

**【심포지움-광촉매 04】**

## **Photo-induced Interfacial Electron Transfer in Some Photosensitive Molecules-Entrapped TiO<sub>2</sub>-Zeolites or MCM41: Design of New Photocatalysts**

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TiO<sub>2</sub> provides very useful photocatalytic systems, capable of converting solar energy to chemical or electrical energy and environmental cleaning. The key step in enhancing photocatalytic efficiency is improving photoinduced interfacial electron transfer like plant photosynthesis. It remains difficult to modify TiO<sub>2</sub> particles as a real analogue of photosynthetic reaction centers of green plants. We attempted to modify the surface of TiO<sub>2</sub> colloids by adsorbing some photosensitive intramolecular charge transfer (ICT) molecules such as N,N-dimethylaminobenzoic acid (DMABA) and Nile Red, or heteropolytungstate (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) (HPA). The interfacial electron transfer dynamics of the ICT molecules or HPA-adsorbed TiO<sub>2</sub> colloids have been studied by using ps-time-resolved fluorescence and ns-transient absorption spectroscopy. These illustrate that the photo-induced charge-carrier generation at the hetero-junction is very efficient, and especially it is found that the interfacial electron transfer mechanism of HPA/TiO<sub>2</sub> is quite analogous to the "Z-scheme" mechanism for plant photosynthetic systems. However, the photo-generated electron undergoes electron-hole recombination within the first 50 ps. In order to retard the electron-hole recombination, we attempted to fix TiO<sub>2</sub> in the cavity of HY zeolites or MCM 41 followed by entrapping the photosensitive molecules. Ti-Y zeolite was prepared by a method of incorporating TiO<sub>2</sub> into zeolite cavities through ion exchange of zeolite Y. DMABA, Nile Red or HPA was entrapped into Ti-Y zeolite in vacuum ( $1.0 \times 10^{-5}$  torr). The entrapped CT molecules show quenching of ICT emission, indicating that an efficient electron transfer from the excited singlet state of the ICT molecules to the conduction band of TiO<sub>2</sub> on the zeolite which consequently relays electron to a certain substrate outside of the zeolite. This is supported by observing more efficient

photoreduction of Methyl Orange as compared to that observed in the colloidal systems. 5,10,15,20-tetraphenyl-21H,23H-porphine manganese(III) chloride (MnTPP) was also encapsulated into MCM41 and Ti-MCM41, and the photoinduced electron transfer has been studied by using femtosecond diffuse reflectance photolysis. Two different ( $\sim 10$  ps and  $\sim 80$  ps) were observed. Also MnTPP<sup>\*</sup> radicals are detected, and its formation is easier in Ti-MCM41 than in MCM41. This indicates that framework modification by incorporating Ti<sup>4+</sup> into the porous molecules enhances the electron-accepting ability of the framework of porous molecules.

[참고문헌]

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