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Preparation of self-cleaning surfaces with a dual functionality of superhydrophobicity and photocatalytic activity

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ABSTRACT

Thin film of polydimethylsiloxane (PDMS) was deposited on SiO_2 nanoparticles by chemical vapor deposition, and SiO_2 became completely hydrophobic after PDMS coating. Mixtures of TiO_2 and PDMS-coated SiO_2 nanoparticles with various relative ratios were prepared, and distributed on glass surfaces, and water contact angles and photocatalytic activities of these surfaces were studied. Samples consisting of TiO_2 and PDMS-coated SiO_2 with a ratio of 7:3 showed a highly stable superhydrophobicity under UV irradiation with a water contact angle of 165° and UV-driven photocatalytic activity for decomposition of methylene blue and phenol in aqueous solution. Our process can be exploited for fabricating self-cleaning surfaces with dual functionality of superhydrophobicity and photocatalytic activity at the same time.

1. Introduction

"Self-cleaning" behavior refers to the phenomenon that various contaminants on solid surfaces can be eliminated under natural circumstances [1–3]. One of the most widely known self-cleaning surface structures mimics lotus leave surface, on which nano-structured hydrophobic domains and micrometer-scale roughness superimpose, resulting in a surface dual roughness and hydrophobic surface functionality at the same time. On such surfaces, air pockets existing between dual-roughness surfaces and water droplet can repel water, and therefore, water droplet does not wet but roll on the surface [1,4–8]. Superhydrophobicity generally refers to the surface structure with a water contact angle exceeding 150°. Water droplets on superhydrophobic surfaces can sweep dust particles existing on the surface, i.e., dust particles deposited on such surfaces can efficiently be removed under rain.

Photocatalysis can be used in various research and application fields of environmental and energy sciences [9]. Photocatalytically active materials are generally wide band-gap semiconductive inorganic compounds, which can absorb either UV or visible light with their energies exceeding band-gap energy of photocatalyst. Light absorption leaves electrons in the conduction band and holes in the valence band, which can participate in redox reactions with adsorbed species such as water and oxygen. For example, TiO_2, which has a band-gap energy of 3.0–3.2 eV, can absorb UV light. In this case, the photogenerated electrons can be trapped by O_2 to form O_2^-, and the holes in the valence band can react with water to form OH radical [10–12]. Therefore, organic molecules adsorbed on photocatalytically active surfaces can be decomposed by these strongly oxidizing agent (O_2^- and OH radicals), ultimately being transformed into H_2O and CO_2. Particularly, interaction of H_2O and hole forming OH radical has been regarded as the most crucial step for the photocatalytic reactions [13]. Photocatalytic activity of TiO_2 was correlated with the number of hydrophilic surface functional groups such as OH-group, showing importance of TiO_2–water interaction in photocatalysis [14–19].

The aim of our work is preparing surface structures, which are superhydrophobic and photocatalytically active at the same time, by distribution of nanoparticles on various solid surfaces of a large area. Superhydrophobicity is a macroscopic phenomenon: superhydrophobicity can appear even when a surface is not completely covered by hydrophobic functionality, i.e., surfaces covered with superhydrophobic domains with a sufficiently large coverage on the surface can show superhydrophobicity [20,21]. Photocatalysis is based on interaction between photo-excited electron-hole pairs and oxygen/water molecules, i.e., photocatalysis can be regarded as a molecular phenomenon. When a photocatalytically active

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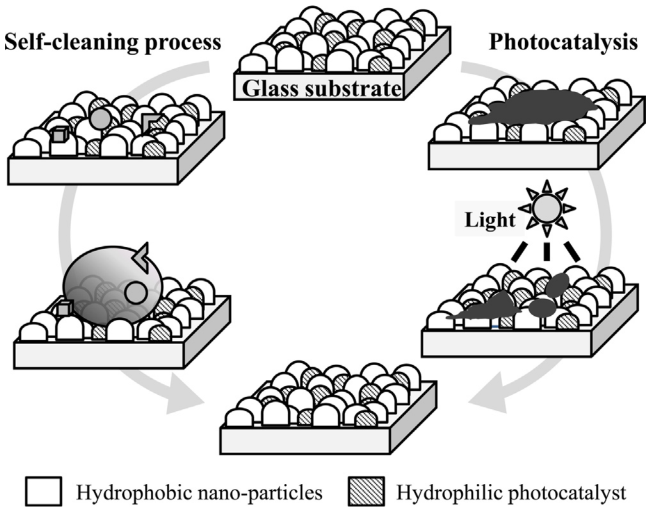

Fig. 1. Schematic diagram of self-cleaning process on photocatalyst film with superhydrophobicity is presented.

surface is properly structured and a sufficiently large portion of surface is covered by hydrophobic functionality, the surface can repel water droplets, yet molecular entity of water vapor can still strongly interact with non-hydrophobic part of the surface, initiating photocatalytic process [22–25]. Such surface structures with both superhydrophobicity and photocatalytic activity can show self-cleaning behavior in various environments: when dust particles are deposited on the surface, water droplets (for example from rain) can roll on the surface, sweeping the dust particles. On the other hand, the organic pollutants deposited on the surface can be photocatalytically decomposed into CO_2 and H_2O vapor (Fig. 1).

2. Experimental

2.1. Sample preparation

The first step of fabrication of dual functional self-cleaning surface is coating SiO_2 nanoparticle (Sigma–Aldrich, purity 99.8%, mean particle size = 12 nm) with hydrophobic polydimethylsiloxane (PDMS) layer. PDMS-coated SiO_2 nanoparticles were prepared by stacking fluidic PDMS (Dow Corning, Sylgard 184) and SiO_2 nanoparticles (weight ratio between fluidic PDMS and SiO_2 nanoparticle was 1:1) in a stainless steel chamber and subsequently heating it up to 300 °C. This temperature of the chamber was maintained for 12 h. During the heating process, PDMS vaporized and deposited on SiO_2 nanoparticles forming hydrophobic thin films. Previously, we have shown that the resulting PDMS-layer thickness does not exceed ~5 nm [26].

Photocatalytically active surfaces can be prepared by dispersing TiO_2 nanoparticles (Degussa, p-25) on an adhesive surface (Fig. 2). On a glass substrate (2 cm × 2 cm), thin layer of a mixture of PDMS and curing agent was homogeneously dispersed and partially cured for 40 min at 60 °C (the weight ratio of Sylgard 184 to curing agent was 10:1). Subsequently, TiO_2 nanoparticles were placed on top of the partially cured PDMS elastomer layer and pressurized to improve the adhesion of nanoparticles on the surface. After the PDMS substrate was completely cured, particles not adhering to the surface were removed using compressed air. In order to make the photocatalyst film surface superhydrophobic, TiO_2 nanoparticles were mixed with PDMS-coated SiO_2 and dispersed on glass substrate (the relative amounts of PDMS-coated SiO_2 and TiO_2 were varied). Depending on the ratio of TiO_2 and PDMS-coated SiO_2, hydrophobicity and photocatalytic activity of the surface were altered.

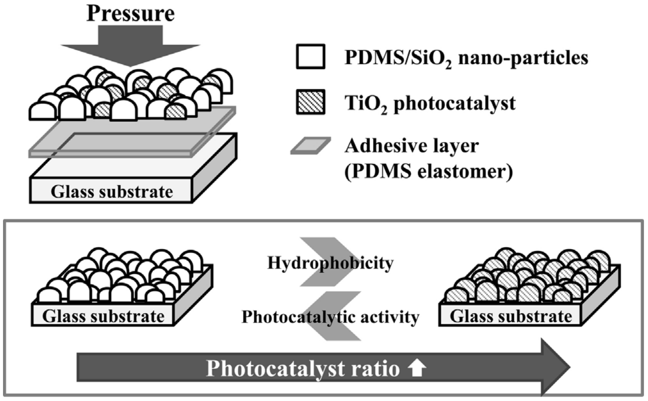

Fig. 2. Schematic diagram of the preparation process of superhydrophobic photocatalyst film is presented. Photocatalyst films with various TiO_2/SiO_2 ratios were prepared.

2.2. Characterization

In order to verify the superhydrophobicity of the prepared surfaces, the water contact angle was measured using Theta Optical Tensiometer modal (KSV instruments, Ltd.) with a digital camera connected to a computer. KSV bundled software, One Attension, was used and Young-Laplace fitting method was employed for contact angle determination. A droplet of distilled water with a volume of 3 μl was deposited and water contact angles were measured three times at different positions on a sample surface and the average value was calculated. In addition, the stability of water contact angle of various films (TiO_2: 0, 20, 30, 40, 50, 80, 100%) under UV irradiation was tested. Prepared photocatalyst films were placed in a petri dish with 20 ml of distilled water and irradiated with UV light (254 nm) for up to 20 h. Every 2 h, the sample was dried for 1 min under dark condition and the water contact angle was measured. In addition, FT-IR spectroscopy was used to characterize the surface

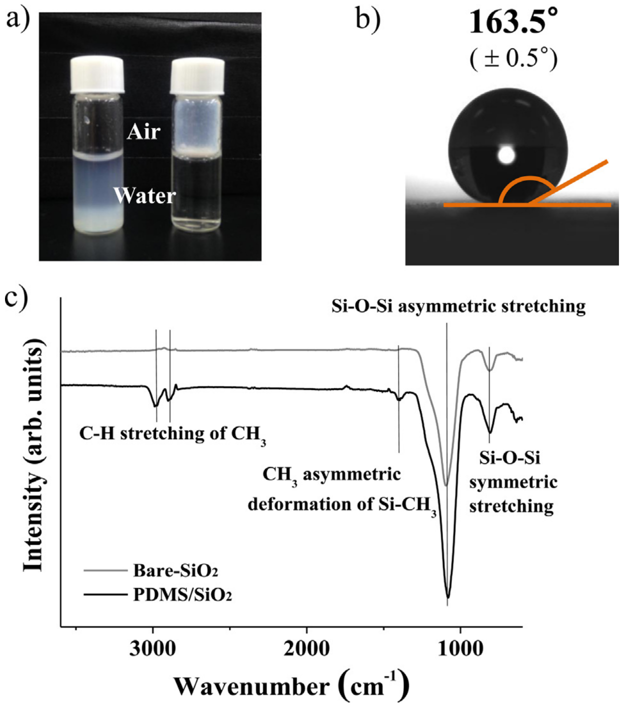

Fig. 3. (a) Optical picture of bare and PDMS-coated SiO_2 nanoparticles on water (b) water contact angle of the surface consisting of PDMS-coated SiO_2 nanoparticles (c) FT-IR spectra of bare and PDMS-coated SiO_2 nanoparticles are displayed.

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