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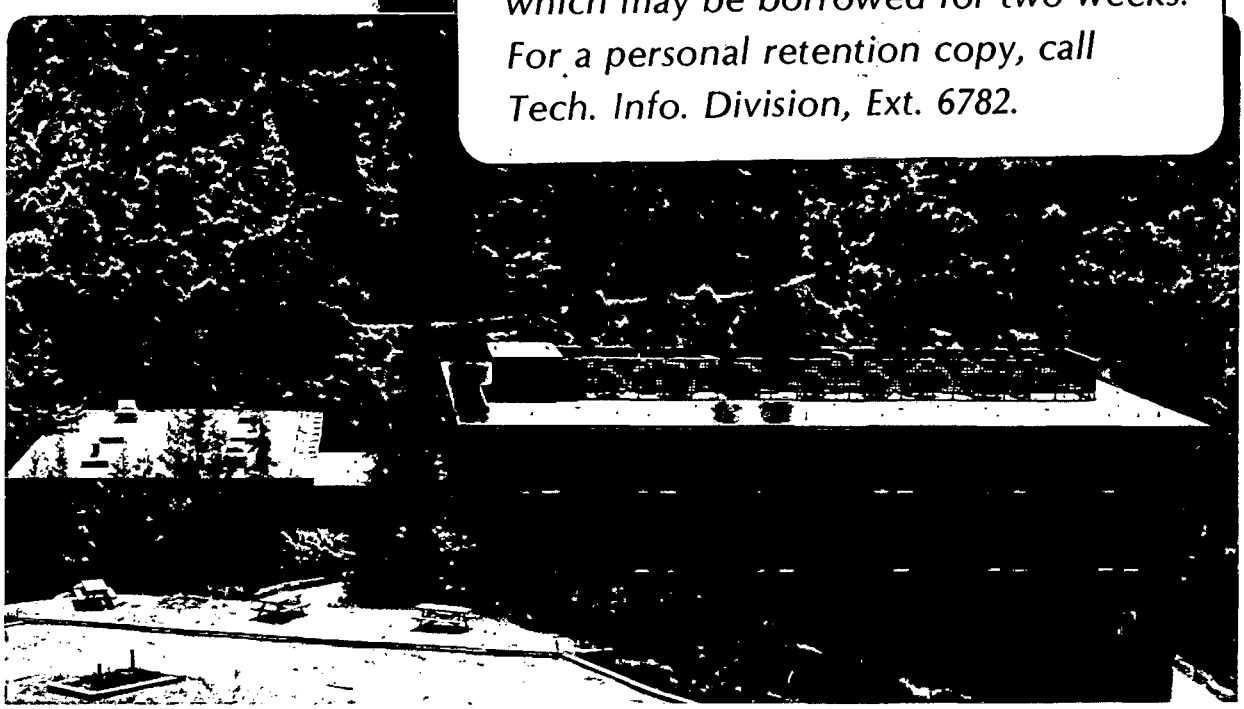

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THE PHOTOCATALYTIC PRODUCTION OF HYDROGEN FROM WATER BY A p- AND n-TYPE POLYCRYSTALLINE IRON OXIDE ASSEMBLY

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Abstract

The photodissociation of water to produce hydrogen has been accomplished using light in the solar range of the electromagnetic spectrum and in the absence of any external potential at 300K. The catalyst for the reaction is a polycrystalline p/n diode assembly made out of Mg- and Si-doped iron oxide. In 0.1 M Na_2SO_4 solution (pH = 6) the device produces hydrogen catalytically with rates of 1-2 H_2 molecules per site per minute and its power conversion efficiency is about 0.05%. Iron oxide containing minerals could have played important roles in the photochemical evolution of the planet in the pre-chlorophyl era.

We report the successful photochemical conversion of water to hydrogen using light in the solar region of the electromagnetic spectrum and at 300K. The catalysts for this reaction are polycrystalline iron oxide discs that are doped with silicon and magnesium. Iron oxide, Fe_2O_3, is a semiconductor with a band gap of 2.2 eV. It becomes n-type when doped with silicon and p-type when doped with magnesium. By connecting n-type and p-type iron oxide polycrystalline pressed discs with a conducting wire, a diode assembly is produced as shown in Figure 1. When this assembly is immersed in a 0.1 M Na_2SO_4 aqueous solution and illuminated with visible light both hydrogen evolution and photocurrent across the samples are detectable The hydrogen production rate is in the range of 1 to 2 hydrogen molecules per site per minute and the photocurrent is of the order of 10 $\mu A/cm^2$. The reaction is thus catalytic and can be carried out for 6-8 hours without any sign of poisoning. When the photoinduced hydrogen production and the corresponding photocurrent eventually decline they can be regenerated by passing oxygen gas over the catalyst iron oxide surfaces. The poisoning effect is not observed as long as oxygen is continuously passing over the surfaces.

The apparatus that is used to photodissociate water is shown in Figure 2. It consists of a glass cell that houses the iron oxide assembly immersed in the Na_2SO_4 aqueous solution. Photogenerated hydrogen is transported from the cell through a closed circulation loop to a gas chromatograph. Argon is used as a carrier gas and is circulated through the loop by means of a mechanical pump. Air leaks in the cell and in the loop hinder accurate detection of photoinduced oxygen production. The sample is illuminated by light from a 500 W lamp which passes through a water filter and a visible pass filter ($E \leq 2.7$ eV). The apparatus also permits photoelectrochemical measurements of p- and n-type iron oxides separately. This is accomplished by a potentiostat and a standard three

electrode configuration consisting of the iron oxide sample, a reference electrode and a platinum counter electrode (see Figure 2).

Iron oxide discs with n-type behavior were produced by mixing fine powders of α-Fe_2O_3 and SiO_2 so that $0 < Si/Si + Fe \leq 20$ atomic %. Similarly, p-type iron oxide discs were produced by mixing powders of α-Fe_2O_3 and MgO so that $0 < Mg/Mg + Fe \leq 20$ atomic %. By pressing the powders into pellets, heating them in air at 1340-1390 C and allowing them to cool rapidly, the resulting mixed iron oxide discs had resistivities in the range $10^3 - 10^4$ $\Omega \cdot cm$.

Scanning electron microscopy studies show all mixed iron oxide surfaces to be heterogeneous. The n-type surfaces consist of a silicon doped iron oxide matrix with a grain size of 10-20 μm and smaller precipitates highly enriched in silicon oxides. The p-type surfaces consist of a magnesium doped iron oxide matrix and precipitates enriched in magnesium oxide. Scanning Auger spectroscopy measurements reveal the same heterogeneity and show, furthermore, that the chemical composition of the outermost 5 nm thick surface region is not significantly changed upon exposure of the iron oxide discs to the Na_2SO_4 aqueous solution. When immersing the p/n-type iron oxide assembly in the Na_2SO_4 aqueous solution a dark current of a few $\mu A/cm^2$ is observed which decreases with time. Upon illumination of both iron oxide samples a photocurrent is measured which ranges between 5-10 $\mu A/cm^2$ during the first hours of illumination and which tends to increase slightly with time. Simultaneous detection of photoinduced hydrogen evolution by gas chromatography reveals a hydrogen production rate of between 5 and 10×10^{16} molecules/hour from the p-type iron oxide with area ≈ 0.6 cm^2.

After about 6-8 hours of operation in 0.1 M Na_2SO_4 the rate of photoinduced hydrogen evolution declines. Simultaneously the photocurrent of the p-type magnesium doped iron oxide also declines. By flowing oxygen gas through the reaction cell for a few minutes to an hour the device can be reactivated and

both the hydrogen evolution rate and the photocurrent between the p- and n-type iron oxide discs return to the original values. Periodic flowing of oxygen gas through the reaction cell results in a stable photocatalytic hydrogen production rate of 1-2 hydrogen molecules per site per minute giving around 2000 monolayers of hydrogen molecules per 24 hours of exposure to the light. X-ray photoelectron spectroscopy studies showed that the oxygen treatment resulted in a higher oxygen content of the iron oxide lattice (Figure 3) indicating a reoxidation of the iron oxide surface. No significant change in the Fe 2P peak position was observed after flowing oxygen gas through the cell.

The deterioration of the p-type samples is most probably caused by a gradual reduction of the iron oxide surfaces by a small fraction of the photoproduced hydrogen. The oxidation treatment restores the iron oxide at the surface to its higher oxidation state and also regenerates the photochemical activity. The deposition of platinum on $SrTiO_3$ single crystal surfaces greatly aided the production of hydrogen from water upon irradation with band gap (3.2 eV) or larger energy photons.(1) In an attempt to increase the hydrogen production rate and possibly to reduce the gradual reduction of the iron oxide surface a grid of platinum was deposited over the p-type sample having a thickness larger than 20 nm. However, no improvement was observed. The photocurrent between the p- and n-type samples was reduced and the hydrogen evolution rate declined in proportion. On the other hand the photocurrent of the n-type Si-doped iron oxide does not deteriorate or show any other sign of poisoning. Thus, the surface at which oxygen is evolving remains stable under present reaction conditions.

The power conversion efficiency can be calculated to be about 0.05% using the H_2 production rate of 8×10^{16} H_2 molecules per hour and incoming photon flux with 17 mW power. This is about an order of magnitude lower than those

reported using single crystals and radiation in the ultraviolet range of the electromagnetic spectrum.[2,3] The photochemical conversion efficiency can be improved in several ways. The particle size of the polycrystalline iron oxide grains can readily be increased from the average 10^{-3} cm size utilized in the present device. While the deposition of a thick (> 20 nm) grid of platinum over the p-type iron oxide surface did not improve its photocurrent or hydrogen production rate, perhaps a thinner coating of Pt or the use of another metal might accelerate the recombination of hydrogen atoms. Improvements of the cell geometry, changes of the iron oxide stoichiometry and doping levels and modification of other experimental conditions are likely to improve the rate of hydrogen production from water over the iron oxide diode assembly using visible light, in the near future. A redesigned, leak tight cell will permit us to detect oxygen in addition to hydrogen using the gas chromatograph.

The successful photoproduction of hydrogen from water using radiation in the solar region over magnesium and silicon containing polycrystalline iron oxide raises the question of the possible importance of this process during the evolution of our planet in the pre-chlorophyl era. Si, Fe and Mg containing minerals are most abundant in the mantle and cold have been catalysts not only for the photochemical conversion of water to H_2 and O_2 but for subsequent reactions of these molecules with CO_2 and N_2. The reactions of hydrogen with CO_2 and N_2 have negative free energies. Furthermore, iron and its compounds are excellent catalysts for the formation of organic molecules from gas mixtures of H_2, CO_2 or CO and of ammonia synthesis from H_2 and N_2. We shall be exploring the feasibility of inorganic photosynthesis over the iron oxide p/n diode assemblies in the near future

Acknowledgment

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References

1. F. Wagner and G.A. Somorjai, Nature 285, 559 (1980).
2. A.J. Nozik, Appl. Phys. Lett. 30, 567 (1977).
3. K. Ohashi, J. McCann and J.O'M. Bockris, Nature 266, 610 (1977).

Figure Captions

Figure 1: p/n-type iron oxide assembly. $\phi \approx 9$ mm.

Figure 2: Apparatus for simultaneous photocurrent and gas evolution studies.

Figure 3: X-ray photoelectron spectra of the O 1s peak before (lower curve) and after (upper curve) oxidation treatment of a mixed iron oxide with Si/Si + Fe = 10 atomic %. Indicated in the figure are the peak positions of O 1s in the iron oxide matrix and in the silicon enriched precipitates.

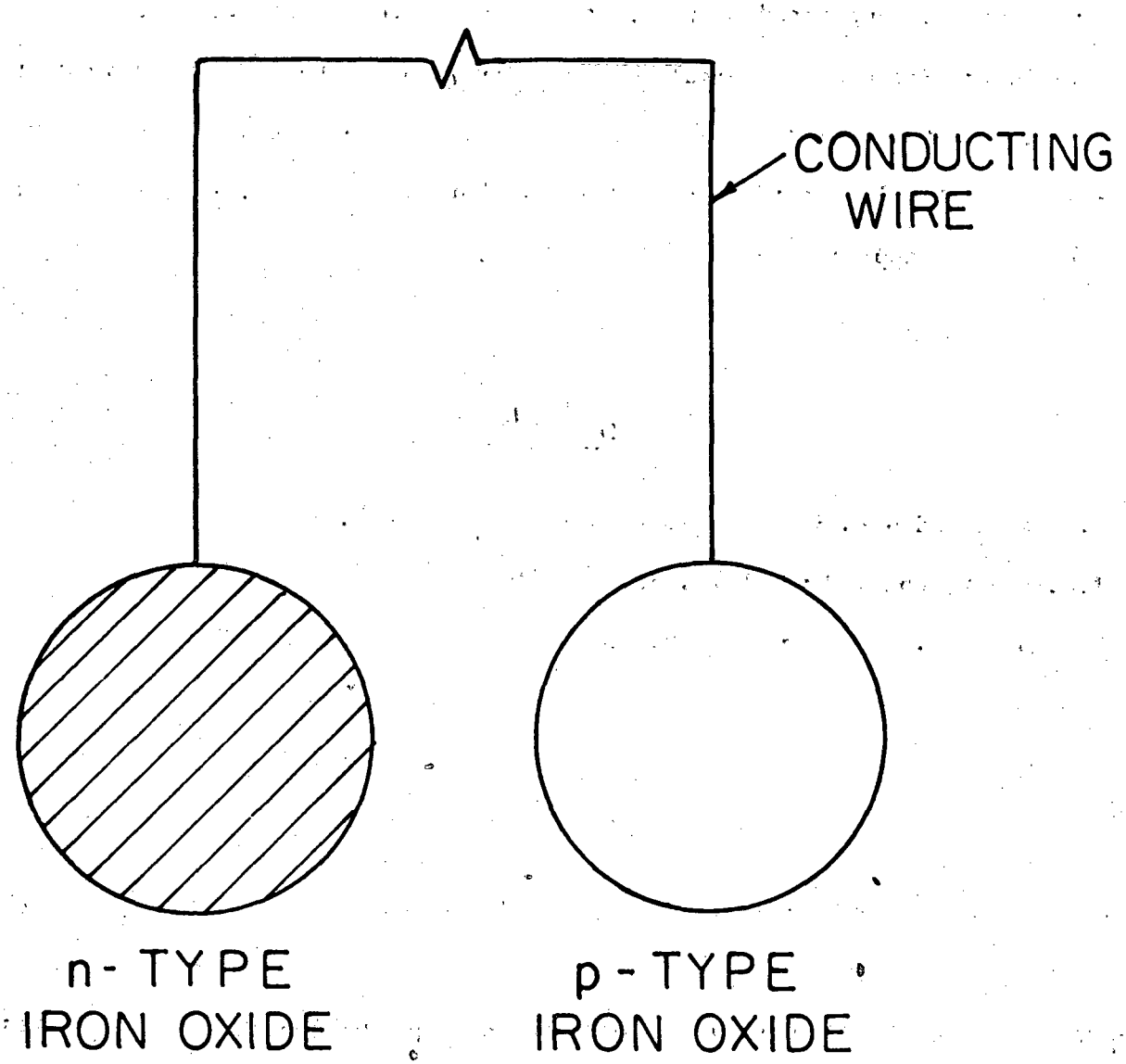

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Fig. 1

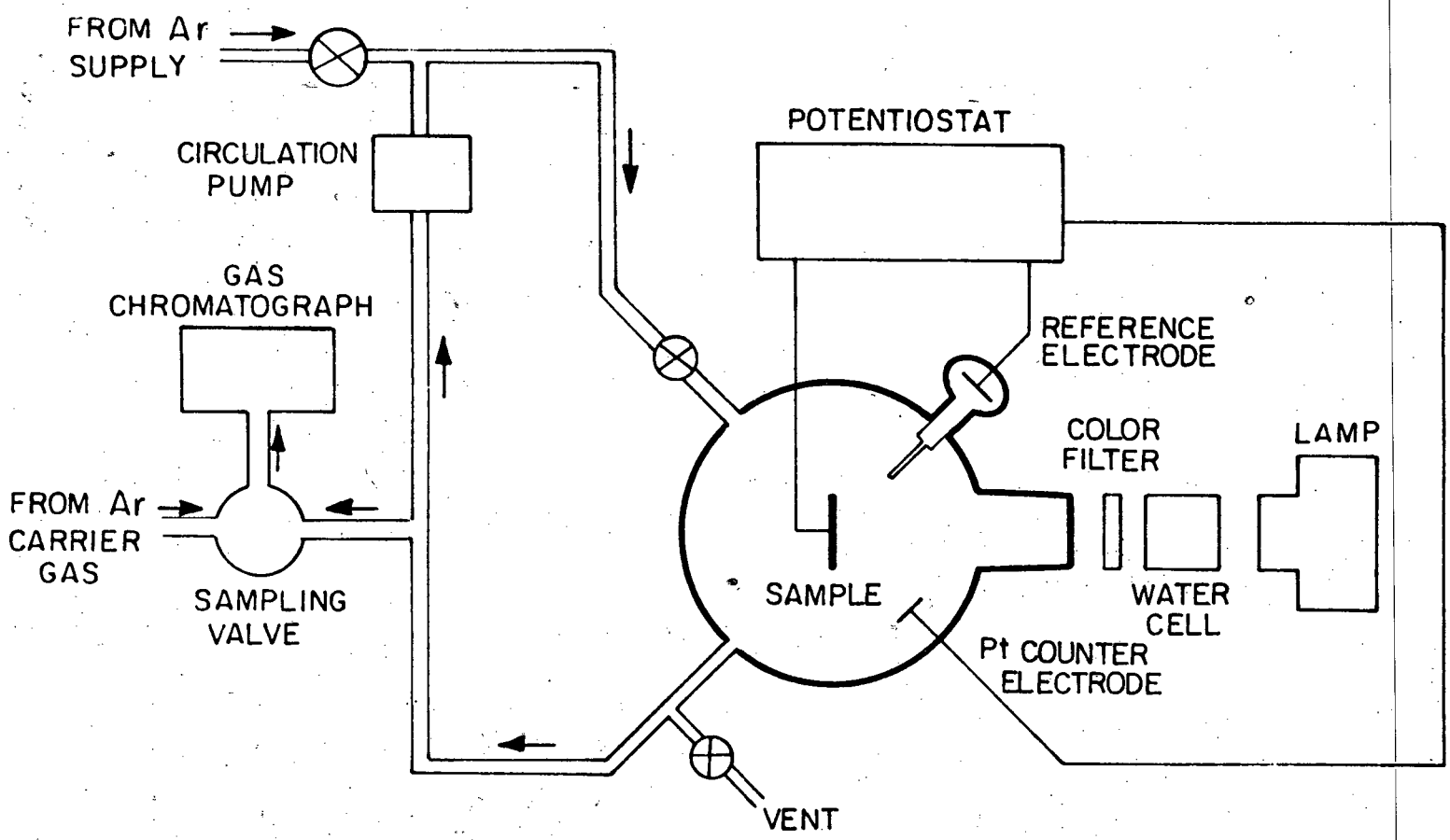

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Fig. 2

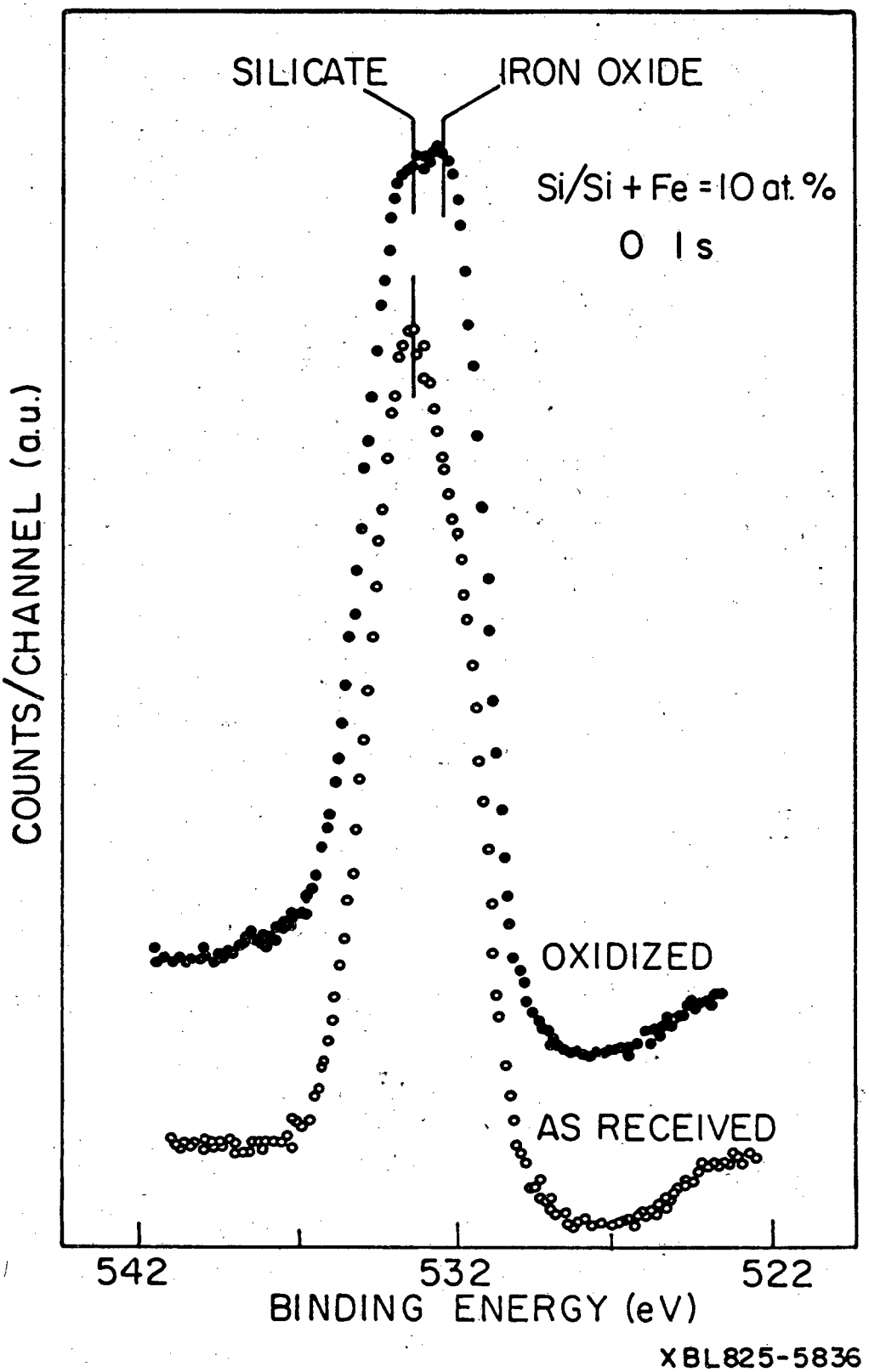
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Fig. 3

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