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Dioxygen Evolution from Inorganic Systems. Reactions and Catalytic Properties of Loaded TiO_2 Particles in Photochemical Dioxygen Generation

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The efficiency of differently prepared TiO_2 particles in photochemical water splitting through band gap irradiation of aqueous suspensions has been investigated. The effect of pH and loading with noble metals and RuO_2 has been examined. Particular attention has been devoted to dioxygen evolution and photoadsorption.

Introduction

During the last few years there has been increasing interest in the use of semiconductors in photosynthetic and photocatalytic processes [1]. In particular, since the work of Fujishima and Honda with TiO_2 electrodes [2], the photochemical cleavage of water has received considerable attention [3]. The water splitting was then achieved photoelectrochemically [4] but, in this case, only the light absorbed at the semiconductor–liquid interface can initiate the reactions.

It now seems possible to carry out many reactions previously carried out with electrodes using the semiconductors in powder or colloidal form [3, 5]. Such systems have a large surface area and are simpler and less expensive to construct and use than the corresponding photoelectrochemical cells.

The irradiation of a semiconductor with light of energy equal to or higher than the band gap creates an electron–hole pair near the surface [6].

$$\text{semiconductor} + h\nu \longrightarrow h^+ + e^- \qquad (1)$$

The generated electron and hole can be used to drive a thermodynamically uphill reaction (heterogeneous photosynthesis) or to increase the rate of a thermodynamically favoured reaction (heterogeneous photocatalysis) [1]. The first type of reaction is of considerable interest in energy storage and the use of semiconductor particles, eventually loaded with metals or metal oxides, has been investigated in a wide variety of processes involving numerous substrates, *e.g.* water [7–17], hydrogen sulphide [18], and dehydrogenation of alcohols [29–21]. Indeed the photodecomposition of water on semiconductor particles has received considerable interest recently and several papers report on water photolysis by illuminating suspensions of TiO_2 [7–15], $SrTiO_3$ [16, 22], CdS [17] and photochemical diodes consisting of n-TiO_2/p-GaP [23].

Since some aspects of the process are still unclear, the present paper reports on the use of differently prepared TiO_2 particles for the photochemical cleavage of water, with particular attention to dioxygen evolution.

Experimental

Materials

All reagents were analytical grade and were used as supplied. RuO_4 (Alfa) and $RuCl_3 \cdot H_2O$ (Fluka) were *purissimum* grade. The following TiO_2 were used: TiO_2 Degussa P 25, TiO_2 Bayer sol, TiO_2 Montedison, TiO_2 British Tioxide. Most of them are commercially available; more details on TiO_2 Montedison have been previously reported [24].

Deionized water was refluxed over alkaline permanganate and subsequently distilled three times in a quartz vessel.

Preparation of the Catalysts

TiO_2 were used as supplied without any further modification of the surface. In Table I the surface area and the pH of a solution containing 0.5 g l^{-1} of the different TiO_2 preparations are reported. Each experiment was performed with 0.5 or 1.0 g l^{-1} of TiO_2.

The loading of TiO_2 with RuO_2 can be carried out via RuO_4 decomposition, according to $RuO_4 \rightarrow RuO_2 + O_2$. The process is catalyzed by light. When the surface is not modified by temperature treatment the $RuCl_3$ method is preferred to the previous one. In this preparation the sample is treated at up to 320 °C for two hours in the presence of air. The RuO_4 method is mainly used for colloidal TiO_2 [25], while the

TABLE I. Characteristics of Differently Prepared TiO_2.

Sample	Surface area ($m^2\ g^{-1}$)	pH of solution containing $0.5\ g\ l^{-1}$
TiO_2 Degussa P25	55	4.9
TiO_2 British Tioxide	60	6.0
TiO_2 Bayer sol (anatase)	200	3.9
TiO_2/RuO_2 Bayer sol (anatase)	220	3.5
TiO_2 Montedison (anatase)	200	3.2
TiO_2(Nb doped)/RuO_2 Montedison	240	3.5

$RuCl_3$ method is used for powders. A modification of the $RuCl_3$ method was employed to load TiO_2 Montedison with RuO_2; in this preparation $RuCl_3$ is dissolved in KOH and the mixture $RuCl_3-TiO_2$ is heated up to 100 °C overnight in the presence of air [24]. The resultant RuO_2 loading is 0.1%.

The final step of the catalyst preparation consisted of loading with Pt particles. An aqueous solution of H_2PtCl_6 is prepared and reduced with citrate as previously described [26]. The resultant ultrafine Pt sol (particle diameter is $\leqslant 30$ Å) is subsequently mixed with the solution containing TiO_2 or TiO_2-RuO_2 particles and sonicated. The final Pt concentration was 40 mg l^{-1}, except for cyclic water splitting experiments where the Pt loading was 1%.

The activities of Cu, Ag, Pd, Rh and Pt loading on TiO_2 were compared using the following procedure: a solution of the chloride or nitrate salt of the metal was reduced in H_2 on TiO_2. The powder was subsequently heated at 150 °C for 2 hours. The metal loading was 1%.

Apparatus

Continuous illumination was carried out with an Osram X BO 450 W Xe lamp equipped with a 15 cm water jacket to remove IR radiation. The solution volume for O_2 uptake experiments was 15 ml and was contained in a Pyrex flask equipped with optically flat entry and exit window. The filter effect of the Pyrex for UV light is significant. The transmission of the entry window is 50% at 325 nm and virtually zero below 300 nm.

For H_2 evolving experiments a 25 ml solution was employed. H_2 production was analyzed by gas chromatography with a Gow Mac system, carbosieve column (35 °C) and Ar as carrier gas. O_2 was analyzed using a Teledyne B1 oxygen-specific microfuel cell. The setup has already been described in a previous paper [25]. Alternatively a gas chromatographic method, Poropack Q column and He as carrier gas, was used.

BET measurements were performed by a Micromeritics 2205 High Speed Surface Area Analyzer, using Ar and assuming the area of an Ar atom to be 13.8 $Å^2$.

Results and Discussion

Dioxygen Photoadsorption

This process has been found to occur efficiently on highly hydroxylated anatase [27] and evidence of $HO_2\cdot$ radicals [11] leads to the suggestion that dioxygen may be preferentially reduced at the conduction band of the semiconductor.

The amount of O_2 taken up by differently prepared TiO_2 was determined by carrying out blank experiments; Table II lists the O_2 percentage detected 1 hour after the injection of a known amount of O_2. The Table offers evidence that O_2 is adsorbed by the particles [28] and that UV light and the deposited redox catalysts (Pt and RuO_2) favour the photoadsorption. Besides, differently prepared TiO_2 exhibit different properties in this process as in other photocatalytic reactions [21]; a possible explanation may be the different surface properties, outlined in Table I, which strongly affect the catalytic behavior [29].

The kinetics of O_2 photouptake are illustrated in Fig. 1. It is evident that *ca.* 50% of the O_2 is adsorbed in *ca.* 30 minutes under the reported experimental conditions, in the presence of $TiO_2/RuO_2/Pt$ (Montedison). After 1 hour of illumination, O_2 decreased to

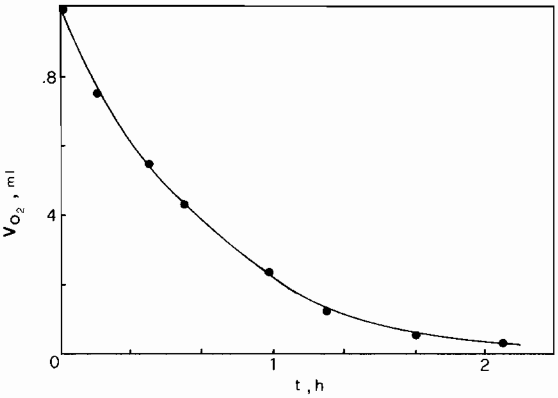

Fig. 1. Kinetics of O_2 uptake (measured with microfuel cell). 1 ml of O_2 injected in 15 ml of solution containing 0.5 g l^{-1} of $TiO_2(Nb)/RuO_2/Pt(8\%)$ Montedison.

TABLE II. O_2 Photouptake by TiO_2 Dispersions.[a]

Sample	% O_2 detected		
	no light no Pt	with light no Pt	with light Pt 40 mg l^{-1}
TiO_2 Degussa P25	77	75	45
TiO_2 Bayer sol	75	75	44
TiO_2/RuO_2 Bayer sol	74	50	44
TiO_2 Montedison	75	75	30
$TiO_2(Nb)/RuO_2$ Montedison	77	50	20

[a]Experimental conditions: TiO_2 0.5 g l^{-1}; 15 ml solution;pH adjusted to 4.5 by addition of HCl or NaOH. Injection of 0.2 mol of O_2 and measurements performed after 1 hour of irradiation. In absence of TiO_2, the solubility of O_2 in water allows only *ca.* 78–80% of O_2 injected to be detected.

20% of its initial value. Further injection of O_2 leads again to photoadsorption till the limiting capacity is reached.

In order to check the possibility of preventing O_2 adsorption, the effect of added anions was investigated. The TiO_2/RuO_2 (Montedison) catalyst was prepared in a solution containing H_3PO_4 (2%) or HCl (2%), stirred for some hours and then the pH was raised to 4.7. The photouptake (UV light) of O_2 was 50% for untreated catalyst and 30% and 20% when phosphate and chloride, respectively, were present.

Phosphate ions are known to be strongly adsorbed at TiO_2 surfaces [30] and the concentration used allows a very high surface coverage. Many other anions, such as sulphate, carbonate, perchlorate, are adsorbed in a similar manner; however little adsorption is reported for nitrate and chloride [30].

The treatment of TiO_2/RuO_2 (Montedison), by heating at 600 °C overnight, does not however change significantly the O_2 photouptake.

Sacrificial Dioxygen Generation

To test the efficiency of the photocatalyst for O_2 evolution, an electron acceptor (A) can be added to scavenge the electron generated in the conduction band by irradiation of the semi-conductor. This allows the hole which remains to be available at the semiconductor surface where the oxidation process takes place

$$A + e^- \longrightarrow A^- \qquad (2)$$

$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+ \qquad (3)$$

As sacrificial agents, $AgNO_3$, K_2PtCl_6, $FeCl_3$ and $Co(NH_3)_5Cl^{2+}$ were used. Table III reports the O_2 evolution rates with TiO_2 Degussa P 25 as catalyst. The effect of several parameters was explored using $AgNO_3$. In this system the conduction band electrons reduce Ag^+ to elemental silver, which is deposited onto the TiO_2 particles [31]. The decrease of Ag^+ concentration during photolysis can be followed with the aid of a Ag^+ specific electrode.

TABLE III. O_2 Evolving Systems. TiO_2 Degussa P25 in the Presence of Ag^+ as Electron Acceptor.[a]

pH	$[Ag^+]_0$ [b]	$\Delta[Ag^+]$ [b]	O_{2calc} [c]	O_{2det} [c]
1.0	2.8×10^{-2}	4.0×10^{-3}	350	50
3.5	5.0×10^{-2}	6.3×10^{-3}	520	170
4.9	3.3×10^{-2}	9.6×10^{-3}	780	290
4.9	5.3×10^{-2}	7.6×10^{-3}	630	220
3.5	7.2×10^{-3}	4.9×10^{-3}	410	180
3.5[d]	7.2×10^{-3}	4.2×10^{-3}	350	280

[a]TiO_2 1 g l^{-1}; 1 hour of irradiation. [b]*M*. [c]μl. [d]Added $NaNO_3$ 5×10^{-2} *M*.

Table III shows the effect of pH, Ag^+ initial concentration and ionic strength on O_2 generation. In the presence of 5×10^{-2} *M* $NaNO_3$ the evolved O_2 accounts for 80% of the reduced Ag^+. Also with TiO_2/RuO_2 (Montedison), after irradiation in the presence of $AgNO_3$ and $NaNO_3$, 80% of the stoichiometric quantity of O_2 can be detected.

Table IV lists the O_2 detected with different TiO_2 preparations: also in this case the influence of the method of preparation and hence of the surface chemistry is evident.

Figures 2 and 3 show the effect of TiO_2 concentration and RuO_2 loading on O_2 evolution. The trend of Fig. 2 can be explained by the increase in absorbed light with increasing TiO_2 concentration. When all the incident light is absorbed a further increase in the particle concentration only reduces the penetration of incident light.

The RuO_2 loading shows however a moderate beneficial effect up to 2%; further increase of RuO_2 does not improve the O_2 evolution rate. This acceleration can be attributed to a selective function of RuO_2 as a hole-transfer catalyst [14]. RuO_2 colloids [32] and RuO_2 deposited onto TiO_2 [33, 34] were also shown to increase strongly the reaction rate of oxidizing agents with water or hydroxide ion.

TABLE IV. Comparison of Differently Prepared TiO_2 in O_2 Evolving Systems with Ag^+ as Electron Acceptor.[a]

Sample	pH	$[Ag^+]_0$[b]	$\Delta[Ag^+]$[b]	O_{2calc}[c]	O_{2det}[c]
TiO_2 Degussa P 25	3.5	5.0×10^{-2}	6.3×10^{-3}	520	170
TiO_2 Montedison	3.2	6.9×10^{-2}	7.6×10^{-3}	630	50
TiO_2 Bayer sol	3.9	5.8×10^{-2}	5.2×10^{-3}	435	40
TiO_2/RuO_2 Bayer sol	3.5	4.4×10^{-2}	1.8×10^{-3}	150	15
$TiO_2(Nb)/RuO_2$ Montedison	3.5	5.0×10^{-2}	2.2×10^{-3}	185	25

[a] TiO_2 1 g l^{-1}; 1 hour of irradiation. [b] *M*. [c] μl.

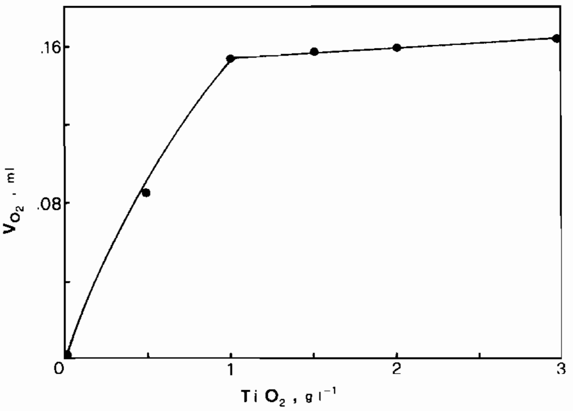

Fig. 2. Effect of the amount of TiO_2 Degussa P 25 on the O_2 (measured with microfuel cell) evolution (ml in 1 hour) (pH 3.5; 15 ml sample; $[Ag^+]_0 = 5 \times 10^{-2}$ *M*).

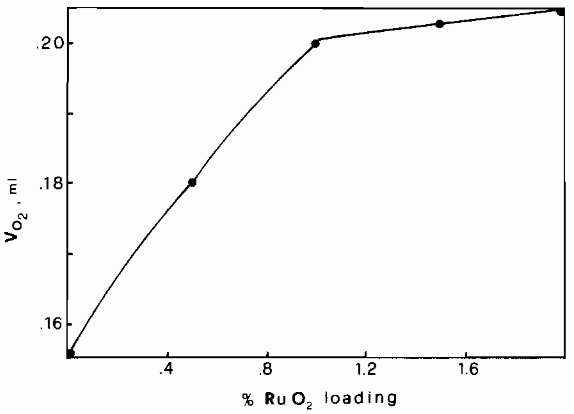

Fig. 3. Effect of RuO_2 loading on O_2 (measured with microfuel cell) evolution (ml in 1 hour) (TiO_2 Degussa P 25 1 g l^{-1}; pH 3.5; 15 ml sample; $[Ag^+]_0 = 5 \times 10^{-2}$ *M*).

The deposition of Pt or Pd onto the catalyst has no relevant effect on O_2 evolution rate. In experiments carried out at pH 4.9 with Ag^+ 2.5×10^{-2} *M* and 12.5 mg of catalyst in 25 ml, the O_2 evolution rate was 150 μl h^{-1} with TiO_2 Degussa P 25; 230 μl h^{-1} with TiO_2 Degussa P 25 loaded 1% Pt and 150 μl h^{-1} loaded 1% Pd; 45 μl h^{-1} with TiO_2 Bayer and 30 μl h^{-1} loaded 1% Pd.

The results concerning $FeCl_3$ as sacrificial agent are reported in Table V. The crucial effect of the presence and type of semiconductor and UV light as well as pH dependence is evident from these results.

TABLE V. O_2 Evolving Systems. TiO_2 Degussa P 25 in the Presence of $FeCl_3$ as Electron Acceptor.[a]

$[Fe^{3+}]_0$[b]	pH	O_{2det}[c]
2.5×10^{-2}	0.5	40
	1.9	160
	2.5	95
	3.0	85
	4.9	20
2.5×10^{-2}	2.6	100
1.25×10^{-2}		90
2.5×10^{-3}		80

[a] TiO_2 1 g l^{-1}; 1 hour of irradiation. [b] *M*. [c] μl.

Sacrificial Dihydrogen Generation

The activity of different photocatalysts was tested by addition of an electron donor (EDTA) to scavenge the hole generated on irradiation of the semiconductor with band-gap light. The remaining electron in the conduction band can give rise to reduction process

$$\mathrm{EDTA} + h^+ \longrightarrow \text{products} \tag{4}$$

$$2H^+ + 2e^- \longrightarrow H_2 \tag{5}$$

Table VI reports the effect of the loading with metals (Cu, Ag, Pd, Rh, Pt) on differently prepared TiO_2. While Pt exhibits a strong increase in the H_2 evolution rate [25, 35–38] only Pd and Rh appear to enhance appreciably the photocatalytic activity. RuO_2 deposition shows only a moderate effect although it has been recently reported that RuO_2 can also be an effective redox catalyst for H_2 evolution [39].

Nonsacrificial Systems

It has been shown in the preceding sections that TiO_2 can reduce or oxidize water in the presence of a proper electron donor or acceptor, respectively. If a cyclic system is the goal, reactions (3) and (5)

TABLE VI. H_2 Evolution by Band Gap Irradiation in Sacrificial Systems.[a]

Sample	H_2 ml h^{-1}
TiO_2 Degussa P 25	0.32
TiO_2 Degussa P 25 + 1% Cu	0.76
TiO_2 Degussa P 25 + 1% Ag	0.22
TiO_2 Degussa P 25 + 1% Pd	4.0
TiO_2 Degussa P 25 + 1% Rh	2.0
TiO_2 Degussa P 25 + 1% Pt	2.4
TiO_2 Degussa P 25 + 1% RuO_2	0.50
TiO_2 Bayer sol	0.26
TiO_2 Bayer sol + 1% Pt	7.0
TiO_2 Bayer sol + 1% Pd	3.6

[a] TiO_2 0.5 g l^{-1}; 25 ml sample; pH 4.7; EDTA 0.1 *M*.

TABLE VII. H_2 Evolution by Band Gap Irradiation in Non-sacrificial System.[a]

Sample	H_2 μl h^{-1}
TiO_2 Montedison	5
$TiO_2(Nb)/RuO_2$ Montedison	35
$TiO_2(Nb)/RuO_2/Pt(1\%)$ Montedison	350
$TiO_2(Nb)/RuO_2/Pt(1\%)$ Montedison + 3% Cl^-	75
$TiO_2(Nb)/RuO_2$ Montedison + 3% phosphate	3
$TiO_2(Nb)/RuO_2$ Montedison + 3% Cl^-	traces
TiO_2 Bayer sol	6
TiO_2/RuO_2 Bayer sol	12
$TiO_2/Pt(1\%)$ Bayer sol	90
$TiO_2/RuO_2/Pt(1\%)$ Bayer sol	100
TiO_2 Degussa P 25	4
$TiO_2/Pt(1\%)$ Degussa P 25	60
$TiO_2/Pt(1\%)$ Degussa P 25 + 3% Cl^-	8
$TiO_2/Pt(1\%)$ Degussa P 25 + 3% ClO_4^-	0
$TiO_2/Pt(1\%)$ Degussa P 25 + 3% SO_4^{2-}	0

[a] TiO_2 0.5 g l^{-1}; 25 ml flask; pH 4.7; Pt citrate method; H_2 evolution rate averaged over 5 hours.

would occur simultaneously. Water splitting on TiO_2 [7–14] and $SrTiO_3$ [16] powders has been observed before, although with low efficiency.

Table VII reports the H_2 evolution rate with different photocatalysts under different conditions. Again the H_2 evolution rate is influenced by the origin of the TiO_2; RuO_2 is moderately beneficial and Pt deposit has a considerable effect on the efficiency. The effects of semiconductor concentration, of pH and of Pt deposition are similar to those observed in related photosynthetic processes [13–15].

The presence of anions which can be adsorbed at the particle surface strongly inhibits H_2 formation. Similar effects due to the occupation of surface sites have already been reported [15, 40]. It is noteworthy that if TiO_2/RuO_2 (Montedison) is saturated with O_2 (a sample was irradiated in the presence of O_2 until no more O_2 was adsorbed), even after 12 hours of exposure to UV light no H_2 is detected.

Only traces of O_2 can be observed after some hours of irradiation, and this can be attributed to the O_2 adsorption and photoadsorption at the catalyst surface, as reported above. Attempts to desorb O_2 after addition of an inert salt were only partially successful, and, if the adsorbed species are added before photolysis, they prevent H_2 evolution.

When prolonged irradiations are performed, the rate of H_2 evolution levels off. This effect could be due to H_2 and O_2 recombination [8, 10, 13, 14]. In fact if the system is allowed to stay in the dark, H_2 is slowly consumed; after addition of 3% of $NaClO_4$ the decrease in H_2 starts again (see Fig. 4).

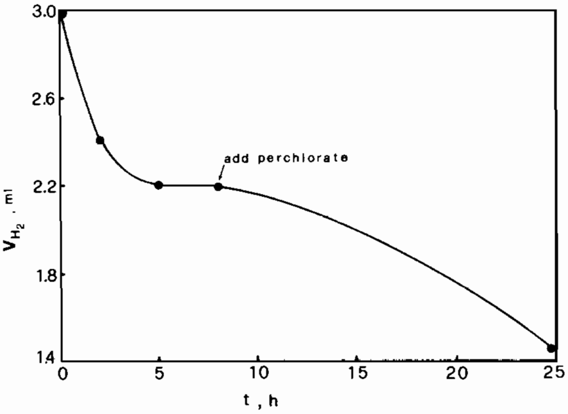

Fig. 4. $H_2 + O_2$ recombination rate on $TiO_2/Pt(4\%)$ Bayer sol (TiO_2 0.5 g l^{-1}; 25 ml sample irradiated for several hours).

Conclusions

Several basic features concerning the properties of semiconductor particles relevant to H_2 and O_2 evolution from water have been reported. The crucial aspects of TiO_2 preparation and the consequent surface chemical properties as well as the importance of noble metal and RuO_2 loading (and of the method of bifunctional catalyst preparation) have been demonstrated.

Photouptake of O_2 has also been investigated and appears as an important phenomenon in the process.

Understanding of these fundamental parameters is essential in the development of more efficient catalysts for water cleavage devices.

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