

# This Week's Citation Classic

**Bard A J.** Photoelectrochemistry and heterogeneous photocatalysis at semiconductors. *J. Photochem.* 10:59-75, 1979. [Department of Chemistry, University of Texas, Austin, TX]

The principles and applications of semiconductor electrodes in photoelectrochemical cells (liquid junction photovoltaic, photoelectrosynthetic, and photocatalytic) are described. The extension of the principles of these cells to the design of simple particle systems for carrying out light-driven chemical reactions is discussed. [The SC<sup>®</sup> indicates that this paper has been cited in more than 245 publications, making it the most-cited article published in this journal.]

## Towards Artificial Photosynthetic Systems

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This paper is based on a lecture delivered at the Second International Conference on the Photochemical Conversion and Storage of Solar Energy, held in Cambridge, England, August 10-12, 1978. The "energy crisis" of 1973 kindled renewed interest in the use of solar energy for the generation of electricity and for the production of alternative fuels (such as hydrogen), and many research groups around the world had begun research efforts in this field. Most of the work was being carried out on the photochemistry of homogeneous systems involving dissolved reactants, but these generally showed very low efficiencies.

A key paper in 1972 by A. Fujishima and K. Honda,<sup>1</sup> on the use of a single crystal semiconductor electrode (titanium dioxide) in a photoelectrochemical cell for solar energy conversion, suggested a useful new approach. This work, which built on earlier studies by Brattain, Garrett, Gerischer, and others, showed that single crystal semiconductors (e.g., Si, Ge) could be studied as electrodes in liquid media. Our research group at

Texas, and many others, began studying such semiconductor-based electrochemical cells, and the effect of semiconductor material and solvent on their behavior and efficiency. My paper summarized the basic principles and concepts of such cells and suggested a number of approaches for improved conversion efficiencies in such cells. The paper has been widely cited, however, probably because it reviewed, for the first time, our work on the use of semiconductor particles for photoprocesses. Because single crystal semiconductors were expensive and unlikely to be used in practical systems, we immediately began to study alternatives, such as polycrystalline materials, that could be used as electrodes. We then thought of simply using semiconductor powders (e.g., TiO<sub>2</sub>, CdS) in liquid solutions for similar purposes. S. Frank and I showed that TiO<sub>2</sub> alone could be used to photooxidize cyanide and suggested possible applications to waste destruction.<sup>2</sup> B. Kraeutler and I then showed that, by metallizing the particles with platinum as a catalyst, other reactions, such as the decomposition of acetate to methane, were possible.<sup>3</sup> We explained such photoprocesses in terms of each particle behaving as a miniature photoelectrochemical cell and sketched a schematic representation that is now commonly used by others in the field. Indeed, in the following years, the study of particulate semiconductors, later extended to include colloidal dispersions, became an area of intense research, and hundreds of papers on TiO<sub>2</sub>, CdS, and other semiconductors have since appeared.<sup>4</sup> The interest in solar energy continues and, recently, large systems for water purification based on photoprocesses on TiO<sub>2</sub> particles have been constructed and tested.

1. Fujishima A & Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37-8, 1972. (Cited 605 times.)
  2. Frank S N & Bard A J. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions at TiO<sub>2</sub> powder. *J. Amer. Chem. Soc.* 99:303-4, 1977.
  3. Kraeutler B & Bard A J. Heterogeneous photocatalytic synthesis of methane from acetic acid—new Kolbe reaction pathway. *J. Amer. Chem. Soc.* 100:2239-40, 1978. (Cited 145 times.)
  4. Serpone N & Pelizzetti E, eds. *Photocatalysis—fundamentals and applications*. New York: Wiley. 1989. 650 p.
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