

Photochemical Production of Hydrogen from Alkaline Solution Containing Polysulfide Dyes

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Abstract—Efficient hydrogen production was achieved by irradiating solutions containing polysulfide dyes as a photoabsorber. In the presence of polysulfide only, considerable amount of hydrogen was initially evolved and followed by the rapid decrease of the evolution rate. On the contrary, in the co-presence of $\text{NiO}_{(x<1)}/\text{TiO}_2$ and polysulfide, steady evolution of hydrogen was observed even after long period of illumination. The photocatalytic evolution of hydrogen was divided into two stages: i) in the first stage within 1 hour irradiation, the hydrogen evolution rate was abruptly increased due to the conversion of polysulfide to partially oxidized sulfur, $\text{S}_2\text{O}_4^{2-}$; ii) in the secondary stage after 1 hour irradiation, steady evolution of hydrogen was observed due to the conversion of partially oxidized sulfur to fully oxidized sulfur. The oxidation/reduction of sulfur occurred more favorably over SiC catalyst where more steady evolution of hydrogen was achieved.

Key words: Hole Scavenger, Polysulfide, NiO/TiO_2 , SiC, Hydrogen Evolution

INTRODUCTION

A photochemical system of hydrogen production by spending sacrificial agents has been an important topic in view of solar energy harvesting [Fujishima and Honda, 1972; Pichat et al., 1981; Domen et al., 1982; Kawai and Sakata, 1979; Sato, 1988]. As one of the metal oxide semiconductors, TiO_2 has been widely used, but it shows a low quantum yield. For promoting the hydrogen evolution rate, therefore, several researches have been performed with hole scavengers such as methanol, carbonate, and sulfide [Pichat et al., 1981; Pellizetti et al., 1984]. Contrasted with frequent use of metal complexes in the so-called sacrificial systems, organic dyes have been rarely used as sensitizers for the photoreduction of water. The common availability of organic dyes, however, initiated the exploration of potential use of polysulfide dye as a photoabsorber [Kalyanasundaram and Dung, 1980; Hashimoto et al., 1983]. Pellizetti et al. reported the high activity of sulfide over CdS colloid in the photocatalytic decomposition of water [Pellizetti et al., 1984]. Owing to the high oxidation ability of sulfide, it can play as an effective hole scavenger even in the visible region. The advantages in using polysulfide are its good sacrificial ability, feasibility of preparation, and economical aspects (low cost and easy recycling of sulfur) [Lee and Lee, 1998]. In this study, the effect of a hole scavenger on the photoreduction of water was investigated by the use of aqueous polysulfide prepared by directly dissolving sulfur powder in alkaline solution.

EXPERIMENTAL SECTION

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1. Photocatalytic Reaction System

A photoreactor of carrier-gas flow type was made of Pyrex cylinder (ca. 600 cm³) whose inner part was jointed by the quartz cylinder as a lamp window. UV irradiation was carried out with a high-pressure mercury lamp (450 W, Kum-Kang Co.), and operation temperature was controlled at 25±1 °C during illumination. In each experiment, the volume of illuminated solution was maintained as 500 ml, and oxygen-free N_2 gas was bubbled continuously through the solution at a rate of 20 cc/min. For the analysis of hydrogen production, 0.5 cc gas sample from the reaction vessel was analyzed by gas chromatography (Yanaco, G1800T, Porapak Q). For the analysis of quantum yield, photon flux from the lamp was measured by chemical actinometry method using potassium ferrioxalate, $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ [Rabek, 1982]. The measured photon flux was 3×10^6 einstein/sec which corresponded to 4.75 mmole H_2 per hour. UV/Vis spectroscopy, ion chromatography and mass spectroscopic techniques were also employed to analyze the reaction solution.

2. Preparation of Catalyst and Polysulfide Materials

5 wt% NiO -doped TiO_2 was used as a catalyst for photoreduction of water. The crystal structure of TiO_2 from Aldrich Co. was mainly anatase (99.9%). For a better activity, partially reduced nickel oxide catalyst, $\text{NiO}_{(x<1)}$ -doped TiO_2 , was prepared by the reduction of NiO -doped TiO_2 in H_2 stream at 500 °C for 2 hours and oxidation in O_2 at 473 K for 1 hour.

Polysulfide in aqueous phase was prepared by dissolving sulfur powder in alkaline solution as follows: i) 80 g NaOH was dissolved in 2,000 ml water, and 6.4 g of sulfur powder was put into the solution, ii) 5 ml of CS_2 was dropped into the solution, iii) after stirring for 24 hours, undissolved sulfur powder was filtered out to obtain aqueous polysulfide. The color of the solution containing polysulfide was yellow-to-red. The content of sulfur dissolved was calculated as 1.51 mg/ml from the quantitative analysis of UV-Vis

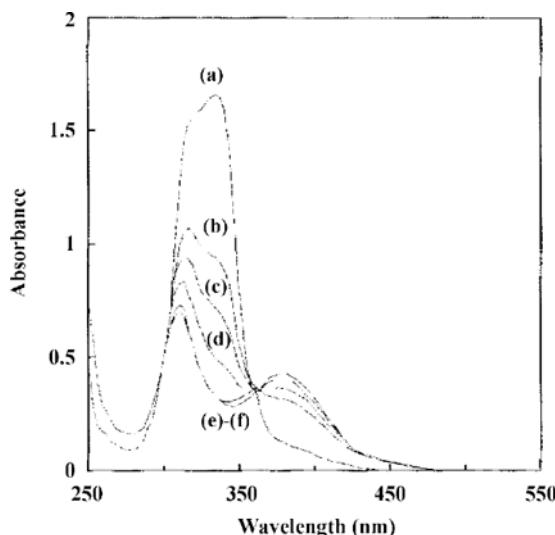


Fig. 1. Changes of polysulfide in UV absorbance in the presence of 5 wt% NiO_x/TiO₂ catalyst as a function of stirring time.
(a) initial, (b) 1 hour, (c) 2 hours, (d) 3 hours, and (e)-(f) 4-5 hours.

absorption spectra.

RESULTS AND DISCUSSION

1. Properties of Polysulfide

UV-Vis spectrum was obtained to characterize the properties of polysulfide dissolved in alkaline solution. As shown in Fig. 1(a), aqueous polysulfide gave three absorption peaks at 315, 335 and 390 nm which were assigned, respectively, to S₄²⁻ (peak at 335 nm) and S₆²⁻ (peaks at 315 and 390 nm) [Kalyanasundaram and Dung, 1980]. In the presence of NiO_x-doped TiO₂ catalyst, the peak intensity and location were changed even in the absence of light [Fig. 1(b)-(f)], whereas the peak change was not observed in the presence of single TiO₂ catalyst. During illumination with NiO/TiO₂ catalyst, the peak was gradually decreased and shifted down to 310 and 370 nm. This indicated that the initial state of polysulfide was so unstable as to reestablish stable species in the presence of a small amount of catalyst, i.e., the initial species of S₄²⁻ and S₆²⁻ were recombined into the final species of S₄²⁻ and S₆²⁻ over NiO_x-doped TiO₂ catalyst [Schwarzenbach and Fischer, 1960]. Mass spectroscopy for polysulfide sample showed the signals of S₄²⁻ (m/e=128) and S₆²⁻ (m/e=192), respectively.

2. Activity of Polysulfide

The hydrogen evolution was observed in the presence of polysulfide without catalyst [Fig. 2(a)]. Its rate was abruptly increased within one hour illumination and followed by rapid decrease for longer period of illumination. The abrupt increase of hydrogen evolution in the early stage of illumination was attributed to the decomposition of polysulfide, which was verified from the rapid variation of UV-Vis spectra of polysulfide with illumination time. Namely, the polysulfide peak disappeared with the increase of illumination time, and only a trace of polysulfide peak was detected after one hour illumination. The decomposition of polysulfide during illumination was also confirmed with no detection of S₄²⁻ and S₆²⁻ peaks by mass spectroscopy.

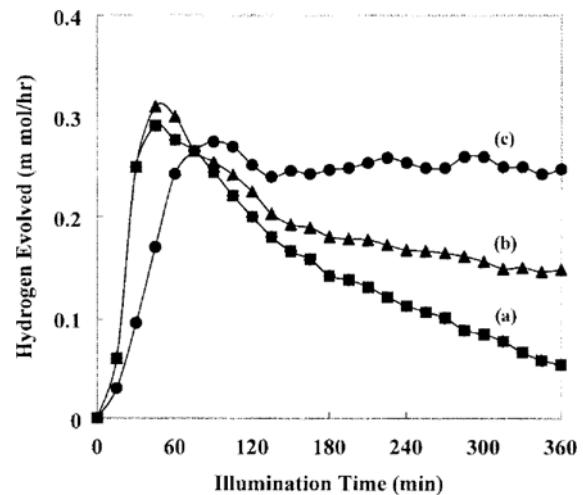
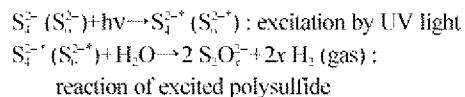
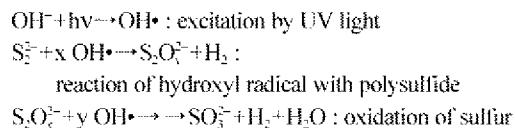


Fig. 2. The rate of hydrogen evolution during illumination.
(a) without catalyst, (b) with TiO₂, and (c) with 5 wt% NiO/TiO₂ catalyst.

Even in the presence of polysulfide without catalyst, a durable evolution of hydrogen was observed for long period of illumination, which was attributed to the instantaneous recombination of fragmented (or depolymerized) polysulfide into polymerized sulfides and/or the oxidation of partially oxidized sulfur to fully oxidized sulfur. Even though the short-lived recombination process has not been verified yet, a favorable reaction scheme could be suggested as follows where the superscript * denotes the activated state of polysulfide by UV light.



In the case of TiO₂ catalyst added to the polysulfide solution, higher photocatalytic activity was induced after 3 hours illumination, compared with polysulfide-only case [Fig. 2(b)]. To explain the above result, it was assumed that the fragmented polysulfide was oxidized to SO₃²⁻ and/or SO₄²⁻. During the oxidation process of fragmented polysulfides, hydrogen could be evolved by the following reactions.



In the case of NiO_x-doped TiO₂, the rate of hydrogen evolution was rapidly increased at early stage within 2 hour illumination and remained at 280 μmole/hour up to 6 hours of illumination [Fig. 2(c)]. The steady evolution of hydrogen for longer period of illumination was due to the ability of partially reduced-Ni on TiO₂ surface to collect the photogenerated electron. It meant that the photogenerated electrons and holes could accumulate separately on NiO and TiO₂ and participate in the evolution of hydrogen as well as the oxidation of polysulfide.

The maximum of hydrogen production rate was correlated with the amount of aqueous sulfur as a polysulfide (Fig. 3). As the amount of aqueous sulfur was increased, the hydrogen evolution rate was

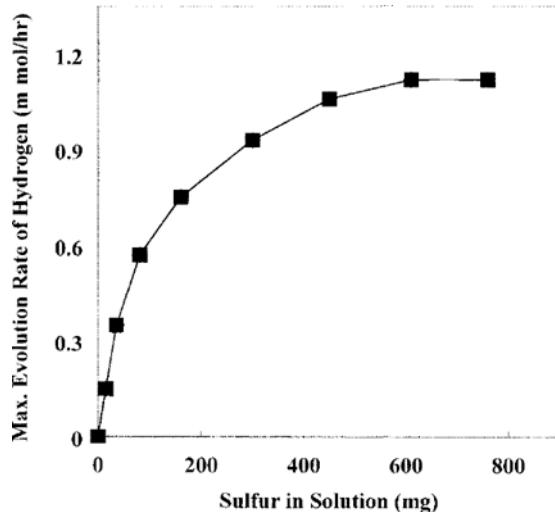


Fig. 3. Maximum rate of hydrogen production in the presence of polysulfide as a function of sulfur amount in the solution of 0.05 M NaOH.

proportionally increased and finally reached an asymptotic value, i.e., hydrogen production rate did not increase any more over a certain amount of sulfur. In conclusion, the polysulfide was an active photoabsorber of UV light, and the quantum yield was about 25% at the maximum production rate.

Ion chromatographic analysis of polysulfide was conducted by the variation of illumination time. As shown in Fig. 4(a), a small amount of sulfite was observed in the initial state of polysulfide, but the oxidized sulfur (such as sulfate and sulfite) was increased with the increase of illumination time. Eventually, after 9 hours of illumination the peak intensity of sulfite was higher than that of sulfate. As shown in Fig. 5, the total oxidized sulfur was increased in proportion to illumination time up to 9 hours and remained at a constant value after then. However, the evolution of hydrogen occurred continuously even after 9 hours albeit at a reduced rate.

3. Enhancement of Photocatalytic Activity

The previous activity test with polysulfide as a sacrificial agent indicated that the oxidation and reduction of sulfur occurred over

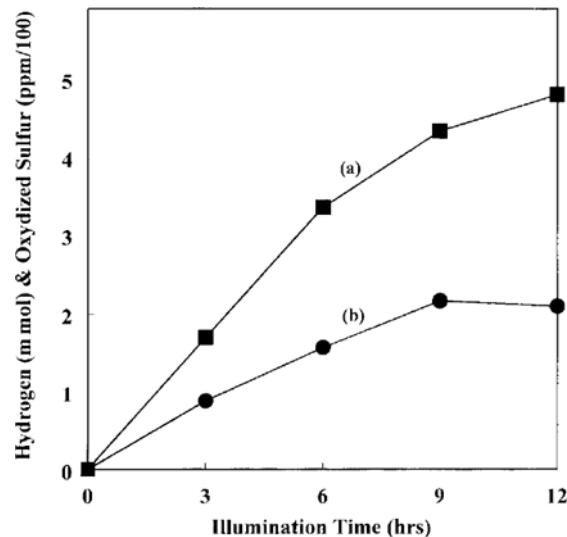
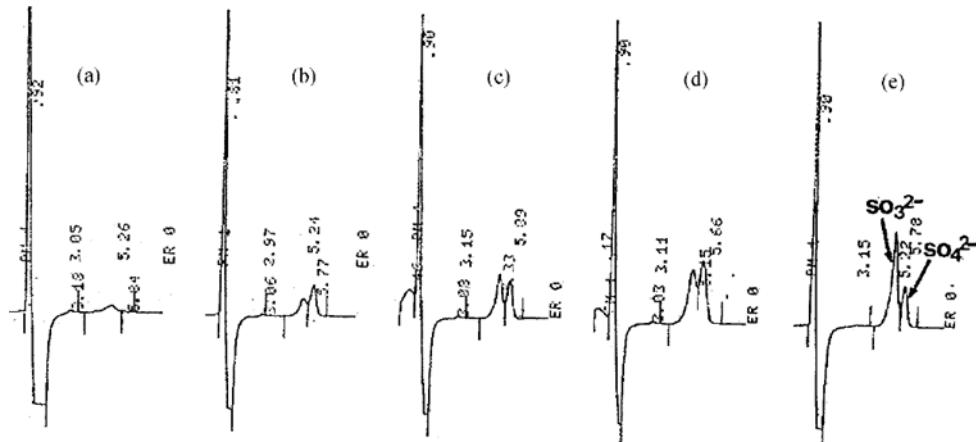


Fig. 5. (a) The amount of hydrogen evolved, and (b) the amount of oxidized sulfur during illumination.

the catalyst during illumination. However, NiO-deposited TiO₂ catalyst did not favor the reduction of oxidized sulfur to partially oxidized sulfur because the position of conduction band of TiO₂ is slightly higher or even lower than reduction potential of various oxidized sulfur species. A new catalyst of SiC was adopted for enhancing the reduction of oxidized sulfur, which was an n-type semiconductor with bandgap energy of 3.0 eV, i.e., the conduction band position=-1.5 eV and valence band position=+1.5 eV. Fig. 6 showed the comparative photocatalytic activities of NiO-doped TiO₂ catalyst and the mixture of NiO/TiO₂ and NiO/SiC catalysts. In the case of NiO-deposited TiO₂ catalyst alone, the hydrogen evolution rate was decreased with the increase of illumination time [Fig. 6(a)]. On the contrary, the mixture of NiO/TiO₂ and NiO/SiC exhibited higher activity in hydrogen evolution than NiO/TiO₂ catalyst [Fig. 6(b)]. The reduction process of oxidized sulfur favorably proceeded over SiC catalyst, i.e., more durable evolution of hydrogen was achieved.

SiC, as a semiconductor with bandgap energy of 3.0 eV, could not produce hydroxyl radical because its valence band was located



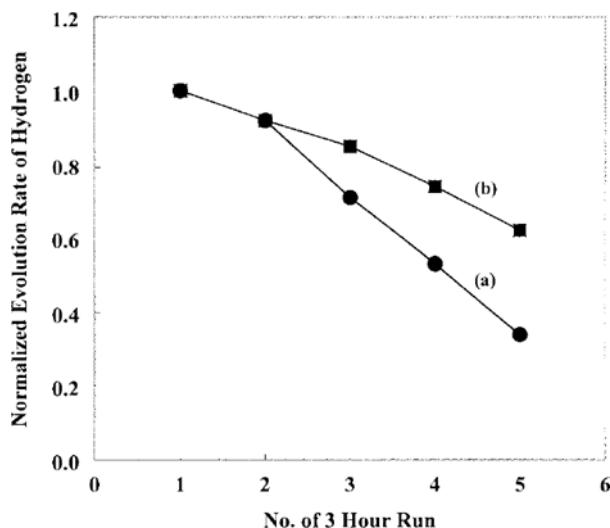


Fig. 6. Activities of (a) 5 wt% NiO/TiO₂ catalyst and (b) the mixture of 5 wt% NiO/TiO₂ and 5 wt% NiO/SiC catalyst.

at higher position than that of oxidation potential of hydroxyl ion induced by UV light. In junction with TiO₂ semiconductor, however, SiC provided a reduction site for oxidized sulfur like sulfite or polysulfide, as previously described in literature [Schiavello, 1988]. Furthermore, higher photocatalytic activity in conjunction with NiO/TiO₂ and NiO/SiC was observed in our experiment. Therefore, a repeating cycle of oxidation and reduction of sulfur species during illumination was suggested.

CONCLUSIONS

Polysulfide, a model compound of sulfur, performed as an effective hole scavenger for the photoreduction of water to hydrogen, i.e., 25% of high quantum yield was obtained. Polysulfide, which was prepared by direct dissolving sulfur powders in the alkaline solution, was initially composed of S₂²⁻, S₃²⁻ and S₄²⁻. However, these species were so unstable as to reestablish to S₂²⁻ and/or S₄²⁻ in the presence of catalyst. By using NiO/TiO₂ catalyst and polysulfide, steady evolution of hydrogen was maintained for long period of illumination. At the early stage of illumination within 1 hour, an abrupt increase of hydrogen evolution was observed, which was attributed to the conversion of polysulfide to monomeric sulfur or partially oxidized sulfur, S₂O₂²⁻. At the later stage of illumination after 1 hour, steady evolution of hydrogen was observed, which was attributed to the partially oxidized sulfur to fully oxidized sulfur. By adopting SiC catalyst, the oxidation and reduction of sulfur progressed in a cyclic manner, and more durable evolution of hydro-

gen was achieved. In conclusion, polysulfide performed as a good hole scavenger during illumination, resulting in formation of oxidized sulfur such as sulfite and/or sulfate as final products.

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