

TiO₂ photoelectrochemistry and photocatalysis

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Water splitting into hydrogen and oxygen with minimum possible consumption of energy is one of the most important energy related chemical processes, because water is an inexhaustible natural resource, and hydrogen is known to be a renewable, sustainable and non-polluting energy source. Solar energy is another renewable energy source, which is considered as a major alternative to deal with the present energy and environmental problems.

By analogy with natural photosynthesis, it is attractive and useful to combine the above two processes and drive the decomposition of water by the use of light energy. We have succeeded in 1969, to photoelectrochemically decompose water at a titanium dioxide (TiO₂) and published their finding in a Japanese Journal (1). This finding has generated hope in photoelectrochemists and it has, in fact, become an active area of research in chemistry.

In 1972, we succeeded for the first time, in the photoelectrochemical decomposition of water under irradiation with light and without any applied electric power. In this experiment, we used n-type TiO₂ as the anode and Pt as the cathode. When the TiO₂ electrode was illuminated under short circuit conditions, hydrogen was evolved at the Pt electrode, while oxygen was evolved at the TiO₂ electrode.

This discovery attracted world-wide attention and triggered enormous research activity in numerous laboratories, especially after the oil crisis in 1973. Efforts are being made all over the world to find semiconductors that utilize the solar spectrum effectively to decompose water photoelectrochemically.

We named this negative shift of oxidation potential by light excitation as the photosensitized electrolytic oxidation. We have pointed out that this observation shows that the photoelectrochemical oxygen evolution reaction is analogous to that in natural photosynthesis. This has in turn spawned a tremendous amount of work on so-called "artificial photosynthesis." In the course of studying the fundamental behavior of semiconductor electrodes under irradiation, the above-mentioned electrochemical cell with TiO₂ anode and Pt cathode was conceived; and the hydrogen production at the cathode without any input of electrical energy was demonstrated by irradiating the TiO₂ electrode with light of the band-gap energy (3).

The principles and measurements obtained with photoelectrochemical studies at semiconductor electrodes have also lead to the research activity on heterogeneous photocatalysis. Again, TiO₂ was the first material that was tested, in the form of powder, for the photocatalytic oxidative decomposition of cyanide in aqueous solution by Frank and Bard in 1977, and it has continued to be the best photocatalyst (3).

We have demonstrated that gas-phase photocatalysis using TiO₂ nanoporous films is even more practical in comparison to liquid-phase photocatalysis. Their dream was to make use of TiO₂ photocatalytic activity for practical applications using normal sunlight and interior room light, which do not contain high UV

light intensities. We have carried out both mechanistic and application-oriented studies in this field and showed that TiO₂ works efficiently under very low light intensities, on the order of sub-microwatts, to decompose indoor air pollutants, which occur on the order of parts per million by volume (4). This means that the UV light available from ordinary fluorescent lighting should be sufficient to decompose such compounds on TiO₂ photocatalysts. We have shown that there are mass transport-limited and purely light intensity-limited regimes for the photodegradation of gas-phase organics (5).

We have also found another novel phenomenon, which they have termed "superhydrophilicity" (6). The water contact angle for TiO₂ surface changes to zero degrees upon UV irradiation and reverts when it is left in the dark. We found that the mechanism of this phenomenon is different from that of photocatalysis. Whereas in photocatalysis, the photogenerated electrons and holes react with molecular oxygen and water to produce superoxide radical anions and hydroxyl radicals, respectively, in superhydrophilicity, the photogenerated electrons tend to reduce Ti(VI) cations to the Ti(III) state, and the holes oxidize the O²⁻ anions and eject them from the surface. Adsorption of water molecules at these vacant sites has been found to be the reason for the increased hydrophilicity.

TiO₂ has been realized as a photoelectrochemical anti-corrosion coating material in 1995. The attractiveness of this material is also due to its self-cleaning property. If illuminated TiO₂ is brought in contact with a metal, electrons would be injected from the semiconductor to the metal via the conduction band. As a result, the potential of the metal can be shifted to negative direction of the corrosion potential of the metal, which then can be protected from corrosion. The photoelectrochemical protection is effective in the daylight. We went another step forward to see if we could retain this anticorrosion effect after the light is turned off. We coupled the TiO₂ film with an energy-storing component, WO₃, which can be charged during the illumination (7). Thus, WO₃ can protect the metal from corrosion even after the light is turned off until it is discharged. This research is progressing with an aim to enhance the lifetime of the charged WO₃.

References

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