Temperature Dependence of Photoinduced Hydrogen Production and Simultaneous Purification in TiO_2 Nanotubes/Palladium Bilayer Membrane

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Photocatalytic hydrogen (H_2) production with widegap semiconductor materials has been expected as one of the new clean energy sources. To provide H_2 gases for practical uses, all the H_2 reforming units must be followed by hydrogen purification units for separating generated H_2 from other byproduct and residual gases such as carbon dioxide and oxygen. This issue can limit the miniaturization of H_2 production systems and the further development of on-site reformers toward mobile application of hydrogen energy. With this background, we have developed photoactive hydrogen production/separation membrane with a bilayer structure of an anodized titanium dioxide (TiO_2) nanotube array (TNA) and a hydrogen permeation film of palladium (TNA/Pd membrane) [1,2].

In this work, the temperature dependence of photoinduced H_2 production and purification in the TNA/Pd membrane was examined. This membrane was fabricated by transferring a TNA embedded in a titanium foil onto an electroless-plated 10-μm-thick palladium film. This membrane can reform a methanol/water (1:1) mixture photocatalytically under ultraviolet (UV) irradiation and concurrently purify generated hydrogen gas through the Pd layer. The H_2 production rate (r_{H_2}) with the membrane at various temperatures was evaluated by using a home-made characterization system (Fig. 1(a)). As shown in Fig. 1(b), the measured r_{H_2} showed larger values at higher temperature of the membrane. r_{H_2} increased abruptly after several hours of UV irradiation and this inflection point appeared faster at higher temperature of the membrane. These behaviors can be probably related to the permeation characteristics of hydrogen through the Pd layer.

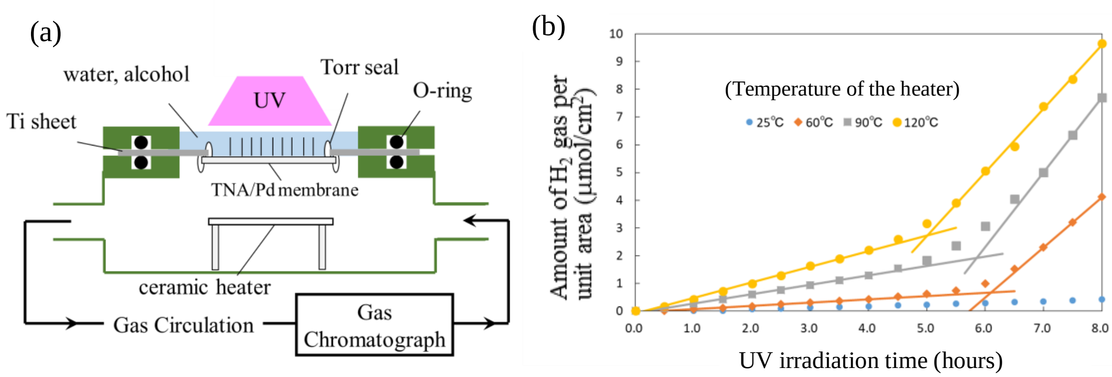

Figure 1. (a) A schematic drawing of home-made characterization system for photocatalytic high-purity H_2 production with the TNA/Pd membrane. (b) A data-plot of the amount of high-purity H_2 produced from the methanol/water mixture versus the duration of UV irradiation onto the TNA/Pd membrane. The temperature of the membrane was controlled by using a ceramic heater depicted in Fig. 1(a).

[1] M. Hattori, K. Noda, and K. Matsushige, Appl. Phys. Lett. **99**, 123107 (2011).
[2] M. Hattori and K. Noda, Appl. Surf. Sci. **357**, 214 (2015).

Supplementary Page

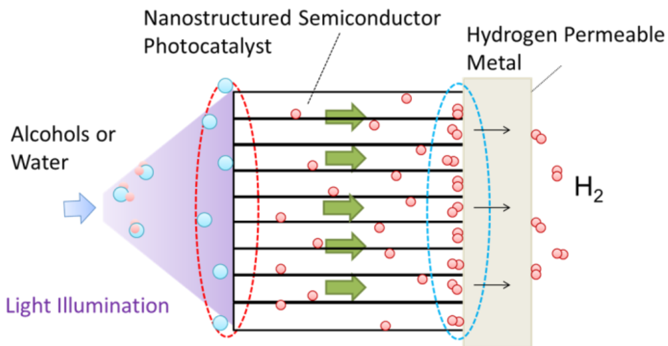

Figure S1. A schematic drawing of a photoinduced hydrogen production/purification membrane based on a bilayer structure of an array of nanotubular photocatalyst and a hydrogen permeable metal. Fuels (e.g., methanol/water mixture) are photo-oxidized on the surface of nanotubular photocatalyst, forming protons or H_2 gas, and only H_2 gas can be separated from other byproducts.

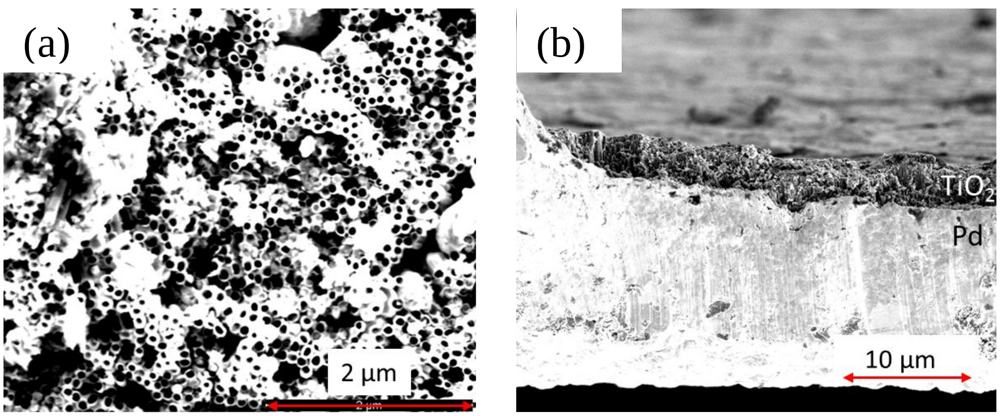

Figure S2. (a) Top-view (TNA side) and (b) cross-sectional scanning electron microscope (SEM) images of the TNA/Pd membrane.