Solvent Effect of the Adsorption of Titanium Dioxide Nanoparticles onto Microporous Polymer Films

Till T. Meiling and Hans-Gerd Löhmannsröben
Potsdam University, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, Haus 25, 14476 Potsdam-Golm, Germany and Innovation Center innoFSPEC, 14476 Potsdam-Golm, Germany

Kenichi Kon and Olaf Karthaus∗
Graduate School of Photonic Science, Chitose Institute of Science and Technology, Bibi 65-758, Chitose 066-8655, Hokkaido, Japan
(Received 7 April 2010; Accepted 21 May 2010; Published 19 June 2010)

We prepared honeycomb films of a crosslinkable poly(maleic anhydride-co-styrene). It was found that the surface modification of the polymer by ethanolamine had a profound effect on the adsorption of TiO2 nanoparticles from alcoholic suspensions. The other important parameter to control adsorption density of the TiO2 film on the honeycomb substrate was the water content of the alcohol. Furthermore, we found that other organic solvents can also be used to form adsorbed films with various morphologies. After pyrolysis, the microscopic honeycomb morphology was retained. [DOI: 10.1380/ejssnt.2010.309]

Keywords: Titanium oxide; Alcohols; Water; Adsorption; Nanoparticles; Organic solvent; Honeycomb; Pyrolysis

I. 1. INTRODUCTION

Since their discovery in the 1970’s [1], titanium dioxide photocatalysts are becoming more and more important for water purification, air cleaning and as coatings for antimicrobial, antifogging, or self-cleaning surfaces [2]. Common preparation techniques include spray coating, either of the TiO2 nanoparticles themselves, or of a precursor titanium alkoxide, or coating of a TiO2 suspension in a polymer solution. The polymer assists the film formation and after pyrolysis, nanometer-size voids are formed. Besides having just nanometer size voids, it would advantageous to have a wider pore size distribution, which will facilitate material transport within the film. Furthermore, pore sizes of around 1 micrometer scatter light which leads to opaque and, in the case of ordered pores, iridescent films.

Even though there are other commonly used methods for producing microporous ordered materials, such as backfilling of colloidal crystals followed by template removal [3], or etching of blockcopolymers [4], the water-droplet templating method of polymers [5] is intriguing, because of its low cost, easy pore-size control, and large area production. A polymer solution is cast under high humidity and the evaporating solvent leads to surface cooling, which induces the condensation of water droplets that act as templates for the formation of a porous polymer film.

We have already reported on the preparation and photocatalytic activity of microstructured honeycomb TiO2 films prepared by coating a honeycomb polymer template with an ethanol suspension of nanocrystalline TiO2. The resulting TiO2 films, after pyrolysis at 400°C to remove the polymer, show a hierarchic structure with nanometer and micrometer-sized pores [6]. Such a type of structure is produced, because the crosslinked polymer template is stable enough to initially retain its three dimensional structure at the temperature necessary for pyrolysis [7]. The hierarchic pore structure facilitates diffusion of reactants to and from the catalyst surface and also is responsible for the effective light scattering in the film, which leads to a higher efficiency.

Here we report on the evaluation of a variety of liquids used for making nanoparticle suspensions and how surface modification and crosslinking of the polymer honeycomb affects the adsorption of titanium dioxide nanoparticles.

II. EXPERIMENTAL

Figure 1 shows the chemical formulae of the used polymers. Honeycomb films were prepared from poly(styrene-co-maleic anhydride) random copolymers containing approx. 11 mol% maleic anhydride groups. Chloroform solutions containing 9 mg/mL copolymer and 1 mg/mL of a polyion complex were cast on a glass slide (20 mm x 50 mm) under high humidity as previously described [7]. The polyion complex is a powerful additive to stabilize the water droplets and thus lead to highly ordered microporous films. The pore diameter in the honeycomb films was between 1 μm and 2 μm. Before coating with

*Corresponding author: kart@photon.chitose.ac.jp
TiO₂, some of the honeycomb films were treated by immersion in one of the following ethanol solutions for 4 hours: For crosslinking a 50 mmol/L diamino octane solution was used. For surface functionalisation, a 50 mmol/L ethanolamine solution was used. For both, crosslinking and surface functionalisation, a solution containing 25 mmol/L diamino octane and 25 mmol/L ethanolamine was used [6].

TiO₂ nanoparticles (P 25, Degussa) were suspended in distilled water or in reagent grade organic liquids at a concentration of 1 mg/mL which were then sonicated for 3 h. A cylindrical flat-bottom flask with an inner diameter of 4 cm was filled with 50 mL of suspension and placed on a hot plate kept at 55°C. The honeycomb films were suspended in the liquid, which was constantly stirred with a magnetic stirrer bar (length 5 mm) at 1000 rpm for 72 h, then taken out, briefly rinsed with ethanol and dried. The surface morphology of the coated honeycomb films was imaged with a scanning electron microscope (S-3500N, Hitachi Corp.).

III. RESULTS AND DISCUSSIONS

All together, four different honeycomb modifications (unmodified (non-hc), crosslinked (cr-hc), surface functionalized (sf-hc), surface functionalized and crosslinked (cr-sf-hc)) and seven different organic liquids (methanol, ethanol, iso-propanol, acetic acid, methylethylketone, tetrahydrofurane, and chloroform) were used. Furthermore, some of the water-miscible liquids were mixed with water in various ratios. In total, more than 100 combinations were screened and here we will present the most significant differences between the samples.

Figure 2 shows the scanning electron images of three different honeycomb films, non-hc (Fig. 2(A)), sf-hc (Fig. 2(B)), and cr-sf-hc (Fig. 2(C)) after immersion for 72 h in an ethanol suspension of TiO₂.

From our previous studies we knew that ethanol is a good dispersing liquid for TiO₂ nanoparticles at room temperature [6]. The present study was carried out at 55°C, because at this temperature the nanoparticles contained only a few aggregates with sizes larger than 100 nm. Figure 2 shows a significant difference in the adsorption density depending on the surface functionalization. The non-hc film showed only partial coverage of the polymer surface with nanoparticles, while both, sf-hc and cr-sf-hc showed a dense coverage. This can be explained by the presence of hydrophilic hydroxyl, amino, and carboxylic acid groups on the honeycomb surfaces, that interact with the surface groups of TiO₂ nanoparticles, either electrostatically or via hydrogen bonding. Some of the micrometer-sized holes of the honeycomb are completely covered with nanoparticles, but this is just a minor effect, and only a small fraction of the holes are covered with nanoparticles, as can be seen in Fig. 2.

In order to evaluate the effect of hydrophilic interaction between the polymer and nanoparticles on the adsorption and aggregation behavior, we prepared suspensions with increasing water content, and immersed surface functionalized honeycomb films. We found that already 30% water leads to a drastic decrease in adsorption of nanoparticles (Fig. 3(A)). Using ethanol with a water content of 50% (Fig. 3(B)), less than half of the honeycomb surface is covered with nanoparticles, and a pure water suspension (Fig. 3(C)) nearly completely inhibits nanoparticle adsorption onto the honeycomb. It has to be noted that the number of adsorbed clusters decrease, too. In a 30% suspension, a small number of clusters can be seen on the honeycomb, but at higher water contents they are nearly completely absent. This is due to the high dielectric constant of water which leads to a stable hydrate layer around the nanoparticles [8]. But this hydrate layer does not only assist in making a stable suspension—it also prevents interaction of the nanoparticles with the honeycomb surface, leading to a reduced adsorption.

Fig. 2: Scanning electron micrographs of honeycomb films after adsorption of TiO₂ for 72 hours ([TiO₂]: 1 mg/mL ethanol suspension). Unmodified film (A), ethanolamine modified (B), ethanolamine modified and crosslinked (C). The insets in A and C are magnified images. Scale bar = 10 μm.
leads to a complete coverage (Fig. 4(B)), which makes it the best solvent up to now for this type of surface functionalization. Other organic liquids, such as acetic acid (Fig. 4(C)), methylethylketone (Fig. 4(D)), chloroform (Fig. 4(E)), and THF (Fig. 4(F)) cannot suspend the nanoparticles effectively. Acetic acid still allows the nanoparticle aggregates to adsorb on the honeycomb film, but a complete coverage of the honeycomb holes was observed. The thickness of the homogeneous nanoparticle layer is about 100 nm. With acetic acid as a dispersant, the use of a honeycomb-structured substrate has lost its meaning. The other three, more hydrophobic liquids also lead to a significant aggregation of the nanoparticles in suspension [9, 10] and a heterogeneous adsorption of aggregates with a broad size distribution at random places on the honeycomb.

Finally, pyrolysis at 500°C for 6 hours removes the polymer from the samples, resulting in purely inorganic TiO₂ films. Figure 5 shows the top and side views of a sample obtained by pyrolysis of a sample similar to the one shown in Fig. 2(C).

The in-plane microporous structure of the polymer honeycomb is preserved during pyrolysis and a network of interconnected TiO₂ nanoparticles is produced. The three dimensional honeycomb structure, on the other hand, is collapsed, because the adsorption mainly occurred on the upper rim of the honeycomb, and not inside the pores and the pillars connecting the lower and upper honeycomb surface. Still, similar to the sample before hydrolysis, the postpyrolysis samples show strong light scattering, which is advantageous for various applications in photonics, such as in photocatalysts, solar cells, or light diffusors.

IV. CONCLUSIONS

In conclusion, we could show that titanium dioxide nanoparticles can be successfully adsorbed onto microporous polymer films that were surface functionalized with ethanolamine. The choice of dispersing medium, especially its water content, critically influences the ad-
sorption behavior. We found that isopropanol is the best solvent for TiO$_2$ nanoparticle adsorption onto hydroxyl group functionalized polymer honeycomb structures, since it can tolerate 40% water content.

Acknowledgments

This research was partially supported by the Collaborative Development of Innovative Seeds of Japan Science and Technology Agency (JST, SEEDS). A part of this work was conducted in Hokkaido Innovation through NanoTechnology Support (HINTS), supported by “Nanotechnology Network Project” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. T. T. M. acknowledges financial support from Photonic World Consortium, Chitose, and from InnoF-SPEC, Potsdam.