Hierarchically porous Au nanostructures with interconnected channels for efficient mass transport in electrocatalytic CO₂ reduction

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Electrocatalytic CO₂ reduction is a promising way to provide renewable energy from gaseous CO₂. The development of nanostructures improves energy efficiency and selectivity for value-added chemicals, but complex nanostructures limit the CO₂ conversion rates due to poor mass transport during vigorous electrolysis. Herein, we propose a three-dimensional (3D) hierarchically porous Au comprising interconnected macroporous channels (200–300 nm) and nanopores (~10 nm) fabricated via proximity-field nanopatterning. The interconnected macropores and nanopores enable efficient mass transport and large active areas, respectively. The roles of each pore network are investigated using reliable 3D nanostructures possessing controlled pore distribution and size. The hierarchical nanostructured electrodes show a high CO₂ selectivity of 85.8% at a low overpotential of 0.264 V and efficient mass activity that is maximum 3.96 times higher than that of dealloyed nanoporous Au. Hence, the systematic model study shows the proposed hierarchical nanostructures have important value in increasing the efficiency of expensive Au.

Hierarchically porous nanostructures | gold nanostructures | mass transport | proximity-field nanopatterning | carbon dioxide reduction

With increasing emissions of carbon dioxide (CO₂) and depletion of fossil fuels, an attractive answer is the electrochemical conversion of CO₂ into useful chemicals. To achieve this goal, a key technological issue is the development of an efficient electrocatalyst for selective and robust CO₂ reduction reactions (1). Many studies have been conducted to improve selectivity because the CO₂ reduction reaction occurs competitively with the hydrogen evolution reaction (HER) at similar redox potentials. In general, the enhanced selectivity is derived from the modulation of intrinsic properties, such as high index plane (2–5), grain boundary (6, 7), and surface structure (8–11), contributing to increases in active sites. Additionally, the thickness and structural changes of electrocatalysts result in the effective suppression of the HER by forming a local pH gradient (12–16), which occurs when the OH⁻ generated by the cathodic reaction is prevented from being neutralized. These studies have primarily been conducted through the synthesis of nanostructures and have already demonstrated the high selectivity of target products at a very low overpotential (SI Appendix; Table S1).

Despite higher catalytic activities in terms of selectivity and overpotential with nanostructures, a massive CO₂ conversion rate should be achieved for practical use (14, 17–19). The previously studied one-dimensional and two-dimensional structures (20–22) have difficulty forming thick electrodes with the desired pore size due to their easy aggregation property, resulting in a limited conversion rate per area. As increased number of active sites with a thick catalyst layer does not guarantee a higher CO₂ conversion rate. In complex nanostructured catalysts, the path toward the reaction sites on the catalyst for protons and reactant CO₂ becomes tortuous enough to disturb the reactions. This mass transport limitation leads to the formation of localized inactive sites accompanying the depletion of reactants, bringing on a decrease in the CO₂ conversion rates. Thus, an optimized, three-dimensional (3D) hierarchical structure, that is capable of improving mass transport while maintaining a large active area, is necessary for achieving efficient CO₂ reduction (19, 23–29). The 3D hierarchically porous nanostructures produce 1) a great number of electrochemical active sites, 2) facile transport of reactants (30, 31), and 3) short ion and electron pathways, surpassing the limits of previous nanostructures. Herein, we proposed a 3D hierarchically porous gold (N/M-Au) nanostructures having interconnected macroporous channels and numerous nanopores via Proximity-field nanoPatterning (PnP). Using this optical lithography, N/M-Au nanostructures were produced with well-controlled pore size and connected networks for supplying fresh electrolyte. The effect of electron and ion transport on the CO₂ reduction reaction was systemically investigated and compared using different 3D Au nanostructures: nanoporous Au (N-Au), macro-porous Au (M-Au), and N/M-Au. In N/M-Au nanostructures, the nanopores contributed to the superior selectivity due to the highly active and large surface area, and the interconnected channels with submicrometer pores offer efficient mass transport pathways.

Significance

A hierarchical structure with multiscale pore networks has been explored to enhance electrocatalytic performance in CO₂ reduction. Here, we thoroughly analyze the effect of each pore network on catalytic performances using nanostructures composed of nanopores and periodic macroporous channels. The tough mass transport within complex nanostructures has attracted much attention as increasing selectivity. However, the productivity improvements of hierarchical nanostructure by efficient mass transport have been rarely investigated in CO₂ reduction. This paper systematically reports the structural effect on both selectivity and productivity by controlling pore sizes and distributions. Therefore, the proposed hierarchically nanostructures show improved mass activity and can further be applied to other electrochemical systems in the same way.


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for electrolytes, including ions and protons. As a result, hier-
archically porous Au shows a CO partial current density 2.40
times higher per mass of Au than the nanoporous Au at a low
potential of 0.324 V (vs. reversible hydrogen electrode [VRHE]).

Our 3D hierarchically porous electrode provides a strategy for
efficient Au utilization in the various electrochemical system.

Results and Discussion

Fig. 1 depicts a schematic illustration of the fabrication pro-
cedures for 3D Au nanostructures having a continuous pore net-
work of various sizes and distributions. Three types of Au
nanostructures (N-, M-, and N/M-Au) with a thickness of
14.7 µm were fabricated by 3D nanopatterning and electroplating
processes. The Au and AuAg alloys are electroplated into a 3D
epoxy (SU-8) template made by the PnP technique (32–45)
that presents a defect-free and periodically interconnected pore net-
work. The advanced lithography, PnP technique, has shown the
possibility of producing a reliable large area (>1 in²) with a single
exposure, and we produced a pattern with a diagonal length of
~3.5 in by multiple exposures, as shown in Fig. 1A (Inset). The
interconnected pore network of 3D epoxy nanostructures composed
of different sizes and distributions could be designed using this li-
thography technique. After the fabrication of a 3D epoxy nano-
structure, the metal is electroplated into the template. Then, the
epoxy template is removed by a remote plasma etcher,
resulting in the formation of an interconnected macroporous
nanostructure. SI Appendix, Fig. S1 shows stepwise cross-sectional
scanning electron microscope (SEM) images of the templating
method. To produce the nanostructures with the sizes of ~10 nm, an
AuAg alloy infiltrates into the template, and the silver component
is selectively etched in diluted nitric acid (70%) for 12 h. The
nanostructures and the macropores are evenly distributed in the 3D
Au nanostructured electrodes. As shown in Fig. 1B, N-Au fabric-
cated with the AuAg alloy directly on the substrate without the
epoxy template only possesses nanopores in the structure. Fig. 1C
shows the M-Au with only macropores, and Fig. 1D shows N/M-Au
with the two different sizes of macropores and nanopores. All
nanostructured electrodes were controlled to have the same
thickness by changing the electroplating time.

To investigate the catalytic activity of the various Au nanostructures,
the CO selectivity is measured in CO2-saturated 0.2 M KHCO3
solutions with different applied potentials. Nontemplated Au
(nt-Au) with a rough morphology (SI Appendix, Fig. S2) is pre-
cpared by electroplating on a Cr/Au (5/200 nm) deposited-flat SiO2
substrate as a control group. According to X-ray photoelectron
spectroscopy analysis in SI Appendix, Fig. S3, clear Au 4f peaks
arouse at ~84.7 and 88.2 eV for the four different types of Au
electrodes (nt-, M-, N-, and N/M-Au). Less than 10.3 at % of Ag
component remained in N/M- and N-Au after the removal process
of Ag in nitric acid because of the atomic diffusion. Although the
residual Ag has a slightly lower CO selectivity than Au, nanopor-
ous Ag with a curved surface is known to provide stable active
sites for the CO2 intermediate, showing excellent performance
under an overpotential of <0.50 V (9, 13). The small amount of
Ag is thus not expected to severely affect the overall reaction from
a structural point of view (25). All 3D nanostructured Au electrodes
are evaluated after the same plasma treatment in the remote
plasma etcher to exclude the effects of the plasma treatment
(46) causing the occurrence of the N 1s peak at ~398 eV and the F
1s peak at ~685 eV (SI Appendix, Fig. S4). As shown in Fig. 2A, all
of the fabricated Au nanostructures, i.e., N-, M-, and N/M-Au,
show improved CO selectivity compared to nt-Au due to the effect
of the porous structure. N/M-Au comprising both nanopores and
macropores shows CO selectivity close to that of N-Au over the
entire potential region, which has higher selectivity than M-Au. In
the comparison of the Tafel plot in Fig. 2B, N/M- and N-Au
having nanopores show lower Tafel slopes of ~106 mV dec⁻¹,
whereas the others have higher values (120 and 186 mV dec⁻¹ for

Fig. 1. Fabrication procedures for various Au nanostructures via the PnP technique and electroplating method. (A) Schematic illustration of fabrication procedures for nanoporous gold (N-Au), macroporous gold (M-Au), and hierarchically porous gold (N/M-Au). Digital images of a 3D epoxy template electroplated with AuAg alloy and N/M-Au on a 4-in SiO2 wafer deposited with Au. Low- and high-magnification SEM images of (B) N-, (C) M-, and (D) N/M-Au. (Scale bars, 5 µm; Inset scale bars, 500 nm.)

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M- and nt-Au, respectively). This result indicates that the nanopores in the Au nanostructures might allow a faster first-electron transfer step in the CO₂ reduction reaction than the samples without nanopores (47–49). The crystallinities of the Au nanostructured electrodes were examined using X-ray diffraction (XRD) analysis, as shown in Fig. 2C. The XRD patterns show the existence of a high index plane of (200) for N/M- and N-Au, while M- and nt-Au have almost no (200) peak. The peak intensity ratios of (200) to (100) are 0.02, 0.14, and 0.27 for M-, N/M-, and N-Au, respectively. In fact, it has been reported that a high index plane produces stable sites for the CO₂⁻ intermediate species (2–5). Thus, these results support the higher CO selectivity and lower Tafel slope of the N/M- and N-Au samples as compared to M- and nt-Au. In addition, the local pH effect is analyzed with two different electrolytes in K₂HPO₄ and KClO₄ (SI Appendix, Fig. S5). Due to the complex nanostructures having many pores, the CO selectivity of all of the electrodes in the KHCO₃ electrolyte is close to the selectivity in the KClO₄ electrolyte, which has no buffering ability. This result means that all our prepared Au nanostructure samples form a local pH gradient well.

We investigated the effect of surface area on the current-density trends for all of the prepared electrodes in a range of applied potentials from −0.174 to −0.574 V_RHE. The partial current densities of CO (j_CO) and H₂ (j_H₂) using N- and N/M-Au are slightly higher than that of M-Au over the whole potential range, as shown in Fig. 3A and B. The roughness factors (RF) of the Au electrodes are calculated using cyclic voltammetry (CV) curves (SI Appendix, Fig. S6) reflecting on the electrochemical surface area, as summarized in SI Appendix, Table S2. Although the

Fig. 2. Measurement and analysis of catalytic activity for electrocatalytic CO₂ reduction. (A) CO selectivity and (B) Tafel slope of various gold nanostructures of N/M-, N-, M-, and nt-Au. (C) XRD pattern for analyzing the electrochemical activity.

Fig. 3. Electrochemical performance for CO₂ reduction electrolysis to CO and H₂ on Au nanostructured electrodes. Partial current density of (A) CO (j_CO) and (B) H₂ (j_H₂) for comparing different nanostructured electrodes. Specific (C) j_CO and (D) j_H₂ divided by RF of each nanostructured electrode.
RF of N/M-Au is half that of N-Au, N/M-Au shows a slightly higher \( j_{\text{CO}} \) of 0.891 mA cm\(^{-2}\) than 0.759 mA cm\(^{-2}\) for N-Au at an applied potential of -0.324 V\(_{\text{RHE}}\). To investigate the surface-area effect, we derived the specific \( j_{\text{CO}} \) and \( j_{\text{H}_2} \) values by normalizing the partial current density with RF, as shown in Fig. 3 C and D. Interestingly, the Au nanostructures possessing macropores (N/M- and M-Au) show higher specific \( j_{\text{CO}} \) than N-Au over the entire potential range. In particular, the specific \( j_{\text{CO}} \) of M- and N/M-Au is 1.33 and 1.52 times larger than that of N-Au, respectively, at a potential of -0.574 V\(_{\text{RHE}}\). This means that the whole surface area of N-Au having only a nanoporous network does not effectively work on the CO\(_2\) reduction reaction. The specific \( j_{\text{H}_2} \) curves are also shown to follow the same trend as the specific \( j_{\text{CO}} \). At applied potentials lower than -0.374 V\(_{\text{RHE}}\), M-Au having poor CO selectivity shows a higher specific \( j_{\text{CO}} \) than that of N/M-Au.

To further understand the relationship between the specific \( j_{\text{CO}} \) and the electrochemical surface area, we compared the specific \( j_{\text{CO}} \) by modulating the thickness at two different potentials (-0.274 and -0.574 V\(_{\text{RHE}}\)). In detail, we prepared various samples with different thicknesses of T1 (~4.41 μm), T2 (~7.95 μm), and T3 (~14.7 μm) for M-, N-, and N/M-Au by controlling the electroplating time in the fabrication process (Fig. 4 A–C). As shown in Fig. 4 D and E, the specific \( j_{\text{CO}} \) for all 3D nanostructured Au decreases as the thickness increases regardless of the applied potentials. Interestingly, it is noteworthy that M-Au with only T1 and T2 shows a noticeably higher specific \( j_{\text{CO}} \) than N- and N/M-Au at -0.574 V\(_{\text{RHE}}\), which is the vigorous reaction condition. We estimated that this is because a well-ordered macroporous network assists smooth transport of the electrolyte and the active surface can be utilized more efficiently when the reaction occurs rapidly, accompanying the prompt consumption of reactants in the electrolyte. However, the specific \( j_{\text{CO}} \) for M-Au with T3 dramatically drops to a similar level as N- and N/M-Au, indicating that a thicker layer extremely disturbs the diffusion of the reactant and

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**Fig. 4.** Thickness-dependent electrocatalytic performance and mass activities of various Au nanostructures. Cross-sectional SEM images of (A) M-, (B) N-, and (C) N/M-Au with various thicknesses of T1, T2, and T3. (Scale bars, 3 μm.) Comparison of specific \( j_{\text{CO}} \) using M-, N-, and N/M-Au with different thicknesses at (D) -0.274 V\(_{\text{RHE}}\) and (E) -0.574 V\(_{\text{RHE}}\). (F) CV of various electrocatalysts in 0.5 M of H\(_2\)SO\(_4\) with a scan rate of 25 mV s\(^{-1}\). (G) Relative mass activity comparing between M-, N-, and N/M-Au. Schematic illustration (Left) and the cross-sectional view with the expected reaction pathway (Right) for (H) N/M-Au and (I) N-Au electrodes.
products even during the vigorous CO₂ reduction reaction. In fact, N/M-Au with a thickness of T3 shows the optimal specific jCO regardless of the applied potentials due to the combined effects of the nanoporous and macroporous channels. On the other hand, the diffusion issue with different nanostructures is found in CV curves performed in 0.5 M H₂SO₄ in Fig. 4F. The reduction peaks for M-Au, N/M-Au, and N-Au are located at 1.108, 1.015, and 0.951 V_RHE, respectively. That is, the peak position is shifted to the lower potential side with nanopores. This shift might be attributed to the slow kinetics of electrons and ions during electrolysis in nanopore-included structures (25, 50). As shown in SI Appendix, Fig. S7, the linear scanning voltammetry (LSV) curve also shows that N/M-Au has the highest current density, indicating the structural advantages of N/M-Au with both nanoporous and macroporous networks. For instance, the current densities at −0.60 V_RHE for M-, N-, and N/M-Au are −12.6, −13.2, and −19.0 mA cm⁻², respectively. Finally, we evaluated the mass activity of our prepared Au nanostructures for electrochemical CO₂ reduction by estimating the mass of the Au nanostructures (see SI Appendix, Fig. S8 for the method of calculation of mass activity). In detail, the mass activities for all nanostructures are relatively compared based on N/M-Au at each potential from −0.174 to −0.574 V_RHE as shown in Fig. 4G. The mass activity of N-Au is approximately half that of N/M-Au at −0.574 V_RHE while M-Au has a much lower value of 16.3% due to the large amount of unexposed Au. These results clearly show the importance of the catalyst structure design for mass activity. Although N-Au has the largest CO selectivity with nanopore effects, the interconnected macropores in N/M-Au show the optimal CO₂ conversion activity in terms of productivity.

Fig. 4H and I show a schematic illustration of the expected mass transport pathways in N/M-Au and N-Au. The macroporous network of N/M-Au assists the efficient electrolyte circulation to utilize the entire area of Au. At the same time, the nanopores possessing a high-index Au surface contribute high CO selectivity and a large electrochemical surface area. While N-Au with only nanopores has the largest surface area, the mass transport of reactants can be disturbed in complex structures, resulting in the poor mass activity of Au as compared to that of N/M-Au. According to the gas-evolution observation during the CO₂ reduction reaction, the generated gas bubble is detached from the electrode after the growth of the bubble to micrometer size (29, 30). The bubbles generated in the complicated 3D nanostructures imperatively not only block active sites until the bubble grows but also cause an insufficient supply of fresh aqueous CO₂. At this point, the interconnected macropores provide a bubble-growth site and efficient transport pathways enabling the mass transport of CO₂. Therefore, our N/M-Au having highly active nanopores and interconnected macroporous channels suggests a direction for the development for CO₂ reduction technology with practical application. This hierarchically porous network can be produced to target useful reactions using other metals including Cu and alloys. In addition, the suggested structural design will be applicable for different energy applications, such as batteries and fuel cells, which are strongly affected by mass transport during a reaction.

In conclusion, we successfully fabricated 3D hierarchically porous Au nanostructures consisting of interconnected macroporous channels and nanopores. This 3D Au nanostructure can be easily modified and scaled up to wafer size due to the simple fabrication process using PnP and electroplating techniques. Numerous nanopores in the hierarchical nanostructures provide a 66.1x larger active electrochemical surface area than that of an electroplated Au film and a maximum of 3.96x times higher jCO per mass than that of a nanoporous Au film. The interconnected macroporous network produces efficient mass transport even in the robust electrolysis, resulting in high mass activity compared to previously reported nanostructured electrodes (SI Appendix, Table S3). Thus, we have suggested an efficient structural design for 3D hierarchical nanostructures having both high specific jCO and jCO relative to the mass of Au. The study of the mass transport effect within 3D nanostructures has important value as the systematic model study. Furthermore, the hierarchically porous nanostructures with simulated optimal pore size and distribution can be efficiently used in next gas-phase CO₂ reduction or other electrochemical systems that need mass production.

Materials and Methods

Fabrication of a 3D Epoxy Template on a Conductive Substrate. A metal conductive layer consisting of Cr (5 nm) and Au (200 nm) was deposited on the SiO₂/Si wafer (TASCO) at a deposition rate of 0.5–0.7 Å s⁻¹ using an e-beam evaporator (SNTEK). The flat-Au and N-Au do not need to form epoxy-based nanostructured templates on the substrate, and gold and gold-silver alloy were directly electroplated on the oxygen-plasma (45 sccm, 40 mTorr, 60 W, CUTEMP, Femtoscience) pretreated substrate. To fabricate 3D epoxy templates, a photolithography of SU-8 (Microchem) with a thickness of 17 μm was spin-coated on the substrate at 4000 rpm for 40 s. The photoresist-coated substrate was soft-baked at 95 °C for 1 h. Then, a conformal phase mask containing square arrays with a cylindrical surface grating was placed on the photoresist-coated substrate, and a collimated laser (Nd:YAG [neodymium-doped yttrium aluminium garnet] laser) 355 nm, 50 mW, Advanant Optics_1700) was irradiated using a high-power phase mask with an exposure dose of −16.0 mJ cm⁻². After exposure, the resist-coated substrate was heated at 65 °C for 6 min on a hotplate and developed in the SU-8 developer (Microchem).

Fabrication of Various Gold-Nanostructured Electrodes. The electrolyte for gold consisted of 0.02 M KAu(CN)₂ and 0.25 M Na₂CO₃, and 0.03 M KAgI(CN)₂ was additionally added into the electrolyte for the gold–silver (AuAg) alloy. All of the fabricated substrates were treated by oxygen-plasma before electroplating. The fabricated substrate, a platinum wire, and KCl-saturated Ag/AgCl (AT FRONTIER) were used as the working electrode, counter-electrode, and reference electrode, respectively. Gold and a gold–silver (AuAg) alloy were electroplated at an applied potential of −0.95 and −1.1 V, respectively, with pulses (5 s on and 5 s off) using a potentiostat system (300 mA, Advance Optics_2100). The electroplated metals was controlled by the different number of pulsed cycles. To remove silver from the alloy, the electroplated metals were soaked in nitric acid (Sigma-Aldrich) for 12 h. Then, the removal of the template and plasma treatment was conducted by a remote plasma etcher (STOP, Muegge) for all electrodes.

Characterization. The structural details of various gold nanostructures were observed using a field-emission SEM (S4800, Hitachi) with an accelerating voltage of 10 kV. The composition distributions of gold and the remaining silver were investigated after the fabrication procedures using X-ray photoelectron spectroscopy (X-alpha, Thermo VG scientific). All of the graphs were calibrated to the peak corresponding to C 1s peak. The crystal phases of the fabricated electrodes were identified by X-ray diffraction (Ultra IV, RIGAKU) from 20° to 60° with a scanning speed of 4° min⁻¹.

Electrochemical Measurements. All nanostructured Au electrodes were reduced at an applied potential of −0.574 V_RHE for 30–60 s. CV was conducted in 0.05 M H₂SO₄ (Sigma-Aldrich) from 0.45 to 1.95 V (vs. Ag/AgCl) at a scan rate of 25 mV s⁻¹. The different gold nanostructures and platinum wires were used as the working electrodes and counter electrodes, respectively. Electrochemical CO₂ reduction was conducted in CO₂-saturated 0.2 M KHCO₃ (pH 6.8) with a single-compartment cell. The working electrode was fabricated gold nanostructures. Graphite and Ag/AgCl (in 3 M NaCl) were used as the counter-electrode and the reference electrode, respectively. All measurements were performed with stirring at 400 rpm. LSV was carried out at a scan rate of 50 mV s⁻¹. Chronoamperometry was conducted at different applied potentials for 15–70 min to analyze the CO selectivity during the CO₂ reduction reaction under gas-tight conditions. After electrolysis, the composition of the gas products was assayed by gas chromatography (Micro GC 3000, Inficon).

Data Availability. All data needed to evaluate the conclusions in the paper are present in the paper and/or SI Appendix.

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