

# Hydrogen production from water by visible light using zinc porphyrin-sensitized platinized titanium dioxide <sup>☆</sup>

Evgenii A. Malinka <sup>a</sup>, Gerbert L. Kamalov <sup>a</sup>, Sergei V. Vodzinskii <sup>b</sup>, Vasili I. Melnik <sup>b</sup>,  
Zinaida I. Zhilina <sup>b</sup>

<sup>a</sup> Department of Catalysis, Physico-Chemical Institute, National Academy of Sciences of Ukraine, Chernomorskaya Doroga 86, 270080 Odessa, Ukraine

<sup>b</sup> PNIL-5, Odessa State University, Petra Velikogo 2, 270000 Odessa, Ukraine

Received 11 January 1995; accepted 31 March 1995

## Abstract

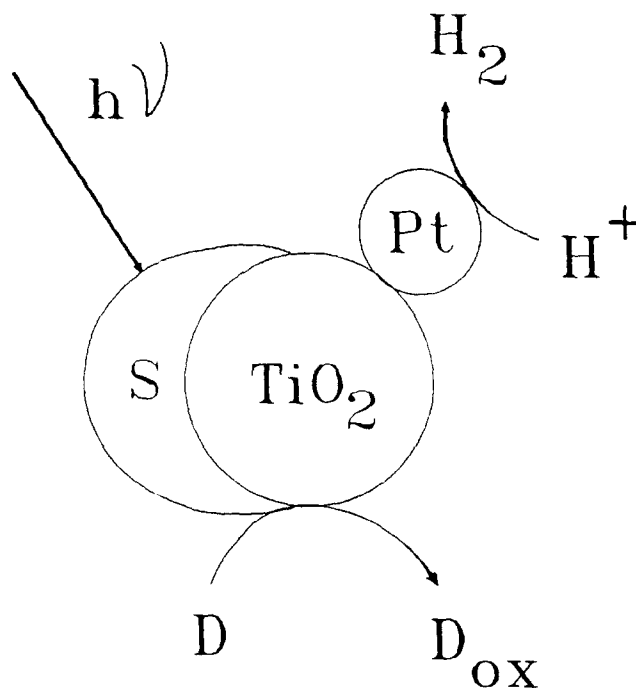
The rate of H<sub>2</sub> evolution from aqueous suspensions of Pt/TiO<sub>2</sub> with deposited zinc porphyrin in the presence of an electron donor (EDTA, triethanolamine, ascorbic and oxalic acids) during irradiation by visible light ( $\lambda > 520$  nm) was optimized with respect to the concentrations of platinum, zinc porphyrin and electron donor. The relationship between the rate of hydrogen evolution and pH has a maximum at pH 4–5 for EDTA, ascorbic and oxalic acids, as does the adsorption of these donors on TiO<sub>2</sub>. In the case of triethanolamine, H<sub>2</sub> production increases sharply in alkaline solutions when the triethanolamine molecules are deprotonated. The photostability of the photosensitizer increases on the semiconductor. Turn-over numbers for the zinc porphyrins varied from 50 for water-soluble zinc porphyrin up to 150–185 for water-insoluble sensitizers.

**Keywords:** Hydrogen production; Photosensitization; Titanium dioxide; Electron donor; Irradiation

## 1. Introduction

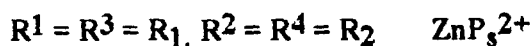
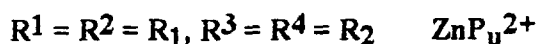
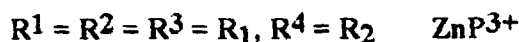
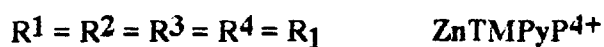
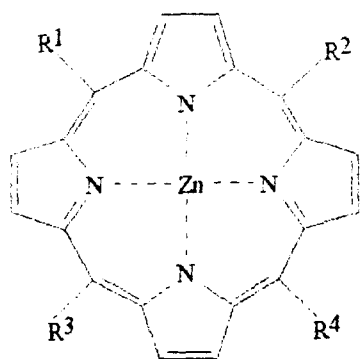
Spectral sensitization of wide band gap semiconductors in visible light for the photolysis of water has been a subject of investigation from the viewpoint of photochemical solar energy conversion. Dyes [1–5], Ru(II) bipyridyl [2,6–11], Ti(IV), Pt(II), Ir(III), Bi(III) and Pb(II) 8-quinolinol [11,12] and Pt(alizarine)<sub>2</sub> [13] complexes and water-soluble metalloporphyrins [2,14] have been shown to sensitize the production of hydrogen from water (Scheme 1).

The present work deals with the sensitization of TiO<sub>2</sub> by both water-soluble and insoluble zinc porphyrins. The effects of the concentrations of platinum, sensitizer and electron donor and the pH and temperature of the suspension on the rate of H<sub>2</sub> evolution, *R*, were investigated. These results were compared with data obtained for Pt/TiO<sub>2</sub> upon UV illumination. The photostability of zinc porphyrins was also tested. Previously it has been found that these zinc porphyrins sensitize H<sub>2</sub> production from aqueous suspensions of Pt/TiO<sub>2</sub> in the presence of a sacrificial electron donor [15,16].

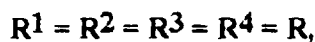


Scheme 1. S is the sensitizer; D is the electron donor.

<sup>☆</sup> Presented at the Xth International Conference on Photochemical Conversion and Storage of Solar Energy, Interlaken, Switzerland, 24–29 July 1994.



where  $R_1 = N$ -methyl-4-pyridyl and  $R_2 = n$ -nonyl;



where  $R =$



Fig. 1. Structure of zinc porphyrins.

Excited metalloporphyrin molecules adsorbed on  $\text{TiO}_2$  colloids are known to inject electrons into the conduction band of the semiconductor [17,18]. On the other hand, the anion radicals of metalloporphyrins formed by photoreduction of a metalloporphyrin with a donor evolve hydrogen from water on platinum [19,20].

## 2. Experimental details

### 2.1. Materials

All chemicals were at least reagent grade and were used as supplied. Details of the synthesis of zinc porphyrins (Fig. 1) – zinc(II) 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphine tetratosylate ( $\text{ZnTMPyP}^{4+}$ ), zinc(II) 5-monokis(*n*-nonyl)-10,15,20-trikis(4-*N*-methylpyridyl)porphine tritosylate ( $\text{ZnP}^{3+}$ ), zinc(II) 5,10-dikis(*n*-nonyl)-15,20-dikis(4-*N*-methylpyridyl)porphine ditosylate ( $\text{ZnP}_u^{2+}$ ), zinc(II) 5,15-dikis(*n*-nonyl)-10,20-dikis(4-*N*-methylpyridyl)porphine ditosylate ( $\text{ZnP}_s^{2+}$ ), zinc(II) 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphine ( $\text{ZnTPPC}$ ), zinc(II)

5,10,15,20-tetrakis(benzo-12-crown-4)porphine ( $\text{ZnTCP(4)}$ ), zinc(II) 5,10,15,20-tetrakis(benzo-15-crown-5)porphine ( $\text{ZnTCP(5)}$ ) and zinc(II) 5,10,15,20-tetrakis(benzo-18-crown-6)porphine ( $\text{ZnTCP(6)}$ ) – were given elsewhere [21–24].

$\text{TiO}_2$  powder (particle size 0.1–5  $\mu\text{m}$ , surface area about 150  $\text{m}^2 \text{g}^{-1}$ ) was prepared by thermal hydrolysis of titanium(IV) sulphate in a concentrated solution of sulphuric acid. Colloidal Pt was obtained by the reduction of  $\text{H}_2\text{PtCl}_6$  with citrate at 90 °C according to Ref. [25]. Excess citrate was removed by an ion exchange resin at 0 °C. The Pt sol was mixed with the  $\text{TiO}_2$  powder, the dispersion was sonicated and water was removed by using a vacuum rotary evaporator. The dried Pt/ $\text{TiO}_2$  powder was resuspended in alcoholic zinc porphyrin solution and the photosensitizer was deposited on the surface of the Pt/ $\text{TiO}_2$  particles by evaporation of ethanol.

Doubly distilled water was used to prepare all solutions and suspensions. The pH of the solutions was adjusted with either NaOH or HCl. Oxalic and ascorbic acids, triethanolamine (TEOA) and the disodium salt of ethylenediamine-tetraacetic acid (EDTA) served as electron donors.

### 2.2. Apparatus and analysis

Photolysis experiments were carried out in a cylindrical Pyrex glass cell (18 ml) equipped with a rubber septum. After sonication of Pt/ $\text{TiO}_2$  with deposited zinc porphyrin in 7 ml aqueous solution of an electron donor, the suspensions were placed in the cell and stirred magnetically. Oxygen was removed by argon bubbling. The suspensions were irradiated by visible light ( $\lambda > 520 \text{ nm}$ ) from a 1000 W xenon lamp through water and a glass filter OS-11 (LOMO). The temperature of all suspensions was about 35 °C.

The volume of evolved hydrogen was measured by gas chromatography. The spectra of solutions and powders were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. The changes in pH values were monitored using a model 340 pH meter.

## 3. Results and discussion

### 3.1. Effect of Pt concentration

Fig. 2 shows that the dependence of  $R$  on the amount of platinum has a maximum at 0.2–0.4 wt.% Pt. These maxima occurred for the Pt/ $\text{TiO}_2$ –electron donor systems upon band gap illumination of the semiconductor [25–28]. The optimum Pt content varied from 0.05% to 5%. This is probably because Pt,  $\text{TiO}_2$  and Pt/ $\text{TiO}_2$  were prepared by various methods.

### 3.2. Effect of electron donor concentration

Fig. 3 presents the dependence of  $R$  on the initial concentration of electron donor,  $C$ . Taking into account the maximal

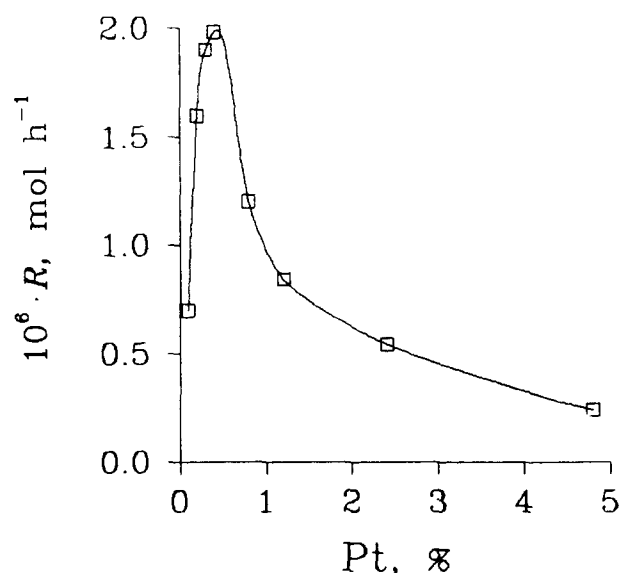


Fig. 2. Rate of  $H_2$  evolution,  $R$ , as a function of Pt loading ( $1.33 \text{ g dm}^{-3} \text{ ZnP}_u^{2+}/\text{Pt}/\text{TiO}_2$  ( $20 \mu\text{mol ZnP}_u^{2+}$  per  $1 \text{ g Pt}/\text{TiO}_2$ ) and  $0.05 \text{ mol dm}^{-3}$  EDTA).

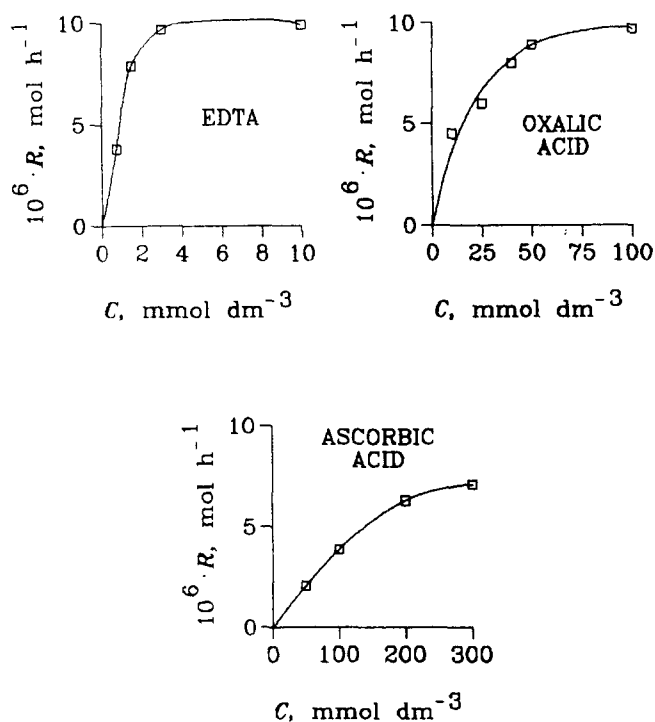


Fig. 3. Rate of  $H_2$  evolution,  $R$ , as a function of electron donor concentration  $C$  ( $3 \text{ g dm}^{-3} \text{ ZnP}^{3+}/\text{Pt}/\text{TiO}_2$  ( $20 \mu\text{mol ZnP}^{3+}$  per  $1 \text{ g Pt}/\text{TiO}_2$ ,  $0.4\%$  Pt) and  $0.05 \text{ mol dm}^{-3}$  electron donor).

rates of hydrogen evolution,  $R_{\text{max}}$ , and the  $C$  values at which the concentration dependences of  $R$  reach a plateau, the efficiency of the electron donors follows the order EDTA > oxalic acid > ascorbic acid. Furthermore, the adsorption isotherms of EDTA, oxalic and ascorbic acids on  $\text{TiO}_2$  [29–31] show that the near-saturation coverage of the electron donors also follows the above order. These facts suggest that  $R$  is determined by the surface concentration of

electron donor on the semiconductor. For the  $\text{Pt}/\text{TiO}_2$ -EDTA system upon band gap irradiation [28,31]  $R$  was determined by the surface concentration of electron donor and the dependence of  $R$  on the EDTA concentration was of a similar type to the dependences in Fig. 3.

### 3.3. Effect of pH

Fig. 4 shows that the relationship between  $R$  and pH has a maximum at pH 4–5 for EDTA, oxalic and ascorbic acids. The adsorption maxima of these donors on  $\text{TiO}_2$  were also observed at the same pH [32–34]. Thus  $R$  and the adsorption of electron donor on the photocatalyst exhibit similar pH dependences. These findings also indicate that  $R$  is determined by the surface concentration of electron donor on the semiconductor.

The results for the  $\text{ZnP}_u^{2+}/\text{Pt}/\text{TiO}_2$ -EDTA system are in contrast with the behaviour of the ruthenium(II) bipyridyl complex/ $\text{Pt}/\text{TiO}_2$ -EDTA system, where the efficiency of sensitized hydrogen production was reduced when the pH was increased from 3 to 7 because of sensitizer desorption [9]. If ZnTPPC is used instead of  $\text{ZnP}_u^{2+}$ , the observed behaviour of the dependence of  $R$  on pH is similar to that seen in Ref. [9]:  $R = 1.4, 0.5$  and  $0.2 \mu\text{mol h}^{-1}$  at pH 3, 5 and 7 respectively. This is because ZnTPPC has  $-\text{COOH}$  groups like the ruthenium complex. ZnTPPC is practically insoluble at  $\text{pH} < 5$ , because the  $-\text{COOH}$  groups are protonated in acid solution [17], and the maximum coverage of ZnTPPC on  $\text{TiO}_2$  is attained at pH 3. Desorption of ZnTPPC from the  $\text{TiO}_2$  surface in neutral and alkaline solutions is known to reduce the efficiency of sensitization of the colloidal

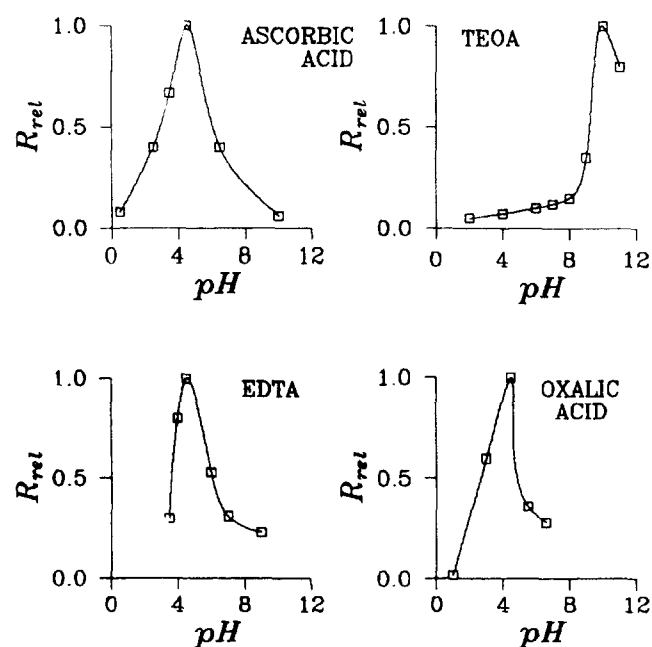


Fig. 4. Relative rate of  $H_2$  evolution,  $R_{\text{rel}}$  ( $R_{\text{rel}} = R/R_{\text{max}}$ ), as a function of pH (the maximal rate  $R_{\text{max}}$  was taken for each electron donor separately) ( $1.33 \text{ g dm}^{-3} \text{ ZnP}_u^{2+}/\text{Pt}/\text{TiO}_2$  ( $20 \mu\text{mol ZnP}_u^{2+}$  per  $1 \text{ g Pt}/\text{TiO}_2$ ,  $0.4\%$  Pt) +  $0.05 \text{ mol dm}^{-3}$  electron donor).

TiO<sub>2</sub> particles [17]. However, the ZnP<sub>u</sub><sup>2+</sup> concentration on TiO<sub>2</sub> is not changed when the pH is varied, since ZnP<sub>u</sub><sup>2+</sup> is insoluble in water.

Fig. 4 shows that *R* increases sharply at pH > 8 in the case of TEOA as electron donor. Similar dependences were observed for the dibromofluorescein/Pt/TiO<sub>2</sub>-TEOA system upon visible light illumination [3] and for the Pt/TiO<sub>2</sub>-TEOA system upon UV illumination [34]. To explain this dependence, we proposed [34] that the rate of oxidation of the amine in alkaline solution is higher than that of the protonated amine in acid solution, since the rate constant for oxidation of the amine is known to be significantly lower in acid solutions [35].

### 3.4. Effect of zinc porphyrin concentration

The diffuse reflectance spectra of the zinc porphyrins deposited on the TiO<sub>2</sub> surface exhibit the same absorbance bands as the visible absorption spectra in solution (the Soret band and two Q bands). However, as can be seen in Table 1, the spectra show a red shift of all absorption bands. This shift of the absorbance bands was attributed to the interaction between porphyrins and supports [17,36].

In organic solvents in the presence of K<sup>+</sup> ions ZnTCP(5) forms a twisted face-to-face dimer owing to the formation of a complex between four K<sup>+</sup> ions and eight benzo-15-crown-5 meso substituents of two molecules of ZnTCP(5) [37]. The formation of the dimer is followed by broadening, a red shift of the Q bands and a blue shift of the Soret band in the visible absorption spectra. There is no blue shift of the Soret band in the diffuse reflectance spectrum of ZnTCP(5)/TiO<sub>2</sub> when ZnTCP(5) is deposited on TiO<sub>2</sub> from an ethanolic solution containing the K<sup>+</sup>-induced dimer (see Table 1). The spectrum is very similar to those observed for ZnTCP(4)

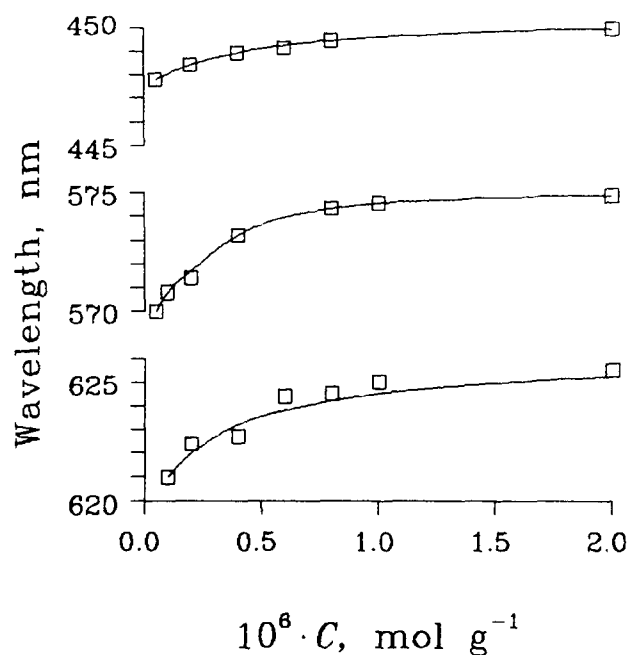


Fig. 5. Absorbance band maxima of ZnP<sup>3+</sup> deposited on TiO<sub>2</sub> as a function of ZnP<sup>3+</sup> concentration on support.

and ZnTCP(6) as well as ZnTCP(5) in the absence of K<sup>+</sup> ions. These facts indicate that the face-to-face dimers with the blue-shifted Soret band are absent on the TiO<sub>2</sub> surface.

Fig. 5 and Table 1 show that increasing the zinc porphyrin concentration on a support causes a bathochromic shift of the band maxima in the diffuse reflectance spectrum. Chlorophyll on some supports demonstrated the same behaviour owing to pigment aggregation [36]. The formation of aggregates was also found for zinc 5,10,15,20-tetraphenylporphine and H<sub>2</sub>TMPyP<sup>4+</sup> on glasses covered by SnO<sub>2</sub> or In<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub>

Table 1  
Band maxima of zinc porphyrins in visible absorption and diffuse reflectance spectra

Zinc porphyrin	Soret (B) and Q bands of zinc porphyrin, λ <sub>max</sub> (nm)						
	Ethanol			Zinc porphyrin on TiO <sub>2</sub>			
	B	Q(1,0)	Q(0,0)	Conc. <sup>a</sup>	B	Q(1,0)	Q(0,0)
ZnTCP (4)	426	559	599	A	430	559	601
				B	–	564	605
ZnTCP (5)	427	559	599	A	431	562	602
				B	–	566	607
ZnTCP (5) (dimer)	413	564	610	A	432	562	605
				B	–	566	610
ZnTCP (6)	427	559	599	A	432	562	605
				B	–	566	610
ZnTMPyP <sup>4+</sup> <sup>b</sup>	433	561	606	A	453	575	613
ZnP <sup>3+</sup> <sup>b</sup>	436	565	614	A	447	571	621
				B	449	576	626
ZnP <sub>u</sub> <sup>2+</sup>	427	568	620	B	448	575	624
ZnP <sub>s</sub> <sup>2+</sup>	426	564	628	B	442	571	639
ZnTPPC	420	556	594	A	436	566	608

<sup>a</sup> A and B denote 2 and 20 μmol zinc porphyrin per 1 g TiO<sub>2</sub> respectively.

<sup>b</sup> The spectra were recorded in aqueous solutions.

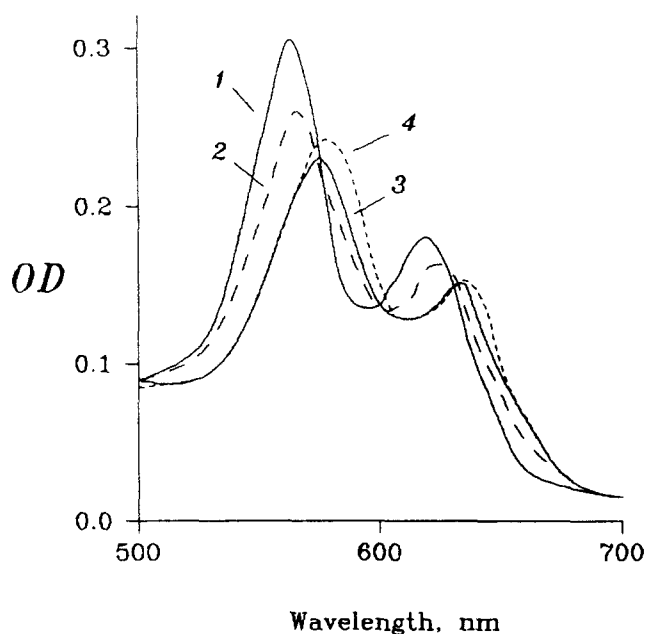


Fig. 6. Absorption spectra of (1)  $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ ZnP}^{3+}$  and (2–4) electrolyte-induced aggregates of  $\text{ZnP}^{3+}$  (0.45, 2.25 and  $4.5 \text{ mol dm}^{-3} \text{ LiCl}$  respectively) in aqueous solutions.

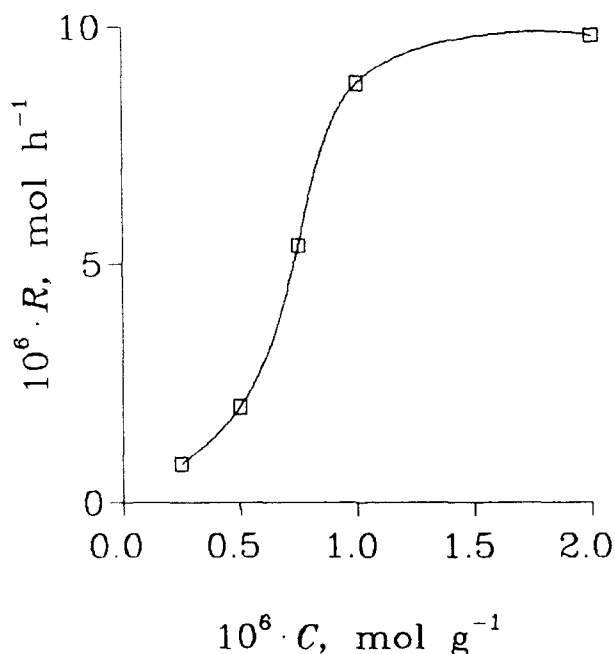


Fig. 7. Rate of  $\text{H}_2$  evolution,  $R$ , as a function of zinc porphyrin concentration ( $3 \text{ g dm}^{-3} \text{ ZnP}^{3+} / \text{Pt/TiO}_2$  (0.4% Pt) and  $0.05 \text{ mol dm}^{-3} \text{ EDTA}$ ).

[38] and for porphyrins containing alkyl and pyridyl meso substituents on  $\text{SiO}_2$  [39].

The red shift and broadening of all adsorption bands are also observed upon addition of  $\text{LiCl}$  to an aqueous solution of  $\text{ZnP}^{3+}$  owing to the formation of electrolyte-induced aggregates [e.g. 40,41]. Fig. 6 illustrates these spectral changes. More than one type of particle is present in solution, since there are no isobestic points in the spectra.

Fig. 7 presents the dependence of  $R$  on the concentration of  $\text{ZnP}^{3+}$ .  $R$  increases with increasing  $\text{ZnP}^{3+}$  concentration up to  $10 \mu\text{mol ZnP}^{3+}$  per  $1 \text{ g Pt/TiO}_2$ . Comparison with Fig. 5 shows that a plot of  $\lambda_{\text{max}}$  against the concentration of  $\text{ZnP}^{3+}$  reaches a plateau at the same  $\text{ZnP}^{3+}$  concentration. This is probably because aggregation is complete at this concentration of  $\text{ZnP}^{3+}$ .

Since  $\text{ZnP}_u^{2+} / \text{Pt/TiO}_2$  powder is hydrophobic, ultrasonic treatment in water is required in order to make it hydrophilic. The porphyrin molecules may have a flat or stacked orientation on the support with respect to its surface. A model with the stacked orientation of porphyrin on the  $\text{SiO}_2$  surface was proposed for a porphyrin containing two long-chain alkyl and two methylpyridyl meso substituents [42]. We believe that ultrasonic treatment changes the orientation of zinc porphyrin on the  $\text{TiO}_2$  surface. It must be noted that the orientation on the support surface of a porphyrin containing alkyl and methylpyridyl meso substituents depends on its concentration and this dependence is complex [42].

### 3.5. Effect of temperature

The apparent activation energy of hydrogen evolution is  $36 \text{ kJ mol}^{-1}$  for the  $\text{ZnP}_u^{2+} / \text{Pt/TiO}_2\text{-EDTA}$  system. This value is nearly half that for platinum(II) oxinate as a photosensitizer (about  $65 \text{ kJ mol}^{-1}$ ) in the same system [12].

### 3.6. Photostability of zinc porphyrins

The turn-over numbers for the zinc porphyrins are collected in Table 2. The metalloporphyrins photobleach because their  $\pi$  ion radicals are unstable in aqueous solutions. Thus water-soluble  $\text{ZnTMPyP}^{4+}$  forms hydroproducts in the presence of EDTA during prolonged illumination [19,20,43]. Some improvement in the photostability of  $\text{ZnTMPyP}^{4+}$  in the  $\text{ZnTMPyP}^{4+} / \text{Pt-EDTA}$  system was obtained at high concentrations of Pt catalyst owing to faster scavenging of electrons by Pt from the anion radical of the porphyrin [19].

Table 2  
Turn-over numbers (TN) for photosensitizers

Zinc porphyrin <sup>a</sup>	TN <sup>b</sup>	Time (h)
$\text{ZnTMPyP}^{4+}$ <sup>c</sup>	50	12
$\text{ZnP}^{3+}$	182	9 <sup>d</sup>
$\text{ZnP}_u^{2+}$	154	9 <sup>d</sup>
$\text{ZnP}_s^{2+}$	148	9 <sup>d</sup>

<sup>a</sup>  $1.33 \text{ g dm}^{-3}$  zinc porphyrin/ $\text{Pt/TiO}_2$  ( $20 \mu\text{mol}$  zinc porphyrin per  $1 \text{ g Pt/TiO}_2$ , 0.4% Pt) and  $0.05 \text{ mol dm}^{-3} \text{ EDTA}$ .

<sup>b</sup>  $\text{TN} = 2(\text{moles of H}_2 \text{ evolved}) / (\text{moles of zinc porphyrin})$ .

<sup>c</sup>  $10^{-4} \text{ mol dm}^{-3} \text{ ZnTMPyP}^{4+}$ .

<sup>d</sup> The zinc porphyrin/ $\text{Pt/TiO}_2$  photocatalyst was removed from suspension every 3 h and then added to fresh EDTA solution, since the donor concentration decreased and the pH increased during prolonged irradiation; such changes in both parameters results in decreasing  $R$ , as shown in Figs. 3 and 4.

Some retardation of zinc porphyrin degradation is also observed when the photosensitizers are deposited on the Pt/TiO<sub>2</sub> surface. For example, about 70% of ZnP<sub>u</sub><sup>2+</sup> is removed into solution from the Pt/TiO<sub>2</sub> particles by organic solvents (DMF, DMSO or ethanol) after irradiation of the ZnP<sub>u</sub><sup>2+</sup>/Pt/TiO<sub>2</sub>-EDTA suspension for 9 h. However, irradiation of the Pt/TiO<sub>2</sub> suspensions containing ZnP<sub>u</sub><sup>2+</sup> and ZnP<sub>s</sub><sup>2+</sup> solubilized with Triton X-100 leads to colourless products after 1 h. In the case of ZnTMPyP<sup>4+</sup>, *R* drops to about 1–1.5 μmol h<sup>-1</sup> owing to the photobleaching of zinc porphyrin in solution and this steady value of *R* is maintained for 7–8 h. The same rate is observed for a light green photocatalyst which is filtered and placed in fresh EDTA solution. These results indicate that during prolonged illumination H<sub>2</sub> evolution is sensitized by adsorbed ZnTMPyP<sup>4+</sup> molecules, since a Pt/TiO<sub>2</sub> sample does not evolve H<sub>2</sub> during visible light irradiation.

#### 4. Conclusions

The rate of hydrogen production depends on the surface concentrations of platinum, zinc porphyrin and electron donor on titanium dioxide. The adsorption of the electron donor is determined by the pH value of the suspension. The photostability of zinc porphyrins increases on the semiconductor surface.

#### Acknowledgment

This work has been financially supported by the National Academy of Sciences of Ukraine.

#### References

- [1] Yu.I. Kiryukhin, Z.A. Sinitzina, L.V. Romashov, V.A. Borovkova and K.S. Bagdasarjan, *Dokl. Akad. Nauk SSSR*, 261 (1981) 416.
- [2] K. Hashimoto, T. Kawai and T. Sakata, *Nouv. J. Chim.*, 7 (1983) 249.
- [3] K. Hashimoto, T. Kawai and T. Sakata, *Nouv. J. Chim.*, 8 (1984) 693.
- [4] T. Shimidzu, T. Iyoda and Y. Koide, *J. Am. Chem. Soc.*, 107 (1985) 35.
- [5] I. Willner, Y. Eichen and A.J. Frank, *J. Am. Chem. Soc.*, 111 (1989) 1884.
- [6] E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, *Nature*, 289 (1981) 158.
- [7] E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, *J. Am. Chem. Soc.*, 103 (1981) 6324.
- [8] D. Duonghong, N. Serpone and M. Grätzel, *Helv. Chim. Acta*, 66 (1984) 1012.
- [9] D.N. Furlong, D. Wells and W.H.F. Sasse, *J. Phys. Chem.*, 90 (1986) 1107.
- [10] M.M. Taqui Khan, R.C. Bhardwaj and C. Bhardwaj, *Inorg. Chim. Acta*, 130 (1987) 153.
- [11] V.H. Houlding and M. Grätzel, *J. Am. Chem. Soc.*, 105 (1983) 5695.
- [12] E. Borgarello, E. Pelizzetti, R. Ballardini and F. Scandola, *Nouv. J. Chim.*, 8 (1984) 567.
- [13] V.S. Zakharenko, A.V. Bulatov and V.N. Parmon, *React. Kinet. Catal. Lett.*, 36 (1988) 295.
- [14] T. Shimidzu, T. Iyoda, Y. Koide and N. Kanda, *Nouv. J. Chim.*, 7 (1983) 21.
- [15] E.A. Malinka, A.M. Khutornoi, S.V. Vodzinskii, Z.I. Zhilina and G.L. Kamalov, *React. Kinet. Catal. Lett.*, 36 (1988) 407.
- [16] E.A. Malinka, V.I. Melnik, Z.I. Zhilina, A.M. Khutornoi and G.L. Kamalov, *Zh. Obshch. Khim.*, 61 (1991) 1256.
- [17] K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier and M. Grätzel, *J. Phys. Chem.*, 91 (1987) 2342.
- [18] K. Kalyanasundaram, J.A. Shelnett and M. Grätzel, *Inorg. Chem.*, 27 (1988) 2820.
- [19] A. Harriman and M.-C. Richoux, *J. Photochem.*, 15 (1981) 335.
- [20] A. Harriman, *J. Photochem.*, 29 (1985) 139.
- [21] A.V. Bogatskii, Z.I. Zhilina, S.V. Vodzinskii and R.M. Zakharova, *Zh. Org. Khim.*, 24 (1985) 649.
- [22] Z.I. Zhilina, S.V. Vodzinskii and S.A. Andronati, *Ukr. Khim. Zh.*, 56 (1990) 1084.
- [23] A.V. Bogatskii, Z.I. Zhilina and D.E. Stepanov, *Zh. Org. Khim.*, 18 (1982) 2309.
- [24] Z.I. Zhilina, V.I. Melnik, S.A. Andronati and A.E. Abramovich, *Zh. Org. Khim.*, 25 (1989) 1070.
- [25] A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 3659.
- [26] T. Sakata, T. Kawai and K. Hashimoto, *Chem. Phys. Lett.*, 88 (1982) 50.
- [27] P. Pichat, M.-N. Mozzanega, J.D. Disdier and J.-M. Herrmann, *Nouv. J. Chim.*, 6 (1982) 559.
- [28] D.N. Furlong, D. Wells and W.H.F. Sasse, *J. Phys. Chem.*, 89 (1985) 1922.
- [29] S.J. Hug and B. Sulzberger, *Abstracts Xth Int. Conf. on Photochemical Conversion and Storage of Solar Energy, Interlaken, July 1994*, p. 375.
- [30] E.A. Malinka and G.L. Kamalov, *Proc. VIIIth Int. Symp. on Relations between Homogeneous and Heterogeneous Catalysis, Balatonfüred, September 1995*, in press.
- [31] D.N. Furlong, D. Wells and W.H.F. Sasse, *J. Phys. Chem.*, 89 (1985) 626.
- [32] D.N. Furlong, D. Wells and W.H.F. Sasse, *Aust. J. Chem.*, 39 (1986) 757.
- [33] J. Domenech and J. Peral, *J. Chem. Res. (Synop.)*, (1987) 360.
- [34] E.A. Malinka and G.L. Kamalov, *J. Photochem. Photobiol. A: Chem.*, 81 (1994) 193.
- [35] G. Scholes and R.L. Willson, *Trans. Faraday Soc.*, 63 (1967) 2983.
- [36] L.I. Nekrasov and N.A. Mamleeva, *Zh. Phys. Khim.*, 52 (1978) 2721.
- [37] V. Thanabal and V. Krishnan, *J. Am. Chem. Soc.*, 104 (1982) 3643.
- [38] S.M.B. Costa, N. Tamai, Y. Yamazaki and I. Yamazaki, *Abstracts XIIIth Int. Conf. on Photochemistry, Budapest, August, 1987*, Vol. 1, p. 231.
- [39] J.M. Kroon, P.S. Schenkels and E.J.R. Sudhölter, *Abstracts Xth Int. Conf. on Photochemical Conversion and Storage of Solar Energy, Interlaken, July 1994*, p. 417.
- [40] K. Bütje and K. Nakamoto, *Inorg. Chim. Acta*, 167 (1990) 97.
- [41] J.A. Shelnett, M.M. Dobry and J.D. Satterlee, *J. Phys. Chem.*, 88 (1984) 4980.
- [42] J. Wienke, F. Kleima, R.B.M. Koehorst and T.J. Schafsma, *Proc. XIIth Eur. Photovoltaic Solar Energy Conf., Amsterdam, April 1994*, p. 1–4.
- [43] K. Kalyanasundaram, *J. Photochem. Photobiol. A: Chem.* 42 (1988) 87.