Surface modification of polypropylene non-woven fibers with TiO₂ nanoparticles via layer-by-layer self assembly method: Preparation and photocatalytic activity

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ABSTRACT

Polypropylene (PP) meltblown fibers were coated with titanium dioxide (TiO₂) nanoparticles using layer-by-layer (LbL) deposition technique. The fibers were first modified with 3 layers of poly(4-styrenesulfonic acid) (PSS) and poly(diallyl-dimethylammonium chloride) (PDADMAC) to improve the anchoring of the TiO₂ nanoparticle clusters. PDADMAC, which is positively charged, was then used as counter polyelectrolyte in tandem with anionic TiO₂ nanoparticles to construct TiO₂/PDADMAC bilayer in the LbL fashion. The number of deposited TiO₂/PDADMAC layers was varied from 1 to 7 bilayer, and could be used to adjust TiO₂ loading. The LbL technique showed higher TiO₂ loading efficiency than the impregnation approach. The modified fibers were tested for their photocatalytic activity against a model dye, Methylene Blue (MB). Results showed that the TiO₂ modified fibers exhibited excellent photocatalytic activity efficiency similar to that of TiO₂ powder dispersed in solution. The deposition of TiO₂ 3 bilayer on the PP substrate was sufficient to produce nanocomposite fibers that could bleach the MB solution in less than 4 hr. TiO₂-LbL constructions also preserved TiO₂ adhesion on substrate surface after 1 cycle of photocatalytic test. Successive photocatalytic test showed decline in MB reduction rate with loss of TiO₂ particles from the substrate outer surface. However, even in the third cycle, the TiO₂ modified fibers are still moderately effective as it could remove more than 95% of MB after 8 hr of treatment.

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those in solid form, it may require additional, often costlier and more sophisticated, process, such as special functionalization of surface substrate, to maintain TiO$_2$ attributes in final product.

Many researchers have been interested in integrating TiO$_2$ NPs onto fiber membrane since substrate in fiber form renders high surface area with small pore sizes, and can be used directly and effectively in water/air filtration and other applications (Gurrajani and Gupta, 2011; Gashiti et al., 2012; Wang et al., 2014). Some concepts used physical or chemical route to modify conventional fibers with TiO$_2$ NPs such as a plasma treatment of PP fibers to enhance TiO$_2$ NP adhesion with a substrate (Szabová et al., 2009), a direct TiO$_2$ NP synthesis on fiber surface by seed-hydrothermal (Yang et al., 2012) or a simple spray on and dip-dry coating on polyester fibers (Han et al., 2012). Several approaches had been developed to produce TiO$_2$ fibers directly, such as electrospinning of TiO$_2$ blending in nylon 6 (Pant et al., 2011), coaxial electrospinning to produce hollow TiO$_2$ nanofibers (Chang et al., 2013) and self-cleaning textiles (Bedford and Steckl, 2010). These methods have different advantages and limitations and could be employed effectively depending on a requirement for particular applications.

Layer by layer (LbL) self assembly technique, a low cost and simple method, is another approach that could be very useful for fiber surface modification. Fundamentally, LbL process is based on electrostatic attraction between cationic and anionic polyelectrolyte solutions that leads to the formation of polyelectrolyte multilayer thin film on a solid surface with its thickness in the range of tens of nanometers to micrometers. The alternate positive and negative layers of LbL film can be replaced with any material containing appropriate polarity. Therefore, surface property of substrate that the film deposited on can be tailored with ease to have desirable property such as to enhance cell–matrix interaction (Dubas et al., 2009), to improve mechanical property of electrospun fiber (Park et al., 2007), and to protect underlining surface (Carosio et al., 2013). Several research had also functionalize substrate surface with LbL film in tandem with TiO$_2$ and other metal oxide nanoparticles. Such approach had been employed to enhance antibacterial property (Wang et al., 2013), to enhance UV protection property of cotton fabrics (Uğur et al., 2010, 2011), to produce a stable hydrophilic–biocompatible surface (Kommireddy et al., 2005), to improve thermal stability of polypropylene (PP) nonwoven fibers (Stawski et al., 2014) and to induce photocatalytic property on nanofiber and fiber media (Pan et al., 2009; Lee et al., 2007; Limmongkon et al., 2013).

In this present contribution, we attempted to fabricate a photocatalytic membrane to be used in water and air treatment application from a low cost and commercial available materials. PP meltblown nonwoven media was used as a substrate for anchoring TiO$_2$ nanoparticle clusters via LbL fabrication. LbL film formation steps were revised to obtain uniform and thorough deposition of TiO$_2$ on the substrate. Photocatalytic activity of obtained membranes against model dye was studied to demonstrate their efficiency. We expected that the media would provide desirable photocatalytic property while reducing potential risk of TiO$_2$ contamination into the environment.

1. Materials and methods

1.1. Materials and chemicals

Polypropylene meltblown nonwoven fibers with 95% bacterial filtration efficiency (BFE) were obtained from Foshan Guide Nonwoven (Foshan Guide Nonwoven, Foshan, Guangdong, China). Poly(4-styrenesulfonic acid) (PSS) with molecular weight (MW) of 70,000 Da and poly(diallyldimethylammonium chloride) (PDADMAC, 20 wt.% MW 200,000–350,000) were purchased from Sigma Aldrich (Sigma Aldrich, St. Louis, Missouri, USA). Sodium chloride (NaCl, analytical grade) was purchased from Carlo Erba (Carlo Erba, Cornaredo, Milan, Italy). Titanium dioxide particles (TiO$_2$, anatase type) were obtained from Wilson Hangzhou Import & Export (Wilson Hangzhou Import & Export, Hangzhou, China). All chemicals were used as received without any further purification. Deionized water was used as solvent media for polyelectrolyte solvent and TiO$_2$ dispersing media.

1.2. Fabrication of polypropylene fiber media coated TiO$_2$ by LbL technique

Polypropylene (PP) non woven fabric, to be used as a TiO$_2$ powder supporting structure, was cut into a circle with 2.6 cm diameter, then rinsed off any loose fibers or particulate contaminants in tap water for a few times with final rinsing in distilled water. The PP pieces were oven dried at about 80°C for 6 hr and kept in electronic dehumidifying cabinet (20% Rh) prior to use. To prepare polyelectrolyte solutions for LbL coating, appropriate amounts of PSS and PDADMAC were weighted and dissolved in 1 mol/L NaCl in deionized water to obtain a final concentration of 10 m mol/L TiO$_2$ suspension, with 1% (W/V) concentration, was prepared by stirring 2.5 g of TiO$_2$ powder in 250 mL deionized water vigorously for 5 min. The suspension was kept agitated with mechanical stirrers at all times until LbL fabrication was finished.

Fig. 1a–c illustrates LbL film fabrication protocol used in this study. In short, the PP disc was placed inside a 25 mm filter holder attached on a tip of 60 mL syringe. The syringe was loaded with 50 mL of liquid media to be used at any particular step in the process, and placed in the syringe pump (NE 300, New Era Pump Systems Inc., Farmingdale, New York, USA). The media flow rate was kept constant at 10 mL/min by the pump. First, PP fibrous disc was flushed with anionic polyelectrolyte solution (PSS), then any excess PSS was rinsed off with deionized water to form the first half of the LbL film. The first Lbl double layer was then completed by flushing the PP disc with cationic polyelectrolyte solution (PDADMAC) and to get rid of excess polyelectrolyte with deionized water. The process was repeated 3 times to obtain 3 PSS-PDADMAC double layers which were used as a base primer for TiO$_2$ layer deposition. The TiO$_2$-PDADMAC double layers were fabricated using the same method for PSS-PDADMAC construction with additional step during TiO$_2$ layer construction. For each TiO$_2$ layer, after the PP disc was flushed with TiO$_2$ suspension and rinsed off, the disc was taken out, flipped over, reinserted into the holder, and flushed with TiO$_2$ suspension again so TiO$_2$ particles would adhere on both sides of PP disc in similar fashion. Up to 7 TiO$_2$-PDADMAC double layers were
constructed with the outermost layer TiO2. The effect of LbL films on TiO2 nanoparticle adhesion was compared with TiO2 direct impregnation where 50 mL of 1 wt.% TiO2 suspension was pumped through neat PP discs and then rinsed in clean water to wash away loose TiO2 particles.

1.3. Material and TiO2-LbL-PP composite characterization

TiO2 crystal structure was determined by X-ray diffraction (“XRD) analysis (PW3710, Philips Analytical, Almelo, Netherlands) and its surface charge in deionized water was determined by zeta potential measurement (Nano-ZS series Model ZEN3600, Malvern, UK). The morphology of fibers and TiO2 coating was observed by using scanning electron microscope (SEM) (XL 30 CP, Philips, Eindhoven, Netherlands). Fourier transform infrared spectrophotometer (Nicolet 6700 FTIR, Thermo Fisher Scientific, Waltham, Massachusetts, USA) was used to analyze functional group of material to follow uniformity of LbL film coverage. Fiber sizes were assessed using FibraQuant program version 1.3.149 (nanoScaffold Technologies, Chapel Hill, North Carolina, USA). TiO2 mass fraction deposited on the fibers was determined by thermogravimetric analysis (TGA) method (TG 209F3, Netzsch, Selb, Germany) under nitrogen atmosphere at 10°C/min heating rate from room temperature to 600°C.

1.4. Photocatalytic activity of TiO2-LbL-PP composite

In this study, Methylene Blue (MB) was used as a model pollutant in water. To assess photocatalytic activity of obtained composite, TiO2-LbL PP membranes with 1 and 3 TiO2 double layers were chosen due to TiO2 deposition quality. About 0.1 g of the modified fibrous discs (5–6 discs depending on number of TiO2 construction layers) was put in a 250 mL glass beaker containing 80 mL of MB solution with 5 ppm concentration. MB solution was mechanically stirred at constant rate for up to 8 hr. Ultraviolet lamp (6 W with 254 nm wavelength) was placed 15 cm away directly above the beaker. MB solution was taken out at a predetermined time point, for up to 8 hr. The photocatalytic activity of the TiO2-PP composite was followed by measuring MB concentration with UV-visible spectrophotometer (Specord S100, Analytik Jena, Jena, Germany) at 663 nm wavelength. To make a comparison, TiO2 powders weighted equivalent to that embedded on TiO2-LbL-PP disc were used as reference materials. Stability and efficiency of the composite with 3 TiO2 bilayer after multiple use were also assessed, where the composite was subjected up to 3 successive cycles of photocatalytic tests. All measurements were carried out in triplicate.

2. Results and discussion

2.1. Properties of TiO2 in deionized water

Due to their point of zero charge (PZC) being at 4.5, TiO2 nanoparticles in solution can possess either a cationic or anionic surface charge depending on the pH of the solution (Lee et al., 2010). In this experiment, the surface zeta potential of the TiO2 in deionized water (pH 5.8) was measured to be −34 mV, confirming its anionic character. The nanoparticles could therefore be deposited in sequence with cationic polyelectrolyte (PDADMAC). SEM images (Fig. 2) revealed that after vigorous agitation step, TiO2 particle clusters broke up into small clusters with irregular shape ranging in size from a few hundreds of nanometers to a few micrometers. These clusters consisted of many TiO2 primary nanoparticles about 80–120 nm in size.

2.2. Preparation of TiO2 coated polypropylene (PP) fibers and TiO2-LbL-PP composites

For direct impregnation method, TiO2 particles appeared to deposit mostly where several fibers are bundling together and

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**Fig. 1** – (a) Experiment set up of layer by layer (LbL) coating, (b) scheme of LbL-TiO2 deposited on fibers and (c) diagram of LbL-TiO2 coating layer used in this experiment.

**Fig. 2** – SEM image of TiO2 clusters used in this study.
form a small opening between the fibers. These opening behaved like a sieve that restrained TiO$_2$ clusters as the suspension flowed through the fabric. Many TiO$_2$ small clusters deposited directly on the fiber surface (Fig. 3a). SEM images also revealed minimal TiO$_2$ deposition inside the PP media.

In the impregnation approach, the PP fibers were simply flushed with TiO$_2$ suspension. The LbL approach was more complex and required two kinds of independent coatings. To change the fiber nature from being hydrophobic to hydrophilic, the fibers were first modified with 3 layers of PSS-PDAD as primer layers followed by the deposition of 1, 3, 5 and 7 bilayer of PDADMAC-TiO$_2$. From SEM images, the LbL approach clearly provided a much denser and more homogeneous coating on the fibers compared to the impregnation method (Fig. 3b). The TiO$_2$ cluster adhesion on the fiber surface was facilitated by the electrostatic interactions with cationic PDADMAC. The primer coating (PDADMAC/PSS) was used because previous attempts to directly deposit TiO$_2$ nanoparticles using the LbL on the fiber were unsuccessful due to the hydrophobic nature of the fiber. Use of the primer coat was found to provide sufficient surface modification to allow further growth of the PDADMAC/TiO$_2$ film. Results from ATR-FTIR analysis showed that the intensity of FTIR peaks corresponding to PDADMAC and PSS was decreased as the number of TiO$_2$ layers increased and yielded fuller and thicker TiO$_2$ coverage throughout PP fibrous substrate.

2.3. TiO$_2$-LbL-PP composite morphological assessment

Native PP fibers had smooth surface with wide fiber size variation ranging from around 2 to 10 $\mu$m (Fig. 4a). The spunbond fiber mesh was chosen as a supporter because it had relatively small diameter and high surface area compared to conventional non-woven fabric, while possessed a better mechanical integrity over a much smaller electrospun nanofibers. Fig. 4b shows a fairly uniform and smooth PDADMAC/PSS primer (3 layers) deposited on PP fiber surface. Upon the fabrication of the first TiO$_2$ layer, most of the fiber surface was covered with a thin layer of numerous TiO$_2$ nanoparticle clusters (Fig. 4c). Evidently, the image showed high effectiveness of fabrication method employed here, as TiO$_2$ coverage was consistent throughout the whole PP substrate even deep inside the PP membrane. Building up TiO$_2$ to 3 bilayers provided almost full coverage over the entire fiber surface.

With addition build up of TiO$_2$ to 5 and 7 bilayer (Fig. 4e–f), the TiO$_2$ layers appeared to be a dense layer wrapped around the fiber. TiO$_2$ was also found to clog over small opening between fibrous substrate. This was due to the difficulty in rinsing off any excess polyelectrolyte trapped inside polymer membranes, especially at high LbL layers, leading to a clogging of the fiber mesh (Dubas et al., 2006; Joshi et al., 2011). The optimum number of TiO$_2$ bilayer construction appeared to be 1 and 3 bilayer as they provided the best fiber coverage with low clogging and blocking of the porous structure of the fiber mat.

2.4. TGA analysis

Although SEM image can be used to confirm the improved coating with the LbL approach, TGA can provide a quantitative measurement of the weight fraction of TiO$_2$ particles deposited on the PP fibers (Srikulkit et al., 2006). After thermally decomposed polymers in the sample at 600°C, at which all polymer components in PP fibers and LbL coated fibers were completely removed, only TiO$_2$ would remain. Table 1 summarizes the TGA results and the weight fraction of TiO$_2$ presented in each sample. TiO$_2$ mass fraction increased steadily from about 25% to 80% as the TiO$_2$ layers increased from 1 to 7 layers. Beyond the first TiO$_2$ layer, the TiO$_2$ mass fraction increased about 8% to 10% for each additional TiO$_2$ layer. Therefore, conceptually, one can construct the membrane with TiO$_2$ mass fraction beyond reported value simply by adding more TiO$_2$ layers. However, fiber pore clogging would be a limiting factor in real practice.

2.5. Photocatalytic activity

To demonstrate potential use of the developed nanocomposite membrane, photocatalytic activity of the native PP fiber media, PP coated TiO$_2$ and TiO$_2$ powder against MB were investigated. Methylene Blue (MB) was used as a model organic compound because its degradation and bleaching could be easily followed by UV–vis spectroscopy. Since the TiO$_2$-LbL-PP composite with 5 and 7 TiO$_2$ bilayer suffered from clogging problem, only the nanocomposites with 1 and 3 TiO$_2$ bilayer were chosen to be studied in this part. Since the nanocomposites with 1 and 3 TiO$_2$ bilayer contained about 25 and 45 mg of TiO$_2$, TiO$_2$ powders weighted 25 and 45 mg were used as their respective benchmark to evaluate their MB
decomposition efficiency. Fig. 5 presents the relationship between $C_t / C_0$ of MB solution treated with different materials as a function of UV irradiation time, where $C_t$ and $C_0$ represent the concentration of MB solution at any given time ($t$) and its initial concentration, respectively.

The results showed that, after 8 hr, UV irradiation and surface adsorption on PP substrate under UV irradiation accounted for about 0.3% and 10.1% of MB reduction, respectively. After 8 hr of treatment, surface adsorption on 25 and 45 mg of TiO$_2$ powder without UV irradiation reduced MB concentration by 22.5% and 24.6%, respectively. Comparing MB reduction efficiency of 1 and 3 TiO$_2$ bilayer nanocomposites with their powder counterpart revealed an interesting observation. After 1 hr of UV irradiation, 25 mg-powder and 45 mg-powder could reduce 77.7% and 91.1% of MB, compared to 50.1% and 74.5% of the 1 and 3 TiO$_2$ bilayer composites. Faster MB reduction rate of the TiO$_2$ powder could be a result of higher surface area and free movement of the powder within testing media. However, after 7 hr, both 25 mg-powder and the 1 bi-layer nanocomposite exhibited similar efficiency where both of them could reduce more than 99% of MB. Furthermore, the 3 bilayer nanocomposite could decompose all MB within 4 hr compared to the time that the 45 mg powder used at about 3 hr. Most of the TiO$_2$ particles on the 3 bilayer nanocomposite still retained in their packed dense layer on PP substrate after 8 hr.

Table 1 – TGA (thermogravimetric analysis) results of polypropylene (PP) coated TiO$_2$ (LBL-TiO$_2$-PP) with various numbers of layers of TiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (wt.%)</th>
<th>PP/ PSS-PDAD (wt.%)</th>
<th>TiO$_2$ (wt.%)</th>
<th>Decomposition peak position (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP fibers</td>
<td>98.99</td>
<td>–</td>
<td>–</td>
<td>452.0</td>
</tr>
<tr>
<td>0 layer</td>
<td>n/a</td>
<td>98.69</td>
<td>–</td>
<td>453.9</td>
</tr>
<tr>
<td>1 layer</td>
<td>n/a</td>
<td>74.86</td>
<td>25.14</td>
<td>468.9</td>
</tr>
<tr>
<td>3 layers</td>
<td>n/a</td>
<td>55.93</td>
<td>44.06</td>
<td>472.8</td>
</tr>
<tr>
<td>5 layers</td>
<td>n/a</td>
<td>38.94</td>
<td>61.06</td>
<td>472.8</td>
</tr>
<tr>
<td>7 layers</td>
<td>n/a</td>
<td>19.77</td>
<td>80.23</td>
<td>466.6</td>
</tr>
</tbody>
</table>

LBL: layer by layer; PSS: poly(4-styrenesulfonic acid); PDAD: poly(diallyldimethylammonium chloride); n/a: data not available.
of MB treatment (Fig. 6a and b). The result clearly elucidated that TiO2-LbL-PP nanocomposite still retained photocatalytic efficiency within the same order of TiO2 powder while offered benefit of TiO2 handling in separation step.

For multiple use of the 3 TiO2 bilayer composite, we found that after 4 hr of treatment, overall MB removal efficiency of the composite decreased from 100.00% to 98.2% and 77.3% for 1, 2 and 3 successive treatment cycles, respectively. It was apparent that the MB removal rate of the composite declined more with each treatment cycle (Fig. 7). The cause for performance deterioration was due to a loss of TiO2 particles from the substrate as evidently shown in Fig. 8, where TiO2 was drastically absent from many parts of the membrane outer surface. Since LbL film is constituted via Coulombic’s attraction between opposite charged polymers, interference from other charged species presented in media, in combination with mechanical agitation the film had to withstand in our test, could disrupt and disintegrate the film structure, resulting in TiO2 loss. Nonetheless, the mechanical integrity of the film was fairly robust, as TiO2 embedded inside the membrane appeared to still be intact after 3 testing cycles. Furthermore, despite the TiO2 loss, the composite could still remove 100.0% and 95.9% of MB after 8 hr, in the second and third successive treatment cycles.

3. Conclusions

TiO2-LbL-PP nanocomposite fibers were successfully fabricated. TiO2 nanoparticle clusters were affixed on PP meltblown nonwoven media via LbL method. LbL and TiO2 layers were constructed by flushing solution through PP membrane in optimized condition to obtain uniform and thorough deposition of TiO2 on the PP substrate. The LbL technique showed higher TiO2 loading efficiency coating than the impregnation approach and the LbL techniques displayed a tunable TiO2 loading. The TiO2 composition could be varied from about 25% to 80% by weight depending on the number of TiO2 layers. Photocatalytic study against MB showed that TiO2-LbL-PP nanocomposite still retained photocatalytic efficiency within the same order of TiO2 powder while lower potential risk of TiO2 contamination into the environment. Overall MB removal rate and MB removal efficiency of the composite were found to decline slightly over the 2nd and 3rd successive testing cycles.
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Fig. 8 – SEM image of (a) as prepared TiO2-LbL-PP nanocomposites with 3 TiO2 bilayer, (b) after 1 cycle, (c) after 2 cycles and (d) after 3 cycles of 8 hr of photocatalytic test.


