Catalysis Today 300 (2018) 145–151

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Enhanced photoelectrochemical CO_2-reduction system based on mixed Cu_2O – nonstoichiometric TiO_2 photocathode

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ARTICLE INFO

Keywords:
Mixed-layered copper-titanium oxides
copper(I) oxide
CO_2 reduction
Electrocatalysis
Photoelectrochemistry

ABSTRACT

Photoelectrochemical reduction of CO_2 is explored here with respect to the possible production of simple organic fuels. While the photoelectrochemical system is based on *p*-type Cu_2O semiconductor, special attention has been paid to its stabilization, intentional modification and fabrication, as well as to optimization of experimental conditions permitting control and diversification of the CO_2 reduction products. Utilization of the mixed oxides photoelectrochemical system consisting of the electrodeposited, onto transparent conductive oxide (TCO) coated glass support, Cu_2O catalyst and next coupled to non-stoichiometric TiO_2, acting as a charge transfer enhancing layer. Such a heterojunction allows, from one side, increase density of charge carries in the conduction band of the photocathode and, on the other side, improve conductivity of the whole system. Moreover, the outer-most over-layer of Nafion is expected to facilitate attraction of CO_2 (dissolved in the sodium sulfate electrolyte) at the photoelectrochemically active mixed-metal-oxides interface. Consequently, the overall photoelectrochemical efficiency is improved, and the cathodic photocurrent (related to the CO_2-reduction) of *ca.* 1.2 mA cm − 2 (at 0.1 V *vs.* RHE). The reported hierarchical (layered mixed-oxide) system consisting of copper(I) oxide and titania over-layer (covered with the Nafion outer-most film) exhibits remarkable stability with time.

1. Introduction

Recent approaches to activation of the CO_2 molecule toward its electrocatalytic and photoelectrochemical reduction covers various experimental and theoretical studies aiming at designing specific and possibly selective catalytic and photochemical systems capable of transforming electrical or solar energy into chemical energy thus allowing its storage indirectly in chemical bonds of fuels. Later, energy can be released in a carbon neutral cycle or be reused in any carbon based technology (feedstock) or by inducing chemical reactions to convert pollutants to environmentally friendly compounds (e.g. by electro/photo-catalysis) [1–5]. Utilization of solar energy (coming from the Sun to upper atmosphere of the Earth) is of particular importance because resources of this energy are, in principle, several orders of magnitudes higher than those originating from other sources of renewable energy. This fact is of particular importance when it comes to the reduction of carbon dioxide since the CO_2 molecule is very stable and resistant to direct splitting even at temperatures as high as 2000 °C. Indeed, a highly positive change in Gibbs free energy is required to overcome the uphill reduction of CO_2 to hydrocarbons or other fuels; and this sizeable energy input might be provided by illumination with the incident light. On mechanistic grounds, activation of the CO_2 molecule would initiate multi-step sequential reactions leading to the formation of $CO_2\cdot^-$ radical species by transferring an electron from the excited photocatalyst to the lowest unoccupied molecular orbital (LUMO) of CO_2. But particular reactions (steps) are not well separated by the potential applied, and the appearance of distinct products would require careful choice of a selective catalyst and application of specific reduction conditions. Based on comparison of the CO_2 electroreduction activities at various metallic cathodes, the highest conversion efficiency has been found at "medium hydrogen overvoltage" metals [6–8]. Indeed, the formal electrode potentials (E°) corresponding to the CO_2 reduction into a series of C_1 products in aqueous media ($pH = 0$) are close to the E° of the standard hydrogen electrode [9]. The optimum electrocatalyst requires a compromise between its activity toward hydrogen evolution and its ability to promote reductive adsorption of CO_2 and to generate moderate coverages of H atoms capable of generating stabilizing subsequent reduced intermediates [10]. Such features exist at metallic copper electrode, and it has been shown that, depending on the applied potential, the reduction process could result in formation of

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http://dx.doi.org/10.1016/j.cattod.2017.05.099
Received 9 October 2016; Received in revised form 14 April 2017; Accepted 30 May 2017

hydrocarbons, methane and ethylene [6,11], in addition to simple alcohols or aldehydes. But electrocatalytic reduction of CO_2 at metallic copper under conventional electrochemical conditions still requires large overpotentials and suffers from hydrogen evolution as well as from poisoning of the Cu surface resulting in a partial suppression of the reduction currents [12,13]. Therefore, attention has been paid to photoelectrochemical approaches based on application of the *p*-type semiconductors as the main component of the CO_2-reduction photocathodes. Among important issues is the use of visible (solar) light as the driving force in order to affect the reaction thermodynamics and dynamics and push it at potentials even lower than that the standard one. This well-known concept relies on the fact that, under the bandgap illumination of the *p*-type semiconductor, the photogenerated electrons reach the potentials close to the conduction band edge − substantially more negative than the photocurrent onset potential determined by the edge of the valence band where majority of charge carriers (positive holes) are located [3,14]. However, the intrinsic drawback of *p*-type semiconductor photocathodes lies in low electron density in the conduction band (in comparison to metals) and, as generally observed, the lack of catalytic properties towards CO_2 reduction. To overcome this limitation and thus, to increase the conduction band electron population, we explore in this paper a build-up mixed photoelectrode utilizing the *p*-type − *n*-type semiconductors junction. In such configuration, the energy of the conduction band edge of the chosen *n*-type semiconductor should be lower than that of the *p*-type semiconductor in order to make possible capture of the photogenerated electrons. Furthermore, a position of the band edge of the selected *n*-type semiconductor is affected, and extension of the conduction band to higher energies should allow the negative shift of the quasi Fermi level of the heterojunction towards more negative potentials necessary for the CO_2 reduction. These requirements are fulfilled by several metal oxide *n*-type semiconductors including such as TiO_2 or $SrTiO_3$ or $KTaO_3$ [15–17]. An additional advantage of creating such *p*-type − *n*-type semiconductor heterojunction is a protection of the *p*-type component against photocorrosion induced by largely negative potentials that offers, at the same time, the possibility to enlarge the choice of employed *p*-type semiconductors to relatively unstable ones such as sulfides and selenides.

In the present work, we report on a bifunctional mixed system relying onto *p-n* junction consisting of copper(I) oxide (Cu_2O) and titanium oxide (TiO_{2-x}) capable of driving either electrocatalytic reduction or photoelectrochemical reduction of CO_2 mainly to methanol or formic acid which subsequently may be reused as energy carriers. In recent years, a large interest has been devoted to the copper oxide based materials due to its diversity in applications, including catalysis, gas sensing, superconducting, biosensors or photoelectrochemistry [16,18–21].

Because synthesis of methanol requires six electrons, the efficient conversion of CO_2 toward such a low-mass aliphatic alcohol is challenging. In this respect, important recent reports [22,23] on hybrid structures of the CuO/Cu_2O nanorod arrays (fabricated by thermal oxidation of Cu foil and subsequent electrochemical deposition of the copper(I) oxide) should be mentioned here. An important advantage of that system was related to the formation of two-dimensional structures enabling electrodeposition of the extremely thin Cu_2O deposits on the bottom part of the support, and thus allowing further growth of the copper(II) oxide crystals and formation of porous and hybrid structures. The hybrid system of the CuO/Cu_2O nanorod arrays was capable of pursuing the solar-light-driven conversion of CO_2 to methanol [22,23]. The relatively high efficiency of this hybrid system was attributed to the existence of double pathway for injection of photoelectrons.

Contrary to the above-mentioned hybrid system, the approach presented in this paper, relies on the mixed bi-layered copper(I) oxide − titania system and explored formation the *p-n* heterojunction favoring increase of density of the electron population within the conduction band following deposition of TiO_2 over the electrodeposited large crystals of Cu_2O. Upon illumination (from the copper(I) oxide side), charge transport to the reaction sites should be enhanced and the overall electric conductivity (at the catalytic interface) increases. Having in mind both hydrophilic and hydrophobic properties of Nafion [24], the outer-most ultra-thin film of Nafion, having properties of both robust (protective) layer and wetting (favoring proton mobility) medium, has been applied. Special attention has been paid to synthesis, characterization and optimization of the hybrid photocathode, namely the Nafion-protected mixed-oxides (Cu_2O-TiO_2) system (deposited on fluorine-doped tin oxide covered glass, FTO) toward photoelectrochemical reduction of carbon dioxide.

2. Experimental

2.1. Materials

All chemicals in this study, that were utilized as precursors, solvents and substrates for the photo-electro-catalytic experiments, were used as received, and they were of analytical grade. Copper(II) sulfate pentahydrate ($CuSO_4{*}5H_2O$, 98% Sigma-Aldrich), lactic acid ($CH_3CH(OH)CO_2H$, MW: 90.08 g/mol Sigma-Aldrich), sodium hydroxide (NaOH, 98.8% POCH BASIC), P-25 (TiO_2, Degussa Ag), dimethylformamide (DMF, 99.8% Sigma-Aldrich), Nafion perfluorinated resin solution (5 wt% in mixture of lower aliphatic alcohols and water, contains 15–20% water, Sigma-Aldrich) were used as the precursors for preparation of the mixed working system. Sodium sulfate decahydrate ($Na_2SO_4{*}10H_2O$, ACS reagent 99% from Sigma-Aldrich) saturated either with Argon (Ar, 99.999% Air Products) or carbon dioxide (CO_2, 99.999% Air Products) was used as a supporting electrolyte subjected for the reduction process. Methanol (CH_3OH, 99.8% POCH BASIC) and carbon oxide (CO, 99.999% Air Products) were used as reference molecules for detection of the reduction products by the gas chromatography equipped with the mass spectroscopy detector (GC–MS). The electrolyte solutions were prepared with deionized water of a resistivity of about 18 MΩ cm.

2.2. Synthesis of copper(I) oxide layer

A typical synthetic protocol for electrochemical deposition of the copper(I) oxide, described elsewhere [23,25], involved application of the three-electrode electrochemical cell arrangement with the fluorine-doped tin oxide covered glass (FTO) as the working electrode, a Pt wire as the counter electrode and Mercury Sulfate Electrode (MSE, Hg/Hg_2SO_4) as the reference electrode. A clear solution of a lactate stabilized copper(II) sulfate was prepared following dissolution of 1.92 g of $CuSO_4$ and 6.71 ml of lactic acid in 30 ml of deionized water. The precursor solution was then adjusted to pH 9 by controlled addition of sodium hydroxide crystals. The copper(I) oxide film was electrodeposited onto fluorine-doped tin oxide glass substrate (FTO, resistivity ~ 8 Ω/sq, Sigma-Aldrich) from the precursor solution at −0.64 V *vs.* MSE. The temperature of the reaction bath was kept at 60 °C for 1800s during the whole cathodic electrodeposition run. The CH Instruments 660C electrochemical workstation was used to control, impose and maintain potential during the chronoamperometic Cu_2O-deposition at the conductive support. Thereafter the resulting film of Cu_2O was calcined in air at 150 °C for 30 min.

2.3. Preparation of Cu_2O/non-stoichiometric-TiO_2 photocathode

Once the active layer of Cu_2O was prepared, the thin layer of TiO_2 (P-25) was suspended in 10 ml of DMF and deposited by spray deposition over the electrodeposited Cu_2O. The whole electrode was then left for 30 min at room temperature followed by calcination at 150 °C to allow evacuation of the organic medium. The non-stoichiometry of TiO_2 upper layer was effected by applying very short pulses of 1–2 s of hydrogen flame. Finally, the photoelectrode was coated with the ultrathin film of Nafion polyelectrolyte (by over-coating with 4 μdm^3 Nafion solution, prepared by introducing 5% (mass) commercial Nafion