

Photoinduced electron transfer in some photosensitive molecules-incorporated semiconductor/zeolites: New photocatalytic systems

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Abstract. An intramolecular charge transfer (ICT) molecule, *p*-N,N-dimethyl-aminobenzoic acid (DMABA) has been studied in zeolite and colloidal media. The ratio of ICT to normal emission (ICT/LE) is greatly enhanced in zeolites compared to that in polar solvents. The ICT emission of DMABA was quenched by increasing the concentration of TiO₂ colloids, while the normal emission was slightly enhanced. Upon illumination of the heteropoly acid (HPA) incorporated TiO₂ colloids, interfacial electron transfer takes place from the conduction band of TiO₂ to the incorporated HPA which is also excited to catalyze the photoreduction of Methyl Orange. It is found that the interfacial electron transfer mechanism of HPA/TiO₂ is quite analogous to the Z-scheme mechanism for plant photosynthetic systems. In DMABA-adsorbed TiO₂/Y-zeolite the ICT/LE ratio of DMABA is quite small implying that electron transfer takes place from DMABA to the conduction band of TiO₂. This results in drastic enhancement in the photocatalytic activity of DMABA-adsorbed TiO₂/Y-zeolite compared to free TiO₂/Y-zeolite.

Keywords. Semiconductor; photocatalytic; photosensitive molecule; intramolecular charge transfer; TiO₂/Y-zeolite.

1. Introduction

The consumption of energy has grown exponentially over the last two decades due to rapid industrialization and better living standards throughout the world. Among the various forms of energy available on the earth, solar energy has the greatest potential because it is available in adequate quantity in almost all parts of the world. In nature, solar energy is utilized efficiently by plants through the process of photosynthesis. Many research groups have tried to mimic this natural process in their laboratories during the past decades. One of the approaches in this direction is by employing semiconductors as the light-harvesting unit. Semiconductors under band-gap excitation produce electron-hole (e^-h^+) pairs, which initiate the oxidation and reduction processes of the adsorbed substrates. Several metal oxides^{1–5} and chalcogenides^{6–10} have been investigated for their photophysical and photocatalytic properties till date. They have been used to study the redox reactions of substrates like biological molecules,^{11,12} dyes,^{13,14} alcohols^{15,16} etc. Colloidal semiconductors have also been employed for the decomposition of toxic substances present in waste-water. The photocatalytic degradation of 4-chlorophenol,¹⁷

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2-chlorophenol,¹⁸ 1,10-dichlorodecane,¹⁹ carbaryl²⁰ and insecticides²¹ have been reported recently.

Zeolites are crystalline Al–O–Si materials containing pores of molecular dimensions, interconnected by smaller windows. By using zeolites as hosts it is possible to synthesise well-defined clusters inside these pores. They have recently been used for the preparation of semiconductors like CdS^{22,23} and TiO₂.²⁴ Zeolites possess unique properties like rigidity and polarity and therefore attract further studies for the clear understanding of the behaviour of the semiconductor particles in their cavities. There have been several reports on the photocatalytic activity of semiconductors entrapped in zeolite cages.^{25–28} Photosensitive molecules like *p*-N,N-dimethylaminobenzoic acid (DMABA) have attracted considerable attention due to the formation of an intramolecular charge transfer (ICT) state which is characterised by a phenomenon of dual fluorescence. In the present paper the photoinduced intramolecular charge transfer of DMABA in zeolite and colloidal media has been discussed. The enhanced photocatalytic efficiency upon additional incorporation of photosensitive molecules in semiconductor based colloidal and zeolite systems has also been described.

2. Experimental

2.1 Preparation and spectroscopic characterisation of colloidal samples

Colloidal TiO₂ was prepared by the method described by Grätzel *et al.*²⁹ One gram of titanium (IV) tetraisopropoxide was dissolved in 20 ml of 2-propanol. A 10 ml sample of this solution was slowly dropped into 100 ml of acidified water (*pH* 1.5). This mixture was stirred until it was virtually clear. After vacuum evaporation of the solvent, a transparent solution of colloidal TiO₂ particles was obtained.

The absorption spectra were measured on a Cary 3E UV-Vis spectrophotometer. A high-pressure Hg arc lamp in conjunction with a monochromator or 450 W Xe lamp with cutoff filters ($\lambda \geq 320$ nm) were used as the light source. The steady-state fluorescence spectra were recorded on a scanning SLM AMINCO 4800 spectrofluorometer. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method, employing a dual-jet ps dye laser (Coherent; Model 702) synchronously pumped by a mode-locked Ar-ion laser (Coherent; Innova 200). Transient absorption measurements and laser flash photolysis experiments were carried out using a Q-switched nanosecond Nd:YAG laser (10 Hz, pulse width 7 ns) with 355 nm excitation light and a 250 W tungsten lamp as the monitoring light source. The monitoring light was oriented perpendicularly to the exciting laser beam, passed through a grating monochromator and detected with a photomultiplier (Hamamatsu R-928) and a storage oscilloscope (LeCroy 9310A, 400 MHz). The laser flash photolysis with DMABA samples was performed using a dye laser (Spectron) synchronously pumped by a Q-switched nanosecond Nd:YAG laser.

2.2 Preparation and characterisation of zeolite samples

The titanium-exchanged zeolite was prepared by a method of ion exchange of HY zeolite with an aqueous solution of ammonium titanyl oxalate monohydrate, (NH₄)₂TiO(C₂O₄)₂·H₂O (from Aldrich). The HY zeolite was synthesized by ion exchanging NaY zeolite (Si/Al = 2.47, from Aldrich) with 0.1 M NH₄Cl. After rinsing the zeolite with

triply distilled water several times, calcination was carried out at 500°C for 15 h. The temperature of the sample was elevated with a rate of 3.3°C/min. The amount of the exchanged titanium cation in the zeolite was calculated by taking the amount of TiO₂ left in the supernatant liquid. The ion-exchanged zeolite had 7.2 Ti species per unit cell. The TiO₂/Y-zeolite was characterised by X-ray diffraction and IR spectroscopic measurements (figure 1). TiO₂/Y-zeolite was transferred to a Pyrex cell and activated at 200°C for 2 h under vacuum (10⁻⁵ Torr). Then it was shaken with a certain volume of solvent containing the photosensitive molecule for 12–15 h. To remove the solvent the solid was dried under vacuum for 18 h. The dried solid was transferred to quartz cell under vacuum for the spectroscopic measurements. The photosensitive molecule adsorbed-TiO₂/Y-zeolite was directly mixed with the aqueous solution of the probe molecule (Methyl Orange) under argon gas flow. The samples were irradiated in a merry-go-round equipped with Xe-arc lamp. After a certain period of irradiation, the sample was filtered with 0.2 μm PVDF filter to remove the zeolite and its absorption spectra measured.

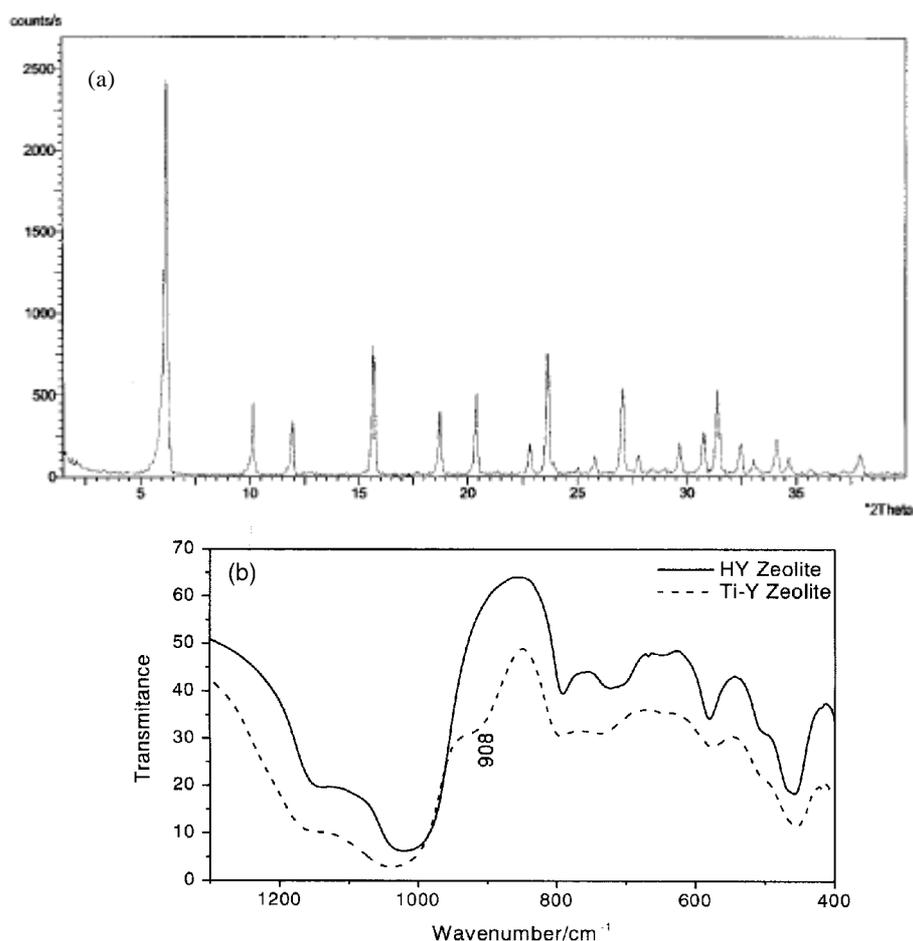


Figure 1. (a) The X-ray diffraction pattern of TiO₂/Y-zeolite, and (b) the IR spectra of HY and TiO₂/Y-zeolite.

3. Results and discussion

3.1 Photoinduced intramolecular charge-transfer of *p*-*N,N*-dimethylaminobenzoic acid in zeolite and colloidal media

In certain molecules like dimethylaminobenzonitrile derivatives, a photoinduced intramolecular charge transfer (ICT) takes place from the initially local excited state (LE) resulting in the formation of an ICT state with a large dipole moment. The formation of the excited ICT state is characterised by a phenomenon of dual fluorescence exhibiting a large Stokes' shifted emission in addition to the normal emission from the LE state. We have investigated the excited state intramolecular charge transfer properties of *p*-*N,N*-dimethylaminobenzoic acid (DMABA) in NaY and HY zeolite by steady-state and time-resolved fluorescence.³⁰ The ratio of the ICT/LE emission is greatly enhanced in zeolites compared to that in homogeneous polar solvent (acetonitrile) as shown in figure 2. The time resolved fluorescence experiments showed that the decay times of ICT emission are increased from 1.4 to 2.1 ns with a rise time of about 20 ps. This is in accordance with the steady-state fluorescence results. The ICT/LE emission is reduced upon illumination of DMABA in NaY zeolites, which is attributed to the efficient electron transfer from the excited state of DMABA to the NaY zeolite through hydrogen bonding interaction.

The photoinduced intramolecular charge transfer in DMABA was also investigated in the presence of colloidal TiO₂.³¹ The ICT emission of DMABA was quenched by increasing the TiO₂ concentration, while the normal emission was slightly enhanced. The fluorescence lifetimes and relative amplitudes of the ICT emission of DMABA are little affected by the addition of colloidal TiO₂, while those of normal emission are greatly changed. An examination of the position of energy levels of LE and ICT states of

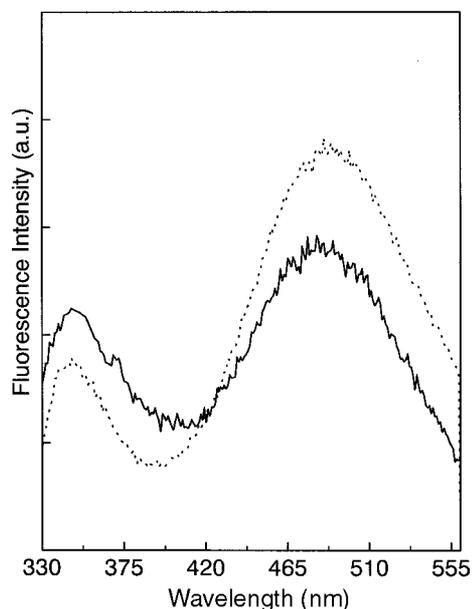


Figure 2. Fluorescence emission spectra of DMABA in acetonitrile (—) and NaY zeolite (.....). The excitation wavelength is 310 nm.

DMABA and conduction band of TiO_2 reveals that the ICT state of DMABA is energetically lower than the conduction band edge of TiO_2 whereas the LE state is energetically higher than it. This indicates that the quenching of ICT emission by TiO_2 is not due to electron transfer and the quenching is static in nature. Thus the participation of the ICT state of DMABA in the electron transfer can be ruled out. In order to further elucidate the electron transfer process between DMABA and TiO_2 , ns time-resolved transient absorption spectra of DMABA were measured at various concentrations of TiO_2 in acetonitrile. For this purpose a dye laser pumped by a Q-switched ns Nd-YAG (10 Hz, pulse width 7 ns) was used as the excitation source. The output of the dye laser was frequency doubled to give a laser pulse of 300 nm. These spectra displayed two different peaks at 435 and 500 nm. The peak at 435 nm was attributed to the triplet state of DMABA, while the 500 nm peak originated from the cation radical of DMABA. The lifetime of the triplet state of DMABA was little affected by the presence of TiO_2 colloids as can be seen in figure 3 indicating that the possibility of the participation of the triplet state in the electron transfer process can be ruled out. These results support the conclusion that the

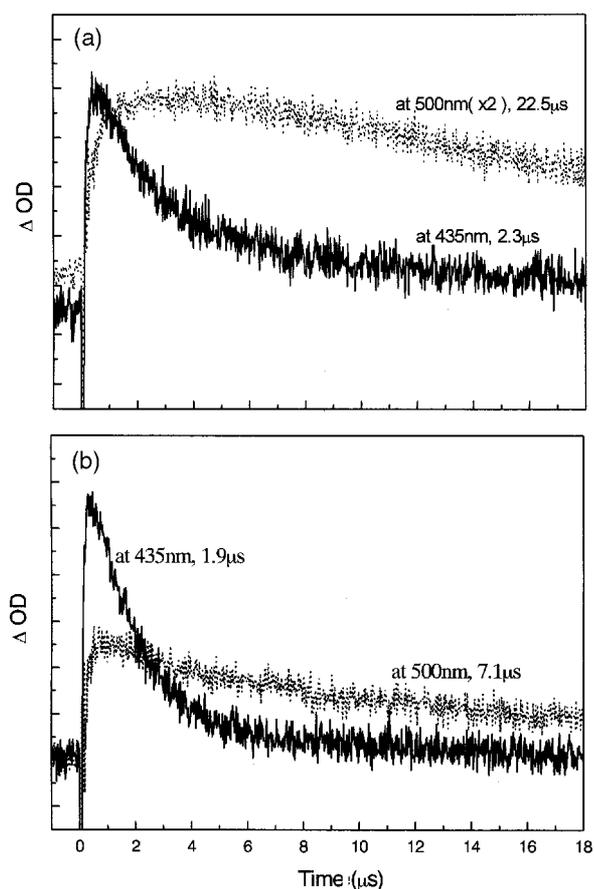


Figure 3. (a) The decay profiles of 0.1 mM DMABA in acetonitrile, and (b) in acetonitrile containing 4×10^{-5} M TiO_2 colloids. ($I_{\text{ex}} = 300$ nm.)

electron transfer into the TiO_2 colloids takes place from the singlet excited state of adsorbed DMABA.

3.2 Heteropoly acid-incorporated TiO_2 photocatalytic system

Various research groups have tried to increase the photocatalytic activity of the colloidal semiconductor system by using coupled semiconductors,³² doping with different transition metal ions³³ etc. Recently Grätzel *et al.*³⁴ have developed the dye-sensitized mesoporous TiO_2 solar cells with the highest photon-to-electron conversion quantum yield (33%). We attempted to incorporate photoreactive heteropoly acid (HPA) such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ into TiO_2 colloids in aqueous polyvinyl alcohol (PVA), 0.1% solution.³⁵ Upon illumination of the HPA/ TiO_2 system with near UV light (300–375 nm), the interfacial electron transfer takes place from the conduction band of TiO_2 to the incorporated HPA. The nanosecond laser flash photolysis of deaerated TiO_2 solution in the presence of PVA showed a transient trapped conduction electron (120 ns) at 600 nm as observed by Bahnemann *et al.*,¹ while in the presence of HPA it is quenched by generating a longer lived transient with maximum absorption around 450 nm (~40 ns) instead of the trapped electron (figure 4). The extent of the photoreduction of the HPA adsorbed on TiO_2 particles depends on the concentration ratio of the HPA and TiO_2 colloids, irradiation wavelength and intensity of radiation. The enhancement results can be best explained if one were to assume that the electron transfer proceeds via two photochemical reactions as the 'Z-scheme' mechanism for the plant photosynthetic system shown in (a) of scheme 1. In scheme 1, (b) shows how the electron transfer in HPA/ TiO_2 system proceeds via two photochemical reactions pathway. The near-UV

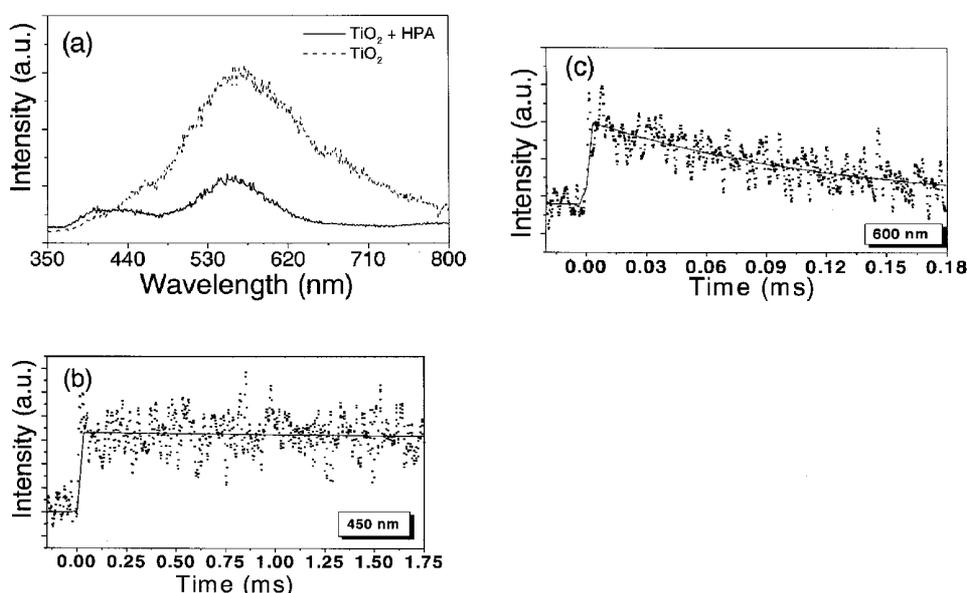


Figure 4. (a) Transient absorption spectra of 5×10^{-3} M HPA with colloidal TiO_2 (5 g/l) in 0.1% PVA aqueous solution; time profiles of the absorption at 450 (b) and 600 nm (c).

illumination of HPA/TiO₂ in the presence of PVA results in the charge separation in TiO₂ as well as the excitation of HPA. Thus the formation of heteropoly blue (HPB) occurs by direct electron transfer from the TiO₂ conduction band to the ground state of HPA as well as by photoreduction through the excited state of HPA. The catalytic activity of the HPA/TiO₂ colloids was assessed by carrying out the photoreduction of Methyl Orange in aqueous medium. When anaerobic aqueous solutions of Methyl Orange (5×10^{-5} M) in the presence of naked HPA, TiO₂ or HPA/TiO₂ colloids were illuminated with near-UV radiation (cutoff ≥ 320 nm), the visible absorption band of Methyl Orange at 502 nm started to disappear without a wavelength shift while no bleaching was observed in the absence of the colloid or HPA. Figure 5 shows the comparison of the photoreduction rate of Methyl Orange in the three cases. From this data, the catalytic activity of HPA/TiO₂ colloids (100% bleaching within 20 min) is tremendously increased as compared to that of naked TiO₂ or HPA itself (only 60% bleaching within 60 min). On the basis of the above results and using the following expression for quantum efficiency (Φ),

$$\Phi = \frac{\text{no. of photoreduced methyl orange molecules}}{\text{no. of absorbed photons}},$$

the photon-to-electron conversion yield in the presence of HPA/TiO₂ was almost 34% with 320 nm monochromatic light. This yield is higher than that reported by Grätzel *et al.*³⁴. Furthermore, it was found that upon additional illumination with visible light (400–600 nm), the photocatalytic reduction of methyl orange was much faster as compared to the results obtained by near-UV light only (320–390 nm). This is consistent with the two photochemical pathways shown in scheme 1.

3.3 Photosensitive molecule incorporated TiO₂/Y-zeolite photocatalytic system

We incorporated an ICT molecule *p*-N,N-dimethylaminobenzoic acid (DMABA) in the TiO₂/Y-zeolite framework.³⁶ The fluorescence spectrum of DMABA in TiO₂/Y-zeolite exhibited dual emission bands. However the ratio of ICT emission to the local emission (ICT/LE) was quite small as compared to that of DMABA in polar zeolite cavity³⁰ or SiO₂ colloidal solution.³⁷ This implies that there is a certain photochemical interaction between DMABA and TiO₂/Y-zeolite. The photochemical interaction should be an electron transfer from DMABA to the conduction band of TiO₂ attached inside the nano-

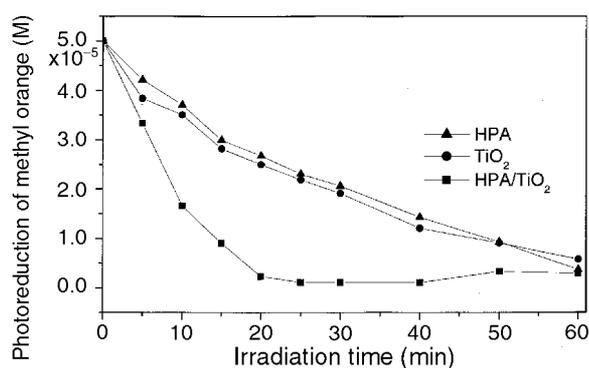
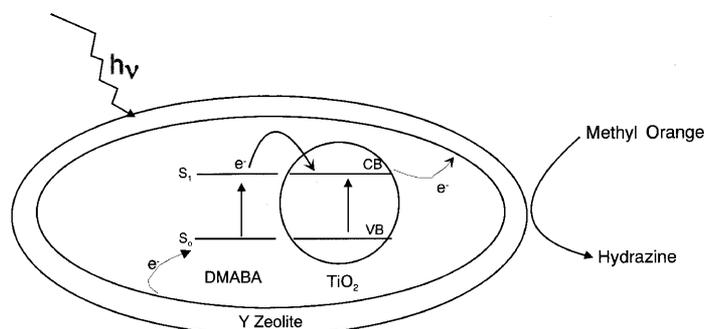


Figure 5. Photoreduction of Methyl Orange in the presence of HPA, naked TiO₂, or HPA/TiO₂ in 0.1% PVA aqueous solutions as a function of irradiation time by Xe lamp ($I \geq 320$ nm). $[\text{TiO}_2] = 5 \times 10^{-3}$ M, $[\text{HPA}] = 5 \times 10^{-5}$ M.



Scheme 2. Schematic diagram showing the reduction of Methyl Orange by DMABA adsorbed TiO_2/Y -zeolite.

pore frame of the zeolite. The photoinduced electron transfer from the locally excited singlet state of DMABA to the conduction band of TiO_2 has been observed earlier in the DMABA-adsorbed TiO_2 colloidal system.³¹ This could result in the enhancement of electron transfer efficiency to the frame of TiO_2/Y -zeolite and the electron should be subsequently accessible for the reduction of a substrate outside the zeolite framework. In order to test the above speculation the photoreduction of Methyl Orange (5×10^{-6} M) was tried using DMABA-adsorbed TiO_2/Y -zeolite as the photocatalyst with light of $\lambda \geq 320$ nm. The photocatalytic activity of DMABA-adsorbed TiO_2/Y -zeolite was found to be six times higher than that of free TiO_2/Y -zeolite. The reduction of Methyl Orange is shown in scheme 2. The quantum efficiency of the photocatalytic reduction of Methyl Orange was about 34% with 320 nm light. This is same as that obtained with colloidal HPA/ TiO_2 system. Similar experiments with Nile Red-adsorbed TiO_2/Y -zeolite showed the photocatalytic activity of about eight times higher than free TiO_2/Y -zeolite.³⁸ This indicates that Nile Red-adsorbed TiO_2/Y -zeolite is even more efficient than the DMABA-adsorbed TiO_2/Y -zeolite system.

Incorporation of heteropoly acid (HPA) in the TiO_2/Y -zeolite pores has been carried out in our laboratory and the photocatalytic efficiency of this new catalyst is currently under investigation. We anticipate that this photocatalytic system will be highly efficient for both water purification and recovery capability. We also plan to use MCM-41 molecular sieves as support for photocatalytic systems. These materials have hexagonal channels of size tunable between 15 to 100 Å. Thus they can be used to trap bulky molecules which cannot be encapsulated in zeolite cavities. The determination of the photocatalytic activity of DMABA adsorbed colloidal TiO_2 is also under consideration.

4. Conclusions

The intensity ratio of ICT emission to normal emission of DMABA is dependent on the nature of chemical environment. In the HPA incorporated TiO_2 colloidal system an interfacial electron transfer occurs from the conduction band of TiO_2 to the HPA upon illumination by near-UV light. The photon-to-electron conversion efficiency of HPA/ TiO_2 system is 34%. The Nile Red-incorporated TiO_2/Y -zeolite is more efficient than DMABA-adsorbed TiO_2/Y -zeolite. Such photocatalytic systems would be useful for the detoxification of water using the ultraviolet and visible portions of the sunlight. The

photolysis of water to produce hydrogen by employing such systems can also help to solve our future energy problems. Further research is underway to develop more efficient photocatalytic systems.

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