Environmental remediation, Disinfection, Energy production

Sunlight-driven photocatalytic production of H_2 from H_2O_2

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Abstract

Hydrogen peroxide (H_2O_2) is an important chemical used for bleaching and disinfection, and is a promising energy carrier as a fuel for fuel cell power generation. It is, however, difficult to generate hydrogen gas (H_2), and has been considered not to be used as a hydrogen carrier. In this research, we succeeded in generating H_2 from H_2O_2 by adding phosphoric acid (H_3PO_4) and a metal-free powder photocatalyst to an H_2O_2 solution under sunlight irradiation. Social implementation can be expected toward the realization of a new energy society with H_2O_2 as a hydrogen/energy carrier.

Background & Results

For the social implementation of H_2O_2 as an energy carrier, it is indispensable also to use it as a hydrogen carrier. That is, as shown in Fig. 1, the on-site generation of H_2 from H_2O_2 ($H_2O_2 \rightarrow H_2 + O_2$, $\Delta G° = +131$ kJ mol_{-1}, equation (1)) is necessary. However, the reduction of H_2O_2 ($H_2O_2 + H^+ + e^- \rightarrow H_2O + \cdot OH$, $H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$, equation ④) proceeds in preference to the H^+ reduction (equation ③) Furthermore, typical metal/metal oxide semiconductor, when used as a photocatalyst, promotes the decomposition of H_2O_2 on the surface ($H_2O_2 \rightarrow H_2O + 1/2O_2$, $\Delta G° = -117$ kJ mol^{-1}, equation ⑤). Therefore, there has been no example of generating H_2 from an H_2O_2 solution.

We made a meta-free photocatalyst consisting of graphitic carbon nitride (g-C_3N_4) organic semiconductor and graphene quantum dots (GQDs) cocatalysts. We found that sunlight (visible light) irradiation of an H_2O_2 solution containing the catalyst and phosphoric acid (H_3PO_4) successfully produces H_2 (Fig. 2). The metal-free catalyst scarcely promote the H_2O_2 decomposition (equation ⑤), and the hydrogen bonding interaction between H_2O_2 and H_3PO_4 forms a stabilized complex (Fig. 1, right) to suppress the H_2O_2 reduction(equation ④), thus promoting H^+ reduction (equation ③). H_3PO_4 has long been added to commercially available aqueous H_2O_2 solutions as a stabilizer. Therefore, the H_2O_2 solution containing H_3PO_4 obtained after the reaction can be stored and transported and can be used for on-site H_2 generation on an inexpensive metal-free photocatalyst. This may open a new possibility for the use of H_2O_2 as a new hydrogen/energy carrier.

Significance of the research and Future perspective

Energy carriers are considered to be the key material for realizing a non-fossil fuel dependent society. H_2O_2 is a promising candidate but cannot be used for H_2 generation. H_2O_2, therefore, has been considered to be unusable as a hydrogen carrier. Our results indicated that the use of H_3PO_4 and an inexpensive metal-free photocatalyst facilitates H_2 generation by sunlight. Although it is essential to improve the selectivity and H_2 production activity, the results open a new possibility towards sustainable energy society using H_2O_2 as a hydrogen/energy carrier.

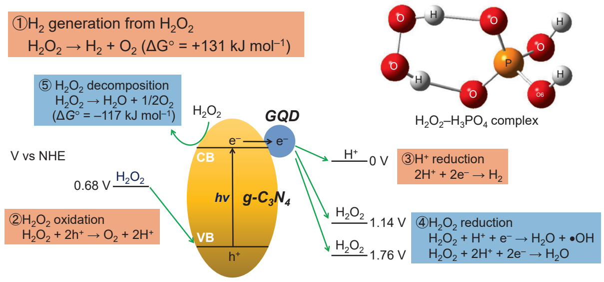

Fig. 1 Mechanism for H_2 generation from H_2O_2 (H_3PO_4 stabilizes H_2O_2 by hydrogen bonding interaction with H_2O_2 and suppresses the reduction by excited electrons)

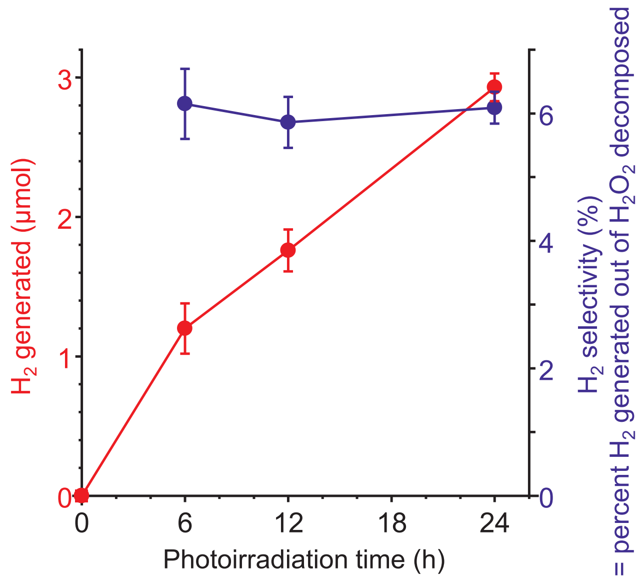

Fig. 2 Time change in the amounts of H_2 produced and the H_2 selectivity during simulated sunlight irradiation (λ >420 nm) (H_2 is continuously generated by photoirradiation, and H_2 selectivity is almost constant).

Patent: Japanese Patent No. 6765132

Treatise: Shiraishi, Yasuhiro; Takii, Takahiro et al. Resorcinol-Formaldehyde Resins as Metal-Free Semiconductor Photocatalysts for Solar-to-Hydrogen Peroxide Energy Conversion. Nat. Mater. 2019; 18(9): 985-993. doi: 10.1038/s41563-019-0398-0
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Keyword: photocatalyst, sunlight, hydrogen peroxide