and excitation spectra of the St/ SiO_2 under vacuum conditions are similar to the spectra in polar solutions (fluorescence maxima 540-560 nm, excitation maximum 390 nm) (Fig. 3). After the contact of the samples with air, fluorescence spectra of S2, SiO_2 are blue-shifted, fluorescence maximum is located near 460 - 470 nm (Fig. 4). Spectral behavior of adsorbed St is different on the surfaces of Ti/Si-1 and Ti-Si-2. Fluorescence spectra of the stilbene on the surfaces

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of the Ti/Si-1 systems (0.1 - 10 % TiO₂) are akin to the ones in the polar solutions. Intensity of emission is decreased with the titania content increase (Fig. 5).

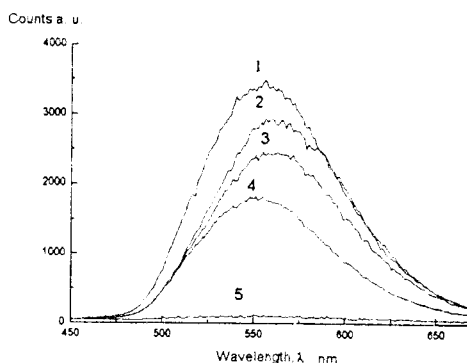
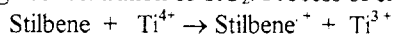


Fig. 5. Fluorescence spectra of St on SiO₂ and SiO₂/TiO₂ powders, prepared by sol-gel method, in vacuum conditions under Nd-YAG excitation at 470 nm:
1- SiO₂, 2-0,6% TiO₂, 3-1% TiO₂, 4-3% TiO₂, 5- pure TiO₂

Change of the spectral position of the fluorescence maxima of adsorbed stilbene in air may be connected with the change of local polarity around the adsorbed species due to competitive adsorption of water molecules from air and removing of adsorbed stilbenes to the places with lower polarity. One of the evidences to support this point of view is the invariability of fluorescence spectrum of St during first minutes of the contact with air. Then adsorption of water occurs and adsorbed stilbenes remove from its initial adsorption sites.

The nature of silica and silica-titania samples active centers is different. Since the adsorbed stilbenes on the surfaces are more rigid than that in the solutions, their adsorption will result in a decrease in internal conversion, leading to the longer lifetimes. Kamat [11] had proposed that fluorescence quenching of sensitized molecules adsorbed on the TiO₂ surface is due to electron injection from excited dye to the conduction band of titania. The fluorescence emission quenching on pure TiO₂ surface should be attributed to electron transfer from the excited state of stilbene to the titania particles, with the appearance of blue color of Ti³⁺ ions. The same is true on the silica-titania surfaces with high concentration of TiO₂. Process of electron transfer



proceeds effectively already at the dark conditions.

Conclusions

1. Pyrene and push-pull stilbene are used as sensitive fluorescent probe for the characterization of surface structure of the molecularly dispersed TiO₂/SiO₂ D-A substituted stilbene is sensitive to the polarity of the environment on the solid surfaces. Silica and silica-titania surfaces are contained the adsorption places with different polarity of OH groups.
2. Photochemistry of Py molecules in microheterogeneous media titania-silica colloids is controlled at presence of cyclodextrine. Quenching of the fluorescence and the interaction of photoactive Py molecules with heterogeneous polar environment of titania-silica colloids is suppressed due to inclusion complex formation.

3. Stilbenes fluorescence quenched effectively when titania amount is 1% wt in the mixed silica-titania system prepared by the impregnation method. The quenching is attributed to electron injection from excited stilbene to titania.
4. Change of the spectral position of the fluorescence maxima of stilbene on SiO_2 surface may be connected with the change of local polarity around the adsorbed species due to competitive adsorption of water molecules from air and removing of adsorbed stilbenes to the places with lower polarity.

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