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Ultrafine and Specific Catalysts Affording Efficient Hydrogen Evolution from Water under Visible Light Illumination

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Abstract: Platinum particles of 32-Å diameter were produced in aqueous solution by citrate reduction of hexachloroplatinate. A variety of synthetic polymers were tested with respect to their protective action and activity to catalyze hydrogen evolution from reduced methylviologen (MV^+) and water according to $2MV^+ + 2H_2O \xrightarrow{Pt} 2MV^{2+} + 2OH^- + H_2$. MV^+ is produced in a light-induced redox reaction of methylviologen with $Ru(bpy)_3^{2+}$. Carbowax-20M-protected Pt particles were found to give outstanding stability and achieve high hydrogen generation rates even at concentrations as low as 1.4-mg Pt/L. An even higher activity is obtained when the microparticles are protected by the cationic polysoap PVP-C_{16}. In a photoredox system containing $Ru(bpy)_3^{2+}$ or zinc tetrakis(*N*-methylpyridyl)porphyrin as a sensitizer and *N*-tetradecyl-*N'*-methyl-4,4'-bipyridine as an electron relay, the latter catalyst can intercept the thermal back reaction by specific interaction with the reduced relay. The access of the oxidized sensitizer to the PVP-C_{16} protected microparticles is impaired by electrostatic and hydrophobic forces.

Introduction

Previously, a number of homogeneous or microheterogeneous solution systems were reported which under illumination with visible light produce hydrogen from water.[1] The essential ingredients of such a system are a sensitizer (S), an electron relay (R), and a catalyst. Excitation of the sensitizer induces electron transfer

$$S + R \xrightarrow{h\nu} S^+ + R^- \tag{1}$$

which is followed by a catalytic step

$$R^- + H_2O \xrightarrow{\text{catalyst}} {}^1/_2H_2 + R + OH^- \tag{2}$$

leading to H_2 generation. The back conversion of S^+ into S may be achieved by sacrificing a donor added to the solution through irreversible oxidation:

$$D + S^+ \rightarrow D^+ + S \tag{3}$$

Alternatively, the recycling of the sensitizer can be coupled to water oxidation

$$S^+ + {}^1/_2H_2O \xrightarrow{\text{catalyst}} S + {}^1/_4O_2 + H^+ \tag{4}$$

via catalysis by noble metal oxides such as PtO_2, IrO_2,[2] and RuO_2.[3]

For the successful operation of such a cyclic water decomposition system, it is mandatory that both catalysts operate selectively and at a high rate.[3f]

Recently, we investigated light-induced hydrogen evolution from a photochemical system in which $Ru(bpy)_3^{2+}$ was used as a sensitizer, methylviologen (MV^{2+}) as an electron relay and a centrifuged Pt sol stabilized by a polymeric material as a catalyst.[4] These studies established a trend to higher activity as the radius of the Pt particles decreased. The results obtained encouraged us to search for Pt aggregates having minimal size and low polydispersity. We report here on the preparation, stabilization, and performance of such a sol in the photoinduced H_2 generation from water. Furthermore, pathways are exploited to achieve specificity of the Pt microelectrodes with respect to their intervention in the water reduction process.

Experimental Section

Preparation and Characterization of the Catalysts. The colloidal platinum was obtained via reduction of hexachloroplatinate solutions by sodium citrate. The reduction procedure was similar to the one described by Turkevich et al.[5] A solution of 255 mL of H_2O containing 15 mg of Pt (in the form of H_2PtCl_6) was brought to boiling temperature; 30 mL of sodium citrate (1% weight aqueous solution) were added and the mixture refluxed for 4 h. Thereafter the solution was cooled in an ice bath. For excess citrate and electrolyte removal, the solution was stirred with an Amberlite-MB-1 exchange resin in its H^+ and OH^- form until the conductivity of the solution was smaller than 5 μS/cm. After filtration the protective agent was added and allowed to equilibrate with the Pt sol for at least 1 h. A schematic summary of this preparation mode is given in Figure 1. The platinum content of the solution was determined by atomic absorption spectroscopy using a Pye Unicam-SP 191 spectrophotometer. The size of the platinum particles was determined by transmission electron microscopy (TEM). Samples were prepared by spraying the colloidal solutions in small droplets (1–10-μm diameter) with a nebulizer on Formvar membranes coated with carbon. Observations were made with the Hitachi HU-12 electron microscope of the Centre de Microscopie Electronique de l'Université de Lausanne.

Apparatus: Continuous photolysis experiments were carried out with an XBO 450-W xenon lamp. Experimental details are given below. The volume of the irradiated solution was always 35 mL. Prior to photolysis, the samples were flushed with highly purified argon for removal of oxygen. A ferrioxalate chemical dosimeter was employed to measure the photon flux. Hydrogen was analyzed by gas chromatography, using a Carbosieve 5-Å column at 35 °C and a Gow-Mac thermal conductivity detector with a detection limit of 1 nmol. Laser photolysis experiments

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[1] (a) B. V. Koryakin, T. S. Dzhabiev, and A. E. Shilov, *Dokl. Akad. Nauk. SSSR*, **238**, 620 (1977); (b) J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, **1**, 441 (1977); (c) K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, **61**, 2720 (1978); (d) A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, *Nouv. J. Chim.*, **2**, 547 (1978); (e) B. O. Durham, W. J. Dressick, and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 381 (1979); (f) P. J. Delaive, B. P. Sullivan, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **101**, 4007 (1979); (g) A. I. Krasna, *Photochem. Photobiol.*, **29**, 267 (1979); (h) T. Kawai, K. Tanimura, and T. Sakada, *Chem. Lett.*, 137 (1979); (i) M. Kirsch, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979); (j) K. Kalyanasundaram and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1138 (1979); (k) A. I. Krasna, *Photochem. Photobiol.*, **31**, 75 (1980); (l) G. M. Brown, S. F. Chan, C. Creutz, H. A. Schwarz, and N. Sutin, *J. Am. Chem. Soc.*, **101**, 7638 (1979); (m) G. M. Brown, B. S. Brunschwig, C. Creutz, J. F. Endicott, and N. Sutin, ibid., **101**, 7638 (1979).

[2] J. Kiwi and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **17**, 860 (1978).

[3] (a) J. Kiwi and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **17**, 860 (1978); (b) *Chimia*, **33**, 289 (1979); (c) M. Graätzel in "Dahlem Conferences 1978 on Light-Induced Charge Separation", H. Gerischer and J. J. Katz, Eds., Verlag Chemie, Weinheim, Germany, 1979, p 299; (d) J. Kiwi and M. Grätzel, *Angew. Chem.*, **91**, 659 (1979); (e) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979); (f) K. Kalyanasundaram and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **18**, 701 (1979).

[4] (a) J. Kiwi and M. Grätzel, *Nature (London)* **281**, 657 (1979); (b) J. Kiwi and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7214 (1979).

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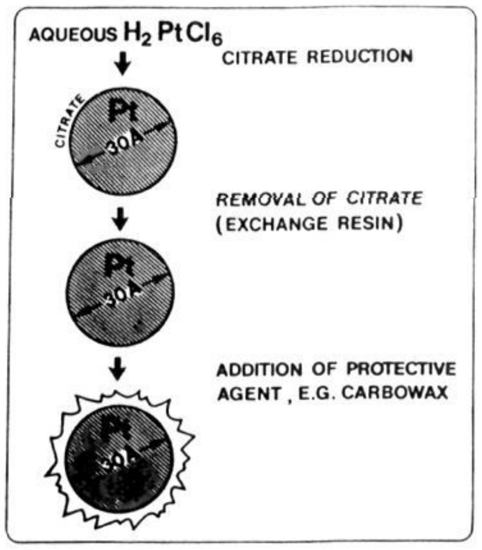

Figure 1. Scheme for the preparation of ultrafine Pt particles.

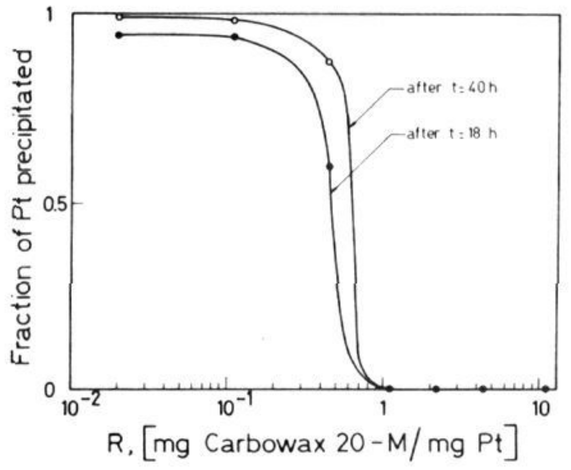

Figure 2. Fraction of Pt precipitated after different times as a function of the Carbowax 20 M–platinum ratio; NaCl = 1% (wt/v), Pt = 45 mg/L.

were performed with a J. K. frequency doubled neodymium laser. The Q-switched pulse had a duration of 20 ns. Details of the fast kinetic detection method have been reported elsewhere.[6]

Materials. Hexachloroplatinic acid hexahydrate (Merck, p.a.), sodium citrate (Fluka, p.a.), $Ru(bpy)_3Cl_2$ (Strem), and methylviologen (BDH) were used as supplied. The synthesis of *N*-tetradecyl-*N'*-methylviologen has been previously described.[7] The polymer protective agent Carbowax-20M was supplied by Union Carbide. The poly(ethylene glycols) (M_r 5000, 10 000, 20 000) were generous gifts from Dr. Tadros, ICI Corporation. The cationic polysoap was synthesized by Dr. Humphrey-Baker in our laboratory according to the following procedure: 0.5 g of poly(4-vinylpyridine) (M_r 68 700), supplied by Ciba-Geigy Corp, was dissolved together with 0.16 g of bromohexadecane in 25 mL of dimethylformamide. The solution was heated at 50 °C for 1 h and the solvent rapidly evaporated under vacuum. The solid residue was taken up in a mixture of 10-mL methanol and 40-mL diethyl ether. After decanting it was refluxed for 2 h in ether, filtered, and dried. NMR analysis shows that approximately 50% of the pyridine groups are quaternized by hexadecyl chains.

Results and Discussion

Effect of Polymers on the Stability of the Pt Sol Against Flocculation by Salts. In these experiments the Pt sol prepared according to the procedure given above was added to an aqueous solution of NaCl and the concentration of platinum measured as a function of time. The platinum content of the solution was determined either by atomic absorption spectroscopy or more simply from optical absorbance measurements. (This sol shows a characteristic absorption rising steadily toward the UV.[8] Precipitation diminishes the intensity of the band without changing its shape. Hence, at a given value, the absorbance of the solution is proportional to the Pt concentration.) Amongst a variety of polymers tested as protective agents for the ultrafine particles, Carbowax-20M[9] and PVP-C_{16} were found to be particularly effective. Figure 2 illustrates the flocculation behavior in 1% NaCl solution as a function of polymer concentration. In the case of Carbowax-20M stability is achieved when the mass ratio of polymer to platinum is at least 1. A somewhat higher value, i.e., $R = 2$ is required for efficient protection by PVP-C_{16}.

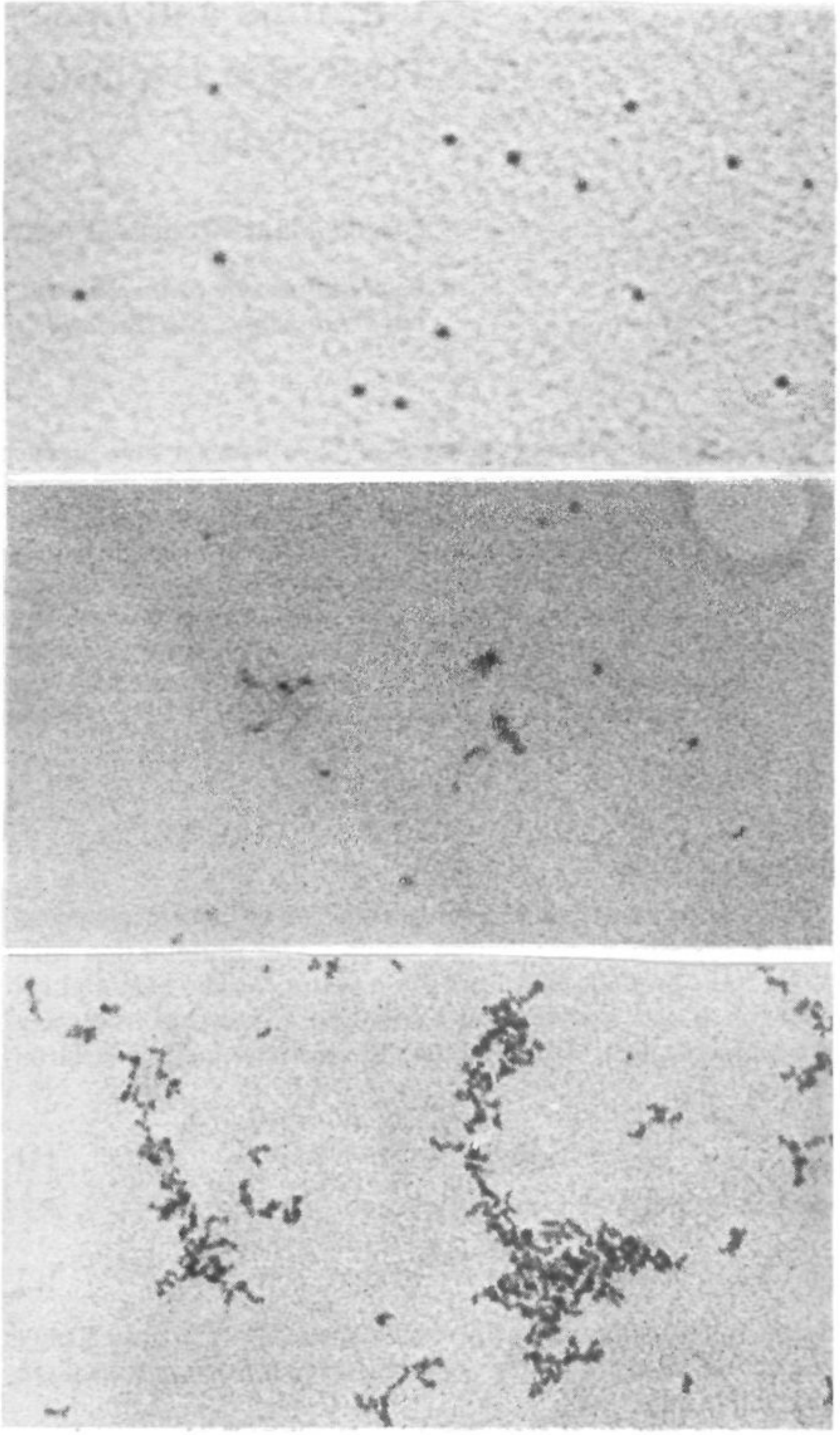

Figure 3. Electron micrographs from different Pt sols. (a, top) Unprotected platinum, magnification 340 000×, Pt = 0.4 mg/L in the original solution. (b, middle) Carbowax/Pt, magnification 180 000×, Pt = 4 mg/L in the original solution, $R = 2.5$. (c, bottom) Carbowax/Pt, magnification 300 000×, Pt = 40 mg/L in the original solution, $R = 2.5$.

In view of the excellent stabilization achieved with Carbowax-20M, it is interesting to note that simple poly(ethylene glycols) (M_r 10 000 or 20 000) are very poor protective agents. A subtle difference in the structure of these compounds brings about this opposing behavior. Carbowax-20M is a block copolymer containing two poly(ethylene glycol) chains (each, M_r 6000) linked by a short hydrophobic epoxide chain.[10] The presence of the latter is crucial in that it is anchored in the Pt surface, the remaining chain segments forming loops that protrude into the aqueous bulk.[11,12] These loops afford the repulsive forces required to

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(6) G. Rothenberger, P. P. Infelta, and M. Grätzel, *J. Phys. Chem.*, **83**, 1871 (1979).

(7) M.-P. Pileni, A. M. Braun, and M. Grätzel, *Photochem. Photobiol.*, **31**, 423 (1980).

(8) The UV-absorption spectrum of the sol has been published previously, cf. ref 5d.

(9) Carbowax-20M was first noted by Horisberger to be the best stabilizer of colloidal gold used as a marker for electron microscopy (M. Horisberger, *Biol. Cell.* **36**, 253 (1979).

(10) "Carbowax Polyethylene Glycols", Union Carbide Corporation Chemicals and Plastics, New York, 1978.

(11) (a) B. Vincent, *Adv. Colloid Interface Sci.*, **4**, 193 (1974); (b) Th. F. Tadros, review to be published in *Colloids Surf.*, and references cited in these reviews.

prevent aggregation of colliding particles. The poor protective effect exhibited by the simple poly(ethylene glycols) reflects weak adsorption on the Pt particles.

Structure and Constitution of the Pt/Polymer Particles. The extraordinary stability and activity (see below) of the Pt/Carbowax catalyst prompted us to perform more detailed investigations on the nature of the colloidal aggregates present in such a solution. Electron microscopy was selected as the most suitable method relative to other alternatives such as light scattering. This technique was previously applied by Turkevich et al. to characterize a variety of colloidal metal dispersions.[5] Results are given in Figure 3 which shows electron micrographs of three different sols: (a) was taken in the absence of protective agent. It reveals the presence of spherical monodisperse particles having a diameter of 30–35 Å. When Carbowax is present as a protective agent the dilute solution (4 mg of Pt/L) gives a similar result. Particle diameters are between 30 and 35 Å. At high concentrations (40 mg of Pt/L, Figure 3c), the formation of clusters becomes apparent. A fraction of the Pt particles form loosely connected assemblies extending over regions of several hundred nanometers.

From these data, it may be inferred that the unprotected as well as the protected Pt sol in dilute aqueous solution consists of uniformly sized particles having a diameter of 30–35 Å. This finding is in agreement with the results obtained by Turkevich et al.[5] who obtained 32-Å Pt aggregates with a mean deviation of 12% in particle size.

Catalysis of Photoinduced H_2 Production from Water. (a) Sacrificial Systems. In these experiments the 32-Å Pt particles were tested for their activity in H_2-generating photolytic systems. The aqueous solution contained $Ru(bpy)_3^{2+}$ (4×10^{-5} M) as sensitizer and methylviologen (MV^{2+}) as an electron relay. Kinetics and mechanism of the processes occurring under illumination have been investigated earlier.[1d,4,13] The excited state of the ruthenium complex transfers an electron to MV^{2+}

$$*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow MV^{+} + Ru(bpy)_3^{3+} \quad (5)$$

which in the presence of Pt catalyst is reoxidized by water under hydrogen generation:

$$MV^{+} + H_2O \rightarrow MV^{2+} + {}^{1}/{}_{2}H_2 + OH^{-} \quad (6)$$

We shall first describe experiments in which $Ru(bpy)_3^{3+}$ is reconverted to the 2+ oxidation state by ethylenediaminetetraacetic acid (EDTA) (10^{-2} M). The latter is used as a sacrificial donor which undergoes irreversible oxidation. The aim of these studies was to establish optimum conditions for H_2 production. The procedure is now described in detail for the Pt/Carbowax catalyst.

Irradiations were carried out in the cell device consisting of an Osram XBO 450-W lamp in conjunction with a cutoff filter (400 nm) and a 15-cm water cell to absorb the infrared radiation. The solution (35 mL) is contained in a cylindrical cell (path length 15 mm) which is equipped with side arms for deoxygenation prior to illumination and for volumetric determination of hydrogen. Both the H_2 burette and the cell are imbedded in a water jacket which was thermostated at 25 °C. The light beam after traversing the cell impinges on a monochromator connected to a photodiode (Hamamatsu R 314), allowing for the measurement of optical density changes in the solution during illumination.

We first examined, for a fixed Carbowax/Pt ratio (R = 2.7), the effect of catalyst concentration on the hydrogen evolution rate. Results are presented in Figure 4. The hydrogen output under photostationary conditions rises steeply with Pt concentration up to 1.4 mg of Pt/L from where on further augmentation is relatively slow.[14] At the break point, the rate is already astonishingly high in view of the very small Pt concentration (~7 × 10^{-6} M) present

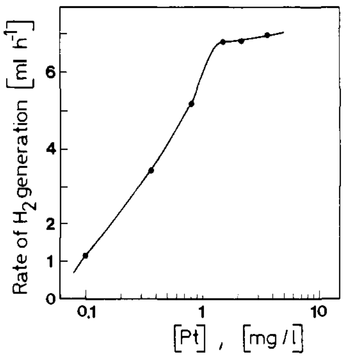

Figure 4. Effect of Pt/Carbowax concentration on the H_2 generation rate (R = 2.7), $Ru(bpy)_3^{2+} = 4 \times 10^{-5}$ M, $MV^{2+} = 2 \times 10^{-3}$ M, EDTA = 10^{-2} M, potassium hydrogen phthalate buffer 5×10^{-3} M, pH 4.5.

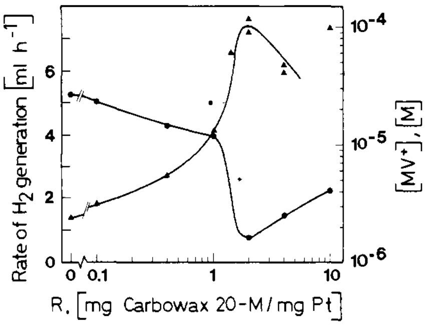

Figure 5. Effect of mass ratio of Carbowax 20 M–platinum on (a) the rate of H_2 generation and (b) the photostationary concentration of MV^{+} measured 30 s after beginning of photolysis. Pt = 6 mg/L, other conditions as in Figure 4.

in solution. In fact, this figure can even be further improved, since at the $Ru(bpy)_3^{2+}$ concentration employed only a fraction of the incident light—the maximum percentage is 86 for λ = 452 nm—is absorbed by the solution. This condition was selected intentionally for our kinetic studies in order to avoid inhomogeneities due to complete light absorption over a small path length. Given these facts, the hydrogen evolution obtained with 1.4 mg of Pt/Carbowax per L becomes comparable with that observed[4] for Pt/PVA at ca. 100 mg of Pt/L.

Secondly, it was attempted to check the effect of Carbowax concentration on the rate of light-induced H_2 evolution. Figure 5 shows that upon increasing the mass ratio of polymer to platinum (R) from 0 to 2, the hydrogen output augments by a factor of more than 4. At the same time the MV^{+} level present under photostationary conditions decreases. This effect is particularly pronounced between R values of 1 and 2 where the MV^{+} concentration diminishes abruptly by a factor of 8. At R values above 2, one notes a decrease of the hydrogen output concomitant with a rise of the MV^{+} level present in the photostationary state. Apparently, at very high Carbowax concentrations, the coating of the Pt surface by the polymer blocks the access of the electron relay to the active sites. At R values below 1 the Pt sol is unstable as was shown above. Larger aggregates are formed which leads to a decreased activity under these conditions.

A final noteworthy point concerns the surprisingly stable operation of this catalytic system. Thus under optimum conditions ($R \simeq 2$, Pt = 1–10 mg/L), the H_2 evolution rate establishes itself at 7–8 mL/h in the presence of 10^{-2} M EDTA. H_2 formation continues at this rate until more than 90% of the EDTA is consumed, yielding one H_2 per EDTA molecule. At this time the turnover numbers for the sensitizer and electron relay are 200 and 4, respectively. Interested in the performance of the Carbowax system at longer times, we photolyzed a solution containing 10^{-1} instead of 10^{-2} M EDTA over a longer period. After an induction time of several minutes, H_2 is generated here at 9 mL/h. This can be sustained for several hours without any noticeable degradation of the sensitizer, turnover numbers being in excess of 1000. The process of hydrogen generation slows down once the

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(12) W. Heller and W. Tanaka, *Phys. Rev.*, **82**, 301 (1951); W. Heller and T. C. Pugh, *J. Chem. Phys.*, **22**, 1778 (1954); W. Heller and T. C. Pugh, *J. Polym. Sci.*, **97**, 203 (1960).

(13) C. R. Bock, J. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).

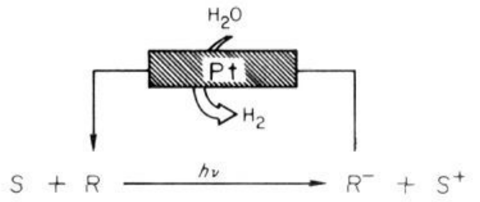
(14) At higher Pt levels the H_2 evolution rate decreases again. This effect is caused by absorption of light by the Pt particles. The extinction coefficient of the Pt solution is 2.3×10^{3} M^{-1} cm^{-1} at 450 nm.

solution pH raises due to exhaustion of the buffer. Higher pH conditions are detrimental[15] for both the sensitizer and the electron relay.[16]

Apart from Carbowax-20M, we tested a series of other polymers with respect to their H_2 generating activity. Only polymers that prevent effectively aggregation of the 32-Å Pt particles were found to be satisfactory. Amongst those one notices still a surprisingly large difference in catalytic activity. Thus, the protective agents PVP-C_{16}, Carbowax-20M, and PVA M_r 60 000 all give stable sols at a polymer/Pt ratio of ca. 2. However, the PVP-C_{16} protected catalyst is 4 times more active than PVA and 1.5 as active as Carbowax/Pt. Evidently, these agents differ in their degree of interaction with active sites while maintaining the same size and shape of the Pt aggregates.

(b) Development of Ultrafine and Selective Catalysts for Cyclic Water Decomposition Systems. In the preceding chapters, the salient features of catalytic H_2 generation with ultrafine platinum particles were explored. The results obtained serve now as a basis for the development of catalysts which, apart from their high activity, are operating selectively on one redox species. Only such mediators are suitable for cyclic water decomposition systems.

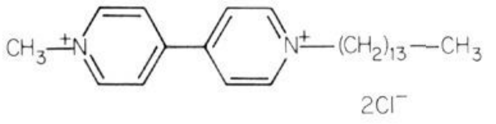
The problem which has to be solved in this case is to make the Pt particle selectively interact with the reduced electron relay (MV^+). Contact of the cathodically tuned particle with the oxidized donor [$Ru(bpy)_3^{3+}$] has to be avoided, since this could lead to short circuiting of the back reaction: reduction of $Ru(bpy)_3^{3+}$ would occur instead of hydrogen production. Such a photocatalytic system performs the transformation



$$S + R \xrightarrow{h\nu} R^- + S^+ \qquad (7)$$

The cycle of light-induced water decomposition can then be closed either by addition of RuO_2 catalyst[3f] or by coupling to an oxygen-producing half-cell.[17]

In the search for such a system, we based our strategy on the use of the methylviologen derivative



$C_{14}MV^{2+}$

as an electron relay. Due to its strongly hydrophilic nature, this surfactant shows little tendency to form micelles[18] or interact with amphiphilic agents. By contrast, the monoreduced form ($C_{14}MV^+$) exhibits pronounced hydrophobicity and hence is prone to solubilization by surfactant assemblies. This effect has been exploited to achieve charge separation in the photoinduced redox reaction between $Ru(bpy)_3^{2+}$ and $C_{14}MV^{2+}$. The $C_{14}MV^+$ produced is rapidly entrapped into a cationic micelle to which $Ru(bpy)_3^{3+}$, for reasons of electrostatic repulsion, has no access.[18] Hence, a drastic retardation of the back reaction is observed.

A similar principle was applied in the development of a platinum catalyst that achieves both charge separation and hydrogen formation. In this case, it is desirable to employ the cationic polysoap PVP-C_{16} as the protective agent. As shown above by the flocculation studies, the latter is an excellent stabilizing agent for the 32-Å particles. Mass ratios of surfactant platinum of 2.0 are sufficient to produce stable sols. However, the Pt particles protected by PVP-C_{16} are different from the Carbowax catalyst in that they are positively charged and their surface has amphiphilic properties.

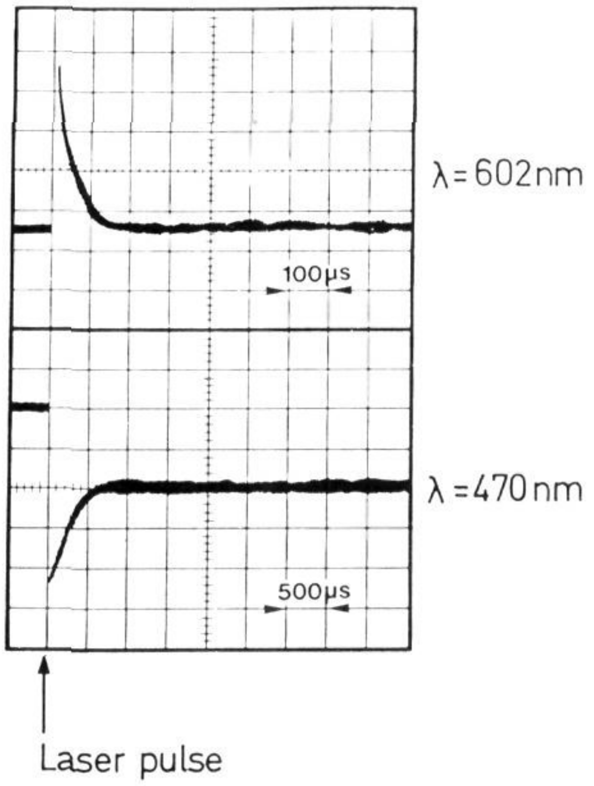


Figure 6. Oscilloscope traces obtained from a deaerated solution of $Ru(bpy)_3^{2+}$ (10^{-4} M), $C_{14}MV^{2+}2Cl^-$ (5×10^{-4} M), PVP-C_{16} (40 mg/L), and colloidal Pt (20 mg/L). Upper trace, transient absorbance at 602 nm; lower trace, transient absorbance at 470 nm.

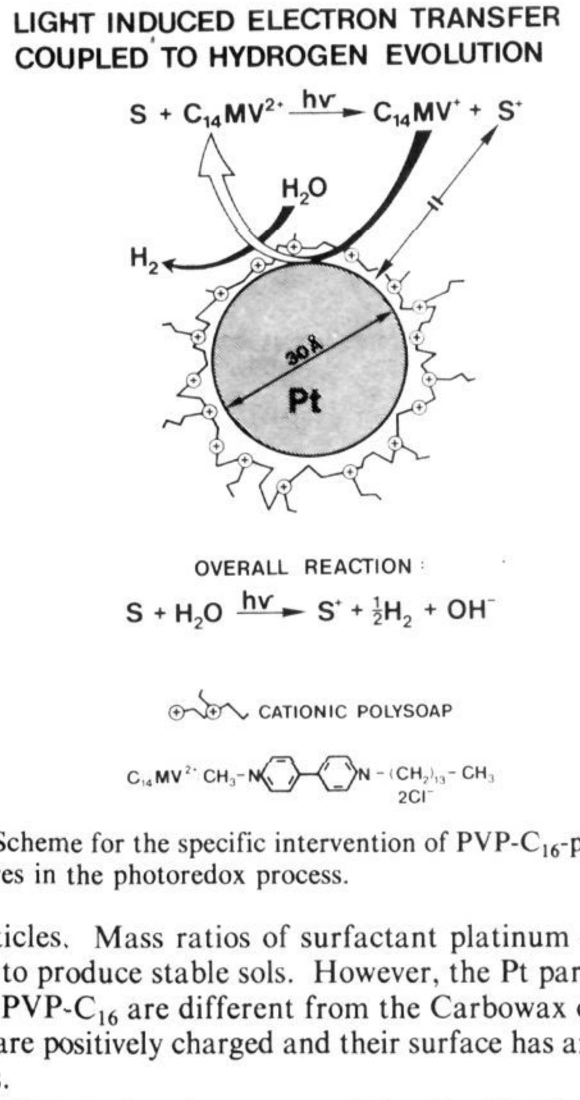


Figure 7. Scheme for the specific intervention of PVP-C_{16}-protected Pt microspheres in the photoredox process.

Photolysis experiments were carried out with solutions containing 10^{-3} M $C_{14}MV^{2+}$, 10^{-4} M $Ru(bpy)_3^{2+}$, 10^{-4} M of colloidal Pt, and 40 mg of PVP-C_{16}. The excited state of $Ru(bpy)_3^{2+}$ reduces $C_{14}MV^{2+}$ with a specific rate of 8×10^8 M^{-1} s^{-1}.[18] The back reaction

$$C_{14}MV^+ + Ru(bpy)_3^{3+} \rightarrow C_{14}MV^{2+} + Ru(bpy)_3^{2+} \qquad (8)$$

has a rate constant of 2×10^9 M^{-1} s^{-1} under the conditions employed. We shall now investigate the fate of $C_{14}MV^+$ and $Ru(bpy)_3^{3+}$ in solutions containing PVP-C_{16}-protected platinum particles. Laser photolysis results are presented in Figure 6. The temporal behavior of the two transient species was monitored by following the absorbance of the solution at 602 and 470 nm, respectively. The initial rise of the signal at 602 nm is due to the

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[15] M. Gohn and N. Getoff, *Z. Naturforsch. A* **34a**, 1135 (1979).

[16] MV^{2+} can be reduced by H_2 to MV^+ in the presence of Pt/Carbowax catalyst. In neutral aqueous solution the latter was found to decay over a period of 2 h, probably due to catalytic hydrogenation (W. F. Sasse, private communication). The rate of this process decreased drasticly on lowering the pH. Interesting, $C_{14}MV^+$ even under neutral conditions appears to be resistant to hydrogenation.

[17] M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel, and M. Grätzel, *Helv. Chim. Acta*, **63**, 1111 (1980).

[18] P.-A. Brugger and M. Grätzel, *J. Am. Chem. Soc.*, **102**, 2462 (1980). P.-A. Brugger, P. P. Infelta, A. M. Braun, and M. Grätzel, *ibid.*, **103**, 320 (1981).

formation of $C_{14}MV^+$ after laser excitation of $Ru(bpy)_3^{2+}$. The absorption decays sharply ($\tau_{1/2} \simeq 30$ μs) back to the zero level, indicating rapid consumption of $C_{14}MV^+$. The formation of $Ru(bpy)_3^{3+}$ is apparent from the bleaching at 470 nm. There is a fractional recovery of the negative signal to a plateau constituting 40–50% of the initial value from where on no further changes are noted. This indicates that a major part of $Ru(bpy)_3^{2+}$ formed in the photoredox reaction is preserved and does not undergo back reaction with $C_{14}MV^+$.

The rapid disappearance of $C_{14}MV^+$ may be interpreted by a mechanism involving first scavenging by the Pt particles through hydrophobic interaction with the protective agent (Figure 7). Charge transfer and water reduction occur simultaneously on the Pt surface. The formation of hydrogen is readily seen in continuous photolysis. Selectivity is achieved by making use of electrostatic and hydrophobic interaction: $Ru(bpy)_3^{3+}$ has no access to the surface of the Pt aggregates. Hence, neither the reduced relay nor the particle itself can interact with $Ru(bpy)_3^{3+}$ which explains its astonishingly long lifetime in such a system.

Figure 6 demonstrates that the electron transfer from the reduced viologen to the Pt particles is fast enough at 10^{-4} M Pt to intercept efficiently the back reaction. Under typical conditions employed in our laser experiments, the latter proceeds with a first half-lifetime of ca. 65 μs (initial concentration of $Ru(bpy)_3^{3+}$ and $C_{14}MV^+ \simeq 4 \times 10^{-6}$ M, $k_8 = 2 \times 10^9$ M^{-1} s^{-1}). In Figure 7, the first half-lifetime of the $C_{14}MV^+$ decay is 35 μs. From the difference in the decay times obtained in the absence and presence of catalyst one calculates a pseudo-first-order rate constant for the electron transfer from $C_{14}MV^+$ to the Pt particles of $\sim 10^4$ s^{-1}. This corresponds to a second-order rate constant of ca. 10^8 M^{-1} s^{-1} if the analytical Pt concentration is used as a reference. However, on the basis of particle concentration (the aggregation number of Pt is 1200), the specific rate is 10^{11} M^{-1} s^{-1}. This shows that the reaction with the colloidal particles occurs at a very high rate essentially controlled by the diffusion of the reactants. Similar rates have been obtained for the discharge of ketyl radicals on ultrafine Pt particles in a water/alcohol mixture.[19]

Selective intervention of the Pt microelectrodes is not restricted to the case where $Ru(bpy)_3^{2+}$ serves as a sensitizer. A similar effect can be achieved, for example, also with zinc tetrakis(*N*-methylpyridyl)porphyrin ($ZnTMPyP^{4+}$) as the photoactive donor. Electron transfer from the porphyrin triplet to $C_{14}MV^{2+}$ produces $C_{14}MV^+$ and $ZnTMPyP^{5+}$.[18] In the presence of 32-Å Pt particles (10^{-4} M Pt) protected by PVP-C_{16}, the $C_{14}MV^+$ dissappears within 200 μs effecting H_2O reduction. By contrast, $ZnTMPyP^{5+}$, which is readily identified by its characteristic absorption between 600 and 750 nm, is stable over many milliseconds. This is due to repulsion of the porphyrin cation from the surface of the Pt particles by electrostatic and hydrophobic interactions. The case of $ZnTMPyP^{4+}$ is particularly interesting as the photoredox reaction occurs here with a solvent cage escape yield of practically 100% compared to 30% for the $Ru(bpy)_3^{2+}$/viologen couple.[18] The choice of the protective agent is crucial in order to obtain Pt microelectrodes capable of operating specifically. Thus, selectivity is lost when PVP-C_{16} is replaced by Carbowax-20M. If the latter catalyst is employed in a system which does not contain a sacrificial agent, there is no hydrogen formation. Instead, it was noted from laser photolysis experiments that the rate of the back reaction between oxidized sensitizer and reduced relay was increased significantly in the presence of this catalyst: both the rate of decay of the viologen radical as well as the bleaching recovery of $Ru(bpy)_3^{2+}$ are enhanced. Apparently, in the case of Carbowax protection, the Pt particles simply short circuit the back electron transfer from reduced viologen to $Ru(bpy)_3^{3+}$.

These data are corroborated by results obtained from continuous photolysis experiments. Carbowax-20M-protected Pt catalyst when coupled to RuO_2 fails to split water under illumination of a cyclic system containing $Ru(bpy)_3^{2+}$ as a sensitizer and methylviologen as an electron relay. By contrast, if the Pt microspheres are protected by PVP-C_{16} and $C_{14}MV^{2+}$ is used as relay, simultaneous H_2 and O_2 production are observed. The lack of specificity of the Carbowax-20M-protected particles is attributed to the strongly hydrophylic nature of this protective polymer, providing facile access of the $Ru(bpy)_3^{3+}$ cation to the platinum surface. Uncharged hydrophylic polymers are thus unsuitable for Pt protection in cyclic water decomposition systems.[20]

Conclusion

An important fact emerging from the present study concerns the activity of colloidal redox catalyst operating in H_2-producing systems. The trends established earlier[4] relating high activity to small particle size are unambiguously confirmed. This finding corroborates a fundamental principle of electrocatalysis: a small particle size is advantageous, both from the viewpoint of mass transport of the electroactive species and from the viewpoint of surface area per gram of catalyst employed. Further optimization is possible by employing a particle size below 30 Å. A separate paper[21] will deal with the synthesis and catalytic action in the photolytic water cleavage of such ultrafine Pt aggregates.

High activity is only one prerequisite to be satisfied if such catalysts are to be used in cyclic water decomposition systems. Equally important but more difficult to obtain is the specificity of intervention in the water reduction step. The present study for the first time establishes pathways to achieve selective performance of the Pt microspheres. The development of such catalysts is of primordial importance to improve the performance of cyclic water decomposition systems.

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(19) C. K. Grätzel and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7741 (1979).

(20) The use of protective polymers can be avoided by employing mineral supports which yield excellent activity and also selectivity. Thus, water decomposition using a bifunctional Pt/RuO_2 redox catalyst and $Ru(bpy)_3^{2+}$ as a sensitizer has recently been achieved; e.g., E. Borgarello et al., *Angew. Chem.*, **92**, 663 (1980).

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