

These structures consist of alkyl groups which, on average, experience a crystalline-like environment, are canted from the surface normal, and packed to high densities sufficient to form high-quality barriers for both electron- and ion-transfer processes. Defects in these structures would be expected because of the complex surface morphology of the polycrystalline gold including crystallographic faceting and surface roughness as well as the complexities of the thiol head-group attachment chemistry and mismatches of ideal lattice parameters for the alkyl chains and the substrate-bound head groups. However, for the case of the long-chain thiols, the van der Waals interactions of the chains appear to sustain a structure which is a very effective dielectric barrier. Shorter chain lengths promote a loss of film organization. This results in a decreased packing density and the onset of permeability by Cl^- and ClO_4^- .

This study clearly shows that significant potential exists to adapt these *n*-alkyl thiol monolayer assemblies for use as model systems for fundamental studies of heterogeneous charge-transfer, ion transport and double-layer phenomena. There are several po-

tentially fruitful modifications, not considered in this first study, that could lead to improve the properties of this model system. These include the use of smooth, single-crystal gold substrates and the optimization of adsorption conditions as well as variations in the molecular structures of the thiols. Utilization of these approaches for various applications is presently underway.

Acknowledgment. The authors gratefully acknowledge many valuable discussions with G. Whitesides, B. Troughton, and their co-workers at Harvard University. We thank B. Troughton for the gift of $\text{CH}_3(\text{CH}_2)_{21}\text{SH}$. Also acknowledged are discussions with H. Finklea and J. Sagiv in the initial stages of this study. We are particularly grateful to R. Nuzzo for critical discussions during the course of this study. The useful comments of one reviewer are acknowledged.

Registry No. $\text{CH}_3\text{CH}_2\text{SH}$, 75-08-1; $\text{CH}_3(\text{CH}_2)_3\text{SH}$, 109-79-5; $\text{CH}_3(\text{CH}_2)_5\text{SH}$, 111-31-9; $\text{CH}_3(\text{CH}_2)_7\text{SH}$, 111-88-6; $\text{CH}_3(\text{CH}_2)_9\text{SH}$, 143-10-2; $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, 1322-36-7; $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, 2917-26-2; $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$, 2885-00-9; $\text{CH}_3(\text{CH}_2)_{21}\text{SH}$, 7773-83-3; Au, 7440-57-5.

Improved Charge Separation and Photosensitized H_2 Evolution from Water with TiO_2 Particles on Colloidal SiO_2 Carriers

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Abstract: Laser flash photolysis and steady-state photolysis studies show that electrostatic interactions have a dramatic influence on the kinetics for charge separation and hydrogen production in aqueous systems (pH 9.8) of 20-nm diameter TiO_2 -modified SiO_2 colloids in various combinations with an electron relay, a photosensitizer, and a Pt catalyst. Either direct excitation of the semiconductor or the photosensitizer $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine), electrostatically adsorbed to the colloid, initiate electron transfer to either the zwitterionic electron relay, N,N' -bis(3-sulfonatopropyl)-4,4'-bipyridinium (PVS^0), or N,N' -bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS^0), or methyl viologen (MV^{2+}). The rates and quantum yields for the formation of the radical $\text{PVS}^{\cdot-}$ anion in both the $\text{TiO}_2\text{-SiO}_2/\text{PVS}^0$ and the $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{PVS}^0$ systems decline with increasing ionic strength. The rate and quantum yields for H_2 production in both the $\text{TiO}_2\text{-SiO}_2/\text{DQS}^0/\text{Pt}$ and the $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{DQS}^0/\text{Pt}$ systems also show a similar ionic strength dependence. Kinetic analysis of the data infers that repulsion of the reduced zwitterionic relay $\text{PVS}^{\cdot-}$ and $\text{DQS}^{\cdot-}$ from the negatively charged colloidal interface inhibits back electron transfer to both the semiconductor and the surface-attached oxidized photosensitizer $\text{Ru}(\text{bpy})_3^{3+}$. Formation of the cation $\text{MV}^{\cdot+}$ radical and its back electron transfer to the semiconductor are rapid and imply that the MV^{2+} electron relay is in close proximity to the colloid. Both the photogenerated valence-band holes and the oxidized photosensitizer $\text{Ru}(\text{bpy})_3^{3+}$ oxidize surface Ti-O^- groups of TiO_2 . This redox process has the important effect of recycling the photosensitizer for further reaction. The addition of the superoxide dismutase enzyme to the oxidized $\text{TiO}_2\text{-(SiO}_2)$ system regenerates, in part, the activity of the semiconductor to evolve H_2 and to release molecular oxygen.

Light-induced electron-transfer reactions in colloidal and particulate semiconductor dispersions have become an active area of research in photochemistry.¹ Extensive studies have demonstrated the potential utility of semiconductor particles as light-harvesting units in the photochemical conversion and storage of solar energy. Semiconductor particles of minute size (diameters of 5–50 nm) can have high efficiencies for the photogeneration of electron-hole pairs because of the short transit time of charge carriers from the particle interior to the surface compared with the long relaxation time for charge recombination in the bulk of the semiconductor.² A crucial problem inherent to microheterogeneous systems is, however, the rapid surface recombination of photogenerated electrons and holes as well as the back electron transfer between the semiconductor and reactive intermediates formed at the semiconductor particle-liquid interface. A second obstacle to the exploitation of small semiconductor particles for photochemical solar energy conversion is the absence of materials

that not only form colloids but also have good photostability and high solar spectral response. One approach that addresses this

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latter problem is to develop new materials (e.g., molecular semiconductors³) having the appropriate properties. Another strategy is to use known materials that form colloids and then to modify them to obtain the other desired properties. Toward this end, a considerable amount of work has been concerned with the photosensitization of stable wide-bandgap semiconductors such as TiO₂^{4,5} with chromophores that absorb strongly in the visible and near-infrared regions of the solar spectrum. Photosensitizers have also been used in nonsemiconductor-based systems to bring about the cleavage of water,⁶ CO₂ fixation,⁷ and other chemical transformations.^{8,9} Efficient conversion of light energy requires that back charge transfer to the oxidized (or reduced) photosensitizer be suppressed. Charged colloids such as SiO₂ and ZrO₂ have been shown to provide effective microenvironments for controlling electron-transfer reactions between photosensitizers and electron relays.^{10,11} With SiO₂ colloids, for example, good charge separation between the oxidized photosensitizer and the reduced electron relay has been accomplished. The mechanism involves the selective electrostatic association of one of the redox products with the charged colloid and the specific repulsion of the partner product from the colloid interface. In these photochemical systems, a sacrificial electron donor is generally required to recycle the photosensitizer. Hydrogen is evolved upon reaction of the reduced electron relay with an appropriate catalyst under suitable conditions.

We report here the first example of the application of electrostatic effects to control electron transfer in a colloidal or a particulate semiconductor-based system. Electrostatic effects are found to produce a marked improvement in the kinetics for charge separation and hydrogen production in aqueous media. The representative system consisted of TiO₂ particles immobilized on negatively charged SiO₂ colloids in various combinations with a zwitterionic electron relay, a photosensitizer, and a colloidal Pt catalyst. The photosensitizer was Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) and the zwitterionic electron relay was either *N,N'*-

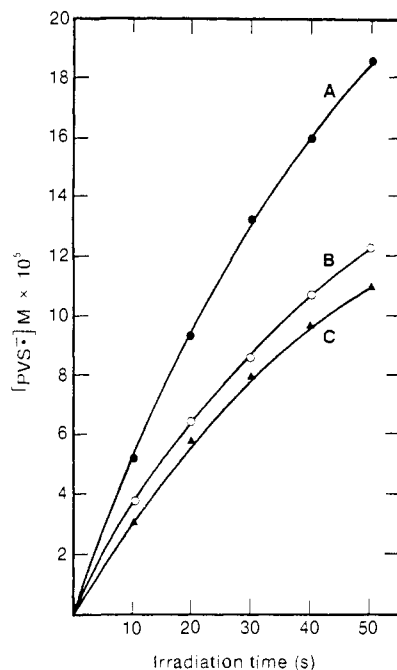
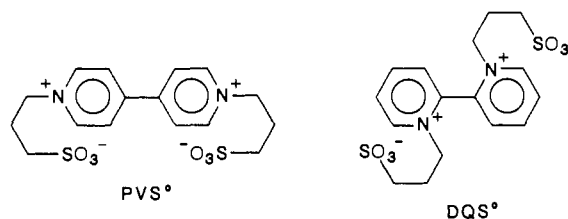


Figure 1. Production of PVS^{•-} with irradiation time ($\lambda_{\text{ex}} > 305$ nm) for 2×10^{-3} M PVS⁰ with 0.5% TiO₂-SiO₂ colloids in aqueous solutions at pH 9.8 with (A) no added salt, (B) 0.06 M NaCl, and (C) 0.14 M NaCl.

bis(3-sulfonatopropyl)-4,4'-bipyridinium (PVS⁰) or *N,N'*-bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS⁰).



Experimental Section

Materials. *N,N'*-Bis(3-sulfonatopropyl)-4,4'-bipyridinium (PVS⁰) and *N,N'*-bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS⁰) were prepared as described elsewhere.^{11a,12} The titania-modified silica (TiO₂-SiO₂) colloids (24.2% (w/w)) were obtained from Nalco Chemical Co. The colloids were dialyzed for 10 h and diluted to the desired concentrations. Transmission electron microscopy (TEM) measurements of the TiO₂-SiO₂ dispersion show that the TiO₂ particles (4-nm diameter) are distributed nonhomogeneously onto spherical SiO₂ colloids (30-nm diameter). Some SiO₂ particles have no TiO₂ sites, whereas others have one or more TiO₂ particles on the surface. Still others have a cluster of TiO₂ particles present at the interface of several SiO₂ colloids. Whether the latter type of aggregation also exists in aqueous solution is speculative. Although both TiO₂ and SiO₂ are each charged negatively at the pH of the solution (pH 9.8), the TEM indicates that they are present as co-colloids. In other words, the TiO₂ is associated with the silica and is not free in solution. Colloidal Pt (12 mg l⁻¹; 2 nm particle diameter) was prepared by the citrate reduction of H₂PtCl₆¹³ and dialyzed just prior to use.

Apparatus. Laser photolysis experiments employed a Molecron UV-IU nitrogen-pumped Molecron DL200 dye laser combined with fast kinetic spectroscopy to detect transient species. Continuous illumination was carried out with a PTI Model A-1000 Xe lamp equipped with a 3 cm path length copper sulfate solution to remove IR radiation and a cutoff filter ($\lambda > 400$ nm, incident photon flux = 1.8×10^{-7} einstein s⁻¹ cm⁻²; $\lambda > 305$ nm, incident photon flux = 2.3×10^{-7} einstein s⁻¹ cm⁻²). Absorption spectra were recorded on a Uvikon-820 (Kontron) spectrophotometer equipped with a ψ -80 computer (Kontron) for data acquisition and reduction. Hydrogen and oxygen were measured with a

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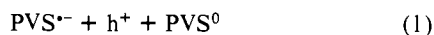
Packard Model 427 gas chromatograph equipped with a 5-Å molecular sieve column, a thermal conductivity detector, and argon or helium as the carrier gas for H₂ or O₂ analyses, respectively.

General Photolysis Samples and Procedures. In the UV-photolysis studies of PVS⁰, the samples consisted of 0.5% (w/w) TiO₂-SiO₂ colloids and 2 × 10⁻³ M PVS⁰ in 3 mL of aqueous solutions at pH 9.8. In the investigation of H₂ production in the ultraviolet region, the samples contained 2.4% (w/w) TiO₂-SiO₂ colloids and 2 × 10⁻³ M DQS⁰ in 3 mL of aqueous solutions at pH 9.8. In the photosensitization studies of H₂ evolution, 6 × 10⁻⁵ M Ru(bpy)₃²⁺ was added to the above samples and the concentrations of the TiO₂-SiO₂ were either 1.2% or 0.6% (w/w). The photolysis vessel was a 1-cm cuvette fitted with a microvalve and rubber septum. Prior to photolysis, the solutions were deaerated by repeated evacuation and argon bubbling cycles. During irradiation, the cuvette was maintained at 23.6 °C. The absorbed light intensity was determined with the Reinecke's salt actinometer.¹⁴ Quantum yields for the formation of the methyl viologen MV^{•+} and PVS^{•-} radical ions were determined from the knowledge of the concentrations of the species at 602 nm (MV^{•+}, ε = 12 800 M⁻¹ cm⁻¹; PVS^{•-}, ε = 13 800 M⁻¹ cm⁻¹). The amount of light absorbed by Ru(bpy)₃²⁺ was determined from its absorption spectrum. In the case of the TiO₂-SiO₂ colloids, the amount of light absorbed was estimated from the difference in light intensity that was transmitted through a reaction vessel containing only water and then water plus TiO₂-SiO₂ particles. In studies in which H₂/O₂ production was investigated, gas samples were taken at regular intervals during photolysis and injected into the gas chromatograph for analysis.

Results and Discussion

Electron Transfer and H₂ Production in the Ultraviolet Region.

Figure 1 describes the effect of ionic strength on the generation of PVS^{•-} radical anions in the bandgap-illuminated (λ > 305 nm) TiO₂-SiO₂/PVS⁰ systems in aqueous solution at pH 9.8. At this pH, the TiO₂-SiO₂ colloids are negatively charged, since TiO₂ and the silanol groups of SiO₂¹⁵ are ionized at pH 9.8. Figure 1 shows that the rate and the yield of PVS^{•-} production decline with increasing ionic strength. In the absence of added salt, the quantum yield φ for the formation of PVS^{•-} is 2.3 × 10⁻². At 0.06 and 0.14 M NaCl, the quantum yields are 1.5 × 10⁻² and 1.2 × 10⁻², respectively. The dependence of the quantum yield for PVS^{•-} formation on the ionic strength is attributed to electrostatic interactions between the colloids and the PVS^{•-} radical anion. Also, since no photoreduction of the PVS⁰ charge relay occurs in the SiO₂/PVS⁰ system (i.e., in a system without TiO₂), we infer that TiO₂ is the photoactive component involved in the electron transfer to PVS⁰. Thus, at low ionic strength, the surface potential of the TiO₂-SiO₂ colloid is sufficiently negative to inhibit the approach of PVS^{•-} radical anions to the immobilized TiO₂ sites. With increasing ionic strength, the electrical field of TiO₂-SiO₂ is screened and the rate of reaction of the PVS^{•-} radicals with the photogenerated valence-band holes of TiO₂ increases.



It is important to note that the photoreduction of PVS⁰ in the TiO₂-SiO₂/PVS⁰ system occurs without the addition of a sacrificial electron donor (or hole acceptor) such as triethanolamine for reasons that are discussed below.

To further investigate the role of electrostatic forces in controlling electron transfer, methyl viologen was substituted for PVS⁰. Whereas PVS⁰ is a zwitterion that becomes negatively charged when reduced, methyl viologen MV²⁺ forms the positively charged MV^{•+} radical upon reduction. Several studies^{16,17} have examined the photoreduction of MV²⁺ by TiO₂ colloids. In the case of TiO₂-SiO₂ colloids, we have found that the quantum yield for

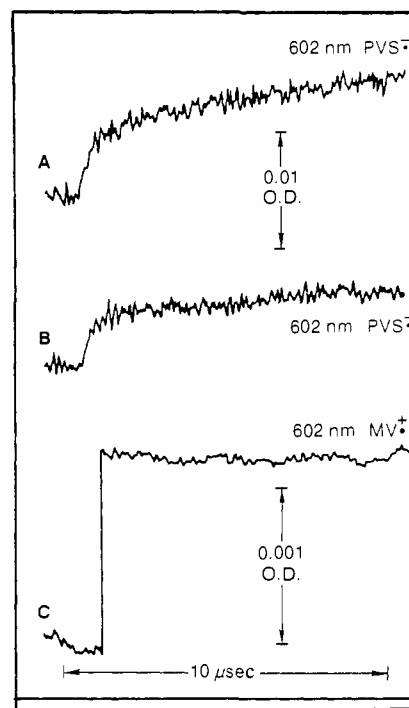


Figure 2. Absorption transients for the production of PVS^{•-} (A and B) and MV^{•+} (C) for aqueous solutions (pH 9.8) of 0.5% TiO₂-SiO₂ colloids with 2 × 10⁻³ M PVS⁰ or 2 × 10⁻³ M MV²⁺, respectively. Ionic strength effects: no added salt in part A and 0.11 M NaCl in part B. 337-nm laser excitation.

reduction of MV²⁺ (φ = 9.6 × 10⁻³) without added salt is close to that observed for PVS⁰ (φ = 1.2 × 10⁻²) at high ionic strength (μ = 0.14 M = [NaCl]). Furthermore, in contrast to the absorption spectrum of the reduction product of PVS⁰ which corresponds to that of the monomeric PVS^{•-} radical anion (λ = 602 nm; ε = 13 800 M⁻¹ cm⁻¹), the absorption spectrum of the photoproduct of MV²⁺ corresponds to that of the dimeric cation radical (MV^{•+})₂ (λ_{max} = 550 nm), even when MV²⁺ is present at low bulk concentrations in aqueous solutions. Dimer formation is, however, observed only at high concentrations of MV^{•+},¹⁸ suggesting the buildup of a high local concentration of the MV^{•+} radical cation at the negatively charged TiO₂-SiO₂ colloid interface. The electrostatic attraction between the oppositely charged species also favors oxidation of the viologen radical cation by the valence-band holes of TiO₂ and accounts for the relatively low quantum yield for reduction of MV²⁺ compared to that of PVS⁰.

Figure 2 shows the respective transient absorption spectra of MV^{•+} and PVS^{•-}, following the pulsed 337-nm laser excitation of TiO₂ in the TiO₂-SiO₂/MV²⁺ and the TiO₂-SiO₂/PVS⁰ systems. The upper and middle traces indicate that the growth of the PVS^{•-} radical anion occurs over a period of 10 μs. The lower trace shows that the MV^{•+} radical cation (λ = 602 nm) is present immediately after the laser pulse. One can infer from these results that the prompt reduction of MV²⁺ is due to its close association with the TiO₂-SiO₂ interface. The slower growth kinetics of PVS^{•-} indicates that subsequent to excitation of the semiconductor, PVS⁰ must diffuse to the particle surface before electron transfer occurs. A comparison of the absorption transients in Figure 2, A and B, shows that the ionic strength of the solutions affects the steady-state concentration of PVS^{•-}. At low ionic strength, the back reaction of PVS^{•-} with the photogenerated valence-band holes of TiO₂ is impeded by the establishment of an electrostatic barrier between PVS^{•-} and the negatively charged TiO₂-SiO₂ colloids. At high ionic strength, the negative surface potential of TiO₂-SiO₂ is screened and the relative rate of the reverse process (reaction 1) is accelerated, thus decreasing the net yield of PVS^{•-}. The

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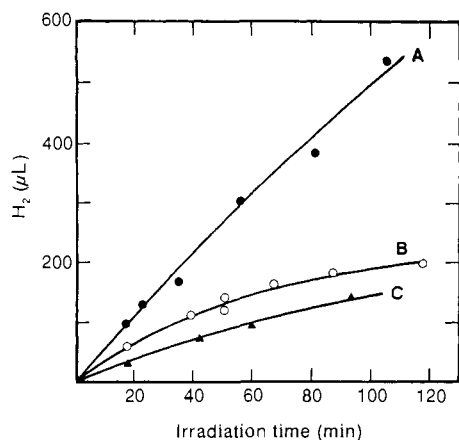


Figure 3. Production of H₂ with irradiation time ($\lambda_{\text{ex}} > 305$ nm) for aqueous solutions (pH 9.8) of 2.4% TiO₂-SiO₂ colloids, 2×10^{-3} M DQS⁰, and 12 mg L⁻¹ Pt colloids with (A) no salt, (B) 0.08 M NaCl, and (C) 0.11 M NaCl.

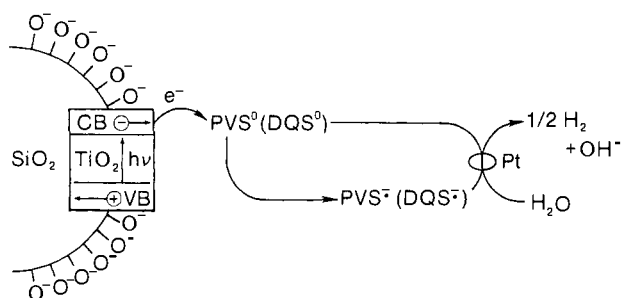


Figure 4. Representation of electrostatic effects: Following photoinitiated electron transfer from TiO₂ to an electron relay PVS⁰ or DQS⁰, the negatively charged SiO₂ colloidal support repels PVS⁻ or DQS⁻ from the semiconductor, thus inhibiting the back reaction. The escaped DQS⁻ is recycled through a reaction with a colloidal Pt catalyst to evolve H₂.

transient and steady-state photolysis data illustrate the influence of electrostatic forces in controlling both the forward and the reverse electron transfer between the two-electron relays (PVS⁰ and MV²⁺) and the TiO₂-modified SiO₂ colloids.

The possibility that the negative surface charge of the TiO₂-SiO₂ particles might be effective in promoting the redox chemistry for H₂ production was also explored. In these experiments, *N,N'*-bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS⁰) was used as an electron relay. The redox potential of the DQS⁰/DQS⁻ couple in aqueous solutions is -0.65 V (vs. NHE) and the radical anion DQS⁻ can reduce water to H₂ at pH 9.8.¹⁹ The flatband potential of TiO₂ is pH dependent.^{16,20} At this pH, the flatband potential of colloidal TiO₂ is -0.70 V (vs. NHE)¹⁶ which is sufficiently negative, thermodynamically, to reduce DQS⁰. Figure 3 demonstrates that bandgap illumination ($\lambda > 305$ nm) of the TiO₂-SiO₂ colloids with DQS⁰ and a catalytic Pt sol (12 mg/L) in aqueous solution at pH 9.8 does indeed produce molecular hydrogen. The quantum yield for H₂ production is 1.6×10^{-3} . However, the H₂ production exhibits a strong dependence on the ionic strength, indicating electrostatic interaction between DQS⁻ and the negatively charged TiO₂-SiO₂ colloids. On decreasing the ionic strength, both the yield and rate of H₂ production increase, implying that the DQS⁻ radical anion was repelled from the surface of the colloid before back reaction with the valence-band holes of TiO₂ could take place. Inhibition of the back reaction stabilizes DQS⁻ for subsequent reaction with the Pt catalyst and H₂ production. Figure 4 summarizes schematically the respective mechanisms for electron transfer and H₂ production in the TiO₂-SiO₂/PVS⁰ and the TiO₂-SiO₂/DQS⁰/Pt systems.

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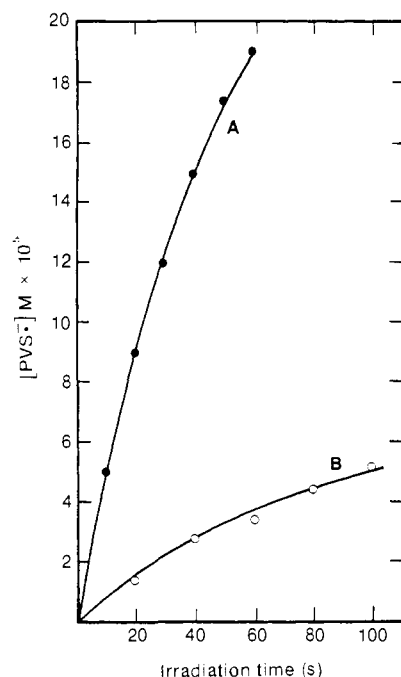
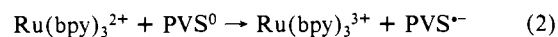


Figure 5. Production of PVS⁻ with irradiation time ($\lambda_{\text{ex}} > 400$ nm) for 6×10^{-5} M Ru(bpy)₃²⁺, 2×10^{-3} M PVS⁰, and 0.5% TiO₂-SiO₂ colloids with (A) no added salt and (B) 0.12 M NaCl.

Electron Transfer and H₂ Production in the Visible Region.

Several studies⁵ have dealt with the photosensitization of TiO₂ particles to visible light by employing chromophores that can serve as electron donors to the semiconductor. It has been found^{5j} that the Ru(bpy)₃²⁺ complex is a relatively poor sensitizer for TiO₂ compared to the carboxylic acid derivative of Ru(bpy)₃²⁺ which is electrostatically attached to the semiconductor surface. The close association of the latter complex with the semiconductor surface is presumed to facilitate charge injection into the conduction band of TiO₂. It has been shown^{10b,d} that Ru(bpy)₃²⁺ may be electrostatically adsorbed to the interface of colloidal SiO₂. We anticipated therefore that a similar electrostatic association of Ru(bpy)₃²⁺ with the TiO₂-SiO₂ particle interface might lead to effective electron transfer from the excited state of the complex to the conduction band of TiO₂. Steady-state fluorescence quenching and laser flash photolysis studies indicated, however, that the emission from excited Ru(bpy)₂²⁺ is not quenched and that no photoinitiated electron transfer to TiO₂(-SiO₂) takes place, suggesting that the Ru(bpy)₃²⁺ may be associated with the SiO₂ colloidal support and not with the TiO₂ sites.

We thought that the presence of a zwitterionic electron relay such as PVS⁰ or DQS⁰ might promote electron transfer in the TiO₂-SiO₂/Ru(bpy)₃²⁺ system. For example, the reduction of PVS⁰ or DQS⁰ by excited Ru(bpy)₃²⁺ occurs rapidly in the presence of SiO₂ and a sacrificial electron donor.^{10,11} In this system, the negatively charged SiO₂ colloid stabilizes the intermediate viologen radical anion against back electron transfer by repelling the reduced PVS⁻ or DQS⁻ from Ru(bpy)₃³⁺ species adsorbed to the colloidal SiO₂ interface. Similar electrostatic effects are anticipated to inhibit the reverse electron transfer between the viologen radical anion and Ru(bpy)₃³⁺ in the presence of TiO₂-SiO₂ colloids. Figure 5 shows the production of PVS⁻ in aqueous solution at pH 9.8 when Ru(bpy)₃²⁺ is excited by sub-bandgap light ($\lambda > 400$ nm).



The quantum yield ϕ for PVS⁻ formation declines with increasing ionic strength. With no added salt, $\phi = 2.4 \times 10^{-2}$, and at 0.12 M NaCl, the quantum yield for PVS⁻ formation decreases to 4.6×10^{-3} . The ionic strength dependence implicates electrostatic effects in controlling the electron transfer. The ionic strength effects suggest that the PVS⁻ radical anion is repelled from the TiO₂-SiO₂ surface to which the oxidized sensitizer Ru(bpy)₃³⁺

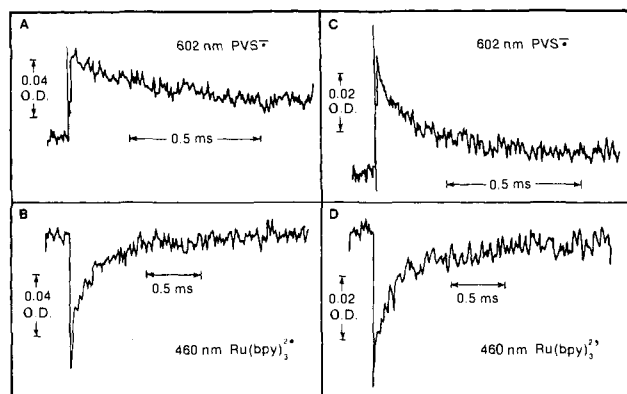
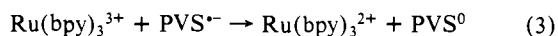
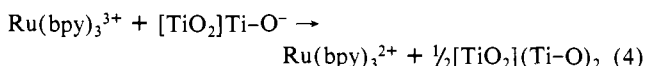


Figure 6. Absorption transients for the decay of $\text{PVS}^{\bullet-}$ (A and C) and the recovery of bleached $\text{Ru}(\text{bpy})_3^{2+}$ (B and D) for aqueous solutions (pH 9.8) of 0.5% $\text{TiO}_2\text{-SiO}_2$ colloids, 3×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$, 2×10^{-3} M PVS^0 , with no added salt in parts A and B and 0.11 M NaCl in parts C and D. 457-nm laser excitation.

is bound. With increasing ionic strength, the electrostatic effects diminish and the back electron transfer becomes increasingly favorable.



The efficient photoproduction of $\text{PVS}^{\bullet-}$ in the aqueous $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{PVS}^0$ system was unexpected since no sacrificial electron donor was added to the solution to recycle $\text{Ru}(\text{bpy})_3^{3+}$ to $\text{Ru}(\text{bpy})_3^{2+}$. To determine whether TiO_2 was the source of electrons for the reduction of $\text{Ru}(\text{bpy})_3^{3+}$, additional experiments were carried out. We found that in either the absence of the $\text{TiO}_2\text{-SiO}_2$ colloids or a system in which the $\text{TiO}_2\text{-SiO}_2$ colloids were replaced by a SiO_2 sol, no photoreduction of PVS^0 occurred. These results suggest that TiO_2 did indeed participate in the conversion of $\text{Ru}(\text{bpy})_3^{3+}$ to $\text{Ru}(\text{bpy})_3^{2+}$ in basic media. These studies also infer that TiO_2 is the source of electrons for the reduction of $\text{Ru}(\text{bpy})_3^{3+}$ and is, in turn, oxidized presumably by means of a surface reaction.



The surface oxidation of TiO_2 by photogenerated valence-band holes has been suggested to occur during the photooxidation of water.²¹

Figure 6 provides information on the temporal behavior of $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ in aqueous solutions with $\text{TiO}_2\text{-SiO}_2$ colloids at different ionic strengths. With no added salt, the transient absorption of $\text{PVS}^{\bullet-}$ ($\lambda = 602$ nm; $\epsilon = 13800$ $\text{M}^{-1} \text{cm}^{-1}$) is present immediately after the laser pulse but then decays to a nonbaseline level in 1 ms (Figure 6A). The transient behavior of $\text{Ru}(\text{bpy})_3^{3+}$ is more complex than that of $\text{PVS}^{\bullet-}$. Figure 6B records the bleaching and recovery of the absorption of $\text{Ru}(\text{bpy})_3^{2+}$ ($\lambda = 460$ nm; $\epsilon = 14600$ $\text{M}^{-1} \text{cm}^{-1}$), following the laser pulse. The bleaching and recovery of the absorption of $\text{Ru}(\text{bpy})_3^{2+}$ corresponds to the growth and disappearance of $\text{Ru}(\text{bpy})_3^{3+}$, respectively. In contrast to the decay kinetics of $\text{PVS}^{\bullet-}$, $\text{Ru}(\text{bpy})_3^{3+}$ decays to baseline within 1 ms, indicating that $\text{Ru}(\text{bpy})_3^{3+}$ is consumed by more than one pathway as may be anticipated by reactions 3 and 4. A comparison of the transient absorptions in Figure 6, A and B, shows that after $\text{Ru}(\text{bpy})_3^{3+}$ is completely consumed, no further reaction of $\text{PVS}^{\bullet-}$ takes place over the period of observation. From the residual absorption of $\text{PVS}^{\bullet-}$ obtained after steady state (Figure 6A), one can estimate that 42% of $\text{Ru}(\text{bpy})_3^{3+}$ is reduced by the surface groups of TiO_2 , according to reaction 4. In other words, 58% of $\text{Ru}(\text{bpy})_3^{3+}$ back reacts with $\text{PVS}^{\bullet-}$ via reaction 3. Figure 6C shows that at high ionic strength (0.11 M NaCl), the decay rate of $\text{PVS}^{\bullet-}$ is substantially accelerated and a lower steady-state concentration is reached compared

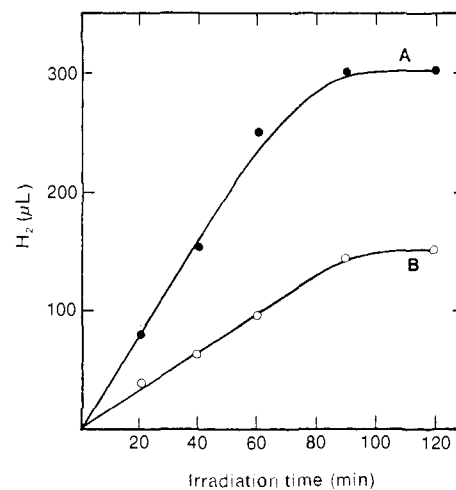


Figure 7. Production of H_2 with irradiation time ($\lambda_{\text{ex}} > 400$ nm) for aqueous solutions of 6×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$, 2×10^{-3} M DQS^0 , and 12 mg L^{-1} Pt colloids with (A) 1.2% $\text{TiO}_2\text{-SiO}_2$ colloids and (B) 0.6% $\text{TiO}_2\text{-SiO}_2$ colloids.

to the system without added salt. The rate constant²² for recombination of $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ at 0.11 M NaCl is

$$k_3 = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

which is a factor of 6 higher than the system without added salt, which has a rate constant of

$$k_3' = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Furthermore, from the residual absorption of $\text{PVS}^{\bullet-}$ after reaching steady state, one can conclude that about 19% of $\text{Ru}(\text{bpy})_3^{3+}$ is consumed by reaction with the TiO_2 surface (reaction 4) in the presence of 0.11 M NaCl. Thus, the effect of the increased ionic strength is to promote the back electron transfer between $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ at the expense of the oxidation of the TiO_2 surface (reaction 4). The kinetics for electron transfer in the $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{PVS}^0$ system are in marked contrast to those in the $\text{Ru}(\text{bpy})_3^{3+}/\text{PVS}^0$ system. In the homogeneous media, flash photolysis studies indicate that the back reaction of $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ is diffusion controlled with a rate constant of

$$k_3'' = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

This value of the rate constant for recombination of $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ in homogeneous media is identical with k_3 obtained in the microheterogeneous $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{PVS}^0$ system at high ionic strength. However, in the homogeneous system, the decay kinetics of $\text{PVS}^{\bullet-}$ are concomitant with and match those of $\text{Ru}(\text{bpy})_3^{3+}$, indicating the absence of side reactions. The results of these studies suggest that the negatively charged $\text{TiO}_2\text{-SiO}_2$ colloids improve the stability of the intermediate photoproducts $\text{PVS}^{\bullet-}$ and $\text{Ru}(\text{bpy})_3^{3+}$ against back electron transfer at low ionic strengths. In addition, the data indicate that $\text{TiO}_2\text{-SiO}_2$ colloid provides electrons to the oxidized intermediate, $\text{Ru}(\text{bpy})_3^{3+}$, thus recycling the complex for further reaction.

The possibility that the $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{Pt}$ system with an appropriate electron relay could be used to photogenerate H_2 from water with visible light was also investigated. For these studies, the DQS^0 zwitterion was employed as the electron relay. Figure 7 shows the H_2 production with illumination time in the $\text{TiO}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}/\text{DQS}^0/\text{Pt}$ system in aqueous media at pH 9.8. When the $\text{TiO}_2\text{-SiO}_2$ colloids are present at a concentration of 1.2%, a total of 300 μL of H_2 was generated in 90 min with an initial rate of 230 $\mu\text{L/h}$ (Figure 7; curve A). When the

(22) The recombination rate constant was determined with use of eq i and ii.

$$d[\text{PVS}^{\bullet-}]/dt = k_3[\text{PVS}^{\bullet-}]_t[\text{Ru}(\text{bpy})_3^{3+}]_t \quad (i)$$

$$\ln \{d[\text{PVS}^{\bullet-}]_0/[\text{PVS}^{\bullet-}]_t\} = k_3 \int [\text{Ru}(\text{bpy})_3^{3+}]_t dt \quad (ii)$$

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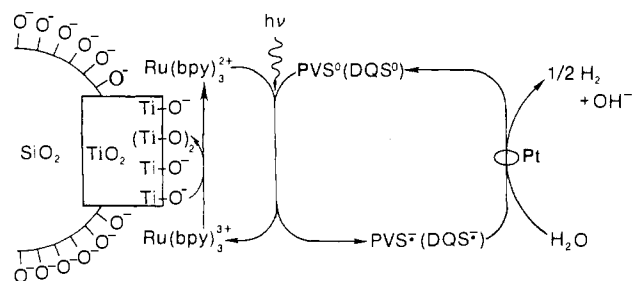


Figure 8. Representation of mechanisms: Following photoinitiated electron transfer from sensitizer $\text{Ru}(\text{bpy})_3^{2+}$ to an electron relay PVS^0 or DQS^0 , the negatively charged SiO_2 colloidal support repels PVS^- or DQS^- from $\text{Ru}(\text{bpy})_3^{3+}$ at colloidal interface, thus inhibiting the back electron transfer. The escaped DQS^- is recycled through reaction with a colloidal Pt catalyst to evolve H_2 . The oxidized sensitizer, $\text{Ru}(\text{bpy})_3^{3+}$, is recycled through the oxidation of the TiO_2 surface.

concentration of TiO_2 - SiO_2 was decreased by one-half, the H_2 yield was also cut by one-half (Figure 7, curve B). Furthermore, when the enzyme superoxide dismutase was added to the system after cessation of hydrogen generation, the photoproduction of H_2 resumed. Along with the hydrogen production, oxygen was also formed. The role of superoxide dismutase to catalyze O_2 production in biological systems has been well studied.²³ Superoxide dismutase catalyzes the disproportionation of two molecules of superoxide O_2^- to O_2 and hydrogen peroxide in two steps that are in equilibrium. The catalytic reaction of the enzyme is highly specific to superoxide. In the case of TiO_2 , the mechanism suggests the possibility for the interconversion of peroxide and superoxide. Since the equilibrium favors peroxide in the biological system, it seems reasonable that only a small fraction of the oxidized surface groups of TiO_2 would be present in the superoxo form. Consistent with this notion is the observation that in the TiO_2 - SiO_2 system to which superoxide dismutase had been added, the amount of O_2 produced represented about 15% of the expected 1:2 stoichiometric ratio of O_2/H_2 . Several other studies^{21,24} also implicate peroxo or superoxo compounds as the oxidized product of surface TiO_2 groups. The dependence of the H_2 production on the concentration of the TiO_2 - SiO_2 colloids can thus be explained by the decline in the number of surface $\text{Ti}-\text{O}^-$ groups available for the reduction of $\text{Ru}(\text{bpy})_3^{3+}$. Similarly, the leveling off of the H_2 production with illumination time is likely due to the exhaustion of $\text{Ti}-\text{O}^-$ groups available for the reduction (or recycling) of the oxidized $\text{Ru}(\text{bpy})_3^{3+}$ species.

In the absence of $\text{Ru}(\text{bpy})_3^{2+}$, sub-bandgap irradiation ($\lambda_{\text{ex}} > 400 \text{ nm}$) of the TiO_2 - SiO_2 / DQS^0 /Pt system did not produce molecular H_2 . However, illumination of the TiO_2 - SiO_2 / DQS^0 /Pt

system with bandgap irradiation ($\lambda > 305 \text{ nm}$) did generate H_2 . The $\text{Ru}(\text{bpy})_3^{2+}$ sensitizer was thus an essential component for the visible-light-induced production of hydrogen. The quantum yield for H_2 production was markedly dependent on the ionic strength. With no added salt, the quantum yield ϕ for H_2 formation was 1.4×10^{-3} . At 0.12 M NaCl, the quantum yield was 2×10^{-4} , representing a factor of 7 decrease with respect to the solution with no added salt. The dependence of the quantum yields for H_2 production on ionic strength illustrates the importance of electrostatic effects in controlling electron transfer and the subsequent photogeneration of molecular hydrogen. Figure 8 is a conceptual representation of the mechanism at low ionic strength. The negative surface charge of the TiO_2 - SiO_2 colloid stabilizes the DQS^- and $\text{Ru}(\text{bpy})_3^{3+}$ intermediates against back electron transfer, thus allowing the DQS^- reaction with the catalytic Pt colloid to produce H_2 . $\text{Ru}(\text{bpy})_3^{3+}$ is converted to $\text{Ru}(\text{bpy})_3^{2+}$ by oxidation of the TiO_2 surface. The oxidation of the TiO_2 surface thus recycles the sensitizer for further reaction. The decrease of the quantum yield for H_2 production at high ionic strength is due to the dampening of the negative surface potential of the TiO_2 - SiO_2 colloids, resulting in the facile recombination of the intermediate photoproducts DQS^- and $\text{Ru}(\text{bpy})_3^{3+}$.

Final Remarks

This study has demonstrated that electrostatic effects produce a dramatic improvement in the kinetics for charge separation and fuel generation in illuminated colloidal or particulate semiconductor systems. Titanium dioxide was immobilized on negatively charged SiO_2 colloids. Direct excitation of the semiconductor or an electrostatically bound sensitizer initiates electron transfer to a neutrally charged zwitterionic relay. Repulsion of the negatively charged reduced electron relay inhibits the reverse electron transfer. The reducing power of the reduced electron relay serves to generate molecular hydrogen in the presence of a Pt catalyst. Surface redox reactions between $\text{Ti}-\text{O}^-$ groups of TiO_2 and the photogenerated valence-band holes or the oxidized sensitizer probably form peroxo or superoxo groups. The ability of TiO_2 to store O_2 as an intermediate peroxide provides a potentially important mechanism for achieving the separation of H_2 and O_2 in dispersed systems. Heat treatment and additives such as metal oxides have been employed to regenerate the surface-oxidized TiO_2 with the accompanying release of molecular oxygen.²⁵ The use of enzymes such as superoxide dismutase is an alternative approach for the regeneration of TiO_2 and the discharge of surface bound oxygen. Further studies are now in progress to characterize the surface oxidation product of TiO_2 and to determine the effectiveness of enzymes to decompose it to molecular oxygen.

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