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Photocatalytic decomposition of gaseous methanol over anodized iron oxide nanotube arrays in high vacuum

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ABSTRACT

Real-time monitoring of photocatalytic methanol decomposition over anodized iron oxide nanotube arrays (FNAs) in high vacuum was performed. Switching phenomena in the partial pressures of H_2, CO and H_2O were observed simultaneously according to the ON/OFF sequence of visible and ultraviolet light illuminations over Pt-loaded FNAs prepared with photodeposition, while no change in these gas species appeared for bare FNAs and iron foils. The absence of formaldehyde (CH_2O) in the intermediates during methanol photodecomposition suggests that Pt-loaded FNAs can possibly work as a catalyst for oxidation of CH_2O. The photoreforming of methanol to hydrogen without any external bias in Pt-loaded FNAs presumably indicate some differences in photocatalytic reaction mechanisms between in liquid and in high vacuum. The dependence of the Pt photodepositon time on gas phase photocatalysis suggests that the selective deposition of Pt cocatalyst particles on the aperture parts of the nanotubes is necessary for efficient gas phase photoreforming.

1. Introduction

Gas phase photocatalysis with wide gap semiconductor materials has been expected and widely studied as one of the environmentally benign technologies for not only air purification, but clean and renewable hydrogen production [1–9]. One of the benefits of applying gas phase photocatalysis is that effects of mass transfer resistance in the whole reaction process can be alleviated in comparison to those in commonly-used liquid phase reactors [7–9]. Actually, a large number of actual applications of photocatalytic oxidation are based on gas phase reactions. The usage of gas phase photocatalysis has another advantage of facilitating to measure intermediate products during photocatalytic reaction processes, which is of great use for clarifying the basic reaction mechanisms. Therefore, the investigation of gas phase photocatalysis plays a highly important role in both understanding photocatalytic functions and promoting commercial applications of photocatalyst materials.

Materials research for visible light responsive photocatalysts plays a greatly important role from the viewpoint of the effective use of solar energy. In these years, a variety of novel materials such as $BiVO_4$, Cu_2O, graphitic carbon nitride ($g\text{-}C_3N_4$), graphene-metal oxides, Ti_3C_2 MXenes, and those composites have been synthesized and showed excellent photoelectrochemical properties [10–14]. Surface plasmon resonance of metal particles has been also applied to extend light absorbance of photocatalytic materials in the ultraviolet-visible range [15,16]. In the meanwhile, hematite ($\alpha\text{-}Fe_2O_3$) is a traditional but promising candidate with an indirect band gap energy of ~2.2 eV [17]. The potential application of hematite will be economically viable, since iron is one of the most abundant metals on the earth. However, hematite has rapid electron-hole pair recombination and poor electrical conductivity. To overcome these shortcomings, various researches including materials synthesis [17–24], elemental doping [25–28], and theoretical calculation [29] are underway. Particularly, in order to enhance photocatalytic activity of hematite, self-aligned nanoporous/nanotubular structures with large specific surface area prepared by electrochemical anodization have been intensively studied due to their attracting features such as simplicity and low cost fabrication [30–34]. Electrolytes including both fluoride and ethylene glycol for anodic iron oxide have been widely employed owing to their better controllability for obtaining different nanostructures. In fact, well-aligned iron oxide nanotubes with smooth walls were produced and those applications toward water photooxidation with high performance were demonstrated [30–32].

Methanol is well known as a test molecule for gas phase photocatalytic oxidation, since methanol is a typical organic pollutant as well as one of the efficient resources for hydrogen production. So far, the adsorption/desorption behaviors of methanol molecules onto TiO_2 surfaces have been investigated under high vacuum or ultrahigh vacuum conditions, by using various surface-sensitive measurement techniques such as scanning probe microscopy (SPM) and temperature

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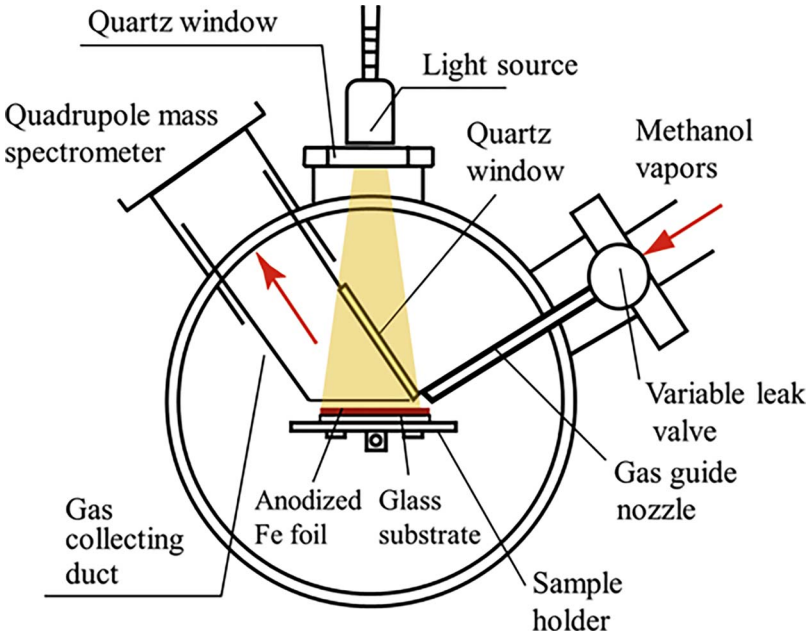

Fig. 1. Schematic drawing of a home-made apparatus for monitoring gas phase photocatalysis in high vacuum. The photocatalytic decomposition process for a small amount of gaseous molecules over nanostructured photocatalysts can be investigated with the aid of a quadrupole mass spectrometer, home-made gas guide nozzle and gas collecting duct.

programmable desorption (TPD) [35,36]. Recently, photooxidation process of methanol to formaldehyde and methyl formate have been monitored sequentially on TiO_2 (110) on a molecular scale [37]. The molecular hydrogen formation induced by methanol photooxidation on TiO_2 (110) was also monitored [38]. However, most of these surface science studies focused on TiO_2, and mechanisms of photocatalytic methanol decomposition on visible-light-responsive photocatalysts are not clear. In addition, operando analysis on photocatalysis in high vacuum environments has not been fully performed.

In the present work, we have studied the photocatalytic decomposition process for methanol vapors over iron oxide nanostructures in high vacuum. The methanol decomposition process was examined not only as a model reaction, but also for potential uses toward fuel cells and on-site reforming for mobile applications [39,40]. We fabricated anodized iron oxide nanotube arrays (FNAs), accompanied by loading platinum nanoparticles for promoting photo-generated electron-hole separation. Real-time observation of gas phase photocatalytic oxidation of methanol over FNAs in high vacuum was conducted under visible and ultraviolet light illuminations and the reaction intermediate products were experimentally identified. From the results in this study, plausible reaction pathways of photocatalytic methanol decomposition and hydrogen production are discussed. Differences in photocatalytic reaction mechanisms between in liquid and in high vacuum are also considered.

2. Experimental details

2.1. Preparation and characterization of iron oxide nanotube arrays

Iron oxide nanotube arrays (FNAs) were prepared as follows. 100-μm-thick pure Fe foils (Sigma Aldrich, purity 99.9%) with a size of 3 cm × 2 cm were cleaned with acetone and water by sonication. FNAs were fabricated by anodizing the Fe foils in a two-electrode electrochemical cell with iron as anode and platinum as cathode. Ethylene glycol (99.0% purity, Nacalai Tesque) containing 0.5 wt% NH_4F (99.0% purity, Nacalai Tesque) and 2.62 wt% pure water (10 MΩcm) was employed as electrolyte for the anodizing treatment. The temperature of the anodization cell was controlled with a water circulating bath (CTB-1, IKUTA Sangyo). After the anodization at a constant voltage of 50 V for 5 min at 60 °C, the Fe foils were soaked in methanol and sonicated again for a few tens of seconds to clean the sample surface. Finally, the foils were annealed at 400 °C in air for 1.5 h for crystallization.

Successively, platinum nanoparticles as cocatalyst were deposited onto the anodized iron foils by photodeposition method [41]. The anodized iron foils were immersed in a solution containing 20 ml of 1 M aqueous solution of hexachloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, Sigma Aldrich, ≥37.50% Pt basis) and 5 ml of ethanol (99.5%, Nacalai Tesque) and visible light was irradiated onto the foils with different time durations. The incident visible light was generated from a 300 W Xe light source (MAX-303, Asahi Spectra) with a band-pass filter between 385 and 740 nm, and the intensity was set to be 30 mW/cm^2 onto the FNA surface. Finally, the foils were rinsed with pure water and blow-dried in a nitrogen stream.

The surface morphology and microstructure of the nanotubular arrays were studied with a scanning electron microscope (SEM; FEI, Inspect F50) with an acceleration voltage of 3 kV. Images of single nanotubes were obtained with transmission electron microscopy (TEM; FEI, Tecnai G^2). X-day diffraction (XRD) analysis for checking the crystalline phase of the anodized Fe foils was carried out with D8 ADVANCE (BrukerAXS). The Raman spectroscopy was also performed by using a Renishaw inVia Raman microscope, with a laser excitation wavelength of 532 nm and at an intensity of 15 mW. The chemical status of the specimens was examined with X-ray photoelectron spectroscopy (XPS; JPS-9010TR, JEOL). Diffuse reflectance ultraviolet-visible (UV–VIS) spectra were measured with a Shimadzu UV-3600Plus spectrophotometer equipped with an integrating sphere. The actual deposition amount of platinum nanoparticles on anodized FNAs was estimated by an energy-dispersive x-ray fluorescence (ED-XRF) instrument (BrukerAXS M4 TORNADO) equipped with a Rh X-ray tube (50 kV, 10 W). The integrated counts for the Pt Lα peak at 9.44 keV were calculated from the observed ED-XRF profiles, and this XRF signal intensity was converted to the deposition amount of platinum by using a reference XRF data measured for a standard specimen. This standard specimen was prepared by depositing and drying a 0.2 ml droplet of a Pt standard solution (1000 ppm, Nacalai Tesque) onto a bare Fe foil.

2.2. Gas phase photocatalysis measurement

Photocatalytic activity of FNAs was evaluated by utilizing a home-made apparatus for investigating gas phase photocatalysis in high vacuum. A schematic drawing of the main measurement chamber was