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ORIGINAL PAPER

Novel cellulose fabric with multifunctional properties through diverse methods of Ag/TiO_2/β-cyclodextrin nanocomposites synthesis

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Abstract Multifunctional cotton fabric with excellent antibacterial efficiency and enhanced durable self-cleaning activity was introduced as a novel substrate with potential benefit for hosting various compounds such as drugs and pollutants providing medical and environmental remediation applications. For this purpose, Ag/TiO_2/β-cyclodextrin (β-CD) nanocomposites was synthesized and deposited on cotton fabric using three different methods namely exhaustion, pad-dry-cure and in-situ synthesis, following by post-treatment with citric acid and sodium hypophosphite. The samples were analyzed by different characterization tests including FESEM, EDX, XRD and FTIR. Response surface methodology based on one factor design was applied to study the influence of β-CD:Ag^+ molar ratio and treatment method on self-cleaning activity, obtaining the optimized condition. Exhaustion method was found as the best technique providing maximum nanocomposites adsorption and self-cleaning properties based on statistical analysis. The optimized sample possessed enhanced self-cleaning properties toward methylene blue degradation, excellent antibacterial activity against *Staphylococcus aureus*, maximum chrome ion adsorption, slightly increased tensile strength and crease recovery angle.

Keywords Ag/TiO_2/β-CD nanocomposites · Cotton fabric · Self-cleaning properties · Antibacterial activity

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Introduction

The potential of nano TiO_2 for imparting multifunctional properties to different textile materials has been widely discussed in literature (Akhavan and Montazer 2013; Gorjanc and Sala 2016; Doakhan et al. 2013; Lessan et al. 2011; Tomsic et al. 2015) ranging from reducing the photo yellowing of wool (Montazer and Pakdel 2010) and nano-photo-scouring of cotton (Montazer and Morshedi 2012) to simultaneous self-cleaning, antimicrobial, and UV protection properties (Nazari et al. 2011). Moreover, different textile

materials with improved self-cleaning and antibacterial efficiencies have been prepared using Ag/TiO_2 nanocomposites (Dastjerdi et al. 2010; Montazer et al. 2011; Rana et al. 2016). Several studies have been also published concerning with synthesis and deposition of silver nanoparticles on textile substrates (Aladpoosh and Montazer 2014; Li et al. 2015).

Biodegradable non-toxic cyclodextrins (CD) with cone-shaped hydrophobic cavity enable to trap various low-molecular-weight substances forming host–guest complexes are famous environmentally friendly compounds in textile finishing (Abdel-Halim et al. 2014). Functional textiles possessing deodorant, insect repellency, antibacterial activity, flame retardant, hydrophilicity, UV protection and slow release of drugs have been prepared using β-CD providing medical, cosmetic, aromatherapy, environmental and domestic applications (Peila et al. 2012; Hebeish et al. 2014; Veerappagounder et al. 2016).

Cyclodextrins have been also used in synthesis of nanoparticles acting as reductive and stabilizing agents controlling the shape and size of nanoparticles (Pande et al. 2007). There are a number of studies focusing on synthesis of nanoparticles using cyclodextrins as environmentally friendly reducing and capping agents for the synthesis of noble metal nanoparticles. Reducing and capping properties of β-cyclodextrin for synthesis of mono- and bimetallic nanoparticles have been reported (Huang et al. 2009). β-CD also acts as electron acceptor, retarding the electron–hole recombination rate of excited semiconductors such as TiO_2, enhancing the photocatalytic activity (Lu et al. 2004).

Following our successful study on synthesis of Ag/TiO_2/β-CD nanocomposites as novel environmentally friendly nanocatalysts with enhanced photocatalytic activity (Attarchi et al. 2013), here we aimed at producing a multifunctional cotton fabric with efficient antibacterial activity and enhanced self-cleaning property. For this purpose, three different methods namely exhaustion, pad-dry-cure and in-situ synthesis have been used for deposition of Ag/TiO_2/β-CD nanocomposites on cotton fabric. All three methods were followed by post-treatment with citric acid (CA) and sodium hypophosphite (SHP) as fixation step. Statistical analysis was carried out to investigate the effect of β-CD concentration on photocatalytic activity, introducing the optimum method with the maximized nanocomposites adsorption. The prepared fabric has the potential to be introduced as a novel substrate hosting various compounds such as drugs and pollutants providing medical and environmental remediation applications.

Experimental

Materials and methods

Desized bleached cotton fabric was supplied from Yazdbaf Company, Iran. Nanosized TiO_2 (Degussa P25) was employed as a photocatalyst containing 80% anatase and 20% rutile phase with average particle size of 25 nm. β-CD was purchased from X'ian Hong Chang Pharmaceuticals Co. China. Silver nitrate ($AgNO_3$ extra pure $> 99.8\%$), citric acid (CA) and sodium hypophosphite (SHP) were supplied from Merck (Germany).

Prior to the treatment, the fabric was washed with 1 g/L nonionic detergent at 50 °C for 30 min and rinsed with distilled water to remove any impurities. Cotton fabrics treated with Ag/TiO_2/β-CD nanocomposites were prepared using three different methods as described below:

(a) Pad-dry-cure

Firstly, 1 g nano TiO_2 particles were dispersed in distilled water and homogenized with homogenizer for 10 min. Based on provided ratios (Table 1) the pre-calculated amount of silver nitrate and β-CD were added to TiO_2 dispersion (Ag^+:$TiO_2 = 0.4\%$). The dispersions were exposed to UV-C lamp (8 W, TUV, Philips, Poland) for 3 h, forming Ag/TiO_2/β-CD nanocomposites dispersion. Cotton fabrics were then immersed in the prepared dispersion for 1 min and padded with wet pick-up of 100%. Finally the treated samples were dried and post treated by immersing in CA (10 W/W %) and SHP (6 W/W %) solution and padding with pick-up 100%, following by drying at 80 °C and curing at 140 °C for 4 min. The fabric samples were finally rinsed with distilled water.

(b) Exhaustion

After preparing the Ag/TiO_2/β-CD nanocomposite dispersions as described in pad-dry-cure method, cotton fabrics were immersed in the dispersion and treated at boil for 1 h. Finally the treated samples were dried and post treated by immersing in CA (10 W/W

Table 1 Statistical design for self-cleaning property of treated fabrics with Ag/TiO_2/β-CD nanocomposites

Run	(A): β-CD:Ag^+	(B): Method	Coded values (A)	Coded values (B)	Self-cleaning (ΔRGB)
1	0.5	Pad-dry-cure	− 1	{1 0}	61
2	0.5	Pad-dry-cure	− 1	{1 0}	63
3	2.6	Pad-dry-cure	− 0.5	{1 0}	66
4	4.7	Pad-dry-cure	0	{1 0}	70
5	6.8	Pad-dry-cure	0.5	{1 0}	68
6	9	Pad-dry-cure	1	{1 0}	54
7	9	Pad-dry-cure	1	{1 0}	50
8	0.5	In-situ	− 1	{− 1 − 1}	66
9	0.5	In-situ	− 1	{− 1 − 1}	64
10	2.6	In-situ	− 0.5	{− 1 − 1}	73
11	4.7	In-situ	0	{− 1 − 1}	78
12	6.8	In-situ	0.5	{− 1 − 1}	75
13	9	In-situ	1	{− 1 − 1}	57
14	9	In-situ	1	{− 1 − 1}	55
15	0.5	Exhaustion	− 1	{0 1}	74
16	0.5	Exhaustion	− 1	{0 1}	77
17	2.6	Exhaustion	− 0.5	{0 1}	80
18	4.7	Exhaustion	0	{0 1}	100
19	6.8	Exhaustion	0.5	{0 1}	95
20	9	Exhaustion	1	{0 1}	60
21	9	Exhaustion	1	{0 1}	65

%) and SHP (6 W/W %) solution and padding with pick-up 100%, following by drying at 80 °C and curing at 140 °C for 4 min. The fabric samples were finally rinsed with distilled water.

(c) In-situ synthesis

Ag/TiO_2/β-CD nanocomposites were in-situ synthesized on cotton fabric treated in a bath containing TiO_2, $AgNO_3$ (Ag^+:TiO_2 molar ratio = 0.4%), and β-CD, irradiating under UV light (8 W) for 3 h. Different concentration of β-CD:Ag^+ was applied according to Table 1. Finally the treated samples were dried and post treated by immersing in CA (10 W/W %) and SHP (6 W/W %) solution and padding with pick-up 100%, following by drying at 80 °C and curing at 140 °C for 4 min. The fabric samples were finally rinsed with distilled water.

Response surface methodology based on one factor design was used to investigate the impact of β-CD concentration (β-CD:Ag^+ molar ratio = 0.5, 2.6, 5, 6.8 and 9) and deposition method (in-situ synthesis, pad-dry-cure and exhaustion) on self-cleaning property of the treated fabrics as summarized in Table 1.

Characterization tests

X-ray diffraction analysis (XRD) was performed with XRD-3003 PTS, Seifert, Germany using CuK_α radiation source ($\lambda = 1.5418$ Å) operating at 40 kV to investigate the crystalline size and phases of the synthesized nanocomposites on cotton fabric. Energy-dispersive spectroscopy (EDX) was used to characterize the elemental composition of the treated fabric.

The surface morphology of the treated sample and particle size of the synthesized nanocomposites were analyzed by field emission scanning electron microscope (Hitachi, S4160, Japan). A Nicolet Fourier transform infrared spectroscopy (FTIR) was employed by taking the spectra between 400 and 4000 cm^{-1}.

In order to confirm the presence of β-CD in the treated samples, chrome ion adsorption was studied. For this purpose, potassium dichromate solution (2 g/

L) was prepared and samples including untreated cotton, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics (0.3 g) were added to the solution and remained for 2 h to adsorb the metal ion. The absorbance spectra of the remaining solutions were obtained using a UV–visible spectrophotometer (Optizen, Mecasys, Deajoen, Korea, 2120 UV).

Self-cleaning properties of the samples was determined by staining the fabrics with 0.01% Methylene Blue (MB). Stained samples were scanned by scanner and exposed to sunlight irradiation for 24 h, in autumn, Tehran, Iran. The color differences between the samples before and after the irradiation were evaluated by image processing in RGB color space according to Eq. (1) using Matlab software:

$$\Delta RGB = \left[(R_2 - R_1)^2 + (B_2 - B_1)^2 + (G_2 - G_1)^2\right]^{1/2} \quad (1)$$

where $R_2G_2B_2$ and $R_1G_1B_1$ are color coordinates of samples after and before irradiation, respectively and the higher ΔRGB values relate to the higher self-cleaning property.

Quantitative antibacterial efficiency of the treated fabrics was determined against *Staphylococcus aureus* (*S. aureus*) a Gram-positive bacteria according to AATCC test method 100-2004. The circular samples were individually placed in a sterile 250 mL beaker and inoculated with 1 mL bacterial suspension (10^7 CFU/mL). After exposure time (0 and 3 h), 100 mL neutralizing solution [sodium thiosulphate ($Na_2S_2O_3$) 1% and Tween 80, 0.1% (W/V)] was added to inoculated samples to neutralize microbial growth and stirred for 15 min at 25 °C. The antibacterial efficiency was calculated according to Eq. (2).

$$R\% = [(A - B)/A] \times 100 \quad (2)$$

where R is the reduction rate, A and B are the number of bacteria at zero and 3 h contact time, respectively.

The contact angle between water and fabric surface was calculated based on plate method by Tensiometer Kruss K100-SF, Germany.

Shriley instrument was used to measure the crease recovery angle (CRA) of the folded treated cotton fabrics pressing by 1 kg weight for 1 min and reporting the angles between two open edges of the fabric. Moreover, the tensile strength of the treated samples was measured using Instron instrument with gauge length of 7 cm and extension rate of 25 mm/min for three replicates, and the average value was recorded.

The stability of Ag/TiO_2/β-CD nanocomposites adsorbed on cotton fabric was tested by washing the samples with 1 g/L non-ionic detergent, rotated under at 60 °C for 90 min.

Results and discussion

Mechanism

Ag/TiO_2/β-CD nanocomposites preparation

TiO_2 nanoparticles were excited under UV light irradiation, forming electron–hole pair (reaction 1). The generated electrons were responsible for the reduction of silver ions to silver metal nanoparticles (reaction 2) (Attarchi et al. 2013). In this contribution, silver nanoparticles formation was assisted by β-CD acting as a weak reducing agent (Attarchi et al. 2013; Pande et al. 2007).

$$TiO_2 \xrightarrow{hv} e^- + h^+ \quad (r.1)$$

$$e^- + Ag^+ \rightarrow Ag^\circ \quad (r.2)$$

Moreover, oxygen vacancies formed on TiO_2 surface under UV light irradiation provide hydroxyl groups responsible for silver nanoparticles adsorption on TiO_2 surface. Besides, β-CD monolayer is formed around TiO_2 due to coordinate bond between hydroxyl groups of β-CD and oxygen of TiO_2 (Attarchi et al. 2013). Detailed mechanism of Ag/TiO_2/β-CD nanocomposites preparation is schematically shown in our previous paper (Attarchi et al. 2013).

Moreover, the capability of cellulosic substrates to reduce various metal ions such as silver has been widely reported. For example, the Ag nanoparticles were in-situ synthesized on cotton fabric using cellulose as reducer and stabilizer. High temperature reaction at 90 °C was effective for enhancing the reactivity of hydroxyl groups and reducing ends of cellulose molecules (Jiang et al. 2011). According to the study carried out by Pinto et al. (2009) if reducing ends of cellulose are removed, silver nanoparticles are not synthesized through UV irradiation of silver nitrate solution. Thus, synthesis of silver nanoparticles has been promoted through photo and chemical

methods with the aid of electrons generated from TiO_2 photo excitation together with the role of β-CD as a weak reducing agent and the reducing ability of cellulosic chains.

Ag/TiO_2/β-CD nanocomposites deposition on cotton fabric

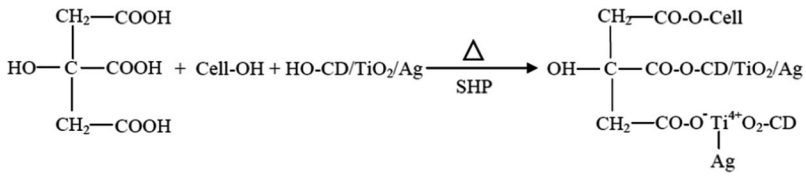
In-situ synthesis Cellulosic cotton fibers possess slightly negative charge on the surface due to ionization of hydroxyl groups when immersed in water (Aladpoosh and Montazer 2015). Thus, TiO_2 nanoparticles can be absorbed to the cotton fiber due to the electrostatic interaction. Under UV light irradiation, Ti(III) species are generated via the reduction of Ti(IV) by the photo-generated electrons, and oxygen vacancies are formed by the photo-generated holes. Subsequently, hydroxyl ions adsorb and fill the oxygen vacancies on TiO_2 surface (Attarchi et al. 2013). The produced hydroxyl groups are responsible for absorption of silver nanoparticles on TiO_2 surface. Besides, the coordinate bond between hydroxyl groups of β-CD and oxygen of TiO_2 leads to the adsorption of β-CD on TiO_2. Thus, Ag/TiO_2/β-CD nanocomposites can be electrostatically absorbed on cellulosic chains. Through in-situ synthesis, adsorption of TiO_2 nanoparticles alone and Ag/TiO_2 nanocomposites on cotton fabric is also possible. Moreover, hydrogen bonding between β-CD and cellulose can be also formed. The involved mechanism is schematically shown in Fig. 1. On the other hand, Ag/TiO_2/β-CD nanocomposites can be synthesized in the preparation bath and transferred to cotton fabric during 3 h stirring. In addition to the physical adsorption, the transferred nanocomposites can be absorbed to cotton fiber through ionic and/or hydrogen bonding.

Exhaustion In exhaustion method cotton fabric was treated with Ag/TiO_2/β-CD nanocomposite dispersions at boil for 1 h. Effective role of boil temperature in fiber swelling and enhanced contact between nanocomposites and fiber surface provides physical, ionic and hydrogen bonding of nanocomposites with cotton fibers as illustrated in Fig. 1.

Pad-dry-cure Through this method the prepared nanocomposites were physically adsorbed on cotton fabric (Fig. 1). Chemical bonding of the nanocomposites was achieved after post-treatment with CA/SHP and curing.

Through post-treatment of all samples with CA/SHP, two forms of interactions between cotton fabric and Ag/TiO_2/β-CD nanocomposites are possible. Firstly, ester bond formation between hydroxyl groups of β-CD and carboxyl groups of citric acid covalently bond to cellulose (Nazari et al. 2009). Secondly, TiO_2 with positive surface charge can electrostatically bond to negative carboxylate groups (Fig. 1).

Finally all the treated samples were rinsed with distilled water, removing the nanocomposites only physically adsorbed on the fibers (Fig. 1; reaction 3).



(r.3)

What has been shown in Fig. 1 is the different ways of nanocomposite deposition on the treated fabrics speculated based on the applied methods/preparation conditions and possible reaction mechanisms reported in previous literatures. Hydrogen bonding of nanocomposites on cotton fiber is possible due to the presence of hydroxyl groups on cellulosic chains of cotton and β-CD component of nanocomposite. Moreover, physical and ionic bonding are probable. Based on previous studies focusing on use of carboxylic acids as crosslinking agents, CA/SHP is effective as cross-linker when cured at 140–150 °C (Nazari et al. 2009) with less detrimental effect on whiteness and tensile strength. Although higher curing temperatures will result in enhanced crosslinking at the expense of increased yellowing effect and decreased tensile strength (Abou Okeil 2008; Gawish et al. 2009). Here, we aimed at cellulose crosslinking with minimum detrimental effect on fabric inherent properties.

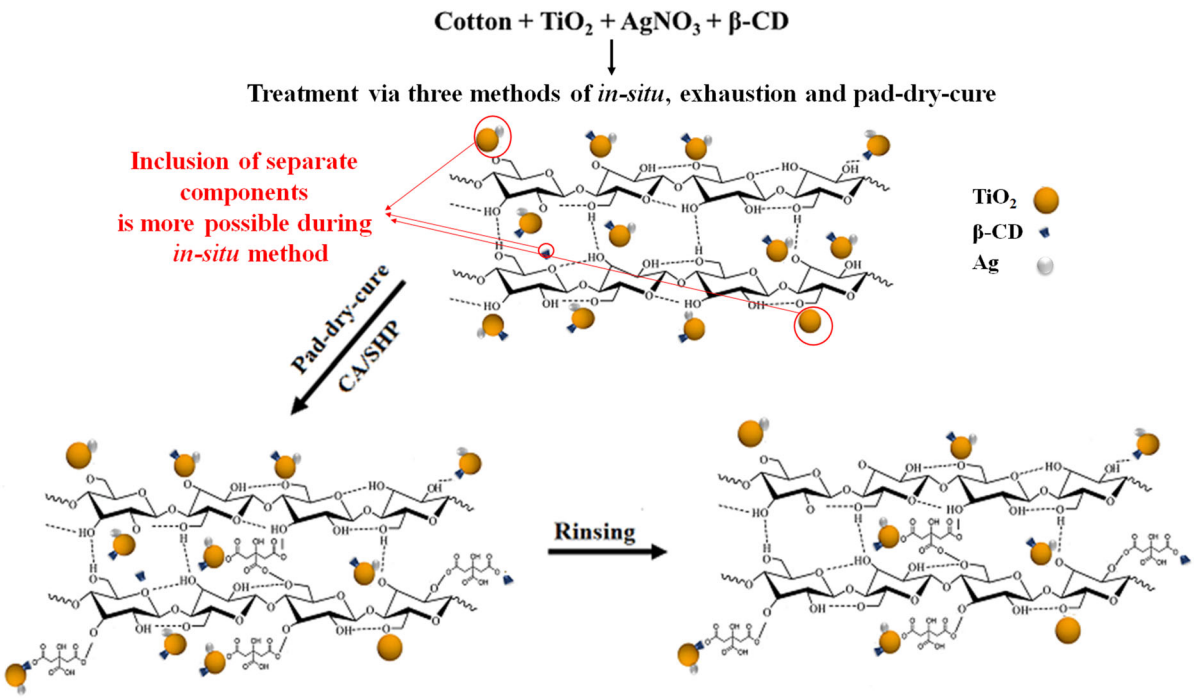


Fig. 1 Schematic representation of Ag/TiO_2/β-CD nanocomposites deposition on cotton fabric via three methods of in-situ synthesis, exhaustion and pad-dry-cure

What is shown in Fig. 1 is cellulose crosslinking with citric acid which is also confirmed by the other authors. Martel et al. (2002) proved that the esterification reaction between citric acid and cellulose occurred at a lower temperature of 150 °C. Thus, at the applied curing temperature and time in our research the cellulose crosslinking by citric acid will be definitely occurred. Although use of higher curing temperature may lead to higher esterification, this would also lead to more tensile strength loss and yellowing, as commented by almost all scientists (Bhaskara et al. 2014). Figure 1 shows all the possible ways of the nanocomposite bonding to cotton. We are not focusing on the yield of the reactions or the amount of citric acid crosslinking nor the amount of nanocomposite bonding from β-CD part. The focus is only on the possibility of the occurrence of all the linkages.

XRD

Comparing with XRD spectrum of untreated cotton fabric (Fig. 2a) with characteristic peaks at $2\theta = 15$, 17, 23 and 32°, the peaks at $2\theta = 25.40$, 38.30, 48.00, 54.04 and 55.10° are attributed to TiO_2 anatase phase for cotton fabric treated with Ag/TiO_2/β-CD nanocomposites using three methods (Fig. 2b–d) (Thamaphat et al. 2008). The peaks are assigned to 100, 004, 200, 105, 211 lattice planes, respectively. Main peak of silver in XRD spectrum is located at $2\theta \sim 38°$, which is overlapped with TiO_2 anatase phase peak (Attarchi et al. 2013). Thus, it is difficult to distinguish silver peak from TiO_2. Using Scherrer's equation and from the widths of the peak at $2\theta = 25.40°$, the crystallite size of the synthesized nanocomposites was 20, 15 and 14 nm using exhaustion, pad-dry-cure and in-situ synthesis, respectively.

Morphological and EDX analyses

Comparing with FESEM images of untreated cotton fabric (Fig. 2a) with smooth surface, surface of cotton fabrics treated with Ag/TiO_2/β-CD nanocomposites using three methods was uniformly covered by nanoparticles (Fig. 2b–d). Nanoparticles were in semi-spherical shape and clustered like a grape. The average particle size was estimated 48, 54 and 42 nm using exhaustion, pad-dry-cure and in-situ synthesis, respectively. As shown in Fig. 2b–d, in addition to C and O relating to β-CD and cotton substrate, presence of Ti and Ag elements were confirmed in the EDX

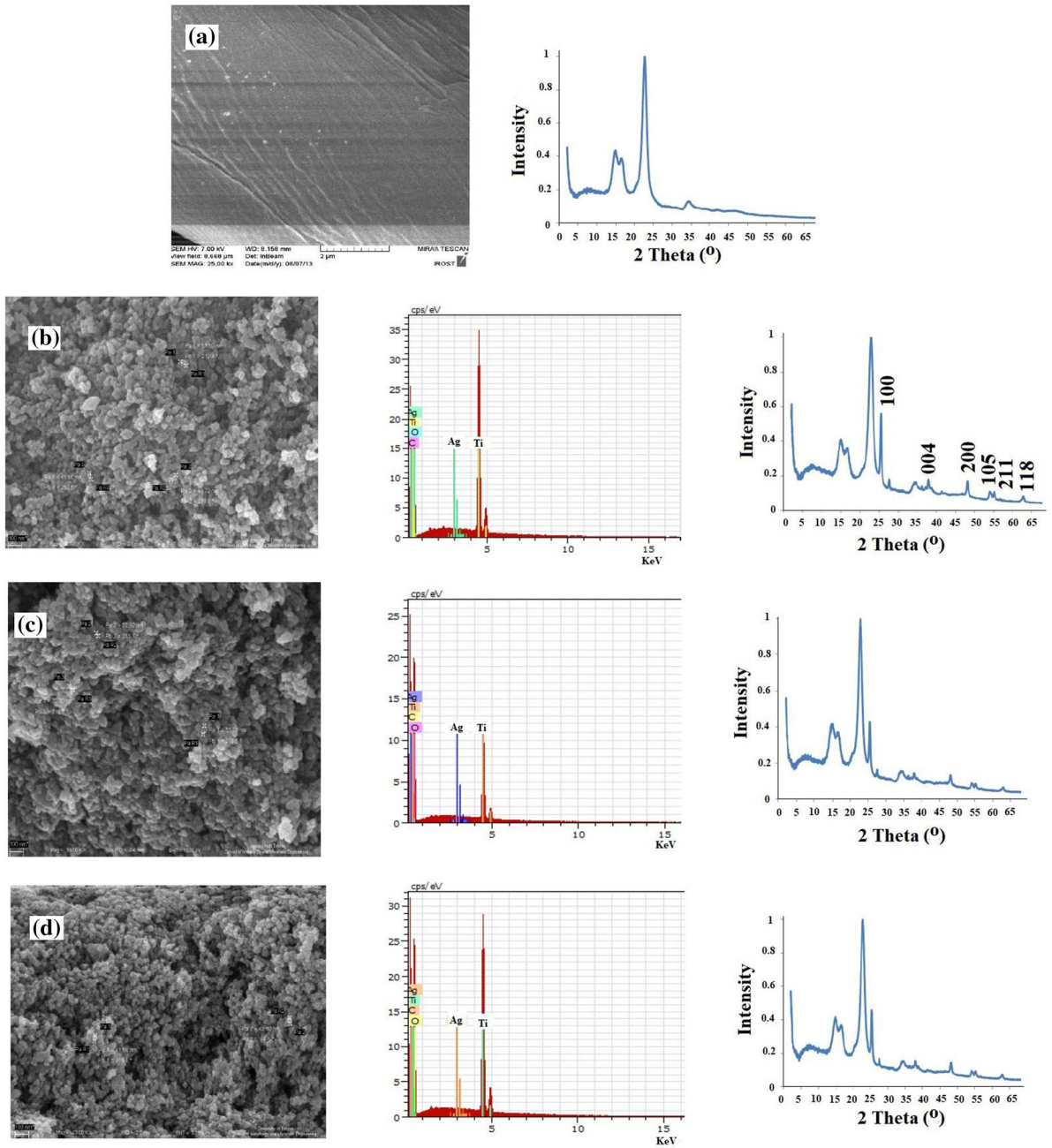


Fig. 2 FESEM and XRD of **a** untreated fabric (×25,000 magnification), FESEM, EDX and XRD results for cotton fabric treated with Ag/TiO_2/β-CD nanocomposites using **b** exhaustion, **c** pad-dry-cure and **d** in-situ synthesis (images are at ×50,000 magnification)

spectra of cotton fabrics treated with Ag/TiO_2/β-CD nanocomposites using three methods.

Weight and atomic percentages of the elements in the cotton fabrics treated with Ag/TiO_2/β-CD nanocomposites using three methods based on EDX analysis is summarized in Fig. 2b–d. Weight percentage of silver was 0.09% for sample treated by exhaustion, which was decreased to 0.06 and 0.02% using in-situ synthesis and pad-dry-cure methods. The same trend was obtained for Ti element decreasing

from 11.27% in exhaustion method to 8.16 and 4.27% for in-situ and pad-dry-cure methods. Thus, exhaustion method was more effective in deposition of more Ag/TiO_2/β-CD nancomposites on cotton fabrics comparing with in-situ synthesis and pad-dry-cure.

For more clarity, mapping images of cotton samples treated with three methods are shown in supplementary data. As indicated in Fig. S1, silver and titanium elements are detected on fibers surface, however with different amount depending on the applied method. The result of mapping images are consistent with the EDX weight percentage results, indicating the deposition of more Ag/TiO_2/β-CD nancomposites on cotton fabrics comparing with in-situ synthesis and pad-dry-cure.

Weight change percentage

Higher adsorption of nanocomposites on cotton fabrics treated by exhaustion method comparing with pad-dry-cure and in-situ synthesis was further confirmed by calculating weight change percentage of the treated fabrics. For this purpose, the percentage of weight change due to the treatment (ΔW %) was determined according to Eq. (3):

$$\Delta W\% = [(W_2 - W_1)/W_1] \times 100 \quad (3)$$

where W_1 and W_2 are weights of samples before and after the treatment, respectively.

Wight gain percentage of fabric treated with Ag/TiO_2/β-CD nanocomposites using exhaustion method was 13%, which was decreased to 6.6 and 2.05% for in-situ synthesis and pad-dry-cure. This is consistent with the results obtained from EDX analysis. Effective role of boil temperature in fiber swelling and enhanced contacts between nanoparticles and fiber surface resulted in more nanoparticles adsorption in exhaustion method. On the other hand, in-situ synthesis of nanocomposites led to greater nanoparticles adsorption comparing with pad-dry-cure method, presumably due to longer treatment time (3 h under UV irradiation) and stirring intensifying the mass transfer of particles to the fabric.

FTIR

Cotton fabrics treated with Ag/TiO_2/β-CD nancomposite were further analyzed by FTIR spectroscopy (Fig. 3). A sample only padded with CA (10 W/W %)/SHP (6 W/W %) and cured at 140 °C for 4 min was also prepared, as a control fabric. Two samples were also prepared regarding as TiO_2 and Ag/TiO_2 finished fabrics using the same procedure identical to Ag/TiO_2/β-CD nanocomposites preparation using exhaustion method in absence of silver nitrate and β-CD. There is no distinguishable difference between the position of peaks in the spectra of different samples, mostly indicating the main peaks of cellulose at 3345, 1641, 1429, 1370, 1112 and 1032 cm^{-1}, attributing to OH stretching, CH stretching, OH bending, CH bending and C–O–C glucose ring (Yuranova et al. 2006). Detailed band assignments are summarized in Table S1. However as indicated in Fig. 3, as the spectra are normalized, the only difference was in the intensity of the peaks. The intensity of peaks at 500–600 cm^{-1} was increased for TiO_2 treated sample, arising from the Ti–O–Ti groups. Sample treated with Ag/TiO_2/β-CD nanocomposites possessed the highest intensity absorbance at 3345 cm^{-1}, due to hydroxyl groups of glucose rings of β-CD. Comparing with untreated cotton fabric, the intensity of peak at 3345 cm^{-1} was decreased for TiO_2 and Ag/TiO_2 treated samples due to binding formation between hydroxyl groups of cellulosic substrate and nanoparticles diminishing the absorbance intensity.

Chrome adsorption

Chrome absorbance of untreated cotton, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics using exhaustion, pad-dry-cure and in-situ synthesis was measured at 255 and 355 nm and the result is shown in Fig. 4a. Comparing with untreated cotton fabric, samples treated with Ag/TiO_2 using all three methods possessed higher chrome adsorption with smaller absorbance at 255 and 355 nm. Maximum chrome adsorption was in presence of β-CD in Ag/TiO_2/β-CD treated fabrics. The potential of β-CD as adsorbent of metal ions have been previously reported in literature (Montazer and Jolaei 2010). It has been reported by researchers that electrostatic attraction is the main mechanism of metal ion adsorption in β-CD based materials, and no distinctive interaction between metal ion and β-CD cavities has been proved (Zhao et al. 2015; Huang et al. 2016; Euvrard et al. 2016). As indicated in Fig. 4a, the maximum chrome absorbance was decreased from 2.2 in Ag/TiO_2 treated sample to 1.5 in presence of β-CD in Ag/TiO_2/β-CD treated

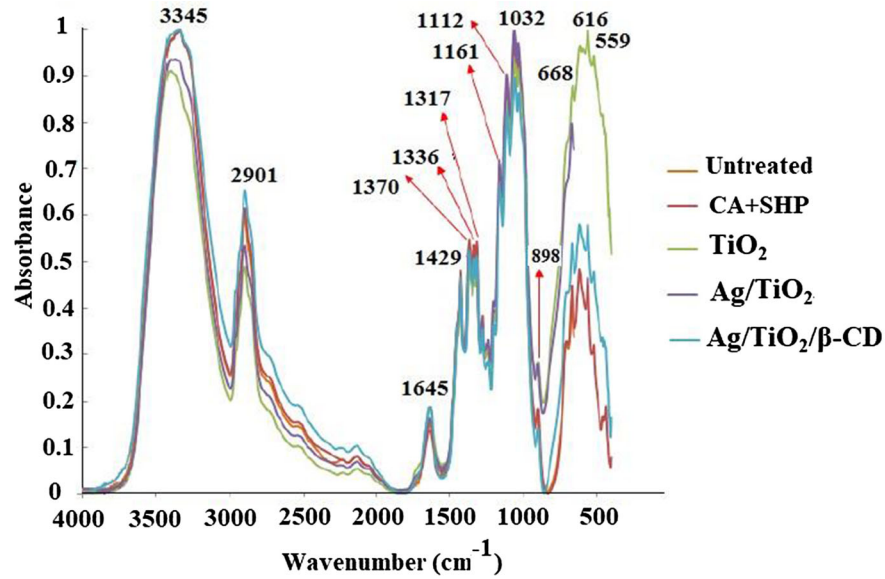


Fig. 3 FTIR spectra of untreated, CA/SHP treated and TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics

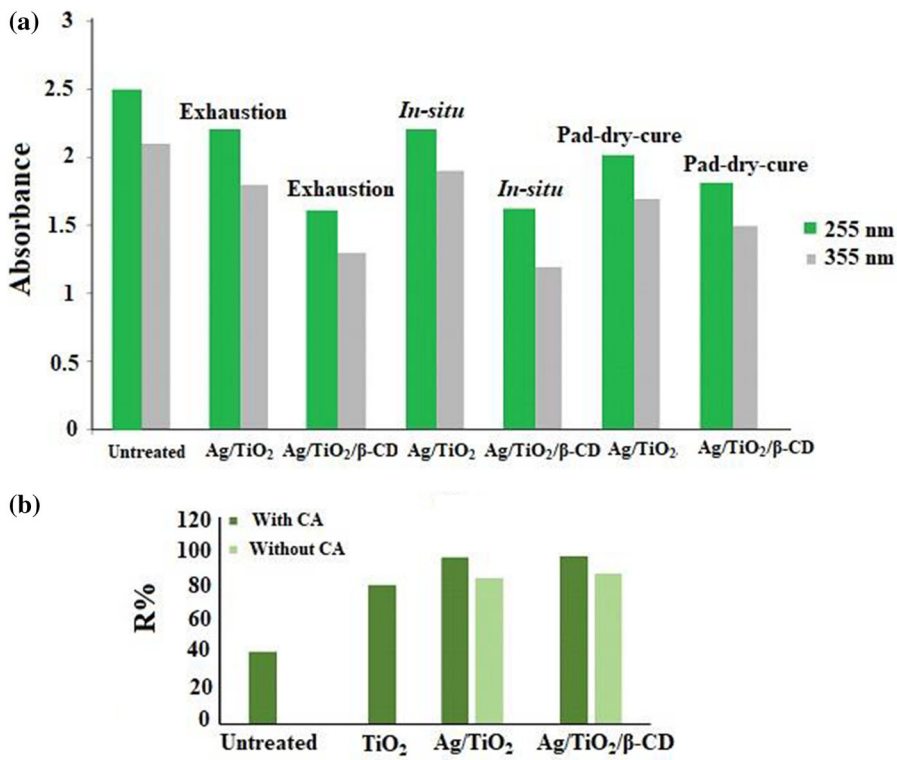


Fig. 4 **a** Chrome ion adsorption of untreated cotton, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics using exhaustion, pad-dry-cure and in-situ synthesis. **b** Antibacterial efficiency of untreated, TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics (β-CD:Ag^+ = 5, exhaustion method)

fabrics (exhaustion method) (almost 30%). This difference is significant considering the low amount of applied materials namely β-CD.

Self-cleaning activity

β-CD:Ag^+ ratio and deposition method including exhaustion, pad-dry-cure and in-situ synthesis were

selected as the most effective factors and our goal was to find the optimized conditions for Ag/TiO_2/β-CD treatment of cotton fabrics based on maximized self-cleaning activity. Thus, statistically-approached experimental design was used to investigate the effect of β-CD:Ag^+ concentration (A) and deposition methods (B) on ΔRGB values as summarized in Table 1.

The design matrix of experimental conditions with the corresponding response value (Table 1) was fitted to a cubic mathematical model [Eq. (4)] (The provided equation is in terms of coded values in which, B(1) and B(2) refer to {1 0 − 1} and {0 1 − 1}, respectively). Based on ANOVA test (Table S2), the designed model for ΔRGB was statistically significant at F value of 48.06 and Prob > F < 0.0001. A good precision and reliability of the experiment was also proved by R-squared of 0.9628.

$$\begin{aligned}\Delta RGB = {} & 81.71 + 10.22A - 11.54B(1) - 3.54B(2) \\ & - 0.19AB(1) + 0.26AB(2)19.62A^2 \\ & + 6.46A^2B(1) + 1.88A^2B(2) - 15.56A^3\end{aligned} \quad (4)$$

Figure S2 shows the effects of β-CD:Ag^+ molar ratio on the photoactivity of the cotton fabrics treated with Ag/TiO_2/β-CD nanocomposites using three different methods. Increased self-cleaning ability in terms of ΔRGB was observed by an increase in β-CD content in the nanocomposites. This arises from several reasons including:

1. Adsorption of more β-CD on TiO_2 causing lower free dye molecule remaining in the solution and more interaction between dye molecules and TiO_2 due to more dye molecules entrapped in the cavity of β-CD (Attarchi et al. 2013).
2. Increased silver nanoparticles formation in presence of more β-CD, acting as a weak reducing agent.
3. Reduced electron–hole recombination rate, enhanced visible light absorbance and increased electron transfer rate to the oxidant due to more silver nanoparticles synthesized on nano TiO_2 surface.

However, this enhancement was limited and a higher β-CD:Ag^+ ratio resulted in lower self-cleaning property which can be due to two reasons namely:

1. Lower contact between the dye molecules and TiO_2 due to more β-CD molecules forming multilayer around TiO_2 surface.
2. Lower Ag/TiO_2/β-CD nanocomposites adsorption on cotton fabric in high β-CD:Ag^+ ratio due to increase in nanocomposites size caused by β-CD multilayer formation.

Thus, there is an optimum limit for β-CD content in the prepared nanocomposites to attain maximum self-cleaning ability (higher ΔRGB). This trend was similar for all three treatment methods.

As indicated in Fig. S2, exhaustion method was superior to pad-dry-cure and in-situ synthesis, providing higher dye degradation efficiency. This is in accord with higher nanocomposites adsorption on cotton fabric through exhaustion method as confirmed by EDX, mapping and weight change percentage analyses.

Finally considering the applied range of the parameters, the software suggested the optimized model factors of β-CD:Ag^+ = 5 and exhaustion method, regarding the highest self-cleaning activity.

The cotton fabric treated with Ag/TiO_2/β-CD nanocomposites at optimum β-CD:Ag^+ ratio was prepared and the self-cleaning activity was compared to untreated, TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated samples using three methods (Table 2).

As indicated in Table 2, cotton fabrics treated with Ag/TiO_2 nanocomposites using three methods possessed higher self-cleaning activity comparing with identical TiO_2 treated fabrics. This confirmed the

Table 2 Self-cleaning activity of untreated, TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated samples using three methods (β-CD:Ag^+ = 5)

Sample	Method	ΔRGB
Untreated	–	29
TiO_2	Pad-dry-cure	40
Ag/TiO_2	Pad-dry-cure	53
Ag/TiO_2/β-CD	Pad-dry-cure	70
TiO_2	In-situ	50
Ag/TiO_2	In-situ	57
Ag/TiO_2/β-CD	In-situ	78
TiO_2	Exhaustion	55
Ag/TiO_2	Exhaustion	63
Ag/TiO_2/β-CD	Exhaustion	100

positive role of silver nanoparticles in enhancing the UV–visible absorbance efficiency, trapping the excited electrons, enhancing the electron–hole separation, and consequently acting as electron donors to O_2, enhancing the photocatalytic activity of TiO_2. This has been previously proved in many scientific literatures (Harifi and Montazer 2014a). Maximum self-cleaning activity was achieved in presence of β-CD in all three methods. β-CD is responsible for enhanced silver nanoparticles synthesis on TiO_2 surface and enhanced dye adsorption in cavities increasing dye accessibility to TiO_2. Moreover, due to electron transfer from TiO_2 to dye molecules trapped in β-CD cavities, electron-holes are separated and their life time prolonged. The superiority of cotton fabric treated with Ag/TiO_2/β-CD using exhaustion method was confirmed possessing the best self-cleaning activity.

Schematic diagram of MB dye degradation by Ag/TiO_2/β-CD nanocomposites is illustrated in Fig. 5.

Antibacterial properties

The antibacterial efficiency of the treated fabrics was determined against *S. aureus* and the bacteria reduction percentage was calculated based on Eq. (2) (Fig. 4b). Only 41.6% bacteria reduction was obtained for untreated sample after 3 h inoculation with *S. aureus*. However, fabric treated with TiO_2 nanoparticles was successful in 80.37% bacteria killing efficiency. The antibacterial activity of TiO_2 nanoparticles have been previously confirmed due to different mechanisms including formation of reactive oxygen species, interaction of nanoparticles with bacteria cell wall and subsequent damage of the bacteria cell (Ashkaran et al. 2011). Exposure of bacteria to Ag/TiO_2 treated fabric resulted in 96.4% antibacterial activity due to effective role of silver nanoparticles in enhancing the bacteria reduction. Silver metal ions, their small particle size and high specific surface area provides close interaction with microbial membranes causing damage to the lipids, proteins and DNA of the microorganisms (Lok 2006). As indicated in Fig. 4b, no significant change was observed for antibacterial efficiency of sample treated with Ag/TiO_2/β-CD nanocomposites, with a slight increase to 96.8% bacteria reduction percentage. Thus, as indicated in Fig. 4b, the antibacterial efficiency of the treated samples was increased from almost 80% for TiO_2 treated cotton to 100% for Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics. Thus, due to the presence of silver in the nanocomposites the treated cotton samples are capable of complete bacteria killing. This is surely a remarkable antibacterial effect, which was achieved by the low silver amount.

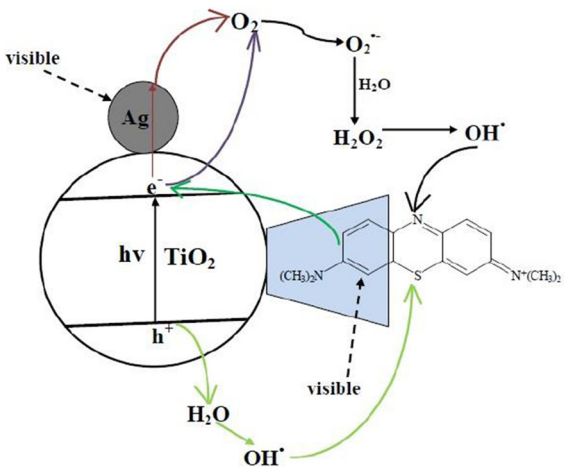


Fig. 5 Schematic diagram of MB dye degradation by Ag/TiO_2/β-CD nanocomposites

As CA is famous for antibacterial activity through alteration in permeability of bacteria cell wall and subsequent bacteria death (Bischof Vukusic et al. 2011), the possible effect of CA/SHP post-treatment of fabrics on enhanced antibacterial efficiency was studied (Fig. 4b). While Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics without CA/SHP post-treatment had 84 and 86.9% bacteria reduction, CA/SHP post-treatment of fabrics effectively enhanced the antibacterial efficiency to 96.4 and 96.8%.

Wettability

The contact angle between water and fabrics surface was quantified and reported in Table 3. In comparison to untreated cotton fabric with contact angle of 18°, fabrics treated with TiO_2 and Ag/TiO_2 possessed lower water adsorption with increased contact angle to 47°. This arises from interaction between hydroxyl groups of cellulose and nanoparticles. Moreover, increased surface roughness through nanoparticles deposition trapped more air bubbles (Harifi and Montazer 2014b).

On the other hand, presence of β-CD in Ag/TiO_2/β-CD treated fabric resulted in higher wettability.

Table 3 Physico-mechanical properties and water contact angle of different samples (β-CD:Ag^+ = 5, exhaustion method)

Sample	Maximum load (N)	Tensile strain (%)	Crease recovery angle (°)	Contact angle (°) before sunlight irradiation
Untreated	212	11.07	189	18
CA/SHP	205	12.20	255	–
TiO_2	214	11.65	245	46
Ag/TiO_2	221	11.93	248	47
Ag/TiO_2/β-CD	212	11.43	251	21

Hydroxyl groups of glucose ring of β-CD are responsible for the decreased contact angle to 21°.

As the photo-induced wettability of TiO_2 treated textiles has been reported in previous studies, contact angle measurement was repeated after 24 h sunlight irradiation of samples. Owing to photo-activity of TiO_2 nanoparticles, wettability of the treated fabrics was increased reaching to 0° for all the samples after sunlight irradiation. The negative electrons and positive holes get involved in the reduction process of Ti^{4+} to Ti^{3+} and produce the superoxide anions which can be changed to oxygen molecules and ejected from the surface, remaining oxygen vacancies increasing the wettability of the fabrics (Harifi and Montazer 2014b).

Physico-mechanical properties

Mechanical properties of untreated, TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics (β-CD:Ag^+ = 5, exhaustion method) are reported in Table 3. For comparison maximum load and tensile strain of fabric only padded with CA/SHP was also measured as a control sample. The maximum load of the control sample was 3.3% less than that of untreated fabric, possibly due to detrimental effect of citric acid on cellulosic chains (Harifi and Montazer 2012). Although there is no significant change in maximum load of samples treated with TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD nanocompositess comparing with control fabric, the data shows a slight increase. Thus, citric acid was more effective in covalent linkage formation between cellulose and nanocomposites rather than damaging to cellulosic chains. Hence, the applied Ag/TiO_2/β-CD nanocomposites treatment had no negative effect on mechanical properties.

The crease recovery angle (CRA) of untreated, control, TiO_2, Ag/TiO_2 and Ag/TiO_2/β-CD treated fabrics (β-CD:Ag^+ = 5, exhaustion method) are also reported in Table 3. Comparing with untreated cotton fabric, the CRA of control sample only padded with CA/SHP was increased by 35%, due to cross-linking effect of citric acid (Harifi and Montazer 2012). Increased CRA of Ag/TiO_2/β-CD treated fabric comparing with untreated cotton can be attributed to decreased free hydroxyl groups of cellulose due to interaction with the deposited nanocomposites and possible crosslinking through CA/SHP post-treatment. However the extent of cross-linking between cellulosic chains is decreasing due to nanocomposites aggregation between cellulosic chains.

Washing durability

The washing durability of Ag/TiO_2/β-CD nanocomposites adsorbed on cotton fabric was evaluated, and the change in self-cleaning ability of the washed sample was studied. Moreover, FESEM images of the washed sample were taken to confirm the presence of nanocomposites on the surface after washing. The appropriate stability of the synthesized Ag/TiO_2/β-CD nanocomposites on the treated fabric was confirmed by negligible change in the self-cleaning activity (still three times higher than untreated fabric). Durable treatment of fabric with Ag/TiO_2/β-CD nanocomposites was further confirmed by FESEM images (Fig. S3), indicating complete coverage of fiber surface with nanocomposites after washing. Formation of ester bond between hydroxyl groups of β-CD and carboxyl groups of citric acid covalently bond to cellulose is the most important factor providing durable finishing.

Conclusion

This study designed a novel multifunctional cotton fabric with excellent antibacterial efficiency and durable enhanced self-cleaning activity through synthesis and deposition of Ag/TiO_2/β-CD nanocomposites utilizing three different methods including exhaustion, pad-dry-cure and in-situ synthesis, following by CA/SHP post-treatment. Based on statistical approach exhaustion method was introduced as the optimized technique for Ag/TiO_2/β-CD nanocomposites deposition providing maximum nanocomposites adsorption, as evidenced by EDX and weight change percentage analyses, and the best self-cleaning activity. According to FESEM pictures, semi-spherical nanoparticles with 48 nm size were completely covered the surface of the optimized treated fabric (β-CD:$Ag^+ = 5$). β-CD was responsible for enhancing the photocatalytic activity of TiO_2 due to higher silver nanoparticles synthesis, enhanced dye adsorption in cavities increasing dye accessibility to TiO_2 and increased electron-holes separation. The optimized treatment not only had no detrimental effect on physico-mechanical properties of cotton fabrics, but also led to increase in maximum load and crease recovery angle. The prepared substrate is applicable in medical and environmental remediation fields due to the potential of hosting various compounds such as drugs and pollutants.

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