Photosensitized Hydrogen Evolution from Basic Aqueous SiO_2 Colloids

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Photosensitized hydrogen evolution from basic aqueous SiO_2 colloids is accomplished using *N,N'*-dipropyl-2,2'-bipyridinium disulphonate, DQS^0, (**1**) as electron acceptor and platinum as catalyst; the charged SiO_2 colloid allows the formation and stabilization of the intermediate photoproducts and the subsequent formation of hydrogen.

The photosensitized decomposition of water is of great interest as a means of solar energy conversion and storage.[1,2] The reduction and oxidation potentials of water to hydrogen and oxygen depend on the pH of the aqueous solution. While hydrogen evolution is favoured in acidic media, oxygen formation is thermodynamically facilitated in basic environments. Photoreduction of water to hydrogen has been accomplished using 4,4'-bipyridinium (viologen) as a mediating electron acceptor and colloidal platinum.[3,4] The use of viologens is limited to acidic and neutral solutions owing to the relatively weak reducing power of the corresponding radical (E^0 *ca.* -0.4 V). Recently, we have examined the photoreduction of a zwitterionic neutral viologen in colloidal SiO_2.[5,6] We have demonstrated that the charged colloid controls the recombination reaction of the intermediate photoproducts by means of electrostatic interactions with the interface. However, hydrogen evolution could not be accomplished with this system since the SiO_2 colloid is effective only in a basic aqueous media (pH 8.5—10).

Here we report the efficient photosensitized formation of hydrogen from basic SiO_2 colloids (pH 9.2), using *N,N'*-dipropyl-2,2'-bipyridinium disulphonate, DQS^0, (**1**), and platinum as mediating catalyst. The formation of hydrogen is accomplished only in the SiO_2 colloid, which controls the formation and stabilization of the intermediate photoproducts.

The system under investigation consisted of a 0.3% aqueous SiO_2 colloid with tris(2,2'-bipyridine)ruthenium(II) [$Ru(bipy)_3^{2+}$] (1.4×10^{-4} M) as sensitizer, (**1**) (1×10^{-2} M) as electron acceptor, and triethanolamine (TEOA) (2×10^{-3} M) as electron donor.† The resulting mixture was adjusted to pH 9.2. Illumination of the deaerated mixture ($\lambda > 400$ nm) resulted in the photoreduction of (**1**) to the corresponding radical anion $DQS^{\bullet -}$. The photoreduction of (**1**) was followed spectroscopically, ϕ 2×10^{-2}. No photoreduction of DQS^0 occurred in a homogeneous aqueous solution with the same components. The function of the charged SiO_2 colloid in the electron transfer reaction was studied by flash photolysis‡ and is represented schematically in Figure 1. The positively charged sensitizer, $Ru(bipy)_3^{2+}$, is adsorbed onto the negatively charged colloidal interface (surface potential -170 mV).[6] Electron transfer from the excited sensitizer to DQS^0 ($k_q = 3.9 \times 10^8$ dm^3 mol^{-1} s^{-1}) results in the separation of the initial complex formed by the photoproducts by means of electrostatic ejection of $DQS^{\bullet -}$ by the colloidal interface. The recombination reaction of the separated photoproducts is also retarded owing to repulsion of $DQS^{\bullet -}$ by the colloidal interface. This stabilization of the photoproducts allows the subsequent oxidation of TEOA by the oxidized sensitizer. In a homogeneous aqueous solution no charge separation of the

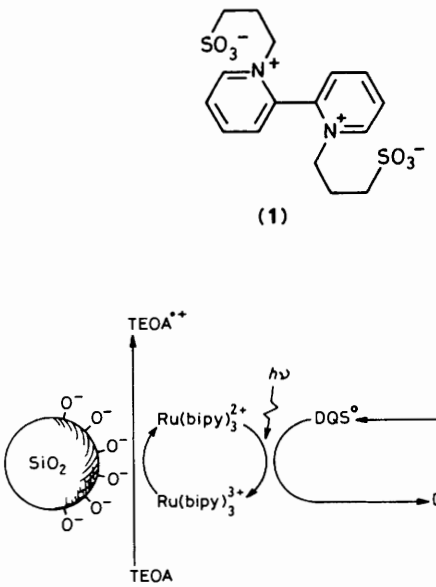

Figure 1. Scheme for photosensitized hydrogen formation in SiO_2 colloids.

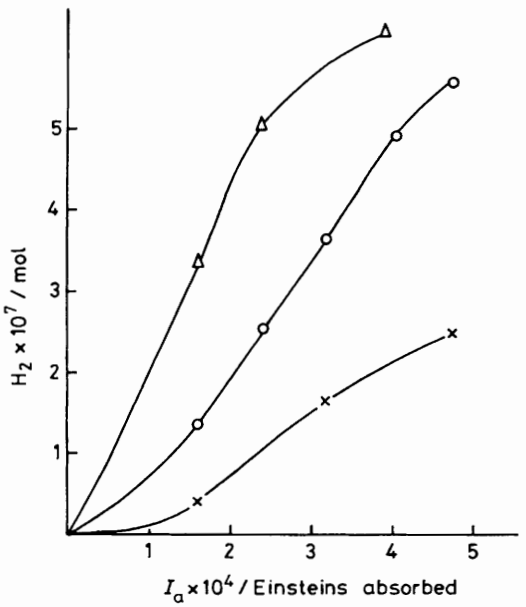

Figure 2. Yield of hydrogen formation from SiO_2 colloids at different pH values as a function of absorbed light: Δ pH 8.5; ○ pH 9.2; × pH 10.

† SiO_2 particles 40 Å diameter, Nalco Inc.; DQS^0, (**1**), prepared by the reaction of 2,2'-bipyridine with propane-1,3-sultone at 120 °C.

‡ The separated photoproducts [$Ru(bipy)_3^{3+}$ and $DQS^{\bullet -}$] recombine in the SiO_2 colloid, $k_b = 1.0 \times 10^7$ dm^3 mol^{-1} s^{-1}. Addition of salt (0.4 M-NaCl) enhances the recombination rate, $k_b = 8 \times 10^8$ dm^3 mol^{-1} s^{-1} owing to reduction of the colloid surface potential.

intermediate photoproducts was observed, despite effective quenching of $Ru(bipy)_3^{2+}$* by DQS^0 ($k_q = 5.9 \times 10^8$ dm^3 mol^{-1} s^{-1}). Thus, the SiO_2 colloid assists the separation of the caged photoproducts and stabilizes them against recombination reactions.

The redox potential of DQS^0 ($E^0 = -0.75$ V) is adequate for hydrogen evolution from basic environments. Indeed, introduction of colloidal platinum (12 mg/l), prepared by citrate reduction, into the previously described system results in the production of hydrogen.§ Its rate of formation depends on the pH of the SiO_2 colloid (Figure 2). At pH 8.5, 9.2, and 10 the quantum yields of hydrogen formation are ϕ 2.2 $\times$ 10^{-3}, 1.4 $\times$ 10^{-3}, and 7.1 $\times$ 10^{-4}, respectively. No hydrogen formation is observed from homogeneous aqueous solutions that include DQS^0, TEOA, and platinum. This is expected since no net separation of the reduced photoproduct, $DQS^{\bullet -}$ could be achieved. Below pH 8.5 the yield of hydrogen in the SiO_2 colloid declines. This is attributed to the decrease of the colloidal surface potential due to protonation of the ionized sites,[7] as well as the reduction of the scavenging capability of $Ru(bipy)_3^{3+}$ by TEOA.[8] The oxidized donor, $TEOA^{\bullet +}$, decomposes under the basic conditions to a strongly reducing secondary species[8] [equation (1)]. This species might be capable of reducing DQS^0 to $DQS^{\bullet -}$ and subsequently contribute to the yield of evolved H_2. Thus, the observed quantum yields of H_2 might originate from two complementary pathways yielding the intermediary $DQS^{\bullet -}$.

$$>\dot{N}-\bar{C}H-CH_2OH + DQS^0 \rightarrow >\overset{+}{N}=CH-CH_2OH + DQS^{\bullet -} \quad (1)$$

§ Followed by gas chromatography: MS 5 Å column, oven temperature 50 °C, and argon used as the carrier gas.

In conclusion, we have demonstrated that DQS^0 and platinum mediate the photoproduction of hydrogen from basic aqueous SiO_2 colloids (Figure 1). The SiO_2 colloid functions in the separation of the initially formed photoproducts and retards their recombination. The production of hydrogen in basic environments might facilitate oxygen production.

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