CO_2 photoreduction using $NiO/InTaO_4$ in optical-fiber reactor for renewable energy

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Abstract

The photocatalytic reduction of CO_2 into fuels provides a direct route to produce renewable energy from sunlight. NiO loaded $InTaO_4$ photocatalyst was prepared by a sol-gel method. A uniform $NiO/InTaO_4$ layer of 0.14μm in thickness was observed on the optical fiber. An optical−fiber photoreactor, comprised of ~216 $NiO/InTaO_4$−coated fibers, was designed to transmit and spread light uniformly inside the reactor. Vapor-phase CO_2 was photocatalytically reduced to methanol using the optical−fiber reactor under real sunlight irradiation in a steady-state flow system. The rate of methanol production was 11.1 μmol/g-h with light intensity of 327mW/cm^2 at 25°C. Methanol production rate was 11.30 μmol/g-h by utilizing concentrated sunlight. Increasing the reaction temperature to 75°C increased the production rate to 21.0 μmol/g-h. The quantum efficiencies were estimated to 0.063% in the optical−fiber reactor, per gram $NiO/InTaO_4$ photocatalyst. The quantum efficiency increased due to the superior light-energy utilization of $NiO/InTaO_4$ thin film in the optical−fiber reactor.

Introduction

The production of greenhouse gas, carbon dioxide(CO_2), is one of the primary causes of global warming. One of the promising solutions to both problems is that photosynthesis may be implemented via the photoreduction of CO_2 to produce fuel. Eq.1 shows the overall conversion of CO_2 to methanol via photoreduction. The Gibbs free energy (△G) of Eq.1 is 698.7kJ at 298K indicating that the equilibrium is highly unfavorable to the product, methanol and oxygen. A bundle of optical fibers can provide a very high exposure surface in a photoreactor[1, 2]. Our motivation is to seek photo−driven chemical reactions using solar energy directly. The idea is to use highly intensive sunlight to accelerate a photoreaction, so that mass production of fuel is viable.

$$CO_2 + 2H_2O \xrightarrow{h\nu} CH_3OH + \tfrac{3}{2}O_2$$

[1]

Experimental

Photocatalysts were prepared by aqueous sol−gel method. $InTaO_4$ was prepared by mixing equimolar amounts of $In(NO_3)_3$ H_2O and $Ta(OC_4H_9)_5$. Calculated amount of $Ni(NO_3)_2 \bullet 6H_2O$ was added for 1 wt% Ni loading and PEG(polyethylene glycol) solution(0.5ml) was added into the above $InTaO_4$ sol to increase viscosity and to prevent cracking during drying. The powder form was obtained by calcined at 1100°C for 12 hrs after drying sol at 80°C. The other part of sol was used for optical−fiber coating. Optical fibers were obtained from the E−Tone Technology Company of Taiwan. It is a commercial communication fiber of OD 250μm. The bare fiber was immersed vertically into the above $NiO/InTaO_4$, dried at 80°C then heated to 1100°C. Vapor-phase photocatalytic reaction was carried out in a continuous circular Pyrex glass reactor(216cm^3) with a quartz window for conduction of light irradiation as shown in Fig.1. The partial pressure of CO_2 was near 101kPa.

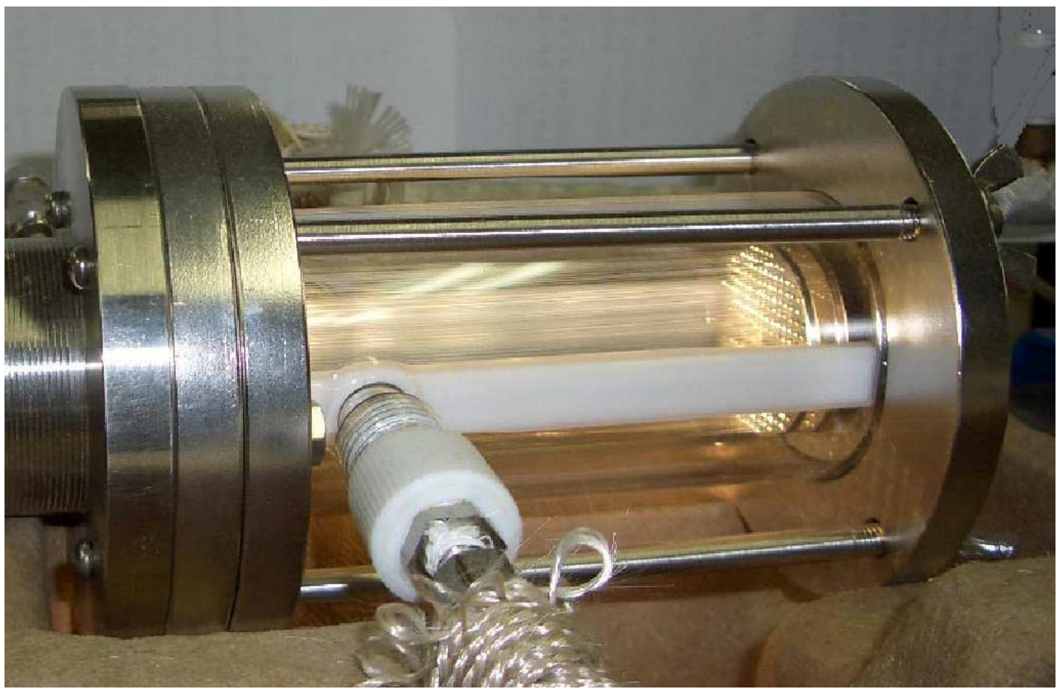

Fig1: optical-fiber reactor with light irradiation

Results and Discussion

Figure2 shows SEM photos of NiO/$InTaO_4$ layer on optical fiber. From the top view in Fig.2(a), the NiO/$InTaO_4$ exhibits the size of particles ranged from 0.1 to 0.3μm. The layer thickness was approximately 0.14μm as shown the cross section in Fig.2(b). The layer was uniformly coated on the surface of optical fiber.

Fig2(a):SEM top view of NiO/$InTaO_4$ layer

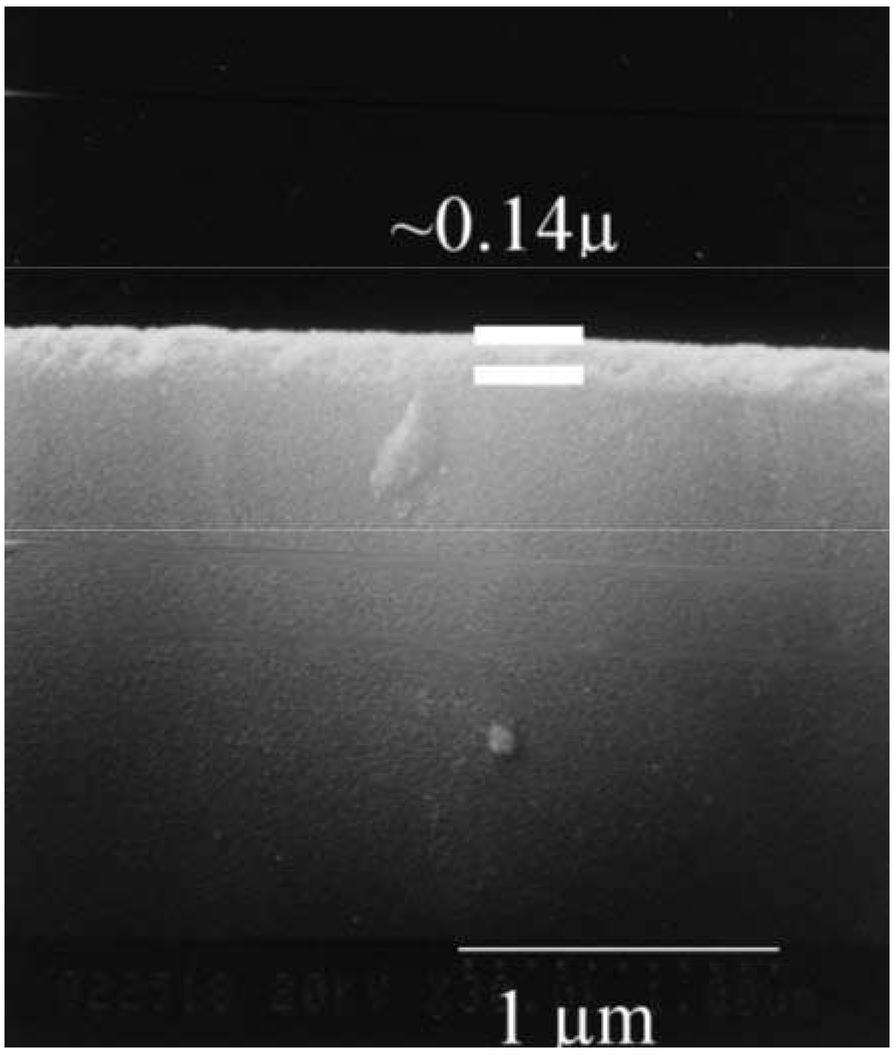

Fig2(b): SEMcross section of NiO/$InTaO_4$ layer

The performance of photocatalytic CO_2 reduction in the optical-fiber reactor under real sunlight is shown in Fig.3. The experiment started at 11 am till 5 pm on 22 June 2008 at Taipei, Taiwan, and the actual time is labeled in the x-axis of Fig.3. The uniform distribution of sunlight by optical fibers provides an efficient utilization of solar energy inside the reactor. As shown in Fig.3, the rate of methanol production increased with the intensity of sunlight in the morning, and reached a maximum rate of 11.3 μmol/g-h at 3 pm. The production rate quickly decreased due to the sunset in the afternoon. In addition, the reaction temperature was also an important factor. The higher the temperature, the higher the rate of methanol production was. The reactor did not require additional heating source. The IR portion of sunlight would raise the reactor temperature.

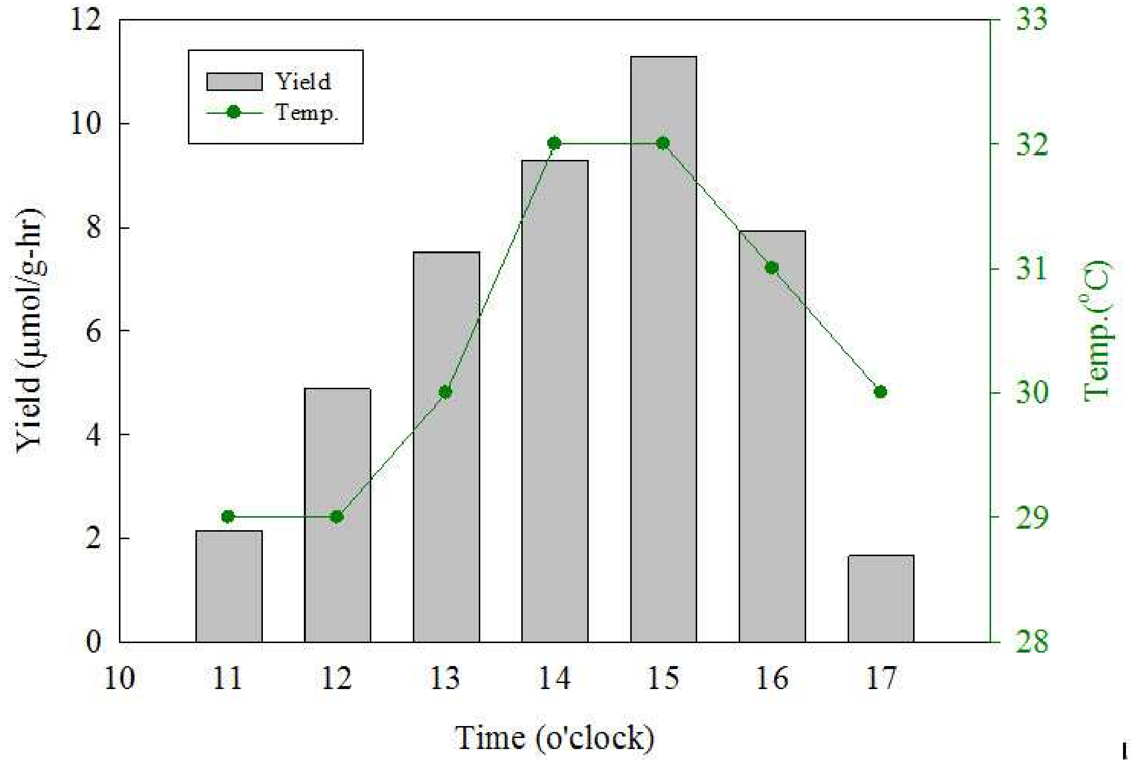

Fig3: Rate of methanol production under real sunlight on 22 June 2008 at Taipei, Taiwan

Summary

[1] The-Vinh Nguyen, Jeffrey C. S. Wu. Applied Catalysis A: General, 335, 112-120 (2008)

[2] Zhen-Yi Wang, Hung-Chi Chou, Jeffrey C. S. Wu, Din Ping Tsai, Guido Mul, Applied Catalysis A: General (2010) DOI: 10.1016/j.apcata.2010.03.059