

Photophysical Studies of TiO₂-Y-Zeolites and MCM41 Entrapped by Some Photosensitive Molecules: Design of New Photocatalysts

Minjoong Yoon

Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea

TiO₂ provides very useful photocatalytic systems, capable of converting solar energy to chemical or electrical energy and environmental cleaning. The key step in enhancing the photocatalytic efficiency is improving photoinduced interfacial electron transfer like plant photosynthesis. However, it remains difficult to modify TiO₂ particles as a real analogue of the photosynthetic reaction center of green plant. Primarily we attempted to modify the surface of TiO₂ colloids by adsorbing some photosensitive molecules such as N,N-dimethylaminobenzoic acid (DMABA), porphyrin derivatives and Nile Red or heteropolytungstate (H₃PW₁₂O₄₀)(HPA), and the interfacial electron transfer dynamics have been studied by using ps-time resolved fluorescence and ns-transient absorption spectroscopy. These illustrate that the photoinduced charge-carrier generation at the hetero-junction is very efficient, and it is found that the interfacial electron transfer mechanism of HPA/ TiO₂ 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 e-h recombination, we attempted to fix TiO₂ in the frame of HY zeolites or MCM41 followed by entrapping the photosensitive molecules. The entrapped molecules show emission quenching, indicating the efficient electron transfer from the excited singlet state of the entrapped molecules to the conduction band of TiO₂ zeolites which consequently relays electron to a certain substrate outside of the zeolites as shown by more efficient photoreduction of Methyl Orange or the photoinduced hydrolysis of water than in the colloidal systems. Some porphyrin derivatives were also encapsulated into MCM41 and Ti-MCM41, and the photoinduced electron transfer has been studied by using femtosecond diffuse reflectance photolysis. Two different (~ 10ps and ~ 80 ps) transient species and porphyrin radicals were observed, and their formation is easier in Ti-MCM41 than in MCM41. This indicates that framework modification by incorporating Ti⁴⁺ into the porous materials enhances the electron-accepting ability of the porous materials.

References

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