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Cu^+-incorporated TiO_2 overlayer on Cu_2O nanowire photocathodes for enhanced photoelectrochemical conversion of CO_2 to methanol

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ABSTRACT

In this paper, we report photoelectrochemical (PEC) conversion of carbon dioxide (CO_2) using photocathodes based on Cu_2O nanowires (NWs) overcoated with Cu^+-incorporated crystalline TiO_2 (TiO_2–Cu^+) shell. Cu_2O NW photocathodes show remanent photocurrent of 5.3% after 30 min of PEC reduction of CO_2. After coating Cu_2O with TiO_2–Cu^+ overlayer, the remanent photocurrent is 27.6%, which is an increase by 5.2 fold. The charge transfer resistance of Cu_2O/TiO_2–Cu^+ is 0.423 kΩ/cm^2, whereas Cu_2O photocathode shows resistivity of 0.781 kΩ/cm^2 under irradiation. Mott–Schottky analysis reveals that Cu^+ species embedded in TiO_2 layer is responsible for enhanced adsorption of CO_2 on TiO_2 surface, as evidenced by the decrease of capacitance in the Helmholtz layer. On account of these electrochemical and electronic effects by the Cu^+ species, the Faradaic efficiency (FE) of photocathodes reaches as high as 56.5% when TiO_2–Cu^+ is added to Cu_2O, showing drastic increase from 23.6% by bare Cu_2O photocathodes.

1. Introduction

Growing concern over the ever-increasing level of carbon dioxide (CO_2) in atmosphere has been strong impetus to search for solutions to mitigate the issue [1–3]. An ultimate formula for lowering CO_2 concentration would include conversion of CO_2 into chemicals that can be harnessed in a form of value-added product. For chemical conversion of CO_2, various approaches have been proposed and investigated: heterogeneous catalysis, electrocatalysis, and bio-mitigation using microalgae, to name a few [4–9]. Yet, it requires high external energy (in the range of several tens to hundreds kJ/mol) to convert thermodynamically stable CO_2 (standard heat of formation for CO_2, $\Delta H^\circ_f = -393.51$ kJ/mol) [10,11], demanding high temperature in gas-phase reactions [6–8] or large overpotential in electrochemical reactions [4]. In photocatalytic and photoelectrochemical (PEC) reduction of CO_2 into hydrocarbons (e.g., formic acid, methanol, or methane), sunlight serves as an energy source, hence increasing possibility of completely carbon-neutral energy production. Critical to the efficiency of the photocatalytic and photoelectrochemical conversion of CO_2 is to design structure of photocatalysts or photoelectrodes in such a way that (i) photogenerated charge carriers in semiconductors are effectively utilized in the CO_2 reduction and (ii) catalytic surface lowers the energy of intermediate species as a result of controlled adsorption of CO_2 on the surface [12,13].

PEC reduction of CO_2 is an excellent test bed to quantify these effects; however, the poor stability of photoelectrodes and low Faradaic efficiency (FE) of overall system have posed major challenges.

Among all the semiconductors under investigation for developing efficient PEC CO_2 reduction, cuprous oxide (Cu_2O) has been studied for the use in photocatalysis due to its low toxicity, high abundance and low processing cost compared with other p-type semiconductors [14–17]. In addition, Cu_2O has narrow band gap energy (1.9–2.2 eV) to utilize sunlight and thermodynamically favorable energy band positions with the conduction band lying more negative of the CO_2 reduction potential [18]. Cu_2O shows the theoretical maximum solar-to-fuel conversion efficiency 18% and maximum photocurrent density is calculated to be 14.7 mA/cm^2 [19]. However, photocurrents generated from PEC CO_2 reduction in reported studies have been much lower than the theoretical value, with the photocathodes exhibiting poor stability due to photocorrosion [16,20–22]. Photocorrosion is a common problem for narrow band gap semiconductors (i.e., $E_g < 2$ eV) in an electrolyte solution since their self-reduction/oxidation potential levels lie between the conduction and valence band energy levels of semiconductors. The photocorrosion of semiconductors lowers the overall FE of PEC system since a large portion of the photo-generated charges are lost

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by photocorrosion of Cu_2O and/or by the trapping process at the trap sites induced by photocorrosion [23]. Thus, the design and fabrication with high FE are important.

Several approaches have been reported in the way of increasing FE of photocathodes for CO_2 reduction. Won et al. investigated the FE and selectivity of Cu_2O/CuO photocathodes by introducing various metal co-catalysts for methanol and formic acid production from CO_2 [20]. To produce more valuable hydrocarbons such as methanol with high selectivity, Cu^+ incorporation to TiO_2 has been suggested as well. Liu et al. reported that Cu(I)/TiO_{2-x} provides the active adsorption and reaction site of CO_2 and also can spontaneously dissociate CO_2 by in-situ FTIR analysis [24]. It is suggested that Cu^+ state on TiO_2 surface is the primary active site for photoreduction of CO_2 and selectively produced methanol [25]. Slamet et al. also showed that Cu-doped TiO_2 catalyst selectively produce methanol from CO_2 [26]. In addition to the experimental proof, computational calculation revealed that selective methanol production from CO_2 on Cu(I) oxide nanolayers and clusters is favorable considering the binding and activation energy of intermediate species [10]. However, to the best of our knowledge, Cu^+-incorporated TiO_2 has not been used as a protective overlayer of narrow band gap semiconductor and has not been applied to PEC CO_2 reduction yet.

In this study, we examine Cu_2O nanowire (NW)-based photocathodes for PEC conversion of CO_2. Our primary focus lies on understanding what affects the FE of Cu_2O-based photocathodes during PEC reduction of CO_2. Various electrochemical analyses were performed in order to elucidate the characteristics of photogenerated charge carriers in Cu_2O-based photocathodes.

2. Experimental

2.1. Materials

The following chemicals were purchased from Sigma-Aldrich and used without additional treatment: copper(II) sulfate pentahydrate ($CuSO_4$•$5H_2O$, ≥ 99.99%), copper(II) chloride dihydrate ($CuCl_2$•$2H_2O$, ≥ 99.99%), potassium hydroxide (KOH, ≥ 85%), sodium hydroxide (NaOH, ≥ 97%), titanium butoxide (TOB, 97%), potassium bicarbonate ($KHCO_3$, 99.7%) and ethanol (anhydrous, ≥ 99.5%).

2.2. Fabrication of photocathodes

Cu film was prepared by electrodeposition from saturated copper(II) sulfate pentahydrate ($CuSO_4$•$5H_2O$) aqueous solution at 10 V for 20 s and 5 V for 150 s on fluorine-doped tin oxide (FTO) using a Pt counter electrode. After Cu deposition, the substrate was washed with deionized water (DI-H_2O) and ethanol and then dried under air flow. The $Cu(OH)_2$ nanowires (NWs) were prepared by anodizing Cu coated FTO substrates at constant current density (10 mA/cm^2) at room temperature in 3 M KOH solution for 180 s and then washed with DI-H_2O and ethanol [14]. The $Cu(OH)_2$ NWs were transformed into Cu_2O NWs by thermal annealing at 600 °C in Ar atmosphere for 4 h. The heating rate was 30 °C/min.

Deposition method of amorphous TiO_2 (*a*-TiO_2) was slightly modified from the literature [27]. *a*-TiO_2 was deposited on Cu_2O NWs by dip coating. The precursor solution was 0.5 mL TOB in 20 mL anhydrous ethanol. The Cu_2O NWs were immersed into the solution for 1 min followed by air drying for 1 min. The dipping process was carried out five times. To crystallize *a*-TiO_2, Cu_2O/*a*-TiO_2 electrode was annealed in Ar atmosphere for 5 h at 550 °C.

Cu^+ species was incorporated onto *c*-TiO_2 surface by immersing a Cu_2O/TiO_2 electrode in 3 mM $CuCl_2$ in 0.25 M NaOH/ethanol solution. After 12 h, the electrode was washed with ethanol and annealed in Ar atmosphere for 1 h at 300 °C. Finally, the samples were stored in an Ar-filled glove box.

2.3. Physiochemical characterization

Different types of photocathodes were characterized by field emission scanning electron microscopy (SEM), field emission transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and X-ray diffraction (XRD). SEM measurements were performed with a NOVA230 (FEI). TEM measurements were performed with a Tecnai F20 (FEI) operated at an acceleration voltage of 200 kV. XPS and AES measurements were performed with a Sigma Probe (Thermo VG Scientific). XRD measurements were performed with an Ultima IV (RIGAKU) operated with a CuK_α source ($\lambda = 1.54$ Å). The data was collected with a scan rate of 3°/min ranging from 20° to 80°.

2.4. PEC measurement

We conducted PEC reduction of CO_2 in a three electrode configuration cell using Pt wire with glass tube and membrane as the counter electrode to prevent backward reaction on Pt electrode and Ag/AgCl (3 M NaCl) as the reference electrode. The potential measured using a Ag/AgCl reference electrode has been converted to the reversible hydrogen electrode (RHE) using the following formula:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059\ pH$$

Different photocathodes with an exposed surface area of 0.25 cm^2 were connected to custom-made Teflon reactor. An aqueous solution of CO_2-saturated 0.3 M $KHCO_3$ (pH 6.8) was used as the electrolyte during the measurement. Linear sweep voltammetry (LSV) was carried out using a VERTEX potentiostat (Ivium Technologies) at a scan rate of 50 mV/s under a chopped illumination of 100 mW/cm (using LS 150 with AM1.5 G filter, Abet Technologies). We performed the stability test under chopped illumination with 1 min of time interval at 0.3 V (vs. RHE) for 30 min.

2.5. Impedance measurements

The electrochemical impedance measurements were carried out using the same experimental setup. The Nyquist plots were obtained in the dark and under AM1.5 G illumination at an applied potential of 0.3 V (vs. RHE) within the frequency range of 100 kHz–100 mHz using an amplitude of 10 mV. We also performed the Mott–Schottky experiments with the potential range of 0.3–0.8 V (vs. RHE) using three different frequencies of 15, 25, and 50 Hz.

3. Results and discussion

3.1. Structural characterization of Cu_2O nanowires and TiO_2–Cu^+ overlayer

Fig. 1(a) shows the fabrication process of different photocathodes. First, $Cu(OH)_2$ NWs were transformed into crystalline Cu_2O NWs via thermal annealing at 600 °C (Fig. 1(b)). After dip-coating in TiO_2 precursor solution, thin layer of *a*-TiO_2 was formed on the surface of Cu_2O NWs and TEM images are presented in Fig. S1 (Supplementary materials). *a*-TiO_2 was transformed into crystalline anatase TiO_2 (*c*-TiO_2) by annealing at 550 °C in Ar atmosphere. Crystal structure of TiO_2 was confirmed to be anatase using both XRD and TEM analyses (Fig. 1). Because of the volume shrinkage of the *a*-TiO_2 during crystallization [28], thickness of *c*-TiO_2 shell was not as uniform as that of *a*-TiO_2, but the *c*-TiO_2 shell also appear to coat entire Cu_2O surface (Fig. S1). After incorporation of Cu species, we did not notice change in SEM and TEM analysis, and also could