Photocatalytic and photoelectrochemical CO₂ reduction with water as an electron donor

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Morphology controlled brookite TiO₂ nanorod with exposed crystal faces was developed. Exposed crystal surfaces play different roles such as oxidation and reduction, respectively. This property is a great advantageous for multi-electron reaction such as CO₂ reduction under UV light. We also investigated the co-catalysts loading effects for improving CO_2 reduction.

CH₃OH was obtained as a main product for CO₂ reduction over brookite TiO₂ under UV light. The photocatalytic activity of brookite TiO₂ is depends on its Fig. 1 Photocatalytic CO₂ reduction on brookite aspect ratio because the ratio between reduction site for CO₂ reduction and

oxidation site for water oxidation on the surface of brookite TiO₂ was controlled by changing its aspect ratio. In order to improve the photocatalytic activity, an effect of metal cocatalysts loaded only on the reduction site of brookite TiO₂ was evaluated (Fig. 1). The photocatalytic activates of brookite TiO₂ nanorods loaded with Ag or Rh were about 10 times

higher than that of brookite TiO₂ without co-catalysts loading. The apparent quantum efficiency of the CO₂ reduction reached to about 3 % under UV light. Furthermore, we had developed $g-C_3N_4/WO_3$ nanocomposite photocatalysts for CO₂reduction to generate methanol, CO, CH₄, and formic acid under visible light. These results will also be discussed in the presentation.

We had also developed several kinds of photoelectrochemical CO₂ reduction system. Cu₂ZnSnS₄ (CZTS) electrodes modified with different n-type buffer layers (CdS and In2S3) were used as photocathodes for CO2 reduction



TiO₂ nanorod with or without co-catalysts loading under UV light.



Fig.2 Photocurrent response as a function of irradiation time for CO₂ reduction over CZTZ covered with or without CdS.

under visible light irradiation ($420 < \lambda < 800$ nm) in aqueous media. Compared to a bare CZTS electrode, CZTS electrodes modified with n-type buffer layers (CdS and In2S3), by which a p–n heterojunction between CZTS and the n-type buffer layer is formed, showed a significant increase in the photocurrent assigned to CO₂ reduction. In addition, product selectivity of CO₂ reduction was improved by surface modification with an n-type buffer layer: that is, selective CO₂ reduction into CO was achieved by using a CdS/CZTS electrode, while HCOOH selectivity was observed over an In₂S₃/CZTS electrode. In this study, we investigated the photoelectrochemical properties of CZTS electrodes modified with n-type buffer layers (CdS and In₂S₃) in conjunction with the structural and optical properties, and we investigated their activity for PEC CO₂ reduction. The detailed results of photoelectrochemical reduction of CO₂ by CZTS and other our developed p-type electrode will be presented in the presentation.

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