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Photocatalytic soot oxidation on TiO_2 microstructured substrate

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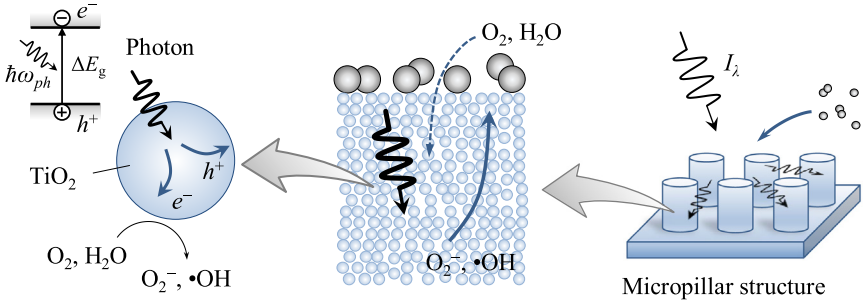
HIGHLIGHTS

- Photocatalytic soot oxidation using TiO_2 microstructured substrates was proposed.
- Photon absorption in TiO_2 substrate to generate electron-hole pairs was analyzed.
- Soot oxidation rate on plain TiO_2 substrates increased with substrate thickness.
- Micropillar substrate showed enhanced soot oxidation rate.
- Multiscale phenomena presented here can be optimized for further improvement.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic soot oxidation was investigated using TiO_2 microstructured substrates. Plain and micropillar substrates of sintered TiO_2 nanoparticles were prepared using a soft lithography process. Photon absorption analysis revealed substantial photon transmission for plain substrate within the current substrate thickness range (<2.5 μm). The porous structure of substrate was confirmed by electron microscopy and by dimensional changes due to sintering, allowing gaseous species and radicals to diffuse across micrometer-thick substrates. It was found that the soot oxidation rate increased with the thickness of the plain TiO_2 substrate; this was related to the increase in electron-hole pair generation associated with increased photon absorption. The soot oxidation rate increased further with the use of TiO_2 micropillars, enhancing photon absorption through multiple scattering. These multiscale phenomena in the photocatalytic soot oxidation on TiO_2 microstructured substrates were analyzed.

1. Introduction

Soot is a fine solid particulate matter of carbon generated in various incomplete combustion processes of hydrocarbons and is considered an environmental pollutant when emitted into the atmosphere [1]. It is oxidized to carbon dioxide at high temperatures often with the help of an oxidation catalyst (e.g., platinum), which indicates that soot removal is an energy-consuming process [2]. Techniques based on renewable energy and using inexpensive materials are desirable for oxidizing soot. Photocatalysis using TiO_2 offers a potential pathway with the direct use of sunlight in this endeavor [3].

Photocatalytic soot oxidation has been studied using TiO_2 photocatalyst [4–7]. Lee et al. reported that the radicals generated by TiO_2 migrated tens of micrometers to oxidize soot [4], which was also confirmed later by another group [5]. Using infrared spectroscopy, Mills et al. revealed that photocatalytic soot oxidation exclusively yielded carbon dioxide as the product [6]. Smits et al.

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studied self-cleaning building materials and examined soot oxidation on mortar coated with TiO_2 [7]. These previous studies examined some fundamental aspects of soot oxidation using plain TiO_2 films with thicknesses of approximately 1 μm [4] and 0.9 μm [6]; however, there appears to be no report on the attempt to improve the efficiency of photocatalytic soot oxidation from the viewpoint of photocatalyst substrate structure.

The efficiency of photocatalytic soot oxidation depends on several factors. Soot is a strong absorber of ultraviolet (UV) rays, so the amount of photons generating electron-hole pairs is reduced when soot covers the TiO_2 substrate [4,8]. The recombination of the generated electron-hole pairs occurs while the carriers diffuse in TiO_2. The diffusion length of the carriers, or the characteristic length of carrier diffusion l_c, for anatase TiO_2 is found to be only about 3 nm [9]. In contrast, the characteristic length of radical diffusion l_r is tens of micrometers [4]. Considering the large gap between the characteristic lengths ($l_c \ll l_r$), one possible strategy to minimize the carrier loss is to use TiO_2 nanoparticles for allowing the carriers to diffuse only a few nanometers to the solid–gas interface and letting the produced radicals diffuse across the micrometer-thick substrate. The characteristic length of photon penetration in a TiO_2 substrate is also important when optimizing the thickness of TiO_2 substrate.

In the present study, we investigate the effect of TiO_2 substrate microstructure on photocatalytic soot oxidation. First, we analyze photon absorption in a TiO_2 substrate. Subsequently, we show the fabricated TiO_2 substrates of sintered TiO_2 nanoparticles and the dependence of soot oxidation rate on the TiO_2 substrate microstructure. The underlying mechanism is presented to interpret the experimental results.

2. Experimental

2.1. Fabrication of TiO_2 structured substrates

We fabricated two types of TiO_2 microstructured substrates: plain and micropillar substrates of sintered nanoparticles. The micropillar substrate comprised a periodic array of cylindrical pillars. Micrometer-scale surface structure was controlled via a soft lithography process wherein TiO_2 nanoparticles were assembled using a polydimethylsiloxane (PDMS) stamp. The outline of soft lithography processes is schematically shown in Fig. 1. A flat glass plate and a patterned photoresist master were prepared as a master for the plain and micropillar TiO_2 substrates, respectively. A room-temperature-vulcanizing silicone rubber, ELASTOSIL® RT601 (Wacker Asahikasei Silicone, Japan), was used to prepare the PDMS stamp. A TiO_2 nanoparticle suspension (Sakai Chemical Industry, Japan), in which TiO_2 nanoparticles were dispersed in methanol, was used in the process. The concentration of TiO_2 particles was 15.4 wt%. The crystal phase of the TiO_2 nanoparticles was anatase. The mean diameter of the TiO_2 nanoparticles was 3.7 nm, which was measured using a dynamic light-scattering instrument and supported by transmission electron microscopy [10]. After the TiO_2 suspension was dropped onto a glass plate, the PDMS stamp was placed on the suspension. Drying of the suspension due to methanol evaporation and particle compaction proceeded at room temperature. Then, the PDMS stamp was released and the sintering of particles to obtain the final form of TiO_2 substrate was performed at 600°C for 20 min in an electric furnace. In our previous research, we confirmed that the anatase phase of the TiO_2 particles was maintained under this sintering condition [10].

The microscale structure of the obtained TiO_2 substrates was characterized prior to soot oxidation experiments. We performed optical transmission measurements using a Flame-S spectrometer with a halogen light source (Ocean Optics, USA) and determined the thickness of the plain TiO_2 substrate by analyzing the interference pattern in the spectral transmittance [11]. We employed Bruggeman's effective medium approximation to estimate the refractive index of the porous substrate [12]. To validate this optical measurement for substrate thickness, we also conducted direct observations of the substrate's cross section using a scanning electron microscope (SEM; JSM-7500F, JEOL, Japan). We fractured the entire sample (TiO_2 substrate and glass plate) after making a scratch on the glass plate using a glass cutter. The glass plate caused surface charging during SEM observation; therefore, we

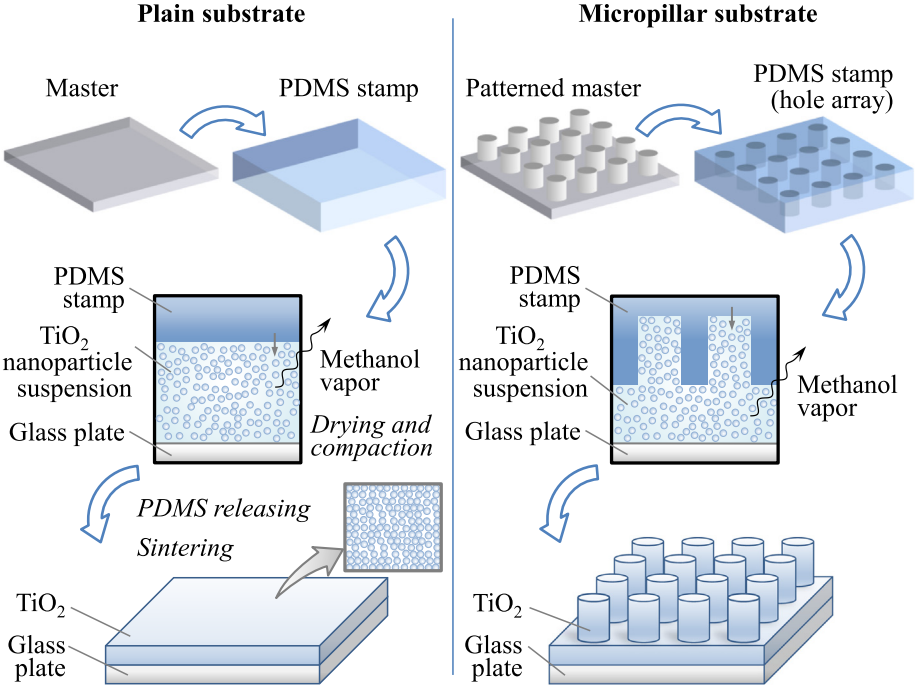

Fig. 1. Schematic of soft lithography processes for the fabrication of TiO_2 sintered-nanoparticle substrates (left: plain substrate; right: micropillar substrate).