



Photophysical properties of phenosafranine (PHNS) adsorbed on the TiO₂-incorporated zeolite-Y

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Abstract

Investigation of photophysical properties of phenosafranine dye ion-exchanged with zeolite-Y samples has been carried out to understand the host–guest interactions of the dye and the zeolite. Photosensitization of titanium dioxide, encapsulated in the supercages and anchored on the external surface of the zeolite-Y by the visible light excited dye molecules, has been studied using steady state and time resolved fluorescence techniques. Titanium dioxide loaded zeolites at the external surface and at the interior of the supercages are found to show different characteristics in the sensitization process.

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1. Introduction

Supramolecular organization of molecules in molecular sieves is of interest to develop efficient systems for controlling chirality and the nanoscale-advanced materials [1–3]. The non-deformable zeolite structure offers the ordered assembly of multicomponent systems spatially in a single roof for stabilizing the light induced charge separated state by preventing the energy wasting back electron transfer process [4]. However, a formidable task in these systems is to devise a competent method to organize the guest molecules. Many reports are available that demonstrate the occurrence of energy [5] and electron-transfer [6] photosensitization processes using zeolites as host materials.

Titanium dioxide semiconductor nanoparticles have been extensively studied for significant applications in

photocatalysis [7] and dye sensitized solar cells [8]. The incorporation of titanium dioxide in zeolite cavity offers advantages due to size quantization resulting in different optical and electronic properties [9–12]. In order to improve the efficiency of the titanium dioxide doped zeolite catalyst to operate in the visible region, attempts are made to assemble the semiconductor and sensitizer in the internal and external zeolite surfaces. Ru(bpy)₃²⁺ ion encapsulated in titanium dioxide co-doped zeolites [13–15] shows enhanced photocatalytic activity and also the mechanism of photochemical water splitting using these materials was elucidated by Kim et al. [16]. The efficiency of charge transfer from the sensitizer to the titanium dioxide is modulated by capping the nanocrystals with insulating layers [17,18] for applications like photonic crystals and in paint industry.

The role played by the zeolite surface, water molecules, and charge balancing cations [19] on the guest molecules for developing efficient systems of interest is not understood well. In this report, we have used phenosafranine (PHNS) as sensitizer which is an azine class

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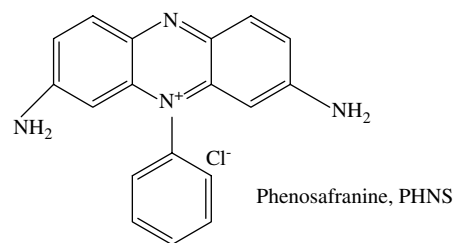
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of dye and the dye behaves as an electron acceptor and donor in the ground and excited state [20]. The dye has been used in photogalvanic cells in homogeneous solution as well as coated on the electrode surface by covalently linking the dye with the polymer [21]. The electron injection from the singlet excited state of phenosafranine to the conduction band of the bulk titanium dioxide semiconductor was investigated by diffuse reflectance laser flash photolysis technique [22]. In this report, we discuss the photophysical properties of phenosafranine dye and the sensitization of titanium dioxide nanoparticles located in the zeolite surface as well as encapsulated in the cavities of the zeolite.

2. Experimental

Zeolite-Y (Suid Chemie, India), washed with 1 M NaCl for about 2 h, was calcined at 530 °C for 12 h. Titanium dioxide anchored on the external surface of the zeolite (1–5% loading (w/w)) was prepared by sol–gel method using tetraisopropyl orthotitanate as reported [23]. In brief, 15 ml of tetraisopropylorthotitanate (E-Merck) was hydrolyzed in water containing 0.75 ml of conc. HNO₃ and was peptized for 15 h. The resulting sol is added to the pre-hydrated zeolite and then the suspension is stirred for 2 h and the solvent is evaporated slowly. Finally, the samples were calcined at 450 °C. TiO₂ encapsulated in the zeolite cavity was prepared by ion-exchange method [10]. In this method, zeolite was stirred with potassium titanoxalate in aqueous solution for 24 h and the zeolite samples were heated at 150 °C for 2–3 h. Different loading of titanium dioxide was achieved by successive ion-exchange followed by heat treatment. Actual amount of titanium present in the zeolite samples was determined by atomic absorption spectroscopy and chemical analysis [16,24]. The calculated quantity of titanium dioxide loaded zeolite is digested in concentrated sulfuric acid for about 5 h and small quantity of this parent solution is diluted with water. To this solution, 10% H₂O₂ is added in excess and titanium is estimated by using the absorbance of the peak at 408 ± 1 nm. Previously the absorbance value is calibrated using pure anatase titanium dioxide under the same experimental conditions.

Phenosafranine (PHNS) chloride (3,7-diamino-5-phenylphenazinium chloride) obtained from Fluka was purified by column chromatography [20]. The aqueous solution of the dye and the zeolite when stirred for 3–4 h at room temperature results in the loading of PHNS in zeolite. The concentration of the dye in zeolite is kept at 3 μM per gram of the zeolite-Y. The studies reported are concerned with the samples, titanium dioxide encapsulated in zeolite TY(e) and titanium dioxide on the external surface of the zeolite TY(s).



UV–visible diffuse reflectance spectra of the samples were recorded using a Shimadzu spectrophotometer equipped with integrating sphere attachment. The steady state fluorescence measurements for opaque samples were done with Fluomax spectrophotometer as front face configuration at 45°. Powder X-ray diffraction measurements were recorded using Philips X-ray diffractometer. EDAX measurements were carried out with JSM-840 scanning electron microscope. Time resolved fluorescence measurements were carried out with time correlated single photon counting fluorescence spectrometer (IBH) by exciting the sample at 470 nm with Ti: Sapphire laser of pulse width 2 ps FWHM and the instrument response time of ~50 ps. Fluorescence decay was measured at the front face configuration with suitable cutoff filters to avoid scattered light and the decay curve was analyzed using the software (DAS6, IBH) provided with the instrument.

3. Results and discussion

The titanium dioxide nanoparticles present in the zeolites are found to be either amorphous in nature or the particle sizes are too small to be detected by the powder XRD, as no evidence for crystalline titanium dioxide was found in the XRD pattern of the samples used for the experiments. The titanium dioxide loading in zeolite, which is lower than that reported earlier [11] (7% decrease in crystallinity at 0.83% for TY(e) samples), does not change the crystallinity of the zeolite to any appreciable extent as shown by XRD pattern. The external surface area of the zeolite samples is about 1% of the inner surface area, which is close to 6 m² g⁻¹ for the particle size of the zeolite around 0.5–1 μm. TiO₂ formed by sol–gel method is known to have particle size larger than that of the zeolite pore opening (7.4 Å), and are anchored on the external surface of the zeolite [16], which was confirmed by EDAX measurement as well. When the ion-exchange method was used for the preparation of TiO₂ incorporated zeolite samples, titanium dioxide nanoclusters thus formed are entrapped in the supercages of the zeolite-Y. The maximum size of the TiO₂ cluster present in the supercage may not be larger than 1.3 nm, the diameter of the supercage [10]. This is further confirmed by the UV–visible spectra shown in

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