Production of valuable chemicals on oxide semiconductor photoelectrodes under visible light for solar chemical conversion process

Kazuhiro Sayama *
* Country Research Center for Photovoltaics (RCPV), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565 Japan
Fax number: +81-(0)29-861-4760, E-mail: k.sayama@aist.go.jp

Abstract:
The photoelectrochemical reaction for the efficient production of hydrogen and high-value-added oxidation reagents (H$_2$O$_2$, HClO, S$_2$O$_8^{2-}$, Ce$^{4+}$, etc.) using porous oxide photoanodes under solar simulated light was investigated. These faradaic efficiencies were significantly improved up to 100% by the optimization of the reaction conditions and surface modification of photoanodes. This solar-to-chemicals reaction is one of the practical artificial photosynthesis technologies for the solar energy conversion and utilization.

Keywords: Photoelectrodes, oxidation reagents, artificial photosynthesis.

1. Introduction
The expansion of utilization methods on clean, huge and limitless solar energy is very important issue. The development of inexpensive, simple and innovative technologies is needed for using fluctuant and low-density solar light energy. An artificial photosynthesis, which converts photon energy into chemical energy directly, is considered as one of a few promising choices. In the field of artificial photosynthesis using semiconductor photocatalysts and photoelectrodes, various oxidative products except O$_2$ have been scarcely paid attention. Our group have investigated on the photoelectrochemical reaction for the efficient production of hydrogen and high-value-added oxidation reagents such as H$_2$O$_2$, HClO, S$_2$O$_8^{2-}$, Ce$^{4+}$, IO$_4^{-}$ and organic compounds using porous oxide photoanodes prepared by simple processes (Fig. 1)1-7. We also recognized the significance and impact of these reactions on the aspects of not only the basic science in artificial photosynthesis reaction but also the useful applications in industries within a short period. Various kinds of chemicals are produced by a large amount of consumption of fossil energy directly and indirectly, and the improvement of the energy efficiency and the significant reduction of CO$_2$ emission in these chemical industries are very important subject. The efficient photoelectrochemical production of high-value-added chemicals with low voltage using solar energy is one of the desirable processes, however these research and developments are very few so far. It is very difficult to obtain an economical benefit only by producing and selling of H$_2$ from water photo-electrochemically, because the H$_2$ market price from competitors using fossil energy is very cheap. The economical O$_2$ production is also difficult because of the lower O$_2$ market price than H$_2$. However, if some high-value-added chemicals which are a few ten or hundred times expensive than H$_2$ and O$_2$ per electron (per photon) can be produced on photoanode oxidatively in addition to the H$_2$ production on cathode, the economic performance in the total photoelectrochemical system will be tremendously and practically improved. In this presentation, some recent progresses in our group and the significance of the production of various oxidizing reagents by photo-electrochemical reactions using simple and inexpensive oxide semiconductor photoanodes are reported for “Solar Chemicals”.

2. Experimental
Porous photoelectrodes of WO$_3$ or BiVO$_4$ on FTO conducting glass were prepared by spin coating of metal precursor solutions and calcination1-4. The photoelectrochemical performance of the photoanodes was measured using an electrochemical analyzer and a solar simulator calibrated to AM-1.5 (1 sun, 100 mW cm$^{-2}$) with a spectroradiometer. The oxidation reagents were mainly analyzed by color reactions and UV-vis spectrometer.

3. Results and discussion
WO$_3$ photoelectrode enabled the production and accumulation of O$_2$, S$_2$O$_8^{2-}$, Ce$^{4+}$ or IO$_4^-$ as oxidation products, as shown in Fig. 1. Most notably, S$_2$O$_8^{2-}$, which possesses the highest oxidizability among all peroxides, was generated with high applied bias photon-to-current efficiency (ABPE (H$_2$, S$_2$O$_8^{2-}$) = 2.2 – 2.45%) and faradaic efficiency (FE(S$_2$O$_8^{2-}$) = ca. 100%) on irradiation from the back side of the WO$_3$ photoelectrode$^1$$^3$. Furthermore, we investigated oxidative H$_2$O$_2$ production from water on a WO$_3$/BiVO$_4$ photoanode simultaneously with production of hydrogen on a Pt cathode in bicarbonate electrolyte even at a voltage far lower than the theoretical electrolysis voltage (1.77 V) under simulated solar light$^2$. An unprecedentedly efficient simultaneous production and accumulation of H$_2$O$_2$ was achieved in 2.0 M KHCO$_3$ at low temperature, and the maximum FE(H$_2$O$_2$) generated reached > 54%. I was surmised that the bicarbonate anion played as catalyst through peroxo-carbonates for H$_2$O$_2$ production. In order to improve the FE, the surface of the photoanode was modified with various metal oxides. A mesoporous and amorphous aluminum oxide (Al$_2$O$_3$) layer on WO$_3$/BiVO$_4$ photoanode significantly facilitated inhibition of the oxidative degradation of generated H$_2$O$_2$ into oxygen (O$_2$) on the photoanode, resulting in unprecedented FE(H$_2$O$_2$) (ca. 80%) and the accumulation (>2500 $\mu$ M at 50 C)$^5$. Moreover, the Au cathode facilitated two-electron reduction of O$_2$, resulting in reductive H$_2$O$_2$ production with high current efficiency. Combining the WO$_3$/BiVO$_4$ photoanode with a HCO$_3^-$ electrolyte and an Au cathode also produced a clean and promising design for a photoelectrode system specializing in H$_2$O$_2$ production (FE$_{\text{anode}}$(H$_2$O$_2$) = ca 50%, FE$_{\text{cathode}}$(H$_2$O$_2$) = ca 90%, FE$_{\text{total}}$(H$_2$O$_2$) = ca. 140%) even without applied voltage after connected electrically at a clip between photoanode and cathode under simulated solar light via 2-photon process; this achieved effective H$_2$O$_2$ production using an Au-supported porous BiVO$_4$ photocatalyst sheet$^4$. It was also found that both BiVO$_4$ and bicarbonate anion are very effective for H$_2$O$_2$ production in not only photo-electrochemical reaction under solar light but also simple electrochemical reaction in the dark for compact systems$^6$. It is suggested that BiVO$_4$ played not only as light absorption material but also as real catalyst for H$_2$O$_2$ generation.

4. Conclusions

Various high-value-added chemicals (H$_2$O$_2$, HClO, S$_2$O$_8^{2-}$, Ce$^{4+}$, Br$^-$, organic compounds, etc.) could be produced and accumulated using porous WO$_3$ or BiVO$_4$/WO$_3$ photoanodes under solar simulated light, with the production of H$_2$ or H$_2$O$_2$ on various cathodes such as Pt and Au. The oxidation reagents can be utilized in future for bleaches in laundry and household use detergents, treatment of dye wastewater, and sterilization of food, and disinfection for virus, bacteria, spore etc.

References