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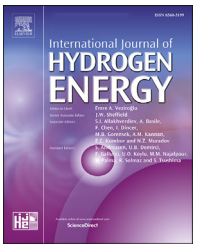

Photoelectrochemical reduction of carbon dioxide to methanol on *p*-type $CuFe_2O_4$ under visible light irradiation

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ABSTRACT

Artificial photosynthesis has the potential to produce solar fuels from CO_2 and H_2O using an efficient photocatalyst. Semiconductor with low band gap and high stability is always the right candidate to be used as photocatalyst. Photocatalytic (PC) reduction of CO_2 suffers from slow reaction kinetics and poor yield of product. Photocatalytic reaction in assistance with judicious bias potential is a solution to increase the catalytic activity and reduce the electron/hole (e^-/h^+) recombination rate. In the present work, a *p*-type $CuFe_2O_4$ was synthesized and used for photoelectrochemical (PEC) CO_2 reduction. The catalyst was characterized by UV-visible spectroscopy (UV-vis), Mott-Schottky (MS), chronoamperometry, X-Ray powder diffraction (XRD), X-Ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Methanol was found as only product in liquid phase produced by photoelectrochemical reduction of CO_2 at a bias potential of −0.5 V (vs NHE) under light irradiation (at 470 nm). The quantum efficiency and incident photon to current efficiency (IPCE) were found as 14.4% and 5.1% respectively revealed that, $CuFe_2O_4$ is a potential photocathode for PEC of CO_2 reduction.

Introduction

Carbon dioxide (CO_2) is a major inevitable gas molecule produced in fossil fuel combustion. Unfortunately, large amounts of CO_2 production lead to the collapse of the natural carbon cycle and accelerate climate change. One way of offsetting the large influx is to convert CO_2 to hydrocarbons or oxy-hydrocarbons under solar irradiation, which is an idea gleaned from how plants combine CO_2 and water to produce

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carbohydrate over chlorophyll (catalyst) through utilizing sunlight as the energy source. The mimic photosynthesis process has gotten a tremendous amount of attention in recent years, sparking hopes of being able to recycle the CO_2 produced from fuel that may have a huge impact in solving the two major issues of our time: climate change and energy shortage [1,2]. Photocatalysis (PC) is a very promising technique for reducing CO_2 into gaseous or liquid fuels such as CO, methane, methanol and formic acid [3–9] at relatively low temperature and atmospheric pressure. The use of photon energy to mimic the photosynthesis process requires photo-responsive materials to interact with light which leads to the generation of high-energy electrons with a high probability of e^-/h^+ recombination leading to very poor quantum efficiency. In PC, the photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time leading to low separation efficiency of photo-generated e^-/h^+ pairs [10]. To produce hydrocarbons or oxygenated hydrocarbons from CO_2 requires proton-coupled multiple-electron path ways which generally experiences slow kinetics and poor product selectivity [11]. Single electron reduction of CO_2 to $^{\bullet}CO_2^-$ is reported to occurs at −1.90 V vs NHE at neutral pH (pH = 7) in aqueous solution at 25 °C under 1 atm pressure [12]. Proton-coupled multiple-electron reaction steps for CO_2 reductions are thermodynamically more favourable than the single electron reductions [13]. The $2e^-$ pathway of CO_2 reduction produces CO (E = −0.53 V vs NHE) and formate (E = −0.61 V vs NHE) while the $6e^-$ pathway leads to the production of methanol (E = −0.38 V vs NHE) [14]. Electrocatalytic reduction of CO_2 has been extensively studied using various metals and metal oxide based electrocatalysts, but it requires large over potentials and suffers from hydrogen evolution [15,16]. In PEC reduction of CO_2, the product distribution depends on the bias potentials [17]. In this regard, to achieve the desired products, PC with judicious bias potentials may be used to prohibit the quick recombination of photogenerated electrons with holes to drive the reactions efficiently. Moreover, the bias potential effectively reduces the e^-/h^+ recombination rate in the photocatalyst leading to higher quantum efficiency [10,18]. Thus, integration of electrocatalysis and photocatalysis generates a unique synergistic photoelectrochemical (PEC) catalysis system [19]. The catalytic activity of a photocatalyst towards CO_2 reduction depends on its band gap and appropriate positioning of the conduction and valence bands [20]. For efficient CO_2 reduction, the conduction band (CB) level of the semiconductor should be more negative than CO_2 redox potential while the valence band (VB) level should be more positive than the water oxidation potential [21]. The *p*-type metal oxides, which act as the photocathodes are essential for PEC reduction of CO_2 which can produce a variety of products such as carbon monoxide, methanol and formate depending on the catalyst, light irradiation and applied bias potential [17,22–26]. Yuan. J. et al. [25] reported the formation of methanol over cuprous oxide foam cathode with a bias potential of −1.27 V vs NHE, whereas CO and hydrogen were found as products by using the RuRe/$CuGaO_2$ photocathode at a bias potential of −0.1 V vs NHE [27]. The mechanism of interaction between catalyst site and CO_2 was found to be crucial to determine the product distribution along with the applied bias potential. $CuFe_2O_4$ is a *p*-type compound [28,29] possessing inverse spinnel structure where electron hoping can be occurred [29]. Moreover, the presence of cation site [30] in the $CuFe_2O_4$ acts as basic side which can chemisorb the CO_2 that makes it attractive to be used as photocathode. However, in our previous study, $CuFe_2O_4$ was used for photocatalytic reduction of CO_2 where it suffered from the high e^-/h^+ recombination rate leading to a very low quantum efficiency for methanol formation [31]. The bias potential may effectively interfere with the e^-/h^+ recombination process and can further enhance the photo current leading to increased PEC reduction of CO_2. To the best of our knowledge, *p*-type $CuFe_2O_4$ has never been investigated as photocathode for PEC reduction of CO_2 in aqueous solution.

In this context, the present study is focused on evaluating the PEC characteristics of $CuFe_2O_4$ for CO_2 reduction. The catalyst was characterized using UV-Vis, XRD, XPS, TEM, and Mott-Schottky and chronoamperometry analysis. The PEC and EC behaviour of the catalyst for CO_2 reduction were evaluated by linear sweep voltammetry (LSV). The products of the PC, EC and PEC of CO_2 reduction were analyzed by using GC-FID.

Methodology

Materials

Iron nitrate ($Fe(NO_3)_3.9H_2O$), copper nitrate ($Cu(NO_3)_2.3H_2O$), hexachloroplatinic acid ($H_2PtCl_6.6H_2O$), sodium bicarbonate ($NaHCO_3$), potassium bicarbonate, ($KHCO_3$), nitric acid (HNO_3, 65%), isopropanol (C_3H_8O, 96%), nafion solution (5 wt%), and agar all were in analytical grade (Sigma-Aldrich, Malaysia) and used without further purification. Toray carbon paper and commercial 10% Pt/C were procured from Kuantan Sunny Scientific Collaboration Sdn. Bhd. Malaysia and Sigma-Aldrich (Saint Louis, MO 63103, USA) respectively.

Catalyst preparation

Nanostructured $CuFe_2O_4$ was prepared by using Sol-gel method as reported in our previous study with slight modifications [28,32]. A required amount of $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ were dissolved in 400 mL of distilled water which contained 40 mL HNO_3 (2M) and 6 g agar, and the solution was stirred for 3 h at room temperature. Thereafter, the mixture was sonicated for ~3 h at 80 °C in ultrasound bath to obtain a green gel. The gel was dried for 24 h at 130 °C in vacuum oven and then ground in a mortar. The powder was calcined at 700 °C with a heating rate of 10 °C/min for 8 h.

Electrode preparation

The electrode was prepared with the method described by Woon et al. [33]. Briefly, the catalyst ink for photocathode was prepared by mixing 22 mg of $CuFe_2O_4$ with 140 μL of 5 wt% Nafion and 280 μL isopropanol (C_3H_8O) followed by ultrasonication for 24 h. The Pt/C ink for anode was also prepared using the same method. Afterwards, the inks were evenly brushed on the toray carbon paper with an area of 1 cm^2. The electrodes were dried in a vacuum oven at 60 °C for 6 h.

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