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Synthetic multiscale design of nanostructured Ni single atom catalyst for superior CO_2 electroreduction

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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 CO_2 reduction (CO_2RR) 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 CO_2 reactants during CO_2RR, 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 CO_2 reduction reaction (CO_2RR) [1–8]. Among several different electrochemical CO_2RR products, CO is the basic chemical resource for methanol production, Fischer-Tropsch synthetic oils, and various carbonylation reactions [9]. The electrochemical conversion of CO_2 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 CO_2 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 CO_2RR.

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

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