VOLATILE ORGANIC COMPOUND TREATMENT UNDER VISIBLE LIGHT BY USING A FUNCTONALIZED TEXTILE

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ABSTRACT

The aim of this study is to develop functionalized textile substrates (PES – woven fabric) with TiO_2 to photodegrade Volatile Organic Compounds (COVs) in order to improve the Indoor Air Quality (IAQ). As the visible light is more interesting for indoor applications, TiO_2 was doped with silver (Ag) and the physical vapour deposition (PVD) was preferred for doping process. In addition to Ag-doped TiO_2, cellulose nanocrystals (CNCs) were desired as the incorporation vector between textile substrate and TiO_2 in order to increase the binding effect by encapsulating TiO_2 into the porous structure of CNC. The padding process was used for functionalization.

Key Words: Indoor air quality, photocatalysis, TiO_2, volatile organic compounds.

1. INTRODUCTION

As people in industrialized countries spend the majority of their time (over 90%) in various indoor spaces, the Indoor Air Quality (IAQ) has become an important health and safety concern [1]. The majority of pollutants, which are present indoors, are Volatile Organic Compounds (VOCs) that originate from different sources like building products (room furnishings, paints, glues, varnishes etc.) and occupant activities [2]. Indoor air treatment is a complex phenomenon because of the wide variety of potential pollutants and the low level of pollutant concentration. In addition to these, the airflow to treat these VOCs remains modest. Photocatalysis presents a real advantage for indoor air applications as it is able to treat low concentrations and flow rates [3]. The semiconductor photocatalysis has been widely applied in removing the organic pollutants from air [4]. The titanium dioxide (TiO_2) is a semiconductor photocatalyst which can be presented as an effectual, easily available, relatively inexpensive and chemically stable one. However, it has two major inconvenient: (i) it can be only triggered by near UV radiation because of its wide band gap and (ii) the photogenerated electron/hole pairs are liable to recombination, leading to low quantum yields [5, 6]. In order to eliminate these disadvantages, its band gap can be reduced using various dopants (nitrogen, silver, vanadium, carbon…) and it can have a photocatalytic activity under visible light [7 - 10]. The aim of this study is to develop a functionalized textile substrate with a hybrid photocatalytic material based on TiO_2 and cellulose nanocrystals (CNC) to photodegrade VOCs in order to improve the IAQ. As the visible light is more interesting for indoor applications and a large part of the UV light is blocked by outside glass windows, TiO_2 was doped with silver (Ag), iodine (I) and azote (N) and the magnetron sputtering method was preferred for doping process. In addition to doped TiO_2, CNC were preferred as the incorporation vector between textile substrate and TiO_2 in order to increase the binding effect of TiO_2 by encapsulating them into the porous structure of CNC. The textile substrate was functionalized with this hybrid photocatalytic material by using padding process. In this study, polyester (PES) woven fabric with acoustic properties was tested as textile substrate.

The functionalized samples were characterized with different methods, i.e. ATR, TGA, SEM-EDX. The first results showed the presence of TiO_2 on textile substrate.

2. MATERIALS AND METHODS

2.1 Materials

100% white PES fabric with acoustic properties was used as textile substrate. A commercial TiO_2 P25® (Evonik, Germany) was preferred as a reference in order to see the influence on the photocatalytic activity under visible light. This commercial TiO_2 P25® was doped with silver (Ag), iodine (I) and azote (N) in order to obtain a photocatalytic activity with visible light. Cellulose nanocrystals (CNC) were used as the incorporation element.

2.2 Methods

The procedures for preparation of (i) CNC, (ii) doped TiO_2, (iii) CNC/TiO_2 suspension and padding process are presented below.

Preparation of CNC

Two different methods were used to prepare CNC. For the first method, 450 mL of a sulfuric acid solution at 64 wt. % was placed in a water bath at 45 ^{0}C. Meanwhile, 29.6 g of cotton wool was torn apart in small pieces in order to facilitate the acid hydrolysis. When the acidic solution reached 45 ^{0}C, the cotton wool was added for 20 minutes under mechanical stirring. The hydrolysis reaction was allowed to continue for 40 minutes and the resulting slurry was diluted with 2 L of deionized water to give a milk-like mixture. Subsequently, the mixture was washed from the excess of acid by centrifugation until a well-dispersed mixture in deionized water was obtained, which was dialyzed against tap water for 48 h. The dialyzed suspension was sonicated in order to re-disperse the aggregates formed during the dialysis prior to filtration through a sintered glass of porosity 2. Finally, the filtered suspension was purified with a strong acid ion exchange resin for 48 hours before removing the resin by filtration to result in the CNC suspension. Rotational evaporation was used to concentrated the suspension to the desired concentration For the second method, the cotton wool (50 g), previously cut in small pieces, was added to a 64 wt. % sulphuric acid solution (450 mL) preheated at 45 °C under moderate mechanic stirring. The total cotton addition time was 15 minutes. The hydrolysis was allowed to continue for 45 minutes under strong magnetic stirring. The hydrolysis was quenched by diluting the resulting grey viscous slurry into deionized water (2 L) to give a milk-like mixture. Subsequently, the as-prepared mixture was washed with deionized water by successive centrifugation and the supernatant was discarded each time until no separation was observed between the deposited product and the supernatant. Each centrifugation was conducted for 20 minutes at 4 °C and 7500 rpm. The washed product was further purified by dialysis against deionized water over 72 hours. The dialysed mixture was tip-sonicated for 3 minutes per fraction of 150 mL using a Branson Digital Sonifier® adjusted to an amplitude of 25 % and the temperature of the mixture remained below 35 °C throughout the sonication. The mixture was filtered through a fritted glass of porosity 2 before passing it through a fritted glass column of 1.9 cm inner diameter filled at the height of about 30 cm with previously rinsed Dowex Marathon C hydrogen form strong acid cation exchange resin.

Preparation of doped TiO_2

TiO_2 P25® was doped with three different types of doping agents (Ag, I, N). The magnetron sputtering method (R2QU14XGX, Kurt J. Lesker Compant Ltd., UK) was used to produce the doped samples. The powder of TiO_2 P25® was used as the substrate for sputtering deposition and the materials for the sputtering targets were Ag, I and N. The samples were named Ag-doped TiO_2 P25®, I-doped TiO_2 P25® and N-doped TiO_2 P25®.

Preparation of CNC/ TiO_2 suspension and padding process

Four different TiO_2, i.e. TiO_2 P25®, Ag-doped TiO2 P25®, I-doped TiO2 P25®, N-doped TiO2 P25®, with a weight of 0.5 g was mixed with 20 g (2.8 wt. %) CNC suspension using a high-shear disperser (Ultra-Turrax, IKA) operated at a speed of 7000 rpm during 15 minutes at room temperature. Afterwards, the suspension was sonicated in an ultra-sonication bath (Bandelin, Germany) for 15 minutes at room temperature. Hence, I-doped TiO_2 P25® and N-doped TiO_2 P25® were not totally soluble in CNC, 10 minutes of mechanical stirring was added in the explained procedure. The prepared suspensions, i.e. CNC/TiO_2 P25®, CNC/Ag-doped TiO_2 P25®, CNC/ I-doped TiO_2 P25®, CNC/ N-doped TiO_2 P25®, were applied to the samples by using padding process. For this process, the applied pressure was 4 Bar and the speed of the rollers was 7 rpm. After the padding process, the samples were dried and cured at 120 °C and at 150 °C for 1 minute, respectively.

3. RESULTS AND DISCUSSION

As mentioned in the section of CNC preparation, two different methods were used for synthesis. By using second method, it was supposed to have a purer CNC suspension by increasing chemically bounded sulphates groups to the CNC instead of unattached groups [11]. However, this second method had an influence on the thermal properties of samples and their color changed from white to dark grey after curing them at 150 °C. Thus, the results obtained with first CNC method were presented for the rest of experimental section.

Different methods were used for characterization of produced samples: Attenuated Total Reflectance (ATR), Scanning Electron Microscope (SEM) - Energy Dispersive X-ray (EDX) and Thermogravimetric Analysis (TGA).

3.1 Attenuated Total Reflectance (ATR)

Functionalized PES fabrics were characterized by IR spectroscopy (Varian, USA). The samples were analyzed in reflectance mode in the range of 400 – 4000 cm^{-1}. Each spectrum was collected by cumulating 64 scans at a resolution of 4 cm^{-1}. The experimental data was collected and analyzed using the Varian Resolutions Pro software. Each sample was analyzed three times for the reproducibility.

The Figure 1 presents the ATR spectra of functionalized samples. As there isn't any significant difference between Ag, I and N doped samples, the results of CNC/ TiO_2 P25® and CNC/Ag-doped TiO_2 P25® treated samples were presented.

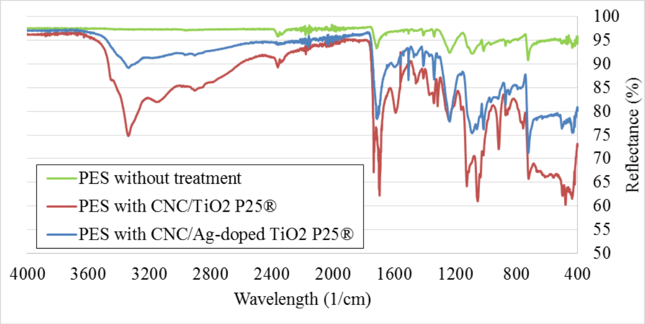


Figure 1. The spectra of non-treated and functionalized PES samples

ATR spectra of the CNC showed bands at 3400 cm^{-1} and 2897 cm^{-1} indicating the stretching vibration of OH and the CH stretching vibration, respectively. The intense band at 1621 cm^{-1} indicated the presence of CO stretching vibration of cellulose rings as well as OH bending vibration of absorbed water molecule and the 1028 cm^{-1} band is related to the C−OH stretching vibration of secondary and primary alcohols of cellulose. In addition, it is worthwhile to note peak at 614 cm^{-1} indicates the C−OH out of plane bending vibration [12]. In case of TiO_2, the broad vibration band between 3650 and 2600 cm^{-1} is associated with the OH stretching mode of water molecules (physisorbed molecular water), while that at 1620 cm^{-1} is assigned to their bending modes. The bands in the range 1600-1300 cm^{-1} are generally associated with carbonate groups; thus, the bands at around 1420 cm^{-1} are assigned to carbonate species formed by the adsorption of atmospheric CO_2. The absorption in the range 1000-600 cm^{-1} is due to the surface vibrations of the Ti-O bonds [13].

3.2 Thermogravimetric Analysis (TGA)

All samples were characterized thermally by using a TGA 4000 thermogravimetric analyzer (Perkin Elmer, USA) in the temperature range of 30 – 700 °C. The heating rate was maintained at 20 °C.min^{-1}. The measurements were made under a constant air flow rate of 20 mL.min^{-1}. The experimental data was collected and analyzed using the Perkin Elmer Pyris Manager software. Each sample was characterized three times in order to confirm the repeatability of the measurement and homogeneity of the treatments.

The Table 1 presents the TGA results of non-treated and functionnalized samples.

Table 1. The weight loss of non-treated and functionalized samples (%) obtained by TGA at 700 °C

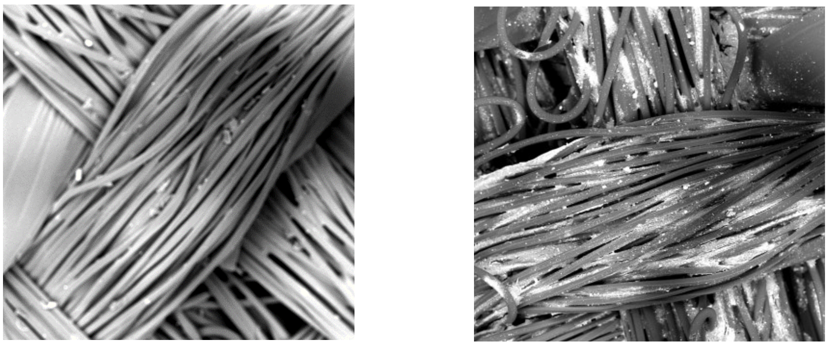
Sample	Weight loss (%)
PES without treatment	0.85 ± 0.10
PES with CNC/TiO_2 P25®	2.02 ± 0.08
PES with CNC/Ag-doped TiO_2 P25®	1.76 ± 0.12
PES with CNC/I-doped TiO_2 P25®	1.63 ± 0.25
PES with CNC/N-doped TiO_2 P25®	1.53 ± 0.03

The TGA results confirms the presence of TiO_2 on the samples. The thermogravimetric analysis showed that the degradation of fabrics started at around 340 °C and reached a maximum rate around 600 °C. From 580 °C onwards, the weight loss was 0.85 ± 0.10 % for PES fabric without treatment. This percentage can be caused by particles used during the spinning and finishing processes. However, the weight of residue for treated samples was higher comparing to non-treated samples at 700 °C. As it was presented in our previous study, the CNC was fully degraded at 600 °C while TiO_2 remained stable at this temperature. Thus, the weight loss percentages listed in Table 1 represent the quantity of TiO_2 on fabric surface [14].

3.3 Scanning Electron Microscope (SEM) - Energy Dispersive X-ray (EDX)

A scanning electron microscope (Phenom ProX, ThermoFischer Scientific, US) was used. The identification of different chemical elements in the samples was accomplished with the Energy Dispersive X-ray (EDX) spectroscopy.

The SEM images and EDX analysis of non-treated PES and CNC/Ag-doped TiO_2 P25® treated PES are presented in Figure 2.



Element Symbol	Atomic Concentration	Weight Concentration
C	64.11	57.28
O	35.89	42.72

(a)

Element Symbol	Atomic Concentration	Weight Concentration
C	58.77	49.32
O	39.17	43.79
Ti	2.06	6.89

(b)

Figure 2. The SEM - EDX analysis of (a) non-functionalized and (b) CNC/Ag-doped TiO_2 P25® PES fabrics

The obtained EDX and SEM results on Figure 2b confirmed our previous results concerning the presence of TiO_2 on functionalized samples.

4. CONCLUSION AND PERSPECTIVES

During this study, a polyester fabric with acoustic properties was functionalized with a hybrid photocatalytic material consists of CNC and doped-TiO_2. The CNC solutions were prepared with two methods. Due to the thermal properties of CNC, the color of samples changed with second method. Thus, the results with first CNC method were presented in this study. To obtain a photocatalytic activity under visible light, the TiO_2 P25® was doped with Ag, I and N. The suspensions produced by I-doped TiO_2 P25® and N-doped TiO_2 P25® were not stable therefore Ag-doped TiO_2 P25® will be used for future studies. The first results showed the feasibility of the process and the presence of doped TiO_2 on textile substrate. The efficiency of photocatalytic activity will be analyzed by using a measuring unit, which is developed during this study.

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