

Multielectron storage and hydrogen generation with colloidal semiconductors

(energy conversion/charge transfer/semiconducting particles/amphiphilic viologens/photoreactions)

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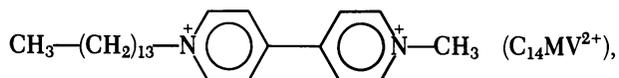
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ABSTRACT Multielectron storage and hydrogen generation by light is achieved in aqueous dispersions of ultrafine TiO₂ particles (120-Å diameter) when the amphiphilic viologen derivative *N*-tetradecyl-*N'*-methyl-4,4'-dipyridinium dichloride (C₁₄MV²⁺) is used as an electron relay. Consecutive reduction of C₁₄MV²⁺ to the radical ion (C₁₄MV^{•+}) and neutral (C₁₄MV[°]) was observed after band-gap excitation of the semiconductor particle. Through surface adsorption of the relay, these electron-transfer reactions can occur very rapidly and are completed within less than 100 μsec (pH 11). Two-electron reduction of C₁₄MV²⁺ can be coupled with H₂ generation in alkaline medium in the presence of Pt catalyst codeposited onto the TiO₂ particle. Electron-relay-free systems are 1/15th as efficient in producing H₂ at the same pH.

Colloidal semiconductors have several advantageous features (1–7) that make them attractive candidates to be used as light-harvesting units in solar energy devices. The idea of using colloidal semiconductors in photoconversion devices has been discussed by Nozik (8, 9). The concept of photoelectrochemical reactions on semiconductor particles dates back to the discoveries of Emil Baur (10). For a recent review, see ref. 11.

Particularly intriguing is the possibility of surface modification of the semiconductor particle by chemisorption, derivatization, or catalyst deposition to achieve light-induced charge separation (12) and subsequent fuel-generating dark reactions. The present study illustrates successful molecular engineering with such systems. By using aqueous dispersions of ultrafine TiO₂ particles in conjunction with the amphiphilic redox relay,



striking electron storage and hydrogen generation effects are demonstrated.

MATERIALS AND METHODS

Colloidal solutions of TiO₂ were prepared by slowly adding 5 g of TiCl₄ (Fluka purissimum) distilled under vacuum to 200 ml of water at 0°C. The solution was dialyzed until the pH reached a value of ca. 3. Precise determination of the TiO₂ content was carried out as described (5). Application of electron microscopy and quasielastic light-scattering technique showed that the sol consisted of 110-Å-diameter particles. At pH > 3, poly(vinyl alcohol) (PVA) was used to stabilize the colloidal particles. Commercial PVA (Mowiol 98110, Hoechst, Federal Republic of Germany) was pretreated by UV light (5) to remove impurities that absorb 347.1-nm light. Laser photolysis experiments were carried out with 347.1-nm pulses (10-nsec duration) of a JK-2000

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ruby laser. An Osram XBO 450-W Xe lamp equipped with a water jacket was used for continuous illuminations. C₁₄MV²⁺ was synthesized as described (13).

RESULTS AND DISCUSSION

Illumination of an aqueous TiO₂ sol containing C₁₄MV²⁺ with light of wavelength λ > 300 nm results in the immediate appearance of a blue color, which can be attributed to formation of viologen cation radicals (C₁₄MV^{•+}) (Fig. 1). However, this color does not persist under continuing exposure to light. A striking and rather rapid change from blue to intense yellow is noted. The resultant spectrum, also shown in Fig. 1, exhibits a weak absorption at 500 nm and a strong peak at 380 nm. Whereas the former absorption can be attributed to viologen dimer radicals (C₁₄MV^{•+})₂ (14) present at low concentration, the latter was identified as doubly reduced viologen—i.e., 1-methyl-1'-tetradecyl-4,4'-bipyridylene (C₁₄MV[°]). The two-electron reduction of the analogous compound methylviologen by chemical (15, 16) and electrochemical (17, 18) means yields dimethylbipyridylene with similar spectral features [solvent, acetonitrile: λ_{max} 404 nm, 340 sh, 315 nm (19); solvent, cyclohexane: λ_{max} 348 nm (log ε = 4.77), 377 nm (log ε = 4.66) (20); λ_{max} 400 nm, 376 sh (16)].

To substantiate the assignment of the 380-nm peak to C₁₄MV[°], two-electron reduction of C₁₄MV²⁺ was performed chemically by using dithionite as a reductant (16) and aqueous micellar solutions of Triton X-100 as a reaction medium. The spectrum of the product obtained has features (Fig. 2) identical with those of the photoproduct shown in Fig. 1 except that the absorption maximum of the bipyridylene is at 400 instead of 380 nm. We attribute this shift of the absorption maximum to adsorption of the doubly reduced viologen to the surface of the TiO₂ particles. Spectral shifts due to adsorption onto mineral supports have been shown for a large number of chromophores including Ru(bipy)₃²⁺ (21) and other transition metal ion complexes (22).

Independent experiments involving oxygen confirmed the two-electron nature of the C₁₄MV²⁺ reduction in the colloidal TiO₂ dispersion. When a solution containing the yellow product of C₁₄MV²⁺ photoreduction by colloidal TiO₂ is exposed to air, the blue color of C₁₄MV²⁺ is formed first, which subsequently fades to yield colorless C₁₄MV²⁺. (This reduction-reoxidation cycle can be repeated many times.) Apparently the reoxidation of C₁₄MV[°] occurs in two distinct steps,



Interestingly, the first reaction was found to occur much less rapidly than the second one, showing that C₁₄MV[°], despite its more reducing nature, is less reactive towards O₂ than is C₁₄MV^{•+}.

Abbreviation: PVA, poly(vinyl alcohol).

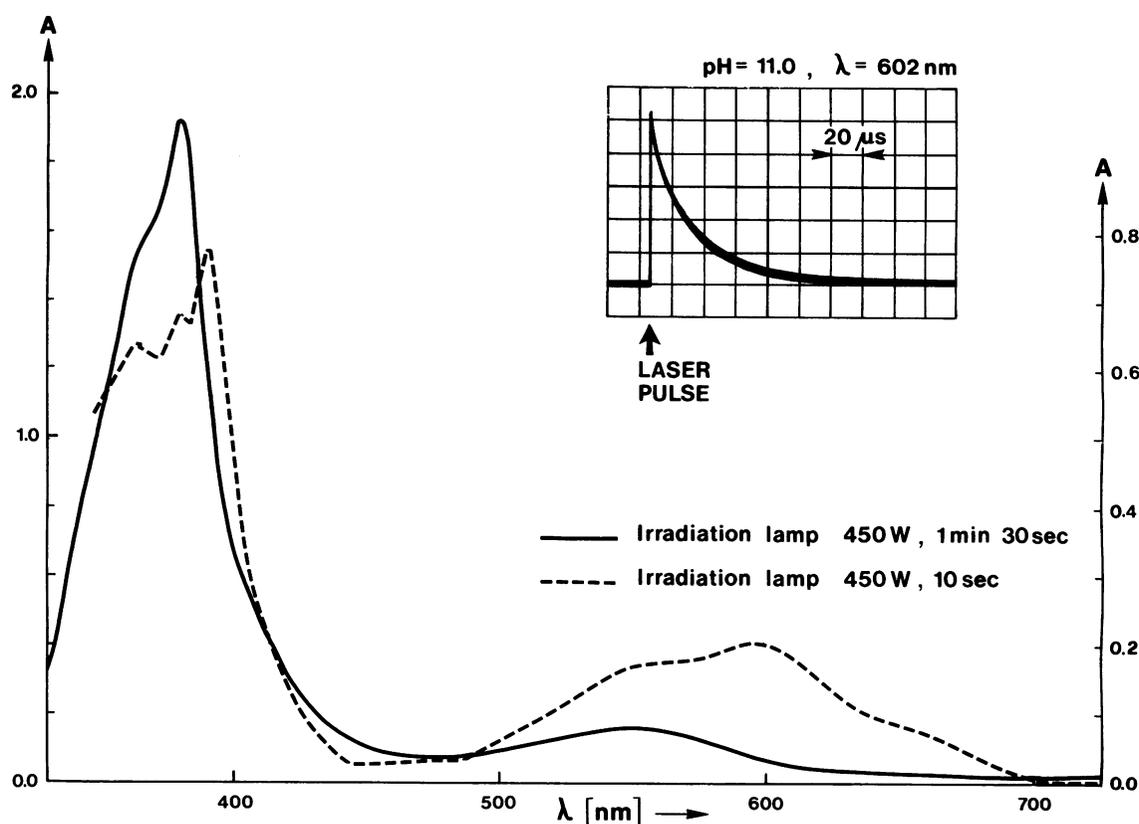
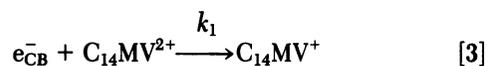
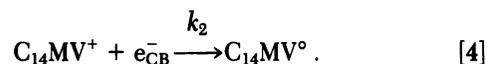


FIG. 1. Spectral changes observed upon illumination ($\lambda > 300$ nm) of a solution of TiO_2 (500 mg/liter) containing $\text{C}_{14}\text{MV}^{2+}$ (0.2 mM) and PVA (1 g/liter; Mowiol 10-98). —, Left ordinate scale; ---, right ordinate scale. A solution of TiO_2 (500 mg/liter; pH 11) was used in the reference light beam. (Inset) Laser flash photolysis (347.1 nm) of the preirradiated (1 min, 30 sec) solution: temporal behavior of the 602-nm absorption of the C_{14}MV^+ radical. All solutions were flushed with nitrogen prior to irradiation.

The mechanism of light-induced $\text{C}_{14}\text{MV}^\circ$ formation involves band-gap excitation of TiO_2 particles generating electron-hole pairs (Fig. 3). Conduction band electrons, e_{CB} , reduce $\text{C}_{14}\text{MV}^{2+}$ first to the radical cation



and subsequently to the bipyridylene



Adhesion of the amphiphilic relay to the surface of TiO_2 particles allows both electron-transfer processes to occur at a very rapid rate. Application of the laser photolysis technique yields for pH 11 the rate constants $k_1 = 10^8 \text{ sec}^{-1}$ and $k_2 = 5 \times 10^4 \text{ sec}^{-1}$.^{*} Therefore, two-electron reduction is completed in less than 100 μsec . This contrasts sharply with the behavior of simple methylviologen,[†] which at comparable light intensity and

concentration does not appear to undergo two-electron reduction at $\text{pH} \leq 12.5$. Only at high alkalinity does slow formation of doubly reduced product become apparent. Apart from kinetic reasons, there are thermodynamic reasons for this drastically different behavior of the two electron relays. The second reduction of methylviologen requires a potential of -0.83 V (vs. the normal hydrogen electrode). Taking into account that the conduction-band position of the TiO_2 particle changes with pH according to $E_{\text{CB}} = -0.11 - 0.059 \text{ pH}$ (2), one predicts that a pH of at least 12 is required to render this process thermodynamically feasible. In the case of the amphiphilic viologen, adsorption to the surface of TiO_2 apparently shifts the potential of the $\text{C}_{14}\text{MV}^+/\text{C}_{14}\text{MV}^\circ$ redox couple by more than 100 mV, facilitating the second reduction step. Blank photolysis experiments with solutions of $\text{C}_{14}\text{MV}^{2+}$ did not lead to appearance of $\text{C}_{14}\text{MV}^\circ$ or C_{14}MV^+ , showing that light absorption by TiO_2 particles produces the electron-transfer events.

As to the valence-band process occurring in parallel with the reaction of conduction-band electrons, it is indicated in Fig. 2 that this comprises oxidation of water to oxygen, competing with hole-scavenging by the PVA polymer used to stabilize the sol. However, the latter process has been shown to be rather inefficient on TiO_2 colloids (5). Therefore, hole reaction with water prevails even in the presence of PVA. [TiO_2 acts as an oxygen carrier. From our own experiments (unpublished data), we conclude that the capacity of the carrier is *ca.* 20 μl of O_2 per mg of TiO_2 .] However, it cannot be excluded that intermediates from the water oxidation attack subsequently the protective polymer. So far we have not analyzed these processes in more detail, our main interest being the storage of conduction-band electrons by the adsorbed relay.

^{*} Because the reduction of e_{CB}^- with $\text{C}_{14}\text{MV}^{2+}$ (C_{14}MV^+) occurs on individual TiO_2 particles, it fits in the general framework of fast electron-transfer processes in colloidal aggregates, which has been elaborated upon previously (23). Similar to intracellular electron-transfer processes, such intraparticle reactions follow first-order kinetics. The observed rate constant is expressed in units of sec^{-1} and is expected to increase with $\text{C}_{14}\text{MV}^{2+}$ association of the particle until saturation of surface sites available to the electron relay is reached. Under our experimental conditions (temperature, pH, TiO_2 concentration), the saturation is practically reached at 0.2 mM $\text{C}_{14}\text{MV}^{2+}$.

[†] Simple methylviologen is not adsorbed to the TiO_2 surface (2). The rate of electron transfer in this case is limited by the diffusional approach of the reactants. For both $\text{C}_{14}\text{MV}^{2+}$ and MV^{2+} , the quantum yield of radical ion formation is approximately 1.

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