Polymer Honeycomb Templated Microporous TiO$_2$ Films with Enhanced Photocatalytic Activity

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(Received 15 April 2008; Accepted 3 June 2008; Published 20 June 2008)

It was found that mesoscale patterned films of titanium dioxide nanocrystals have superior photocatalytic activity as compared to unstructured films. The nanocrystals were adsorbed onto surface-functionalized and crosslinked polymer honeycomb films. After calcination, the porous structure remained and photocatalytic activity was evaluated by the photolytic decomposition of a cyanine dye in aqueous solution. [DOI: 10.1380/ejssnt.2008.161]

Keywords: Surface structure, morphology, roughness, and topography; Titanium oxide

I. INTRODUCTION

Titanium dioxide is a well-known photocatalyst [1, 2] and surface coatings exhibit antimicrobial and self-cleaning properties. It has been used in waste water treatment, and as coatings to reduce smog.

The surface topology of a thin film of titanium dioxide particles has an effect on the photocatalytic activity, because increased surface roughness leads to a higher surface area as well as allows better diffusion of reactants. A microporous architecture could also be useful for filter applications. Furthermore, enhanced light scattering allows for multiple passes of photons through the film and thus to an increased absorption of photons and a higher quantum efficiency [3]. There have been reports on the formation of microporous polymer honeycomb films by templating with water droplets [4–6]. Since these films are made of organic polymers, they tend to collapse at temperatures higher than their glass transition temperature, thus limiting their use for high temperature applications [7]. Adsorption of inorganic nanoparticles is possible, but calcination to remove the organic polymer has to be carried out carefully, not to collapse the three dimensional honeycomb structure [8]. Recently, we have reported that by photochemical crosslinking [9] thermally stable honeycomb films of up to 350°C can be obtained. Maleic anhydride containing polymers can be processed into honeycomb films [10] and we could show that crosslinking with diamino-octan produces thermally stable honeycomb films [11]. One additional side effect of the chemical crosslinking of carboxylic acid anhydrides with diamines is that a hydrophilic carboxylic acid group is produced. This then can interact with oxygen at the surface of titanium dioxide particles and lead to increased adsorption. Furthermore, other reactive species, such as functionalized amines, can be added while crosslinking takes place, thus tailoring the surface properties of the resulting crosslinked honeycomb films.

II. EXPERIMENTAL

Honeycomb films were prepared from poly(styrene-co-maleic anhydride) random copolymers containing ca 11 mol% maleic anhydride groups. Chloroform solutions containing 3 mg/ml copolymer and 0.3 mg of a polycation complex were cast under high humidity as already described in the literature [6, 11]. The resulting honeycomb films were immersed in one of the following ethanol solutions of amines: A: 50 mmol/l of 1,8 diamino octane; B: 50 mmol/l of ethanol amine; C: mixture of 25 mmol/l of 1,8 diamino octane and 25 mmol/l of ethanol amine.

After several hours of immersion, the films were removed, dried and immersed in a water/ethanol suspension of TiO$_2$ nanoparticles (Sakai Kagaku Inc.) for 12 hours. Calcination was carried out at 500°C in a muffle oven. Photoactivity was evaluated by placing a “black light” (As One Corp., Japan, 9 W) at a distance of 10 cm on top of an aqueous cyanine dye solution. The concentration of the dye was adjusted so that the absorbance at 429 nm was 1.48.

III. RESULTS AND DISCUSSION

As can be seen in the reaction scheme in Fig. 1, crosslinking leads not only to amide and carboxylic acid groups, but due to steric reasons, unreacted amino groups may be present. Adding aminoethanol to the crosslinking solution then contributes to yet another type of hydrophilic groups on the surface.

Figure 2 shows the scanning electron micrographs of honeycomb films. All films have a pore diameter of ca. 3 µm and have a base-film, meaning that there are no through-pores perpendicular to the film. On the other hand, the hexagonally arranged pores are connected laterally. Four types of honeycomb films (non-crosslinked; non-crosslinked, but surface functionalized with aminoethanol; crosslinked; crosslinked and surface functionalized with aminoethanol) were immersed in an ethanol suspension of TiO$_2$ nanoparticles for 12 hours. As can be seen in Fig. 2, both crosslinked or non-crosslinked,

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The exact role of ethanolamine for this behavior is not yet understood. Hydrogen bonding of the ethanolamine OH group to surface oxygen atoms of TiO$_2$ nanoparticles is possible. Contact angle measurements show that the honeycomb surface changes from superhydrophobic, with a contact angle of more than 100$^\circ$, to hydrophilic, with a contact angle of 30$^\circ$ after surface modification or crosslinking, showing that hydrophilic surface groups are present [10], but the exact ratio of amino, hydroxy and carboxy groups is not known and is the subject of future studies.

Since a self-supported honeycomb structure of TiO$_2$ needs a thicker, continuous coating of the inorganic nanoparticles, the adsorption conditions were modified. An aminoethanol/diamino octane modified honeycomb film was immersed in a 5 mg/ml ethanol suspension of TiO$_2$ nanoparticles for three days. Figure 3 shows the scanning electron micrographs after immersion and after subsequent calcination at 500$^\circ$C for 6 hours. The three-dimensional honeycomb structure is completely intact after calcination.

In order to assess the photocatalytic activity, a solution of a sulfonated cyanine dye was irradiated with 365 nm UV light. Three different samples were compared: a blank solution, a solution with an immersed glass plate with a TiO$_2$ film prepared by adsorption of a flat polymer film with subsequent calcination, and a glass plate with a honeycomb TiO$_2$ film. The cyanine dye was selected because of its good water solubility and a minimum in the adsorption at 365 nm. This ensures that enough photons reach the TiO$_2$ surface through the aqueous solution, while minimizing the photobleaching of the dye itself. The change in photodegradation of the dye over time was monitored at its maximum absorption at 429 nm. The initial concentration of the dye was set at an absorbance of 1.48 at 429 nm. The blank sample without any photocatalyst did not show a decrease in absorbance over time. The results are summarized in Fig. 4. The flat film induced some photodegradation, and the dye concentration decreased by approximately 5% to 1.40.

The honeycomb film, on the other hand, led to a steady decrease of absorbance and after 6 hours an absorbance of 0.97 was recorded, meaning that 34% of the dye was...
decomposed. Part of this increase can be attributed to the increase in surface area, but the dramatically increased activity is also due to other factors, like enhanced diffusion of the dye through the hierarchic structure and increased photon scattering leading to an increase in quantum yield. We did not observe any coloration of the film, thus the decrease in adsorbance is not due to physisorption of the dye onto the film.

IV. CONCLUSION

We prepared micropatterned films of titanium dioxide nanoparticles by adsorption on surface-functionalized polymer honeycomb films. After calcination the films retained their 3-dimensional honeycomb structure and showed drastically enhanced photocatalytic activity.

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