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Title: Ag-induced Phase Transition of Bi₂O₃ Nanofibers for Enhanced Energy Conversion Efficiency towards Formate in CO₂ Electroreduction

Author(s): Wang, X (Wang, Xin); He, WH (He, Wenhui); Shi, JL (Shi, Jialin); Junqueira, JRC (Junqueira, Joao R. C.); Zhang, J (Zhang, Jian); Dieckhoefer, S (Dieckhoefer, Stefan); Seisel, S (Seisel, Sabine); Das, D (Das, Debanjan); Schuhmann, W (Schuhmann, Wolfgang)

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Abstract: Bi-based electrocatalysts have been widely investigated in the CO₂ reduction reaction (CO₂RR) for the formation of formate. However, it remains a challenge to achieve high Faradaic efficiency (FE) and industrial current densities at low overpotentials for obtaining both high formate productivity and energy efficiency (EE). Herein, we report an Ag-Bi₂O₃ hybrid nanofiber (Ag-Bi₂O₃) for highly efficient electrochemical reduction of CO₂ to formate. Ag-Bi₂O₃ exhibits a formate FE of >90% for current densities from -10 to -250 mA cm⁻² and attains a yield rate of 11.7 mmol center dot s(-1) center dot m(-2) at -250 mA center dot cm(-2). Moreover, Ag-Bi₂O₃ increased the EE (52.7%) by nearly 10% compared to a Bi₂O₃ only counterpart. Structural characterization and in-situ Raman results suggest that the presence of Ag induced the conversion of Bi₂O₃ from a monoclinic phase (alpha-Bi₂O₃) to a metastable tetragonal phase (beta-Bi₂O₃) and accelerated the formation of active metallic Bi at low overpotentials (at > -0.3 V), which together contributes to the highly efficient formate formation.

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Addresses: [Wang, Xin; He, Wenhui; Shi, Jialin; Junqueira, Joao R. C.; Zhang, Jian; Dieckhoefer, Stefan; Seisel, Sabine; Das, Debanjan; Schuhmann, Wolfgang] Ruhr Univ Bochum, Fac Chem & Biochem, Analyt Chem Ctr Electrochem Sci CES, Universitatstr 150, D-44780 Bochum, Germany.

Corresponding Address: Schuhmann, W (corresponding author), Ruhr Univ Bochum, Fac Chem & Biochem, Analyt Chem Ctr Electrochem Sci CES, Universitatstr 150, D-44780 Bochum, Germany.

E-mail Addresses: wolfgang.schuhmann@rub.de

Affiliations: Ruhr University Bochum

Author Identifiers:

Author	Web of Science ResearcherID	ORCID Number
Shi, Jialin	HKN-9997-2023	0000-0002-6853-619X
Wenhui, He		0000-0003-0001-9177
Schuhmann, Wolfgang	S-2626-2016	0000-0003-2916-5223
Coelho Junqueira, João Ricardo	AAW-9007-2021	0000-0003-1685-7861

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