

Photoelectrochemical conversion of methane to ethane and hydrogen under blue light irradiation

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Abstract: Activation of methane at room temperature is challenging topic in chemistry in the absence of the use of deep ultraviolet light. We show that a photoelectrochemical cell composed of a membrane electrode assembly (MEA) with WO₃-based photoelectrode, proton-conductive polymer membrane, and Pt/Carbon catalyst induces direct conversion of methane to ethane and hydrogen under visible light irradiation at room temperature. The incident photon-to-current conversion efficiency (IPCE) was 11% at applied voltage of 1.2 V under 453-nm blue light irradiation, and the selectivity toward C₂H₆ production was 56% on carbon basis under CH₄ stream with water vapor.

Keywords: Methane conversion, Membrane reactor, Tungsten oxide.

1. Introduction

A process of direct conversion of CH₄, which is abundant natural resources, into chemical products such as higher hydrocarbons is desired because of environmental and potentially financial incentives. However, there are no available commercial process for direct conversion owing to the difficulty for activation of C-H bond of methane with a large dissociation energy (438 kJ/mol). High temperature conditions required for catalytic oxidative coupling of methane (OCM) resulted in the limited C₂ yields due to the formation of thermodynamically favorable byproducts such as CO₂. Therefore, it is desired to develop a new catalytic process for activation of CH₄ at low temperature. There are reports on using UV irradiation and wide-bandgap photocatalysts for CH₄ conversion to C₂H₆, H₂, and CO₂. However, UV irradiation ($\lambda < 400$ nm) is necessary and the quantum efficiencies are still low.^{1, 2} In this study, we aimed to develop a photoelectrochemical reaction system in which C₂H₆ is produced over semiconductor electrode under visible light irradiation.

2. Experimental

Unlike the conventional "liquid-solid" photoelectrochemistry, we developed a "gas-solid" photoelectrochemical system. Figure 1 shows SEM images of WO₃ electrode deposited on porous Ti microfibers as a three dimensional conductive substrate for the gas-phase reaction.³ Figure 2 shows the designed photoelectrochemical cell and a schematic illustration of a MEA composed of a proton-conductive polymer membrane (DuPont, N117) sandwiched between the WO₃ electrode as a photoanode and a Pt/carbon catalyst electrode as a cathode. It is expected to induce oxidation of CH₄ into C₂H₆ by positive hole over the photoexcited WO₃ electrode, and H₂ production over Pt/C counter electrode with the photoexcited electrons via an external circuit and protons passed through the Nafion membrane.

3. Results and discussion

The IPCE was evaluated to be 11% at bias voltage of 1.2 V under 453-nm blue light irradiation. Gas chromatograph measurement revealed the production of O₂, CO₂, and C₂H₆ in the anode compartment, and the production of H₂ in the cathode compartment. It was found that the product distribution in anode compartment significantly depends on the CH₄ concentration in feed. Increase in the CH₄ concentration decreased O₂ production rate and increased C₂H₆ production rate, suggesting the competitive reaction of CH₄ and water vapor. Under 100% CH₄ flow, Faraday efficiency of O₂, CO₂, and C₂H₆ was estimated to be

0.7%, 72.8%, and 11.6%, respectively. The selectivity toward C_2H_6 and CO_2 was 56% and 44% on carbon basis, respectively.

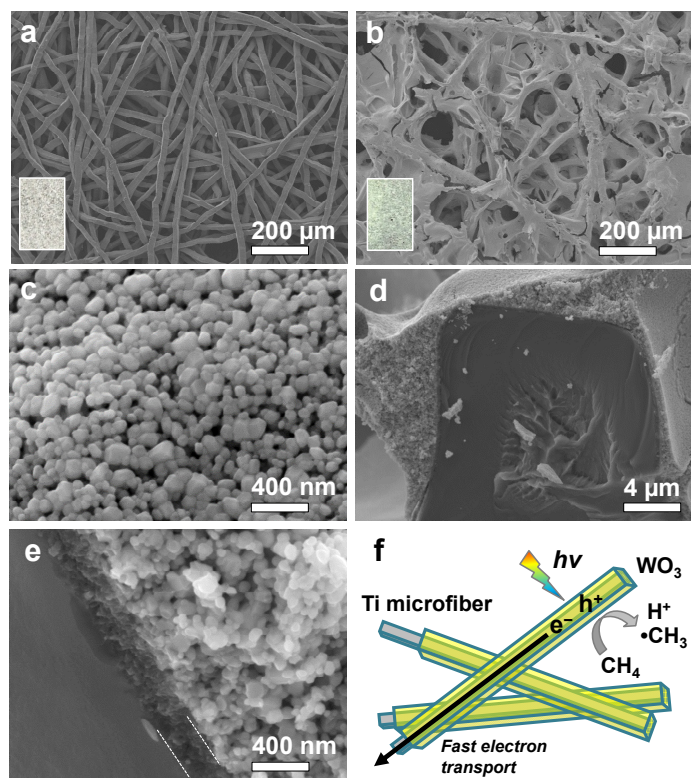


Figure 1. FE-SEM images of (a) Ti microfibers, (b–e) WO_3 particles coated on Ti microfibers, and (f) schematic illustration of photoelectrochemical oxidation of CH_4 over WO_3 /Ti-microfibers electrode under visible light.

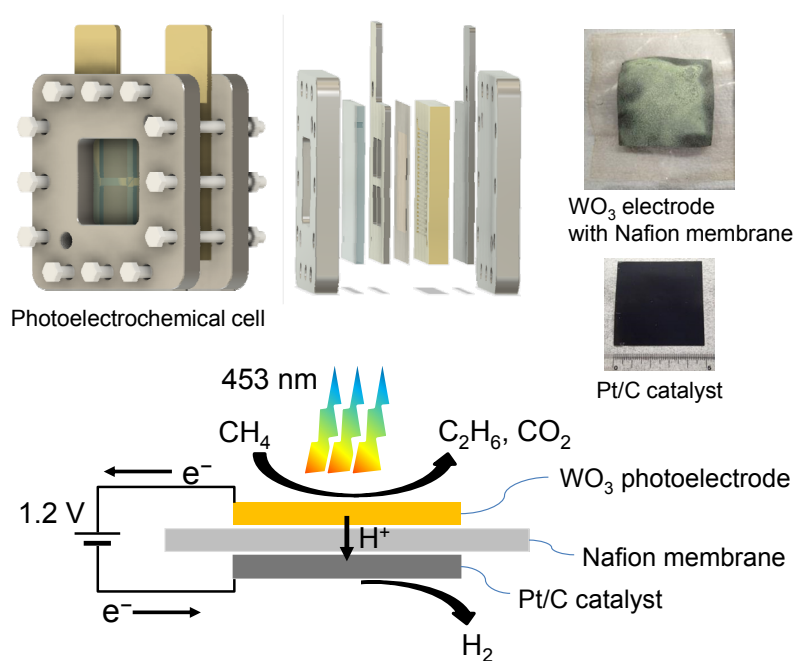


Figure 2. Schematic illustrations of photoelectrochemical cell for conversion of gas-phase CH_4 .

References

1. L. Li, G.-D. Li, C. Yan, X.-Y. Mu, X.-L. Pan, X.-X. Zou, K.-X. Wang, J.-S. Chen, *Angew. Chem. Int. Ed.*, 50 (2011) 8299-8303.
2. L. Yu, Y. Shao, D. Li, *Appl. Catal. B*, 204 (2017) 216-223.
3. F. Amano, A. Shintani, K. Tsurui, Y.-M. Hwang, *Mater. Lett.*, 199 (2017) 68-71.