

Interaction of TiO₂ Films on Carbon Fibers with Toluene

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TiO₂ thin films were synthesized on carbon fibers using chemical vapor deposition. We show that these films can exhibit extraordinarily high absorption capacities of toluene vapor. Such an absorption phenomenon of toluene at room temperature was not found for other TiO₂ samples. Upon toluene absorption change in the color (darkening) of the film was found, indicating that these films can be used as an indicator of the existence of volatile organic compounds in the indoor environments. By X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM), a high concentration of OH species and a unique layered structure were found for the TiO₂ films and these could be related to their high absorption capacity of toluene.

Key Words: Thin films, Chemical vapour deposition, TiO₂, C fiber, Volatile organic compound (VOC)

Introduction

As is well-known, sick building syndrome is caused by high concentrations of the volatile organic compounds (VOCs) inside buildings. Molecules with an aromatic ring framework such as benzene, toluene, xylene and phenol are widely used as solvents and are known to be toxic. Development of novel materials for sensing and removing toxic VOCs in the environments could be important.

TiO₂ has been widely used in a variety of application fields due to its unique optical properties and chemical stabilities.¹ TiO₂ is a semiconductive material with a band gap of ~3.2 eV, and electron-hole pairs created in TiO₂ by absorption of UV light can survive sufficiently long time for the creation of O₂⁻ and OH radicals.¹ Note that the electrons and holes of TiO₂ can react with O₂ and H₂O to create O₂⁻ and OH radicals, respectively.¹ The strong oxidizing agents such as O₂⁻ and OH radicals created here can decompose organic pollutants, and therefore, TiO₂-based photocatalysts can be useful in environmental science.¹ A drawback of TiO₂ as a photocatalyst is that it can absorb mostly UV light due to their wide band gaps and, therefore, their photocatalytic activity under sunlight can be low. Much effort has been made to improve the photocatalytic activity of TiO₂ by using various dopants, which can narrow the band gap of TiO₂, and surface modifications.²⁻⁷

Besides photocatalysis, efficient absorbents and adsorbents can be used for removing organic pollutants. Note that adsorption refers to the interaction between gas or liquid molecules with substrate surfaces, whereas absorption includes diffusion of molecules into deeper layers. Amount of adsorption should be related to surface area, whereas that of absorption to mass of a substrate. One advantage of using absorbents and adsorbents is that they can reduce the concentrations of harmful organic pollutants even under dark conditions (without light). Activated carbon and carbon fibers have been regarded as potential candidates for removing VOCs such as toluene by adsorption.⁸⁻¹² As mentioned above, it has been extensively reported that TiO₂ is a good photocatalyst for decomposing organic pollutants; however, capability of TiO₂ for adsorbing or absorbing organic

pollutants has not been reported so far. In the present work, TiO₂ films were prepared by chemical vapor deposition (CVD) on carbon fibers. We show that our novel method can produce TiO₂ films with unique structures, resulting in their having an extraordinarily high absorption capacity of toluene. Upon absorbing toluene, change in the color of TiO₂ films could be found, implying that this material can be used as indicator of the existence of VOCs.

Experimental

In the atomic layer deposition (ALD) process, two precursors (e.g., titanium tetraisopropoxide TTIP and H₂O for synthesizing TiO₂ films) are separately introduced into the chamber. The growth process is self-limiting, since the precursors chemisorbed on the surface can only participate in the film growth.¹³ The growth rate of TiO₂ is typically 0.2 - 0.7 Å/cycle, which depends on the various experimental parameters.¹³ In the present work, the two precursors (TTIP and H₂O) were introduced sequentially into the chamber in a manner analogous to the ALD process. However, the two precursors were not completely separated from each other, that is, before H₂O was completely removed from the chamber by purging, TTIP was introduced. The film deposition process used in the present work can be regarded as chemical vapor deposition (CVD). The major difference between conventional CVD and that of the present work is that discrete pulses of H₂O and TTIP were used instead of the continuous flow of the precursors. For each cycle, TTIP and H₂O pulses were injected for 1.5 sec and 2.0 sec, respectively, and the exposure time for both of the precursors was 30 sec. N₂ was used as a purging gas and carrier of TTIP and H₂O. During deposition, the temperature of the TTIP bottle was 60 °C, whereas that of H₂O was room temperature. The base pressure of the chamber was 25 mtorr. At the moment of injection of each TTIP-pulse, the pressure of the chamber (~ 100 mtorr) was much higher than the base pressure, due to the residual water vapor which was not completely pumped out. As a substrate, carbon papers (Toray 060) with a Brunauer-Emmett-Teller (BET) surface area of 0.4 m²/g were used. During film deposition, the

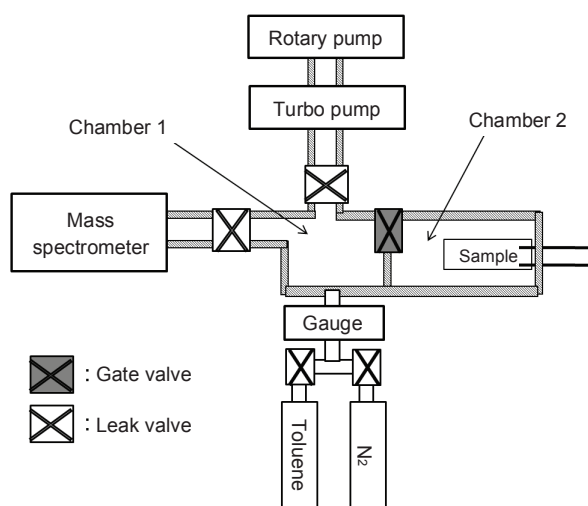


Figure 1. Schematic description of the experimental set-up used for measuring the toluene absorption capacity of the TiO₂ films and Degussa P-25 samples prepared in the present work.

sample temperature was kept at 110 °C.

The TiO₂ films produced in this way were analyzed using scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were performed in the main chamber (base pressure 2×10^{-10} torr) equipped with a concentric hemispherical analyzer (CHA, PHOIBOS-Hsa3500, SPECS), a dual Al/Mg X-ray source, and a quadrupole mass spectrometer (QMS). XPS spectra were obtained at room temperature by using Mg K α -source (1253.6 eV). The aperture of the analyzer was located normal to the sample surface, and the distance between the sample surface and the aperture of the analyzer was 35 mm.

The toluene absorption capacity of the TiO₂ films on carbon fiber was measured. In Fig. 1, the experimental set-up used for measuring the toluene absorption capacity is schematically shown. After the reactor was evacuated with a rotary pump, the two chambers were separated by closing the gate valve. In the first chamber, N₂ (3 torr) and toluene (1 torr) were introduced and, then, the gate valve was opened in order to expose the samples to the toluene + N₂ atmosphere. The change in the gas composition was quantitatively analyzed as a function of time using a quadrupole mass-spectrometer (HIDEN) connected *via* a leak valve. The pressure in the chamber was monitored by a Convectron vacuum gauge (CVM-201, Instru Tech, Inc.) during the experiment.

Results and Discussion

Fig. 2 shows the SEM images of the TiO₂ films deposited on the carbon fiber. The structure of the carbon fiber was preserved after TiO₂ deposition, indicating that TiO₂ was homogeneously deposited on the carbon fiber surfaces. From the cross section images, the TiO₂ films deposited on the surface of carbon can be clearly identified. A close inspection of the SEM cross section image suggests that a layered structure formed on the surface, instead of a vertically continuous one. These structural properties are probably related to the unique preparation method

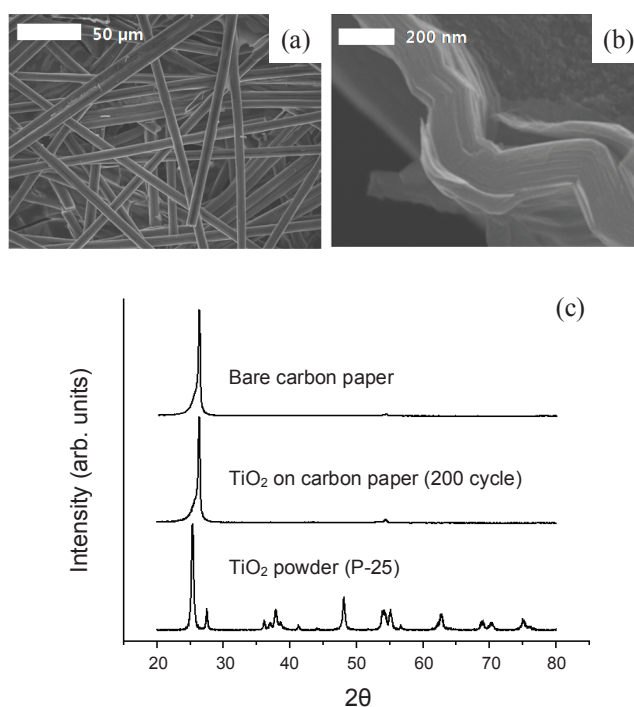


Figure 2. SEM images (a) top and (b) cross section views) of TiO₂ film on carbon paper. For the deposition of TiO₂, 50 cycles were used. A detailed description of each cycle can be found in the text. (c) The XRD pattern of the TiO₂ film on carbon paper in Fig. 2 a,b and that of the P-25 sample are compared.

used in the present work; two precursors (TTIP and H₂O) were sequentially introduced into the chamber. The XRD data in Fig. 2 indicate that the TiO₂ films were mostly amorphous. The poor crystallinity of the TiO₂ films is most likely due to the low film deposition temperature used in the present work. For comparison, the XRD pattern of a commercially available Degussa P-25 sample is shown, for which peaks corresponding to anatase and rutile phases can be identified.

In Fig. 3, the XPS spectra of the TiO₂ films prepared in the present work are compared with those of the P-25 samples. The binding energies of the Ti 2p states agree with those of TiO₂ in the literature, i.e., Ti was fully oxidized. The spectrum of the O 1s state shows a major peak centered at ~530 eV. The shoulder at higher binding energies (~532 eV) can be attributed to the OH groups formed from TiO₂.¹⁴ Comparing the O 1s spectra of the TiO₂ films prepared in the present work with that of a commercially available Degussa P-25 sample, a significantly higher population of OH groups can be seen on the surface of the present TiO₂ films.

The TiO₂ films synthesized in the present work have an extraordinarily high capability of removing toluene from the gas phase. As shown in Fig. 4, a decrease in the relative partial pressure of toluene with respect to that of N₂ can be seen as a function of the exposure time (time passed after the gate valve between chambers 1 and 2 was open). Without the sample or with a bare C fiber sample, no change in the partial pressure of toluene as a function of time was identified. As the film thickness increased, the amount of toluene removed became larger, indicating that toluene was not only adsorbed on the surface of

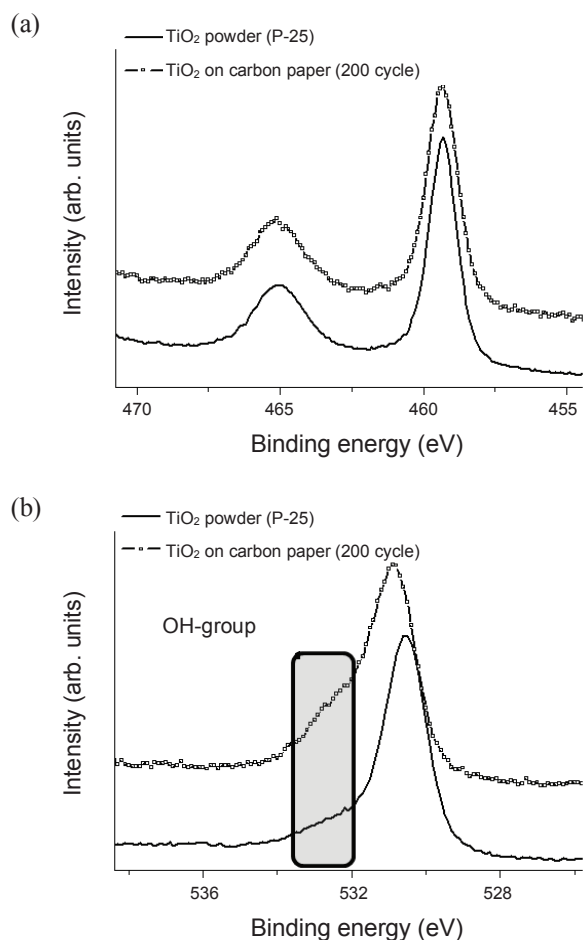


Figure 3. The XPS results of the TiO₂ film (200 cycles) on carbon paper and those of the P-25 sample are compared. The Ti 2p (top) and O 1s (bottom) states are shown.

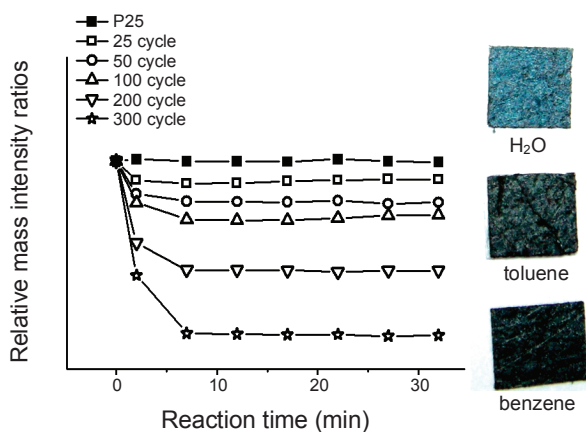


Figure 4. Change in the relative partial pressure of toluene as a function of time corresponding to the amount of toluene absorbed by the TiO₂ films. The initial partial pressure of toluene and N₂ were, 1 and 3 torr, respectively. The absorption capacities of the TiO₂ films with various thicknesses as well as that of the P-25 sample are compared. The change in the color of the TiO₂-coated carbon papers by exposing to water, toluene and benzene vapors under atmospheric conditions is also illustrated. For these experiments, the TiO₂ films were prepared by 50 deposition cycles.

the TiO₂ film, but also absorbed.

Considering the volume of the chamber used in this experiment and the change in the partial pressure of toluene in Fig. 4, the number of toluene molecules removed by the TiO₂ films can be estimated. For the sample prepared with 300 deposition cycles, the amount of toluene removed corresponds to more than 300 monolayer equivalents, confirming that toluene is not only adsorbed on the surface of the TiO₂ film, but also absorbed by TiO₂.

For comparison, similar experiments were carried out using commercially available P-25 (Fig. 4). For the P-25 samples, little change in the partial pressure of toluene could be identified as a function of time, implying that the absorption of toluene is unique for the TiO₂ films prepared in the present work. For the experiments shown in Fig. 4, the amount of the P-25 sample used was 0.11 g, whereas that of the TiO₂/C sample was 0.03 g. In addition, the BET surface area of the P-25 sample (~55 m²/g) is much higher than that of the C paper (0.4 m²/g). We suggest that the higher OH group concentrations of the TiO₂ films prepared in the present work, in combination with their unique layered structure, are responsible for their extraordinarily high capability for removing toluene. Hydroxylated TiO₂ surface has been suggested to more strongly interact with toluene than regular TiO₂ surfaces without OH groups due to the interaction between OH groups and π electrons of toluene.¹⁵

It is worth mentioning that the color of the sample was changed after the toluene absorption experiments, indicating that the color of the TiO₂ thin films can be used as an indicator of the existence of toluene in the vapor (Fig. 4). Under ambient pressure conditions, a similar change in the color of the TiO₂ thin films could be found after exposing the samples to toluene vapor. Also, exposure to benzene vapor resulted in the same color change of TiO₂ films. For these experiments, the samples were placed at the upper parts of half-filled liquid (water, toluene, or benzene) bottles and the exposure time was 30 min. (Fig. 4).

Conclusion

In summary, we prepared TiO₂ films using CVD method on C fibers. The TiO₂ films prepared in this way showed a very high capability of absorbing toluene, and the color of the film was changed by the toluene adsorption i.e., these materials can be useful for removing and sensing indoor VOCs. Using SEM and XPS, we found that their high capacity of toluene absorption is likely related to their high population of OH groups and unique layered structure.

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