



Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synthetic multiscale design of nanostructured Ni single atom catalyst for superior CO₂ electroreduction

Gyoung Hwa Jeong^{a,b,1}, Ying Chuan Tan^{c,1}, Jun Tae Song^d, Gil-Yong Lee^{a,b}, Ho Jin Lee^{a,b}, Jaewoong Lim^e, Hu Young Jeong^f, Somi Won^e, Jihun Oh^{b,*}, Sang Ouk Kim^{a,b,*}

^a National Creative Research Initiative (CRI) Center for Multi-Dimensional Directed Nanoscale, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

^b Department of Materials Science and Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

^c Institute of Materials Research and Engineering (IMRE), A*STAR, 2 Fusionopolis Way, #08-03 Innova 138634, Singapore

^d Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan

^e Department of Chemistry, UNIST, 50 UNIST-gil, Ulsan 44919, Republic of Korea

^f UNIST Central Research Facilities, UNIST, 50 UNIST-gil, Ulsan 44919, Republic of Korea

ARTICLE INFO

Keywords:

Single atom catalyst
CO₂ reduction
Carbon nanostructure
Electrochemistry

ABSTRACT

Rational design of nanoscale structures can greatly strengthen heterogeneous catalysis with the maximal utilization of active sites. Single atom catalysts (SACs) are recently emerging but a systematic design of nanostructured SAC has rarely been demonstrated yet. Here, distinct architectural structure-dependence of electrochemical CO₂ reduction (CO₂RR) on Ni-based SACs is presented. Starting from Ni-imidazolate coordination polymers (Ni-Im) and their supported counterparts with a carbon nanotube (CNT) and a zeolite imidazolate framework (ZIF-8), the respective derivatives, i.e. Ni-SAC, Ni-SAC-CNT, and Ni-SAC-ZIF8, are obtained after pyrolysis. The presence of substrates ultimately results in large surface porous N-doped carbon nanostructures, which facilitate the diffusion of etchants to remove undesired Ni nanoparticles effectively. The dense Ni single atomic sites contained within the nanostructure are easily accessible to CO₂ reactants during CO₂RR, thus promoting high utilization of active sites even at large current densities. Electro-conductive CNT substrates mediate fluent charge transfer and stimulates the intrinsic activity of catalytic sites. Consequently, operating at 400 mA cm⁻², Ni-SAC-CNT attains a high faradaic efficiency of 99% toward CO at a low overpotential of 0.24 V, equivalent to a record cathodic energetic efficiency and turnover frequency of 83.4% and 439,000 h⁻¹, respectively.

1. Introduction

Rapid advent of environmental issues arising from fossil fuel based current industrial system have triggered intensive research interest in the electrochemical CO₂ reduction reaction (CO₂RR) [1–8]. Among several different electrochemical CO₂RR products, CO is the basic chemical resource for methanol production, Fischer-Tropsch synthetic oils, and various carbonylation reactions [9]. The electrochemical conversion of CO₂ into CO is a typical two-electron process favored at the surface of Au, Ag, and Zn [10,11]. Nanostructured Au and Ag catalysts with relatively low energy barriers toward CO show excellent electrochemical reduction catalyst activity with CO Faradaic efficiency (FE) above 90% at overpotentials lower than 300 mV [12–14]. Nonetheless,

most prior studies have been unable to reach the economical viable activity of 200 mA cm⁻² particularly due to the limited CO₂ mass transport in a conventional H-type electrochemical cell. Recently, an increasing number of studies have employed flow electrolyzers based on gas-diffusion electrodes (GDEs) to achieve industrially relevant CO production rates [15–17]. Unfortunately, these results still rely on noble metals, which inevitably suffer from a high economic burden for scaling up. Alternatively, efforts have been spent on identifying cheaper alternatives, such as AgZn alloy and Cu/In hybrid [18,19], though they still suffer from high overpotentials and thus large power consumption for electrochemical CO₂RR.

Lately, single atom catalysts (SACs) are emerging as a novel class of catalysts that can be rationally designed for numerous applications,

* Corresponding authors.

E-mail addresses: jihun.oh@kaist.ac.kr (J. Oh), sangouk.kim@kaist.ac.kr (S. Ouk Kim).

¹ G.H.J. and Y.C.T. contributed equally to this work.