

Carbon microfiber layer as noble metal-catalyst support for selective CO₂ photoconversion in phosphate solution: Toward artificial photosynthesis in a single-compartment reactor



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ABSTRACT

Metal catalysts are known to exhibit high selectivity for electrochemical CO₂ reduction reactions only in a bicarbonate solution. Here, high selectivity was realized even in a phosphate solution using a carbon microfiber support for Au and Ag catalysts, and accordingly high selectivity in CO₂ photoconversion was demonstrated in a single-compartment reactor filled with a phosphate solution.

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1. Introduction

Efficient photocatalytic systems for solar-driven CO₂ reduction to produce organic chemicals using H₂O as an electron donor are required in order to reduce overall CO₂ emissions into the atmosphere and to prepare for future fossil fuel shortages. Metal catalysts for electrochemical CO₂ reduction to organic chemicals such as CO, HCOOH, CH₄, and C₂H₄ have been studied extensively. For instance, Ag and Au are known to produce CO from CO₂, while In, Sn, Cd, Hg, Pb produce formate in bicarbonate solutions at high externally applied potentials, both potentiostatically [1] and galvanostatically [2]. CO, one of the gaseous species that can be produced from CO₂, is useful as a syngas to produce methanol from a mixture containing hydrogen. As an example, Au was used for the electrochemical reduction of CO₂ to CO with high selectivity by Hori et al. [3], and the high selectivity for CO formation was recently applied at the nanoscale using Au nanowires [4]. However, metal catalysts such as Au require very high potentials, such as −2.0 V (vs. SCE), such that H₂ is preferentially produced at lower bias potentials even in the presence of CO₂. A very low potential for producing CO over oxide-derived Au nanoparticles in a bicarbonate solution has recently been reported [5]. This mechanism involves reversible electron transfer to CO₂ to form adsorbed CO₂[−] anion

radicals followed by a rate-determining H⁺ transfer with HCO₃[−] as the H⁺ donor, determined by the electronic and chemical state of the Au catalyst, which is dependent on the synthesis method. A typical detrimental feature in the cases reported to date is that the metal catalysts for electrochemical CO₂ reduction systems exhibit high selectivity for CO₂ only in a bicarbonate solution [6]. This is presumably due to the reaction mechanism for these metallic catalysts, in which carbonate or bicarbonate ions react at the surface of the catalysts. In contrast, a phosphate buffer solution is more beneficial due to the higher current density for gold electrodes. For example, the cathodic current observed in a phosphate buffer solution was about 2–3 times higher than that in a bicarbonate solution, as shown in Fig. 1.

However, a technical issue with a phosphate buffer solution is its low selectivity for CO₂ compared with a bicarbonate solution. Thus, many researchers prefer using a bicarbonate solution for electrochemical CO₂ reduction by metal catalysts. If a phosphate buffer solution becomes available for metal catalysts, it would be highly beneficial for establishing more efficient electrochemical and photochemical systems for CO₂ reduction. Furthermore, a phosphate buffer is advantageous because the CO₂ reduction reaction must be coupled with the water oxidation reaction. For example, cobalt-based catalysts that possess the so-called self-healing property have recently been developed, and they can operate in a phosphate buffer at almost neutral pH and yield a high reaction rate [7]. In the present paper, enhanced selectivity for electro- or photoelectro-chemical CO₂ reduction to produce CO in a

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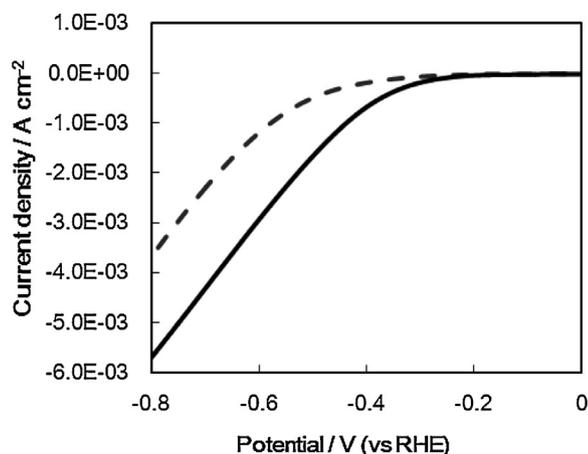


Fig. 1. Current-potential characteristics of Au catalyst (200nm) in a NaHCO_3 solution (dash line) and in a phosphate buffer solution (solid line) under CO_2 atmosphere.

phosphate buffer solution is demonstrated. Porous carbon is the key to the system, which plays an important role in improving the CO_2 selectivity of the metal catalysts in competition with hydrogen generation in the phosphate solution. A monolithic photo-device that produces CO from CO_2 using water as an electron donor is demonstrated by coupling the Au catalyst, porous carbon composed of microfibers for improving CO_2 selectivity in the phosphate buffer, Si-Ge as a light absorber, and IrOx as a water oxidation catalyst. This monolithic tablet-shaped device stoichiometrically produced CO together with H_2 using H_2O as an electron source with a solar-to-chemical conversion efficiency of 0.71% for CO in the phosphate solution at an almost neutral pH of 6.9.

2. Material and methods

2.1. Material

Dipotassium hydrogen phosphate (Wako Pure Chemical Industries, Ltd.), potassium dihydrogen phosphate (Kanto Chemical Co., Inc.), sodium hydrogen carbonate (Kanto Chemical Co., Inc.), carbon dioxide gas (Taiyo Nippon Sanso), formic acid (88%, Kanto), Au, Ag and Pt metal plates (99.9%, Kojundo Chemical Laboratory Co., Ltd.), and SUS304 foil ($0.06 \times 100 \times 300$ mm, Nilako Co., Inc.) were purchased from the indicated supplier and used as received. Pure water ($>18 \text{ M}\Omega \text{ cm}$ resistivity) was provided by Direct-Q (EMD Millipore). Triple-junction amorphous silicon (SiGe-jn) on a stainless steel substrate and carbon cloth (CC: EC-CC1-060, Toyo Corp.) were obtained from Xunlight Corp. and Toyo Corp., respectively.

CC/metal catalysts were prepared by the sputtering method. Au, Ag and Pt (nominally 10 nm thick) were sputter-deposited on a carbon microfiber cloth. A CC/metal cathode such as SUS/CC/metal was connected to the stainless steel using silver paste (Fig. S1).

2.2. Methods

Electrochemical measurements were performed using an electrochemical analyzer (CHI-620, ALS Co., Ltd.). A CC/metal cathode, silver-silver chloride electrode (Ag/AgCl) and platinum wire were used as working, reference and counter electrodes, respectively. A Pyrex glass cell was used as a reactor, and electrolyte aqueous solutions such as 0.1 M of sodium hydrogen carbonate (NaHCO_3) and potassium phosphate buffer (dipotassium hydrogen phosphate + potassium dihydrogen phosphate) were used as the reaction solutions. 65 mL of electrolyte solution was introduced into the reactor and bubbled with Ar gas for 20 min to remove dissolved air, and then the solution was bubbled with CO_2 gas for 20 min before the experiment. Gaseous reaction products such as CO and H_2 were analyzed using a GC-TCD instrument (Shimadzu GC-14A) with an active carbon column, and the products in the solution were analyzed using an IC instrument (Dionex ICS-2100) with IonPacAS15 and IonPacAG15 columns. The column temperature was maintained at 308 K. A solution of 10 mM KOH was used as the first eluent up to 10 min, and then the eluent was changed gradually to 60 mM KOH over 10 min, followed by a change to 10 mM KOH solution over 3 min. All of the analyses were conducted with possible experimental errors of about $\pm 10\%$.

Photochemical measurements were performed using a flow reactor combined with a gas chromatograph (Shimadzu GC-14A). A quartz cell was used as the reactor and 0.1 M potassium phosphate buffer solution was used as an electrolyte. The tablet-shaped IrOx/SiGe-jn/CC/Au or IrOx/SiGe-jn/Au/CC device was immersed in the solution and CO_2 gas was bubbled into the reactor for 20 min before measurement and allowed to flow at 20 mL min^{-1} during the measurement. A solar simulator (HAL-320, Asahi Spectra Co., Ltd.) was used as the light source for irradiation from the IrOx side. The intensity was adjusted to 1.5 SUN (AM 1.5) on the surface of the device using a light intensity checker (CS-20, Asahi Spectra Co., Ltd.).

3. Results and discussion

Carbon materials are known to exhibit an excellent ability for CO_2 capture in the gas phase due to their lack of polarity [8,9]. Although capturing CO_2 with the aid of triethanolamine and porous coordination polymer-based catalysts is one of the hot topics in photochemical or electrochemical CO_2 reduction, these studies have only been conducted in organic solvents [10,11]. Cathodes for electrochemical CO_2 reduction in an aqueous solution were fabricated using carbon and metal catalysts (Fig. S1).

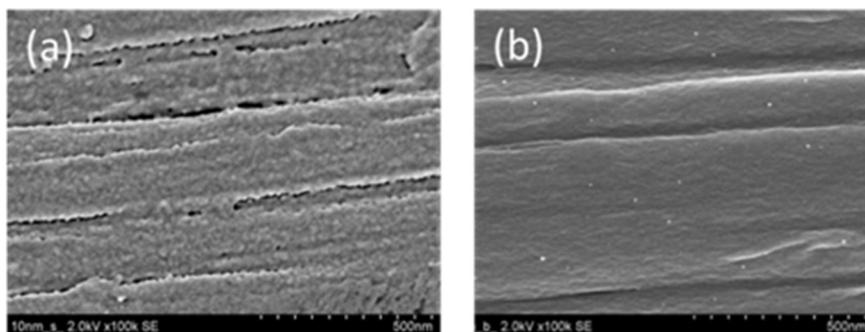


Fig. 2. SEM images of carbon cloth (CC) deposited with Au. (a) Au-deposited side (denoted as CC/Au in the present paper) and (b) back side (Au/CC).

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