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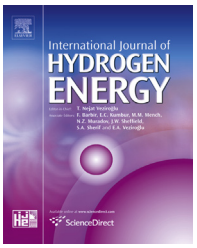

Short Communication

Hydrogen production with CuO/ZnO nanowire catalyst for a nanocatalytic solar thermal steam-methanol reformer

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ABSTRACT

We have fabricated CuO/ZnO nanowire (NW) catalyst for hydrogen production by solar thermal steam-methanol reforming (SMR). Such NW catalyst is expected to be more durable than the conventional nanoparticle catalysts by avoiding agglomeration. ZnO NWs are synthesized by hydrothermal growth on quartz and glass substrates. The ZnO NWs are then coated with CuO by thermal decomposition of copper nitrate using UV pulsed laser as a heat source for prototyping. A solar simulator is used as a heat source for the demonstration of the SMR in water/methanol mixture solution. Gas chromatograph (GC) exhibits increasing mole fraction of produced hydrogen with irradiated time. We then fabricate the catalyst on a large area glass plate substrate by the CuO deposition using an electric heater to confirm the SMR and demonstrate scaling-up. The SMR is briefly demonstrated by feeding water vapor/methanol mixture gas to the catalyst heated by an electric heater, giving thermally produced hydrogen ($CO/H_2 = 0.019$) in the product gas detected by GC.

Introduction

Fuel cells are promising as high efficiency power sources with low environmental load. Methanol has attracted considerable attention as liquid fuel producing hydrogen for the fuel cells [1–4]. Methanol is suitable for the steam reforming owing to its relatively high theoretical conversion efficiency, low conversion temperature, and less byproduct production such as

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carbon monoxide, compared to the other hydrocarbon fuels including ethanol, methane and gasoline.

Since hydrogen is produced by the endothermic steam-methanol reforming (SMR, $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$), a heat source is necessary. One of the advantages of SMR is that it proceeds at relatively low temperatures (200–300 °C).

The heat source for the endothermic reforming reactions in a reformer has been often provided by an electrical heater or a fuel combustor. Researchers focus on the solar thermal energy as the heat source to increase the overall fuel to electricity efficiency and reduce the CO_2 emission [5–10]. To increase the hydrogen production and the reformer efficiency, we have fabricated nanocatalytic particles from commercially available Al_2O_3/CuO/ZnO catalyst by pulsed laser ablation (PLA) technology for nano-structured catalytic reformers in the previous works [7,11].

In the present study, we focus on nanowire (NW) catalyst deposited on a substrate to improve durability by avoiding agglomeration of the conventional nanoparticle catalysts. We deposit CuO layer on ZnO NW backbones synthesized by hydrothermal growth. Depending on the growth conditions, two types of growth modes of ZnO NWs were reported: lengthwise growth (LG) and branched growth (BG) [12]. LG can yield ZnO NWs of increased length by extending the growth at the tip of the backbone ZnO NW. On the other hand, BG produces highly-branched ZnO NWs by multiple generation hierarchical growth. First generation ZnO NWs are grown from ZnO nanoparticle seeds deposited on a substrate immersed in an aqueous precursor solution. Seed nanoparticles added with subsequently applying hydrothermal growth lead to BG. In this paper, however, we employ LG mode as a starting point.

We demonstrate the thermal hydrogen production by the endothermic SMR using a prototype small area catalyst irradiated by focused light of a solar simulator and expand it with large area catalyst heated by an electric hot plate to confirm the feasibility of the scaling-up of the concept.

Experimental

Fabrication of ZnO nanowires

ZnO NWs were grown by the hydrothermal growth approach from the ZnO nanoparticle seeds (ca. 50 nm diameter, Aldrich) in ethanol drop casted on quartz and glass plate substrates in aqueous solutions containing 25 mM zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 25 mM hexamethylenetetramine ($C_6H_{12}N_4$, HMTA) at 95 °C for 8 h. The grown ZnO NWs were thoroughly rinsed with Milli-Q water. Longer ZnO NW in the LG mode was produced by repeating the above hydrothermal growth process, extending the tip of the backbone ZnO NW. In the LG mode, ZnO nanoparticle seeds were added only at the beginning of the growth process. While a single hydrothermal reaction, LG produces 2–8 μm long and vertically aligned ZnO NWs (130–200 nm diameter), the length extension becomes smaller as the step order increases [12].

CuO deposition

CuO was deposited on the ZnO NW backbones by thermal decomposition of copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$) [13] adhered by immersing the quartz substrates with ZnO NWs into ethanol containing copper nitrate hydrate (0.05 g cm^{-3}) for 10 min. Heat source for the thermal decomposition was UV pulsed laser (355 nm, 12 ps, 80 MHz, 125 mW, Vanguard, Spectra Physics) with a spot size of 25 μm for prototyping of CuO deposition on ZnO NWs, taking advantage of the controllable heat flux with digitized parameters and relatively moderate heat production by the UV pulsed MHz-picosecond laser avoiding ablation. The ethanol solvent with copper nitrate hydrate was dried before the UV laser irradiation.

The substrates with the ZnO NWs and CuO–ZnO NWs were then characterized by transmittance measurements with reference to the quartz substrate without the ZnO NWs using an ellipsometer (Sopra 380) between wavelengths of 200 and 800 nm. The surface of the NWs were also observed with a field-emission scanning electron microscope (FE-SEM) (Leo 1550, Zeiss).

An electric hot plate (CHPS-250AN, AS ONE Corp.) was used as the heat source for the demonstration of large area catalyst fabrication. The copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$) with ZnO NWs on the glass substrate was decomposed to produce CuO/ZnO NW catalysts for 45 s on the hot plate set at 250 °C with a thermocouple. Dark brown color of the CuO layer started appearing at a substrate temperature around 165 °C.

Demonstration of hydrogen production

Solar simulator

The prototype catalyst sample was immersed in methanol/water mixture solution (2:1 vol., 1.1:1 M) in a rectangular spectrophotometer vial as illustrated in Fig. 1. The simulated solar light of 1 kWm^{-2} (1 sun) (Model 67005, Newport) was focused at the meniscus on the NW catalyst by a visible achromatic doublet lens (Thorlabs Inc., focal length of ca. 75 mm) for 1.5 and 3 h. The focal spot size of the light was approximately 3 mm in diameter. The intensity of the light through

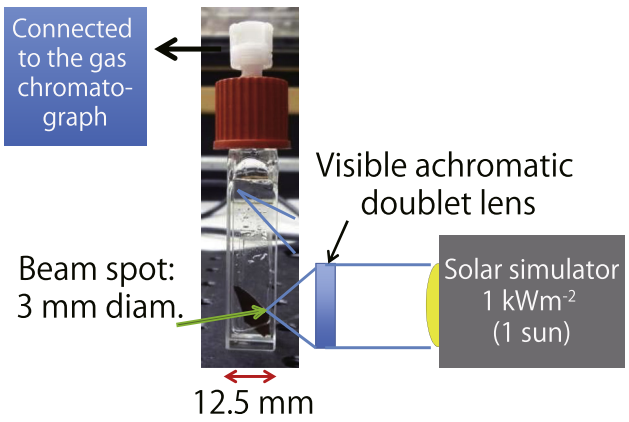

Fig. 1 – Hydrogen production with the solar simulator as a heat source.

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