Nanostructured Au Electrode with 100 h Stability for Solar-Driven Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide

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ABSTRACT: Solar-to-chemical energy conversion is a potential alternative to fossil fuels. A promising approach is the electrochemical (EC) reduction of CO₂ to value-added chemicals, particularly hydrocarbons. Here, we report on the selective EC reduction of CO₂ to CO on a porous Au nanostructure (pAu) cathode in 0.1 M KHCO₃. The pAu cathode anodized at 2.6 V exhibited maximum Faradaic efficiency (FE) for conversion of CO₂ to CO (up to 100% at −0.75 V vs reversible hydrogen electrode (RHE)). Furthermore, commercial Si photovoltaic cells were combined with EC systems (PV-EC) consisting of pAu cathodes and IrO₂ anodes. The triple-junction cell and EC system resulted in a solar-to-CO conversion efficiency (SCE) of 5.3% under 1 sun illumination and was operated for 100 h. This study provides a PV-EC CO₂ reduction system for CO production and indicates the potential of the PV-EC system for the EC reduction of CO₂ to value-added chemicals.

INTRODUCTION

Because of global warming, it is essential to develop sustainable technology and protect the environment. It would be very helpful to reduce or stop carbon dioxide (CO₂) emission into the environment by transforming CO₂ into renewable fuels. Electrochemical (EC) CO₂ conversion is a promising candidate for large-scale carbon management applications because it can operate with high reaction rates and good efficiency under ambient conditions. A typical EC system includes two electrically biased electrodes; CO₂ and protons are converted into products at the negatively charge cathode, and H₂O is oxidized into O₂ and protons at the positively charged anode. The total cell voltage required for CO₂ reduction includes potentials for both anodic and cathodic processes (\(E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}\)). However, compared with water splitting, EC CO₂ reduction often presents significant constraints and high voltage requirements for achieving satisfactory reaction rates. These overpotentials represent wasted energy that can lead to inefficiencies. The insufficient activity and stability both limit the commercialization of the EC CO₂ reduction. Therefore, it is imperative to develop a functional EC electrode and cost-effective EC system that effectively catalyzes both half-reactions with low overpotentials and high selectivities.

For resolving the insufficient activity, using photovoltaic (PV) cells for external energy is a potential approach because PV can harvest abundant solar energy. This energy can be used as an external energy source for carrying out EC CO₂ reduction. The PVs can reduce the voltage required for the EC cell. Solar-driven chemical production involves the use of PV panels, modules, or cells connected in series to an EC system. This requires optimization of the voltage and current to efficiently combine the PV and EC systems, which can make it difficult to obtain a desirable product with high efficiency. Therefore, research has been performed to achieve high catalytic performance and selectivity.

White et al. reported a PV-EC system consisting of a Si PV solar array coupled with In cathode-based EC cells. These cells used a bicarbonate catholyte for the conversion of CO₂ to formate and formic acid. Kaufman et al. used a commercial 6 V Si solar module to power a two-chamber EC reactor with an Au cathode and a Pt anode, which was able to produce >400 L/(gAu·h) of CO with a selectivity of approximately 96%. EC reduction of CO₂ to CO is generally more energy-efficient and kinetically favorable than direct reduction of CO₂ to multicarbon products such as CH₄, C₂H₄, CH₃OH, and C₃H₆OH. Therefore, CO is an attractive product for EC CO₂ reduction. There are efficient metal catalysts for CO₂ reduction to CO, such as Au, Ag, WSe₂, ZnO, and MoS₂. Au thin films are effective for efficient CO₂ reduction to CO at modest overpotentials and high selectivity in comparison to hydrogen
evolution. Specifically, nanoporous Au (pAu) has been reported to have a Faradaic efficiency (FE) of 95.9% at an applied potential of −0.6 V vs RHE for 10 h.24 Thus, we chose a pAu nanostructure that produced CO with high selectivity because of its large surface area and large number of active sites.24−27 We fabricated an EC cell with a pAu electrode as a cathode and an IrO2 electrode as an anode. The pAu electrode was fabricated using an anodization−reduction process. This

![Figure 1](https://pubs.acs.org/doi/abs/10.1021/acsomega.1c06720)

**Figure 1.** (a) Chronoamperometry plots for the as-deposited Au anodized at different applied voltages. (b) Chronopotentiometry plots for the reduction of Au(OH)3, under a constant current density of −1 mA/cm² at different potentials. Front-view FE-SEM images of the Au nanostructures anodized at (c) 2.3 V, (d) 2.4 V, (e) 2.5 V, and (f) 2.6 V.

![Figure 2](https://pubs.acs.org/doi/abs/10.1021/acsomega.1c06720)

**Figure 2.** AFM images of the (a) untreated Au reference electrode (Au ref) and the pAu electrodes anodized at (b) 2.3 V, (c) 2.4 V, (d) 2.5 V, and (e) 2.6 V. (f) XRD patterns of the Au reference electrode and pAu electrodes anodized at different voltages.
Au catalyst exhibited excellent performance, with a CO FE of 100% at −0.75 V vs RHE. Furthermore, by using the catalyst for both the cathode and anode, we demonstrated a solar-driven configuration for a triple-junction Si solar cell as a power source with a solar-to-CO conversion efficiency (SCE) of 5.3% and stability for >100 h.

**RESULTS AND DISCUSSION**

Figure 1a presents the chronoamperometry curves for the 300 nm thick anodized Au films in the 0.2 M KHCO3 electrolyte. Potentials ranging from 2.3 to 2.6 V were applied with steps of 0.1 V for 40 min. The anodic current density increased from 1.5 to 8.5 mA/cm² with increasing applied potential. Furthermore, the anodic current densities at each potential remained approximately constant for 40 min of anodization, although the current density at high applied potentials decreased slightly after prolonged anodization. This may have been due to the oxygen evolution and bubble attachment on the electrode surface.

Figure 1b shows the chronopotentiometry curves for the reduction of the porous Au(OH)₃ nanostructure at a constant current density of −1 mA/cm². As the anodization potential for Au increased, the potential drop time increased, indicating that the anodized Au thickness at high voltage is thicker. The scanning electron microscopy (SEM) images of the pAu in Figure 1c–f show the Au nanostructures with pore-like structures. The Au nanostructure shape is more pronounced in the anodized pAu samples, indicating that the pAu sample surface becomes rougher with higher anodization voltage.

Furthermore, the AFM images of the untreated Au reference electrode (Au ref) and the pAu electrodes are shown in Figure 2a–e. Estimated average surface roughness values of Au ref, pAu-2.3 V, pAu-2.4 V, pAu-2.5 V, and pAu-2.6 V were approximately 2.18, 3.07, 4.14, 4.36, and 5.76 nm, respectively. These results indicate that pAu porosity increased with increasing anodization voltage. The XRD patterns were recorded to determine the phase structure and crystallinity of the pAu electrodes. Figure 2f shows the XRD patterns of untreated Au and anodized Au. Prominent diffraction peaks for planes of polycrystalline Au were observed. Peak intensities corresponding to the (220) and (220) planes increased as the anodization voltage increased above 2.4 V, showing that the morphology of Au changed depending on the applied voltage. Meanwhile, the Ti peak was decreased at 2.5 and 2.6 V, which is possibly explained by a greater thickness of Au at anodization voltages above 2.4 V. From the results, the relative morphology of the Au nanostructure is affected by the anodization voltage, but the specific crystal faces that are present are not.

To evaluate the EC properties of the pAu for CO₂ reduction, LSV was measured in a three-electrode configuration in the CO₂-saturated 0.1 M KHCO3 solution. Figure 3a shows LSV plots of untreated Au and anodized Au samples. It is observed that the current density increased when the applied voltage was increased. The maximum current density was observed for pAu-2.6 V. The FE for the CO product is shown in Figure 3b–f. The CO₂ reduction of all samples was assessed at a constant current density of −4 mA/cm².

The FE for CO is calculated using the following equation

\[
\text{FE} = \frac{z \times n \times F}{Q}
\]

where \(z\) is the number of electrons involved (\(z = 2\) for reduction of CO₂ to CO), \(n\) is the number of moles for a detected CO product, \(F\) is Faraday’s constant (96,485 C/mol), and \(Q\) is the charge passed. The CO FE for untreated Au is
shown in Figure 3b, in which only CO and H$_2$ gas were detected as products in the EC CO$_2$ reduction of Au samples. Figure 3c–f shows the CO FE of the anodized Au at (c) 2.3 V, (d) 2.4 V, (e) 2.5 V, and (f) 2.6 V. The hydrogen evolution reaction (HER) was not observed in the pAu samples other than pAu-2.3 V. This may be because the pores in the Au nanostructure accelerated CO production reaction. The resulting pAu cathodes exhibited significantly higher CO selectivity at a low overpotential than the as-deposited Au, owing to the high density of grain boundaries as shown in Figure S1. This can accelerate the stabilization of the CO$_2^-$ intermediate, facilitate the adsorption/stabilization of key reaction intermediates (such as COOH$^*$) for CO$_2$ reduction to CO, and suppress the HER.  

To investigate the electrochemically active surface area (ECSA), the double-layer capacitance method was used. Figure 4a–e shows the CV plots of untreated and anodized Au samples measured in the potential window from 1.18 to 1.28 V vs RHE. Figure 4f shows the capacitive current density as a function of scan rate. The slope gives the double-layer capacitance ($C_{dl}$) determined by measuring the capacitive current associated with double-layer charging from the various scan rates (20, 40, 60, 80, and 100 mV/s) during CV. It can be seen that the pAu-2.6 V electrode has a large $C_{dl}$ of 455 mF/cm$^2$, which was greater than those of all the other electrodes.
tested, suggesting that it has the largest effective ECSA for the electrochemical reduction of CO₂. This result further confirms that when a larger anodization voltage is applied, the electrocatalytic process is improved.

IrO₂ was selected as an anode electrode owing to its great stability and excellent performance for the oxygen evolution reaction. The oxygen evolution EC properties of IrO₂ were examined in a three-electrode configuration. As indicated by the LSV curve in Figure 5a, the IrO₂ electrode had an onset potential of 1.5 V vs RHE. For the PV-EC system, the LSV curve was assessed in the two-electrode configuration for EC CO₂ reduction with the IrO₂ electrode as the anode and pAu-2.6 V as the cathode (Figure 5b). The LSV curve shown in Figure 5b is similar to that in Figure 5a, indicating that additional Ohmic losses did not occur in our H-type cell (inset of Figure 5b).

The open-circuit operating potential ($V_{oc}$) and open-circuit current density ($J_{oc}$) are the values at the intersection of the current density ($J$)–voltage ($V$) curve of the PV cells and EC cells. These values must be close to the values at the maximum power of the PV cells; otherwise, the photoexcited electrons and/or electron energies partially dissipate. To identify the optimal numbers of PV cells, conventional Si solar cells connected in series were employed. Figure 6a shows a schematic of the PV system under illumination. The $J$–$V$ curves of the solar-array configuration with up to four PV cells and an EC cell (the $J$–$V$ curves extracted from Figure 5b) are shown in Figure 6b. The dependence of the operating parameters, selectivity, and figure of merit of the resulting PV-EC system on the control parameters, including the number of PVs and the individual solar-cell area, were evaluated using these curves (Table 1). Current-matched PV cells can be connected in series to increase the overall voltage. The current densities under the operating conditions ($J_{oc}$) were 0.1 mA/cm², $V_{oc} = 1.1$ V for PV-1; 2.3 mA/cm², $V_{oc} = 2.3$ V for PV-2; 4.0 mA/cm², $V_{oc} = 2.7$ V for PV-3; and 3.6 mA/cm², $V_{oc} = 2.6$ V for PV-4. Under this condition, long-term testing of the PV-EC system was conducted, where the CO₂-saturated 0.1 M KHCO₃ solution was used as the electrolyte circulated during experiments. The PV cells were connected to an EC cell, and the stability experiment on the PV-EC system was

**Table 1. Parameters and Measurement from Solar Experiments, i.e., the Number of PV Panels, PV Area, $V_{oc}$ (Open-Circuit Potential), $I_{oc}$ (Open-Circuit Current), $J_{oc}$ (Open-Circuit Current Density), and SCE**

| number of PV panels | area (cm²) | $V_{oc}$ (V) | $I_{oc}$ (mA) | $J_{oc}$ (mA/cm²) | SCE (%) |
|--------------------|-----------|--------------|---------------|------------------|--------|
| PV-1               | 1         | 6            | 1.1           | 0.6              | 0.1    |
| PV-2               | 2         | 12           | 2.3           | 27.6             | 3.1    |
| PV-3               | 3         | 18           | 2.7           | 72.0             | 4.0    |
| PV-4               | 4         | 24           | 2.6           | 86.4             | 3.6    |

Figure 6. (a) Photograph of solar illumination on solar panels connected in series. Each solar panel area was 6 cm². (b) $J$–$V$ curves of EC cells (black line) and PV cells with different numbers of solar panels (1, red line; 2, green line; 3, brown line; 4, blue line). The star symbols indicate the optimized operation point. (c) Results of a stability test of the PV-EC system performed at the operating current density.
conducted under 1 sun illumination for 100 h as shown in Figure 6c. The current density of the PV-EC system was 4 mA/cm² at the initial stage. It decreased slightly to 3 mA/cm² and held this value for 100 h. The SCE of the PV-EC system can be calculated using the following equation

\[
SCE = \frac{E^0_{\text{CO2RR}} \times FE_{\text{CO}} \times I_{\text{OC}}}{P_{\text{solar}}} \times 100%
\]

where \(E^0_{\text{CO2RR}}\) is the standard equilibrium potential for CO₂ to CO (1.34 V), \(FE_{\text{CO}}\) is the FE of the CO₂ to CO reduction, \(I_{\text{OC}}\) is the operating current density of the PV-EC system, and \(P_{\text{solar}}\) is the incident solar power (100 mW/cm²). When combined with a triple-junction Si solar cell, a SCE of 5.3% was achieved for this system, with an average FE of 100% for CO evolution.

**CONCLUSIONS**

We developed unassisted light-driven electrochemical CO₂ reduction to CO comprising an IrO₂ anode and a pAu cathode using series-connected Si solar cells. The pAu cathode was fabricated by an anodization and reduction process in a 0.2 M KHCO₃ electrolyte. A directly coupled solar-driven CO₂ reduction cell was designed and optimized with a triple-junction Si PV cell under 1 sun illumination. The optimized PV-EC system achieved a SCE of 5.3% and operated for 100 h. Our homemade H-type cell with a circuit flow system exhibited no appreciable degradation. This study paves the way for the development of inexpensive and efficient electrochemical CO₂ reduction.

**EXPERIMENTAL SECTION**

**Preparation and Characterization of Electrodes.** A Au thin film with a thickness of approximately 300 nm was prepared using electron-beam evaporation on a sapphire substrate. A 30 nm thick Ti interlayer was embedded for enhancing the adhesion between the Au film and the sapphire substrate. Oxidized cathodes were prepared via EC anodization as previously described. The Au thin films were cut to an area of 1 cm². Anodization at 2.3, 2.4, 2.5, and 2.6 V vs RHE was conducted in a 0.2 M KHCO₃ aqueous electrolyte (pH 7.8) for 40 min. After reduction of the oxidized Au, these electrodes exhibited a highly porous structure of metallic Au with an increased surface area. The IrO₂ anode was purchased from GANATECH Company (Republic of Korea). IrO₂ was coated onto both sides of a Ti substrate. KHCO₃ (>99.8%) was purchased from Sigma-Aldrich (USA). All chemicals were used as received without further purification. Millipore triple-distilled water was used to prepare solutions. The morphology and structural properties were characterized using field emission scanning electron microscopy (FE-SEM; Gemini 500, Oxford), atomic force microscopy (AFM; NX20, Park Systems) and X-ray diffraction (XRD; Panalytical). The AFM images were rendered using the XEI program (Park Systems). XRD patterns were obtained from an X-ray diffractometer (D2 Phaser, Bruker AXS Analytical Instruments Pvt. Ltd., Germany) and an XPERT PRO MRD PW3040/60 over the 2θ angular range of approximately 20°–90° under grazing angle incidence using Cu Kα irradiation (wavelength \(\lambda = 1.5406 \text{ Å}\)). Au porous structures were characterized using a high-resolution transmission electron microscope (TEM, Tecnai G2, F30 S-Twin, operating at 80–300 KeV, FEI).

**Electrochemistry of Electrodes.** The EC CO₂ reduction performance of the Au electrodes was measured in a CO₂-saturated 0.1 M KHCO₃ aqueous electrolyte (pH 6.8) using an H-type cell with a three-electrode configuration. The electrolyte was prepared by purging CO₂ for 20 min before the experiment. The cathodic and anodic compartments were separated by an anion-exchange membrane (Nafion 117). The Au electrode was used as the working electrode, and Pt wire and Ag/AgCl (saturated KCl) were used as counter and reference electrodes, respectively. All the Au electrodes used in the experiment underwent electropolishing before the CO₂ reduction experiment. The EC polishing steps were as follows: (1) preparation of the polishing solution (H₃PO₄:PEG400 = 3:1); (2) EC treatment at 1.5 V vs counter electrode for 30 min; (3) washing in water; and (4) drying in ambient air. Chronopotentiometry at a selected constant current was performed for 180 min on the cathode using a potentiostat (PARSTAT 4000). The measured current density was not corrected by the solution resistance because the potential drop caused by the solution resistance was negligible. For gas product analysis, the headspace of the cathodic chamber was connected to a gas chromatography system with a thermal conductivity and flame ionization detector (Agilent 7890, Agilent Technologies, Santa Clara, CA, USA). The gas product was monitored every 30 min for 180 min. The activity of the IrO₂ anode toward oxygen evolution was tested using linear sweep voltammetry (LSV) at a scan rate of 20 mV/s in a 0.1 M KHCO₃ electrolyte saturated by CO₂.

**Solar-Driven EC CO₂ Reduction.** PV modules were prepared using a commercially available Si solar cell (A00435, TOY SCIENCE, Korea). The Si PV cell areas were 2 cm × 3 cm (6 cm²). The panel was prepared with four cells connected in series using alligator clips. PV properties were measured using a K3000 Xe55 Solar Cell I-V Parameter Test System (Solar Simulator Class AAA, IEC60904-9, McScience Inc., Korea). The PV-EC module consists of components such as the electrode, membrane, and PV cell. A two-electrode configuration was applied in the EC system to characterize the electrolysis properties of the real device. The light source was a solar simulator equipped with a 1.5 AM filter (Xe55, McScience Inc., Korea). The electrolyte was circulated using a pump during the experiment. The current density of the unassisted PV-EC system under standard light illumination conditions (1 sun, 1.5 AM) was measured using a Keithley 2601A Source Measure Unit (Tektronix, formerly Keithley, Beaverton, OR, USA).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06720. TEM analyses of the Au porous structure; HRTEM images presenting grain boundaries with white lines and the FFTs (fast Fourier transforms) of two boxed areas (PDF)

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This research was financially supported by the Ministry of Trade, Industry, and Energy (MOTIE) and the Korea Institute for Advancement of Technology (KIAT) through the International Cooperative R&D program (no. P0006851) and the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (2018R1A6A1A03024334).

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