Conversion of CO₂ into useful chemicals through photoelectrochemical reaction.

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Introduction
Herein we have been introduced two materials for conversion of CO₂ into useful chemicals with photoelectrochemical method. First of all we used CdTe/FTO as a photocathode, and pyridine was added into the electrolyte. Recent studies demonstrated that pyridine plays a crucial role in the reduction of CO₂.[1,2] Therefore the synergistic effect of photoenhanced electrocatalysis of CdTe/FTO-pyridine for CO₂ reduction is investigated.

Secondly, layered structures of CuO/Cu₂O thin films were simply prepared by the oxidation of Cu foil. To improve performance and increase the reaction selectivity, the surfaces of the CuO/Cu₂O films were modified by various transition metal particles. Using a Me/CuO/Cu₂O thin film as a photocathode (Me = Ag, Au, Cd, Cu, Pb, and Sn), photoelectrochemical reduction of CO₂ to liquid fuels was investigated at higher potential than the standard redox potential of the products under visible light irradiation. In addition, the degradation phenomenon of the CuO/Cu₂O-based films in the photoelectrochemical reduction of CO₂ was also investigated through the correlation with compositional changes and photo current responses in the reactions by using the X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) studies.

Materials and Methods
CdTe is synthesized by electrodeposition method. CdSO₄ is dissolved in deionized water at room temperature and then TeO₂ is added. The pH was adjusted to 2 using 1 M of H₂SO₄. FTO glass is placed in the mixture of CdSO₄, TeO₂ solution and used as electrode. The electrodeposition is carried out on FTO glass at applied potential of -0.6 V with respect of standard calomel electrode (SCE) at room temperature. Finally, the deposited FTO glass is calcined at 400 °C for 2 h in Ar atmosphere.

CuO/Cu₂O layered thin film is synthesized by oxidation of a cleaned Cu substrate at 400°C under air flow for 4 h in a tube furnace. Various transition metals, (i.e., Ag, Au, Cd, Cu, Sn, and Pb) are deposited onto the CuO/Cu₂O photoelectrode by photo-assisted electrodeposition at ~1.0 V (vs. SCE) in the 1 M NaNO₃ solution dissolved in 0.02 M of each metal precursor under UV-visible light illumination for 5 s. The selected metal precursors are AgNO₃, HAuCl₄·3H₂O, CdSO₄, CuSO₄, SnSO₄, and Pb(NO₃)₂.

Results and Discussion
The overall faradaic efficiency of CdTe/FTO-pyridine is increased 30% in optimized concentration of pyridine compared to CdTe/FTO. In CdTe/FTO-pyridine system, the pyridinium radical formed upon addition of pyridine, and forms pyridinium carbamate intermediate and the activation barrier is reduced cooperatively which is resulted in higher faradaic efficiency. The onset potential is shifted toward the higher potential, and the CO₂ is reduced to formic acid on the CdTe/FTO-pyridine surface.

Significance
This system can be used efficiently to get useful chemicals from CO₂ through photoelectrochemical system.

References