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One-dimensional CuIn alloy nanowires as a robust and efficient electrocatalyst for selective CO_2-to-CO conversion

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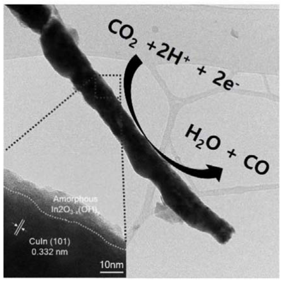
HIGHLIGHTS

- 1-D CuIn nanowire electrocatalyst is prepared by anodization and electrodeposition.
- $In(OH)_3$ layer is formed on CuIn alloy surface by electrochemical pre-activation.
- The catalyst shows best CO_2–to-CO reduction activity among reported Cu-In catalysts.
- 1-D nanostructuring provides higher surface areas and facile charge transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrical anodization of Cu foil produces one-dimensional Cu nanowires of high surface areas, which turns to CuIn alloy nanowires by indium electrodeposition replacing edge site Cu atoms. An electrochemical pre-activation forms a highly conformal amorphous $In(OH)_3$ overlayer with oxygen vacancy on the CuIn alloy that facilitates CO_2 adsorption to promote selective CO formation suppressing competing H_2 adsorption. Thus the activated CuIn alloy nanowires catalyse electrochemical CO_2 conversion to CO with high CO selectivity ($> 68.2\%$) and high current density (*ca.* $-3.9\,mAcm^{-2}$) at $-0.6\ V_{RHE}$, which represents the higher partial CO current density (*ca.* $-2.66\,mAcm^{-2}$) than that of previously reported CuIn alloy powders without nanostructuring. The performance remains stable for more than 15 h without significant degradation.

1. Introduction

Re-utilization of CO_2 has been a subject of immense global interest lately as a carbon-neutral technology by converting the greenhouse gas into useful fuels and chemicals instead of storage in geological or ocean reservoirs. Among diverse ways of CO_2 conversion, electrocatalytic methods are effective and simple because of mild operating conditions, product versatility, and eco-friendliness. Electrocatalytic CO_2 reduction to CO is one of those highly desired processes because CO is a feedstock for a variety of hydrocarbons and oxygenates [1–4]. However, the technology suffers from significant challenges of low efficiency, poor product selectivity, insufficient stability and high cost [4].

Electrocatalytic CO_2 reduction has long been studied over different metal electrodes comparing their reaction rates (or overpotentials required to obtain a given current) and formed products (or selectivity) [5]. Noble metals like Ag and Au are selective for CO production, but high overpotentials and expensive prices are drawbacks [6–8]. On the other hands, Cu has many attractive characteristics for electrochemical CO_2 conversion including low onset potential, low cost, and high activity of CO_2 conversion. However, its low product selectivity is a disadvantage forming diverse product mixtures containing H_2, CO, hydrocarbons and oxygenates [9–12].

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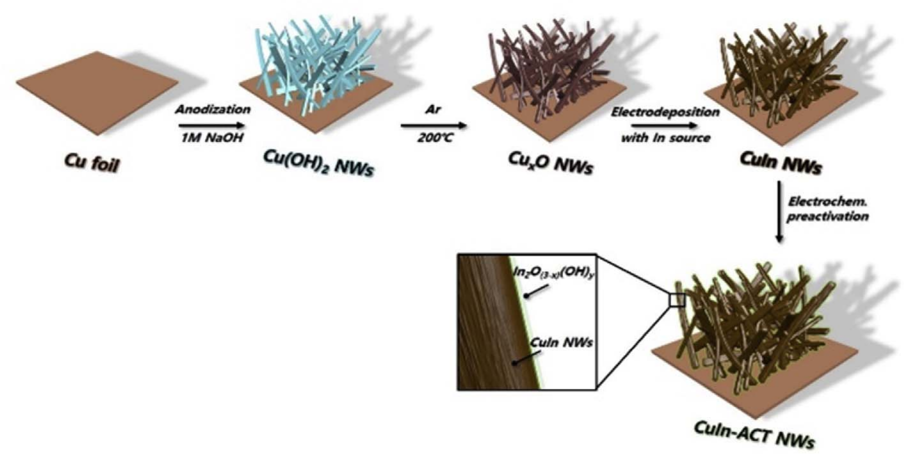

Fig. 1. Schematic procedure to prepare an activated CuIn alloy nanowire electrode.

In attempt to design noble metal-free electrocatalysts of CO_2 reduction with high activity and outstanding product selectivity, metal alloy formation was suggested as an effective strategy [13–16]. Metal alloys can tune electrocatalytic properties of component metals by modifying their electronic structures and rendering ensemble or geometric effects [14,16]. An interesting example is a copper-indium (CuIn) bimetallic alloy fabricated by *in-situ* reduction of copper oxide followed by indium deposition reported by Takanabe and coworkers [17]. By replacing edge-site copper atoms with indium, the nature of active sites for CO_2 conversion was altered. Thus, Cu edge atoms prefer the adsorption of proton in water, while indium atoms occupying edge sites of Cu adsorb CO_2 preferentially. This leads to dominant CO production suppressing H_2 evolution in electrocatalytic CO_2 reduction on CuIn alloys. But their current density was only moderate with $-0.65\,mAcm^{-2}$ at $-0.6\ V_{RHE}$. They also reported a CuIn alloy derived from $CuInO_2$ that showed a high CO faradaic efficiency of *ca.* 55% at $-0.6\ V_{RHE}$, but a marginally improved current density of $-0.8\,mAcm^{-2}$ [18].

Here we report one-dimensional (1-D) CuIn nanowires as an electrocatalyst for electrochemical CO_2 conversion to CO with outstanding CO selectivity ($> 68.2\%$), high current density (*ca.* $-3.9\,mAcm^{-2}$ at $-0.6\ V_{RHE}$) and excellent stability ($> 15\,h$), representing the best performance reported so far for electrocatalysts based on Cu-In. The 1-D nanowire morphology obtained by electrical anodization of Cu foil offers high surface areas and facile charge transfer that lead to the high current density. In particular, an electrochemical pre-activation forms a highly conformal $In(OH)_3$ overlayer with oxygen vacancies on the CuIn alloy surface, which promotes selective CO production suppressing formation of side products like H_2 and HCOOH.

2. Experimental section

2.1. Electrode preparation

Cu foil (Aldrich, 99.98%) was cleaned with acetone, ethanol, 2 M HCl (Aldrich, 37–38%) and distilled water for 5 min. The CuIn bimetallic alloy was prepared in two steps of anodization followed by In replacement. First, copper oxide (Cu_xO) nanowires were grown on cleaned Cu foil through a chronopotential anodization at $2\,mAcm^{-2}$ for 5 min in 1 M NaOH and calcination under Ar flow (100 sccm) at 200 °C for 2 h. The CuIn bimetallic alloy was prepared by a chronopotential galvanic replacement at $-5\,mAcm^{-2}$ for 5 min in an aqueous solution of 0.05 M $In_2(SO_4)_3\ xH_2O$ (Aldrich, 99.99%) and 0.4 M citric acid (Samchun, 98%). The Cu substrate was connected with Cu wire using Ag paste and all area except CuIn was covered by epoxy resin. For electrochemical activation, the electrode was biased at $-0.6\ V_{RHE}$ in CO_2 saturated 0.5 M $KHCO_3$ (Junsei) for 6 h.

2.2. Electrocatalytic CO_2 reduction

Electrocatalytic CO_2 reduction was performed in a standard 3-electrode cell with the CuIn alloy, a Pt mesh and Ag/AgCl as working, counter, and reference electrodes, respectively. The electrolyte was CO_2-saturated 0.5 M $KHCO_3$ (Wako, 99.9%) and all measurements were taken using a potentiostat (Gamry Reference 600TM). The collected gaseous reduction products in head-space (10 ml) were analyzed by a gas chromatography (GC, Agilent 7890) equipped with a thermal conductivity detector (TCD) connected to a Carboxen 1000 packed column, and a flame ionization detector (FID) to an Agilent Poraplot-Q capillary column. Liquid products in a cathode chamber were analyzed by a high-resolution liquid chromatography (HPLC, Agilent 1200) with a C18 Inverse column. Surface roughness factors were evaluated by measuring double layer capacitances. Cyclic voltammetry (CV) was conducted in the same electrolyte and the geometric current density, where no Faraday process was occurring, was plotted as a function of CV scan rate, and the linear slope yielded the capacitance.

2.3. Characterization

Field-emission scanning electron microscopy (FESEM, JEOL JMS-7401F), high-resolution transmission electron microscopy (HR-TEM, Cs-corrected, JEOL JEM-2200FS) were used to obtain microscopic images of the electrodes. For TEM analysis, the CuIn alloy sample powder was obtained by grinding the surface of the electrode with a sharpener and was dispersed in absolute ethanol. X-ray diffraction spectrometry (XRD, Mac Science, M18XHF using Cu K α radiation, $\lambda = 0.15406\,nm$), and X-ray photoelectron spectroscopy (XPS) were applied to investigate crystallinity and oxidation state of the electrocatalyst.

3. Results

The 1-D CuIn bimetallic nanowire electrocatalyst of a high surface area was fabricated in two steps as depicted in Fig. 1: Anodization of Cu foil and indium electrodeposition at Cu edge sites using chronopotential programs shown in Figure S1 of Supporting Information (SI). Electrochemical anodization of Cu foil at $2\,mAcm^{-2}$ for 5 min produces $Cu(OH)_2$ nanowires, which are converted into Cu_xO nanowires through annealing at 200 °C in Ar flow. Then CuIn bimetallic alloy is fabricated by electrodeposition of indium at $-5\,mAcm^{-2}$. X-ray diffraction (XRD) revealed the formation of CuIn alloy (JCPDS no. 00-035-1150) on Cu foil in Figure S2. Scanning electron microscopy (SEM) images in Figure S3 demonstrate a well-preserved nanowire morphology during the transformation of $Cu(OH)_2 \rightarrow Cu_xO \rightarrow CuIn$.

The duration of electrodeposition step was optimized based on