



All electrochemical fabrication of a bilayer membrane composed of nanotubular photocatalyst and palladium toward high-purity hydrogen production



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ABSTRACT

We developed an all-electrochemical technique for fabricating a bilayer structure of a titanium dioxide (TiO₂) nanotube array (TNA) and a palladium film (TNA/Pd membrane), which works for photocatalytic high-purity hydrogen production. Electroless plating was used for depositing the Pd film on the TNA surface prepared by anodizing a titanium foil. A 3- μ m-thick TNA/Pd membrane without any pinholes in a 1.5-cm-diameter area was fabricated by transferring a 1- μ m-thick TNA onto an electroless-plated 2- μ m-thick Pd film with a mechanical peel-off process. This ultrathin membrane with sufficient mechanical robustness showed photocatalytic H₂ production via methanol reforming under ultraviolet illumination on the TNA side, immediately followed by the purification of the generated H₂ gas through the Pd layer. The hydrogen production rate and the apparent quantum yield for high-purity H₂ production from methanol/water mixture with the TNA/Pd membrane were also examined. This work suggests that palladium electroless plating is more suitable and practical for preparing a well-organized TNA/Pd heterointerface than palladium sputter deposition.

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1. Introduction

Hydrogen gas (H₂) has been expected as a clean energy resource in next generation. In particular, solar hydrogen production via water splitting and alcohol reforming with semiconductor photocatalysts has been intensely studied [1–23]. This hydrogen production process is promising for on-demand reforming of various fuels, which will realize instantaneous hydrogen production with the aid of sunlight and will provide portable power sources in our future daily life. Moreover, further development of photocatalytic H₂ production is quite important for establishing safe use of hydrogen and hydrogen systems, because the on-demand reforming can prevent difficulties in hydrogen storage and transportation.

However, photocatalytic H₂ production usually generates byproduct gases such as carbon dioxide and oxygen simultaneously and the generated H₂ should be purified for practical uses from fuels for fuel cells to process gases for semiconductor manufacturing. This concern is not limited to photocatalytic H₂ production. Namely, all conventional H₂ production systems based on steam

reforming [24], partial oxidation reforming [25], and water electrolysis [26] are equipped with both hydrogen production and purification parts. This problem has limited the miniaturization of H₂ production systems and the further development of on-site reformers toward realizing mobile application of hydrogen energy.

With this background, we recently reported a photoactive hydrogen production/separation membrane which has a bilayer structure comprised by an anodized titanium dioxide nanotube array (TNA) [27–37] and a palladium hydrogen permeable film [38–41] (TNA/Pd membrane) as shown in Fig. 1 [42]. In the previous work, the TNA/Pd membrane was fabricated by transferring an anodized TNA embedded in a titanium foil onto a sputtered palladium film, and the UV-induced production of high-purity hydrogen from pure alcohols (e.g., methanol and ethanol) with the TNA/Pd membrane was demonstrated at room temperature. However, the preparation of 10- μ m-thick Pd film by physical vapor deposition methods such as sputtering and electron-beam deposition was quite costly and time-consuming. From the viewpoint of scarcity of resources such as noble metals, another cost-effective deposition method should be introduced. In our present article, an electroless plating process [43–46] was employed for fabricating a high-quality interface between a palladium film and an anodized TNA. Then, the evaluation of the structures and the H₂ production

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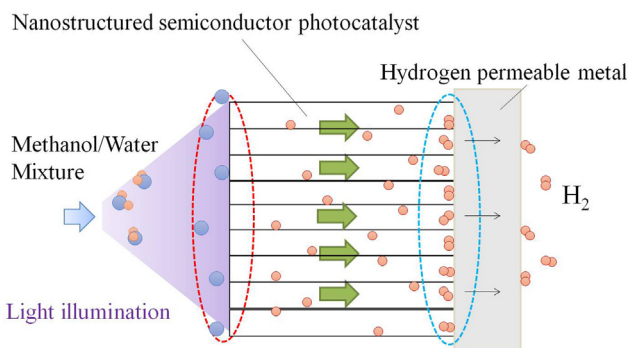


Fig. 1. Functional mechanism of a photoactive hydrogen production/separation membrane based on a bilayer structure of an array of nanotubular photocatalyst and a hydrogen permeable metal. Fuels (e.g., methanol or methanol/water mixture) are photo-oxidized on the surface of nanotubular photocatalyst, forming protons or H_2 gas, and only H_2 gas can be separated from other byproducts.

rate in the TNA/Pd membrane fabricated by all electrochemical processes was performed. In this work, a pinhole-free, ultrathin TNA/Pd membrane with a thickness of a few micrometers was obtained with the aid of electroless plating. The basic properties of the TNA/Pd membrane on photo-induced high-purity H_2 production were also discussed.

2. Experimental

2.1. Preparation and characterization of the TNA/Pd membrane

The TNA/Pd membrane was fabricated according to the process described hereinafter. A titanium foil (100 μm thick, 99.6% purity, Japan Metal Service) was degreased by sonication in acetone. A TNA was formed by anodizing the Ti foil in a two-electrode electrochemical cell with titanium as anode and platinum as cathode, with a constant voltage across the electrodes. A 4:1 mixture of glycerol (99.0% purity, Nacalai Tesque) and highly-pure water (18.2 $M\Omega\text{cm}$) containing 0.5 wt% NH_4F (Special Grade, Wako Pure Chemical Industries) was used as electrolyte. After the anodization at 50 V for 10 h, the foil was annealed at 500 $^\circ\text{C}$ in air for 2 h for crystallization. After the post-annealing of the anodized Ti foil, the TNA was coated with a Pd film via electroless plating. Firstly, Pd nanoparticle cores at which the growth of an electroless-plated Pd film was initiated were formed on the aperture of the TNA by photodeposition. The photodeposition was carried out under UV irradiation for 10 min, in a mixed solution which included 1 ml of palladium standard solution (1000 ppm, Nacalai Tesque), 3 ml of ethanol (99.5%, Nacalai Tesque), and 50 ml of pure water. After the photodeposition process, the TNA was immersed in an electroless plating solution (Palla Top N bath, Okuno Chemical Industries) at 60 $^\circ\text{C}$ for 30 min. After that, the Pd-coated TNA was annealed at 500 $^\circ\text{C}$ for 5 h under N_2 atmosphere. For comparison, another TNA/Pd membrane with a 10- μm -thick sputter-deposited Pd layer was also prepared by RF magnetron sputtering. Here, the TNA used for sputter-deposition was anodized at 50 V for 10 h in the electrolyte which was 9:1 mixture of glycerol and highly-pure water containing 0.5 wt% NH_4F . A pure Pd target (99.9% purity, Furuya Metal) was used as the sputtering source. The sample temperature was kept at 400 $^\circ\text{C}$ for 4 h during the Pd sputter deposition. Finally, the Pd films were mechanically peeled off from the TNA surface for completing the TNA/Pd membranes.

The surface and interface morphologies of the anodized Ti foils and the TNA/Pd membranes were observed using a scanning electron microscope (SEM; S4500, Hitachi) with an acceleration voltage of 5 kV. The phase structure and the elemental chemical status of the TNA/Pd membranes were characterized using X-ray diffraction

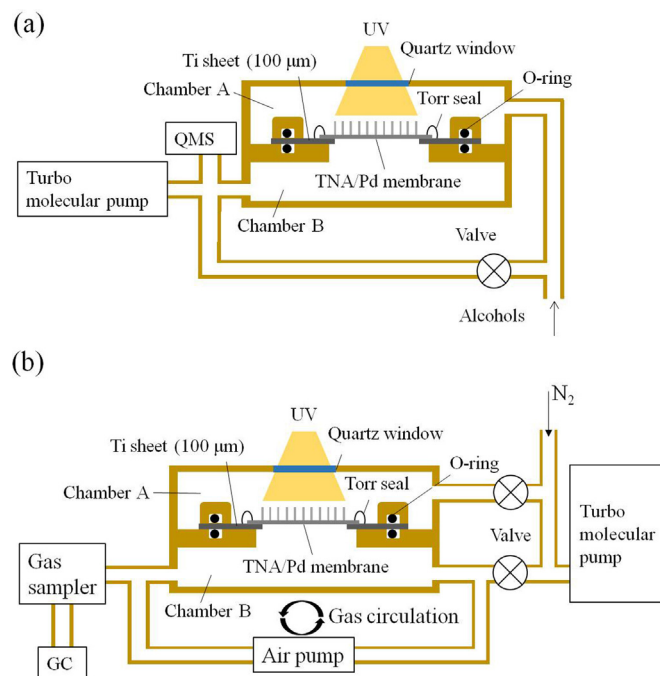


Fig. 2. Schematic drawings of home-made characterization systems for (a) photo-catalytic H_2 production/separation process and (b) the amount of photocatalytic high-purity H_2 production with the TNA/Pd membrane.

(XRD; SmartLab, Rigaku) and X-ray photoelectron spectroscopy (XPS; JPS-9010TR, JEOL), respectively.

2.2. Measurement of photo-induced H_2 production/separation with the TNA/Pd membrane

Hydrogen production from methanol photodecomposition and concomitant hydrogen separation in the TNA/Pd membrane were examined with a home-made high vacuum cell as shown in Fig. 2(a). The cell has two chambers connected to a turbo-molecular pump and spatially separated by the membrane specimen. Hereafter, we call the upper chamber “chamber A” and the lower one “chamber B” for convenience. In order to mount the TNA/Pd membrane in the vacuum cell, the membrane was glued on a Ti sheet (100 μm thick, 3 cm \times 3 cm) with a 1.5-cm-diameter aperture by using Torr seal epoxy resin. After sufficient evacuation of both the chambers A and B to 1.0×10^{-4} Pa with the turbo-molecular pump, the evacuation of the chamber A was stopped and methanol vapors were introduced into the chamber A until the TNA surface of the membrane became fully covered with a methanol droplet. This reactant methanol was stored in a glass flask and evacuated in advance with a rotary pump for a certain time to get rid of air and other unnecessary gases sufficiently. Then, the membrane specimen was illuminated through a quartz window with a Xe lamp (LAX-101, Asahi Spectra). Generated gases filtered through the TNA/Pd membrane were detected at a real-time scale by a six-channel quadrupole mass spectrometer (QMS, Vacscan/Spectra) installed for detecting residual gases inside the chamber B. The incident light was filtered with a band-pass filter between 300 and 400 nm, and the intensity was set to be 30 mW/cm^2 on the TNA surface. All the measurements were performed at room temperature.

2.3. Measurement of the amount of photo-induced H_2 production with the TNA/Pd membrane

The amount of hydrogen gas produced with the TNA/Pd membrane was measured under atmospheric pressure by using a gas

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