



Stable surface oxygen on nanostructured silver for efficient CO₂ electroreduction



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ABSTRACT

We investigated properties involved in the enhancement in electrocatalytic carbon dioxide (CO₂) reduction to carbon monoxide (CO) in electrochemically treated Ag surfaces with surface sensitive analysis methods such as Auger spectroscopy, atomic force microscopy (AFM) coupled with Kelvin probe force microscopy (KPFM) techniques, and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The absence of Ag M_{4,5}VV Auger signals for the electrochemically treated Ag indicate the presence of localized surface oxygen (O) which survives on the best performing Ag electrocatalysts even in the reductive environment of the CO₂ reduction reaction. Higher work functions were located at the nanostructure boundaries observed by KPFM/AFM implying the higher surface O concentrations in these regions. Furthermore, NEXAFS measured the selective prominence of π* states over σ* in the active Ag surfaces which suggests stronger interaction with intermediates of CO₂ reduction while minimizing the –OH interaction contributing to increase CO₂ reduction activity and selectivity. These results provide direction in engineering surfaces for efficient electrochemical CO₂ conversion.

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1. Introduction

The modern energy production infrastructure from fossil fuels accumulates carbon dioxide (CO₂, a major greenhouse gas) in the atmosphere, the increasing concentration of which concerns many scholars of climate change [1,2]. Electrochemical CO₂ reduction, when integrated with rapidly developing renewable energy sources (e.g., photovoltaics and wind), is an attractive process that can reconvert the atmospheric CO₂ into useful chemicals to balance the anthropogenic carbon cycle [2–4].

However, electrochemical CO₂ reduction reaction (CO₂RR) is thermodynamically uphill reaction requiring high overpotential, and only a few metals are capable of facilitating selective electrochemical CO₂ conversion in aqueous media. Furthermore, promising metals such as Ag and Au in their bulk state can pro-

duce carbon monoxide (CO), but the selective CO production dramatically varies and rather produces hydrogen as major product depending on applied potentials [5,6]. In addition, due to fast deactivation, the competitive hydrogen evolution reaction (HER) increase after sustaining CO₂RR, resulting in low conversion efficiency and product selectivity. To overcome these limitations, nanostructures are engineered to take advantage of their unique properties to facilitate the interaction with intermediate species of CO₂RR and thus enhance the catalytic activities.

Oxide-derived nanocrystals are a particular class of active CO₂RR electrocatalysts prepared by oxidation of metals such as Au, Cu, and Pb and subsequent reduction for enhanced CO₂RR activity under low overpotentials [7–9]. An electrochemical mechanism study proposed effective stabilization of the COOH intermediate on oxide-derived Au surface is an important contributor to enhance CO₂RR due to the acceleration of the first electron transfer step [5]. Recent developments on oxide-derived Au identified the grain boundaries are the active sites [10] while another study revealed that the nanostructuring shortens the Au–Au bond length to effectively lower the activation energy and prevents the absorption of species that cause deactivation of the electrocatalyst [11–13]. These

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studies suggest that morphology changes are important for nanostructured Au to enhance the electrocatalytic activity of CO₂RR. Besides the properties metal itself, a report on oxide-derived Pb hypothesizes a surface layer oxygen (O) suppresses H⁺ reduction and achieves selective CO₂ reduction [9]. Therefore, more surface studies are required to understand the contributors to enhancement of CO₂RR activity depending on the metal type because the O binding properties are different on each metal.

Our previous study showed that electrochemically nanostructured Ag surface, also prepared by oxidation and subsequent reduction, enhanced CO₂RR by lowering the onset potential of CO partial current and increasing CO Faradaic efficiency. Unlike other nanostructured Ag electrocatalysts [14–16], nanostructuring alone was not able enough to explain the enhancement of CO₂ reduction activity, and high-resolution X-ray photoelectron spectroscopy (XPS) showed the presence of stable surface O species on the active Ag electrocatalyst [17]. In this study, we prepare Ag electrocatalysts by various electrochemical treatment conditions and investigate an in-depth surface analysis of nanostructured Ag electrocatalysts with Auger spectroscopy, atomic force microscopy (AFM) coupled with Kelvin probe force microscopy (KPFM), and near edge X-ray absorption fine structure (NEXAFS) measurements to find the correlation between the CO₂ reduction electrocatalytic activity and the state of O on Ag surface.

2. Experimental

2.1. Preparation of electrochemically treated Ag

Before electrochemical treatment, Ag foil (99.99%, Dasom RMS) was mechanically polished with 1.0 μm and 0.05 μm alumina polishing slurries (Mirapolish[®], Buhler), sonicated, and washed with deionized (DI) water. The Ag foil was then electrochemically treated via either cyclic voltammetry (CV) or pulsed voltammetry. For the CV method, potential scan was applied between –0.9 and 1.0 V vs. Ag/AgCl in aqueous 0.1 M NaOH (98%, Sigma-Aldrich) for five cycles at a scan rate of 50 or 5 mV/s, where the resulting sample is henceforth denoted CVAg-50 or CVAg-5, respectively. The CV shows three distinct oxidation peaks associated with the formation of Ag oxides (i.e. Ag₂O, AgO, and Ag₂O₃) and their respective reduction peaks as expected from the Pourbaix diagram [18]. As for the pulsed voltammetry method, potential between 1.0 and 0.0 V vs. Ag/AgCl was applied at 100 Hz for 30 min in aqueous 0.1 M NaOH and the resulting oxide layer was reduced by applying –2.3 V vs. Ag/AgCl in CO₂-saturated 0.5 M KHCO₃ (≥99.99%, Sigma-Aldrich) solution. The surface was then generously rinsed in DI water. In all electrochemical processes including the following CO₂RR experiment, Pt and Ag/AgCl were used as the counter and reference electrodes, respectively.

2.2. CO₂ reduction reaction experiment

Electrochemical CO₂RR experiments were conducted in a two-compartment cell made of polyether ether ketone (PEEK) separated by a proton exchange membrane (Nafion[®] 117). Each compartment contains 0.5 M KHCO₃ solution purged in 20 sccm CO₂ (99.999%) continuously for saturation. Constant potential was applied using a potentiostat (CHI Instruments) and gaseous products were analyzed by gas chromatography (GC, Younglin 6500) equipped with a capillary column (Restek, RT[®]-Msieve 5A) and pulsed discharge ionization detector (PDD) using ultra high purity (UHP, 99.9999%) He as the carrier gas. The Faradaic efficiency (F.E.) of i_j ($j = \text{H}_2$ or CO) was calculated according the following equations

$$i_j = y_j \times Q \times \frac{2FP}{RT}$$

$$\text{F.E.}_j(\%) = \frac{i_j}{i} \times 100$$

where i_j is the partial current density of j , y_j is the volume concentration of j measured by GC, Q is the flow rate measured by a universal flow meter (ADM 2000, Agilent Technologies) at the exit of the electrochemical cell, i is the total current density, F is the Faradaic constant, P is the pressure, T is the temperature, and R is the ideal gas constant.

2.3. Characterization

The surface images were obtained by field emission gun scanning electron microscopy (FEG-SEM, Inspect F, FEI). The crystal structure was characterized by using a X-ray diffractometer (XRD-6000, Shimadzu) equipped with Cu K α radiation ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, Ulvac-PHI) with monochromated aluminum Al K α (1486.6 eV) anode (24.5 W, 15 kV) radiation was conducted to analyze surface element's electronic state. Binding energies were calibrated based on the C 1s peak at 284.5 eV as a reference. NEXAFS measurements were taken with a 10D XAS KIST beamline in Pohang Light Source (PLS) with X-ray incidence angle of 90° and were used to obtain the Ag M_{4,5}VV Auger signal from Ag M-edge and the O K-edge was normalized using Athena software. For comparison, samples before and after CO₂RR were measured, where the post-CO₂RR samples were each prepared by applying constant potentials in consecutive 0.1 V steps between –1.0 to –2.3 V vs. Ag/AgCl with each step lasting 10 min.

The surface work function was measured by Kelvin probe force microscopy (KPFM) coupled with an atomic force microscopy system (AFM, XE-100, Park Systems Co.). The topographic mapping was acquired by AC mode with a drive frequency of ~160 kHz and work function mapping was simultaneously obtained by applying an AC modulation voltage of amplitude (V_{ac}) of 2 V and a frequency (ω) of 17 kHz to the tip with a scan speed of 500 nm/s. A capacitive and Coulomb forces contribute to the electrostatic force between the sample and the tip, F_e . The amplitude of the first harmonic component of F_e , F_1 , is expressed as

$$F_{1\omega} = \left[\frac{\partial C}{\partial z} (V_{dc} - V_{CPD}) \right] V_{ac} \sin \omega t$$

where V_{dc} is the DC bias voltage applied to the tip, V_{CPD} is the contact potential difference between the work functions and the tip ($[W_{tip} - W_{sample}]/e$), z is the tip-surface distance, and C is the tip-surface capacitance. The minimum corresponds to the local V_{CPD} and the surface work function can be estimated from the equation since the work function value of the tip is known. An important characteristic of the equation is that the work function is independent of the geometric positioning and the AC modulation voltage of the tip. Conductive Cr-Au coated Si cantilevers (NSC14/Cr-Au, resonance frequency: ~160 kHz, Mikromash) were used to scan the sample surface. All KPFM/AFM measurements were conducted in darkness to eliminate any effect light may cause.

3. Results and discussion

Scanning electron microscopy (SEM) images (Fig. 1a–d) shows the surface morphologies of the bare Ag foil, CV-treated Ag foil at 50 mV/s (CVAg-50), CV-treated Ag foil at 5 mV/s (CVAg-5), and pulsed voltammetrically-treated Ag foil (pulsedAg). As reported in the previous study, Ag foil surface is rather flat, and the electrochemically treated Ag has rough surfaces of agglomerated particles ranging from 30 to 200 nm. X-ray diffraction (XRD) patterns of all samples (Fig. S1a) only contain 2θ peaks that correspond to the face-

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