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Photoprocesses of molecules encapsulated in porous solids XI: Excited state dynamics of proflavine and photosensitization of TiO_2 in nanoporous materials

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ABSTRACT

Photosensitization of titanium dioxide (TiO_2) encapsulated in the nanoporous materials of different pore size using proflavine dye as the sensitizer was studied using steady state and time resolved fluorescence spectral techniques. The titanium dioxide encapsulated nanoporous materials was prepared by ion exchange method and were characterized by UV–visible diffuse reflectance spectra, ICP-OES, BET and powder XRD techniques. The observed results show that TiO_2 were encapsulated in the nanochannels and nanocavities of the host materials. The photophysical properties of proflavine are found to be influenced by the pore size and the Si/Al ratio of the host materials. Photosensitization of TiO_2 in the host by proflavine was inferred from the decreased stead state fluorescence intensity of the dye molecule. In the case of the dye encapsulated TiO_2 loaded ZSM-5, fluorescence intensity decreases with red shifted emission maximum. Excitation of proflavine in presence of TiO_2 nanoparticles leads to protonation of proflavine in the excited state as confirmed in ultrafast time resolved fluorescence and decay associated spectral studies. On the other hand, no protonated proflavine was detected when zeolite-Y and MCM-41 were used as the host material.

1. Introduction

Exploration of chromophore loaded nanoporous materials has potential importance to design systems for different applications such as microlaser, second harmonic generation, frequency doubling, antenna materials, optical sensors, and in photocatalysis [1–9]. The role of the nanoporous silicate materials is to act as a host with desired geometrical properties and also to provide enhanced thermal and photostability to the encapsulated molecules. Encapsulation of the dyes into the nanochannels and nanocavities of silicate materials suppresses the aggregation of dye molecules thus providing enhanced fluorescence quantum yield and photostability. Incorporation of chromophores into the nanoporous cavities is achieved by different methods, depending upon the nature of the guest molecules; from the gas phase [10] or by ion exchange [11] if cations are involved, and by in situ synthesis [12] within the zeolite cages if the molecular size is greater than the size of the pore opening. Photophysics and photochemistry of organic dyes, metal complexes, and semiconductor nanoparticles into the microheterogeneous systems such as vesicles, clays, micelles, polymer matrix, nanoporous silicate materials and metal organic framework (MOF) have been studied extensively [13–17]. Among these micro-heterogeneous systems, nanoporous silicate materials are attractive candidates for encapsulation of dyes, metal complexes and semiconductor nanoparticles due to their uniformly sized, well ordered, nanopores, channels with chemical and thermal stability. Further, these nanoporous silicate materials have large optical band gap and behave as insulators.

In general, energy conversion efficiency or photocatalytic behavior of nanoporous silicate materials containing $Ru(bpy)_3^{2+}$ or related compounds as photosensitizers has been found to be low when there were no electron relays embedded in the structural frame work. The presence of electron relay within the nanoporous silicate materials is mandatory for directed electron transfer which enhances the charge separation processes. Encapsulation of semiconductor nanoparticles of TiO_2, ZnO and CdS in the host enhances the photocatalytic activity of the composite materials, alters the

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band gaps, and in addition provides additional thermal and chemical stability to the encapsulated nanoparticles [11,12,17]. Electron transfer from the photoexcited organic and inorganic sensitizers to the semiconductor nanoparticle incorporated in the nanoporous materials have been widely studied for visible light induced photolysis of water to produce hydrogen which could be used as a fuel [13,14,16]. In nanoporous materials, the thermodynamically favored, unwanted back electron transfer from the semiconductor to photoactive molecules is minimized by several orders of magnitude as compared to that in homogeneous solution. In natural antenna systems such as photosynthesis, formation of aggregates is prevented by fencing the chlorophyll molecules with polypeptide cages. A similar approach is possible by enclosing dyes within the pores of silicate materials by carefully choosing the host with appropriate volume of the cages/channels where only the monomers but not the aggregates are formed. Investigation of femtosecond dynamics of dyes in nanoporous silicate host materials facilitates the understanding of specific interaction between the host and the excited state of dyes. Proflavine belongs to acridine class of dyes and is known to be important for its potential application in solar energy conversion and biological systems [15,18]. Since, proflavine has been known to be a good sensitizer in light induced water splitting, understanding its photophysical and photochemical properties becomes important to improve the efficiency in harnessing solar energy [19–22]. Photophysical properties of proflavine in aqueous, organic and micellar systems have been studied extensively [23,24]. The existence of two closely lying excited singlet states of proflavine dye in solution was also reported using ultrafast time dependent fluorescence studies [24]. Photoinduced electron transfer from the excited state of proflavine to the encapsulated titanium dioxide nanoparticles within the MCM-41 channels was also reported [25].

The present study deals with the excited state dynamics and protonation of proflavine encapsulated in nanoporous host materials containing titanium dioxide nanoparticles using steady state and time resolved fluorescence spectral studies in pico to femtosecond time scale. It has been demonstrated that protonation of the dye is due to confinement effect rather than the acidity of the host materials. The photosensitization of titanium dioxide nanoparticles encapsulated into the nanoporous host materials by co-adsorbed proflavine dye molecules has also been investigated in zeolite-Y and MCM-41.

2. Experimental section

2.1. Materials

Zeolite-Y and ZSM-5 purchased from Sud Chemie, India were washed with 1 M NaCl for 2 h and calcined at 530°C for 12 h. Proflavine (Pf^+) was purchased from Aldrich and used after recrystallization from methanol. Cetyltrimethylammonium bromide (CTAB), tetramethylorthosilicate (TEOS) and ammonium titanium oxalate were purchased from Lancaster. All the other analytical grade chemicals were obtained from Qualigens and were used as supplied.

2.2. Sample preparation

MCM-41 was synthesized following the reported procedure [26]. About 2.4 g of CTAB was dissolved in 120 g of de-ionized water and stirred until a clear homogeneous solution is obtained. 8.0 ml of ammonium hydroxide was added to this mixture and stirred for 5 min; subsequently 10.0 ml of tetraethylorthosilicate was added to give a molar composition of the gel (1 M TEOS:1.64 M NH_4OH:0.15 M CTAB:126 MH_2O). The reaction mixture was stirred overnight and the solution was filtered, washed with de-ionized water and ethanol. The resultant solid was calcined at 523 K for 5 h and the solid obtained was characterized by SAXRD, surface area analysis (BET) and HR-TEM. The results obtained were found to be identical with the reported values [26].

Titanium-exchanged host were prepared by ion exchange method [20] using aqueous titanium oxalate as titanium source. In this method 1.0 g of zeolite was stirred with 5×10^{-3} M stock solution of titanium oxalate for 24 h, and forms TiO^{2+}ions exchanged zeolite. The zeolite was washed with excess water and dried under vacuum in a desiccator. Formation of titanium dioxide nanoparticles into the channels or cavities of zeolites was achieved by heating the sample at 150 °C for 6 h. Higher titanium dioxide loading levels was achieved by the successive ion exchange followed by heat treatment. Actual amount of titanium present in the zeolite host was determined by ICP-OES method. The samples for the ICP-OES method was prepared by dissolving measured quantities of titanium loaded zeolites in 4% HF solution and small quantity of this solution was diluted with distilled water. The solution pH was adjusted to 7.0 using barium sulfate and titanium was estimated.

The proflavine exchanged host materials were prepared by stirring the aqueous solution of the dye with zeolites for 4 h at room temperature. Since, the molecular size of the dye is smaller than the zeolite pore opening; the dye gets encapsulated into the channels or cavities of zeolites. The concentration of the dye in zeolites was varied from 1×10^{-6} to 1×10^{-3} M of dye/g of zeolite. Similar procedure was followed to prepare proflavine encapsulated TiO_2 loaded zeolites, MCM-41, and silica. In all the cases the resulting solid is washed with excess water to remove any physisorbed dyes on the external surface of the zeolite, which was ascertained by monitoring the absorption spectra of the eluent for the presence of dyes. The actual concentration of the dye adsorbed into the host materials was determined by UV–visible absorption spectral studies. The samples were prepared by dissolving measured quantities of dye loaded zeolites in 4% HF solution and then concentration of dye was calculated from the absorbance values at absorption maximum wavelength.

2.3. Characterization

BET surface area, pore volume, and pore size distribution of TiO_2 loaded nanoporous materials were performed using volumetric adsorption equipment (ASAP 2010 micrometric USA) at 77 K. The sample was degassed under vacuum at 373 K prior to data collection. Partial pressure used in the range from 16.49 mmHg to 785 mmHg and BJH model used for measuring pore volume and surface area. Powder X-ray diffraction patterns were recorded using CuK_∞ $1(\lambda = 1.5406$ Å) as a source. UV–visible diffuse reflectance spectra of powder samples were collected using Agilent 8453 spectrophotometer equipped with labsphere RSH-HP-8453 reflectance accessory. Steady state fluorescence measurement of the dye loaded nanoporous materials were carried out using Fluromax spectrophotometer at front face configuration (45°). Time resolved fluorescence measurements were carried out using time correlated single photon counting technique (TCSPC, IBH) by exciting the sample at 420 nm. Fluorescence decay was measured by monitoring the signals at emission maximum in front face configuration using suitable cut-off-filters to avoid scattered light. The data analysis was carried out by the software provided by IBH (DAS6) which is based on deconvolution using non-linear least square method and quality of the fit is identified by the reduced χ^2 and weighted residual.

Femtosecond fluorescence transient have been collected using fluorescence up-conversion technique. In our femtosecond up-conversion setup (FOG 100, CDP, Russia) the sample was excited