Photocatalytic Hydrogen Production by Direct Sunlight: A Laboratory Experiment

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Atıf Koca*
Department of Chemical Engineering, Engineering Faculty, Marmara University, 81040 Kadiköy, Istanbul, Turkey;
**akoca@marmara.edu.tr*

Musa Şahın
Department of Chemistry, Atatürk Faculty of Education, Marmara University, 81040 Kadiköy, Istanbul, Turkey

Human use of energy is natural and necessary; it is fundamental to life. Energy is an essential component of economic activity and required for the production of goods and the provision of services. Therefore, sustainable economic growth must be fueled by energy systems that are increasingly more efficient, less expensive, and cleaner. In other words, we must move from an energy system based on fossil fuels to an energy system based on more efficient, less expensive, cleaner, and renewable energy sources, such as hydrogen. In the future, hydrogen may be produced cost effectively from renewable energy sources. It will be stored and transported for use in home and office heating, generating electricity, industrial processes, and surface and air transportation. Hydrogen can replace some fossil fuels and reduce the use of other fossil fuels, decreasing pollution *(1–3)*.

The benefits of hydrogen make it the ideal component of a renewable and sustainable energy system of the future. It can be produced from water, an abundant supply source, using direct sunlight, renewable electricity, and some biological organisms. When burned directly as a fuel, or converted to electricity, its principal byproduct is water, which can be safely returned to the environment or reused to produce more hydrogen. Hydrogen energy has the potential for substantially contributing to the reduction of climate-changing emissions and other atmospheric pollutants *(4, 5)*.

Hydrogen can be obtained from water by a variety of methods that are currently not feasible for large-scale production, yet are the focus of immense research and development activity. During the last few years, photo–electrochemical processes at semiconductor–electrolyte interfaces, namely, photocatalysis and photosensitization, have attracted interest because of their possible application in the conversion of solar energy into chemical energy *(6–9)*.

Methods and techniques of photocatalytic reactions are described in some detail in many undergraduate chemistry programs *(10, 11)*. However, in instructional settings, little attention is given to how photocatalytic reactions are used for the production of hydrogen. In the present investigation we developed a photocatalytic hydrogen production experiment suitable for use in the undergraduate chemistry laboratory to demonstrate the use of a CdS/ZnS photocatalyst system for hydrogen production from direct sunlight. This experiment is simple to perform and suitable for inorganic chemistry, physical chemistry, chemical engineering, or environmental chemistry laboratories.

Use of this photocatalytic reactor and associated techniques can be adapted to a number of instructional and student research settings. In the design of this experiment we had several pedagogical goals. First, we wanted to introduce the students to the concept of a renewable and sustainable energy system of the future. Second, we wished to show an example of photocatalytic hydrogen production. Finally, we wanted to discuss the advantages and disadvantages of hydrogen and its production techniques.

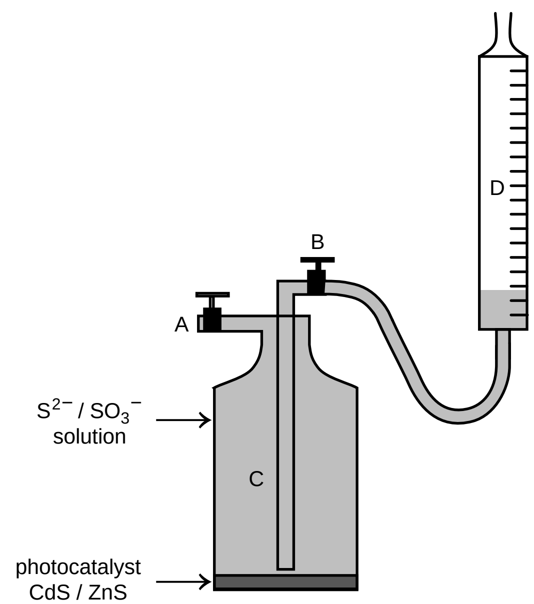

Figure 1. Photocatalytic hydrogen production reactor: A and B–shutoff valves, C–photocatalytic reactor, D–graduated pipet.

overall: H2S + SO3(-) --> H2 + S2O3(-)

$$CdS \xrightarrow{h\nu} e^- + h^+$$

$$e^- + H^+ \rightarrow \tfrac{1}{2}H_2$$

$$h^+ + S^- \rightarrow S$$

$$S + SO_3^- \rightarrow S_2O_3^-$$

Scheme I. Reaction mechanism discussed in detail in ref *13.* The free electron and hole from the catalyst are represented by e^- and h^+, respectively.

Table 1. Compositions of the CdS/ZnS Photocatalyst System and the Volumes of Hydrogen Evolved

Student Groups	CdS:ZnS	CdS/ZnS/mg	w% CdS/mg	w% ZnS/mg	Vol of H_2/mg
1	4:1	100	80.0	20.0	4.20
2	3:1	100	75.0	25.0	8.30
3	2:1	100	66.6	33.4	15.6
4	3:2	100	60.0	40.0	12.5
5	1:1	100	50.0	50.0	5.40
6	2:3	100	40.0	60.0	4.50
7	1:2	100	33.4	66.6	3.80

Experimental

In this experiment an inexpensive and workable photocatalytic hydrogen production system was designed as shown in Figure 1. The photocatalytic reactor used in this system is a 250-mL gas-washing bottle with a two shutoff valves adapted to the bottle. A 25-mL graduated pipet is fitted to the B valve of the reactor to measure the volume of hydrogen gas produced.

Different compositions of CdS/ZnS used as a photocatalyst were prepared by a modification of a published procedure *(12, 13)*. The CdS/ZnS photocatalysts were precipitated by mixing a hot solution of Na_2S with a hot mixture of $CdCO_3$ and $ZnCO_3$ dissolved in acetic acid solutions. By following this procedure, different compositions of CdS/ZnS were prepared.

To determine photocatalytic activity of the CdS/ZnS, the reactor was filled with a mixture of Na_2S and Na_2SO_3 aqueous solutions, which was used as sacrificial material in this system (Scheme I). Then CdS/ZnS photocatalyst was added to this solution. The reactor system was exposed to direct sunlight for approximately 2 hours. The volume of hydrogen evolved was assessed from the displacement of liquid into the graduated pipet.

Results

Student groups carried out different series of experiments to compare the volume of hydrogen evolved by different compositions of CdS/ZnS. The compositions of photocatalysts and the volumes of hydrogen evolved are shown in Table 1. The volume of hydrogen produced varied with the composition of CdS/ZnS. A 2:1 composition of the CdS/ZnS is the most efficient composition of the photocatalyst in this system.

Conclusions

The experiment nicely demonstrated how photocatalysts can be used to produce hydrogen and to predict the most suitable photocatalyst system. It illustrated that CdS/ZnS photocatalyst is a suitable material for hydrogen production in the reactor described. The experiment also indicated that this photocatalytic hydrogen production system is a simple and workable system that can be used in an undergraduate laboratory because it is inexpensive, easy to operate, and suitable for use in a variety of educational settings. The use of this system to treat sulfide and sulfite, undesirable waste products in fossil fuel technology, is another benefit of the system.

If this experiment is included in an undergraduate chemistry laboratory, it provides students a good example of photocatalytic production of hydrogen by direct sunlight from aqueous solution. The experiment also can be used to introduce topics in semiconductors and catalysts.

Hazards

Hydrogen is flammable. Cadmium salts are carcinogens and may be fatal if swallowed. Na_2S is spontaneously flammable, incompatible with acids, metals, and oxidizing agents. It is toxic and corrosive, and causes burns. Na_2SO_3 may cause irritation and allergic reaction. $ZnCO_3$ has no significant hazards.

ʷSupplemental Material

Background, theory, and instructions for the students are available in this issue of *JCE Online*.

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