The Effect of Platinum Deposition on the Water Photo-Reduction at p-Cu₂O Semiconductor Electrodes with Visible Light Irradiation

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The surface of a p-Cu₂O semiconductor photoelectrode was modified by electrodeposition of Pt nanoparticles and analyzed by XRD, SEM, XPS, and EIS (electrochemical impedance spectrometry) methods besides photocurrent measurements. The XRD, SEM, and XPS analyses showed the fabrication of Cu₂O film and the deposition of Pt particles. On the electrodeposition of Pt nanoparticles, cathodic photocurrent was enhanced. The EIS analysis suggested that Pt nanoparticles enhance the charge transfer process to the solution.

Key Words: Cu2O Photoelectrode, Pt Nanoparticles, Hydrogen Evolution, Photoelectrocatalysis,

1 Introduction

Photoelectrochemical water splitting driven by solar light energy is one of the attractive targets for the development of hydrogen fuel production systems, because it is an ultimate solution for solving both the energy and environmental problems. Many metal oxide semiconductors working in a visible light region have been developed as photoelectrodes for water splitting.15) Recently, we have reported BiVO4 electrodes coupled with SnO2 and WO3 thin layers⁶⁷⁾ in order to develop a photo-anode with a high activity of oxygen evolution under visible light irradiation. Moreover, gold nanoparticles were deposited on WO₃/BiVO₄ photoelectrode and the anodic photocurrent was increased.8) Since these electrodes are ype semiconductors and the potential is not enough or water reduction, p-type semiconductors have been expected as a photo-cathode for water reduction. As an efficient photo-cathode was prepared, a tandem-type photoelectrochemical cell9) for solar water splitting can be fabricated with the photo-anode reported.

A p-type copper (I) oxide (Cu₂O) semiconductor is one of the most attractive materials because the band gap energy is so narrow (2.0-2.2 eV) enough to absorb efficiently the solar light, and the conduction band level is negative enough for the reduction of water. (0.11) Various researchers on the photocatalytic properties of Cu₂O have been reported. Hara et al. 12) investigated the photocatalytic water spitting to H2 and O2 on Cu2O powder. However, the mechanism of the process was not clear. To clarify the mechanism, Jongh et al. 13) studied the electrochemical photocatalytic properties of Cu₂O electrode of water decomposition. They concluded that the Cu2O band gap energy is suitable to reduce water to hydrogen than that the water oxidation as consider in the level of energy bands. Although p-Cu₂O is used as a photo-cathode towards hydrogen evolution under visible light irra-

diation, the photocatalytic activity of pure Cu2O is unusually low because of the recombination of the photogenerated electrons and holes. This effect was studied by Nagasubramanian et al. 14) who confirmed the rapid recombination processes of p-Cu₂O in acetonitrile solution. There are many reports on preventing the recombination to enhance charge separation in Cu2O semiconductor. The charge separation could be improved by trapping electrons at the conduction band of Cu₂O. 15) It may possible to improve the charge separation by combining an n-type WO3 with the p-type Cu2O electrode for H₂ evolution. 16 Assembling of metal nanoparticles on the semiconductor surface is one of the strategies to achieve a high catalytic activity. We found in the previous study that the modification with gold nanoparticles could improve the surface properties of a BiVO4 electrode to enhance the water oxidation.8) Therefore, metal nanoparticles were expected to modify the Cu₂O surface to promote the photocatalytic activity for water reduction.

Platinum is an attractive metal because of the high catalytic activity with a low over potential for hydrogen evolution. 17,18) Peruffo et al. reported an electrochemical method which enabled direct deposition of Pt nanoparticles on a fluorine-doped thin oxide (FTO) substrate, exhibiting an enhanced electrocatalytic activity. 19) Therefore, in the present study we examined the electrodeposition of Pt nanoparticles on an FTO/Cu₂O electrode and evaluated their photocatalytic activities for hydrogen evolution under visible light irradiation.

2 Experimental

2.1 Preparation of the FTO/Cu₂O film photoelectrode Cu₂O thin films were fabricated on a conducting FTO substrate by electrodeposition. The electrolyte was consisted of 0.1 M (M = mol dm⁻³) of CuSO₄ and 0.1 M of tartaric acid,200 and the pH was adjusted to 9.0 with 3.0 M



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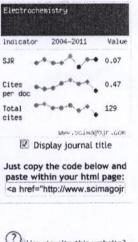
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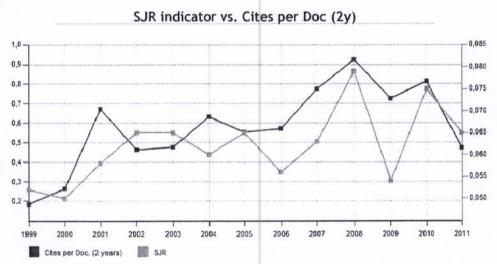




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