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ORIGINAL PAPER

TiO_2/spacer succinate films grafted onto nylon as a new approach to develop self-cleaning textile fibers that remove stains: a promising way to reduce reliance on cleaning water

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Abstract
Succinic acid was used as a spacer to bind titanium dioxide onto nylon as a new approach to develop self-cleaning fibers. Photoinduced decomposition of stains was achieved within acceptable times under ultraviolet A irradiation, a component of both solar light and indoor lamps spectrum. The surface properties of this innovative film were determined by scanning electron microscopy, electron-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. The self-cleaning process was evaluated by analyzing the discoloration of coffee and palm oil stains by ultraviolet/visible diffuse reflection spectroscopy and mineralization via CO_2 evolution, recorded using an infrared sensor. The results indicate that grafting TiO_2 onto nylon, a synthetic fiber, using succinic acid is a successful chemical binding method, leading to a new self-cleaning material for stain discoloration. This new material is a promising solution to save water and reduce wastewater generated by the use of conventional substances used in textile cleaning.

Keywords Chemical binding · Coating · Coffee · Palm oil · Succinic acid · Synthetic fabrics

Introduction

Textile fibers require the use of detergents for cleaning, which result in the discharge of waste chemicals into the environment and cause environmental pollution. These residues include toxic chloro-compounds when dry-cleaning is used (Giagnorio et al. 2017; Yun et al. 2016). Modification of the surface properties of textile fibers is a topic of interest that has potential for large scale applications (Abbas et al. 2018; Ahmad and Kan 2017; Eglītis and Mežinskis 2015; Mejía et al. 2009a, b).

Self-cleaning of natural and artificial fabrics under light irradiation is a relatively new field and has been reported for cotton (Sarwar et al. 2022; Diaa and Hassabo 2022; Pal et al. 2021; Gautam and Yu 2020; Kale et al. 2016; Eglītis and Mežinskis 2015; Lee et al. 2014; Khajavi and Berendjchi 2014; Pakdel and Daoud 2013; Tan et al. 2013; Sobczyk-Guzenda et al. 2013; Palamutcu et al. 2011; Karimi et al. 2010), polyester (Jeong et al. 2021; Pakdel et al. 2020; Li et al. 2018; Gaminian and Montazer 2017; Haji et al. 2016; Tayyar and Alan 2015; Selishchev et al. 2013; Mihailović et al. 2010), wool (Ibrahim et al. 2022; Liu et al. 2017; Haji et al. 2016; Shirgholami et al. 2016; Pakdel et al. 2013; Montazer and Seifollahzadeh 2011a), wool/polyester (Montazer and Seifollahzadeh 2011a; b), cotton/polyester (Sivakumar et al. 2016; Tayyar and Alan 2015), and nylon (Wang et al. 2021; Naebe et al. 2021; Hasan et al. 2020; Ichiura and Kozu 2020; Zhou et al. 2017; Zohoori et al. 2014a, b; Mejía et al. 2009a, b). TiO_2 can be used to modify the textile surface due to its low price, chemical stability, and non-toxic behavior (Noman et al. 2018; Zhou et al. 2017; Radetic 2013).

Coating TiO_2 on textiles has been reported using the physical or chemical treatment of fabrics like sol–gel (Abbas

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et al. 2018; Ahmad and Kan 2017; Palamutcu et al. 2011), dip-coating (Gao et al. 2017; Tan et al. 2013) and dip-pad–dry-cure (Ahmad and Kan 2017; Lee et al. 2014; Pakdel and Daoud 2013; Sundaresan et al. 2012) methods. Pre-treatment of textile surfaces before binding TiO_2 has been carried out using enzymatic treatment (Montazer and Seifollahzadeh 2011a), electro-spinning (Zohoori et al. 2014a, b; Pant et al. 2011), RF plasma, MW plasma and UV irradiation (Sobczyk-Guzenda et al. 2013; Mejía et al. 2009a, b). In addition, spacers have been used as crosslinkers to bind TiO_2 to cotton (El-Naggar et al. 2016; Sundaresan et al. 2012), polyester (Pakdel et al. 2013; Meilert et al. 2005), and wool (Pakdel et al. 2013; Fujishima and Zhang 2006). Succinic acid has been used as a spacer in TiO_2-cotton materials because it is a simple, non-toxic, and low-cost compound. Its double –COOH functional groups allow TiO_2 to bind with the –OH groups of cellulose (Zohoori et al. 2014a, b; Khajavi and Berendjchi 2014; Meilert et al. 2005). According to the literature review, no studies have been published where succinic acid is used to bond TiO_2 to nylon fibers.

The self-cleaning behavior of modified textile surfaces has been tested with dyes like methylene blue (Noman et al. 2018; Pakdel et al. 2014; Sobczyk-Guzenda et al. 2013; Pakdel and Daoud 2013); dark green (Zohoori et al. 2014a; b), direct green 6 (Karimi et al. 2010), methyl orange (Zhou et al. 2017; Eglītis and Mežinskis 2015; Tan et al. 2013), reactive orange (Zohoori et al. 2014a, b; Karimi et al. 2010), orange II (Kale et al. 2016), acid blue 113 (Montazer and Pakdel 2011; Montazer and Seifollahzadeh 2011a), Neolan blue 26 (Qi and Xin 2010) and CI basic blue 9 (Montazer and Seifollahzadeh 2011b), malachite green (Tan et al. 2013) and ink (Tayyar and Alan 2015). The removal of food stains like coffee (Li et al. 2018; Pakdel and Daoud 2013; Pakdel et al. 2013; Meilert et al. 2005), red wine (Li et al. 2018; Lee et al. 2014; Sobczyk-Guzenda et al. 2013; Mejia et al. 2009a, b), tea (Zhou et al. 2017; Khajavi and Berendjchi 2014; Montazer and Pakdel 2011; Palamutcu et al. 2011) and fruit juice (Tayyar and Alan 2015; Sobczyk-Guzenda et al. 2013; Montazer and Pakdel 2011; Karimi et al. 2010) has also been evaluated.

In this paper, succinic acid was used as an induced spacer to bind TiO_2 onto nylon fabric. This led to a new process to bind the photocatalyst to the fiber and produced new self-cleaning materials using a commercial synthetic fabric, in a short time, at low temperature and without fiber preparation requirements. The TiO_2/nylon fabric photoactivity was evaluated by looking at the discoloration of coffee and palm oil stains under UV-A light, and by analyzing stability after reuse. The TiO_2/nylon surface properties were determined by scanning electron microscopy (SEM), electron-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR-ATR) and ultraviolet/visible diffuse reflection spectroscopy (UV/Vis DRS).

Materials and methods

Fabric impregnation

The nylon fabrics were a finished nylon ready for commercial use, provided by a local textile industry.

TiO_2 was bonded to nylon using a succinic acid which has two terminal carboxyl groups. One carboxyl group binds covalently with the nitrogen of nylon, while the second carboxyl group binds to TiO_2 by electrostatic attraction (Fig. 1). The highly stable single bond of the $–CH_2–$ groups in the succinic acid provides the basis of the high stability observed for the spacer.

The preparation of the material (Fig. 2) required the use of two solutions: (a) an aqueous solution of succinic acid 6% w/w (Mallinckrodt, 99%, Ireland) and (b) a solution of NaH_2PO_2 aqueous 4% w/w (Mallinckrodt, 99%, Ireland) as a catalyst. Both solutions were mixed at a 1:1 ratio (30 ml) under constant stirring, leading to anhydrides which are more reactive than the succinic carboxylic groups (Fig. 1b). Subsequently, the nylon fabric without pre-treatment (Mejia et al. 2009a; b) (9 cm^2) was immersed in the mixture for 1 h and the fabric was treated at 85 °C for 3 min, allowing for the formation of amide bonds (Meilert et al. 2005). The fabric was then immersed for 30 min in an aqueous solution 5 g/L of TiO_2 P-25 (80% anatase, 20% rutile, Degussa, Germany) (Bozzi et al. 2005), previously treated by ultrasound (Ultrasonic LC30H, 35 kHz), followed by drying for 1 h at 75 °C. The TiO_2/nylon materials were then heated to 100 °C for 1 h and washed with distilled water. Ultrasound was applied to TiO_2/nylon samples for 5 min to remove the loose particles of TiO_2 that had not chemically bonded onto the nylon. Finally, the fabrics were dried at 100 °C for 1 h. This method for the preparation of the TiO_2/nylon material requires short time, low temperature without fiber preparation requirement.

Characterization of TiO_2/nylon fabrics

Scanning electron microscopy (SEM) was carried out with a JEOL JSM 6490LV field emission scanning electron microscope with a BS-SE-detector. SEM images were taken using a backscattered electron (BSE) detector, WD = 10 mm, with an acceleration voltage of 15 to 20 kV. An Oxford X-ray detector-type EDX spectrometer was used for the surface elemental composition analysis, operating at 15 kV. The fabrics were put in a vacuum to eliminate the humidity, and later a gold layer was deposited on the surface. Fourier transform infrared attenuated total reflectance (FTIR-ATR) was performed employing

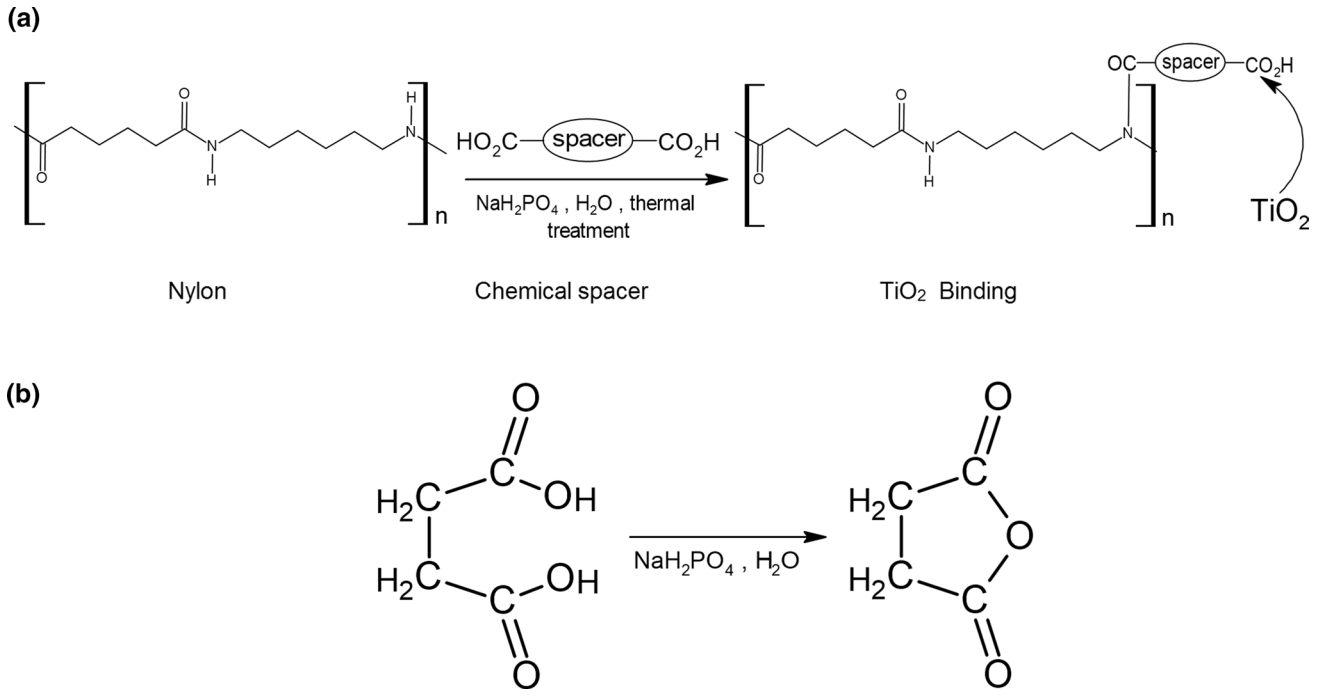

Fig. 1 **a** Chemical bond formation between the fabric, chemical spacer and TiO_2. **b** Reaction mechanism of succinic acid and sodium hypophosphite

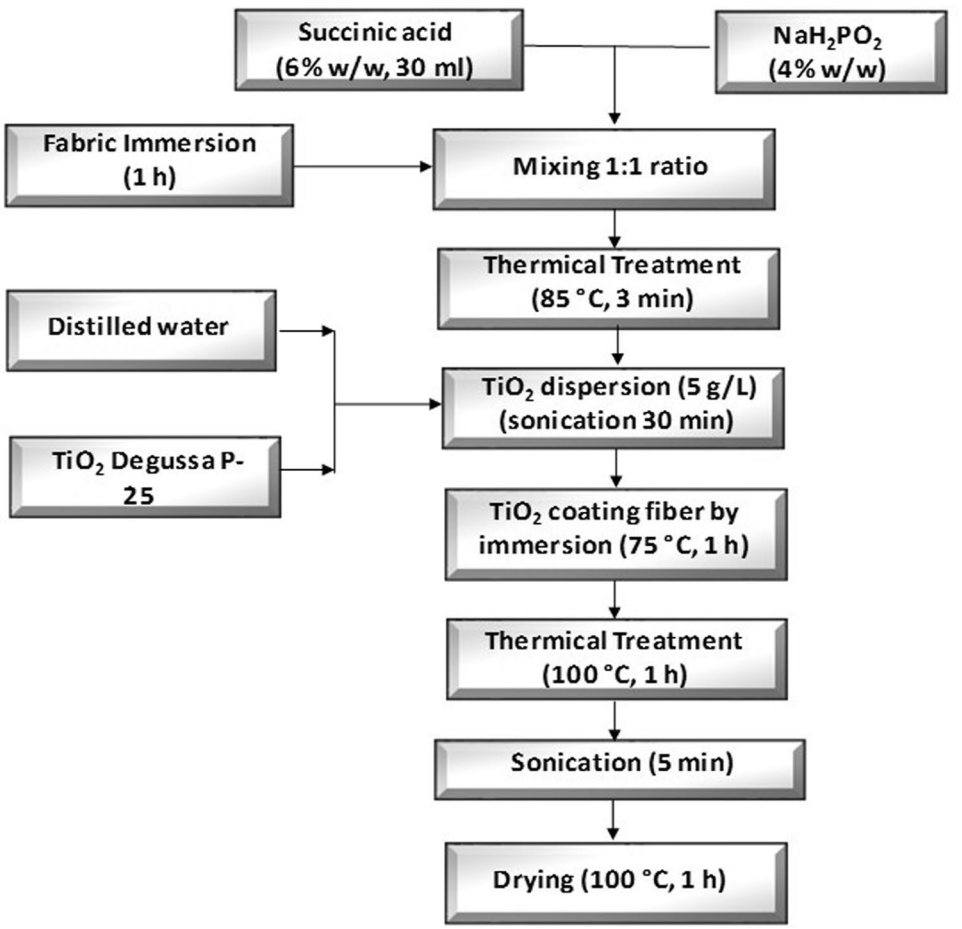

Fig. 2 TiO_2 binding process onto Nylon using succinic acid

an IR-Prestige-21/8400S Fourier infrared transform spectrometer with an attenuated total reflectance attachment. The spectrum was taken in the range of 4000–500 cm^{-1}. The UV/Visible diffuse reflectance spectra (UV/Vis DRS) were analyzed in a Thermo Scientific Evolution 600 UV–Vis spectrophotometer equipped with a diffuse reflectance accessory. Measurements were carried out on samples of 3 cm × 3 cm in size.

Self-cleaning evaluation

The TiO_2/nylon fabrics were immersed in aqueous coffee or palm oil solutions. To remove the stains, the samples were irradiated in a vertical cylindrical Pyrex reactor (effective volume 50 mL) containing TiO_2/nylon fabric samples (9 cm^2). The impregnated fabric was placed vertically inside the cylindrical reactor and irradiated with an axial parallel Nippon 25-W UV-A lamp at 355 nm. Stain discoloration of the TiO_2/nylon materials was analyzed using DRS spectroscopy between 350 and 800 nm. Mineralization of the stains was determined by monitoring the CO_2 produced by infrared absorption in the Telaire 7001 CO_2 sensor. The continuous measurement system included a Pyrex photoreactor that was built with three nozzles. Through A central nozzle, the TiO_2/nylon sample was inserted and later hermetically sealed. The other two photoreactor nozzles were attached to gas hoses. One hose acted as the air inlet and the other hose acted as the air outlet after passing through the reactor. The latter was in contact with the fabric and dragged the CO_2 produced in photodegradation. It was connected to a CO_2 monitor that detected real-time variation in the amount of CO_2 produced in the system during the mineralization of the stain. The initial CO_2 quantity in the reactor was monitored before photodegradation started and taken as a reference value.

Results and discussion

Morphological and compositional properties

The surface morphology of the nylon fibers after impregnation and the physical characteristics of the materials (Fig. 3a, b) characterized by scanning electron microscopy (SEM) showed fibers between 15 and 20 nm in diameter. The

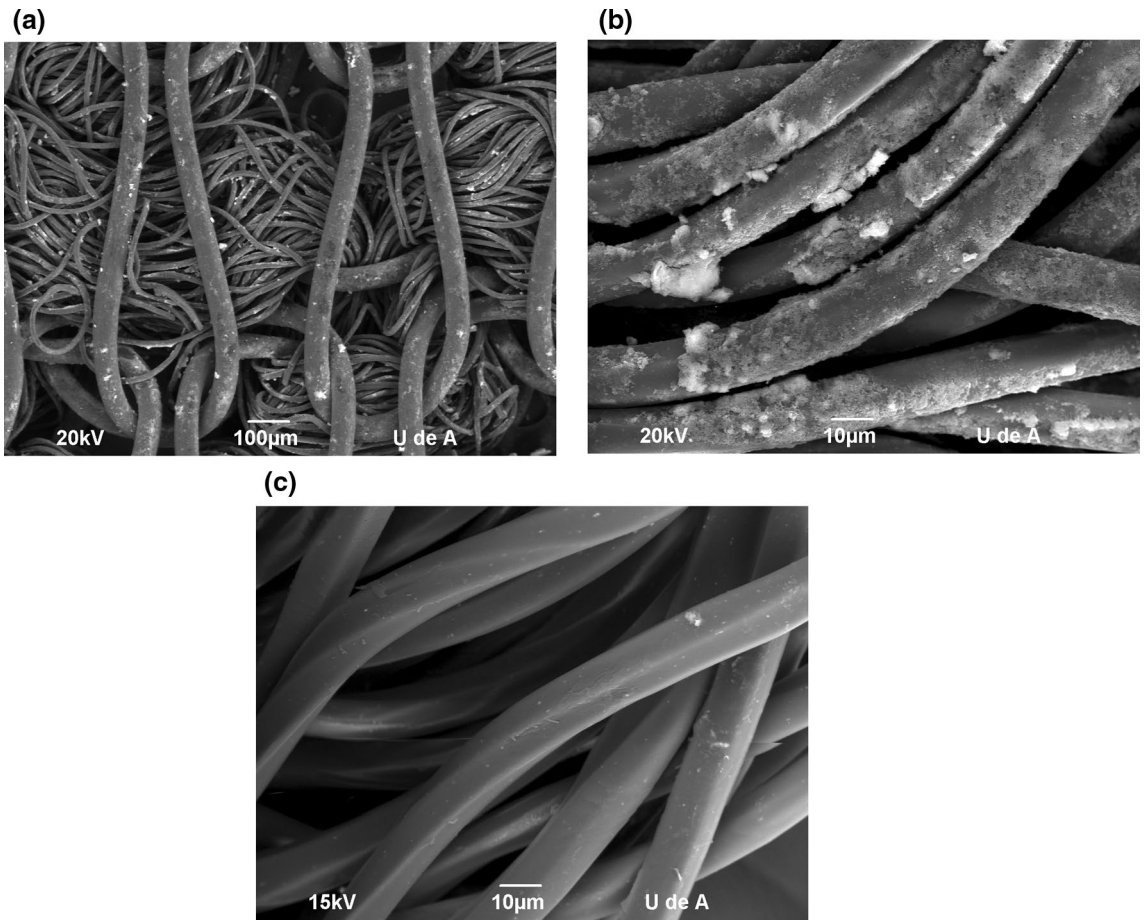

Fig. 3 SEM images for **a**, **b** TiO_2/nylon and **c** bare nylon

TiO_2 was evenly distributed over the nylon with irregular shaped and randomly distributed agglomerates between 5 and 20 nm in size. The chemical composition of the TiO_2/nylon fabrics evaluated by energy-dispersive X-ray spectroscopy (EDX) showed titanium (blue color) and oxygen (green color) homogeneously distributed over the nylon (Fig. 4). The presence of carbon was due to the nylon and succinic acid (red color). Compositional maps indicated that TiO_2 was regularly distributed into all filaments that constituted nylon fabric. These results confirm that the impregnation method employed produces nylon materials with uniform coatings of TiO_2.

Characterization by FTIR-ATR spectroscopy was used to determinate the functional groups of fibers and the way of chemical interaction in which TiO_2 was bonded to the fibers.

The FTIR-ATR spectrum of TiO_2/nylon fabric in the range between 1900 and 600 cm^{-1} is shown in Fig. 5. The bands between 800 and 500 cm^{-1} are related to the TiO_2 on the nylon surface and N–H bending vibration (García-Pérez et al. 2017). The band between 1240 and 1200 cm^{-1} shows the presence of amide III (O=C–N plane bending) (Pramanik et al. 2015; Jeevithan et al. 2014; Guerrini et al. 2009), which indicates that a chemical bond between the nylon and succinic acid has formed (Meilert et al. 2005), as shown in Fig. 1a. The band from 1119 to 925 cm^{-1} is associated with skeletal stretching and the crystalline phase, and amide axial deformation (C–C=O)

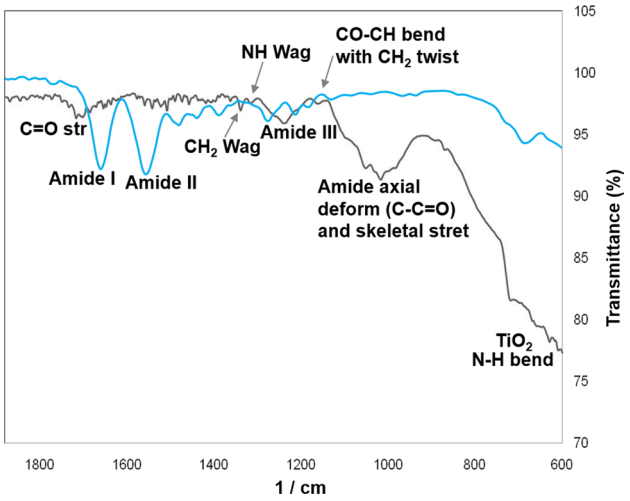

Fig. 5 FTIR-ATR spectra for nylon (blue line) and TiO_2/nylon (black line)

(Pramanik et al. 2015; Jeevithan et al. 2014). The band at ~ 1141 cm^{-1} is related to CO–CH symmetric bending vibration combined with CH_2 twisting (García-Pérez et al. 2017; Guerrini et al. 2009). The bands at 1296 cm^{-1} and 1311 cm^{-1} are due to the wagging of NH amide (Guerrini et al. 2009) and CH_2 (Jeevithan et al. 2014), respectively. The band between 1697 and 1667 cm^{-1} is associated with

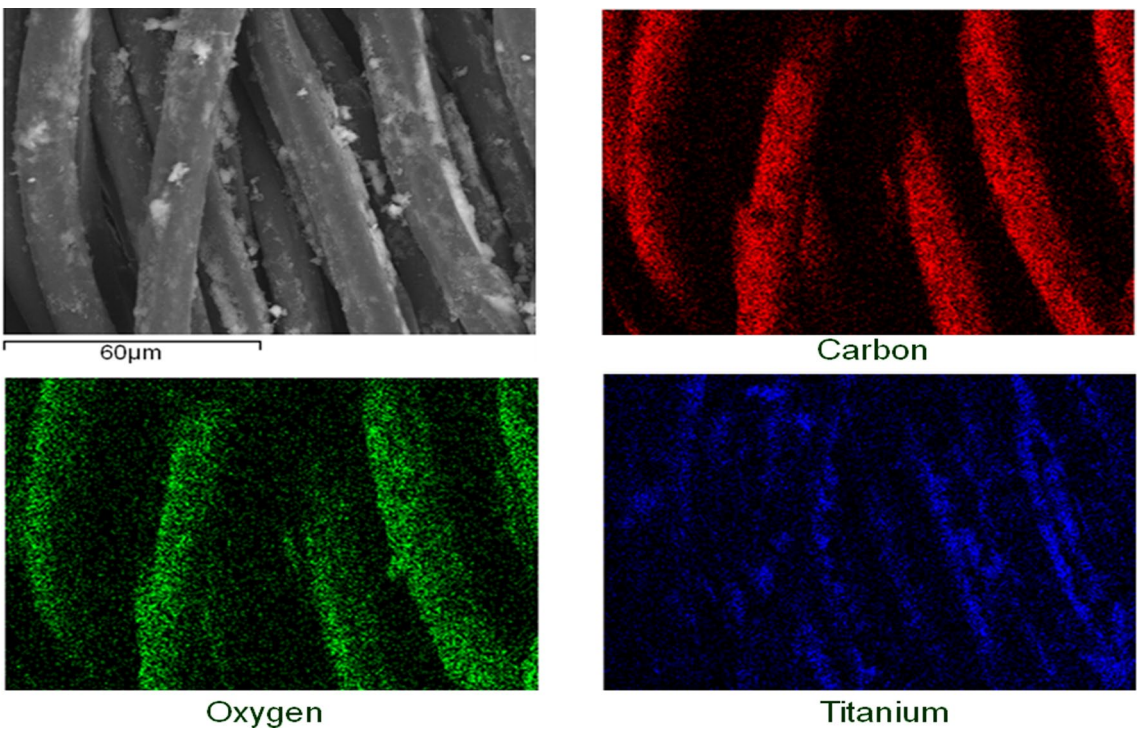

Fig. 4 EDX mapping for TiO_2/nylon

C=O stretching of amide I (Pramanik et al. 2015; Jeevithan et al. 2014).

After the TiO_2 coating, the bands of nylon fabric at 1627 cm^{-1} and 1527 cm^{-1} corresponding to amide I (C=O stretch) and amide II (NH bend coupled with and CN stretch) (Pramanik et al. 2015; Jeevithan et al. 2014; Guerrini et al. 2009) were not observed in the spectrum of TiO_2/nylon fabric due to the TiO_2 being added onto the nylon surface. The EDX analyses in Table 1 show the C, O and Ti percentage loadings on the samples. FTIR and SEM–EDX characterization confirmed TiO_2 deposited onto nylon fibers. The applied conditions in the material preparation did not modify the structure of the photocatalyst.

Table 1 EDX results for TiO_2/nylon fabrics

	% at. C	% at. O	% at. Ti
TiO_2/nylon	68.36	27.79	3.85
Fabric alone	78.83	21.17	

Stains discoloration on the TiO_2/nylon fabric

Coffee stain

Figure 6a, b shows the coffee stain on TiO_2/nylon samples before and after UV-A irradiation. A partial discoloration of the coffee stain was observed within 55 h of irradiation. The coffee stain contains colored molecular and colloidal nature components (Bozzi et al. 2005; Kissa 1995; Braham and Bressani 1979), consisting of quaternary amine such as a cationic surfactant (Kissa 1995).

Some of these components appear during the roasting of coffee beans when saccharides transform into caramel,

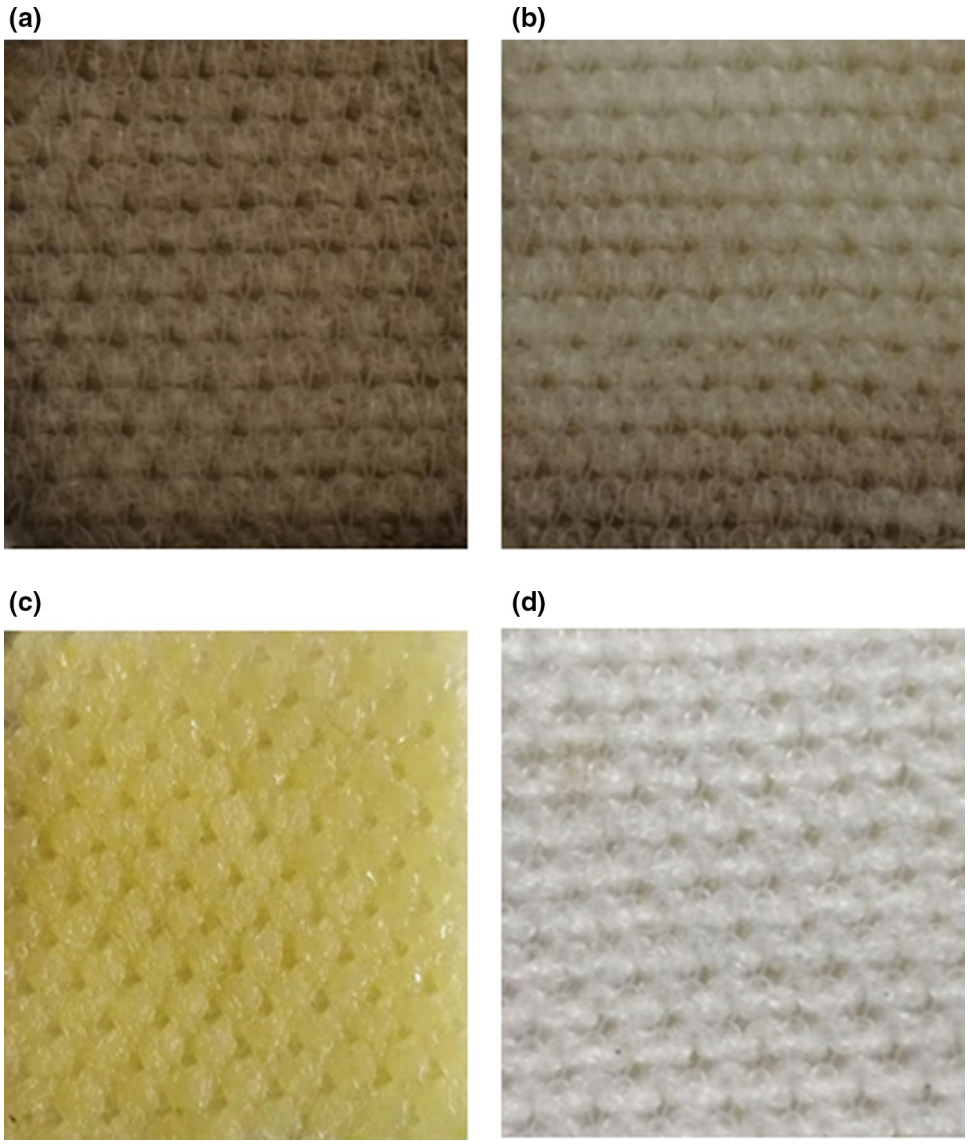

Fig. 6 Discoloration of TiO_2/nylon fabrics with a coffee stain **a** before and **b** after 55 h of UV-A irradiation, and a palm oil stain **c** before and **d** after 24 h of UV-A irradiation

amino acids transform into melanoidins, and chlorogenic acids (CGA) transform into quino-lactones, humic acids and melanoidins. The proportions depend on the roasting process, mainly temperature (Arimi et al. 2015). Coffee contains some phenolic acids and smaller amounts of nicotinic acid, and aliphatic acids that are colorless. However, these acids affect coffee stains by forming colored acid-structured species (Kissa 1995). The phenolic acids present in the green coffee beans are predominantly chlorogenic acid (CGA) pseudo tannins of low molecular weight, compounds of hydroxyl cinnamic and quinic acid (Pramanik et al. 2015; Jeevithan et al. 2014; Guerrini et al. 2009; Kissa 1995; Braham and Bressani 1979).

Palm oil stain

Palm oil stain discoloration was achieved within 24 h (see Fig. 6c, d). Palm oil is composed mostly of low molecular palmitic, oleic and linoleic fatty acids that easily photodegrade (Nagendran et al. 2000; Cottrell 1992). Furthermore, palm oil contains carotenoids, mainly alpha carotenes and beta carotenes, that are photosensitive and help to accelerate the process of stain elimination because they are strongly oxidative (Nagendran et al. 2000; Cottrell 1992).

In addition to photosensitization, Bozzi et al. reported that the photocatalytic discoloration of different types of stains is accompanied by the formation of the superoxides on the TiO_2 surface (Bozzi et al. 2005).

UV/visible DRS monitoring of stain discoloration

The assessment of photoactive behavior by UV/visible diffuse reflectance spectra (UV/Vis DRS) established that the process was efficient at eliminating stains and that the self-cleaning material was stable.

Coffee stain

Figure 7 shows the UV/Vis DRS spectra of the coffee stain as a function of UV-A irradiation time. Unlike the nylon fabric (line 0), the TiO_2/nylon (line 1) spectrum shows a decrease below 400 nm due to the presence of TiO_2. When the coffee stain was added (line 2), a decrease in the spectra at $\lambda > 400$ nm was observed as a result of the stain components (Bozzi et al. 2005; Kissa 1995; Braham and Bressani 1979). After 24 h of irradiation (line 3), the coffee stain was removed, showing an increase in the reflectance percentage at $\lambda > 400$ nm. This result confirms the discoloration shown in Fig. 6. For longer irradiation times (Fig. 7, line 4 and line 5), a slight change in reflectance was observed. Similar behavior was reported for the removal of coffee stains on polyester fabrics (Li et al. 2018). The decrease in the discoloration of the coffee stain in the TiO_2/nylon material after 40 h and 55 h of irradiation was possibly due to the formation of a by-product that adheres to the fiber surface during the first 24 h, preventing the radiation from reaching the photocatalyst, and consequently reducing discoloration of the stain (Arimi et al. 2015).

Palm oil stain

The UV/Vis DRS spectra of TiO_2 derivatized nylon film in Fig. 8 show a band at $\lambda < 400$ nm due to the presence of TiO_2 (line 1). When the palm oil stain was added to the film (line 2), there was a strong decrease in reflectance between 400 and 570 nm due to alpha-carotene, beta-carotene and lycopene, palmitic, oleic and linoleic fatty acids (Marfil et al. 2016; Nagendran et al. 2000). After 4 h (Fig. 8, line 3), 12 h (Fig. 8, line 4) and 24 h (Fig. 8, line 5) of irradiation, a sharp increase in reflectance was achieved, attaining the values of the initial film. Unlike the coffee stains, only 4 h were

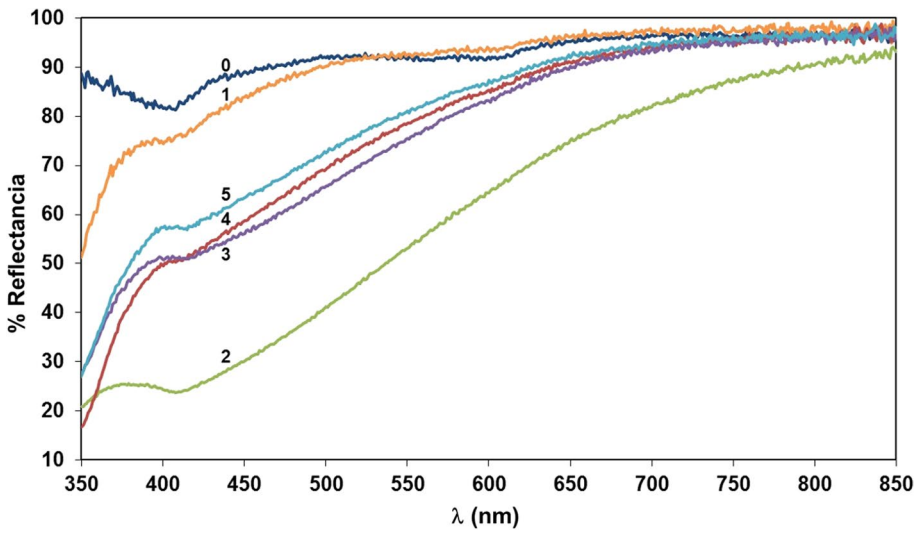

Fig. 7 UV/Vis DRS (line 0) nylon fabric, (line 1) TiO_2/nylon, (line 2) TiO_2/nylon without irradiation and stained with coffee, TiO_2/nylon stained and irradiated for (line 3) 24 h, (line 4) 40 h and (line 5) 55 h

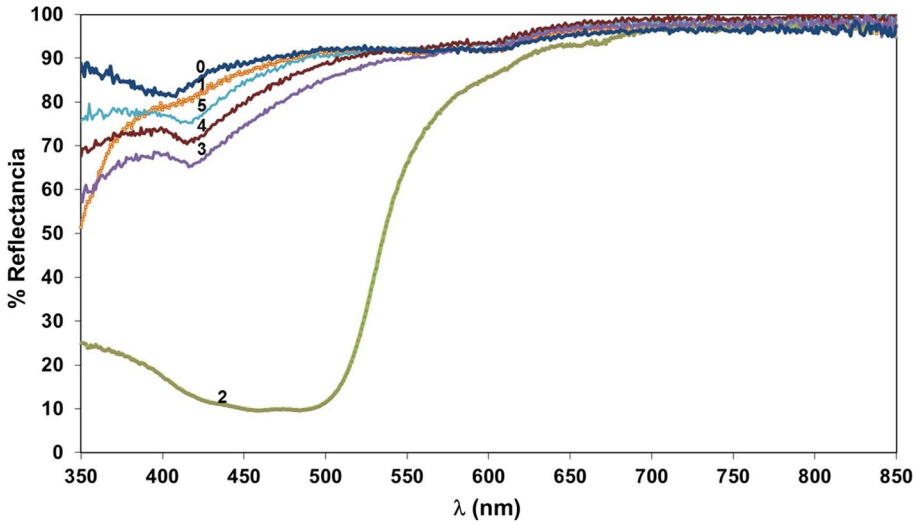

Fig. 8 UV/Vis DRS (line 0) nylon fabric, (line 1) TiO_2/nylon, (line 2) TiO_2/nylon without irradiation and stained with palm oil, TiO_2/nylon stained and irradiated for (line 3) 4 h, (line 4) 12 h and (line 5) 24 h

required for significant stain removal of palm oil. Therefore, an increase in irradiation time above the optimum does not lead to a significant increase in palm oil stain removal considering the resulting increase in energy consumption due to longer irradiation.

CO_2 evolution during stain removal

Stain removal was evaluated through mineralization, which was determined by the CO_2 formation due to oxidation of the organic compounds present in the stains.

The monitoring of CO_2 production during coffee and palm oil stain removal under UV-A light is shown in Fig. 9a, b, respectively. On the TiO_2/nylon samples stained with coffee, the CO_2 production reached ~ 725 ppm, indicating stain mineralization of organic compounds of the stain (Fig. 9a, line 3). For stained nylon fabric without TiO_2, shown in line 2 of Fig. 9a, there was only a slight CO_2 production due to photosensitization of the stain during the irradiation time (Bozzi et al. 2005). In the case of TiO_2/nylon without coffee stains (Fig. 9a, line 1), the CO_2 production was very low showing that fabric did not deteriorate during irradiation. For the palm oil stain (Fig. 9b), similar behaviour was observed. However, the CO_2 production due to photosensitization of this stain was minimal. Therefore, the CO_2 produced was due to the self-cleaning process.

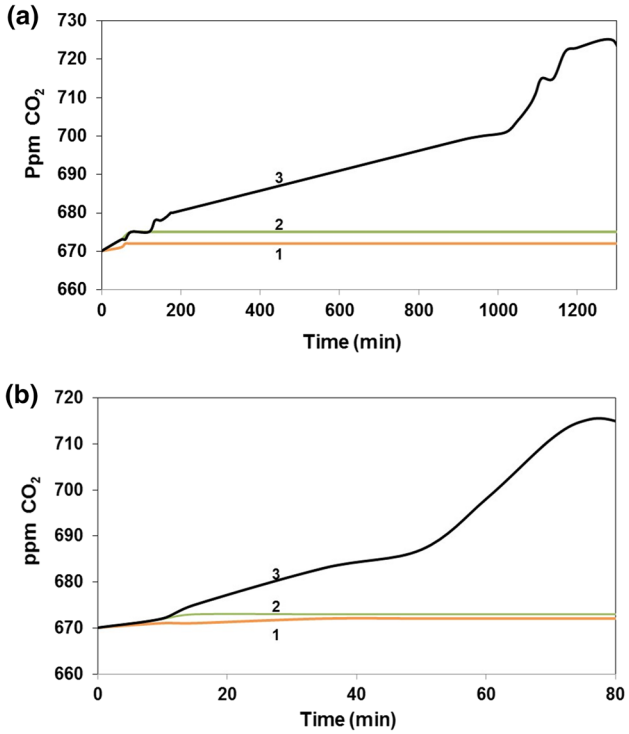

Fig. 9 CO_2 evolution during discoloration of the stains of **a** coffee and **b** palm oil. UV-A irradiation of: TiO_2/nylon fabric (line 1), stained nylon fabric without TiO_2 (line 2), and stained TiO_2/nylon fabric (line 3)

Reuse of the photocatalytic film

Figure 10 shows the discoloration of coffee and palm oil stains after 5 cycles of irradiation. Each self-cleaning cycle involves completely staining the same fabric and irradiating it for 24 h. The decrease in the discoloration percentage of the coffee stain from the second reuse cycle presented the same behavior observed in Fig. 7 after 24 h of irradiation. This result is because of the possible formation of a by-product during the oxidation reaction of the colored compounds deposited on the photocatalyst, which generates a shield against the incident radiation (Arimi et al. 2015). The stability observed in the stain discoloration after the second

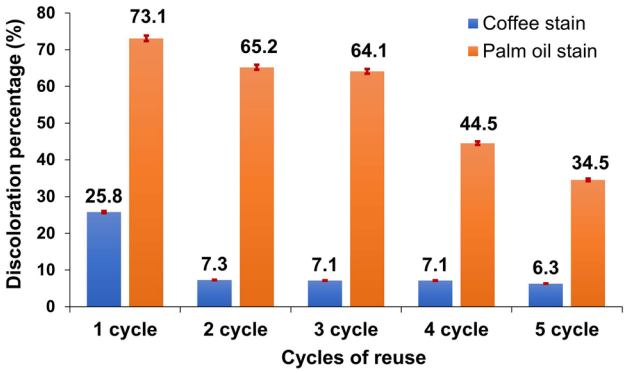

Fig. 10 Reuse cycles of 24 h irradiation of TiO_2/nylon fabric for the removal of coffee and palm oil stains

cycle can be attributed to the effect of photosensitization of the stain, as observed in the evolution of CO_2. The TiO_2/nylon material was effective at self-cleaning the palm oil stain until the third reuse cycle. In the last two cycles, a greater decrease in discoloration percentage was observed, possibly due to the presence of deposited by-products.

Conclusion

TiO_2/nylon self-cleaning materials were successfully prepared using succinic acid as a spacer to bind TiO_2 onto nylon. This was possible due to the action of the carboxyl groups of succinic acid on the nylon through O=C–N plane bending and bonding to TiO_2 by electrostatic attraction. This new approach of linking of the photocatalyst to the synthetic fiber, produced photoactive self-cleaning materials, in a short time, at low temperature and without fiber preparation requirements. The TiO_2/nylon material was photoactive in the discoloration of palm oil and coffee stains. Different maximum irradiation times were found, depending on the type of stain removed. Discoloration and CO_2 production during mineralization indicate that the self-cleaning processes of the TiO_2/ nylon fabric are highly effective at stain removal. These results could be used to develop textiles that can be exposed to stains on a daily basis and help reduce water consumption for textile washing and prevent the effects of water contamination due to the use of cleaning products.

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Author contributions The contribution of each co-author is as follows: JM and MIM prepared the materials and collected data. All authors (MIM, JM, JMM, CP, JK) analyzed the results. All authors drafted or revised the manuscript. MIM, JMM, CP, and JK contributed funding.

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Data availability All data generated or analyzed during this study are included in this article. If needed, further detail on the data can be provided.

Declarations

Conflict of interest The authors declare no competing interests.

Ethics declarations All the authors approved the manuscript and this submission. This manuscript describes an original work, which has not been published before and is not under consideration by any other journal.

Ethics approval and consent to participate This article does not contain any studies with human participants or animals performed by any of the authors.

Consent for publication Not applicable.

Availability of data and materials All data generated or analyzed during this study are included in this article. If needed, further detail on the data can be provided.

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