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High-purity hydrogen generation by ultraviolet illumination with the membrane composed of titanium dioxide nanotube array and Pd layer

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High-purity hydrogen generation was observed by using a membrane composed of a bilayer of an anodized titanium dioxide nanotube array (TNA) and a hydrogen permeable metal. This membrane was fabricated by transferring a TNA embedded in a titanium foil onto a sputtered 10-μm-thick palladium film. Alcohols are reformed photocatalytically and concurrently generated hydrogen is purified through the Pd layer. H_2 with a purity of more than 99% was obtained from liquid alcohols under ultraviolet illumination onto the membrane. Thus, we demonstrated the integration of photocatalytic hydrogen production and purification within a single membrane. © *2011 American Institute of Physics*. [doi:10.1063/1.3643052]

Hydrogen gas (H_2) has been expected as one of the clean energy sources which can replace fossil fuels. H_2 production has been performed with various methods, for example, steam reforming or partial oxidation of natural and synthesized gas,[1–4] and electrolysis of water.[5] In all these processes, the reforming units are followed by hydrogen purification units for separating generated H_2 from other byproduct and residual gases. Moreover, reforming reactions usually need high temperatures of several hundred degrees Celsius. These constraints in H_2 production limit miniaturization of efficient hydrogen production systems toward mobile applications such as on-site reformers.

For solving above-mentioned issues on hydrogen usage, in this communication, we propose a photoactive hydrogen production/separation membrane reactor which consists of an array of nanotubular photocatalyst and a hydrogen permeable metal as shown in Fig. 1. The whole thickness of this membrane reactor was only a few tens of micrometers. Anodized titanium dioxide (TiO_2) nanotube array (TNA)[6–11] was employed as a photocatalyst and sputtered palladium thin film as a hydrogen purification part.[12,13] Liquid and vapor fuels such as methanol and ethanol can be reformed by photocatalysis on TNA even at room temperature (Fig. 1(a)). The hollow parts of TNA serve as a path for generated H_2 or protons to the inner surface of a palladium thin film (Fig. 1(b)), and then highly purified H_2 gas was obtained quickly from the back side of the palladium thin film (Fig. 1(c)). The production of pure H_2 clearly coincides with ON/OFF switching of ultraviolet (UV) illumination. This work demonstrates the integration of photocatalytic hydrogen production and purification within a single membrane, thereby suggesting that our photoactive membrane reactor is quite promising for achieving further miniaturization and lower temperature operation of various hydrogen reformers.

The photoactive hydrogen production/separation 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. 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. Glycerol (99.0% purity, Nakaraitesk) containing 0.5 wt. % NH_4F (96.0% purity, Wako Pure Chemical Industries) was used as electrolyte. Here, the circular area with a diameter of 1.7 cm in the middle of the foil was exposed to the electrolyte. After the anodization at 50 V for 20 h, the foil was firstly annealed at 573 K in air for 30 min then annealed at 773 K in air for 3 h, resulting in the TNA of anatase crystals confirmed by x-ray diffraction (not shown here). The surface morphologies of the TNA was observed using a Hitachi S4500 scanning electron microscope (SEM). SEM images of an anodized Ti foil, represented in Figs. 2(a) and 2(b), clearly show that the TNA with 5 μm length and 40 nm pore size was formed under our experimental condition.

Successively, a 10-μm-thick palladium layer was deposited on the surface of the TNA by RF magnetron sputter deposition. A pure palladium target (99.9% purity, Furuya Metal Co.) was used as the sputtering source. During the Pd deposition, the sample temperature was kept at 673 K to promote the adhesion of Pd layer onto the TNA surface.
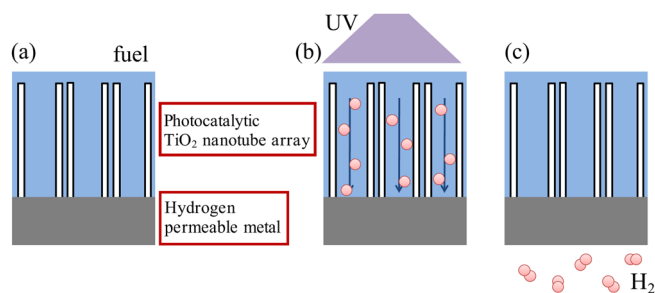

FIG. 1. (Color online) Functional mechanism of a photoactive hydrogen production/separation membrane based on a bilayer structure of an array of nanotubular photocatalyst and a hydrogen permeable metal. (a) A conceptual schematic of the hydrogen production/separation membrane. (b) Fuels (e.g., alcohols) are photo-oxidized on the surface of nanotubular photocatalyst and protons or H_2 gas are formed. (c) Only H_2 gas can be separated from other byproducts.

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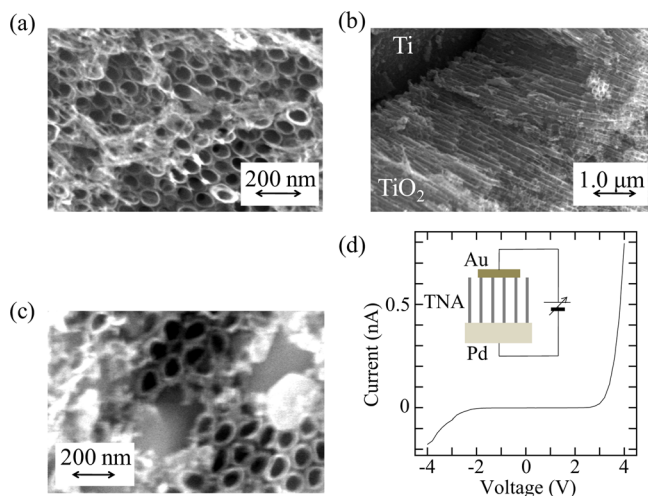
FIG. 2. (Color online) SEM images of the TNA in (a) top view and (b) cross-sectional view. (c) SEM image of the top surface of the TNA/Pd membrane. (d) A current-voltage (*I-V*) curve of the Au/TNA/Pd sandwich structure prepared from the TNA/Pd membrane.

FIG. 3. (Color online) Schematic drawing of a high-vacuum characterization system for the TNA/Pd membrane reactor. The performance of H_2 production and separation was evaluated using a QMS and a home-made vacuum cell.

After the Pd deposition, the palladium layer was mechanically peeled off from the anodized Ti foil. This peel-off process made the TNA cracked at some defect sites on tubular surfaces and transferred onto the Pd surface. Figure 2(c) shows the image of the TNA transferred onto palladium layer, which clearly shows the TiO_2 nanotubes with open apertures are standing on the palladium. Thus, a bilayer structure of the TNA and the Pd layer (TNA/Pd membrane) was prepared.

A current-voltage (*I-V*) curve of the TNA/Pd bilayer structure was obtained with 2-point electrical measurement in air under dark condition using a Keithley 4200-SCS system. For this measurement, 50-nm-thick Au contacts with a diameter of 1 mm were formed on top of the TNA/Pd membrane by vacuum evaporation using a shadow mask. The obtained *I-V* curve of the Au/TNA/Pd structure, shown in Fig. 2(d), displays a nonlinear curve which is typical of metal-semiconductor interfaces with Schottky barriers. The main charge carrier in TiO_2 is electron because TiO_2 is well known as an n-type oxide semiconductor. The work functions of Au (5.1 eV) and Pd (5.1 eV) are much larger than the conduction band level of TiO_2 (4.0 eV). Therefore, the existence of Schottky barriers at both interfaces of Au/TNA and TNA/Pd is thought to be quite reasonable. The obtained *I-V* curve supports the formation of a rigid interface between the TNA and Pd in the TNA/Pd membrane.

Photoinduced hydrogen production and concurrent separation for the TNA/Pd membrane were examined with a home-made high vacuum cell as shown in Fig. 3. The cell was comprised by 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 a turbo-molecular pump, the evacuation of the chamber A was stopped and alcohol vapors were introduced into the chamber A until the TNA surface of the
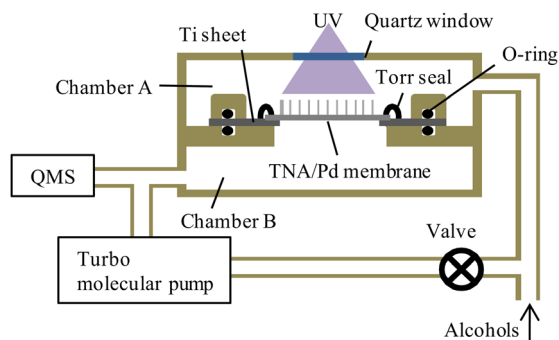
membrane became submerged in an alcohol droplet. Even after the introduction of alcohols into the chamber A, the degree of vacuum in the chamber B was maintained to be 1.0×10^{-4} Pa, suggesting the supreme mechanical robustness of the TNA/Pd membrane. Successively, photocatalytically generated hydrogen and other byproduct 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. Measurements of the gas spectra were performed with the repetitive ON/OFF of illumination from a Xe lamp (LAX-101, Asahi Spectra). 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. All the measurements were performed at room temperature.

In photocatalytic H_2 production from methanol on TiO_2 surface, methanol undergoes oxidative decomposition to CO_2 through intermediates, e.g., formaldehyde (CH_2O).[14,15] Figure 4(a) shows a simultaneous analysis of various gases generated from methanol photocatalytic decomposition with the TNA/Pd membrane; H_2 (m/e = 2), CO_2 (m/e = 44), and CH_2O (m/e = 30). These partial pressures were measured from residual gases in the chamber B. The H_2 pressure revealed a switching phenomenon according to the ON–OFF interval of UV illumination (30 min/20 min) and the net increase in the H_2 pressure under UV illumination was about 1.0×10^{-5} Pa. On the other hand, the CO_2 and CH_2O pressures did not show any switching phenomena regardless of UV illumination. This means that CH_2O and CO_2 detected in
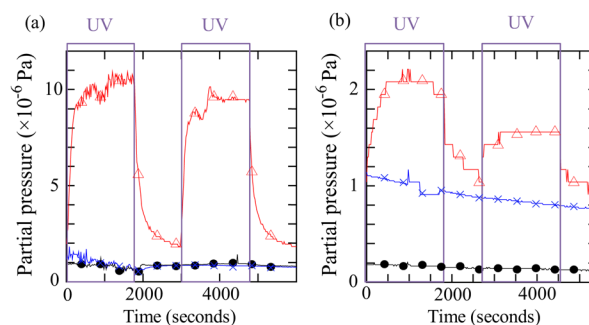

FIG. 4. (Color online) Temporal variation of partial pressures of gas species generated from (a) methanol and (b) ethanol photocatalytic decomposition with the TNA/Pd membrane: H_2 (m/e = 2, open triangle), CO_2 (m/e = 44, cross), and formaldehyde (CH_2O) (m/e = 30, solid circle). These partial pressures were monitored from residual gases in the chamber B.

Fig. 4(a) were not byproducts due to the function of the TNA/Pd membrane but originally existed inside the chamber B as background gases.

Here, the purity of H_2 (x) produced with the TNA/Pd membrane is defined as follows:

$$x = \frac{\Delta P_{H2}}{\Delta P_{H2} + \Delta P_{CH2O} + \Delta P_{CO2}}, \quad (1)$$

where ΔP_{H2}, ΔP_{CH2O}, and ΔP_{CO2} stand for the net increase of partial pressure for each gas species with UV illumination. The increase of partial pressure is obtained by subtracting the background pressure from the average pressure under UV illumination. From the data in Fig. 4(a), the purity of generated H_2 was estimated to be 100% at the first UV illumination and 99% at the second UV illumination. These results reveal that the TNA/Pd membrane reactor produced high-purity H_2 from methanol rapidly with UV illumination.

The simultaneous H_2 production and separation were also confirmed in the case of ethanol decomposition as shown in Fig. 4(b). Only the H_2 pressure displayed a switching phenomenon with the ON/OFF (30 min/15 min) of UV irradiation. Pressures of CO_2 and CH_2O were not changed with the UV irradiation, although the background levels of these gas species were gradually shifted. The net increase in H_2 pressure under UV illumination was about 1.0×10^{-6} Pa, and the purity of produced H_2 calculated from Eq. (1) was 100% at both first and second UV illumination. Accordingly, high-purity H_2 can be also produced from ethanol by using the TNA/Pd membrane reactor.

In the TNA/Pd membrane, two possible processes for high-purity H_2 production are considered. H_2 gas can be formed on the TNA side with the aid of Pd, which can work as cocatalyst for proton reduction, and then penetrate into the Pd layer in the form of proton. However, it is also possible that photocatalytically generated protons on the TNA side can reach the surface of the Pd layer directly without proton reduction. The investigation of the functional mechanism of the TNA/Pd membrane is going on and of great importance for realizing more efficient high-purity hydrogen production.

In conclusion, we developed the photoactive hydrogen production/separation membrane based on a bilayer structure of a TNA with open apertures and a metallic hydrogen permeation film. Integration of nanostructured photocatalyst and hydrogen permeation materials, exemplified in this study, is one of the promising strategies for realizing more efficient, and compact hydrogen reforming systems with the aid of solar energy.

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