Antibacterial and self-cleaning properties of cotton fabric treated with TiO$_2$/Pt

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This study explores a new nanocomposite to produce a cotton fabric with superior self-cleaning and antibacterial properties. The platinum loaded nano titanium dioxide (nanocomposite) has been synthesized through wet impregnation using Pt precursor. The nanocomposite has been applied on cotton fabric and the fabric characteristics such as self-cleaning performance, antibacterial and UV blocking activities are examined. Field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray mapping are utilized to characterize the surface morphology and elemental analysis of the treated cotton fabrics. The chemical composition of the nanocomposite has been investigated using X-ray photoelectron spectroscopy and crystallinity of coatings by X-ray diffraction spectroscopy. Whiteness index, tensile strength, flexibility and wettability of treated fabrics are also assessed. Results show that the photocatalytic self-cleaning performance of the cotton treated with TiO$_2$/Pt nanocomposite is superior to the cotton treated with nano-titanium dioxide alone. Also, adding platinum to nano-TiO$_2$ shows the most promising antibacterial activities against both Staphylococcus aureus and Escherichia coli bacteria.

Keywords: Antibacterial property, Cotton fabric, Self-cleaning property, TiO$_2$/Pt nanocomposite, UV blocking

1 Introduction

In recent decades, different kinds of nanoparticles with unique properties have been utilized to produce high-performance textiles$^1$. Among them, titanium dioxide nanoparticles are highly regarded because of their fascinating properties including optical, catalytic, long-term stability and non-toxicity$^{13}$. Also, its usages in textile finishing produce self-cleaning$^{12}$, antimicrobial$^{5,7}$, ultraviolet (UV) protection$^{8,9}$, mothproofing$^{10}$ and flame retardancy$^{11}$ properties.

Although nano-TiO$_2$ is the most frequently used photocatalyst for textile finishing, it shows some drawbacks. Titanium dioxide only shows photocatalytic activities under UV rays$^{12}$. Moreover, the high electron-hole recombination rate causes low efficiency of nano TiO$_2$$^{13}$. Attempts to overcome these problems have been mainly focused on the use of a second constituent to combine with titanium dioxide. For example, Montazer et al.$^{14,15}$ produced wool fabric with excellent antibacterial and self-cleaning properties using titanium dioxide/silver nanocomposite. Wu and Long$^{16}$ used AgI-N-TiO$_2$ on cotton fabric and obtained photocatalytic fabric with good performance under visible light irradiation. Behzadnia et al.$^{17}$ synthesized TiO$_2$/ZnO nanocomposite on wool fabric and proved the significant improvement in self-cleaning and antibacterial properties of the fabric. Uddin et al.$^{18}$ coated cotton fibre with Au/TiO$_2$ nanoparticles and showed efficient photocatalytic properties upon exposure to solar light. Also, superior self-cleaning property on cotton fabric through adding nano strontium titanate to nano titania was reported by Zohoori and Karimi$^{19}$. Noble metals (Ag or Au) or semiconductors (ZnO or SrTiO$_3$) can mitigate the rate of electrons and holes recombination of titanium dioxide particles by trapping the electrons. Furthermore, expanding the light absorption ability into visible territory improved the photocatalytic performance$^{14}$.

Recently, some studies used carbonaceous-TiO$_2$ nanocomposites like graphene/TiO$_2$$^{20-23}$, graphene oxide/TiO$_2$$^{24}$, carbon nanotube/TiO$_2$$^{25,26}$ and carbon black/TiO$_2$$^{27}$ in textile finishing to impart superior photocatalytic properties to the fabrics. Carbonaceous materials would act as an electron acceptor of the photo-generated electrons for TiO$_2$ and ensure a fast charge transportation in view of its high conductivity$^{28}$.

In this study, TiO$_2$/Pt nanocomposite was prepared through impregnation method, and then immobilized on cotton fabrics with succinic acid as a cross-link agent. The self-cleaning properties, antibacterial activities and UV-blocking performance of the treated fabrics and the synergism effect of titanium dioxide nanoparticles and platinum on these properties were investigated.
2 Materials and Methods

2.1 Materials

The bleached plain weave 100% cotton fabric with warp and weft yarn density of 30 and 28 yarn/cm respectively, and the fabric weight of 105 g/m² was supplied by Yazdbaf Company, Iran. Nano-powder of titanium dioxide (P25) and diammine dinitritoplatinum (II) solution [Pt(NH$_3$)$_2$(NO$_2$)$_2$] as a Pt precursor were provided by Degussa and Sigma Aldrich Companies respectively. Succinic acid (C$_4$H$_6$O$_4$) as a cross-link agent, sodium hypophosphite monohydrate (NaH$_2$PO$_2$·H$_2$O) as a catalyst, and methylene blue (C.I.52015) were purchased from Merck Company.

2.2 Apparatus

A Euronda ultrasonic bath model Eurosonic® 4D, 350 W, 50/60 Hz (Italy) was used. Transmission electron microscopy (TEM) image of titanium dioxide/platinum nanocomposite was obtained on a Phillips EM208 electron microscope, Czech Republic. X-ray photoelectron spectroscopy (XPS) measurements were done on an X-Ray 8025-BesTec XPS system (Germany) with an Al Ka X-ray source (hν = 1,486.6 eV). FE-SEM and X-ray mapping images and EDS patterns were established by MIRA3-TESCAN, field emission scanning electron microscope (FE-SEM) (Czech Republic). The X-ray diffraction (XRD) analysis was performed using a Bruker (model D8 Discover) X-ray Diffractometer, Germany. The UV–Vis reflectance spectra of the fabrics were recorded by using Perkin-Elmer Lambda spectrometer (USA).

2.3 Methods

2.3.1 TiO$_2$/Pt Nanocomposite Preparation

The TiO$_2$/Pt nanocomposite were prepared by impregnation of TiO$_2$ nano-powder with aqueous solution of the platinum precursor [Pt(NH$_3$)$_2$(NO$_2$)$_2$]. Briefly, 1 g titanium dioxide powder was added to 100 mL distilled water under ultrasonic irradiation. Afterward, different portions of diammine dinitritoplatinum (II) solution (100, 200, 300, 400, 500 and 1000 μL) were added, and the solution was sonicated at 70 °C until nearly all the water evaporated. Finally, the samples were dried at 110 °C for 24 h and then calcined at 300 °C for 3 h.

2.3.2 Cotton Treatment with TiO$_2$/Pt Nanocomposite

One gram of titanium dioxide/platinum nanocomposites, succinic acid (6%, wt/wt) and sodium hypophosphite (4%, wt/wt) were mixed in the finishing bath with 100 ml volume. The prepared solutions were sonicated for 20 min in ultrasonic bath to obtain a disperse solution. Next, the cotton fabrics were immersed into the solutions and heated for 45 min at 70 °C. Finally, the treated fabrics were dried at 70 °C for 30 min and then cured at 110 °C for 3 min.

2.3.3 Test Methods

In order to investigate the self-cleaning properties of treated cotton fabrics, colorant stains were created on the fabrics. The treated cotton fabrics were stained by methylene blue with concentration of 100 mg/L. After being stained, the samples were exposed to the sunlight (Yazd, Iran) irradiation for 4 consecutive days. The sample colors were measured before and after illumination, and based on their color difference ($\Delta E^*$), the self-cleaning properties of samples were compared. Color coordinates were determined by color measurement software using the CIE L* a* b* color space at D65/10°. In the CIELAB system, color is expressed in terms of CIE L*, a* and b* values; where L* defines lightness, a* denotes the red-green value and b* indicates the yellow-blue value. The total color difference ($\Delta E^*$) was calculated according to following equation:

$$\Delta E^* = [\Delta L^*]^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad \text{(1)}$$

Also, to evaluate the durability of the nanocomposites on cotton surface, the self-cleaning properties of the samples were measured after laundering. The treated fabrics were washed at 60 °C for 20 min using a solution containing 1 g/l nonionic detergent (Ultravon GPN, Ciba Co., Germany). Finally, samples were rinsed with distilled water and dried at room temperature.

The reflectance values were determined using spectrophotometer and the CIE whiteness index was measured using following equation:

$$WI(CIE) = Y + 800(x_n - x) + 1700(y_n - y) \quad \text{(2)}$$

where WI is the whiteness index; $Y$, the CIE tristimulus value; and $(x, y) \& (x_n, y_n)$, the CIE chromaticity coordinates of the samples and perfect diffuser respectively.

The antibacterial properties of the treated fabrics were measured by AATCC 100-2004 test method against Escherichia coli (E. coli, ATCC 25922, Gram-negative bacterium) and Staphylococcus aureus (S. aureus, ATCC 25923, Gram-positive bacterium) as common pathogenic bacterium. Antibacterial activity was expressed in terms of the percentage reduction of the microorganisms and calculated as:
% Reduction of microorganisms (R) = \[
\frac{(A-B)}{A} \times 100
\]

…(3)

where A and B are the number of microorganisms colonies on untreated and treated fabrics respectively.

Stiffness of fabric samples was determined according to ASTM D 1388-96 (2002) test method. The bending rigidity of the fabrics was measured using the following equation:

\[ G = M \times (C)^3 \]

…(4)

where \( G \) is the bending rigidity (mg cm); \( M \), the fabric weight (mg/cm²); and \( C \), the average bending length (cm). Tensile properties and hydrophilicity of the samples were evaluated according to ASTM D 5035 (strip test) and AATCC 79-2000 standard methods respectively.

3 Results and Discussion

3.1 Characterization

The XRD pattern of the titanium dioxide/platinum nanocomposite is presented in Fig 1. The XRD pattern clearly indicates the existence of anatase and rutile structures of TiO₂ in the nanocomposite as expected. Also, the Pt (1 1 1), Pt (2 0 0) and Pt (2 2 0) crystal faces are detected at around 2\( \Theta \) = 40º, 46.2º, and 67.9º for the nanocomposite, which confirms the presence of metallic Pt. In addition, the average crystallite size by applying the Debye-Scherrer formula has been calculated and for the nanocomposite it is found 288 Å.

The FE-SEM and TEM images of titanium dioxide/platinum nanocomposite with 500 μL platinum precursor are shown in Fig 2. The nanoparticles are seen aggregated at some level with diameter in the range of 20–50 nm. In Fig 2(b), the platinum particles in deep black color are densely distributed on the titanium dioxide nanoparticles. It obviously exhibits the good contact between TiO₂ and Pt nanoparticles.

The chemical state and surface exposition of the titanium dioxide/platinum nanocomposite are investigated by XPS analysis. The XPS survey spectrum [(Fig. 3(a)] clearly indicates the existence of Pt, Ti and O in the nanocomposite. In order to get better insight into the chemical composition of the nanocomposite, a high-resolution scan is accomplished in the Pt and Ti regions. From Pt 4f spectrum [Fig. 3(b)], two peaks are detected and centered at ~70 and ~74 eV, corresponding to Pt 4f½ and Pt 4f½ respectively. It demonstrates the presence of metallic state of platinum (Pt⁰) in the prepared nanocomposite, which is due to the calcination of platinum precursor at a high temperature²⁹. Also, the Ti 2p spectrum [Figure 3(c)] shows two strong peaks centered at ~458 and ~464 eV, corresponding to Ti 2p½ and Ti 2p½.

Fig. 1 — XRD pattern of titanium dioxide/platinum nanocomposite with 500 μL platinum precursor

Fig. 2 — (a) FE-SEM and (b) TEM images of titanium dioxide/platinum nanocomposite with 500 μL platinum precursor
respectively. The peak position at 464 eV is ascribed to the presence of Ti$^{4+}$, while that at 458 eV is attributed to the formation of Ti$^{3+}$ (ref. 30). The presence of Ti$^{3+}$ can be attributed to the deposition of platinum onto the titanium dioxide nanoparticles, which further demonstrates the interaction between Pt and the TiO$_2$. Consequently, the results of XRD, FE-SEM, TEM and XPS analyses establish the successful preparation of the titanium dioxide/platinum nanocomposite.

In order to study the surface morphology of untreated and treated cotton fabrics, a FE-SEM was used. The FE-SEM images of blank cotton (a) and cotton fabric treated with titanium dioxide/platinum nanocomposite (b, c and d) are shown in Figs. 4. As shown in Fig 4(a), the surface of the blank cotton fabric is clean and smooth. It is thoroughly possible to recognize the nanocomposite particles on the surface of treated cotton fabric by comparing Figs. 4(b) & (c) with Fig.4(a). The nanocomposite particles are close to spherical shape with average sizes in the range of 20–30 nm [Fig.4(d)]. Also, it is obvious that the nanoparticles are well distributed on the fibre surface.

Figure 5(a) shows the EDS pattern of treated sample with titanium dioxide/platinum nanocomposite, which indicates the presence of C, O, Ti, Pt and Au elements on the surface of the fabric. The presence of Au element in the EDS pattern is due to coating of gold layer on the fabric before FE-SEM observation. The distribution of Ti and Pt elements in treated sample with the nanocomposite is investigated by the elemental mapping [Figs 5(b) and (c)]. It is clearly illustrated that the distribution of Ti and Pt on the fabric surface is uniform, which confirm the successful formation of titanium dioxide/platinum nanocomposite on the cotton surface.

3.2 Self-cleaning Properties

Self-cleaning performance of the treated cotton fabrics was examined by the discoloration of methylene blue stain on the surface of samples.
Figure 6 compares the results of spectrophotometry of the treated cotton fabrics, exposed to the sunlight. The results acquired indicate that applying of nano-TiO$_2$ in cotton fabric finishing leads to the significant discoloration of methylene blue on the fabric. Self-cleaning of the fabrics treated with titania can be attributed to the oxidizing intermediates on the fabric surface. When a photocatalyst such as TiO$_2$ is illuminated by a light with energy higher than its bandgap energy, electron-hole pairs diffuse out to the surface of the photocatalyst. The created negative electrons and oxygen combine into O$_2^-$, and the positive electric holes and water generate hydroxyl radicals. This highly active oxygen species can oxidize organic pollutants. Thus, nano titanium dioxide can decompose common organic matters, dye molecules, bacterial cell membranes, etc.\textsuperscript{32}

Based on the obtained results, combining titanium dioxide nanoparticles with platinum gives a tangible effect on self-cleaning properties of treated cotton fabrics and its self-cleaning performance is found higher than that of the fabrics treated with nano-TiO$_2$ alone. The sample treated with the TiO$_2$/Pt nanocomposite with 500 μL platinum precursor has the best self-cleaning property. Application of 500 μL platinum improves the self-cleaning performance about 42.3% in comparison with nano-TiO$_2$ treated cotton. The self-cleaning improvement reported in the literature by other authors is as follows. Zohoori and Karimi treated cotton fabrics with TiO$_2$/SrTiO$_3$ nanocomposite and reported self-cleaning improvement ∼ 20%\textsuperscript{19}. Montazer et al.\textsuperscript{15} reported improvement value of 34% for wool fabrics coated with TiO$_2$/Ag nanocomposite. Uddin et al.\textsuperscript{18} used Au/TiO$_2$ nanocomposite for finishing of cotton fabrics and obtained self-cleaning improvement ∼ 25%.

In the case of nano-TiO$_2$ treated cotton, the photogenerated electron-hole pairs have a flash recombination time (10$^{-9}$s). The presence of platinum on the nano-photocatalyst favors the migration of photo-induced electrons towards the metal (Pt), thus improving the electron–hole separation and extending the life time of electrons. Furthermore, the extended light absorption ability of titanium dioxide/platinum nanocomposite improves the photocatalytic performance\textsuperscript{31}.

Also, as shown in Fig.6, laundering does not cause any remarkable changes in self-cleaning properties of the treated cotton samples. It is to be noted that the application of succinic acid as a cross-link agent in finishing treatment leads to produce a durable photoactive fabric. The esterification of one carboxylic group of succinic acid by a hydroxyl group of cellulose leads to succinic acid bonding with cotton

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**Fig. 5** — EDS spectrum (a) and X-ray mapping images (b and c) of treated cotton fabric with titanium dioxide/platinum nanocomposite (500 μL Pt precursor)

**Fig. 6** — Comparative diagram of self-cleaning performance results of treated cotton fabrics with TiO$_2$ nanoparticles and TiO$_2$/Pt nanocomposites
fabric. The second carboxylic group of succinic acid tend to anchor TiO\(_2\) by electrostatic interaction. Thus, in the presence of succinic acid a strong electrostatic interaction between nano-TiO\(_2\) and cotton fabric occurs\(^5\).

3.3 Antibacterial Properties

Antimicrobial efficiency of the treated fabrics has been tested against both Gram-positive (\(S.\) \textit{aureus}) and Gram-negative (\(E.\) \textit{coli}) bacteria. The \(S.\) \textit{aureus} bacterium is a pathogenic micro-organism causing many diseases such as toxic shock, purulence, abscess, fibrin coagulation, and endocarditic. Moreover, \(E.\) \textit{coli} bacterium which causes urinary tract and wound infections is a popular test organism\(^14\).

The result of the antibacterial test is reported in Fig.7. There is no reduction of bacteria found on the raw cotton fabric, but the treated samples with the nanocomposite (500 μL Pt precursor) show the highest antibacterial activity against both \(S.\) \textit{aureus} and \(E.\) \textit{coli} bacteria. The antibacterial activity of treated fabrics with TiO\(_2\) is about 68% and 37% for \(E.\) \textit{coli} and \(S.\) \textit{aureus} bacteria respectively. The nano-TiO\(_2\) treated cotton shows better efficiency against \(E.\) \textit{coli} in comparison with \(S.\) \textit{aureus}. This can be explained by the differences between their cell wall structures. \(S.\) \textit{aureus} has a thicker cell wall; therefore, the reactions between active species and suitable sites of \(S.\) \textit{aureus} are not as efficient as that of \(E.\) \textit{coli}\(^33,34\).

Based on the obtained results, combining titanium dioxide with platinum improves the antibacterial activity of fabric. A similar result has also been reported by Montazer \textit{et al.}\(^14\), indicating that the adding metal nanoparticles like Ag and Pt to titanium dioxide results in producing functional fabrics with proper antibacterial properties. Also, Behzadnia \textit{et al.}\(^17\) reported higher antimicrobial property for wool fabrics loaded with ZnO/TiO\(_2\) nanocomposite in comparison with nano-TiO\(_2\) treated wool, which is due to the combination of two semiconductors together.

3.4 UV Blocking Properties

Figure 8 represents the UV transmittance spectra of raw cotton fabric in comparison with both treated fabrics (TiO\(_2\) treated and TiO\(_2\)/Pt treated). The range of spectra is between 200 nm and 400nm. It is observed that the transmission per cent of raw cotton is higher than that of treated fabrics. Within the two treated samples, TiO\(_2\)/Pt treated sample has a little better UV blocking, but both of them have excellent UV blocking property due to the UV absorption ability of the nano-photocatalyst.

3.5 Fabric Properties

Whiteness index, tensile strength, bending length, bending rigidity and time of water droplet absorption of the cotton samples are summarized in Table 1. It is observed that the properties of the nano-TiO\(_2\)-treated
cotton and the nanocomposite-treated cotton samples are comparable. The whiteness index of samples was measured to evaluate the influence of treatment on fabric whiteness. Application of TiO$_2$/Pt nanocomposite and nano-TiO$_2$ improves the whiteness index by ~7.8 and ~12.5% respectively. On the other hand, loading the nanomaterials on cotton leads to produce lighter fabric. This is due to the existence of titanium dioxide nanoparticles on the fabric surface. The evaluation of bending length and rigidity is as a criterion of the fabric handle. The bending lengths of the nano TiO$_2$-treated and nanocomposite treated samples are reduced in comparison to the raw cotton fabric, indicating higher flexibility and softer handle.

After finishing treatment with nano TiO$_2$ or TiO$_2$/Pt nanocomposite, the tensile strength of the cotton fabric decreases. The decrease in tensile strength of the fabric is mostly due to the acidity of the succinic acid in impregnation bath. This leads to an irreversible depolymerisation of the cellulose molecules$^{35}$. Also, the treatment of the fabric with nano TiO$_2$ or TiO$_2$/Pt nanocomposite changes the water absorption properties of the fabrics. This can be attributed to the reactions between carboxyl groups of succinic acid and hydroxyl groups of cellulose chains$^{36}$. Consequently, the accessibility of water to the hydrophilic groups of cotton fabric decreases, which causes increase in the water droplet absorption time.

### 4 Conclusion

In this study, titanium/platinum nanocomposites are successfully prepared, by impregnation method, and used for functional treatment of cotton fabrics in presence of succinic acid as a cross-linking agent. Through XRD pattern, XPS spectra, FE-SEM and TEM images and EDS pattern the successful preparation of titanium dioxide/Pt nanocomposite on the surface of the treated cotton samples is verified. Further, X-ray mapping images show uniform distribution of TiO$_2$/Pt nanocomposite. Adding platinum to titanium dioxide nanoparticles improves some properties of cotton fabrics such as self-cleaning, antibacterial and UV blocking. Also, the nanocomposite treated sample with 500 μL Pt precursor concentration shows the highest performance. It is expected that the titanium dioxide/Pt nanocomposite might be used to produce high-performance fabrics and smart textiles.

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### References