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THE PHOTOASSISTED DECOMPOSITION OF GAS PHASE 
WATER ADSORBED ON SrTiO₃

by

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Abstract

The photoassisted decomposition of gas phase water molecules adsorbed onto strontium titanate surfaces to hydrogen and oxygen is reported. The decomposition takes place without any externally applied potential and in the absence of liquid electrolyte when the SrTiO₃ surface is illuminated with light of energy greater than the band gap. Reduced SrTiO₃ produces hydrogen and oxygen at higher rates than unreduced SrTiO₃. Experiments with co-adsorbed H₂O and D₂O indicate the scission of OH bonds of the adsorbed water.

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In this Letter, we report the first observation of the photoassisted decomposition of water molecules from the gas phase to hydrogen and oxygen when adsorbed on polycrystalline strontium titanate surfaces. This occurs without applying an external potential and in the absence of any liquid electrolyte.

Ever since the report of photoassisted decomposition of liquid water by Fujishima and Honda,\(^1\) there has been much work on the photoassisted production of hydrogen and oxygen in aqueous solutions using various semiconductor photoelectrodes that were immersed in electrolytes.\(^2\text{-}10\) In some of these systems, a small external potential (less than the necessary 1.23 volts for water) had to be applied, in others none at all, for efficient generation of hydrogen at the metal counter-electrode and oxygen at the illuminated semiconductor photoanode. In all cases, photons of energy greater than or equal to the band gap of the semiconductor electrode has to be used to initiate and sustain the decomposition of water.

There are many advantages in carrying out the photon assisted decomposition of water in the vapor phase over solid-liquid (electrochemical cell) systems. Working in the gas phase at low pressures (less than \(10^{-4}\) torr) allows the direct application of the various analytical tools of modern surface science to monitor the composition, structure and electronic states of the surface during the reaction and to identify the nature and oxidation states of both the substrate and the adsorbate. The reaction mechanism can then be uncovered and understood more clearly this way. One may also be able to change the surface temperature over a broader range to optimize the production rates of hydrogen and oxygen without concern for the adsorption of light by the electrolyte or diffusion limitation of
the products.

Our experiments of the photon assisted decomposition of water vapor were performed inside a multiple-technique ultrahigh vacuum chamber with a base pressure less than $1 \times 10^{-10}$ torr, as was used in our previous characterization studies of titanium dioxide surfaces. (11) It consists of an ion-pumped stainless steel UHV system, equipped with LEED, Auger and UPS capabilities for surface analysis and a quadrupole mass spectrometer for gas analysis. Strontium titanate powders of 99.95% purity were obtained from Electronic Space Products, Inc., Los Angeles. The powders were compressed into 7/8 in. diameter pellets. Two such samples were made. One of them was reduced by heating to 1200°C at a hydrogen pressure of one atmosphere for an hour and showed a slightly greyish color after reduction. The external surface area for both samples was approximately $2.5 \times 10^3$ cm$^2$. Both samples (reduced and unreduced) were immersed into distilled water and then removed to dry. Each powder sample was then mounted on a 1.5 x 1.5 in.$^2$ platinum foil backing and held in place by two spot-welded platinum wires. The arrangement was such that either sample could be illuminated without illuminating the other.

Band gap radiation was provided by a 500 watt high pressure mercury power lamp, which was water and air cooled during maximum operation. The UV light generated was transmitted to the specimen through a sapphire window. A 20 cm focal length quartz lens was used to focus the light onto the sample surface so that only the sample and part of the holder were illuminated directly. An infrared filter, made from filling a quartz cell with nickel sulphate solution, was placed between the mercury UV source and the focusing near lens to absorb the heat and transmit the UV. This limits the temperature
rise of the specimen due to radiation heating to less than +30°C and hence avoids any spurious effects due to thermal desorption. The total photon flux on the sample was estimated to be ~10^{17} photons (energy > 3 eV) per second, as measured by a calibrated Eppley pyrheliometer. To increase the detection sensitivity, the ion pump was throttled to give effective pumping speeds of 2, 20 and 70 liters/sec. for water, oxygen and hydrogen respectively. The approximate wavelength response was checked by inserting various filters and measuring the photo-induced mass spectrometer signal.

Figure 1 shows that by shining UV light onto the strontium titanate samples held at room temperature, the partial pressures of H$_2$(m/e=2), H$_2$O (m/e=18) and oxygen (m/e=32) were found to increase instantaneously to a steady level. This pressure increase was practically constant over a period of an hour or more, and occurred only when the light was incident on the sample. After converting ion currents to pressures and correcting for pumping speed differences, the number of molecules leaving the semiconductor surface per second is plotted in Fig. 2. The reduced sample appears to evolve more hydrogen and oxygen when illuminated. Photodesorption of molecular water (m/e=18) was also observed. However, the amounts of H$_2$ and O$_2$ detected are at least two orders of magnitude greater than could be accounted for by the fragmentation of the photodesorbed water in the mass spectrometer.

The experiment was repeated by co-adsorbing H$_2$O and D$_2$O onto the same SrTiO$_3$ surfaces at a pressure of 10^{-6} torr for 20 minutes and then illuminating with UV light. In addition to the evolution of H$_2$(m/e=2), H$_2$O(m/e=18), D$_2$O(m/e=20) and O$_2$(m/e=32), both HD(m/e=3) and D$_2$(m/e=4) were detected. Again, the reduced sample always gave larger photo-induced signals than the
unreduced sample. In both experiments it was found that only light with energy greater than ~3 eV is effective in giving rise to the observed signals.

Several important observations can be immediately extracted from the above experimental results. First, the ratio of the number of hydrogen molecules to that of oxygen leaving the semiconductor surface is approximately 40 to 1 for the reduced SrTiO$_3$ sample and 140 to 1 for the unreduced one. While these numbers are uncertain to a factor of 2, the ratios are still far from the stoichiometric ratio of 2 to 1 as expected from the decomposition of water. One possibility is the depletion of oxygen by a surface reaction that produces CO and CO$_2$, as inferred from the increased ion currents at m/e=28 and 44 during illumination. Another possibility is the intermediate formation of hydrogen peroxide which is only partially decomposed on the surface. Indeed, small quantities of hydrogen peroxide were detected in electrochemical cells using SrTiO$_3$ as a photoanode.$^6$

Second, the reduced SrTiO$_3$ sample is at least 20% more efficient than the unreduced sample in the photoassisted decomposition of adsorbed water. This may be related to differences in charge carrier mobilities in the two samples. It is also possible that more lower oxidation state titanium species (e.g., Ti$^{3+}$) are present in the reduced sample which may enhance the overall reaction rate. Also, the evolution of HD when the SrTiO$_3$ sample with a co-adsorbed layer of H$_2$O and D$_2$O was illuminated by band gap radiation implies that at least one of the OH bonds in water is broken on adsorption to the SrTiO$_3$ surface. Similar behavior has been found for water adsorbed on reduced titanium dioxide surfaces.$^{12}$ Finally and perhaps most significantly, the D$_2$O experiment clearly demonstrates that the
observed hydrogen evolution is due to water decomposition and not simply to photodesorption.

The successful photoassisted decomposition of adsorbed water vapor opens up a new area of investigation of photoassisted thermodynamically uphill processes on semiconductor surfaces. This result is especially encouraging since they indicate that other photoassisted by thermochemically forbidden oxidation-reduction reactions will also be feasible.

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References

Figure Captions

Fig. 1 Changes of ion currents (ΔI) as detected by the quadrupole mass spectrometer as a result of UV illumination on water adsorbed on strontium titanate powder surfaces.

Fig. 2 Rates of hydrogen, water and oxygen evolution due to UV illumination on water adsorbed on strontium titanate powder surfaces.
Fig. 1

(a) REDUCED SrTiO$_3$

(b) UNREDUCED SrTiO$_3$
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