

화학적 증기 증착 방법을 통해 제조한 소수성 폴리디메틸실록산 박막: 수처리로의 응용

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Hydrophobic Polydimethylsiloxane Thin Films Prepared by Chemical Vapor Deposition: Application in Water Purification

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초 록

폴리디메틸실록산(PDMS)은 화학적 증기 증착 방법을 통해 다양한 물질에 5 nm 두께 이하의 박막 형태로 증착될 수 있다. SiO₂, TiO₂, ZnO, C, Ni 및 NiO와 같은 다양한 종류의 나노입자 표면에도 PDMS 박막은 증기 증착을 통해 고르게 형성될 수 있으며, PDMS가 증착된 표면은 완벽한 소수성을 갖게 된다. 이 소수성 박막은 안정성이 높아 산, 염기 및 자외선 노출 시에도 잘 분해되지 않으며, 또한 PDMS로 코팅된 나노입자는 다양한 환경 분야에 응용될 수 있다. PDMS 코팅된 소수성 SiO₂ 입자는 기름/물 혼합액에서 기름과 선택적으로 반응하고, 기름 유출 사고 시 유류 확산을 억제할 수 있으며, 유출된 기름을 물에서 물리적으로 쉽게 분리할 수 있게 해준다. PDMS 코팅된 TiO₂를 진공 상태에서 열처리 할 경우 TiO₂ 표면은 완전하게 친수성으로 개질되며, 이때 TiO₂가 가시광선을 흡수하여 반응할 수 있게 하는 산소 빈자리 또한 발생하게 된다. PDMS 코팅 후 열처리한 TiO₂는 아무 처리하지 않은 TiO₂에 비해 가시광 하에서 수중의 유기 염료를 분해하는데 더 뛰어난 광촉매 활성을 보인다. 우리는 해당 연구에서 제시하는 간단한 PDMS 박막 코팅 방법이 다양한 환경 과학 및 공학 분야에서 응용될 수 있음을 소개하고자 한다.

Abstract

Polydimethylsiloxane (PDMS) can be deposited on various substrates using chemical vapor deposition process, which results in the formation of PDMS thin films with thickness below 5 nm. PDMS layers can be evenly deposited on surfaces of nanoparticles composed of various chemical compositions such as SiO₂, TiO₂, ZnO, C, Ni, and NiO, and the PDMS-coated surface becomes completely hydrophobic. These hydrophobic layers are highly resistant towards degradation under acidic and basic environments and UV-exposures. Nanoparticles coated with PDMS can be used in various environmental applications: hydrophobic silica nanoparticles can selectively interact with oil from oil/water mixture, suppressing fast diffusion of spill-oil on water and allowing more facile physical separation of spill-oil from the water. Upon heat-treatments of PDMS-coated TiO₂ under vacuum conditions, TiO₂ surface becomes completely hydrophilic, accompanying formation oxygen vacancies responsible for visible-light absorption. The post-annealed PDMS-TiO₂ shows enhanced photocatalytic activity with respect to the bare TiO₂ for decomposition of organic dyes in water under visible light illumination. We show that the simple PDMS-coating process presented here can be useful in a variety of field of environmental science and technology.

Keywords: PDMS, hydrophobicity, hydrophilicity, water purification

1. Introduction

Hydrophobic surface modification of nanomaterials has been extensively studied so far due to its potential applications in a variety of fields. For the preparation of composite materials of organic polymers and inorganic nanomaterials, hydrophobic surface modification of nanomaterials can be useful, since the hydrophobization can inhibit ag-

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glomeration of nanomaterials in a polymer medium[1,2]. It is notable that high dispersion of nanomaterials in the polymer has been shown to be important for enhanced mechanical and electrical properties of composite materials[1,2]. Hydrophobic surface modification of nanostructured surfaces with dual surface roughness can show superhydrophobicity with water contact angle higher than 150° [3-18]. On such surfaces, water droplets can roll on the surface, which can cause self-cleaning of surfaces contaminated by dust particles[5,18-24]. It is worth noting that water droplets on such surfaces can be repelled by air pockets existing between water droplets and hydrophobic and dual-roughness-structured surfaces.

In addition, materials with hydrophobic surface properties can be used for removing spill-oils and nonpolar organic solvents, since these surfaces can selectively interact with those contaminants without having interaction with water[25]. Absorbents of oils and organic solvents in the forms of powder, pad and booms have been developed for protecting water from contamination by oils and organic solvents[25-29].

Most widely used techniques of hydrophobic surface modifications use silane-based agents, and here, condensation reactions between hydroxyl groups on the surface of solid and those of the agents are used for the surface treatments; this method is, however, limited to modification of the surfaces consisting of OH terminal groups. Organic agents such as stearic acid can also be used for hydrophobic surface modification; however, these organic molecules can often be decomposed under harsh conditions such as acidic and basic ones and under UV irradiation. One can rarely find a method for surface hydrophobization, which can provide hydrophobic surface property to various materials independent of the chemical composition of materials, and high stability of hydrophobic layers.

In this article, surface structures of polydimethylsiloxane (PDMS)-coated nanostructures and their applications in wastewater treatments are summarized[4,6,7,9,11,25,30]. For the formation of thin PDMS-layer on various nanomaterials, chemical vapor deposition (CVD) has been utilized. We show that CVD of PDMS layers can be advantageous in applications due to high chemical stability and to the fact that this method of hydrophobic coating can be applied to various nanomaterials with different chemical compositions.

2. Experimental

2.1. Synthesis of PDMS-layers on nanomaterials

There are two different methods for the preparation of PDMS-layers on nanomaterials. PDMS and curing agent can be mixed with a 10 : 1 ratio and cured for 24 hours. Then, small pieces of cured PDMS and substrates (powder) are put in a beaker, the bottom of which is heated to 200-300 $^\circ\text{C}$ for several hours. Note that the heating temperature and time are dependent on the materials we use as substrates. Alternatively, one can put fluidic PDMS without curing agent on the bottom of a reactor. After putting a mesh on top of the fluidic PDMS, powders are heaped on the mesh. This process allows physical separation of fluidic PDMS and powder, and therefore, the relative expensive curing agent is not required. After the reactor is closed, the bottom of the reactor

is heated to 200-300 $^\circ\text{C}$ for several hours. Some of PDMS is vaporized and deposited on the surface of nanomaterials, forming hydrophobic thin layers.

2.2. Structure analyses

The water contact angles of the samples were measured using Theta Optical Tensiometer model (KSV Instruments, Ltd.) and electro-optics comprised of a digital camera connected to a computer (software Attension Theta). For the characterization of functional groups of sample surfaces, a Fourier-transformed infrared spectrometer (FT-IR, BRUKER, Optics/vertex 70) was used. IR spectra were recorded using 64 scans with a 4 cm^{-1} resolution. Morphological images of samples were obtained using scanning electron microscopy (SEM, JEOL, JSM7001F), atomic force microscopy (AFM, NT-MDT, NTEGRA spectra) and transmission electron microscopy (TEM, JEOL, JEM2100F).

2.3. Weight gain determination

10 g of oil and samples were homogeneously mixed in a beaker, and the oil/SiO₂ mixture was put on top of a metal mesh (opening : 595 μm) for 10 minutes[25]. After 10 minutes, the mixture of oil/SiO₂ on top of the mesh was collected and its weight was recorded. The weight of this mixture was divided by the original weight of the absorbents used for the determination of "weight gain".

2.4. Photocatalysis experiments

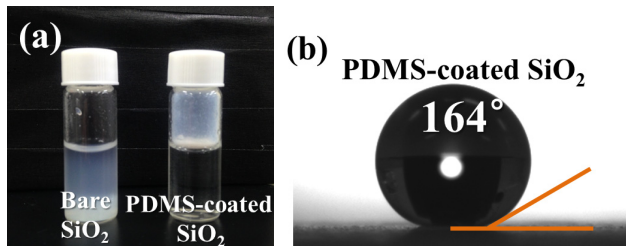
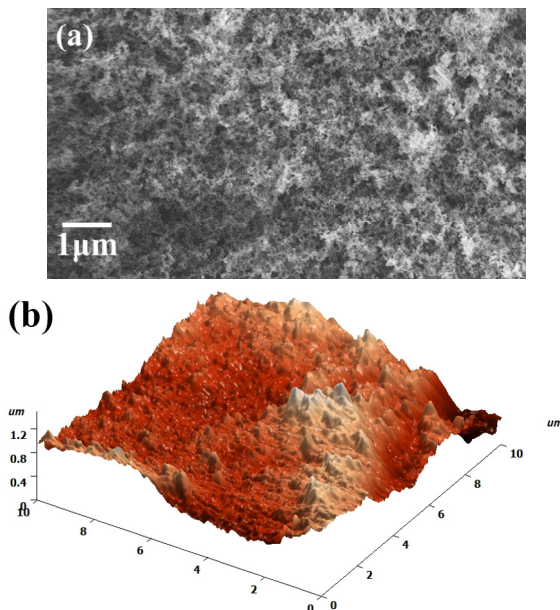
Adsorption and photocatalytic degradation of methylene blue (MB) over bare TiO₂ (Degussa, P-25) and h-TiO₂ were investigated by monitoring the absorbance of MB in aqueous solution as a function of time[30]. For the preparation of h-TiO₂, TiO₂ was coated with PDMS and then the resulting sample was annealed at 800 $^\circ\text{C}$ under rough vacuum conditions. MB absorption spectra were measured using UV-Vis spectroscopy (OPTIZEN 3220UV) in the range from 400 nm to 800 nm and absorbance values at maximum absorbance wavelength were recorded. TiO₂ solution was prepared by dispersing 0.01 g of TiO₂ sample in 50 mL of distilled water with 10 minutes of sonication. Then, an aliquot of TiO₂ solution (0.1 mL) was added to 1 ppm of MB solution (3.9 mL) in a disposable cuvette ($1 \times 1 \times 4.5\text{ cm}^3$). Three cuvettes with resulting solutions were prepared for each TiO₂ sample and the average values were used. The cuvettes were first kept in a dark condition (adsorption step) for 40 minutes and then exposed to the blue light emitting diode (LED) irradiation (photocatalysis step) for 10 hours in a black box with an interval time of 2 hours.

3. Hydrophobic Coating of Nanoparticles Using CVD of PDMS

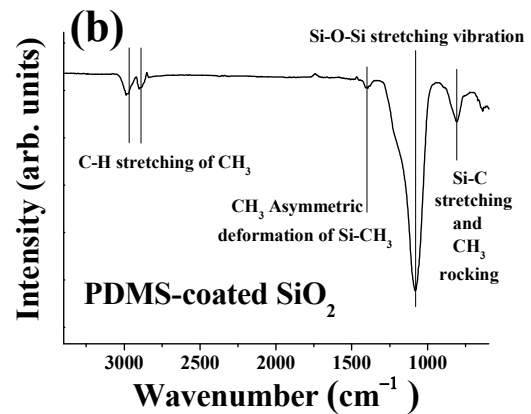
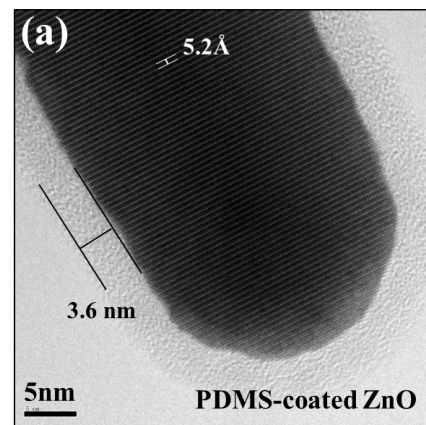
One of the most important advantages of CVD of PDMS for the preparation of hydrophobic coating is that the same methods can be applied to a variety of materials consisting of different chemical elements. So far, hydrophobic PDMS layer was successfully formed on nanostructures of SiO₂, TiO₂, ZnO, Ni, and carbon using chemical vapor deposition, indicating that formation of PDMS thin layers on the

Table 1. Water Contact Angles of Surfaces of Various Nanomaterials Coated by PDMS are Summarized in the Table. Independent of the Chemical Composition of Nanomaterials, Thin PDMS-layers can Successfully be Formed, Resulting in Superhydrophobic Nature of the Surfaces

Substrates	Activated carbon	TiO ₂	ZnO	Ni
Water Contact Angle (°)	166	163	164	166


Figure 1. (a) Picture of bare and PDMS-coated SiO₂ nanoparticles put on water is shown. (b) The result of water contact angle measurement of a surface consisting of PDMS-coated SiO₂ nanoparticles is presented.

Figure 2. (a) SEM and (b) AFM images of PDMS-coated SiO₂ nanoparticles distributed on the surface of a glass are displayed.

solid surface does not necessarily have to accompany strong chemical interaction between PDMS and solid surface[4,6,7,9,11,25]. As shown in Figure 1 and Table 1, surfaces prepared by distributed PDMS-coated nanoparticles of various chemical compositions show superhydrophobicity with a water contact angle higher than 160°. It is remarkable to note that originally hydrophilic SiO₂ nanoparticles with its density higher than that of water can become completely hydrophobic upon PDMS-coating so that PDMS-coated SiO₂ nanoparticles can be perfectly floated on water (Figure 1 (a))[25]. As shown in Figure 2, surfaces of distributed nanoparticles typically show dual surface roughness, in which nanometer-scale roughness of individual particle size is superimposed by sub-micrometer-scale roughness due to aggregation of nanoparticles[9]. Water droplets on such dual-roughness-surface with hydrophobicity can be repelled by air pockets existing at interfaces, re-


Figure 3. Results of analysis of PDMS-coated nanostructures are shown. (a) TEM images of PDMS-coated ZnO. (b) FT-IR spectrum of PDMS-coated SiO₂.

sulting in phenomena that water droplets do not wet but roll on the surface.

As shown in the TEM image of Figure 3 (a), PDMS can typically form a thin homogeneous layer with a thickness of 3-5 nm[4]. FT-IR spectroscopy data of PDMS-coated nanostructures show evidence that molecular framework of PDMS is sustained in these thin PDMS-layers (Figure 3 (b))[25]. After the PDMS-coating, typically, additional peaks appear, and these peaks can be attributed to C-H stretching vibrations (3000 and 2900 cm⁻¹), asymmetric deformations of the Si-CH₃ (1400 cm⁻¹), the Si-C stretching and CH₃ rocking (750-900 cm⁻¹) of PDMS. Mechanism of CVD of PDMS is still to be unveiled. The most probable scenario is that PDMS with relatively low molecular weight can evaporate as a polymeric entity and be deposited on the surface of substrates. Diffusion of this precursor in the vapor seems to be much faster than deposition rate on the surface, resulting in a homogeneous coating of PDMS-layer on nanoparticles heaped in our deposition-reactor.

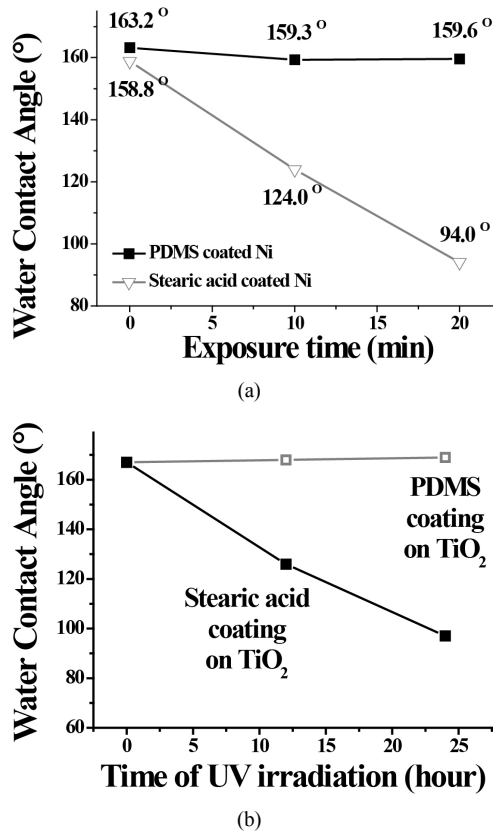


Figure 4. Summary of the stability test of PDMS-layer on nanoparticles. (a) Stearic acid and PDMS layers on Ni were exposed acidic condition (pH = 2.5) and the water contact angle was measured as a function of exposing time to acidic environments. (b) Stearic acid and PDMS layer on TiO₂ were exposed UV light with maximum intensity at 254 nm wavelength.

4. Stability of Hydrophobic PDMS-coating

For a practical application of PDMS-layers on various nanostructures, the stability of these PDMS-layers is an important issue. We compared the stability of stearic acid and PDMS coating on Ni particles under acidic environments (pH 2.5), and the results are shown in Figure 4[11]. The stearic acid coating was not stable and therefore, superhydrophobic nature of surface consisting of Ni particles with stearic acid disappeared upon exposure to the acidic medium. In contrast, PDMS coating was stable, and superhydrophobicity of PDMS-coated Ni was sustained under acidic conditions. We tested the chemical stability of PDMS-coating under even harsher conditions : the PDMS-coated Ni particles were immersed into strongly acidic or basic solutions (HCl(aq) with pH 1 or NaOH(aq) with pH 14, respectively) for 40 minutes at room temperature with vigorous stirring. Particles were then washed out with distilled water and dried for 2 days. Ni particles treated in these ways were distributed on a relatively flat surface, and the water contact angles of these surfaces were measured[11]. For the sample with hydrophobic coating treated with acidic (HCl, pH 1) or basic solutions (NaOH, pH 14), water contact angle was still higher than 160°, indicating that PDMS-layer was still maintained without corrosion after

acid and base treatments.

We also tested the stability of PDMS-layers deposited on TiO₂ nanoparticles under UV irradiation (Figure 4 (b))[7]. Note that TiO₂ is semiconductive with a band gap of ~3.1 eV, and therefore when UV lights are absorbed, electron-hole pairs can be created. These electrons and holes in TiO₂ can interact with O₂ and water vapor, resulting in the formation of O₂⁻ and OH radicals, which are strong oxidizing agents, and are well known to be able to decompose organic molecules. In the case of PDMS-layers on TiO₂, we could verify high stability under UV irradiation; surfaces consisting of PDMS-coated TiO₂ nanoparticles showed water contact angles higher than 160°, which were sustained for 24 hours of UV irradiation. For comparison, a similar test was conducted using surfaces of stearic-acid-coated nanoparticles, and in this case, a drastic decrease in the water contact angle by photocatalytic decomposition of stearic acid was observed. We also performed similar experiments with ZnO, and the results were almost identical to those of TiO₂ in Figure 4 (b)[4].

It was also shown that the PDMS-layer is resistant towards salt water : PDMS-coated SiO₂ did not show any surface property change after treatment with salt water[9].

5. Application of PDMS-coated Nanoparticles for Removing oil and Non-polar Organic Solvent

One of the aims of our recent studies was to identify whether PDMS-coated nanoparticles can be used as gelation agents of spill-oil in seawater and river. We selected PDMS-coated SiO₂ nanoparticles as gelation agent since SiO₂ nanoparticles are commercially available, widely used in various applications and inexpensive. As already shown in Figure 1, SiO₂ is originally hydrophilic, however, it becomes completely immiscible with water after surface modification using PDMS.

We determined “weight gains” of PDMS-coated SiO₂ nanoparticles with a mean diameter of ~10 nm by various types of oils (Figure 5 (a))[25]. Weight gains of PDMS-coated SiO₂ by oils were shown to be 10-15, i.e., 1 g of PDMS-coated SiO₂ nanoparticles can result in gelation of 10-15 g of oil (Figure 5 (b)). Such a large weight gain value determined here seems to be related to a high porosity of SiO₂ nanoparticles (~99%).

When PDMS-coated SiO₂ nanoparticles are mixed with a heterogeneous mixture of oil and water, they can selectively interact with oil, resulting in gelation of oil. The gels comprising of PDMS-coated SiO₂ and oil are very stable on the water surface, and therefore, one can easily remove the oil after mixing with PDMS-coated SiO₂.

It is questionable how the mixture of nonpolar pollutants (oils and solvents) and PDMS-coated particles can be efficiently and selectively removed from the water. We recently verified that magnetic particles coated by PDMS can be used for removing nonpolar organic solvents and oils from water by external magnetic field: PDMS-coated Ni particles are perfectly floated on the water surface and they can selectively interact with nonpolar organic solvents[11]. When external magnetic fields are applied, oils interacting with PDMS-coated magnetic particles can be selectively removed from the water. Probably, a

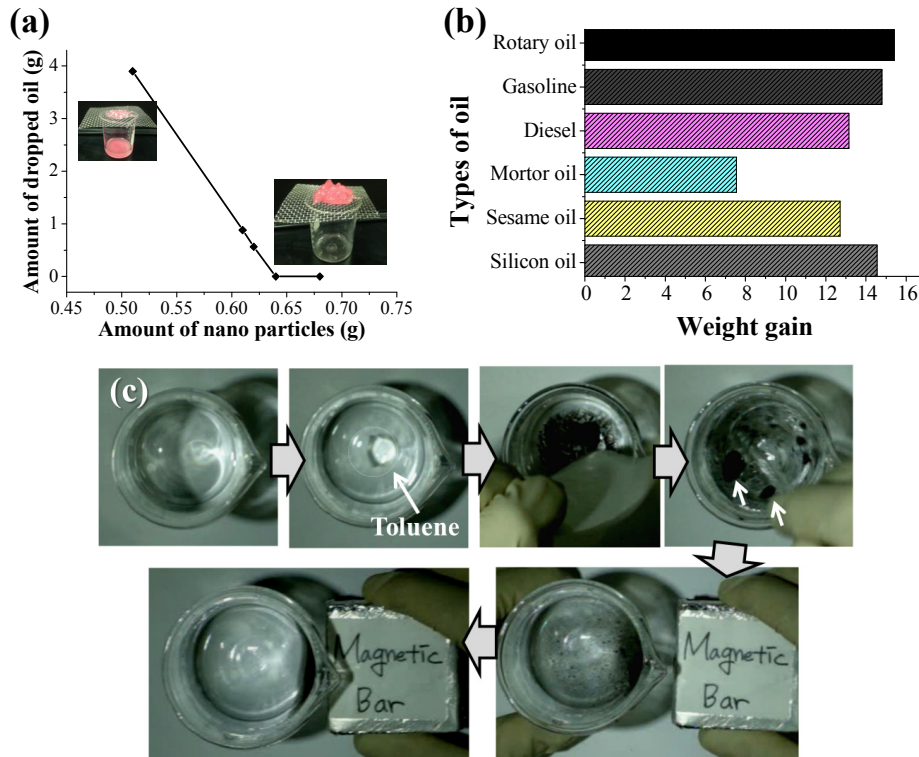


Figure 5. (a) Procedure for determination of weight gain by oil is shown. A mixture of PDMS-coated SiO₂ and oil is deposited on a mesh. After waiting for 10 minutes, the amount of oil dropped down is measured. Weight gain is measured from a mixture, which does not result in a drop of oil for 10 minutes. The weight of the mixture divided by the original weight of PDMS-coated SiO₂ is determined to be weight gain. (b) Weight gains of PDMS-coated SiO₂ by various oils are summarized. (c) Snapshots of the movie showing that Ni particle with PDMS-layer and nonpolar solvents can be removed from the water at the same time by external magnetic fields.

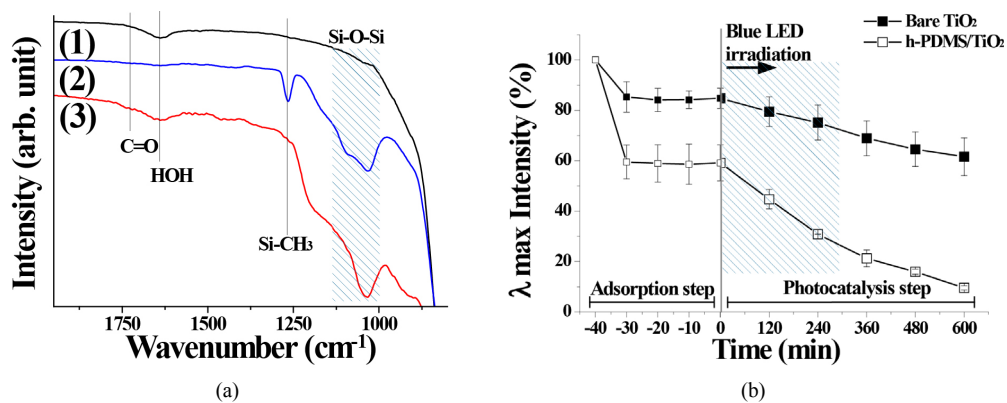


Figure 6. (a) FT-IR spectra of (1) bare TiO₂, (2) PDMS-coated TiO₂ and (3) h-TiO₂ are shown. h-TiO₂ was prepared by PDMS-coating and 800 °C-annealing under vacuum. (b) Results of photocatalysis experiments of bare and h-TiO₂ are compared.

mixture of PDMS-coated SiO₂ and Ni particles can be used for removing nonpolar pollutants from water with high weight gains and efficient removal by external magnetic fields.

6. Surface Modification for Enhanced Photocatalytic Activity

As it has been shown so far, a coating of PDMS-layer renders hydrophobic surface nature of various materials. Such hydrophobic nature

of PDMS-coating can be exploited for removing nonpolar pollutants such as oil and various organic solvents from the water. When PDMS-coated TiO₂ was annealed at 800 °C under vacuum, the PDMS-layer was shown to undergo structural changes, resulting in the formation of a highly hydrophilic layer on TiO₂[30].

Figure 6 shows FT-IR spectrum of PDMS-coated TiO₂ nanoparticles (Degussa, P-25) compared with the spectrum obtained from the same sample after annealing at 800 °C under vacuum conditions[30]. The most important difference between these two samples is the appearance

of the band corresponding to the C=O stretching frequency at ~ 1700 cm^{-1} after annealing. This shows that hydrophobic methyl groups in PDMS can be converted to hydrophilic C=O group upon annealing. Most likely, oxygen from TiO_2 is transferred into the PDMS layer partially oxidizing methyl group to more hydrophilic C=O groups. One can actually see using XPS that oxygen vacancies are created upon annealing PDMS-coated TiO_2 , in line with the aforementioned scenario regarding the mechanism of partial oxidation of PDMS upon annealing[30]. The annealed sample of PDMS-coated TiO_2 was highly miscible in water, in accordance with the FT-IR data that hydrophilic functional groups are created upon annealing.

Photocatalytic activity of the hydrophilically modified TiO_2 sample was studied using MB decomposition under blue LED irradiation[30]. As one can see in Figure 6, both adsorption capacity and photocatalytic activity of TiO_2 towards MB are enhanced upon hydrophilic modification. On one hand, more hydrophilic nature is advantageous for MB adsorption and OH group formation in aqueous solutions, on the other hand, oxygen vacancies created in TiO_2 allows absorption of the visible light, enhancing optical responses of TiO_2 .

7. Conclusion

A homogeneous thin layer of PDMS can be achieved on various nanomaterials using CVD, providing hydrophobic nature of solid surfaces. Hydrophobic layer of PDMS shows high resistance towards degradation under chemically and physically harsh conditions. Hydrophobically modified SiO_2 nanoparticles can be used for efficiently and selectively gelating oil from water. Hydrophobically modified magnetic particles can be used for separating oil from water by external magnetic field. In addition, post-annealing of PDMS-coated TiO_2 (h- TiO_2) allows hydrophilic modification of TiO_2 surface and formation of visible-light responsive defect sites in TiO_2 . h- TiO_2 shows enhanced photocatalytic activity for decomposition of organic dyes in aqueous solutions under visible light illuminations.

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