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An internal-illuminated monolith photoreactor towards efficient photocatalytic degradation of ppb-level isopropyl alcohol

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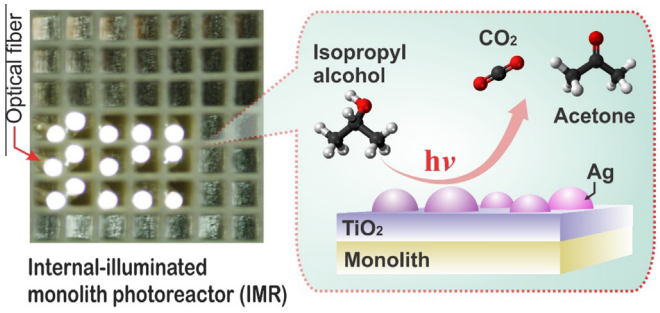
HIGHLIGHTS

- Internal-illuminated monolith photoreactor was designed to transmit light uniformly.
- Catalysts were fully characterized by SEM, TEM, BET, XRD, UV–vis and XPS techniques.
- Photodegradation of IPA at ppb level was studied under various operating conditions.
- The removal efficiency increased up to nearly 80% over Ag/TiO_2 photocatalyst.
- Photoreactor is potentially applicable to cleanroom in the semiconductor industry.

GRAPHICAL ABSTRACT



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ABSTRACT

Isopropyl alcohol (IPA) at ppb level is the airborne molecular contamination regarded as a potential pollutant for semiconductor processes. An internal-illuminated monolith photoreactor (IMR) was designed and assembled to transmit and spread light uniformly by optical fibers inside every monolith channels. TiO_2 and Ag/TiO_2 photocatalysts were synthesized and coated on the surface of the monolith. The coating layer was completely covered the monolith surface and fully characterized by SEM, high-resolution TEM, EDS, BET, XRD, UV–vis, and XPS techniques. The photodegradation of gaseous IPA at ppb level in IMR was then investigated under various operating conditions such as retention time, initial IPA concentration, Ag-decorated contents, and diameter of the optical fiber. The experimental results show that IMR significantly improves the IPA removal efficiency. The enhanced efficiency of light utilization, which can be attributed to the excellent activity performance, is due to unique light distribution by optical fibers and well-coated photocatalyst in every monolith channels. At the optimal operation, 78.6% removal efficiency and 99.5% CO_2 selectivity was achieved over Ag/TiO_2 photocatalyst. It believes that IMR could be potentially applicable to cleanroom in the semiconductor industry.

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1. Introduction

The airborne molecular contamination (AMC) in cleanroom environments have been widely described as a negative impact on a nano-device performance [1,2]. According to the semiconductor manufacturing activities, AMC has been identified widely in the cleanrooms with concentrations at a parts-per-billion (ppb) level [1]. Among such AMC, isopropyl alcohol (IPA) is one of the solvents commonly used in semiconductor industry. Because of high mobility and low vapor pressures, IPA at ppb level can easily condense on the surface of the wafers, resulting in deterioration mechanisms in several device performances and loss of millions of dollars in production line [2,3].

Several studies have been carried out to address this issue. Among various emission control technologies, photocatalytic oxidation/degradation that is chemically converting IPA into nontoxic compounds such as water (H_2O) and carbon dioxide (CO_2) has been considered [4]. This process is low-cost, friendly to the environment and efficiently operated at ambient temperature. Recently, the photooxidation of gaseous IPA (1400 ppm) was carried out to evaluate the photocatalytic activities of Bi_2O_3 photocatalyst under visible-light [5]. Ma et al. studied the decomposition of gaseous IPA by UV/TiO_2 process in an annular photoreactor under various inlet IPA concentrations (140–520 ppm) [6]. Pan and Wu evaluated the photodegradation of IPA (156 ppm) over Cr-doped $TiO_{2-X}N_X$ photocatalysts under visible-light [7]. Sun et al. designed TiO_2-coated filter-type photoreactor and studied the photodecomposition of ppm-level (21 ppm) IPA [8]. It is notable that there are two challenges to remove IPA in the semiconductor industry, i.e., low concentration (ppb) and large volume (hundreds cubic meter per min). However, most case study research has focused at ppm level only. Regarding the low-limit standard for IPA in the semiconductor cleanrooms, individual semiconductor manufacturers tend to set their contamination control criteria due to the industry's competitiveness. It is believed that its standard would be lowered soon due to the demand for better quality in the nanotechnology era. Due to this concern, an internal-illuminated monolith photoreactor (IMR) with distributed optical fibers (OFs) inside every channel of the monolith has been designed and studied. The monolith could provide high surface area per unit volume with a low-pressure loss under high flow rate [9]. Optical fibers can deliver light into deep inside of channels [10]. This idea combined the most advantages of the monolith reactor and the optical fiber.

Regarding the photocatalysts, titanium dioxide (TiO_2), among the various candidates, has been attracted for the degradation of environmental contaminants due to remarkable photocatalytic, non-toxicity, low-cost, and good chemical stability [11,12]. Typically, the major limitation in semiconductor photocatalysis is the recombination of photo-generated charge carriers, resulting in reducing the overall quantum efficiency [13]. Therefore, intensive efforts have been made to decorate the TiO_2 surface by metals/metal oxides loading [14–22]. This concept will impair the recombination of the electron-hole pairs by acting as an electron trap and promoting interfacial charge transfer. Specifically, silver is the classic metal that has mostly received much attractive due to its high photoactivity and specific optical characteristics [15–17,23].

Herein, IMR was considered to explore the photodegradation of gaseous IPA at the ppb level. Photocatalysts, including TiO_2 and silver-decorated TiO_2 (Ag/TiO_2), were coated on the surface of monolith channels, which can be illuminated by the refracted UV light out of the OFs. The photodegradation of gaseous IPA at ppb level was systematically investigated under various conditions such as retention time, initial IPA concentration, Ag contents, and diameter of OFs.

2. Experimental

2.1. Preparation and coating of photocatalysts

The TiO_2 sol was prepared by the controlled thermal hydrolysis method. At first, 87.63 g of the titanium (IV) butoxide (TBOT, 97%, Fluka) was slowly added to 510 ml of 0.1 M nitric acid (HNO_3, J.T. Backer) with a volume ratio of 1:6. Then, 10 g of polyethylene glycol (PEG, Merck) was added to improve the viscosity of the TiO_2 sol and its adhesion on the monolith. The mixture was kept to stir at 80 °C for 8 h.

The monolith substrate was purchased from Chauger Honeycomb Ceramics Co. Ltd. (New Taipei City, Taiwan) with the dimension of 37 mm × 37 mm × 150 mm contained 196 channels (opening area: 2 mm × 2 mm). The chemical composition of monolith consisted mainly of SiO_2 (40%), Al_2O_3 (44%), MgO (13%). A dip-coating method was used to immobilize photocatalysts on the inner walls of the substrate. After dip-coating, TiO_2 coated monolith was calcined at 300 °C for 3 h to remove PEG. Finally, it was calcined at 500 °C for 3 h to transform TiO_2 into anatase phase.

Impregnation method was used to prepare the Ag/TiO_2 photocatalyst. The TiO_2-coated monolith was impregnated with the desired amount of silver nitrate ($AgNO_3$, 99.8%, Sigma–Aldrich) aqueous solution. In a typical case of 0.5 wt% Ag/TiO_2 photocatalyst, if there was 0.7 g of the TiO_2-coated monolith, 5.523 mg of $AgNO_3$ would be used to prepare the silver nitrate solution. At first, the monolith, which was dipped in the silver precursor solution, was put in a sonicator bath for 10 min. After that, it was just soaked at 80 °C until all the precursor solution was evaporated. Finally, it was dried and calcined in air at 80 °C overnight, and then 500 °C for 3 h. The contents of Ag-decorated on TiO_2 ranged from 0.5 to 1.5 wt %. Instead of coating, the powder photocatalysts were also prepared as the same procedures for characterization analysis.

2.2. Characterization of photocatalysts

The TiO_2 layer characterized by a scanning electron microscopy (SEM, NovaTM NanoSEM 230) equipped with Energy Dispersive X-ray Spectroscopy (EDS) for surface morphology analysis. The specific surface area of catalyst was determined by the Bru nauer–Emmett–Teller method (BET, ASAP2010 Micromeritics). Powder X-ray diffraction (XRD, OXFORD X-max) was used to verify the crystalline structure of the photocatalysts. An ultraviolet–visible spectrophotometer (UV–vis, Varian Cary 100) was used to measure the light absorption of photocatalysts. The X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe) was used to determine the oxidation states of the elements. High-resolution transmission electron microscope (HRTEM, Philips Tecnai F20 FEI G^2) equipped with Energy Dispersive X-ray Spectroscopy (EDS) was performed at an acceleration voltage of 200 kV.

2.3. Photodegradation of isopropyl alcohol (IPA)

The internal-illuminated monolith photoreactor (IMR, 55 mm × 55 mm × 180 mm) which consists one UV-lamp (7.5 mW cm^{-2}, 185 + 254 nm) and photocatalyst coated ceramic monolith with 196 OFs. Three different diameters (0.5 mm, 1.0 mm, and 1.5 mm) of OFs were used to prolong the light-illumined into every channel of the monolith. Scheme 1 shows the schematic diagram of the experimental system. The gas stream, which was provided by a gas cylinder of air (21% O_2 and 79% N_2), was passed through desiccants, active carbon, and high-efficiency particulate air filter to remove water, organic compounds, and small particulates, respectively. After that, the gas stream, which was controlled by mass