



Highly-active copper oxide/copper electrocatalysts induced from hierarchical copper oxide nanospheres for carbon dioxide reduction reaction



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ABSTRACT

Novel hierarchical copper oxide (Cu_xO) nanosphere particles are synthesized, and then coated onto gas diffusion layer (carbon) to form a working electrode for catalyzing CO_2 electroreduction. When applying a negative voltage to the working electrode, the metal Cu nanoparticles which are induced by the Cu_xO nanospheres appear. Cu_xO and metal Cu together form the $\text{Cu}_x\text{O}/\text{Cu}$ nanocatalysts which show high catalytic activity for CO_2 electroreduction. The morphology, composition, crystal structure and surface area of the $\text{Cu}_x\text{O}/\text{Cu}$ electrocatalysts are characterized using scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The $\text{Cu}_x\text{O}/\text{Cu}$ nanoparticles are tested as the catalysts for CO_2 electroreduction using cyclic voltammetry and linear sweep voltammetry in CO_2 -saturated 0.5 M KHCO_3 aqueous electrolyte. It is found that the CO_2 electroreduction activity is highly improved using this $\text{Cu}_x\text{O}/\text{Cu}$ nanocatalyst, which remains stable during 20 h of electrolysis, along with the high selectivity with a ~62% of Faradaic efficiency for formate production. Detailed kinetic information relevant to the catalysis is also discussed.

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1. Introduction

Carbon dioxide (CO_2) produced by extensive fossil fuel consumption and excess industrial processes could make carbon imbalance in the world, creating negative impact on environment through greenhouse effect. One of the feasible ways to reduce CO_2 emission is to convert it to useful fuels by using clean and sustainable energy from solar, wind, hydropower, etc. [1–3]. Among different conversion technologies, electrochemical reduction of CO_2 to produce low-carbon fuels, such as CO and HCOOH or HCOO^- , has been demonstrated to be feasible and efficient. However, the CO_2 electroreduction kinetics is extremely sluggish.

Even if some electrocatalysts are employed, the reduction rate seems to be still not fast enough. To speed up the reduction rate, a large negative potential has to be applied onto the electrode, causing low energy efficiency. Furthermore, the electrocatalysts' stability and selectivity are also not sufficient for a practical application [4,5]. In order to improve the energy efficiency of CO_2 electroreduction, exploring highly active, stable and selective electrocatalysts is no doubt the urgent issue.

Recently, low-cost and abundant polycrystalline Cu electrodes have been explored as the working electrodes for CO_2 electroreduction by many researchers [6,7]. However, the smooth polycrystalline and single-crystal Cu electrode surfaces have low catalytic activity. The current efficiency of Cu is limited by the large overpotential (almost 1 V) [5–8] which is still not suitable for the practical usage. In the effort to improve the electrochemical performance of catalyst materials, two significant aspects have to be considered: the composite materials and the nanostructure materials. On the one hand, their unique properties such as high

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specific surface area can provide easy diffusion path lengths for substrates to access, leading to faster kinetics [5], on the other hand, the nanostructures can provide the different surface morphology, thus providing more active sites for CO₂ electro-reduction and in controlling the product selectivity [9]. In view of these facts, in our most recent work, Cu nanostructured electrode surface created using a method containing high-temperature annealing and electroreduction steps has been proven to be dramatically effective in generating highly active Cu catalysts for CO₂ vs H₂O reduction at low overpotential and high resistance to deactivation relative to polycrystalline Cu electrodes [10–12]. The work described below is one of our ongoing activities aimed at synthesizing more active catalysts for CO₂ electroreduction. In this work, a simple hydro-thermal method was used to synthesize novel hierarchically structured Cu_xO nanosphere particles for CO₂ electrocatalysis, and during the electrolysis, these Cu_xO nanosphere particles induce the appearance of metal Cu, which could highly improve the selectivity of produced formate. Such novel Cu_xO/Cu catalysts induced by Cu_xO nanosphere particles with special morphology have never been reported yet. The Cu_xO nanosphere particles were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to obtain their morphologies, structures and compositions. The electrochemical redox reactions of Cu_xO/Cu catalysts at different conditions were characterized using cyclic voltammetry (CV), and their electrocatalytic activity toward CO₂ reduction was studied using both cyclic voltammetry and linear sweep voltammetry in CO₂-saturated 0.5 M KHCO₃ aqueous solution, along with the catalytic durability and the Faradaic efficiency of formate production. For all electrochemical measurements, the Cu_xO nanosphere particles were coated on the gas diffusion carbon paper to form target electrodes.

2. Experimental

2.1. Catalysts and electrodes preparation

In the synthesis of Cu_xO nanosphere particles, Copper(II) acetate monohydrate (Cu(Ac)₂) from Sinopharm Chemical Reagent Co. (SCR) with 99% purity was used as metal precursor [12], and 2,5-dimethoxyaniline purchased from Ourchem Information Consulting Co. with 99% purity was used as the reducing agent in dilute aqueous solution under hydro-thermal condition. For a typical synthesis, 40 mL 0.04 M Cu(Ac)₂ solution was mixed with 10 mL 0.02 M 2,5-dimethoxyaniline solution under stirring till the mixture becoming dark green. Then such a mixture was transferred to 100 mL of Teflon-lined stainless steel autoclaves, and heated at 180 °C for 2 hours. The resulting product was washed by ethanol and then dried overnight. In this way, the Cu_xO nanosphere particles with special 3-dimension (3D) hierarchical structure were synthesized, as shown in Fig. 1. For the electrochemical reduction of CO₂, the Cu_xO nanosphere particles were coated onto a gas diffusion carbon paper to form the electrode which was used as the working electrode and, put into a three-electrode electrochemical cell for measurements. The detailed measurement conditions will be given in the following section. To elucidate the morphology effect, the electrode using Cu_xO nanoparticles (by hydro-thermal method at 180 °C for 15 hours) without any 3D-hierarchical structure was also prepared as the reference and tested under the same measuring conditions.

2.2. Electrochemical measurements

For catalyst ink preparation, Cu_xO powder (15 mg) was suspended in 400 μL isopropyl alcohol (Sinopharm Chemical Reagent Co.) and then dropped in 100 mg Nafion[®] solution (5 wt%)

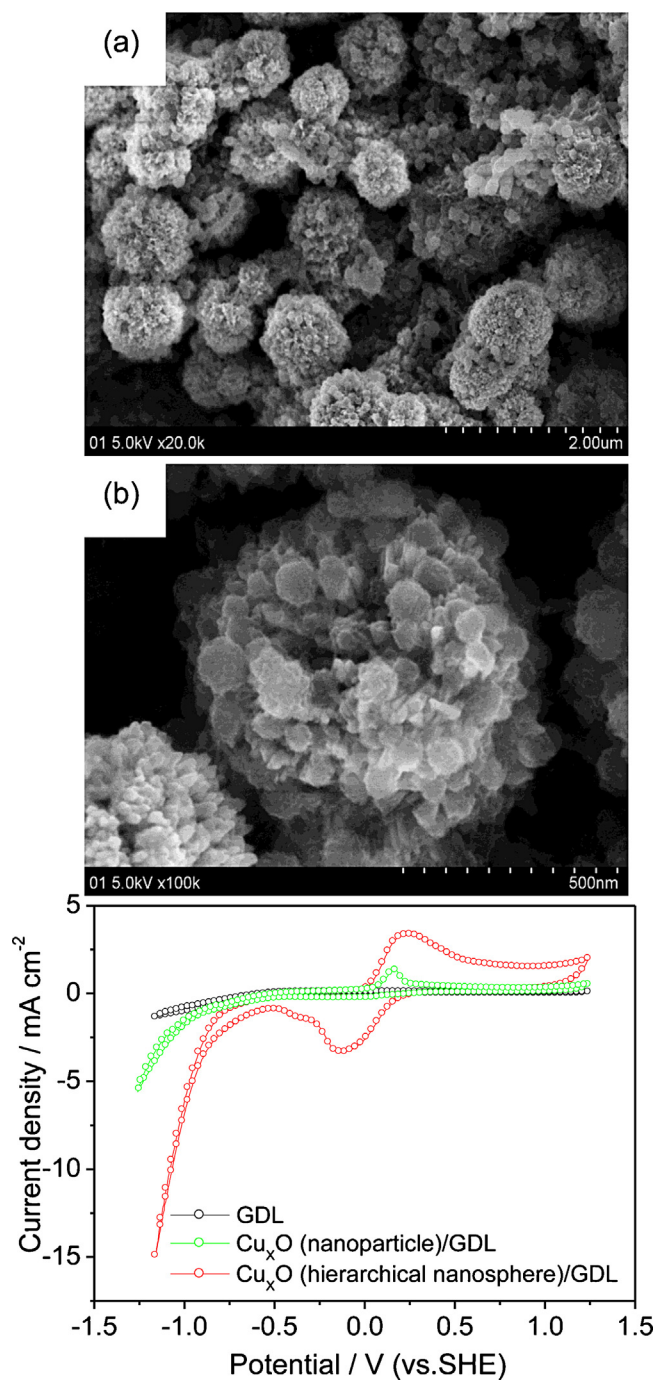


Fig. 1. (a, b) SEM images and (c) XRD pattern of the hierarchical Cu_xO nanospheres synthesized using a hydro-thermal method at 180 °C for 2 hours.

to improve adhesion. A gas diffusion layer (GDL, 4 cm² Toray carbon paper, TGP-H-090) coated by the Cu_xO particles was used as the working electrode (about 80% Cu_xO powder was coated on the GDL) and tested in a conventional three-electrode electrochemical H-type cell, in which a piece of Nafion[®] 117 cation-exchange membrane (H⁺ form) was used as a separator, a platinum foil electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. All measured potentials were converted to a standard hydrogen electrode (SHE). A CH Instrument 600E was used for all electrochemical experiments. For pH effect on the Cu_xO/Cu redox

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