



Gold catalyst reactivity for CO₂ electro-reduction: From nano particle to layer



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ABSTRACT

CO₂ electro-reduction is a promising method for sustainable production of carbon fuels as well as valuable chemicals. Herein, we investigated a direct electro-catalytic CO₂ conversion to CO by nanostructured gold catalysts from the small nanoparticles to aggregated clusters to layered film. The selectivity of CO formation was found to increase as the gold amount increased and it reached a saturation point of ~78% (–0.59 V vs. RHE) at the morphological transition from aggregated cluster to layered film. Furthermore, the ~4 nm gold nanoparticle exhibited a remarkable CO formation mass activity value at 166.1 A/g (–0.59 V vs. RHE).

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1. Introduction

Current energy production methods raise atmospheric concentrations of CO₂, which is known as one of the greenhouse gases that leads to climate change and ocean acidification [1]. Capturing and transforming CO₂ into valuable chemicals or carbon fuels using renewable energy sources is an attractive yet necessary project that could preserve the basic living environment for human beings [2–5]. Among the several pathways to reduce CO₂ concentration, electrochemical reduction is a promising method because of its benign operability under ambient reaction condition and controllability of process (by changing external bias, i.e. overpotential) [6]. CO₂ electro-reduction is a direct electro-catalytic method that can be performed in aqueous or non-aqueous electrolytes [7], to utilize CO₂ to produce carbon fuels such as methane and methanol; useful hydrocarbons such as ethylene and formic acid; and feedstock gases such as H₂ and CO for the Fischer–Tropsch process or hydrocarbon formation [8,9]. However, the initiation of CO₂ reduction

often must be done in very negative potentials [7], because of a thermodynamically unstable intermediate state. In addition, large negative overpotential in CO₂ electro-reduction can promote a competitive reaction such as H₂ evolution in an aqueous electrolyte [10]. To overcome these limitations and produce a targeted product selectively, a highly efficient catalyst should be developed.

Bulk metal catalysts (e.g. Au) have been investigated in detail as catalysts for various CO₂ electro-reductions; however, they often suffer from low activity and are readily deactivated [8]. On the other hand, recent studies in CO₂ electro-reduction catalyst showed that nanostructured catalysts are able to lower the overpotential for CO₂ reduction to CO and to control the reaction pathway to obtain desirable CO/H₂ ratios [6]. Also, similar to the electrochemical H₂ evolution [11], nanoparticles catalysts with high surface area are expected to possess high activity for CO₂ electro-reduction. Recent studies also showed that nanostructured catalysts directly prepared from metal foils or well dispersed nanoparticles catalysts on carbon substrate are able to selectively facilitate CO formation in both aqueous [12–14] and non-aqueous [15,16] electrolytes. These results point to a correlation that structure and morphology of catalyst have important roles in the CO₂ electro-reduction activity [5]. Well dispersed nanoparticles catalysts on carbon substrate can optimize surface area and catalyst loading for CO₂ electro-reduction and has an advantage over direct growth of nanostructured catalyst on metal foils in the cost reduction point of view.

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Here, we deposited Au nanoparticles onto carbon paper with electron beam (e-beam) deposition process, a well-known physical vapor deposition process that deposits metal in a solvent-free environment [17–19]. By controlling Au deposition amount, we could confirm that the morphologies of deposited Au gradually changed from small nanoparticles to a layered film. All states of Au catalysts were electrochemically tested to investigate the correlation between the morphology (i.e. nanoparticles to bulk film) and catalytic activity. Notably, the mass activity of typical sized (~4 nm) Au nanoparticles from e-beam deposition process was found to have a remarkable value of 166.1 A/g at -0.59 V vs. RHE for CO₂ reduction to CO production, which performed better than comparable catalysts reported so far.

2. Experimental

2.1. E-beam deposition of Au

Au catalysts with various sizes (or thicknesses) were prepared on carbon paper (TGP-H, Toray Industries, Inc.) by an e-beam evaporator (KVE-E2006, Korea Vacuum Tech.) using a Au pellet (99.99%, iTASCO) source. The amount of Au was calibrated as the thicknesses (0.5, 1, 2, 3, 4, 5, 7, 10, and 30 nm) of the deposited Au layer measured by a quartz crystal microbalance (QCM) deposition control unit mounted inside the vacuum chamber and evaporation was repeated again to deposit the same amount of Au on both sides of the carbon paper (0.28 mm thickness, TGP-H-090, Toray Industries, Inc.). The Au catalyst deposited on carbon paper will be referred as Au-T (T = Au film thickness on QCM) sample; for example, Au-0.5 on carbon paper is a sample with Au amount corresponding to 0.5 nm thick Au film on QCM. The actual Au loading amount onto the carbon paper was measured from inductively coupled mass spectrometry (ICP-MS, Elan 6100, PerkinElmer Inc.) analysis, and the measured Au mass density (Table S1) was used to calculate mass activities of Au-T samples.

2.2. CO₂ electro-reduction measurement

All CO₂ electro-reduction experiments were conducted by a potentiostat (Ivium stat-potentiostat, Ivium Tech) in a home-built polyether ether ketone (PEEK) two-compartment electrochemical cell separated by a proton exchange membrane (Nafion®, 117). Each compartment contained 38 mL electrolyte and approximately 34 mL headspace. Au deposited on carbon paper as the working electrode with the area $1 \text{ cm}^2 \times 2$ (for both sides) and an Ag/AgCl reference electrode (saturated KCl, BASI Inc.) were placed in the cathodic compartment, and platinum (99.9%, Sigma-Aldrich) counter electrode was positioned in the other compartment. Polycrystalline Au foil (99.99%, Dasom RMS) was cleaned in aqua regia and was used as a reference for the working electrode. 0.5 M KHCO₃ aqueous electrolyte was saturated with CO₂ by bubbling CO₂ (99.999%, Shinyang Sanso Co.) gas for at least 30 min prior to CO₂ reduction measurement, and the pH of the electrolyte was 7.03 after saturation.

During the measurement, CO₂ was delivered to the electrochemical cell at an average rate of 120 mL/min (at room temperature and ambient pressure) and routed directly into gas chromatography (GC, 6500 GC System, Young Lin Instrument Co. Ltd.). The gaseous products were analyzed by GC equipped with a pulsed discharge ionization detector (PDD) with ultra-high purity He (UHP 99.9999%, Shinyang Sanso Co.) as the carrier gas. The gaseous products were analyzed by GC measurement at 5 min after the reaction started, and the individual measurement was repeated by four times with fresh Au-T samples to take the reproducible average values. Steady-state current density was measured by

using chronoamperometry technique with respect to each potential. The solution resistance was measured by electrochemical impedance spectroscopy, and all potentials were compensated for *iR* loss. Potentials were measured against an Ag/AgCl reference electrode and converted against a reversible hydrogen electrode (RHE) reference using the following equation:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 + 0.059 \text{ V} \times \text{pH}.$$

2.3. Characterization

The crystal structures of the Au films deposited on the carbon paper were characterized using a X-ray diffractometer (XRD-6000, Shimadzu) equipped with a Cu K α radiation ($\lambda = 0.15406$). Morphological characteristics were investigated by a high-resolution transmission electron microscope (HR-TEM, Tecnai F-20, FEI Inc.) and field emission gun scanning electron microscope (FEG SEM Inspect F50, FEI Inc.). For the TEM measurements, the TEM grid was loaded on the e-beam chamber at the same time as Au deposition onto carbon paper. ICP-MS measurements were performed for elemental analysis from which Au mass density was obtained.

3. Results and discussion

The morphology changes of e-beam deposited Au on carbon paper were investigated by TEM images with respect to the Au amount (Fig. 1). As the Au loading increased from 0.5 to 30 nm, nano-sized particulate Au (Fig. 1a–c) evolved to aggregated clusters (Fig. 1d–g) and layered film (Fig. 1h). According to the TEM images, the average particle sizes of the initial Au-T samples grew from 2.1 ± 0.1 , 4.4 ± 0.2 , to 6.5 ± 0.4 nm for Au-0.5, Au-1, and Au-2, respectively. Further deposition of Au formed agglomerates of nanoparticles resulting in polycrystalline nanostructures with multiple grain boundaries as shown in HR-TEM (Fig. S1). From Au-3 to Au-10, the average size of the particles increased, and then the entire carbon surface was almost covered by the stacked Au layers when the thickness reached 30 nm (Au-30, Fig. S1).

The crystal structure of the e-beam deposited Au-T samples on the carbon paper was investigated by XRD and HR-TEM analysis, both of which indicated the face-centered cubic (fcc) Au crystal structure. XRD patterns (Fig. S2) show that the evolution of 2θ peaks at 38.2° and 44.4° which correspond to (1 1 1) and (2 0 0) of fcc Au when the Au thin film was thicker than 7 nm. These Au XRD patterns were not detectable for the thinner films (Au-0.5 to Au-5) because of our instrumental limitation. However, for the thinner Au-T samples, HR-TEM images (Fig. S1) also confirmed the same crystalline Au structure with matching *d*-spacing (0.235 nm) of fcc Au (1 1 1) plane.

Au-T samples performance for CO₂ electro-reduction was investigated. For comparison, we used bare carbon paper and polycrystalline Au foil as references for the working electrodes. Fig. 2 shows the total current densities of bare carbon paper, Au foil and Au-T samples. In fact, we measured the total current densities of all samples (also see Fig. S3), but only selected data were presented in Fig. 2 for clearer comparison. It is apparent that the total current densities for the Au-T samples increased with the increasing thickness of Au layer. To be specific, Au-10 sample showed -0.8 mA/cm^2 at -0.59 V vs. RHE while Au-1 showed -0.18 mA/cm^2 at the same potential.

We also investigated Faradaic efficiency with respect to various potentials to investigate the selectivity of each sample (selective data shown in Fig. S4). CO gas started to generate from Au-0.5 while bare carbon paper shows almost inert activity for CO formation and only shows low hydrogen evolution reactivity for the applied potential range of -0.59 to -0.79 V vs. RHE implying bare

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