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Water Detoxification: Photocatalytic Decomposition of Phenol on Au/TiO_2

Anna Dobosz and **Andrzej Sobczyński***

Faculty of Commodity Science, Poznań University of Economics, PL-60967 Poznań, Poland

Summary. Photodeposition of gold on TiO_2 was conducted *in situ* in the photoreactor used for the reaction of phenol photodestruction. The Au/TiO_2 system shows better photocatalytic properties in the destruction of phenol contaminants in water than pure TiO_2. The gold cocatalyst prevents also the decrease of the rate of the photocatalytic reaction at higher phenol concentration observed for pure TiO_2. Hydroquinone, *p*-benzoquinone, and catechol are main intermediates of the photoreaction, which finally leads to total phenol mineralization.

Keywords. Gold; Titania; Phenol; Photodegradation.

Introduction

Photocatalytic water purification on semiconductors is one of the newer AOP (Advanced Oxidation Processes) techniques, developed during the last two decades [1–9]. The process, which takes place on a surface of irradiated semiconductors, leads to water purification from organic substances. It is similar to those described earlier for semiconductor catalyzed hydrogen photogeneration from water in the presence of sacrificial agents [10–12]. In both cases, photogenerated holes react with hydroxyl groups from water giving hydroxyl radicals. The generated $OH^{\cdot}$ radicals react further with organic matter dissolved in water and cause its oxidation, finally to CO_2 and H_2O. Photogenerated electrons in deaerated water reduce H_3O^+ causing hydrogen evolution. In aerated water, the electrons reduce dissolved oxygen.

Hydrogen evolution is not catalyzed well by the titanium dioxide surface. Therefore, it was necessary to modify the surface by introducing a cocatalyst improving H_3O^+ reduction, recombination of the reduced hydrogen atoms to H_2, and gaseous product evolution. Besides platinum [13–17], also other cocatalysts like palladium [18], ruthenium [19], copper [20], nickel [21, 22], ruthenium dioxide [23], molybdenum, and tungsten sulfides [24, 25] have been applied. From the electrochemical point of view, islands of the noble metals or other substances on the TiO_2 surface act as microelectrodes (microcathodes) on which reduction processes occur [26].

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* Corresponding author. E-mail: biuropromocji@novci1.poznan.pl

Besides, the bare titania surface catalyzes the reduction of oxygen dissolved in water. Therefore, photooxidation (mineralization) of organic water pollutants proceeds relatively efficiently on pure TiO_2 particles [1–9, 12]. However, it has been shown [27] that introduction of a Pt cocatalyst enhancees the activity of titania in photoassisted oxidation of hydrocarbons dissolved in water. Based on theoretical considerations, *Gerischer* and *Heller* [28] suggested that the quantum efficiency of oxidation of organic compounds in water on illuminated n-TiO_2 was limited by the O_2 reduction rate. According to these authors, the semiconductor-like n-TiO_2 does not possess a sufficient density of shallow, near-surface electron traps to assist in the O_2 reduction process. It causes, in turn, accumulation of electrons on the semiconductor and acceleration of the rate of radiationless electron-hole recombination, a process which leads to a loss of the semiconductor photoactivity. To improve the efficiency of the photoreactions, they have suggested application of group VIII metals as cocatalysts. The authors' predictions have been proven experimentally [29]. It has been found that incorporation of Pd^0 on titania particles promotes the electron transfer to O_2 dissolved in water, thus eliminating negative charge on TiO_2 and increasing the quantum efficiency of the photoassisted oxidation of 2,2-dichloropropionate. An increased rate of photodegradation of organic compounds like 1,4-dichlorobenzene and salicylic acid upon incorporation of Ag^0, Au^0, and Pd^0 onto the surface of TiO_2 particles has also been observed [30–32]. Recently, papers by *Chen et al.* [33–35] concerning the photocatalytic properties of Pt^0- and Pd^0-loaded titania particles have discussed kinetic processes and possible photocatalytic mechanisms which take place on the metallized surface of TiO_2.

In this paper, the photoactivity of Au/TiO_2 in phenol destruction is reported. The reagent was prepared by *in situ* metal photodeposition in the reaction slurry.

Results and Discussion

As mentioned above, metallic gold was photodeposited on the surface of TiO_2 *in situ* in the reaction vessel under a neutral atmosphere. For that purpose, the slurry of TiO_2 in an aqueous phenol solution to which an appropriate amount of $HAuCl_4 \cdot 3H_2O$ had been previously added was purged with argon in order to remove dissolved oxygen. Next, the mixture was illuminated with a 180 W medium pressure Hg lamp for 30 min. It had been checked before that this illumination time was sufficient for the total reduction of metals like Pt [16], Ru [19], or Cu [20] on the surface of TiO_2. During the metal reduction the slurry was mixed by an argon stream applied at the bottom and flowing through a draft tube placed in the centre of the photoreactor. The photocatalytic reaction was conducted in a non-continuous mode (batch reactor).

The catalytic effect of Au on the photoactivity of TiO_2 has been studied previously by *Gao et al.* [30] in the reactions of 1,4-dichlorobenzene (*DCB*) and salicylic acid photodecomposition. The novelty of the present studies lies in the preparation of the Au/TiO_2 system. Here the metal was photodeposited on TiO_2 *in situ*, *i.e.* in the reaction environment. The method has been described previously for the preparation of such photocatalysts as Pt/TiO_2, Ru/TiO_2, and Cu/TiO_2 used in systems for hydrogen photogeneration from water in the presence of methanol as a sacrificial agent [16, 19, 20]. The method allows to omit steps like filtration/

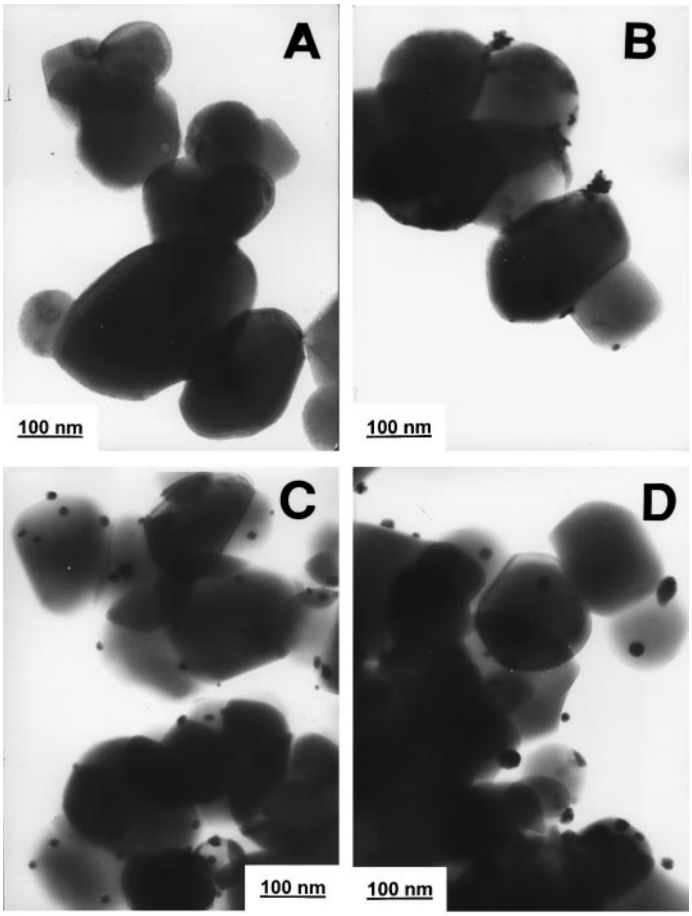

Fig. 1. TEM micrographs of pure TiO_2 (A) and TiO_2 doped with 0.05 (B), 1.0 (C), and 2.0 (D) weight percent of gold

centrifugation and drying which can cause some changes of the photocatalytic activity of Me/TiO_2. This way, photooxidation of phenol proceeds on a freshly prepared active surface.

The metal photoreduction and deposition on the surface of titania was monitored by transmission electron microscopy (TEM). The TEM images of the samples containing 0.05, 1.0, and 2.0% (w/w) Au, and, for comparison, of pure TiO_2, are shown in Fig. 1. The black dots of photodeposited Au islands can well be seen. It follows from the images that the higher metal content favours more dense and bigger gold islands on the titania surface. However, if we turn back to SEM investigations on Ru/TiO_2 [19] it can be predicted that also the naked part of the surface may contain some highly dispersed metal. After photodeposition of Au and 30 min of photoreaction under argon, the slurry was aerated in the dark and illuminated again. Therefore, the real phenol photooxidation on Au/TiO_2 in the presence of air started after 1 hour (Fig. 2).

The rate of phenol photooxidation was monitored by the 4-aminoantipyrine method [4]. The spectrophotometric method gives as a result a so-called phenolic index, *i.e.* the sum of phenolic compounds present in the solution. However, for

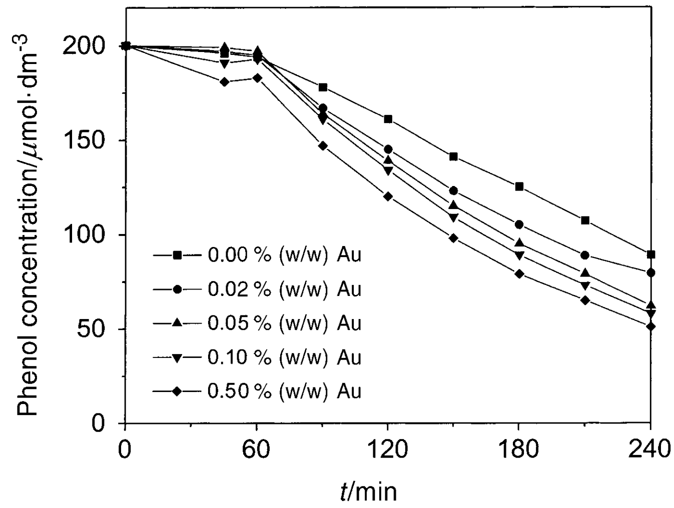

Fig. 2. Changes of phenolic index in the photoreactor during illumination of pure TiO_2 and titanium dioxide with various amounts of gold

simplification, the term phenol instead of phenolic index is used in the paper. Real phenol consumption and the difference between phenol and phenolic index changes during the photoreaction will be shown below. The changes of phenol concentration (changes of the phenolic index) during illumination of the slurry of pure titanium dioxide and Au-loaded TiO_2 are shown in Fig. 2. It can be seen that the photoreaction rate increases with increasing of Au content in the range of 0–0.5% (w/w). For bigger Au contents (0.75, 1.0, 1.5, and 2% (w/w)), the curves of phenol disappearance cover partly that for 0.05% (w/w) Au and are not shown in Fig. 2.

Some conclusions can be drawn from the data of Fig. 2. Firstly, illumination of the slurry under a neutral atmosphere causes – besides metal reduction – also phenol photooxidation. Its consumption increases with rising amount of metal. Secondly, the metal admixture shows a catalytic (electrocatalytic) effect on the photoreaction in the presence of oxygen: the rate of phenol destruction increases with increasing amount of metal in the range from 0.02 to 0.5% (w/w) Au. Further increase of the amount of the photodeposited gold does not influence considerably the photocatalytic activity.

Phenol photodecomposition in the presence of titania obeys 1st order kinetics, and usually the *Langmuir-Hinshelwood* expression is used in order to describe the reaction rate [36–38]. Thus, the comparison between the reaction rates has to be carried out at the same substrate (phenol) concentration, *i.e.* at the beginning of the process.

When studying the photocatalytic activity of titania in *DCB* degradation, *Gao et al.* [30] observed an increase of the activity by 30% caused by deposition of 1 at.% Au on the surface of TiO_2 after 30 min. In the present investigation the increase of the activity amounts to 120% after deposition of 0.5% (w/w) Au on the titania surface (optimum metal loading). The significant difference between the results of *Gao et al.* and those reported here can be accounted for by both different substrates decomposed (*DCB* and phenol) and different ways of Au/TiO_2 preparation. The

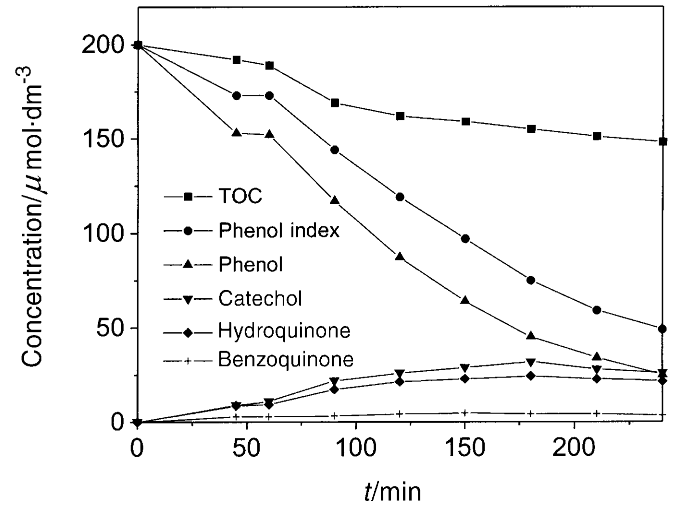

Fig. 3. HPLC and TOC analysis of the products of the photocatalytic reaction on 1% (w/w) Au on TiO$_2$; for comparison, a phenolic index curve is also depicted

observed small decrease of the photoreaction rate at a higher metal loading (> 0.5% (w/w)) can be caused by the so-called screening effect. This effect has been previously described for Pt/TiO$_2$, Ru/TiO$_2$, and Cu/TiO$_2$ systems used for photocatalytic hydrogen production from water (the deposited metal makes part of the surface less accessible for photons) [19, 20].

Figure 3 shows the results of HPLC and total organic content (TOC) studies of phenol photooxidation on Au/TiO$_2$ (1% (w/w)); the curve of the phenolic index is also included. One can see from the figure that the decrease of phenol concentration during the process of Au photodeposition under neutral atmosphere (15–45 min of the process) is much faster than the decrease of the phenolic index. At the same time, hydroquinone, benzoquinone, and catechol appear in detectable amounts. Dark saturation of the reaction mixture with air (45–60 min of the process) does not cause noticeable changes in the concentration of substrate and intermediates.

Illumination of the reaction mixture in the presence of dissolved air causes fast phenol photooxidation. Slower changes of the phenolic index show the existence of phenolic-type reaction intermediates. Hydroquinone, *p*-benzoquinone, and catechol are the main intermediate compounds. Small concentrations of *p*-benzoquinone in relation to that of hydroquinone have been observed before in studies of photooxidation of these compounds on pure titania [37]. Oxidation of catechol also leads to *o*-benzoquinone. However, the absence of *o*-benzoquinone in the reaction mixture is probably a result of its instability and, hence, fast decomposition.

The concentration of the intermediates rises with time at the beginning of illumination; in parallel, that of phenol decreases. Photooxidation of all compounds proceeds *via* a reaction with hydroxyl radicals photogenerated on the surface of titania. It has been confirmed before that the photooxidation of phenol, catechol, resorcinol, and hydroquinone/benzoquinone proceeds according to 1st order kinetics; the corresponding results have been partly published [37, 39]. Therefore, the rate of the photooxidation of the mentioned compounds depends on their con-

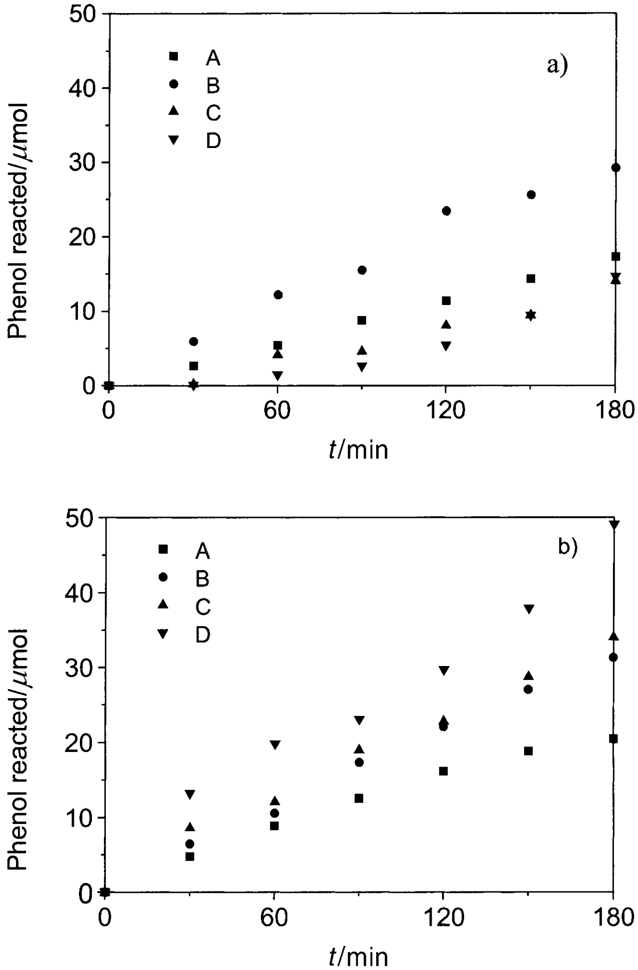

Fig. 4. Degree of phenol photodecomposition on pure TiO_2 (a) and TiO_2 doped with 1.0% (w/w) of Au at different substrate concentrations: $0.2 \cdot 10^{-3}$ (A), $0.6 \cdot 10^{-3}$ (B), $1.0 \cdot 10^{-3}$ (C), and $1.6 \cdot 10^{-3}$ (D) $mol \cdot dm^{-3}$

centration in the reaction mixture. After about 90 minutes of photoreaction, the concentrations of the intermediates remain nearly constant. This means that the rates of their formation and destruction are equal (see flat parts of the curves of catechol, hydroquinone, and benzoquinone). Finally, all organic compounds are fully oxidized to CO_2 and H_2O, although their mineralization is rather slow (see TOC curve in Fig. 3).

Figures 4a and 4b show the amounts of phenol which reacted during illumination of the slurries of pure TiO_2 (4a) and 1% (w/w) Au on TiO_2 (4b) with different initial phenol concentration. The steps of gold photoreduction and dark periods are omitted in the figures. On pure TiO_2, the rate of the photoreaction increases with increasing phenol concentration in the range of $2 \cdot 10^{-4}$–$0.6 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ and is strongly retarded at $1.0 \cdot 10^{-3}$ and $1.6 \cdot 10^{-3}$ $mol \cdot dm^{-3}$. There can be at least three reasons for the observed phenomenon. Firstly, higher substrate concentration can favour the zero-order reaction kinetics (*e.g.* when phenol adsorption is not concentration dependent). Secondly, the fast formation of phenol radicals (in the reaction of phenol with photogenerated hydroxyl radicals) can result in their combining into bi- or polyphenols. The compounds are not water soluble and are expected to adsorb strongly on the surface of TiO_2 as it has been observed before [36]. The third reason lies in the rate of oxygen photoreduction. Limitations of O_2 reduction on pure TiO_2 have been considered and experimentally proved by *Gerischer*, *Heller*, and *Wang* [28, 29] as was mentioned in the Introduction.

No photoreaction rate set-back was observed for 1% (w/w) Au on TiO_2 over the whole phenol concentration range from $1 \cdot 10^{-4}$ to $2 \cdot 10^{-3}\,\mathrm{mol \cdot dm^{-3}}$. Here the influence of the Au additive is distinct: strong enhancement of the photoreaction rate at lower substrate concentration (in comparison with pure TiO_2) and lack of retardation of the rate at higher concentrations. Probably, the gold microelectrodes on the TiO_2 surface cause a strong increase of the rate of oxygen reduction in the reduction route of the photoreaction on the semiconductor as predicted [28, 29]. It is also possible that the faster generation of hydroxyl radicals in the oxidation route of the photoreaction prevents the production of polyphenols.

Conclusions

Introduction of metallic Au on a TiO_2 surface improves the photocatalytic properties of TiO_2. The *in situ* preparation of the cocatalyst results in an increase of the rate of phenol destruction on illuminated TiO_2 of 120%. The Au cocatalyst prevents also the decrease of the rate of the photocatalytic reaction at higher phenol concentrations which has been observed for pure TiO_2. Hydroquinone, *p*-benzoquinone, and catechol are the main intermediates of the process. The existence of higher hydroxylated products confirms a radical mechanism of the photoprocesses on TiO_2 [27, 38]. The photocatalytic phenol destruction leads finally to its total mineralization to CO_2 and H_2O.

Experimental

Photocatalytic experiments

The photocatalytic activities of various catalyst samples were evaluated by degradation of phenol (99+%, Aldrich) in an aqueous environment. A stock solution of $HAuCl_4 \cdot 3H_2O$ (Sigma) containing 5.002 mg Au/cm^3 was prepared. Various amounts of the stock solution were added to 100 cm^3 of the reaction mixture containing $2 \cdot 10^{-4}\,\mathrm{mol/dm^3}$ of phenol and 0.02 g of TiO_2 anatase (99.9%, Aldrich). This reaction mixture was sonicated for 3 min and poured in the photoreactor. The phenol solution was added to achieve a final volume of 165 cm^3. In the case of different initial concentrations of phenol, the same procedure was utilized. To get 1% (w/w) Au per TiO_2, 40 mm^3 of the stock solution of Au were added to 0.02 g TiO_2 suspended in the phenol solution.

The photoreactor consisted of an external glass tube with a conical bottom equipped with a septum and a draft tube placed in the centre of the external one. The slurry in the reactor was mixed by a gas stream (argon or air) applied at the bottom using a needle and flowing up through the draft tube. The dimensions of the reactor were as follows: inner diameter of the external tube, 40 mm; h, 160 mm; inner diameter of the draft tube, 10 mm; h, 120 mm; total volume of the reactor, *ca.* 190 cm^3. The reactor was illuminated from a side wall with a 180 W medium pressure Hg lamp. The Pyrex walls of the reactor determined a lower limit of entering light (about 300 nm cutoff filter). The photoreactor was cooled by a stream of air; the reaction temperature was maintained at 28±2°C. For a detailed reactor description, see Refs. [36, 37].

At first, the reaction mixture was saturated with Ar for 15 min. Then, the mixture was illuminated for 30 min in presence of Ar in order to photodeposit metallic Au on the TiO_2 surface. Afterwards, the reaction mixture was saturated with air for 15 min and illuminated for 3 h.

Subsequently, the apparatus was saturated with air. During the further photoreaction, 1 cm^3 of the slurry was withdrawn every 30 min using a syringe. After filtration over Millipore Millex GV_3 units the samples were analyzed by absorptiometric determination of the phenol index (concentration of phenolic type compounds). The 4-aminoantipyrine method was used according to the procedure described in Ref. [4]. HPLC (Waters) analysis was also used to identify intermediates of the photodegradation of phenol. All reactants were of *p.a.* purity. In all experiments Millipore 18 Mohm water was used.

The photocatalyst

The titania (TiO_2 anatase, 99.9%, Aldrich) possessed a BET specific surface area of 9.85 $m^2 \cdot g^{-1}$ and showed a typical anatase spectrum with an adsorption onset at about 400 nm [23]. The particle size of the TiO_2 Aldrich powder is in the range of 0.10–0.35 µm as was deduced from SEM micrographs.

SEM and TEM investigations

Scanning electron micrographs were taken on a SEM 515 Philips apparatus using an acceleration voltage of 20 kV. TEM analysis was performed using a Jeol JEM-1200 EX electron microscope. An acceleration voltage of 80 kV was applied.

References

[1] Hsiao H-Y, Lee CL, Ollis DF (1983) J Catal **82**: 418
[2] Pruden AL, Ollis DF (1983) J Catal **82**: 404
[3] Nguyen T, Ollis DF (1984) J Phys Chem **88**: 3386
[4] Matthew RW (1984) J Chem Soc Faraday Trans 1 **80**: 457
[5] Matthew RW (1986) Water Res **20**: 569
[6] Okamoto K, Yamamoto Y, Tanaka H, Tanaka M, Itaya A (1985) Bull Chem Soc Jpn **58**: 2015
[7] Barbeni M, Pramauro E, Pelizzetti E, Borgarello E, Grätzel M, Serpone N (1984) Nouv J Chem **8**: 547
[8] Hidaka H, Kubota H, Grätzel M, Serpone N, Pelizzetti E (1985) Nouv J Chem **9**: 67
[9] Al-Ekabi H, Serpone N (1988) J Phys Chem **92**: 5726
[10] Bard AJ (1982) J Phys Chem **86**: 172
[11] Bard AJ (1988) Ber Bunsenges Phys Chem **92**: 1187
[12] Fox MA, Dulay MT (1993) Chem Rev **93**: 341
[13] Sato S, White JM (1980) J Amer Chem Soc **102**: 7206
[14] Chen B-H, White JM (1982) J Phys Chem **86**: 3534
[15] Kiwi J, Grätzel M (1984) J Phys Chem **88**: 1302
[16] Sobczyński A, Bard AJ, Campion A, Fox MA, Mallouk TE, Webber SE, White JM (1987) J Phys Chem **91**: 3319
[17] Nakamtsu H, Kawai T, Koreeda A, Kawai S (1985) J Chem Soc Faraday Trans 1 **82**: 527
[18] Oosawa J, Chen J (1987) J Chem Soc Faraday Trans 1 **80**: 507
[19] Sobczyński A, Jakubowska T, Zieliński S (1989) Monatsh Chem **120**: 101
[20] Sobczyński A (1992) Monatsh Chem **123**: 211
[21] Sakata T, Kawai T (1981) Chem Phys Letters **80**: 341

[22] Prahov L, Disdier J, Herrmann JM, Pichat P (1984) Int J Hydrogen Energy **9**: 397
[23] Sayama K, Arakawa H (1994) J Photochem Photobiol A **77**: 243
[24] Sobczyński A, Yildiz A, Bard AJ, Campion A, Fox MA, Mallouk TE, Webber SE, White JM (1989) J Phys Chem **93**: 401
[25] Sobczyński A (1991) J Catal **131**: 156
[26] Bard AJ (1979) J Photochem **10**: 50
[27] Izumi I, Dunn WW, Wilbourn KO, Fan FRF, Bard AJ (1980) J Phys Chem **84**: 3207
[28] Gerischer H, Heller A (1992) J Electrochem Soc **139**: 113
[29] Wang C-M, Heller A, Gerischer H (1992) J Amer Chem Soc **114**: 5230
[30] Gao Y-M, Lee W, Trehan R, Kershaw R, Dwight K, Wold A (1991) Mater Res Bull **26**: 1247
[31] Papp J, Shen H-S, Kershaw R, Dwight K, Wold A (1993) Chem Mater **5**: 284
[32] Lee W, Shen H-S, Dwight K, Wold A (1993) J Solid State Chem **106**: 288
[33] Chen J, Ollis DF, Rulkens WH, Bruning H (1999) Water Res **33**: 661
[34] Chen J, Ollis DF, Rulkens WH, Bruning H (1999) Water Res **33**: 669
[35] Chen J, Ollis DF, Rulkens WH, Bruning H (1999) Water Res **33**: 1173
[36] Sobczyński A, Gimenez J, Cervera-March S (1997) Monatsh Chem **128**: 1109
[37] Sobczyński A, Duczmal Ł, Dobosz A (1999) Monatsh Chem **130**: 377
[38] Turchi CS, Ollis DF (1990) J Catal **122**: 178
[39] Duczmal Ł, Sobczyński A (1999) React Kinet Catal Lett **66**: 289

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