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A Microfluidic Reactor for Solar Fuel Production from Photocatalytic CO_2 Reduction

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Abstract

Photocatalytic CO_2 conversion into usable chemical fuels is considered as an ideal way to tackle problems such as energy shortage and global warming simultaneously. In this “kill two birds with one stone” approach, CO_2 is used as feedstock and abundant solar light as energy source. For this purpose, a photocatalytic micro-reactor was designed in order to overcome problems of conventional photo-reactors including low surface-area-to-volume ratio, poor mass and photon transfer. Common materials such as Fluorine-doped Tin oxide (FTO) glass, Polymethyl methacrylate (PMMA) and surlyn that widely used in photoelectrochemical and solar cells were employed for the fabrication of the reactor. The feasibility and performance of the proposed reactor was tested in the challenging case of photocatalytic CO_2 reduction on TiO_2 thin film. The experimental results confirmed that one of the main products of CO_2 reduction was methanol. Maximum methanol concentration reached 162 μM at a flow rate of 120 μL/min.

Keywords: CO_2 conversion; microfluidic; solar fuels; energy storage;

1. Introduction

Nowadays, global energy consumption is dominated by fossil fuels such as crude oil, natural gas and coal. However, fossil fuels are non-renewable which means that they are being depleted rapidly. Furthermore, combustion of conventional fuels is one of the most important factors of several environmental issues including global warming and greenhouse effect [1]. Therefore, there is an urgent need to use a renewable and environmentally friendly energy source to meet the energy demand of modern world. Among all clean energy sources, solar energy seems more

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attractive because it can cope with the current and the future energy needs [2]. Specifically, solar energy conversion into chemicals have been extensively investigated the last decades but there is a lot of room for improvements in to order to achieve high efficiencies that will enable the commercialization of this technology.

Photocatalytic CO_2 reduction, which allows the direct conversion of CO_2 into chemicals, seems an ideal approach because it can address both environmental pollution and energy shortage at the same time. In this approach, CO_2 can be used as a raw material for the production of chemicals or usable fuels. Additionally, the produced fuels of this process can be transported and stored in the existing infrastructure systems. Photocatalytic CO_2 reduction process is also known as artificial photosynthesis because it mimics the natural process of plants that convert the atmospheric CO_2 into chemical products. A large variety of semiconductor-based photocatalysts has been studied for this modest goal since Inoue et al. in 1979 reported for the first time photoreduction of CO_2 into methanol, formaldehyde, formic acid and traces of methane using several photocatalysts including TiO_2, CdS, WO_3, ZnO, GaP and SiC [3].

Briefly, heterogeneous phototocatalytic CO_2 reduction can be summarized into the following steps:

- adsorption of CO_2 molecules on the surface of the photocatalyst,
- generation of electron-hole pairs through absorption of photons with energy equal to or higher than the band gap of the photocatalyst
- electron-hole separation and transportation
- reduction and oxidation reactions between the adsorbed species and the charge carriers on the surface.

Although many efforts have been done for the development of highly active semiconductor-based photocatalysts, CO_2 photo-conversion rates are still very poor. Apart from the performance of the photocatalyst, another important factor that plays a significant role in the efficiency of a photocatalytic CO_2 conversion system is the development of an effective photo-reactor. Specifically, mass transfer of CO_2, light distribution and specific surface area of photocatalyst to volume ratio highly depend on the photo-reactor design. Recently, new type of reactors have been introduced in photocatalytic applications known as optofluidic micro-reactors [4-7]. These reactors combine the advantages of microfluidics and optics providing fine flow control, high specific surface area to volume ratio, high light distribution and better light penetration compared to conventional photo-reactors.

In this study, the main objective was the design and fabrication of an optofluidic reactor that can be used not only for photocatalytic but also for photoelectrochemical CO_2 reduction. In photocatalytic CO_2 reduction experiments performed with this micro-reactor several products were obtained. However, only methanol was used to evaluate the photocatalytic performance of the reactor because it was one of the main products. Additionally, the effect of liquid flow rate on CO_2 conversion into methanol was investigated.

2. Experimental

2.1. Design and fabrication of microfluidic photo-reactor

A sandwich-type microfluidic photo-reactor was designed, as shown in fig. 1. FTO glasses were used as bottom and top layer. This type of glass was used not only for its transparency but also for its conductivity (Resistance 10 Ω/square) that will offer the possibility to use the same reactor for photoelectrochemical applications in the future. A PMMA layer (100 μm) was cut by Trotec Speedy 300 laser engraver/cutter. This PMMA layer was made in order to create a reaction chamber between the two FTO glasses. Finally, two gaskets of a thermoplastic film (Surlyn 30μm, Dyesol) were cut in laser cutter and placed between the PMMA layer and the FTO glasses sealing the reactor. Thus, the total volume of the micro-chamber was 32 μL (20 mm x 10 mm x 0.16 mm).