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Plasmonic Cu_xO 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_2O, which exists in abundance as cuprite in nature, has been studied extensively since Cu_2O is a simple metal oxide semiconductor with small bandgap energy of 2.0~2.2 eV. The conduction and valence band edges of Cu_2O are available for the reduction and oxidation of water, respectively. In this study, the H_2 evolution rate of Cu_xO (CuO/Cu2O 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_xO 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_xO 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 is 58 molhr^{-1} with a device area of 0.25cm^2 has been demonstrated using the plasmonic Cu_xO photocatalyst [1]. Similar to most of the photocatalysts with a small bandgap, Cu_xO photocatalyst suffers from the photocorrosion. The photostability of Cu_xO in pure water splitting will be discussed.

2. General Instructions

Quantitative X-ray photoelectron spectroscopy (XPS) analysis of Cu_xO film (annealing at 240^{o}C) 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_2O, respectively. After the photocatalytic water splitting reaction, The Cu-O-Cu / Cu-O peak ratio dramatically drop after the photocatalytic water splitting reaction.

In pure water system, the possible reactants of Cu_2O during water splitting reaction are Cu(OH), CuO, Cu_2O and Cu. All of the reactants are insoluble in pure water. Therefore, the translation of the Cu-O-Cu / Cu-O peak implies the valence number of O 1s changes. Consequently, we can assume that the Cu_2O 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_2O is oxidized to CuO as photocorrosion.

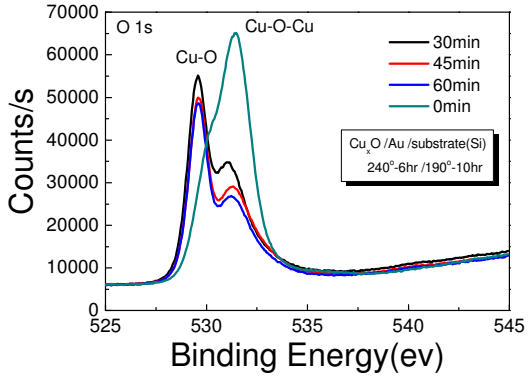

Fig. 1O 1s XPS spectra of Cu_xO after photocatalytic water splitting reaction for 0min, 30min, 45min and 60min, respectively

3. Conclusions

Photocorrosion of p-type Cu_2O electrodes in aqueous electrolytes has already been reported, where photoexcited electrons reduce the Cu_2O to Cu. In this paper, we consider the Cu_2O in pure water which might be different from the Cu_2O electrodes in aqueous electrolytes. Through the XPS spectrum, it was found that the Cu_2O might be oxidized to CuO as photocorrosion.

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References

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