Plasmonic Cu$_x$O photocatalyst for Solar Water Splitting with Visible Light

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1. Introduction

Metal nanostructures possess strong absorptions in the visible spectrum as surface plasmon (SP) resonances are arisen. It has been shown that the absorbed plasmonic energy transfers to an adjacent semiconductor either through resonant energy transfer or directly through hot-electron injection. Therefore, the photoactivity of the semiconductor in the visible region can be improved. The optical response of plasmonic structure is the strong morphology and geometry dependence of SPs, in principle making it possible to design a composite plasmonic/semiconductor system that can harvest photons over the entire solar spectrum and beyond.

Cu$_2$O, which exists in abundance as cuprite in nature, has been studied extensively since Cu$_2$O is a simple metal oxide semiconductor with small bandgap energy of 2.0~2.2 eV. The conduction and valence band edges of Cu$_2$O are available for the reduction and oxidation of water, respectively. In this study, the $H_2$ evolution rate of Cu$_2$O (Cu$_x$O/Cu$_2$O composite) photocatalyst pure water splitting is demonstrated to be enhanced using nanoporous Au film. The nanoporous Au film can simultaneously provide surface-enhanced absorption and built-in potential. The absorption of Cu$_2$O film with only 20nm can be as high as 90% for unpolarized light due to the surface-enhanced absorption. The photogenerated electrons and holes can be effectively separated due to the built-in potential at the Au/Cu$_2$O heterojunction. Consequently, the life-time of the excitons can be prolonged. These activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions. A $H_2$ evolution rate of $58~\text{mol hr}^{-1}$ with a device area of 0.25cm$^2$ has been demonstrated using the plasmonic Cu$_2$O photocatalyst [1]. Similar to most of the photocatalysts with a small bandgap, Cu$_2$O photocatalyst suffers from the photocorrosion. The photostability of Cu$_2$O in pure water splitting will be discussed.

2. General Instructions

Quantitative X-ray photoelectron spectroscopy (XPS) analysis of Cu$_2$O film (annealing at 240℃) after photocatalytic water splitting reaction is performed. O 1s peaks are resolved as shown in Fig. 1. The 529.4eV (O$^2$) and 531.8eV (O$^1$) of XPS peaks are assigned to the presence of CuO and Cu$_2$O, respectively. After the photocatalytic water splitting reaction, the Cu$_2$O-Cu / Cu-O peak ratio dramatically drop after the photocatalytic water splitting reaction.

In pure water system, the possible reactants of Cu$_2$O during water splitting reaction are Cu(OH)$_2$, CuO, Cu$_2$O and Cu. All of the reactants are insoluble in pure water. Therefore, the translation of the Cu$_2$O-Cu / Cu-O peak implies the valence number of O 1s changes. Consequently, we can assume that the Cu$_2$O react to other possible reactants as photocorrosion. It can be seen that the O$^2$/O$^1$ is increased during water splitting reaction. Therefore, the Cu$_2$O is oxidized to CuO as photocorrosion.

3. Conclusions

Photocorrosion of p-type Cu$_2$O electrodes in aqueous electrolytes has already been reported, where photoexcited electrons reduce the Cu$_2$O to Cu. In this paper, we consider the Cu$_2$O in pure water which might be different from the Cu$_2$O electrodes in aqueous electrolytes. Through the XPS spectrum, it was found that the Cu$_2$O might be oxidized to CuO as photocorrosion.

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References