Coatings of Polymers with TiO₂ Nanoparticles by Sonochemical Method

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ABSTRACT

A titania film was deposited on polycarbonate and parylene-coated glass by a one-step, ultrasound-assisted procedure. The TiO₂ nanoparticles formed during the hydrolysis of Ti(i-OPr)₄ were thrown at the solid surface by sonochemical microjets and strongly anchored to the polymers. Polyethylene glycol and polyvinyl pyrrolidone was used to stabilize the uniform distribution of TiO₂ on the polymers surface. The morphology and structure of the coated films were characterized by XRD, TEM, SEM, AFM, and Rutherford backscattering spectrometry. The hydrophilic/hydrophobic properties were evaluated by measuring the water contact angle. The photocatalytic properties of the titania-modified polymers were estimated in the photo discoloration of methylene blue dye, and high activity in its bleaching was demonstrated. The experimental results revealed a correlation between the uniformity of the nanostructured anatase titania film and its photocatalytic properties.

Keywords: coating, sonochemistry, titania, nanoparticles

1 INTRODUCTION

The coating of polymers to impart them with self-cleaning properties significantly increases their area of application in optical and electronic devices, solar cells, gas sensors, anti-fogging windows, etc. Due to their photocatalytic properties, TiO₂ films are widely used for these purposes. A wide range of methods, such as sputtering, chemical vapor deposition, sol-gel and wet coating, were employed for the deposition of titania nanoparticles on the polymeric substrates [1-3]. Although the titania films have already been thoroughly studied, the development of simple and effective techniques for fixing the photocatalytic TiO₂ nanoparticles on the substrate still remains a challenge.

In our previous publications, we reported on the coating of various substrates with inorganic nanoparticles (NPs) by the sonochemical method [4]. The physical phenomenon responsible for the sonochemical process is acoustic cavitation, i.e., formation, growth and explosive collapse of the bubbles. The NPs formed in the precursor's solution under extreme conditions of bubble collapse (temperature >5000 K, pressure >1000 atm) are thrown to the solid substrate by the microjets and the shock waves created after the collapse of the bubble. The speed of these microjets and shock waves is very high (>100 m/s), causing the NPs to adhere strongly to the solid surface [5, 6].

Parylene film is well known as an effective coating that improves the moisture- and corrosion-resistance of microelectronic devices, medical instruments, implants, and prostheses [7, 8]. Polycarbonate became an important engineering material because of its high transparency, light weight, and high chemical and heat resistance [9]. Herein, we report for the first time on the deposition of titania film on polycarbonate and parylene-coated glass by a one-step, ultrasound-assisted procedure.

The TiO₂ NPs formed during the hydrolysis of titanium tetra iso-propoxide Ti(i-OPr)₄ were thrown at the solid surface by the sonochemical microjets and strongly anchored to the polymers substrate. Polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) were used to stabilize the highly homogeneous distribution of TiO₂ on the surface. The morphology and structure of the coated films were characterized by physical and chemical methods. The hydrophilic/hydrophobic properties were evaluated by measuring the water contact angle (WCA). The photocatalytic properties of the titania-modified polymers were estimated by the discoloration of methylene blue dye.

2 EXPERIMENTAL

2.1 Deposition of TiO₂ on polymers

The TiO₂ (NPs) were deposited on the parylene-coated glass or polycarbonate (PC) substrates by the ultrasound-assisted hydrolysis of Ti(i-OPr)₄ (TIP). The procedure was as follows. The polymer substrate was washed with i-propanol, dried in air and placed in water. The solution was sonochemically irradiated with an immersed Ti-horn (20 kHz, 750 W at 70% efficiency). The TIP was added dropwise to the working solution under sonication. The stabilization agents, PVP (MW=89000-98000) or PEG (MW=40000), were added to the solution before sonication at a concentration range of 3-12 g/L. The sonochemical process continued for 0.5 h. After the reaction, the coated polymer was washed with water and ethanol and allowed to dry in air at room temperature.

2.2 Characterization

The structural characterization of the deposited titania was done by X-ray diffraction (XRD) using a Bruker D8 diffractometer (with Cu-Kα = 1.5418 Å radiation). The
particle size of the titania in the working solution was controlled by transmission electron microscopy (TEM) with a 200 kV JEOL JEM 2100 instrument. The morphology of TiO$_2$ films on the polymer's substrate was studied by scanning electron microscopy (SEM) with a JEOL-JSN 7000F device. The atomic force microscopy (AFM) measurements were carried out using a Nanoscope V Multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA). The mean square roughness (RMS) was determined by the analysis of the height images using the Nanoscope Software Version 7.3. The RBS (Rutherford Backscattering Spectroscopy) analysis was performed with a 3.0 MeV He$^+$ beam generated by a Tandetron 1.7 MV accelerator from High Voltage Engineering. The changes in transmittance were controlled on a CARY 100 Scan UV spectrometer taking the transmittance of the bare polymer as 100%.

In the photocatalytic activity test, an aqueous solution of methylene blue (MB) was first adsorbed on the titania-coated polymer in the dark to achieve adsorption equilibrium. The adsorption solution was then replaced with a test solution of MB and irradiated with UV light. For the irradiation experiments, a Vilber Lourmat – 3x15W 315BL lamp with an emission of 365 nm was used. The concentration of dye was determined by UV spectroscopy at a 664 nm wave length, corresponding to the maximum absorbance of MB. For a comparison, the blank sample of a MB solution was tested under the same conditions.

3 RESULTS AND DISCUSSION

3.1 Surface properties and morphology

The deposition of TiO$_2$ on parylene and PC was done by the ultrasound-assisted liquid phase hydrolysis of TIP and the simultaneous deposition of the just-formed NPs on the immersed polymer's plate. In order to achieve the most homogeneous coating of titania on the polymer's surface, the concentrations of the precursor and the stabilizing agent were varied. The results of the optimization on the parylene's coating are presented in Table 1.

![Figure 1. XRD patterns of TiO$_2$ deposited on parylene.](image1)

The XRD studies demonstrated that the sonochemical hydrolysis resulted in the formation of the crystalline phase of titania (Fig. 1). The observed peaks were assigned to the reflection lines corresponding to the body-centered tetragonal structure of anatase (JCPDS 00-021-1272). The peaks were broad because of the small crystallite size of titania forming in the sonochemical reaction. The crystallite's size was calculated by the Scherrer equation according to the direction (101).

![Figure 2. SEM images of the TiO$_2$-coated parylene (x50000); the sample numbers correspond to Table 1.](image2)

The distribution of TiO$_2$ NPs on the parylene surface depended on the concentration of the TIP precursor and the stabilizing agent. Thus, with a precursor concentration of 10 g/L and PVP of 3 g/L, the coating was still non-continuous (sample A) and the deposited layer was not completed. The most homogeneous coating was obtained in a solution containing 10 g/L of TIP and 6 g/L of PVP or PEG, samples B and D respectively. The light transparency of sample B was 70% comparing to the initial parylene (Table 1).

![Figure 3. SEM images of the TiO$_2$-coated parylene (x50000); the sample numbers correspond to Table 1.](image3)

The distribution of TiO$_2$ NPs on the parylene surface depended on the concentration of the TIP precursor and the stabilizing agent. Thus, with a precursor concentration of 10 g/L and PVP of 3 g/L, the coating was still non-continuous (sample A) and the deposited layer was not completed. The most homogeneous coating was obtained in a solution containing 10 g/L of TIP and 6 g/L of PVP or PEG, samples B and D respectively. The light transparency of sample B was 70% comparing to the initial parylene (Table 1).

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>TIP (g/L)</th>
<th>PVP/PEG (g/L)</th>
<th>NPs size (nm)</th>
<th>Light transp. (%)</th>
<th>WCA (°)</th>
<th>Rate const. k (min$^{-1}$)</th>
</tr>
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<tr>
<td>A</td>
<td>10</td>
<td>3</td>
<td>40</td>
<td>75</td>
<td>85</td>
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</tr>
<tr>
<td>B</td>
<td>10</td>
<td>6</td>
<td>30</td>
<td>70</td>
<td>20</td>
<td>0.023</td>
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<td>C</td>
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<td>6</td>
<td>≥40</td>
<td>62</td>
<td>100</td>
<td>0.017</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>6</td>
<td>25</td>
<td>85</td>
<td>10</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

Table 1. Sonochemical deposition of TiO$_2$ NPs on parylene

The distribution of TiO$_2$ NPs on the parylene surface depended on the concentration of the TIP precursor and the stabilizing agent. Thus, with a precursor concentration of 10 g/L and PVP of 3 g/L, the coating was still non-continuous (sample A) and the deposited layer was not completed. The most homogeneous coating was obtained in a solution containing 10 g/L of TIP and 6 g/L of PVP or PEG, samples B and D respectively. The light transparency of sample B was 70% comparing to the initial parylene (Table 1).
1). It can be explained by the fully uninterrupted coating layer covering the entire surface of the parylene glass. The light transparency observed with sample D was rather high (85%) because of the very thin coating produced with addition of PEG. With an increase in the concentration of TIP to 20 g/L, and keeping the PVP concentration as 6 g/L, the size of the particles didn't change significantly, although they were deposited one on top of the other, forming a multilayer coating, as well as aggregates (sample C). The SEM also revealed some cracks in the coated surface (Fig. 2C). As a result of the increase in the thickness and appearance of the aggregates, the light transparency of sample C is relatively low (62%).

The surface morphology of the coated samples was also characterized by the AFM method (Fig. 3). For a comparison, the morphology of the initial parylene-coated glass was presented (Fig. 3P).

![Figure 3. AFM images of the TiO2-coated parylene.](image)

From the height projections it is clear that the sonochemical deposition of TiO2 on the parylene depended significantly on the reagents concentration. In sample A, prepared with a 10 g/L concentration of the TIP precursor and the stabilizing agent PVP as 3 g/L, together with the homogeneously-coated areas, the empty spaces and sections of high-coating density were observed (Fig. 3A). With the two-fold increase in the PVP concentration (to 6 g/L), the coating became smoother and the deposited titania NPs formed a complete uniform layer on the parylene glass (Fig. 3B). Using a higher concentration of the precursor (20 g/L) and concentration of the stabilizing agent 6 g/L, we observed the deposition of TiO2 NPs, one upon the other, forming aggregates (Fig. 3C). As a result, the coating became less homogeneous and some cracks were also found. The mean square roughness of samples A, B, and C was estimated as 60, 32 and 94 nm, respectively. Taking into account the fact that the RMS of the initial parylene was 15 nm, the optimized ultrasound-assisted deposition of the anatase TiO2 film (sample B) resulted in a rather smooth coating of the polymer's surface. The lowest roughness (RMS 20 nm) was found with sample D obtained with PEG as the stabilizing agent. The difference in roughness significantly influenced the water contact angle (Table 1).

The substrates coated with a uniform layer (samples B and D) were sufficient hydrophilic (WCA 20 and 10° correspondingly), but with the high roughness the coating transformed to a more hydrophobic state. The WCA of sample C increased to 100°, comparing with 80° of the initial parylene.

A similar tendency on influence of the reagents concentration was revealed at the coating of the PC with TiO2 under the same conditions as indicated in Table 1 for parylene. The finest coating was observed using the TIP concentration as 10 g/L and stabilizing agent PVP or PEG as 6 g/L (samples B-PC and D-PC). The RMS calculated by the AFM method for samples B-PC, C-PC and D-PC were 37, 104 and 8 nm, respectively. The change in WCA correlated with the sample's roughness, and the best wettability was observed for the finest coating (Fig. 4).

![Figure 4. WCA of PC coated with TiO2 by sonochemistry.](image)

For both polymer substrates, higher hydrophilic properties were found with the addition of PEG as the stabilizing agent. The similar effect of PEG was observed in [1] and may be explained because of the reduction in diffusion resistance within the titania film structure and a higher –OH content on the surface, which enables the water molecules to spread easily across the surface.

### 3.2 Mechanism of sonochemical deposition

The sonochemical mechanism by which the NPs were deposited on the solid substrates is related to the creation of microjets and shock waves as the after effects of acoustic cavitation. The solutions of organometallic compounds in a liquid medium are used as precursors for the sonochemical synthesis of the NPs. The volatile nature of the organometallic precursor allows its decomposition under ultrasonic irradiation, producing NPs. When cavitation occurs near the solid surface, cavity collapse is non-spherical and drives high-speed jets of liquid onto the surface. If ultrasound irradiation is applied in the presence of polymer support, the microjets, with a high speed and temperature, push the just-formed NPs to the surface, leading to the local melting or softening of the polymer. No chemical interaction between metal oxide and the polymer takes place in this collision. Thus, the heat exchange between the polymer surface and the NPs leads to an increase in the local temperature to the crystallization point of an inorganic phase [4-6].

The titania NPs formed in the solution are thrown to the substrate by sonochemical microjets with such a high
speed and temperature that it causes their strong adherence to, and even penetration of, the surface. The penetration depth of TiO2 NPs into the Parylene film was evaluated by the RBS method (Fig. 5). The profile of the atomic concentration of the elements in the parylene was measured to a depth of 1000 nm and detected titanium oxide that “diffused” into the polymer up to 346 nm. The stoichiometry of parylene seems to be slightly modified when the TiO2 concentration is higher and represents up to 30% of the composition (surface). However, at the deep layers, the parylene remained unchanged. The observed depth of penetration can not be achieved by regular spin coating or dip coating.

![Figure 5. Profile of the atomic concentration (in %) of C and Cl (parylene) and TiO2 from the surface.](image)

The titania layer on the parylene is stable and could not be removed by a simple washing procedure with water, ethanol, or acetone. The obtained results clearly demonstrated the advantages of the ultrasound-assisted method for the stable and efficient deposition of titania on the polymer substrate.

### 3.3 Photocatalytic activity

The experiments on photocatalytic activity for degrading the MB dye revealed that the particle size and morphology of the titania layer affected significantly its photocatalytic activity. When the particle size of TiO2 was 25 nm and the deposited layer was very thin, the activity was poor (Fig. 6, sample D). With the formation of the more dense layer, the activity increased (sample A). The best photocatalytic activity (50% degradation for 5h) was observed with the most uniform distribution of titania NPs of 30 nm on the surface of the polymer (sample B). The formation of some aggregates and cracks in the deposited layer (sample C) resulted in a decrease in the photocatalytic activity, as compared with sample B. The rate constant, $k$, for the MB decomposition reaction was derived from the linear slope of the relationship between $\ln(C/C_0)$ and $kt$, where $C_0$ and $C$ were the concentrations of the initial solution after $t$ (min) of UV irradiation, and were shown in Table 1.

The size of the crystals and the homogeneity of their distribution on the surface are important factors affecting the photocatalytic activity of the TiO2 film. The smaller the particle size, the larger is the number of the particles, and the higher is the specific surface area. Both are advantageous for the photocatalytic reaction taking place on the surface of the particle. These factors may explain the best photocatalytic activity observed with sample B.

![Figure 6. Kinetics of the photocatalytic degradation of MB on the TiO2-coated parylene.](image)

### 4 CONCLUSION

TiO2 film was deposited on parylene and polycarbonate by the ultrasound-assisted hydrolysis of TIP and the simultaneous throwing of as-prepared titania NPs to the substrate by sonochemical microjets. The physical and chemical methods revealed a coating layer composed of nanocrystalline TiO2 of anatase structure. The titania NPs were strongly anchored to the polymers' surface by a one-step sonochemical procedure without the use of any binding compounds. The penetration of the TiO2 into the parylene film without any reasonable damage to its structure was demonstrated. The results showed that by varying the concentration of precursor, type and concentration of the stabilizing agent (PVP or PEG), the sonochemical deposition of titania film on the polymers' surface can be adjusted. Thus, the ultrasound-assisted method of coating polymers with titania is well controlled and regulated. The hydrophilic and photocatalytic properties of the coated substrates depend on the uniformity and thickness of the titania-layer on the surface that influence the self cleaning ability of polymers.

### REFERENCES