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-phenyl)amino)phenyl)-4,4'-(2,2'-bithiophen5-yl)-2-cyanoacrylic acid including parent hydrophobic HD (R1 = R2 = H), more hydrophobic PD (R1 = C3H7, R2 = H), slightly hydrophilic MOD (R1 = CH3OCH2, R2 = H), and relatively hydrophilic MO4D (R1 = R2 = CH3OCH2). Efficiencies of hydrogen evolution from aqueous suspensions of dye/TiO2/Pt in the presence of EDTA as an electron donor under illumination at λ > 420 nm were found to considerably depend on the hydrophilic character of R1, varying in the order MOD > 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 R1, 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 × 108 s-1) is ~2.5 times slower than that for PD (1.14 × 109 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).