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F. T. Wagner, S. Ferrer, and G. A. Somorjai

August 1979

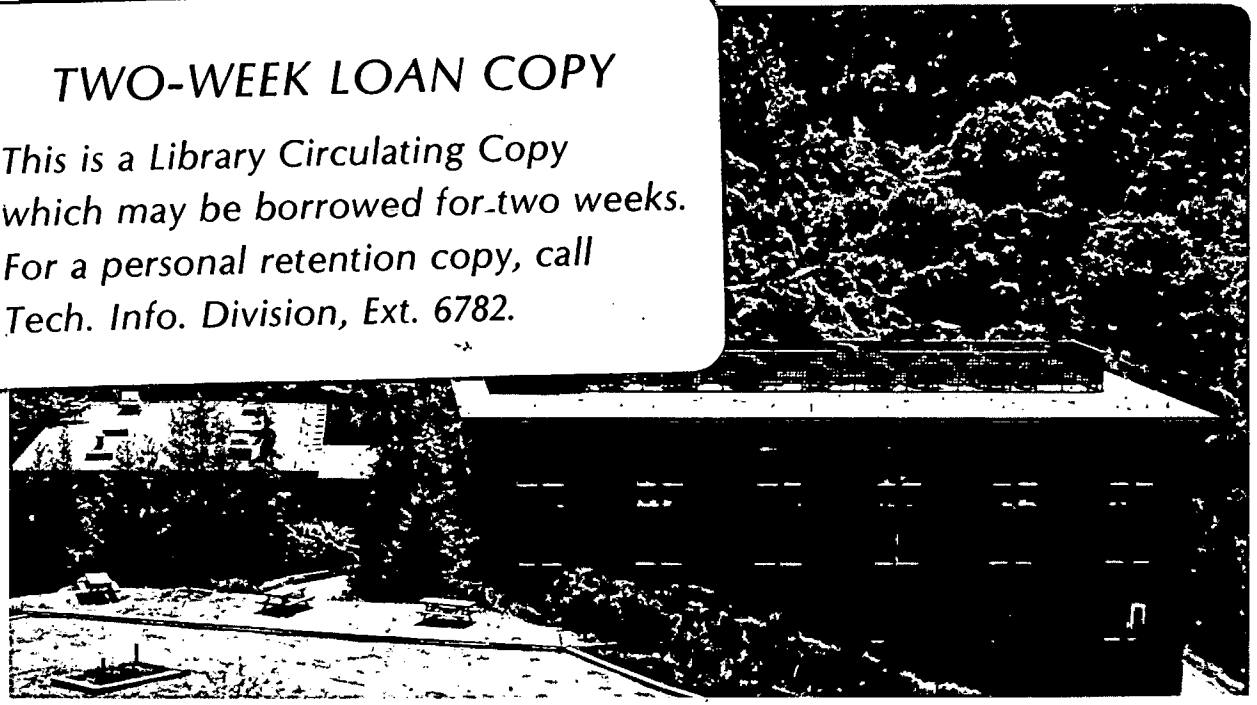
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PHOTOGATALYTIC HYDROGEN PRODUCTION FROM WATER
OVER SrTiO_3 CRYSTAL SURFACES, ELECTRON
SPECTROSCOPY STUDIES OF ADSORBED H_2 , O_2 and H_2O

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Abstract

Hydrogen production from metal-free, as well as from platinized, SrTiO_3 crystals has been observed upon illumination in water vapor saturated films of soluble ionic compounds and in aqueous electrolytes. Hydrogen production occurs at the illuminated surface of metal-free crystals, implying a mechanism rather different from that operating in SrTiO_3/Pt photoelectrochemical cells. Hydrogen production rates increase with increasing hydroxide concentration in the electrolyte. This (OH^-) dependence of the rate is particularly strong in the 5N-20N concentration range.

Photoemission studies have identified a reduced surface species ascribed to Ti^{+3} and hydroxyl groups on $\text{SrTiO}_3(111)$. This surface species is involved in photoactivity related to oxygen adsorption and photodesorption. The concentration of surface hydroxyl groups can be monitored with UPS.

Introduction

The technological challenge of storing solar energy in chemical fuels constantly grows in importance as reserves of fossil fuels dwindle. Most of our present supplies of fuels are obtained from fossil raw materials with the aid of heterogeneous catalysis. Heterogeneous photocatalytic processes may eventually combine the product specificity and high rates presently obtained in ordinary thermodynamically downhill surface catalysis with an overall boost in chemical free energy derived from light. Much of the success of present surface catalytic processes derives from the ability to independently vary the temperature and pressures in gas phase reactions to optimize thermodynamic and kinetic reaction parameters. The study of gas-solid heterogeneous photocatalytic reactions is

thus of considerable interest.

One of the most efficient means of direct solar-chemical energy conversion available at present is not a gas-solid device, but rather the n-type SrTiO_3/Pt photoelectrochemical cell operating in aqueous electrolyte.^{1,2,3} This cell can convert about 1% of incident solar radiation into hydrogen through the photoassisted electrolysis of water. Such cells produce hydrogen and oxygen from water even when no external potential is applied between the SrTiO_3 photoanode and the platinum cathode. But sustained operation of these devices with physically separated anodes and cathodes requires the flow of net ionic currents through the electrolyte. No such ionic currents could be maintained in the gas phase. Thus, a new reaction mechanism involving no long-distance ion transport seems to be necessary for the sustained operation of a thermodynamically uphill gas-surface photoredox reaction. In this paper we report preliminary evidence for the operation of such a mechanism at the liquid-solid interface and summarize the results to date of attempts to further elucidate the nature of photoassisted processes on SrTiO_3 , through detailed surface studies carried out in ultrahigh vacuum.

We have measured sustained hydrogen photo production from metal-free, as well as from partially platinized, SrTiO_3 crystals.⁴ The crystals were illuminated either while covered with water vapor saturated films of basic deliquescent compounds (NaOH , KOH or Cs_2CO_3), or while immersed in aqueous alkaline electrolyte. In agreement with the conclusion of Wrighton, Wolczanski and Ellis,⁵ water dissociation on platinized pre-reduced SrTiO_3 crystals appears to occur, for the most part, via a mechanism analogous to that operating in photoelectrochemical cells. That is, oxygen is evolved from the illuminated exposed SrTiO_3 surfaces while hydrogen is produced on platinized areas. In contrast, hydrogen is evolved from

the illuminated SrTiO₃ surface in the absence of any metallic coating on the crystal. This is indicative of a photocatalytic mechanism distinct from the process operative in photoelectrochemical cells. This photocatalytic process may not require long-range ion transport and probably occurs through surface charge traps. The rates of hydrogen photoproduction from both metal-free and increasing platinized SrTiO₃ crystals increase with / concentration of a sodium hydroxide electrolyte in the range of 10⁻³N - 20N. No hydrogen production was observed in neutral or acidic media. Though a number of explanations for this hydroxide concentration dependence are possible, our data lend support to the suggestion^{6,7} that surface hydroxylation is important to the kinetics of photochemistry on oxide semiconductor surfaces.

We have also undertaken photoelectron spectroscopic studies of clean SrTiO₃ (111) surfaces and their interactions with adsorbed molecules and light.^{8,9} Among other goals, we hope to investigate the chemistry of surface charge-trapping species and of surface hydroxyl groups. Using X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) we can monitor changes in the surface concentrations of a reduced species ascribed to Ti⁺³^{9,10} and identify surface hydroxyl groups. Auger electron spectroscopy (AES) is used to monitor changes in surface elemental composition. Low energy electron diffraction (LEED) gives structural information on ordered surfaces.

We have studied the (111) surfaces of reduced (n-type) and stoichiometric SrTiO₃ single crystals. The argon-sputtered surface of the reduced crystals shows a high concentration of Ti³⁺. Oxygen adsorption on this surface oxidizes Ti³⁺ to Ti⁴⁺, the predominant titanium species in the bulk crystal lattice. Subsequent exposure to bandgap radiation leads to the photodesorption of the oxygen and partially restores the surface Ti³⁺ sites. Hydrogen gives similar but smaller

decreases in surface Ti^{3+} concentration upon adsorption and illumination also restores part of the initial Ti^{3+} concentration. Water adsorption decreases the Ti^{3+} concentration, but no photoregeneration of Ti^{3+} was observed on the water-covered surfaces.

Our surface studies have identified the presence of hydroxyl species on $SrTiO_3(111)$ surfaces that form upon water or hydrogen adsorption. Research is continuing to identify the roles played by these species in the photocatalytic hydrogen production from water and towards the development of sustainable gas-solid heterogeneous photocatalytic processes.

Experimental

Hydrogen production experiments

All hydrogen production experiments were performed in reaction chambers capable of being evacuated and then backfilled with water vapor at room temperature. Products were detected by gas chromatographic sampling of a gas phase consisting of water vapor, argon and products which circulated in a closed loop by the $SrTiO_3$ crystal or, in some experiments, over the electrolyte in which the crystal was immersed. Hydrogen production rates as low as 12×10^{15} molecules per hour were readily measurable, rates one-quarter of this would have been noticed. Technical difficulties placed the smallest detectable oxygen evolution rate above 10^{17} molecules per hour. One monolayer of product is defined as 1×10^{15} molecules/cm² of illuminated surface. This is the order of magnitude of the atomic density on the $SrTiO_3(111)$ surface.

Three series of experiments were carried out in two different reaction cells. In the first series, clean $SrTiO_3$ crystals, with or without platinum, were illuminated in water vapor. In the second series the crystal and its vycor glass mounting bracket were coated with a crust of a water soluble ionic

compound, saturated with water vapor, and illuminated. These two series of experiments were carried out in a stainless steel gas phase reaction cell. In the third series of experiments the crystal rested in a 10 ml pool of thoroughly outgassed aqueous electrolyte in a 25 ml pyrex flask that was inserted into the vacuum line.

Crystal preparation

Crystal wafers about 1 mm thick were cut from single crystal boules supplied by NL Industries and Commercial Crystal Laboratories. The boules were doped to about 100 ppm with tantalum. Wafers were oriented to within 1° of the (111) plane by Laue back reflection X-ray diffraction. Wafers intended for surface studies and some of the wafers for reaction experiments were polished to a mirror finish with 1 μ diamond paste. "Pre-reduced" crystals were treated in a hydrogen furnace at 1000°C for four hours and appeared blue-black and almost opaque, "Stoichiometric" crystals received no heat or hydrogen treatment and were clear and colorless when polished. The backs of "platinized" crystals were coated with platinum metal via the thermal decomposition of aqueous chloroplatinic acid.

Light source

A 500 W high pressure mercury lamp filtered through water to remove infrared radiation was used throughout. Corning 7-51 and 3-74 color glass filters allowed only bandgap or sub-bandgap radiation to impinge upon the crystals. The flux of photons with greater than bandgap energies ($>3.2\text{eV}$) was in the range of 10^{14} - 10^{16} $\text{sec}^{-1} \text{cm}^{-2}$.

Photoelectron spectroscopy

The photoelectron spectroscopy studies were carried out in a commercial ultra-high vacuum chamber with base pressure in the low 10^{-10} torr range. This system has been described in detail elsewhere.⁸ Electron energy analysis was via a

double-pass cylindrical mirror analyzer. Ultraviolet photoelectron spectroscopy was carried out using the He I emission (21.2 eV). A Physical Electronics X-ray source with a Mg anode provided photons for XPS measurements. Auger spectra served to monitor surface cleanliness. ^{Pre-reduced} crystals were routinely sputtered with a 1.5 keV argon beam for about five minutes prior to experiments. The ion beam current to the sample was a few μA .

Results

I. Studies of hydrogen photoproduction on SrTiO_3 crystals

We have observed sustained hydrogen photoproduction on completely metal-free as well as on platinized SrTiO_3 crystals when covered with a water vapor saturated film of NaOH, KOH, CsOH or Cs_2CO_3 , or when immersed in an alkaline aqueous electrolyte. Figure 1 compares hydrogen photoproduction from platinized and metal-free pre-reduced SrTiO_3 crystals. These crystals and their vycor glass mounting brackets were coated with NaOH crusts of ^{thickness} \wedge greater than 30 μ . The crystals were inserted into the reaction cell, saturated with water vapor and illuminated. Under these conditions, hydrogen production rates of up to 1600 monolayers per hour could be obtained on platinized crystals. Metal-free crystals yielded hydrogen at rates up to 100 layers per hour. Pre-reduced and stoichiometric metal-free crystals yielded hydrogen at similar rates. Similar results Table I shows maximum hydrogen production rates observed under a variety of conditions. [^] In solution, these hydrogen evolution rates could be maintained for tens of hours. Experiments carried out in NaOH films exhibited slowly decreasing hydrogen evolution rates, probably due to loss of NaOH from the crystal by gravity flow. No hydrogen production was observed in the dark, under illumination with photons of less than bandgap (3.2 eV) energy, in the absence of water vapor or electrolyte solution, or in the presence of water vapor when there was no film of a basic deliquescent compound

on the crystal surface. Figure 1 also shows that no hydrogen was produced when a piece of platinized platinum foil was mounted in place of the SrTiO_3 crystal, coated with NaOH, saturated with water vapor, and illuminated.

On platinized crystals, photoproduction of oxygen was observed at rates relative to hydrogen evolution somewhat lower than those expected from the stoichiometric ratio in water. If water stoichiometry were followed, oxygen photoproduction rates from metal-free crystals would be too slow to be readily detectable with our present apparatus. Thus, we shall display the experimental data by plotting only the detected hydrogen concentration as a function of different experimental variables.

A. Studies of the locus of hydrogen production on platinized and metal-free SrTiO_3 crystals

When a platinized prereduced SrTiO_3 crystal was placed in a concentrated NaOH solution and illuminated, visible gas evolution occurred from both the illuminated SrTiO_3 surface and the non-illuminated Pt surface. When a metal-free crystal was illuminated, gas bubbles formed only at the illuminated surface. Sealing off the non-illuminated surfaces of metal-free crystals with epoxy caused no diminution of hydrogen production. Blank experiments showed that the epoxy was not a source of hydrogen. Thus hydrogen production on metal-free crystals occurs on the illuminated SrTiO_3 surface. Since stoichiometric metal-free crystals evolve hydrogen at rates similar to those observed from pre-reduced crystals, good electrical conductivity is not a pre-condition for hydrogen production in the absence of platinum.

Sealing off the metal-coated surfaces of platinized crystals attenuated hydrogen production to the rates seen from metal-free crystals. Platinization of the backs of stoichiometric crystals caused, at most, a two-fold increase in hydrogen evolution rates. Platinum foil in pressure contact with a metal-free reduced crystal did not increase hydrogen production rates above those observed in experiments where no platinum was present. A good electrical contact between the SrTiO_3 and platinum is thus necessary for rate enhancement by the platinum.

Platinized crystals do, therefore, appear to behave as short circuited photo-electrochemical cells⁵ wherein oxygen is produced at the illuminated SrTiO₃ surface and hydrogen is produced primarily at the platinum surface. On the other hand, hydrogen production from metal-free SrTiO₃, which takes place at the illuminated surface, appears to proceed via a mechanism distinct from the major reaction path operating in photoelectrochemical cells.

B. Hydroxide concentration dependence of hydrogen photo-production

Films of many water soluble ionic compounds were tested on platinized and metal-free SrTiO₃ crystals. Upon saturation with water vapor and illumination of the crystal, only films of compounds which were both basic and deliquescent (able to extract enough water from moist air to turn the powder into an aqueous solution) gave detectable hydrogen yields. The requirement of deliquescent materials, plus the similarity of results obtained with water saturated films and in bulk aqueous electrolytes, indicate that the films turn into thin layers of aqueous electrolyte upon saturation.

The requirement of the presence of basic compounds for the hydrogen photo-production led to the experiments summarized in Figure 2. Here the rate of hydrogen production from a platinized, preproduced SrTiO₃ crystal is plotted against the (OH⁻) concentration in a NaOH electrolyte. The hydroxide concentration dependence is rather weak below 5 N, but becomes remarkably strong above this concentration. Hydrogen production from metal-free crystals shows similar (OH⁻) concentration dependent rate behavior. No hydrogen production from platinized crystals was seen in 1-10 N HClO₄, 10 N H₂SO₄, Mallinckrodt pH 4.01 BuffAR, 1 N NaF, or 10 N LiCl. The observed change in hydrogen production rate is therefore not

simply a matter of ionic strength or anionic size, it seems quite specific to hydroxide, or at least to a base.

We thus have evidence for a hydrogen-producing photocatalytic process in which all chemistry occurs on the same illuminated metal-free SrTiO_3 surface. We have also shown that the reaction rate is dependent on the hydroxide concentration of the electrolyte. We have then undertaken photoemission studies of the chemisorption and photochemistry of H_2 , O_2 and H_2O on $\text{SrTiO}_3(111)$ surfaces in an attempt to better understand the active surface species and the elementary steps involved in the SrTiO_3 photochemistry.

II. Surface Studies of SrTiO_2 ,

Argon sputtering of SrTiO_3 or TiO_2 surfaces induces oxygen vacancies and produce Ti^{3+} ions in the surface region. These defects profoundly influence the reactivity of the oxide surfaces. We have studied the adsorption of small molecules on argon sputtered hydrogen reduced and thoroughly annealed stoichiometric $\text{SrTiO}_3(111)$ surfaces and have investigated the effects of light on these surfaces.

A. Argon sputtered reduced surfaces.

In the following description we refer to a surface of a hydrogen pre-reduced $\text{SrTiO}_3(111)$ crystal that has been argon sputtered and annealed at around 200°C for a few minutes. UPS and XPS experiments have shown that there is approximately one monolayer of Ti^{3+} on such surfaces.⁹ Figure 3 shows changes in the Ti^{3+} concentration upon adsorption of O_2 , H_2O or H_2 in

the dark, pumping to UHV, and illumination with bandgap radiation. On the vertical axis we show the intensity of the UPS emission ascribed to Ti^{+3} . On the horizontal axis we display first gas exposure in Langmuirs ($1 L \equiv 10^{-6}$ torr-sec) and the illumination time in vacuum. Adsorption of oxygen causes a sharp decrease in the Ti^{+3} signal, with only 2 L of oxygen exposure the Ti^{+3} signal drops to ~50% of its original value. After 2000 L of oxygen the Ti^{+3} signal has dropped to 10% of its initial value. Subsequent bandgap illumination in vacuum restores the Ti^{+3} signal to 20% of its pre-adsorption value in 40 minutes. Monitoring the concentration of surface oxygen by UPS and XPS, we observed that the Ti^{+3} photogeneration was accompanied by a decrease in the surface oxygen content, indicating that oxygen photodesorption was taking place.¹² The Ti^{+3} emission also decreased but to a lesser extent when H_2O or H_2 were adsorbed. Illumination partially regenerated the Ti^{+3} initial concentration in the case of the H_2 exposed surface but not in the case of water.

In Figure 4 we present UPS studies of H_2O adsorption on $SrTiO_3(111)$. The second curve is a $\Delta N(E)$ difference spectrum (water covered surface - initial clean surface) showing the changes in UPS emission induced by exposure to 2000 L of water. This spectrum does not agree with spectra of gas phase molecular water. The top curve in Figure 3 shows the $N(E)$ UPS spectrum of a thoroughly out-gassed 1μ film of NaOH. The spectrum shows emission from OH^- alone, since electrons in Na^+ are too strongly bound to be excited by HeI photons. The similarity of the top and second spectra constitutes evidence that hydroxylation occurs when water or bandgap illumination of the clean surface is adsorbed on the reduced $SrTiO_3(111)$ surface. Hydrogen adsorption produces similar spectra. This surface, therefore, is easily hydroxylated in a variety of ways. Even the 'clean' reference surface appears to be slightly hydroxylated.⁹ This agrees with electron stimulated desorption studies reported by Knotek in which hydroxyl groups were observed on clean argon-sputtered TiO_2 surfaces.

Annealing a stoichiometric $\text{SrTiO}_3(111)$ crystal at around 700°C for a few minutes gave rise to a chemically inert surface. This surface did not show the presence of Ti^{+3} or hydroxyl photoelectron signals and did not adsorb oxygen or hydrogen upon exposure to $10^4 - 10^5$ L. Illumination generated no Ti^{3+} signal. This surface gave a LEED Pattern with a unit mesh consistent with the unreconstructed termination of the bulk crystal structure.

Discussion

Sustained hydrogen production has been obtained from platinized and metal-free SrTiO_3 crystals illuminated in water vapor saturated NaOH films or in concentrated aqueous NaOH. While hydrogen photo-production from platinized crystals appears largely analogous to the operation of ppa photoelectrochemical cell with distinct electrodes, hydrogen production from metal-free crystals appears to proceed by a somewhat different mechanism. This distinction bears further consideration.

We observe hydrogen production and infer the production of oxidized products at the illuminated surface of metal-free SrTiO_3 crystals. Active surface sites for oxidation and reduction may be inter-dispersed on an atomic scale on the same oxide surface. This could prove advantageous to gas phase reactions since it would obviate the necessity of ion transport over long distances. However, we have observed no hydrogen production upon illumination of SrTiO_3 in room temperature water vapor in the absence of an ionic compound film. Our hydroxide dependence data may give a clue to a possible kinetic barrier to such gas-surface photocatalytic reactions.

Schrauzer and Guth have reported photodissociation of water vapor on TiO_2 powders. However, the total hydrogen production they observed was on the order of a monolayer. Boonstra and Mutsaers have observed hydrogenation of acetylene on hydroxylated TiO_2 . Only a monolayer of hydrogenated products was observed and dehydroxylated powders showed no hydrogenation activity. Van Damme and Hall have proposed that the gas-solid photo-"catalytic" reactions reported to date have actually been stoichiometric reactions of surface hydroxyl groups. They believe that immeasurably slow rates of surface rehydroxylation by water vapor have prevented true photocatalytic activity. Munuera has implicated surface hydroxyl groups in the oxygen behavior of TiO_2 powders. Using infrared spectroscopy, he has shown that certain hydroxyl groups are more photoactive than others. After thermal dehydroxylation of the surface, the most active hydroxyls cannot be restored by immersion in water vapor or liquid water at room temperature. Our photoemission studies have shown that adsorption of either water vapor or hydrogen on clean reduced SrTiO_3 (111) gives rise to a hydroxylated surface. Illumination of the surface exposed to hydrogen increases the Ti^{+3} signal, while no photoeffects were seen on the surface exposed to water. This agrees with Munuera's observations that different treatments lead to surface hydroxyl groups of varying photoactivity.

We have shown that the rates of hydrogen production from metal-free, as well as from platinized crystals increase with increased concentration of a NaOH electrolyte. This increase may be due to an increased rate of surface hydroxylation. A number of other explanations are possible, such as increased band-bending or stabilization of new oxidized intermediates or products in highly alkaline media. These hypotheses will be discussed in more detail elsewhere. Here we can only note that the equivalent photochemical behavior of stoichiometric and pre-reduced metal-free crystals with increasing OH^- concentration argues against an explanation of the hydroxide concentration dependence based entirely on changes in band-bending.

We thus have evidence for a mechanism of hydrogen photoproduction which could prove to be more useful for the development of heterogeneous solid-gas photochemical reactions than is the major reaction pathway operating in electrochemical cells. Our results and those of others show that surface hydroxylation may be crucial to the kinetics of gas-phase heterogeneous photocatalysis.

Photoelectron spectroscopic techniques can identify and monitor Ti^{3+} and hydroxyl surface species on $SrTiO_3(111)$. We have shown that Ti^{3+} is involved in oxygen adsorption-photodesorption chemistry on reduced $SrTiO_3(111)$ surfaces. Photodesorption of the product oxygen may be important to sustain water photolysis on semiconductor surfaces. Ti^{3+} may be directly involved in the reductive chemistry observed in aqueous electrolyte at the illuminated $SrTiO_3$.

Local active sites do appear to be important to large band gap semiconductor photochemistry. Continued parallel reaction and surface studies may lead to better understanding of the mechanisms of photocatalysis on these and on other materials.

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A. Hydrogen production from SrTiO₃ crystals covered by thick (>30 μ) NaOH films saturated with water vapor

Crystal	Monolayers* H ₂ /hr
Pre-reduced, platinized	1580
Pre-reduced, metal-free	100
Stoichiometric, metal-free	30

B. Hydrogen production from SrTiO₃ crystals in 20 M NaOH

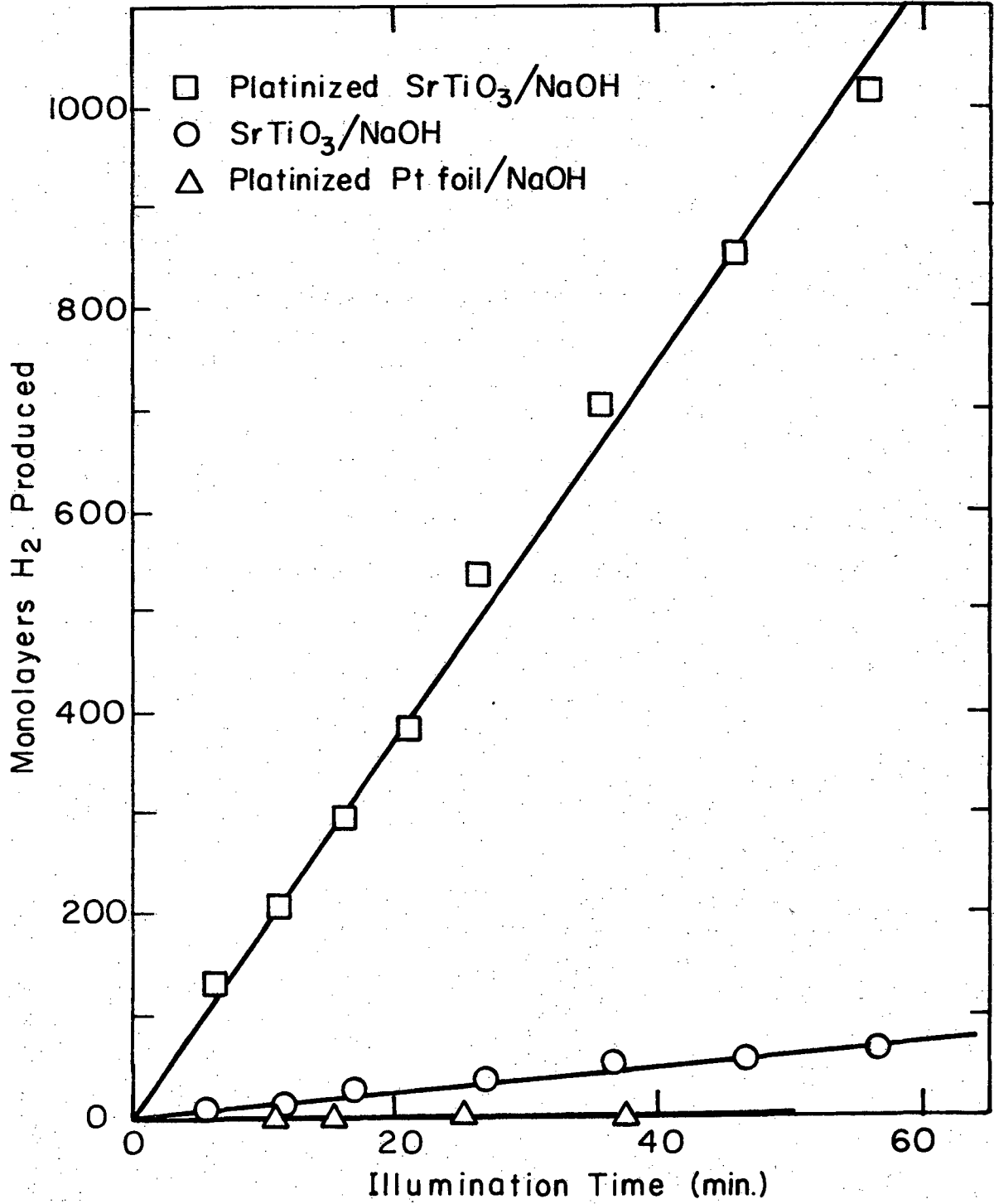
Crystal	Monolayers* H ₂ /hr
Pre-reduced, platinized	4500
Stoichiometric, platinized	120
Pre-reduced, metal-free	30
Stoichiometric, metal-free	50

*1 monolayer $\equiv 1 \times 10^{15}$ molecules/cm² illuminated surface

TABLE I

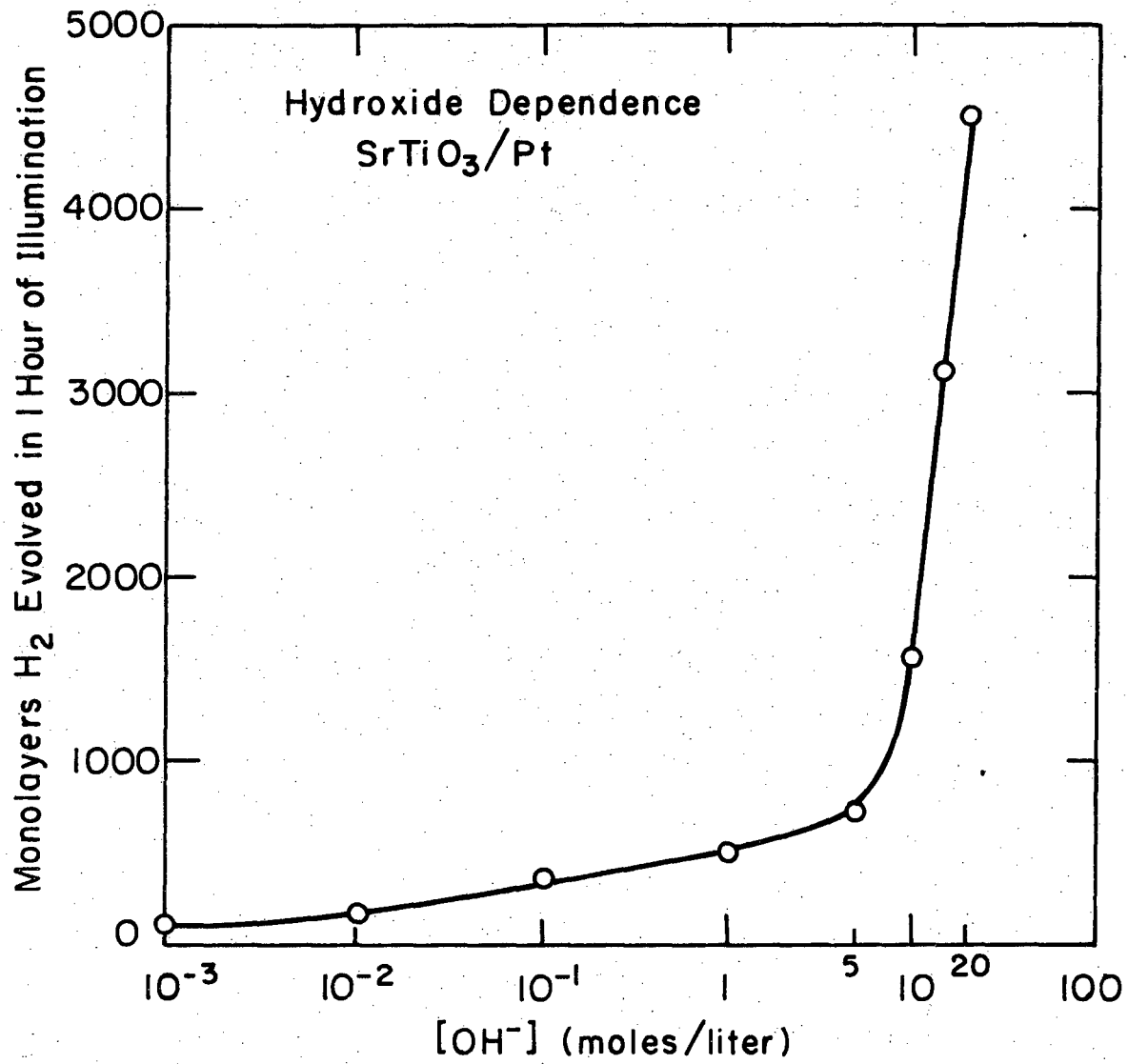
Figure Captions

- Figure 1 Hydrogen production from platinized and metal-free n-type SrTiO₃(111) crystals. Both crystals were coated with >30μ of NaOH and were illuminated in a saturation pressure (c20 torr) of water vapor (1 monolayer ≡ 10¹⁵ molecules H₂/cm² of illuminated surface).
- Figure 2 Hydrogen production from a platinized, pre-reduced SrTiO₃(111) crystal during one hour of illumination as a function of NaOH electrolyte concentration (1 monolayer ≡ 10¹⁵ molecules H₂/cm² of illuminated surface).
- Figure 3 Intensity of the UPS Ti⁺³ emission as a function of H₂O, O₂ and H₂ exposures up to 2000 L in dark, and as a function of the irradiation on the H₂O, O₂ and H₂ surfaces after having pumped away these gases.
- Figure 4 Top curve--UPS, N(E) spectrum of a 1 micron thick NaOH film on the SrTiO₃ reduced crystal.
Second curve--Difference spectrum due to 2000 L of water exposue.
Third curve--the same as second curve, but with H₂ rather than H₂O.
Fourth curve--difference spectrum due to the bandgap irradiation of the clean surface.



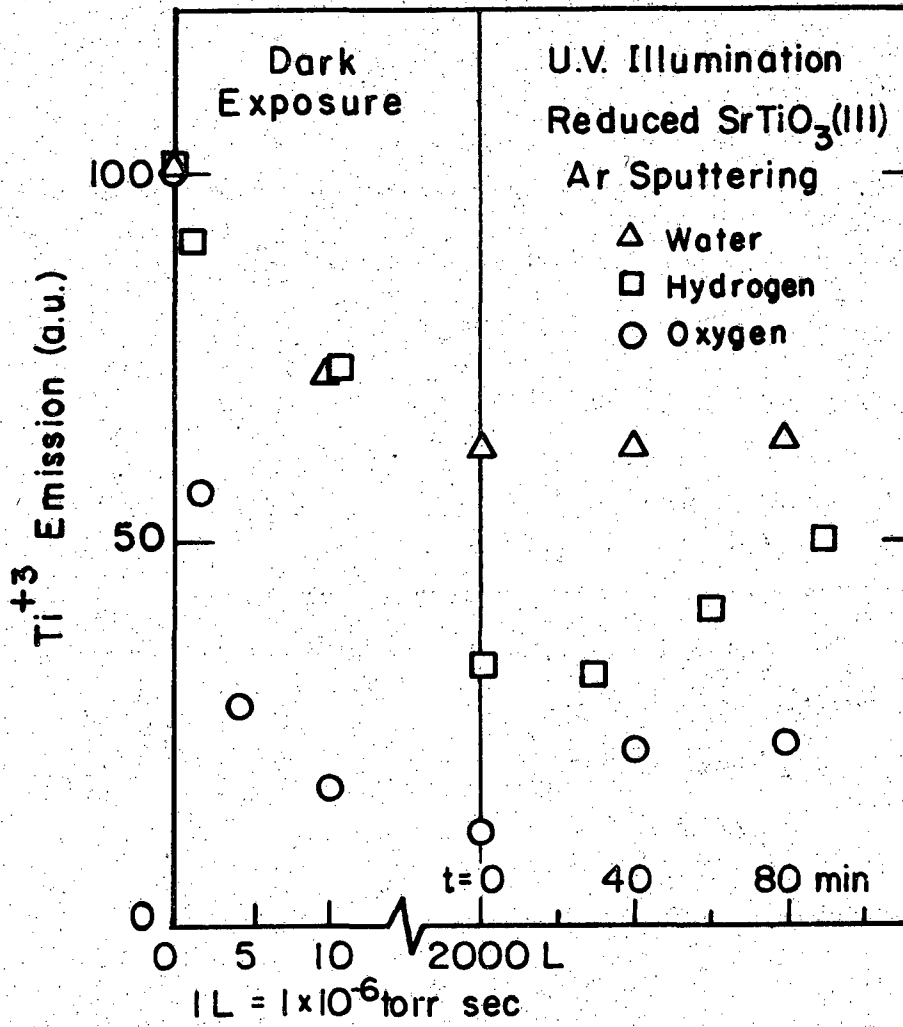
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Fig.1



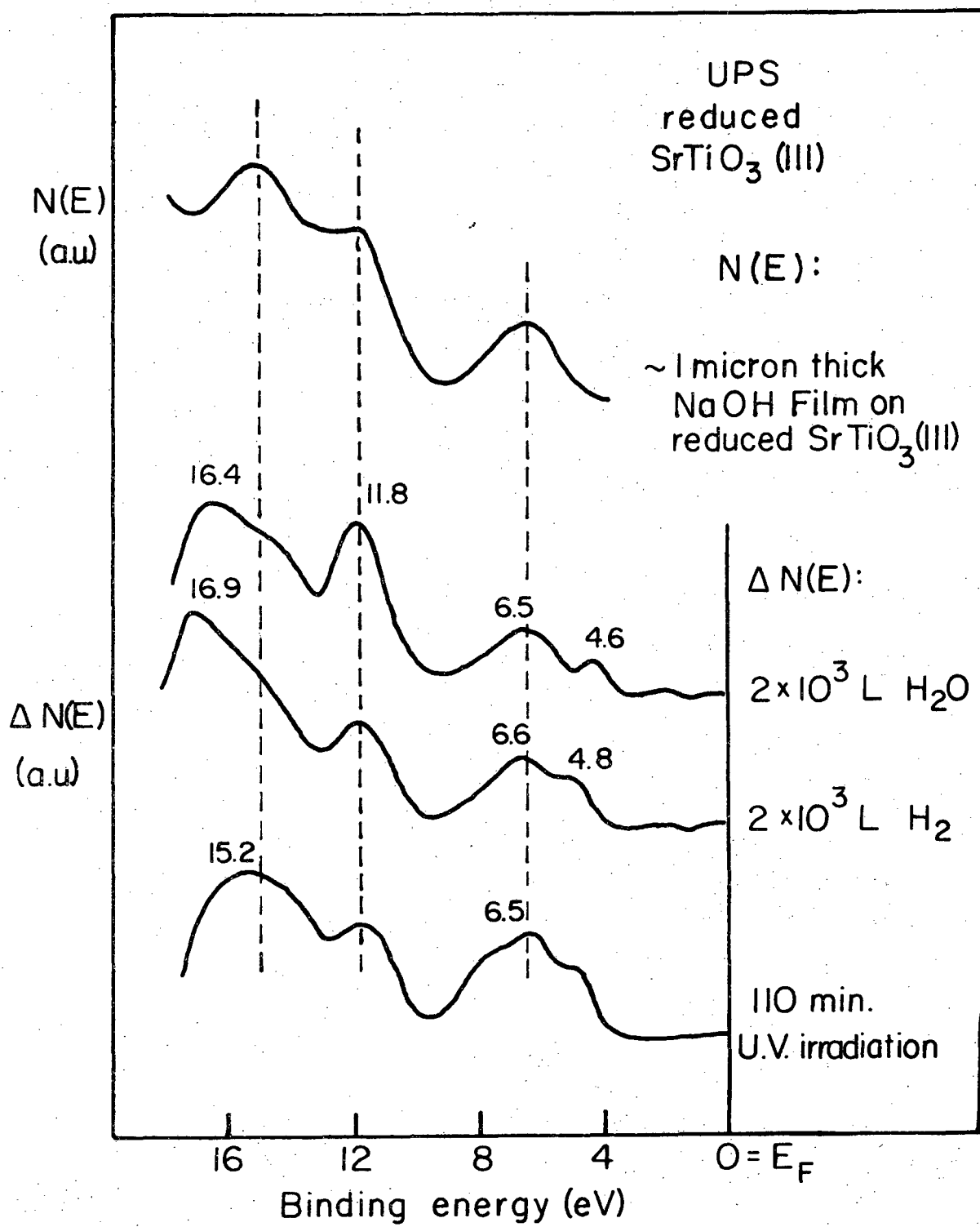
XBL799-7068

Fig.2



XBL 799-7048

Fig. 3



XBL 799-7042

Fig.4

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