Laser flash photolysis study of intermolecular electron transfer processes of adsorbed anthracene-N,Ndimethylaniline pair on titania-silica nanosized photocatalysts

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The introduction of photoreactive molecules into a dispersed oxide composition is an attractive way to create light-transforming photosensitive systems with a wide set of unique spectral properties. It is well-known that light induced charge separation is the key process in heterogeneous photocatalysis. Photoinduced charge transfer and charge separation in heterogeneous media can be enhanced by the process of adsorption and incorporation of guest molecules. The well established charge transfer reaction between An and DMA have been examined recently on silica surface (J.K.Thomas, A.Eremenko et al., J.Phys.Chem 1997).. In competition with the exciplex fluorescence emission, triplet formation, internal conversion, and dissociation into free ions are the non-radiative pathways that deactivate the exciplex on silica. The quenching on silica surfaces was found to be diffusion controlled and gives rise to exciplex formation on silica surfaces. The main goal of this work is to study the effects of titania-silica binaries with 1, 3 and 5wt prepared by sol-gel route on the processes of photoinduced ET between N,Ndimethylaniline (DMA) and Anthracene (An) using fluorescence, diffusion- reflectance and laser flash photolysis methods. Fluorescence quenching of the excited anthracene occurs on Ti/Si surfaces and clearly shows a dependence on titania content. Co-adsorption of well known quencher of An fluorescence - aromatic amine N,N dimethylaniline resulted in unexpected increase of fluorescence intensity of adsorbed An in proportion to the concentration of added amine. Life time of An fluorescence slightly increased in this case. Formation of An-DMA exciplex is not observed in spectra. It means that competition adsorption of DMA and An on the same surface centers occurred, and An molecules have been removed to the weaker surface sites. In this case quenching effect of titanium ions on the fluorescence of An is suppressed. The foregoing proves important role of adsorption of the contaminant molecules on the semiconductor surface in the processes of photocatalytic action of the semiconductor composites, at least in the powder form. Other mechanisms should be considered for the films also. Transient time resolved absorption spectra of An/DMA/Ti/Si system consist with An triplet and DMA radical cation. The triplet state and singlet state of An are quenched by the Ti present in the system and has been attributed to charge transfer processes. Direct evidence of electron injection from adsorbed An-DMA pair to titania particles has been obtained in the diffusion reflectance spectra due to increase of absorption belonging to Ti3+ ions on the surface.