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Publication Date
1982-05-01
To be published in the Proceedings of the National Academy of Sciences

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May 1982

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PHOTODISSOCIATION OF WATER BY p- AND n-TYPE POLYCRYSTALLINE IRON OXIDES USING VISIBLE LIGHT (< 2.7 eV) IN THE ABSENCE OF EXTERNAL POTENTIAL

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.
ABSTRACT

A polycrystalline p/n diode assembly, consisting of pressed Mg- and Si-doped iron oxide powders, has been shown to photodissociate water using visible light in the absence of any external potential. In the investigated pH range (8–14) the device produces hydrogen catalytically in amounts which are readily detectable by gas chromatography. The relatively low power conversion efficient of 0.05% is believed to be due to the poor charge transfer properties of the p-type iron oxide used.
The photodissociation of water using strontium titanate single crystals or polycrystalline powders to produce hydrogen and oxygen has been studied intensively in recent years (1). When platinum was deposited over the oxide and alkali hydroxide was present at its surface illumination by band gap (3.1 eV) or larger photon energies produced hydrogen at rates of several molecules per site per second at 300K. When n-type SrTiO₃ or TiO₂ and p-type GaP or CdTe were used in an electrochemical cell as anode and cathode, respectively, the photodissociation of water could also be carried out without using external potential (2,3). The need of radiation in the ultraviolet, instead of the solar region however, seriously limits the utility of these systems for chemical conversion of solar energy. Recently it was shown that a p/n diode, consisting of single crystal p-GaP and polycrystalline n-Fe₂O₃, could split water at relatively low quantum yields when exposed to visible and near UV radiation (4).

We report the photodissociation of water by radiation in the solar region and in the absence of any external potential. This was accomplished by using samples that were made from silicon doped n-type and magnesium and silicon doped p-type iron oxide pressed polycrystalline disks. These were connected by a conducting silver epoxy as shown in Figure 1. The p- and n-type iron oxide disks were immersed in aqueous solutions of various pH where both disks were illuminated using radiation of E < 2.7 eV.

Hydrogen evolution was readily detectable with rates of several molecules per site per minute using visible light and without external potential. Photoinduced hydrogen production rates are given in Table I. The photoactivity slightly increases between pH = 8 and 12 while the number of detected hydrogen molecules is lowest at pH = 14. The pH dependence of the hydrogen evolution rate is under continued investigation.

A slow poisoning of the hydrogen production is observed as indicated from
the data in Table I. Exposing the sample to air seems to regenerate its photo-
activity and the same sample can be used in several experiments always giving
the highest photoactivity during the first hour of exposure.

More than $3 \times 10^{17}$ hydrogen molecules have been detected in single expo-
sures so far. With an illuminated total p- and n-surface area of 0.6 cm$^2$ this
amounts to hundreds of monolayers of hydrogen. Even if the real surface area
of the pressed polycrystalline iron oxide pellets is larger, perhaps by one
order of magnitude, the number of detected hydrogen molecules per surface site
is of the order of 50. Thus, we believe that the photoinduced hydrogen evolu-
tion is catalytic.

Our apparatus, which permits the measurement of both the photocurrent and
the hydrogen evolution simultaneously, is shown in Figure 2. It consists of an
electrochemical glass cell and a closed circulation loop for transporting the
photogenerated hydrogen, with Argon as a carrier gas and a circulation pump,
to a gas chromatograph (Hewlett Packard 5720 A). The gas chromatograph, fitted
with a thermal conductivity detector, has a detection limit for H$_2$ which cor-
responds to a production rate of $10^{16}$ molecules per hour in the cell. Air
leaks in the cell and the circulation loop hinder accurate detection of the
photoinduced oxygen production. The sample is illuminated by a 500 W lamp.
The light passes through a water filter and a visible pass filter ($E < 2.7$ eV)
to the sample.

n-Type iron oxide samples were prepared by mixing powders of $\alpha$-Fe$_2$O$_3$ and
SiO$_2$ to obtain compositions of $0 < Si/(Si + Fe) < 10$ atomic %, whereas p-type
iron oxide samples were prepared by mixing powders of $\alpha$-Fe$_2$O$_3$, MgO and SiO$_2$ so
that Mg/(Mg + Si + Fe) and Si/(Mg + Si + Fe) = 10 atomic %. The mixed powders
were then pressed into pellets, heated in air at 1340-1390°C and rapidly cooled in air. The resulting resistivity of the samples was in the range of 10$^3$-10$^5$ Ω cm.
While the photocurrent is proportional to the hydrogen evolution rate for homogeneous materials this may not be the case for heterogeneous or polycrystalline materials such as our doped iron oxide polycrystalline pellets. The photoelectrons may recombine at grain boundaries and will not be detectable while the local photoreaction may still produce hydrogen. Electron microscope pictures of the n-type and p-type iron oxide samples (Figure 3) clearly show the structural heterogeneity. Scanning auger electron spectroscopy studies indicate the presence of a multiphase system that includes silicon enriched precipitates in addition to the silicon doped and magnesium doped iron oxide phases.

Blank experiments with no sample but with electrolyte and sample holder in the cell gave no detectable hydrogen production, either in the dark or under illumination. Furthermore, no hydrogen was detected in the dark when exposing the p- and n-type iron oxide surface to the electrolyte. Both iron oxide surfaces must be illuminated to obtain hydrogen evolution. The photocurrent obtained from the p-type iron oxide under potentiostatic conditions is considerably less (50 μA at 300 mV (RHE)) than that obtained from the n-type sample (500 μA at 1200 mV(RHE)). The relatively low hydrogen evolution rate may be due to the poorer charge transfer properties of the p-type iron oxide.

The efficiency of the device for photochemical energy conversion is poor, 0.05%. This is based on a production rate of $8 \times 10^{16}$ hydrogen molecules per hour and incoming radiation with 17 mW power. However, improvement in the architecture of the cell, changes of the iron oxide stoichiometry and doping levels, and modification of the experimental conditions are likely to markedly improve the rate of hydrogen photoproduction in the near future.

The ability of polycrystalline iron oxide, doped only with Si or Mg, to catalyze the production of hydrogen upon solar irradiation raises the question of the possible importance of this system during the evolution of our planet.
The abundance of iron-magnesium-silicon compounds in the mantle assures that hydrogen and oxygen could be photoproduced from water with great probability and in large quantities. Once hydrogen is available its subsequent catalyzed reactions with CO₂ and N₂ to produce hydrocarbons and ammonia are thermodynamically feasible. Iron compounds are also excellent catalysts for these reactions and are used commercially in the chemical technology for this purpose. Thus, the series of reactions that begin with the photodissociation of water can yield organic molecules and oxygen and thus, result in photosynthesis. Photosynthesis by inorganic catalysts like the iron compounds in the mantle may have been of key importance for evolution in the pre-chlorophyll era of the planet.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

REFERENCES

TABLE I: H\textsubscript{2} Production Rates [in units of $10^{16}$ H\textsubscript{2} molecules/hour]

<table>
<thead>
<tr>
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<th>n-type iron oxide:</th>
<th>p-type iron oxide:</th>
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<tbody>
<tr>
<td></td>
<td>Si/Si + Fe = 1 atom %</td>
<td>Si/Mg + Si + Fe = 10 atom %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg/Mg + Si + Fe = 10 atom %</td>
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<td>Solution:</td>
<td>Dist. H\textsubscript{2}O</td>
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<td>2nd hour</td>
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<td>6</td>
</tr>
<tr>
<td>3rd hour</td>
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<td>5</td>
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</table>
FIGURE CAPTIONS

Figure 1: Platinized p-type and n-type iron oxide polycrystalline disks connected by conducting Ag epoxy.

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

Figure 3: Scanning Electron Microscope photographs showing n-type Fe2Si (left) and p-type Fe10Si10Mg (right). The samples consist of a Si- (left) and Si- and Mg- (right) doped Fe2O3 matrix and highly Si-enriched precipitates.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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