

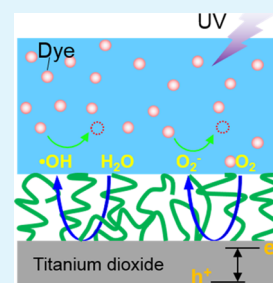
Optimizing Hydrophobicity and Photocatalytic Activity of PDMS-Coated Titanium Dioxide

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ABSTRACT: Polydimethylsiloxane (PDMS) can be linked to the surface of metal-oxide photocatalysts by immersion and UV illumination. The surfaces become hydrophobic and keep their hydrophobicity even under extended UV exposure. Titanium dioxide (TiO_2) is a prominent example of a metal-oxide photocatalyst. Here, we studied the influence of a grafted PDMS layer on the photocatalytic activity and wetting properties of TiO_2 . By varying the molecular weight of PDMS, we controlled the thickness of the polymer layer from 0.6 to 5.5 nm. We recommend a PDMS molecular weight of 6.0 kDa. It leads to a grafted PDMS layer thickness of 2.2 nm, a receding contact angle of 94° , a low contact angle hysteresis of 9° , and the layer is still photocatalytically active.

KEYWORDS: hydrophobic, photocatalytic, wetting, grafted PDMS layer, titanium dioxide



INTRODUCTION

Designing and creating active, robust, and inexpensive catalysts is the basis for practical applications of catalysis.^{1,2} Metal-oxide photocatalysts are one category in the family of catalysts that are broadly applied in both scientific research and industry, from water and air purification to anti-biofouling, water splitting, and organic synthesis.^{3–6} In semiconducting metal-oxide photocatalysis, light generates electron–hole pairs, which are responsible for the catalytic effect.⁷ To make a catalyst more effective, its inner composition and interfacial properties need to be controlled.^{3,8,9} Metal/metal-oxide hybrids have been developed to spatially separate charges within the nanoscale photocatalysts.^{8,9} Specific wetting property of the catalyst surface is also designed to enhance the compatibility of the catalyst to solvent.^{10–13}

When catalysts possess a hydrophobic surface and when they have the appropriate surface nanostructure and microstructure, they become superhydrophobic. Superhydrophobic catalysts were discovered to have enhanced catalytic activity when introducing an air layer between the catalyst and liquid.^{3,14} The charges from the reacting interface are transferred fast to radicals by acceptors such as oxygen.^{3,15–17} Enough oxygen in the air layer can effectively capture electrons and form radicals, thus minimizing the electron–hole recombination.^{18,19} These tri-phase (air–liquid–solid) catalytic systems demonstrate higher photocatalytic activity than conventional liquid/solid di-phase systems.

Two issues need to be considered in designing hydrophobic catalysts: (i) the organic coating is exposed to charges and radicals.^{20,21} As a result, the surface hydrophobicity decreases due to chemical degradation.^{22–24} (ii) The blocking effect of the hydrophobic coating on the transfer of the charges and radicals from the catalyst's surface to reactants decreases the catalytic effect. Therefore, it is still a challenge to combine robust hydrophobicity with high catalytic activity.

Wooh et al.²⁵ found that metal-oxide photocatalysts can be coated with stable polydimethylsiloxane (PDMS) “brush” by simply immersing the photocatalyst in a melt or solution of PDMS and shining UV light. Here, we use the term “grafted polymer layer” because individual chains may have more than one anchor point on the surface. Photocatalysts, which are functionalized in this way, retain their hydrophobicity even under strong UV light illumination ($5 \pm 0.5 \text{ mW/cm}^2$) for more than 30 h. These grafted PDMS layers resist charge and radical degradation under both UV light and catalysis. The question arises to which degree such grafted PDMS layers block the photocatalytic activity. PDMS layers exceeding a certain thickness may hinder the formation of radicals or the transfer of electrons to the water, finally stopping catalysis.

Here, we graft PDMS layers to titanium dioxide (TiO_2) surfaces to investigate the influence of layer thickness, H , on the photocatalytic activity. The aim is to provide scientific guidance to optimize the photocatalytic activity while at the same time keeping hydrophobicity. The thickness of the grafted PDMS layer is regulated by the molecular weight M_w of the PDMS.

EXPERIMENTAL SECTION

Preparation of Substrates. Aqueous solution of TiCl_4 (0.1 M) was spin-coated (4000 rpm, 40 s) onto an oxygen plasma-modified glass or silicon wafer. By annealing at 500°C for 30 min, the TiCl_4 precursor was hydrolyzed to form thin TiO_2 layers with a thickness of ≈ 6 nm. Mesoporous TiO_2 films were prepared by the deposition of TiO_2 pastes (18NR-T and WER2-O) onto glass substrates ($22 \times 22 \text{ cm}^2$) using the doctor blade method.²⁵ The coated pastes were sintered at 500°C for 30 min to remove the organic moieties.

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Grafting PDMS onto the TiO₂ Film. Trimethylsiloxy-terminated PDMS was grafted to the TiO₂ surfaces as shown in Figure 1A.

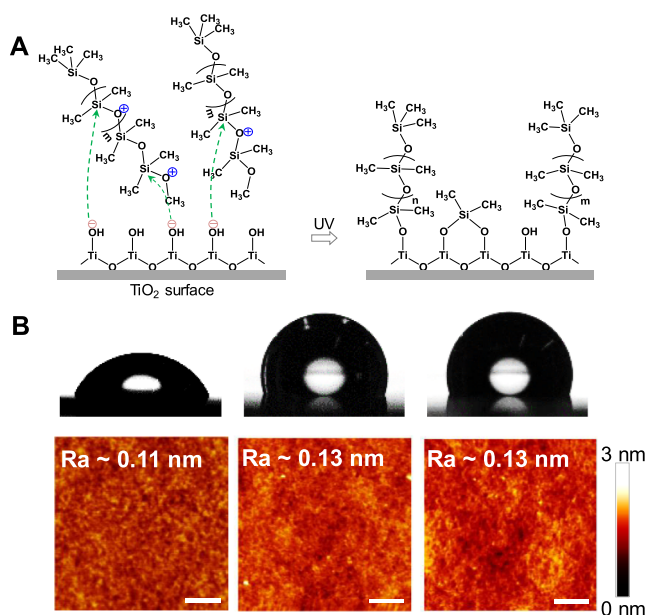


Figure 1. Contact angle and morphology of grafted PDMS layer. (A) Schematic of PDMS grafting reaction on the TiO₂ surface. A top-down method was applied that PDMS could be directly grafted onto the surface via UV illumination through the formation of Si–O–Ti bonds. (B) Contact angles of water droplets (5 μL) on a bare TiO₂ surface (left) and TiO₂ coated with 2.2 nm (M_w : 6.0 kDa, middle) and 4.0 nm (M_w : 17.3 kDa, right) PDMS. AFM images taken with tapping mode show the morphologies of the corresponding surfaces.

Therefore, the samples were immersed in PDMS under UV illumination (wavelength: 315–380 nm; light source: LQ-400, Dr. Gröbel UV-Elektronik GmbH, UV light intensity: 2.6 mW/cm²) for 1 h. The light intensity was measured using an UV radiometer sensor (RM-12 with UV-A (315–380 nm), Dr. Gröbel UV-Elektronik GmbH). After illumination, free PDMS was thoroughly washed away with toluene, *n*-hexane, and tetrahydrofuran. PDMS grafted in this way to TiO₂ cannot be rinsed off again even under extensive washing in toluene or hexane for 30 min. Therefore, we assume that a covalent bond is formed.

Characterization of the Grafted PDMS Layer on the TiO₂-Covered Surface. The morphology of the grafted PDMS layer on the TiO₂-covered glass was characterized using tapping mode of atomic force microscopy (AFM, Multimode TUNA/Torsion). The wetting properties of the surfaces were investigated using a contact angle detector equipped with a side camera (IDS uEye camera) and a goniometer. The thickness of the grafted PDMS layer on TiO₂-covered silicon wafer was measured by ellipsometry (Nanofilm surface analysis EP3, 532 nm, 50 mW).

Measurement of the Photocatalytic Effect. To measure the photocatalytic efficiency, we monitored the degradation of 3 mL fluorescent dye ATTO 488 (concentration 1 μg/mL) by PDMS-modified surfaces in aqueous solution after being illuminated by UV light for different times. The intensity of the UV light was controlled by the distance between the light source and surface. To inhibit the evaporation of water during long-time illumination, the samples were placed in closed chambers with quartz glass caps (thickness 170 μm).

RESULTS AND DISCUSSION

When TiO₂ was modified with PDMS, the static contact angles of water change from $63^\circ \pm 1^\circ$ to $103^\circ \pm 1^\circ$ for $M_w = 6.0$ and 17.3 kDa (Figure 1B). The morphologies of TiO₂ surfaces grafted with PDMS of different layer thicknesses were

characterized by AFM with tapping mode. The TiO₂ layer on-top has a very low roughness of around 0.11 nm. The roughness changes little when grafted with PDMS layers of different thicknesses. The low roughness of surfaces guarantee that all surfaces have a similar contact area between water and substrate.

The advancing and receding contact angles of water on grafted PDMS layers demonstrate a close relationship to UV illumination time (Figure 2). The contact angle hysteresis

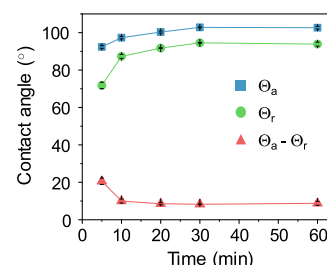


Figure 2. Wetting property of grafted PDMS layer on TiO₂ surfaces. Advancing (Θ_a), receding (Θ_r) contact angles and contact angle hysteresis (Θ_a - Θ_r) of surfaces with different exposure times to UV during the grafting process. $M_w = 6.0$ kDa.

decreases from $\approx 21^\circ$ to $\approx 9^\circ$ when the reaction time was extended from 5 to 20 min. Advancing (Θ_a), receding (Θ_r) contact angles and contact angle hysteresis (Θ_a - Θ_r) almost keep unchanged when the reaction time exceeded 20 min (UV intensity: 2.6 mW/cm²). The unique droplet dewetting performance of the PDMS layer is considered to be related to the high mobility of the chains.²⁶

The PDMS layer thickness increases with the molecular weight. It could be controlled to be 0.6, 2.2, 4.0, and 5.5 nm, respectively (Figure 3A), with M_w of 1.3, 6.0, 17.3, and 28.0 kDa. When plotting the PDMS layer thickness versus the molecular weight in a log–log plot, roughly a straight line with a slope around 0.66 ± 0.3 was obtained. We can determine the grafting density by $\sigma = (H\rho N_A)/M_w$; where ρ is the bulk

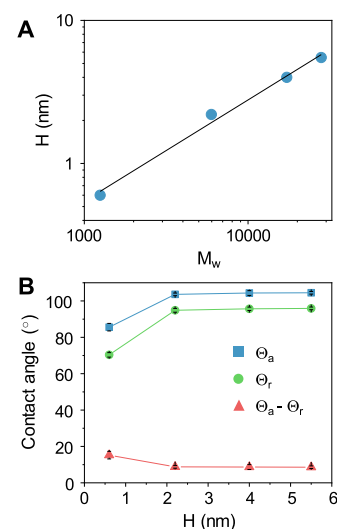


Figure 3. Evolution of wetting property with PDMS layer thickness. (A) Thickness of the grafted PDMS layer on the TiO₂ surface as a function of the molecular weight (reaction time: 1 h, UV intensity: 2.6 mW/cm²). (B) Contact angles of water on grafted PDMS layers on TiO₂ for different layer thickness H .

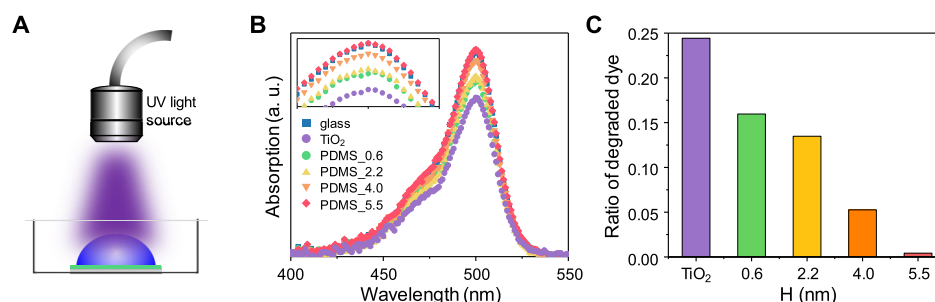


Figure 4. Effect of the grafted PDMS layer thicknesses on photocatalytic activity of TiO_2 surfaces. (A) Illustrated schematic presents the setup used to characterize the photocatalytic activity of surfaces. UV light illumination: 5 h at 2.6 mW/cm^2 . (B) UV-vis spectrum shows degradation of ATTO 488 in aqueous solution as function of H . (C) Ratio of degraded dye by modified TiO_2 surfaces with different PDMS thicknesses.

density of polymer and N_A is the Avogadro's number.^{27,28} Grafting densities between $2.8, 2.1, 1.3,$ and $1.1 \times 10^{17}/\text{m}^2$ are obtained for the four molecular weights (from 1.3 to 28.0 kDa), respectively. For the PDMS with higher molecular weight, the volume or space occupied by one polymer molecule on the surface is bigger. This increases the barrier for the next arriving polymer to form dense polymer brush layer and thus decreases the grafting density. We do, however, not take this high grafting density as an indication for a brushlike structure because each chain may have more than one attachment point. Thus, chains do not have to extend normal to the surface.

The advancing and receding contact angles increases with the thickness of the PDMS layer (Figure 3B). Starting with a thickness of 2.2 nm, they saturate at $\Theta_a = 103^\circ$ and $\Theta_r = 94^\circ$. At the same time, contact angle hysteresis decreases from 15° at $H < 2.2 \text{ nm}$ to $\approx 9^\circ$ for $H \geq 2.2 \text{ nm}$. Thus, a PDMS layer of 0.6 nm thickness is not sufficient to repel water. The grafted PDMS layer blocks the contact with water when $H \geq 2.2 \text{ nm}$.

To measure the photocatalytic efficiency, we monitored the degradation of the fluorescent dye ATTO 488 (concentration $1 \mu\text{g/mL}$) by PDMS-modified surfaces in aqueous solution (Figure 4A). The intensity of the UV light was 2.6 mW/cm^2 , controlled by the distance between the light source and surface. To inhibit the evaporation of water during long-time illumination, the samples were placed in closed chambers with quartz glass caps (thickness $170 \mu\text{m}$). The contact area between the solution and catalyst was fixed by the size of the circular substrate (diameter: 24 mm). The volume of dye solution was 3 mL. As the roughness of TiO_2 and the PDMS-modified surfaces is very low, the contact areas of different surfaces were the same. The degradation ratio of dye was measured at different illumination times via UV-vis absorption spectrometry (Figure 4B). The degradation of dye on a neat glass surface was used as a contrast. We calculated the degradation ratio by dividing the UV absorption of ATTO 488 on glass by that on other surfaces after 5 h illumination (Figure 4C).

For $H = 2.2 \text{ nm}$, the TiO_2 surface is still photocatalytically active and at the same time hydrophobic. When $H > 2.2 \text{ nm}$, the degradation ratio decreases significantly with increasing PDMS layer thickness. At a PDMS layer thickness of 5.5 nm, the photocatalytic activity was lost. Therefore, we conclude that even though the catalyst surfaces are blocked to be in contact with the aqueous solution, they still have some catalytic activity when the PDMS layer thickness is in the range of 2.2–4.0 nm.

Additionally, we monitored the degradation of the fluorescent dye ATTO 488 (concentration $1 \mu\text{g/mL}$) by PDMS-modified porous TiO_2 surfaces (Figure 5A) in aqueous

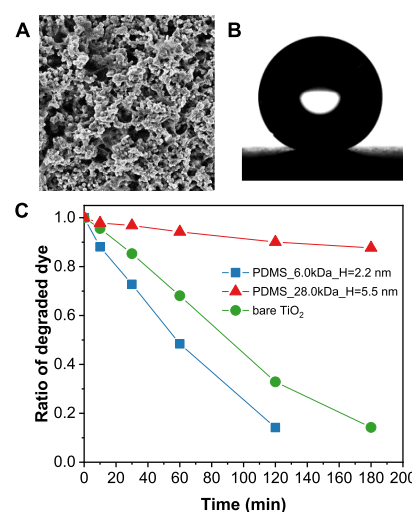


Figure 5. Photocatalytic activity of superhydrophobic TiO_2 surfaces modified with PDMS. (A) Scanning electron microscopy image of PDMS-grafted porous TiO_2 surface. M_w : 6.0 kDa. Scale bar: 300 nm. (B) Side-view image of a water drop ($5 \mu\text{L}$) on a flat PDMS-grafted porous TiO_2 surface. M_w : 6.0 kDa. (C) Variation of the dye concentrations as a function of illumination time under UV light (intensity: 5 mW/cm^2) for porous TiO_2 surfaces. The intensity of the UV light was 5 mW/cm^2 . The volume of dye solution was 3 mL.

solution. Figure 5B shows that the porous TiO_2 surfaces was superhydrophobic and the contact angle of $5 \mu\text{L}$ water droplet was around 160° when the surfaces were modified with a PDMS layer. As shown in Figure 5C, when the surface was modified with a PDMS layer of $H = 2.2 \text{ nm}$, the photocatalytic activity of the surface was enhanced comparing to the bare TiO_2 . In contrast, the surface modified with a PDMS layer of $H = 5.5 \text{ nm}$ demonstrated very low photocatalytic activity, indicating blocking of the photocatalytic activity by the thick PDMS layer.

CONCLUSIONS

In conclusion, we recommend a PDMS molecular weight of 5–15 kDa. It leads to a grafted PDMS layer thickness of 2–4 nm. In that range, the surfaces are already hydrophobic, possess low contact angle hysteresis, and still show significant photocatalytic activity. The photocatalytic activity is enhanced for the superhydrophobic TiO_2 with a PDMS layer of 2.2 nm

comparing with bare TiO₂. The PDMS layer reduces the photocatalytic activity of the superhydrophobic TiO₂ when it is thicker than 5 nm. Our work will be helpful to develop guidelines for modifying catalyst surfaces with hydrophobic properties and simultaneously maintain high catalytic activity.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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