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Enhanced CO selectivity and stability for electrocatalytic reduction of CO_2 on electrodeposited nanostructured porous Ag electrode

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ABSTRACT

Nanostructured electrocatalysts for CO_2 reduction have attracted much attention due to their unique properties compared to their bulk counterparts. Here we report the synthesis of porous Ag foams on a polished Ag substrate via electrodeposition using the hydrogen bubble dynamic template. The as-prepared porous Ag foams has an average pore size of 10–25 μm with the porous wall composed of 40–100 nm Ag nanoparticles. CV tests indicate that the competing hydrogen evolution reaction remarkably slow down on porous Ag electrode and the onset potential of CO_2 reduction occurs at 0.15 V less than that on the Ag foil electrode. Moreover, the high current density and CO faradaic efficiency of over 90% were stable over the course of several hours, whereas Ag foil electrode exhibited the drop of CO faradaic efficiency from 74.4% to 58.6% under identical conditions. We found that the enhanced activity and stability are the result of a large electrochemical surface area (approximately 120 times larger) which can provide more active sites. The noteworthy difference between the two electrodes suggests that the nanostructured surface of porous Ag foams is likely to not only favor the formation of $CO_2^{\bullet-}$ intermediate but also suppress the competitive reaction of hydrogen evolution.

1. Introduction

The ever-increasing worldwide consumption of fossil fuels has caused a steady increase of CO_2 levels in atmosphere. Developing strategies for the prevention of further increase of CO_2 and eventually to lower it are undoubtedly important tasks [1]. In the past decades, electrochemical conversion of CO_2 has received much attention and has devoted great many efforts [2–5]. Electrochemical reduction of CO_2 to CO has been regarded both as a promising route to reduce CO_2 emission and as a source of renewable fuels and chemicals [6,7]. However, the practical applications have been hindered due to a relatively low catalytic activity, insufficient selectivity for desired products and the stability of catalysts. Great efforts are still needed to develop the efficient catalysts, which exhibit both high efficiency and high current density [8].

Metallic electrodes have been studied intensively for electrochemical reduction of CO_2. Hori [6] reviewed the relatively early studies on different metals. Recently, nanostructured metallic eletrocatalysts raise a lot of interests due to their unique properties compared to bulk counterparts [9]. The most distinct advantage is the enhanced surface area, which can provide much more surface active sites than bulk materials. In addition, nanostructured electrocatalysts have been shown to improve catalytic stability. Moreover, a large portion of low-coordinated sites on nanostructured surface make the catalytic behavior different from flat surface in corresponding bulk metals [10,11]. The unique properties have shown in oxygen reduction reaction (ORR) [12], hydrogen evolution reaction (HER) [13] and oxygen evolution reaction (OER) [14]. Comparatively, bulk metal electrode was subject to high overpotential requirement, low current density and especially the rapid loss of activity in aqueous solutions. More recently, the progress on nanostructured metallic electrocatalysts for CO_2 reduction was reviewed by Jiao [15]. When regarding to the reduction of CO_2 to CO, the encouraging results should be especially noted. Lu et al. [16] prepared a nanoporous Ag catalyst by a dealloy process, which achieve a high activity of

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approximately 20 mA cm^{-2} with 92% selectivity at a potential of 0.6 V (vs. RHE) in aqueous $KHCO_3$ electrolyte. Polyansky et al. [17] reported a nanocoral Ag catalyst fabricated by an oxidation–reduction method, demonstrated a 32-fold enhancement in surface-area normalized activity at the low potential of 0.37 V, as compared to Ag foil.

Mentioning the synthesis of porous metal, it is worthy to note an eletrodeposition method via hydrogen bubbles as the dynamic template proposed by Shin [18]. The procedure is simple to be performed. According to Shin's method, we synthesized three-dimensional porous Pb on the copper substrates [19,20], which showed improved catalytic performance in CO_2 electroreduction to formic acid compared with the bulk electrode. In addition, porous Cu was also reported for exhibiting superior performance both in distribution of products and faradaic efficiency in eletroreducing CO_2 to hydrocarbons [21]. All these stimulate us to further explore the synthesis of Ag nanofoam and its application in electro-reduction of CO_2.

Herein we prepared a porous Ag nanofoams on a substrate of polished Ag foil via the hydrogen bubble dynamic template, instead of using Pt/Ti/Si as the substrate in Cherevko's studies [22,23], considering the side effects of metal Pt and the conductivity during the electrolysis. The as-prepared porous Ag foam has an average pore size of 10–25 μm with the porous wall composed of 40–100 nm Ag nanoparticles. Electrochemical measurement shows that the porous Ag electrode has a large electrochemical surface area. It demonstrated higher current density and higher current efficiency for CO than that on a planar Ag foil electrode at lower overpotential. Especially it exhibits the excellent stability over long time electrolysis. In addition, the results reveal that the noteworthy enhancement in CO faradaic efficiency comparing with smooth Ag surface results from that the nanostructured surface of porous Ag foams favors the formation of $CO_2^{\bullet-}$ intermediate while suppressing HER.

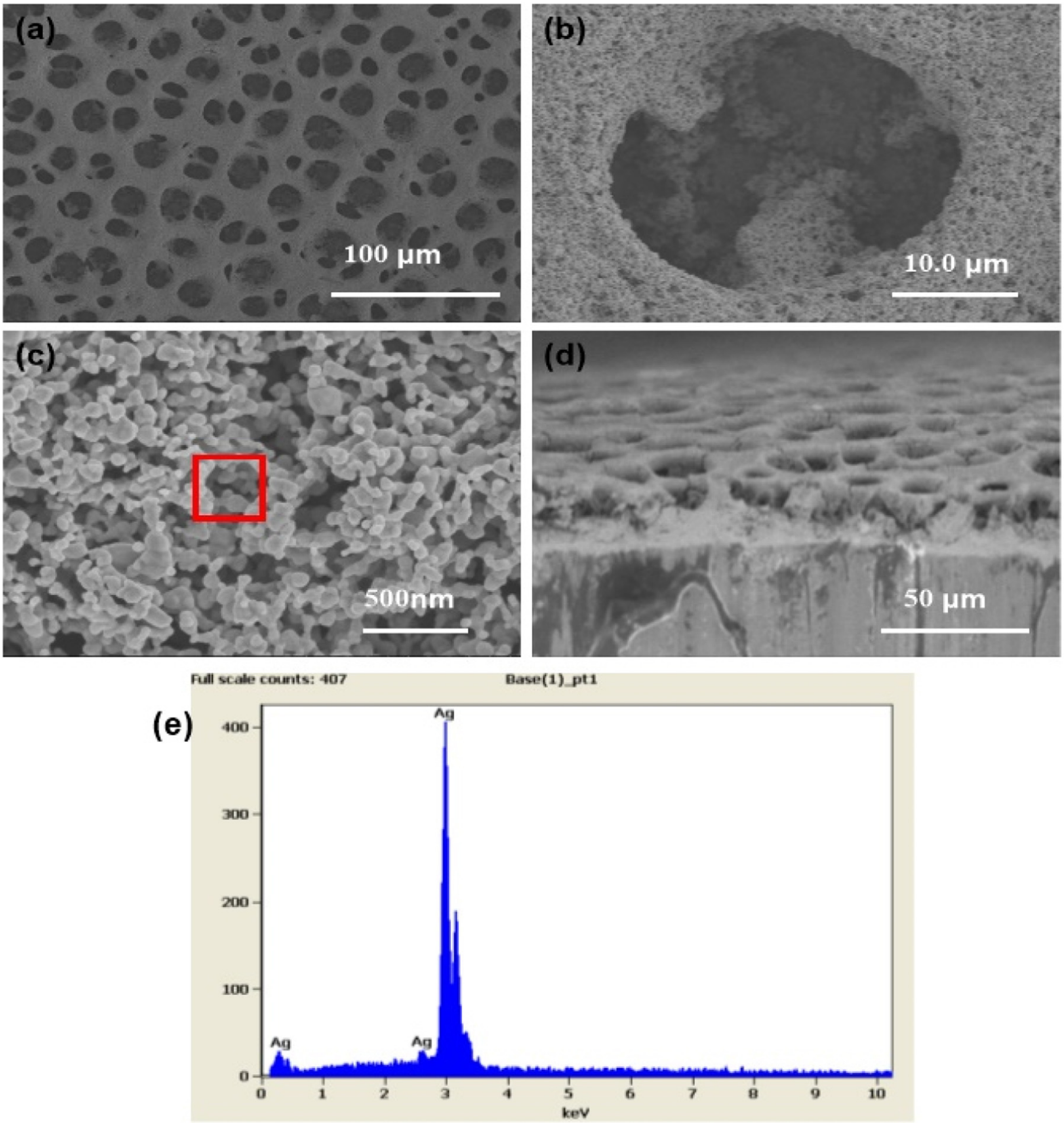

Fig. 1. Structure and morphology of porous Ag foams on Ag substrate (a) Top views; (b,c) magnified views of the porous wall and packed Ag nanoscale grains; (d) cross-sectional views of porous Ag electrode; (e) typical EDS spectra of porous Ag foams.