Silver Nanowire/Carbon Sheet Composites for Electrochemical Syngas Generation with Tunable H₂/CO Ratios

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ABSTRACT: Generating syngas (H₂ and CO mixture) from electrochemically reduced CO₂ in an aqueous solution is one of the sustainable strategies utilizing atmospheric CO₂ in value-added products. However, a conventional single-component metal catalyst, such as Ag, Au, or Zn, exhibits potential-dependent CO₂ reduction selectivity, which could result in temporal variation of syngas composition and limit its use in large-scale electrochemical syngas production. Herein, we demonstrate the use of Ag nanowire (NW)/porous carbon sheet composite catalysts in the generation of syngas with tunable H₂/CO ratios having a large potential window to resist power fluctuation. These Ag NW/carbon sheet composite catalysts have a potential window increased by 10 times for generating syngas with the proper H₂/CO ratio (1.7−2.15) for the Fischer−Tropsch process and an increased syngas production rate of about 19 times compared to that of a Ag foil. Additionally, we tuned the H₂/CO ratio from 2 to ∼10 by adjusting only the quantity of the Ag NWs under the given electrode potential. We believe that our Ag NW/carbon sheet composite provides new possibilities for designing electrode structures with a large potential window and controlled CO₂ reduction products in aqueous solutions.

1. INTRODUCTION

Global climate change accelerated by carbon dioxide emissions has increased the demand to reduce the atmospheric CO₂ concentration by CO₂ capture, storage, and conversion. Among these, CO₂ conversion technologies, such as bioconversion, electrochemical conversion, and combined reforming, have attracted much interest for converting CO₂ into value-added products. Electrochemical CO₂ conversion can produce various fuels and carbon feedstocks, including CO, CH₄, HCOOH, and C₂H₄ at room temperature using renewable energy resources. In particular, CO production by the electrochemical CO₂ reduction reaction (CO₂RR) is attractive because it involves only two electrons and is a main component of syngas, which is widely used to synthesize value-added hydrocarbons in various industries. Syngas, a mixture of H₂ and CO, can be transformed into various hydrocarbons, such as methanol or synthetic crude oil, through the Fischer−Tropsch (F−T) process. In the F−T process, the ratio of syngas is crucial to maximize the product yield. For instance, the optimal H₂/CO ratio for syngas to generate hydrocarbons is 1.7 when using an iron-based catalyst and 2.15 when using a cobalt-based catalyst.

Metal catalysts such as Au, Ag, and Zn can be used as electrochemical catalysts to reduce CO₂ to CO in aqueous solutions. With these metal catalysts, syngas can be directly produced by electrochemical reduction of CO₂ to CO in aqueous solutions because electrochemical CO₂RR in an aqueous solution always accompanies the H₂ evolution reaction (HER) as a competitive reaction. However, this competitive reaction is the main reason for potential-dependent product distribution for typical CO₂RR metal catalysts. For example, in the case of Ag, the CO Faraday efficiency rapidly decreases from about 90 to <20% when the applied potential is changed from −1.02 to −0.75 V (vs reversible hydrogen electrode (RHE)), respectively, in CO₂-saturated 0.1 M KHCO₃. This is due to the fact that the CO₂RR current density for CO generation, jCO, is limited by the low solubility of CO₂ in water (34 mmol/L at 1 atm and 25 °C) and the sluggish reaction kinetics, which requires a high overpotential of more than 1 V to drive a sufficiently high jCO. This leads to considerable generation of the HER current density, jH₂, at a low overpotential. This potential-dependent H₂/CO distribution from a metal catalyst can limit the use of electrochemical CO₂RR for direct syngas production and requires additional facilities to adjust the syngas ratio. Especially in a two-electrode CO₂ electrolysis system, it is difficult to impose an exact electrode potential on a metal catalyst, and it would cause a temporal variation in the H₂/CO ratio. This becomes further aggravated if unstable electricity resources like photovoltaics and wind power are used. Therefore, to achieve cost-effective...
and sustainable syngas production with the optimum H2/CO ratio, it is crucial to develop a CO2RR catalyst capable of tuning the CO2RR and HER rates over wide ranges of operating conditions.

Thus far, the search for a single metal or bimetallic catalyst to convert CO2 to CO has focused on achieving the maximum CO generation rate at a low overpotential by controlling nanostructures and crystal facets.13−21 For example, nanoporous Au and Ag dramatically improve the CO2RR activity, showing nearly 100% CO production in an aqueous solution at a low overpotential.14,16 Also, Ag with an In(OH)3 support shows a higher CO current density than that of pure Ag and In(OH)3.20 In addition, Won et al. show that hexagonal Zn nanostructures with (101) crystal facets are effective in converting CO2 to CO.21 However, dominant CO production would require additional H2 sources for direct syngas production. Recently, Spurgeon et al. reported on the simultaneous production of CO and H2 with tunable H2/CO ratios from ~97 to 0.36 on a Cu foil by controlling the pulse times at a specific bias during pulsed-biased CO2 electrolysis.22 Here, we introduce porous composite materials for producing syngas with tunable H2/CO ratios for extended ranges of electrode potentials in potentiostatic CO2 electrolysis. Our composite material is composed of Ag nanowires (NWs) as the CO2RR catalyst on top of a thick macroporous carbon sheet as the HER catalyst. Compared to a Ag foil, our Ag NWs/carbon sheet composites have an increased syngas production rate of about 19 times with a H2/CO ratio of 1.7−2.15, which is optimum for the F–T process, and an increased range in the electrode potential of about 10 times during potentiostatic CO2 electrolysis in an aqueous solution. In addition, controllability of the syngas composition from ~0.7 to 80 was demonstrated by simply controlling the loading amount of Ag NWs.

2. RESULTS AND DISCUSSION

A schematic diagram of our composite CO2RR catalyst for tunable H2/CO production is shown in Figure 1. Unlike conventional single-component CO2RR catalysts for which the competitive HER and CO2RR occur on the same electrode surface (Figure 1a), our composite catalyst is designed to reduce CO2 and water independently from the corresponding CO2RR and HER catalysts following their own electrochemical characteristics. For instance, as shown in Figure 1b, CO2 will be reduced to CO on the CO2RR catalyst, which is on top of the macroporous HER catalyst. Then, unreacted protons will be
transported to the underlying HER catalyst for \( \text{H}_2 \) production. The macroporosity of our composite catalysts provides facile transport of protons to the HER catalyst as well as enhanced reactivity from the increased surface area. To achieve a tunable \( \text{H}_2/\text{CO} \) ratio over a wide range of electrode potentials, both the \( \text{CO}_2 \text{RR} \) and HER catalysts in the composite should have similar electrochemical current density—potential (\( j-V \)) characteristics, such as the onset potentials for \( \text{CO}_2 \text{RR} \) and HER, respectively. In addition, the products ratio of CO can be independently controlled by changing the loading amount of the \( \text{CO}_2 \text{RR} \) catalyst. In this work, we used Ag NWs as the \( \text{CO}_2 \text{RR} \) catalyst and a macroporous carbon sheet as the substrate for the Ag NWs and the HER catalyst. These Ag NWs simply enable us to tune the \( \text{H}_2/\text{CO} \) ratio by controlling the quantity of sprayed Ag NWs. Also, we chose a carbon sheet although it is known to be a poor HER catalyst because the HER onset potential of the carbon sheet is well-matched with the \( \text{CO}_2 \text{RR} \) onset potential of Ag explained below.

The Ag NWs/carbon sheet composites were fabricated by spraying Ag NWs on a macroporous carbon sheet shown in Figure 2a. The synthesized Ag NWs with a 50 nm diameter and \( \sim 30 \) \( \mu \text{m} \) length were dispersed in solution and sprayed by a sprayer previously described. After spraying, an intimate contact between each Ag NW was made by annealing at 100 °C for 60 min. The loading amount of the Ag NWs on a carbon sheet was controlled by adjusting the spraying time. To quantify the Ag NW loading amount, we measured the sheet resistance of the Ag NWs on a slide glass, which were sprayed for the same amount of time as the spraying time for the carbon sheet (see Figure S1).

Figure 2b–d shows the SEM images of the sprayed Ag NWs on the carbon sheets with different spraying times. The sheet resistances of Ag NWs on the carbon sheet are 1.4, 0.5, and 0.2 \( \Omega/\Box \), respectively. Hereafter, these are referred to as the 1.4 \( \Omega/\Box \) Ag NWs/carbon sheet composite, 0.5 \( \Omega/\Box \) Ag NWs/carbon sheet composite, and 0.2 \( \Omega/\Box \) Ag NWs/carbon sheet composite. As clearly shown in Figure 2b–d, the sprayed Ag NWs are stacked mostly at the top of the macroporous carbon sheets and form a porous structure, which creates a greater surface area for \( \text{CO}_2 \text{RR} \) and could facilitate proton transfer to the bottom of the macroporous carbon sheets for HER. In addition, the Ag NWs/carbon sheet composite with a lower sheet resistance has more densely stacked Ag NWs compared to those in the Ag NW composite with a higher sheet resistance. In other words, the exposed carbon sheet surface area of the topmost region toward electrolyte would be decreased as lowering the Ag NWs/carbon sheet composite sheet resistance. This means that the reaction areas for HER and \( \text{CO}_2 \text{RR} \) are controlled by the quantity of Ag NWs, spontaneously. Therefore, the evolution ratio of \( \text{H}_2 \) and CO through the Ag NWs/carbon sheet composites is adjustable by controlling the amount of Ag NWs. The X-ray photoelectron spectroscopy (XPS) spectrum of the Ag NWs/carbon sheet composites shows peaks at 368.2 and 374.2 eV, indicating no significant surface chemical state changes during the spraying or annealing process (Figure S2). To figure out the \( \text{CO}_2 \text{RR} \) property of Ag NWs themselves, we sprayed different amounts of Ag NWs on Ag foils by adjusting the spraying time. If the activity of Ag NWs for \( \text{CO}_2 \text{RR} \) is different from that of an Ag foil, CO selectivity and electrochemical properties, such as Tafel slope, partial current density (\( j_{\text{CO}} \)), and total current density (\( j_{\text{total}} \)), of Ag NWs sprayed on Ag foil electrodes would be changed with increasing the quantity of sprayed Ag NWs.

However, all of the “Ag NWs on the Ag foil” electrodes and the bare Ag foil had a similar CO selectivity and Tafel slope (~180 mV/decade) as a function of the applied potential (Figures S3–S5) despite different Ag NWs quantities. The similar \( \text{CO}_2 \text{RR} \) characteristics of Ag NWs and Ag foils are believed, mainly, due to the exposed crystal facets of Ag NWs. According to our previous work, our sprayed Ag NWs are single crystalline with the growth direction of {110}: the (100) and (111) facets are mostly exposed in our sprayed Ag NWs.\textsuperscript{25,26} Polycrystalline Ag also mainly expose the (100) and (111) facets rather than (110) because of its low surface energy.\textsuperscript{27–29} Because the Ag(100) and Ag(111) facets are known to have similar \( \text{CO}_2 \text{RR} \) properties,\textsuperscript{30} no significant \( \text{CO}_2 \text{RR} \) property difference between our Ag NWs and an Ag foil was observed from the \( \text{CO}_2 \text{RR} \) performance of the Ag NWs sprayed onto the Ag foil.

To briefly look into the electrode characteristics, linear sweep voltammetry (LSV) was conducted in a \( \text{CO}_2 \)-saturated 0.2 M KHCO\textsubscript{3} aqueous solution (Figure 3). As clearly shown in Figure 3, bare Ag foil and bare carbon sheet show a similar voltage onset of about −0.79 V, although the bare carbon sheet has a higher current density than that of the bare Ag. Interestingly, Ag NWs/carbon sheet composites also have a similar voltage onset of about −0.79 V but exhibit different current densities depending on the Ag NW loadings. Because of the higher exposed surface area of the carbon sheet, for example, the 1.4 \( \Omega/\Box \) Ag NWs/carbon sheet composite has a more carbon sheet like \( j-V \) behavior than that of the 0.5 or 0.2 \( \Omega/\Box \) Ag NWs/carbon sheet composite shown in Figure 3. Note that the LSV curve of the Ag foil shows a similar behavior as that in previously reported results.\textsuperscript{10}

Gas chromatography (GC) showed a dramatic difference in the \( j_{\text{H}_2} \) and \( j_{\text{CO}} \) compositions depending on the applied potentials. Figure 4a–e shows the partial current densities for HER and \( \text{CO}_2 \text{RR} \) of the five electrodes extracted from the chronoamperometry. All data points were converted from the current density–time curves in Figure S6, and 0.1–0.5 C charge was passed through the electrode surfaces. The total Faraday efficiencies of all electrodes are shown in Figure S7. As seen in Figure 4a, the Ag foil has a typical potential-dependent \( \text{CO}_2 \text{RR} \) activity, as reported elsewhere. For instance, the \( j_{\text{CO}} \) of the Ag foil starts to increase at about −0.79 V and becomes saturated at −10 mA/cm\textsuperscript{2} when the applied potential is more negative than −1.39 V. The \( j_{\text{H}_2} \) of the Ag foil is suppressed up to −1.39 V and then rapidly increases. Therefore, the \( \text{H}_2/\text{CO} \) production ratio is highly dependent on the applied potentials. In contrast, a carbon sheet produces mostly \( j_{\text{H}_2} \) with a potential
onset of about \(-0.79\) V. Note that the bare Ag foil and carbon sheet show a similar onset potential of about \(-0.79\) V for CO\(_2\)RR and HER, respectively. When the Ag NWs are deposited onto a carbon sheet, the \(j_{\text{CO}}\) starts to increase, which is affected by the loading amount of Ag NWs. For instance, the \(j_{\text{CO}}\) of the Ag NWs/carbon sheet composites at \(-1.79\) V increases to \(\sim 6\) from \(\sim 2\) mA/cm\(^2\) with increasing Ag NW loading, as shown in Figure 4c–e. Note that the \(j_{\text{H}_2}\) of the Ag NWs/carbon sheet composites originates mostly from the carbon sheets underneath the sprayed Ag NWs when the applied potential is more positive than \(-1.39\) V. Therefore, \(j_{\text{H}_2}\) of the Ag NWs/carbon sheet composites decreases with increasing amount of sprayed Ag NWs as the exposed carbon sheet surfaces, that is, the sites for HER, are blocked by the sprayed Ag NWs. Hence, in contrast to that of the Ag foil, the partial current density difference between \(j_{\text{CO}}\) and \(j_{\text{H}_2}\) of the Ag NWs/carbon sheet composites is dramatically decreased with the 0.2 \(\Omega/\square\) Ag NWs around \(-1.2\) V. Moreover, the partial current density difference can be adjusted in accordance with the amount of Ag NWs: the 1.4 \(\Omega/\square\) Ag NWs/carbon sheet composite has small changes in the partial current density gap compared to those in the 0.2 \(\Omega/\square\) Ag NWs/carbon sheet composite (Figure 4c,e). This leads to a tunable H\(_2\)/CO ratio as a function of the Ag NW loading for a large range of applied potentials.

Figure 5 shows the electrochemically generated H\(_2\)/CO syngas ratios of the Ag NWs/carbon sheet composites with various applied potentials. The yellow box indicates the optimum syngas ratio (1.7–2.15) for transforming syngas to hydrocarbons by the F–T process. As clearly seen in Figure 5, the H\(_2\)/CO ratio is controlled by the amount of Ag NW loading for all potentials: at \(-1.2\) V, the H\(_2\)/CO ratio is tuned depending on the quantity of loaded Ag NWs. More importantly, the Ag NWs/carbon sheet composite can generate syngas at the optimum H\(_2\)/CO ratio for the F–T process with a higher current density and under larger potential ranges than those of the Ag foil. For instance, the 0.5 \(\Omega/\square\) Ag NWs/carbon sheet composite has a 300 mV potential window for the optimal syngas ratio range, whereas the Ag foil has only a 30 mV potential window. Moreover, the 0.5 \(\Omega/\square\) Ag NWs/carbon sheet composite generates syngas at a ratio of 2.15 with a higher production rate of about 19 times compared to that of the Ag foil: the total current densities to produce H\(_2\)/CO at a ratio of 2.15 from the 0.5 \(\Omega/\square\) Ag NWs/carbon sheet composite and the Ag foil are \(\sim 8.72\) and \(\sim 0.45\) mA/cm\(^2\), respectively. In Table S1, we summarize the electrocatalytic syngas production performances of Ag-based composite materials reported in the literature. As clearly seen in Table S1, our Ag NWs/carbon sheet composite is one of the best syngas-producing composite catalysts with the highest syngas-producing current density with wide potential ranges.
Our study shows a new composite catalyst structure for generating syngas with tunable H2/CO ratios by independently providing reaction sites for HER and CO2RR during electrochemical CO2RR in an aqueous solution. Ag NWs/macro-porous carbon composites were selected by considering each electrochemical performance of the carbon and Ag for HER and CO2RR and prepared by spraying the Ag NWs onto a carbon sheet. In our composite, the H2/CO ratio is controlled simply by changing the Ag NW loading on the carbon sheet. Our Ag NWs/carbon sheet composite has potential ranges that are 10 times larger for the generation of syngas with the optimum ratio for the F-T process (from 1.7 to 2.15) and a syngas production rate that is about 19 times higher than that of Ag foil. Finally, we believe that, by identifying composite materials with low overpotentials for HER and CO2RR as well as further engineering of electrolytes for enhanced CO2 solubility, our composite electrocatalyst design could be used to produce syngas with a tunable H2/CO ratio by electrochemical CO2RR using renewable energy resources in large-scale applications.

3. CONCLUSIONS

We present a strategy to develop an electrocatalyst to produce syngas with controllable H2/CO ratios by independently providing reaction sites for HER and CO2RR during electrochemical CO2RR in an aqueous solution. Ag NWs/macro-porous carbon composites were selected by considering each electrochemical performance of the carbon and Ag for HER and CO2RR and prepared by spraying the Ag NWs onto a carbon sheet. In our composite, the H2/CO ratio is controlled simply by changing the Ag NW loading on the carbon sheet. Our Ag NWs/carbon sheet composite has potential ranges that are 10 times larger for the generation of syngas with the optimum ratio for the F-T process (from 1.7 to 2.15) and a syngas production rate that is about 19 times higher than that of Ag foil. Finally, we believe that, by identifying composite materials with low overpotentials for HER and CO2RR as well as further engineering of electrolytes for enhanced CO2 solubility, our composite electrocatalyst design could be used to produce syngas with a tunable H2/CO ratio by electrochemical CO2RR using renewable energy resources in large-scale applications.

4. EXPERIMENTAL SECTION

4.1. Electrode Preparation. Ag NWs were synthesized by the modified polyol process described previously. The solution of synthesized Ag NWs was sprayed onto the carbon sheet (TGP-H; Toray Industries, Inc.) with a spray system to fabricate a Ag NW network structure. The amount of Ag NWs on the carbon sheet was monitored by measuring the sheet resistance of the Ag NWs on a glass substrate, which was fabricated by varying the spraying time of the Ag NW solution. The Ag foil (99.998%; Alfa Aesar) was mechanically polished with sandpaper (CC-400Cw; Daesung) and dipped into a 0.1 M H2SO4 aqueous solution overnight to remove any organic impurities on the metal surface before the CO2RR. All prepared electrodes with an attached copper wire on the back side were sealed by industrial epoxy (Loctite 9460) to confine the reactive area. The geometric surface area of the exposed electrode was then determined by an image processing program (ImageJ) with scanned images (300 dpi resolution).

4.2. Electrochemical Experiments and Product Analysis. All electrochemical experiments were performed with a gas-tight single-compartment electrolysis cell. The total volume of the single-compartment cell was 60 mL with 20 mL of 0.2 M KHCO3 (99.95%; Sigma-Aldrich) and a 40 mL head space. A Ag/AgCl (3 M NaCl) electrode and a graphite rod were used as a reference electrode and a counter electrode, respectively. The reference electrode potentials were converted to RHE with equation E as follows: (RHE) = E (Ag/AgCl) + 0.209 V + 0.0591 V × pH. Prior to the CO2RR electrochemical experiment, a 100 mL/min stream of CO2 gas (99.999%) was purged for at least 30 min to saturate the electrolyte with CO2 and the pH of the solution was 6.8. The electrolyte solution was stirred by a magnetic bar during the experiments. The electrochemical properties of the electrodes were measured with a potentiostat (SP-150; Bio-Logic Science Instruments). LSV curves for each electrode were scanned from −0.3 to −1.8 V with a scan rate of 50 mV/s. The quantification of the gas product was analyzed by GC (micro GC 3000; INFICON) equipped with a thermal conductor detector. Argon (99.9999%) and helium (99.9999%) were used as carrier gases for a PLOT Q and molecular sieve column, respectively. All gas products were generated by constant potential electrolysis at seven different potentials. The gas-phase products were directly injected from the single-compartment cell into the GC column to minimize the contamination of the collected gas product.

4.3. Microscopy Measurement. The surface morphologies of the Ag NWs/carbon sheet composite and carbon sheet were observed by a SEM (JEOL-7600F) operated at 5 kV. The electrochemical properties of the electrodes were measured with a potentiostat (SP-150; Bio-Logic Science Instruments). LSV curves for each electrode were scanned from −0.3 to −1.8 V with a scan rate of 50 mV/s. The quantification of the gas product was analyzed by GC (micro GC 3000; INFICON) equipped with a thermal conductor detector. Argon (99.9999%) and helium (99.9999%) were used as carrier gases for a PLOT Q and molecular sieve column, respectively. All gas products were generated by constant potential electrolysis at seven different potentials. The gas-phase products were directly injected from the single-compartment cell into the GC column to minimize the contamination of the collected gas product.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00846. XPS; gas product analysis results; partial current density; chronoamperometry data information (PDF)

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Notes

The authors declare no competing financial interest.

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