

学 位 論 文 の 要 旨

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学位論文題目	<p>Tin- and bismuth-based catalysts for electrochemical reduction of carbon dioxide to formic acid</p> <p>(スズおよびビスマスベースの触媒を用いた二酸化炭素をギ酸への電気化学的に還元)</p>		
<p>学位論文要旨</p> <p>In recent years, electrochemical reduction carbon dioxide (CO₂) to value-added chemicals has attracted widespread attention because of its efficiency, cleanliness and convenience to face the environmental and energy issues. Electroreduction of CO₂ to formic acid (HCOOH) is considered as one of economically feasible ways. Developing high-efficient electrocatalysts is key for this technology. The tin (Sn)- and bismuth (Bi)-based catalysts have been extensively studied due to their efficiency, low cost, and environmental friendliness. However, in order to meet large-scale industrial applications, more highly-efficient electrocatalysts based on them still should be developed. This study focused on Sn- and Bi-based catalysts prepared by different methods for electrochemical CO₂ reduction reaction (CO₂RR) to HCOOH. Besides, density functional theory (DFT) calculations were performed to help understand the catalytic mechanism.</p> <p>Firstly, we obtained smaller and uniform Sn-based electrocatalysts particles on the carbon paper substrate by using unipolar pulse electrodeposition (UPED) method. It exhibited the maximum HCOOH faradaic efficiency of 89% at -1.7 V (vs. Ag/AgCl) with a current density of 6.0 mA cm⁻² and long-term stability in the 0.1 M CO₂-saturated KHCO₃ solution. Moreover, the effects of surface oxides species on the performance of tin-based electrocatalysts were systematically investigated via DFT calculations. The calculation results indicated that both metal tin and tin oxides had excellent catalytic ability for the electrochemical reduction of CO₂ to HCOOH. Especially, the tetravalent tin (Sn⁴⁺) and divalent tin (Sn²⁺) species can reduce the overpotential and improve the HCOOH selectivity, respectively. In addition, it is found that the tin oxides/metal tin interface can suppress the evolution of H₂ but no obvious effect on the formations of HCOOH and CO. Thusly, we propose that the actual CO₂ catalytic electroreduction process should be synergistically controlled by the complex surface oxide species on the tin-based electrocatalysts.</p> <p>Secondly, a Bismuth (Bi)-doped SnO nanosheets were grown on copper foam (Bi-SnO/Cu foam) by a one-step hydrothermal reaction method and applied for the electrochemical reduction of CO₂ to HCOOH. The experimental results indicated that Bi doping stabilized the divalent tin (Sn²⁺) existed on the surface of the electrocatalyst, making it difficult to be reduced to metallic tin (Sn⁰) during the electrochemical reduction process. In addition, combining with the DFT calculations, it is found that Bi doping and the electron transfer from the catalyst to the Cu foam substrate could enhance the adsorption of *OOCH intermediates. As such, the Bi-doped SnO electrocatalyst exhibited a superior faradaic efficiency of 93% at -1.7 V (vs Ag/AgCl) for the</p>			

reduction of CO₂ to HCOOH, together with a current density of 12 mA cm⁻² and excellent stability in at least 30 h of operation.

Thirdly, we observed an interesting morphological transformation phenomenon accompanied by the formation of petal-shaped bismuth subcarbonate (Bi₂O₂CO₃) nanosheets in Bi-based catalyst. It was found that this transformation improved the electrocatalytic performance of CO₂ reduction to HCOOH. By using this catalyst, the faradaic efficiency of CO₂ to HCOOH reached 92% at -1.6 V (vs. Ag/AgCl) with a current density of 10 mA cm⁻². Also, this electrocatalyst exhibited good stability during the electrocatalysis operation for 20 h. DFT calculations revealed that *in-situ* formed Bi₂O₂CO₃ species can enhance the catalytic activity by stabilizing *OOCH intermediate through the stronger orbital hybridization of Bi 6p of Bi₂O₂CO₃ with O 2p of *OOCH. As such, it can be considered that the rate-limiting step in the CO₂ electroreduction process should rely on the second-step electron transfer, which is consistent with the Tafel slope analysis result.

All in all, in this work, 3 kinds of Sn or Bi-based electrocatalysts were successfully developed for electrochemical CO₂RR to HCOOH. Their physicochemical properties and electrocatalytic performance have been characterized and tested in details, and the catalytic mechanisms have also been analyzed by DFT calculations. It is expected to give guidance for the design and application of electrocatalyst in the practical CO₂RR processes.

注) 和文 2,000 字以内又は英文 800 語以内

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