Development of cathode catalysts for photoelectrochemical and electrochemical CO$_2$ reduction

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CO$_2$ is a major contributor to global warming and greenhouse effect. To reduce the accumulation of CO$_2$ in the atmosphere, various strategies for CO$_2$ conversion to fuels have been developed. Among the various systems for CO$_2$ conversion, photo-electrochemical and electrochemical CO$_2$ reductions have been attracted as a promising system due to their ambient reaction conditions and high energy efficiency. However, the success in this approach requires further in-depth understanding of catalysis because it involves highly complex multi-step reactions. Here, various rational design principles of cathode catalysts for an efficient CO$_2$ reduction to useful fuels were suggested.

As a photocathode material for photo-electrochemical system, p-type semi-conductors (*i.e.* p-CdTe, layered p-CuO/Cu$_2$O thin film, and p-ZnTe) were developed and their performances are improved by various strategies: i) using a homogeneous catalyst (*i.e.* pyridine) with photocathode and ii) decoration of photocathode surface with electrocatalysts such as various transition metals (*i.e.* Ag, Au, Cd, Cu, Pb, and Sn) and conducting polymer, polypyrrole (Fig.1). These modifications effectively enhanced CO$_2$ conversion to fuels in terms of Faradaic efficiency, reaction selectivity, and production rates. It is worth noting that CO$_2$ was photoelectrochemically reduced to useful products (*e.g.* formic acid, carbon monoxide and methanol) without any significant overpotential loss under visible light irradiation on the prepared photocathodes.

In electrochemical CO$_2$ conversion, the various metal candidates, transition metals attracted many attention due to its low-cost, low-toxicity, and high-selectivity for CO$_2$ conversion. Because general electrochemical catalysis is highly correlated with mass diffusion, crystal orientation, surface area, and conductivity, manipulating the architecture of electrode is an effective method for improving catalytic performance. Here we developed hierarchical 3D Cu pillar, Sn dendrite, and hexagonal Zn electrodes as electrocatalysts by facile electrodeposition methods (Fig. 2). Cu pillar, Sn dendrite and hexagonal Zn electrodes achieved significantly enhanced CO$_2$ reduction performances in terms of current density and Faradaic efficiency compared to their pristine metal foils. Furthermore, experimental and theoretical studies additionally elucidated the origin of the catalytic behaviors of the prepared electrodes.[1]
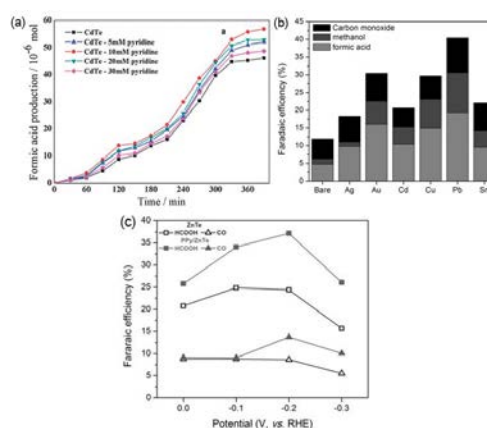

Fig. 1 Catalytic performance of photocathode (a) CdTe with pyridine, (b) metal decorated CuO/Cu$_2$O and (c) polypyrrole deposited ZnTe.
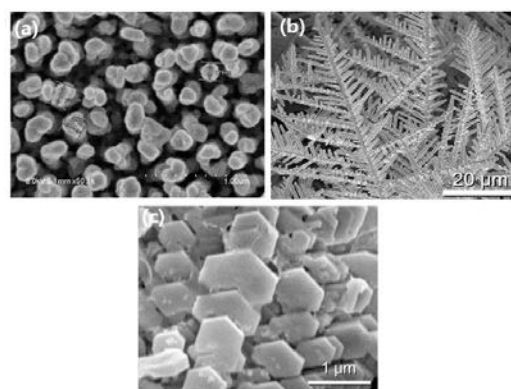

Fig. 2 SEM image of Cu pillar, Sn dendrite and hexagonal Zn catalysts.

REFERENCES
[1] D.H. Won, H. Shin, J. Koh, J. Chung, H.S. Lee, H. Kim, S.I. Woo, Angew. Chem. Int. Ed., 55 (2016) 9297-9300.