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Hydrogen Photoproduction from Water-Methanol on Titania Covered with Copper

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Summary. Hydrogen photogeneration from water-methanol solution was studied on $Cu-TiO_2$ photoactive systems. It was found that Cu-deposit on titania particles could be obtained "in situ" in a reaction cell. The dispersed copper showed satisfactory good activity (quantum yield 4.3%) and stability under H_2 production conditions. The hydrogen evolution catalytic properties of Cu were also proved in an electrochemical study: a graphite electrode immersed in Cu/TiO_2 suspension showed dark cathodic current at about -0.9 V vs. SCE. It was checked in two simple experiments that the reduction of Cu^{2+} by illuminated titania leads to Cu(O) deposited onto semiconductor particles. Using an ion selective electrode it was found that Cu^{2+} reduction was accomplished in 20 minutes. Bigger amounts of copper ($>$ 1 wt.%) were photodeposited on the already existing metal islands. Cu^{2+} preadsorption on titania was small and did not have any influence on the hydrogen evolution activity of Cu/TiO_2. 0.5 wt.% on TiO_2 was found as an optimum metal loading.

Keywords. Photocatalysis; Copper; Titania.

Photoproduktion von Wasserstoff aus Wasser-Methanol auf kupferbeschichtetem Titanoxyd

Zusammenfassung. Es wurde die Wasserstoff-Photogenerierung aus wäßrig-methanolischen Lösungen an $CuTiO_2$ als photoaktivem System untersucht. Es wurde festgestellt, daß die Kupferdepositierung auf Titanoxydpartikeln „in situ" in einer Reaktionszelle erreicht werden kann. Das dispergierte Kupfer zeigte zufriedenstellend gute Aktivität (Quantenausbeute 4.3%) und Stabilität unter den erforderlichen Bedingungen. Die katalytischen Eigenschaften des Kupfers zur Wasserstoffentwicklung wurden auch elektrochemisch untersucht: eine Graphitelektrode in einer $Cu-TiO_2$-Suspension zeigte einen kathodischen Dunkelstrom bei ca. -0.9 V gegen eine SCE. Mittels zweier einfacher Experimente wurde überprüft, daß die Reduktion von Cu^{2+} mittels belichtetem Titanoxyd zu einem Niederschlag von Cu(O) auf den Halbleiterpartikeln führt. Mittels einer ionenselektiven Elektrode wurde festgestellt, daß die Cu^{2+}-Reduktion innerhalb von 20 Minuten erfolgte. Größere Mengen von Kupfer ($>$ 1 Gew.%) wurden auf bereits vorhandenen Metallinseln photo-depositiert. Die Präadsorption von Cu^{2+} auf Titanoxyd war gering und hatte keinerlei Einfluß auf die wasserstoffentwickelnde Aktivität von $Cu-TiO_2$. Als optimale Metallbeladung erwies sich 0.5 Gew.% Cu auf TiO_2.

Introduction

Since the first papers of Fujishima and Honda [1, 2] attention has been paid to designing of both special photoelectrochemical systems and particulate semiconductor systems which can produce hydrogen from water utilizing solar energy. The mechanism of photoelectrochemical action on dispersed semiconductors is regarded to be similar to that in liquid electrochemical photocells [3–7] although an alternate more chemical mechanism has been also proposed [4]. Hydrogen photogeneration on semiconductors, however, is suppressed by a very small rate of the reactions of H_3O^+ reduction and atomic hydrogen recombination: special catalysts with low hydrogen evolution overpotentials are required to be in contact with semiconductor surface to facilitate hydrogen evolution. Hundreds of papers have been devoted to noble metals and especially to platinum supported onto photoactive semiconductors and their catalytic action. Refs. [8–20] show some examples of them. Some other metals or compounds can replace the expensive noble metals. Metallic nickel and cobalt [9, 21–23], nickel oxide [24–26] or ruthenium dioxide [27] have been found to work efficiently as catalysts for hydrogen generation in composition with light sensitive semiconductors like TiO_2, $SrTiO_2$ or CdS. Attempts have been also undertaken to prepare bifunctional photocatalysts i.e. the semiconductor particles loaded with both hydrogen evolution (Pt) and oxygen evolution (RuO_2) catalysts [28, 29]. However, the simultaneous hydrogen and oxygen photoproduction from water is still a great problem [30, 31]. Therefore, sacrificial compounds are usually used in the investigations of hydrogen generation photosystems.

Advantage of noble metals over the other hydrogen generation catalysts is their very high activity (the lowest H_2-evolution overpotentials) and the ease of the catalyst deposition: noble metal ions are reduced by electrons photogenerated in semiconductors [see e.g., 8, 9, 18, 19, 32–37]. The last phenomenon found an application as an efficient method of recovery of precious metals from diluted solutions [20, 38–40]. Among the group of noble metals only the price of copper is reasonably low. Although the reduction potential of copper is the most negative in the group it is still positive enough for the copper(II) ions reduction by photogenerated electrons in some semiconductors. The deposition of metallic copper on irradiated TiO_2, WO_3, and ZnO in the presence of sacrificial electron donors has been described in literature [41, 42]. However, unlike other noble metal ions, copper is not reduced by irradiated titania with simultaneous oxygen evolution from water, i.e. it is not reduced in the absence of any hole scavengers [20, 40].

In previous papers platinum and ruthenium catalysts on TiO_2 particles were prepared "in situ" in hydrogen photoevolution cells [43–45]. The conditions of catalysts preparation and hydrogen photoproduction were optimized and the influence of some factors on both reactions was studied. In this paper attention is focussed on the preparation of a copper catalyst on TiO_2 particles and its activity in the system for hydrogen photoproduction.

Experimental

Characterization of Titanium Dioxide

The specific surface area of TiO_2 (Merck, Lab. # 808) was measured by a BET method on a Perkin Elmer Sorptometer model 212C using low temperature N adsorption. A reflection UV-visible spectrum in a wavelength range 200–600 nm was taken on a Specord M-40 spectrometer using MgO as a standard. X-ray diffraction analysis was performed on a TUR MG2 diffractometer using CuK_α irradiation and an Ni-filter.

Cu^{2+} *Adsorption*

For the adsorption study 0.05 g TiO_2 (Merck) was added to 100 ml of $CuSO_4$ solutions which differed in concentration: 0.36, 0.72, 1.02, 1.43, 1.79, 2.15, and $2.51 \cdot 10^{-4}$ mol $CuSo_4$ dm^{-3}. In a second series of measurements, 100 ml of $0.9 \cdot 10^{-4} m$ $CuSo_4$ solution and different amounts of TiO_2 (0.02, 0.04, 0.06, 0.08, and 0.1 g) were used. The slurries were left for 7 days and then Cu^{2+} concentration in the solutions was measured using atomic absorption spectroscopy.

Rate of Cu^{2+} *Photodeposition on* TiO_2

The rate of Cu^{2+} photoreduction by irradiated titania was measured using an ion selective electrode. An Ag – AgCl electrode was used as reference. The fade of Cu^{2+} in the slurry was monitored on a digital *pH*-meter in 5-min intervals. The slurry was illuminated with a 180 W medium pressure Hg lamp.

The catalyst slurry was prepared by adding 0.1 g TiO_2 to 10 ml H_2O and sonication. A Pyrex reaction cell (100 ml volume) was equipped with an entrance-exit system for argon and two necks to mount electrodes which were additionally tightened with rubber seals. 74 ml H_2O, 25 ml CH_3OH and 1 ml of the catalyst slurry were poured into the reaction cell and the suspension was deaerated by flowing argon. After the electrode potential became stable, i.e. after 1.5–2 h 1 ml $Cu(NO_3)_2$ ($1 \cdot 10^{-4}$ g Cu ml^{-1}) was added and irradiation was started. After all Cu^{2+} was reduced i.e. after the ion selective electrode potential returned to ther starting point 1 ml $Cu(NO_3)_2$ was introduced and the slurry was irradiated again. The procedure was repeated five times.

Measurements of the Hydrogen Evolution Overpotential

Current-voltage curves were taken on a Radius All Purpose Electrochemical Instrument coupled to an *X-Y* recorder. Three electrodes were used: a graphite (12 mm^2) working electrode, a Pt counter-electrode and a saturated calomel electrode as reference. The electrodes were immersed in the slurry of Cu/TiO_2 in water – methanol (3 : 1) – 0.5 *m* KCl. The measurements were performed under flowing argon. The presence of evolving hydrogen was checked by GC.

Cu/TiO_2 was prepared "in situ" in an electrochemical cell by photodeposition of the metal (1 wt.%) onto titania. The slurry of TiO_2 in water – methanol containing $CuSO_4$ was irradiated with a 180 W medium pressure mercury lamp for 2 h.

Studies of Hydrogen Photoproduction

The reaction was carried out in the way described previously [43, 44]. The Pyrex bottle shape reaction cell was equipped with an inlet-outlet system for argon. 100 ml of water – methanol (3 : 1) solution and an appropriate amount of the solution of copper salt were poured into the cell. The cell was placed in a Pyrex water bath with a constant temperature of 298 ± 1 K. The suspension was stirred using a magnetic stirrer. Oxygen-free argon bubbled through the slurry during the experiment. After the suspension had been deaerated (GC analysis of the outlet argon) it was illuminated with a 180 W medium pressure Hg lamp. The evolved hydrogen left the cell in a stream of argon and was analyzed by GC.

The incident light flux was $15.6 \cdot 10^{-2}$ μmol quanta s^{-1}, as measured by an uranyl-oxalate actinometer [43].

All chemicals used in this study were at least p.a. grade. The water used in the electrochemical and photocatalytic measurements was doubly distilled from a quartz vessel.

Results and Discussion

In previous two papers [43, 45] platinum and ruthenium coated titania was studied in connection to the problem of catalytic hydrogen production on irradiated semiconductor particles. A method of "in situ" Pt^{4+} and Ru^{3+} reduction by photogenerated electrons in TiO_2 particles was employed. This simple method has been recommended for studying of a noble metal-semiconductor photocatalysts, especially in sacrificial systems. It was found that there exists an optimum metal coverage on TiO_2 for efficient hydrogen photogeneration from a water – methanol solution. It was also found that preadsorption of platinum and ruthenium ions on TiO_2 influenced an initial step of hydrogen photoproduction.

In this paper copper-covered titania is examined in sacrificial hydrogen production using both photocatalytic and electrochemical methods. Attention is also focussed on the problem of Cu/TiO_2 preparation. Cu^{2+} preadsorption on titania and the rate of copper(II) reduction by photogenerated electrons in TiO_2 are studied.

Titanium dioxide used in the present study was anatase by XRD, its specific surface area was about $6\,m^2g^{-1}$. The UV-visible spectrum of titania (not shown in the paper) showed an absorption edge at 380 nm corresponding to the value of a forbidden gap of anatase which, according to literature (see e.g. [46]), amounts 3.2 eV.

Adsorption of Cu^{2+} on TiO_2 was investigated using either a constant amount of titania and different concentrations of $CuSO_4$ solution or constant concentration of copper sulfate and a different weight of TiO_2. It was established in both experiments that the amount of copper adsorbed on TiO_2 was constant, independent of the Cu^{2+} concentration 29 µg Cu^{2+} adsorbed on 1 g TiO_2. Fig. 1 shows the results of copper(II) adsorption vs. $CuSO_4$ concentration. Taking into account the specific surface area of TiO_2, the specific adsorption amounts $4.4 \cdot 10^{16}$ Cu^{2+} ions per $1\,m^2$. This value is about two orders of magnitude less than the amount of ions needed for monolayer coverage (which amounts to about 10^{18} per $1\,m^2$ [47]).

It was observed in the previous study [43, 45] that Pt^{4+} and Ru^{3+} preadsorption on TiO_2 influenced the hydrogen evolution rates at the beginning of illumination. In other words the adsorption caused fast reduction of metal ions on the particle surface. Such an effect is not expected in this study due to the very small Cu^{2+} adsorption on TiO_2: even for the smallest Cu-coverage used in the photocatalytic studies ($Cu:TiO_2=0.001$, see below) only about ¼ Cu^{2+} ions from the solution can be adsorbed by the suspended TiO_2 particles. The rather high adsorption of Pt(IV) and Ru(III) postulated previously [43, 45] could be caused partly by hydrolysis of H_2PtCl_6 and $RuCl_3$ in highly diluted solutions (*pH* of the starting metal solutions raised with dilution) and precipitation of unsoluble hydroxides or hydrates oxides on the surface of titania.

Fig. 2 shows the fade of Cu^{2+} concentration during irradiation of the slurry of TiO_2 in the presence of $Cu(NO_3)_2$ (weight ratio $Cu:TiO_2=0.001$) in a water – methanol solution. It is seen from Fig. 2 that the complete photoreduction

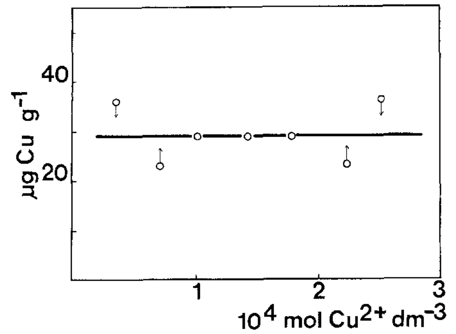

Fig. 1. Amount of Cu^{2+} adsorbed on TiO_2 vs. concentration of $CuSO_4$ solution

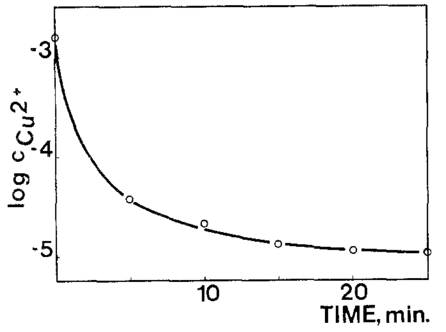

Fig. 2. Rate of Cu^{2+} photoreduction on TiO_2 from the solution of $CuSO_4$

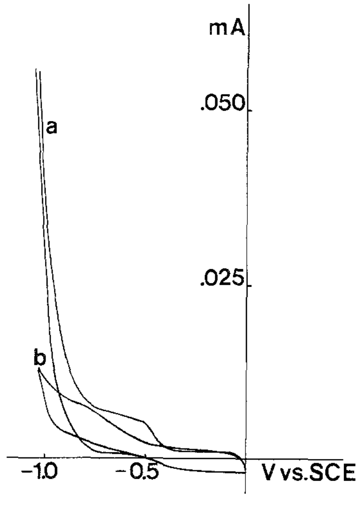

Fig. 3. *I-V* curve for a graphite electrode immersed in Cu/TiO_2 suspension in water – methanol (3 : 1) – 0.5 m KCl (curve *a*), and the electrode immersed in a TiO_2 suspension in water – methanol – KCl (curve *b*)

of Cu^{2+} by photogenerated electrons is accomplished in about 20 minutes. The reduction of the second portion of $Cu(NO_3)_2$ was a little slower. The reduction of the next portions of copper nitrate followed exactly the reduction curve for the second $Cu(NO_3)_2$ portion (not shown in the paper). Therefore it can be concluded that the additional Cu^{2+} ions are photoreduced on the already existing Cu-islets on the surface of titania. Hence, a screening effect of the photosensitive TiO_2 surface by deposited copper for a larger amount of the deposit should not take place.

Fig. 3 shows *I-V* curves taken at a graphite electrode immersed in Cu/TiO_2 suspension. The cathodic current at a negative potential (vs. SCE) in the slurry of Cu/TiO_2 corresponds to the hydrogen evolution overpotential of the copper dispersed on titania. Curve (*b*) represents the results of *I-V* measurements in a slurry of TiO_2 in water – methanol – KCl. Exactly the same curve was observed in water – methanol – KCl solution only. Hence curve (*a*) does not show any changes connected to the presence of titania. The H_2-evolution overpotential of Cu/TiO_2 estimated from Fig. 3 amounts to about – 0.9 V vs. SCE. The value is similar to that found before for silica supported tungsten disulfide [49]. The hydrogen evolution overpotential showed by a graphite electrode immersed in a Pt/SiO_2 slurry was about – 0.6 V vs. SCE [49]. The overpotential showed by Cu/TiO_2 is reasonably small and is an evidence of good H_2-evolution catalytic properties of the dispersed copper on titania.

Figs. 4–6 show results of hydrogen photoproduction from a water – methanol solution. Optimization of the reaction conditions is shown in Figs. 4 and 5. It was

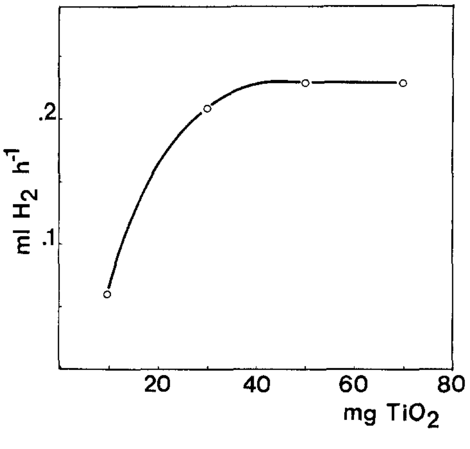

Fig. 4. Rate of hydrogen photoproduction from water – methanol vs. the amount of TiO_2 ($Cu:TiO_2 = 0.005$)

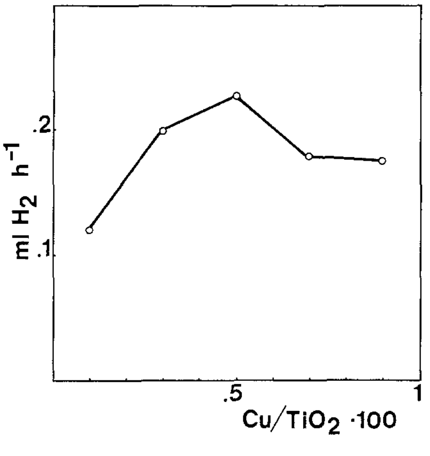

Fig. 5. Rate of hydrogen photoproduction from water – methanol vs. the $Cu:TiO_2$ ratio (amount of $TiO_2 - 0.005$ g)

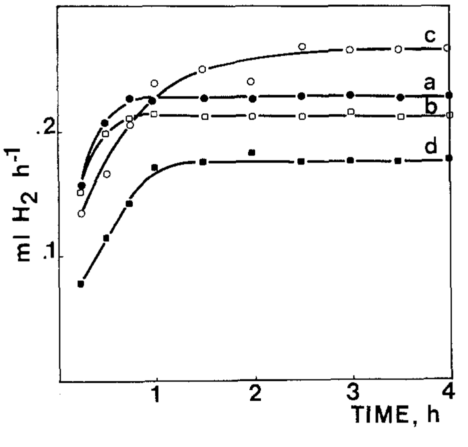

Fig. 6. Rate of hydrogen photoproduction from water – methanol vs. time using different salts of copper ($Cu:TiO_2 = 0.005$); *a*: $CuCl_2$; *b*: $CuSO_4$; *c*: $(CH_3COO)_2Cu$; *d*: $Cu(NO_3)_2$

established from the figures that the optimum amount of TiO_2 was 0.05 g and the optimum $Cu:TiO_2$ ratio was 0.005. Therefore, 0.05 g TiO_2 and the amount of solutions which contained 0.00025 g of copper ($Cu/TiO_2 = 0.005$) were used in further investigations. Fig. 6 shows H_2-photoproduction rates vs. time using different salts of copper. The highest hydrogen yield was found when copper acetate was used as a Cu^{2+} source, the lowest in the presence of copper nitrate. It should be mentioned that CH_3COO^- is the only anion among the ones used here which is consumed (oxidized) during illumination of the semiconductor suspension [30].

The observed lower hydrogen photogeneration rate at the beginning of the process is caused by Cu^{2+} photoreduction and formation of a Cu-deposit on the surface of the titania particles. Note that no hydrogen is photoproduced unless at least traces of a H_2 generation catalyst are present on the semiconductor particles. The quantum yield of hydrogen photoproduction using copper acetate as a source of Cu^{2+} was 4.3%. The quantum yield is defined as the ratio of the hydrogen atoms produced to the incident light flux: $[(\mu mol\ H_2 s^{-1}) \cdot 2/\mu mol\ quanta\ s^{-1}] \cdot 100\%$. The value of the quantum yield was not corrected for light scattering on the catalyst particles.

It was observed in a separate experiment that the yield of hydrogen photoproduction from water – methanol on Cu/TiO_2 [using $(CH_3COO)_2Cu$] did not change remarkably during 48 hours of illumination.

Comparing the above results to these on Pt/TiO_2 [43] one can state that although the hydrogen photoproduction yield from water – methanol on Cu/TiO_2 is about five times less than on platinized titania, it may be considered still reasonably high and the system is stable during long term illumination.

There exist different opinions regarding Cu^{2+} photoreduction on TiO_2 particles. Some authors found that both with and without sacrificial electron donor the deposit consisted of metallic copper [38]. In the opinion of the others [14, 20, 48] the copper(II) ions were reduced to Cu^+. All authors observed the non-stability of the deposit when exposed to the air. The unstability of copper deposit was observed also in this study: the purple-gray suspension turned white after the reaction cell had been opened to air. However, the deposit was stable when the slurry was kept at inert atmosphere.

Two simple experiments were performed in order to establish if Cu^{2+} ions were reduced by irradiated TiO_2 to metallic copper or copper(I) oxide. In two different vessels the slurries of Cu/TiO_2 (photodeposited, see Exp. Part) and Cu_2O (freshly prepared by reduction of Cu^{2+} with glucose) were prepared in water – methanol and kept under flowing argon. In the first experiment a little conc. HCl was added to both slurries, in the second a little conc. H_2SO_4. In both cases changes were observed in the Cu_2O slurries (white CuCl and Cu + $CuSO_4$ after addition of HCl and H_2SO_4, respectively). The Cu/TiO_2 slurry remained unchanged after both acids had been added. Therefore one can conclude that under the hydrogen generation conditions (see Exp. Part) the deposit of metallic copper was formed on the surface of TiO_2 particles.

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