

Hydrophilicity Control of Visible-Light Hydrogen Evolution and Dynamics of Charge-Separated State in Dye/TiO₂/Pt Hybrid System

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We investigated visible-light-driven H₂ evolution based on dye/TiO₂/Pt hybrid photocatalysts using a series of dyes with the structure of (*E*)-3-(5-(4-(bis(4-*R*₁-phenyl) amino)phenyl)-4,4'-(*R*₂)₂-2,2'-bithiophen-5-yl)-2-cyanoacrylic acid including parent hydrophobic HD (*R*₁ = *R*₂ = H), more hydrophobic PD (*R*₁ = C₃H₇, *R*₂ = H), slightly hydrophilic MOD (*R*₁ = CH₃OCH₂, *R*₂ = H), and relatively hydrophilic MO4D (*R*₁ = *R*₂ = CH₃OCH₂). Efficiencies of hydrogen evolution from aqueous suspensions of dye/TiO₂/Pt in the presence of EDTA as an electron donor under illumination at $\lambda > 420$ nm were found to considerably depend on the hydrophilic character of *R*₁, varying in the order MOD \approx MO4D > HD > PD. In the case of MOD/TiO₂/Pt hybrid, the apparent quantum yield for the photocatalyzed H₂ generation at 436 nm was determined to be 0.27 ± 0.03 . The hydrophilic/hydrophobic substituent effects of the dyes were investigated by transient absorption spectra taken in subpicosecond-to-microsecond time domains for MOD- or PD-grafted transparent films of TiO₂ nanoparticles dipped into water at pH 3. Upon femtosecond laser-pulse irradiation, the two samples commonly revealed the ultrafast growth (< 100 fs) of a broad absorption at 600–800 nm due to formation of the dye radical cation (dye^{•+}) followed by multi-component decays. While the fast decays occurring within 5 ps were almost *independent* of *R*₁, major parts of the transient decays in a longer time domain (> 5 ps) showed significant *differences* between the two samples; (1) the early part decay in the major components for MOD (4.55×10^8 s⁻¹) is ~ 2.5 times slower than that for PD (1.14×10^9 s⁻¹) and (2) a red shift of the spectrum occurred for MOD with a time constant of 17 ps, but not for PD. The transient absorption taken after a 20 ns delay was approximately three times higher for the MOD sample than for the PD one. The *substituent-independent* fast events observed within 5 ps have been interpreted in terms of ultrafast electron injection from the excited-singlet dye into TiO₂ followed by fast charge recombination of dye^{•+} with electrons trapped in surface/shallow traps. On the other hand, the major decay processes proceeding in the longer time region have been attributed to *substituent-dependent* charge recombination of dye^{•+} with electrons in inner-trap, interstitial-trap, and/or bulk states, giving different amounts of persistent electrons utilizable for the

reduction of protons. Essential roles of the hydrophilic/hydrophobic character of the dyes in the CR processes associated with net efficiencies of H₂ generation have been discussed in relation to different solvent reorganization as well as to possible molecular orientations on the TiO₂ surface based on theoretical calculations by Density Functional Theory (DFT).

