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# Understanding morphological degradation of Ag nanoparticle during electrochemical CO<sub>2</sub> reduction reaction by identical location observation



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## ABSTRACT

Electrocatalytic systems affording stable performance beyond the initial catalytic activity and selectivity have been actively discussed. Understanding the long-term stability of nanoparticle catalysts requires careful monitoring of the morphological changes. Herein, we demonstrate the relationship between the degradation of the catalytic activity and morphological changes in Ag nanoparticles during the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) for CO production by identical location transmission electron microscopy (IL-TEM) measurements. The synthesized Ag/C catalyst with 95.1% CO Faradaic efficiency ( $FE_{CO}$ ) at  $-0.82$  V vs. RHE showed a gradual decrease in the CO production current density and  $FE_{CO}$ , whereas the H<sub>2</sub> production increased during 12 h of CO<sub>2</sub>RR. IL-TEM images showed that small Ag particles with dimensions of less than 5 nm were newly formed from the original particles within 1 h of reaction, accounting for 80% of the total number of particles, and slowly grew to around 10 nm with multiple domains when the CO<sub>2</sub>RR was prolonged. These morphological changes were explained in connection with the CO current density gradient, where it was proposed that the formation of small particles causes a sharp decrease in the CO production during the first hour, and subsequent growth of the Ag nanoparticles did not restore the CO<sub>2</sub>RR activity of the particles. It was confirmed that degradation of the nanoparticles was more severe at a higher cathodic potential, and occurred during the CO<sub>2</sub>RR, but not in the hydrogen evolution reaction (HER) in N<sub>2</sub>-purged KHCO<sub>3</sub> electrolyte. In this study, we introduce analytical methods for observing morphological changes of nanoparticles in the identical location during CO<sub>2</sub>RR electrolysis.

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## 1. Introduction

The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has been intensively studied as a promising CO<sub>2</sub> utilization technique that can be combined with renewable energy sources. It targets the conversion of CO<sub>2</sub>, a greenhouse gas, to value-added useful chemicals such as CO, formate, and C<sub>2</sub>H<sub>4</sub> [1–4]. CO is a particularly promising target chemical as it can be produced with high selec-

tivity and energy conversion efficiency via the CO<sub>2</sub>RR due to the recent progress in the development of electrocatalysts, membranes, and electrolyzers [5–7]. A mixture of CO and H<sub>2</sub> is industrially used to produce hydrocarbons via the Fischer-Tropsch process [8].

High selectivity for CO with a Faradaic efficiency of over 95% has been achieved with various catalysts such as Au [7], Ag [9], Zn [10], Cu-based bimetallic catalysts [11], and single-atom catalysts [12], with the assistance of nanostructuring. Ag has been used as a model catalyst for understanding the fundamentals of CO production and device applications [13–15]. Defects or edge sites of Ag-based nanocatalysts show high intrinsic activity for selective CO production, but their stability has yet not been systematically

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