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

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Abstract:
The photoelectrochemical reaction for the efficient production of hydrogen and high-value-added oxidation reagents (H_2O_2, HClO, $S_2O_8^{2-}$, 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_2O_2, HClO, $S_2O_8^{2-}$, 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 calcination[1-4]. 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, $S_2O_8^{2-}$, Ce^{4+} or IO_4^- as oxidation products, as shown in Fig. 1. Most notably, $S_2O_8^{2-}$, which possesses the highest oxidizability among all peroxides, was generated with high applied bias photon-to-current efficiency (ABPE (H_2, $S_2O_8^{2-}$) = 2.2 – 2.45%) and faradaic efficiency (FE($S_2O_8^{2-}$) = ca. 100%) on irradiation from the back side of the WO_3 photoelectrode[1,3]. Furthermore, we investigated oxidative H_2O_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_2O_2 was achieved in 2.0 M $KHCO_3$ at low temperature, and the maximum FE(H_2O_2) generated reached > 54%. I was surmised that the bicarbonate anion played as catalyst through peroxo-carbonates for H_2O_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_2O_3) layer on WO_3/$BiVO_4$ photoanode significantly facilitated inhibition of the oxidative degradation of generated H_2O_2 into oxygen (O_2) on the photoanode, resulting in unprecedented FE(H_2O_2) (ca. 80%) and the accumulation (>2500 μM at 50 C)[5]. Moreover, the Au cathode facilitated two-electron reduction of O_2, resulting in reductive H_2O_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_2O_2 production ($FE_{anode}(H_2O_2)$ = ca 50%, $FE_{cathode}(H_2O_2)$ = ca 90%, $FE_{total}(H_2O_2)$ = 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_2O_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_2O_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_2O_2 generation.

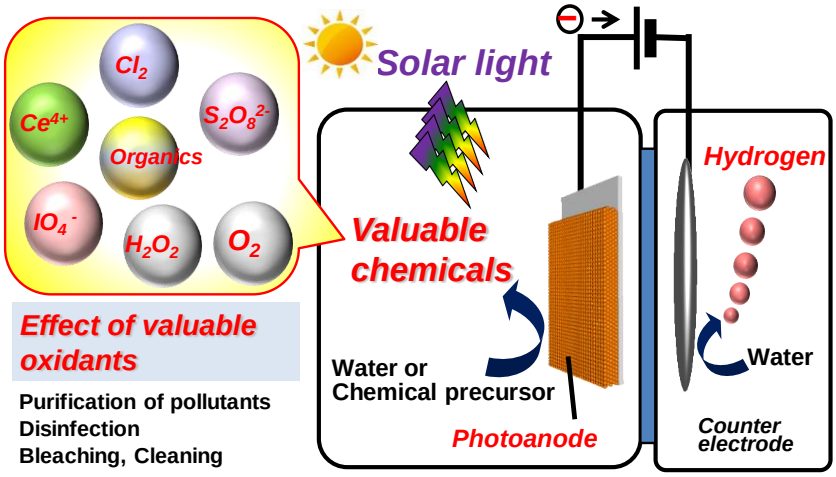

Figure 1. Production of high-value-added oxidants using oxide photo-anode.

4. Conclusions

Various high-value-added chemicals (H_2O_2, HClO, $S_2O_8^{2-}$, 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_2O_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.

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