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TiO_2 nanowire and TiO_2 nanowire doped Ag-PVP nanocomposite for antimicrobial and self-cleaning cotton textile

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ABSTRACT

The TiO_2 nanowire (TiO_2 Nw) was successfully prepared via hydrothermal method through TiO_2 nanoparticle (TiO_2 Np). TiO_2 Np doped silver and TiO_2 Nw doped silver were prepared via photo-reducing Ag^+ ions to Ag metal on the TiO_2 Np or TiO_2 Nw surfaces. The prepared nanomaterials were evaluated using X-ray (XRD) diffraction pattern, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Bleached untreated cotton fabric and PVP treated cotton fabrics were coated with the synthesized nanomaterials using pad-dry-cure method. Photocatalytic activity of untreated and coated cotton fabrics with TiO_2 nanomaterials was investigated through the fabric self cleaning of MB dye stains. Also, the PVP finished cotton fabric modified by nanomaterials demonstrated antimicrobial activity against Gram positive bacteria, Gram negative bacteria and fungi. The mechanical properties of coated cotton fabric (tear strength, surface roughness, tensile strength and elongation at break) were examined.

1. Introduction

Textile industry holds a vast potential in the commercialization of nano technological products. Especially, self cleaning textiles have been holding great promise for military applications, where there is a lack of time for laundering at severe conditions. Also in business life self-cleaning textiles are very helpful for preventing stains on the clothes that would ruin the day. Furthermore, UV radiation that comes from the sun could be very dangerous for human health. UV radiation causes the generation of free radical chemical species (Black, 2004) that are supposed to participate in the development of various pathologies such as cancer, aging, Alzheimer's disease, inflammatory disorders and other ailments (Liebler, 2006). Therefore, protection of body from harmful UV portion of the sunlight is another important attractive area. Many scientists have been working on self cleaning and UV blocking textiles (Elif & Husnu, 2012). Silver nanoparticles (Ag-NPs) are a powerful antimicrobial agent that deactivates several microorganisms, for example *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* (Nassar & Youssef, 2012). Recently, nanocomposites containing silver nanoparticles have been intensively considered for packaging applications and promising biomedical applications, such as wound dressings, tissue scaffolds and antimicrobial filters (Rodrigo, Caue, & Luiz, 2010).

Titanium dioxide (TiO_2), the most promising photocatalyst because of its potential application in the decomposition of pollutants in water and air, has attracted much attention for the past few decades. However, the effective photoexcitation of TiO_2 requires the radiation of light with energy higher than the titania band gap energy (Chan & Barteau, 2005).

TiO_2 is also considered to be the most suitable catalyst for environmental applications owing to its nontoxicity, strong oxidizing power and the long-term stability against corrosion (Varghese, LaTempa, & Grimes, 2009; Wu, Lin, & Lai, 2005). Therefore, a great effort has been spent on revealing and improving its photocatalytic activity for practical applications (Chang, Lin, Chan, Hsu, & Chen, 2006; Kim et al., 2003; Sobana, Muruganadham, & Swaminathan, 2006). It is well known that the photocatalytic activity of titania depends on its crystalline structure, doping, surface area, surface hydroxyl group, etc. Recently, much scientific attention has been attracted by the effect of doping (Herrmann et al., 1997; Liu, Wang, Yang, & Yang, 2008; Yu, Xiong, Cheng, & Liu, 2005). Silver among the other metals thanks to its high stability and excellent electrical and thermal conductivity seems to be promising titania dopant. For those reasons a doping effect of silver on the titania photocatalytic efficiency in decontamination processes has been

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intensively studied (Akpan & Hameed, 2009). Moreover, the silver ability to prevent the backward recombination of a promoted electron (e^-) and a generated hole (h^+) can positively effect the photocatalytic activity of titania (Krejckov et al., 2012).

With the above in mind, we undertake this work with a view to enhance the photocatalytic and antimicrobial activities of TiO_2 nanomaterials. Thus our research was designed to achieve three-fold objective: (1) to synthesize TiO_2 nanowires and TiO_2 nanowires doped Ag; (2) to make a comparison among essential characteristics and basic features of TiO_2 nanoparticles, TiO_2 nanowires, TiO_2 nanoparticles doped Ag, and TiO_2 nanowires doped Ag; (3) to study the impact of application of these nanomaterials when included in PVP-treated cotton fabrics on the newly imparted properties brought about thereof. It is understandable that inclusion of aforementioned nanomaterials in PVP yields nanocomposites that coat the cotton fabric and therefore, would be reflected on the properties of the fabrics, notably antimicrobial and self cleaning.

2. Experimental

2.1. Materials

The bleached plain woven 100% cotton fabric (138 g/m^2) was kindly supplied by Misr Company for spinning and weaving Mehalla El Kobra, Egypt. Poly-N-vinyl-2-pyrrolidone (PVP) 40,000 Da, was supplied by Sigma–Aldrich. Methylene blue was supplied by Ciba. TiO_2 nanoparticles (P_{25}, Degussa), with about 30 nm cross-sectional dimension, silver nitrate and sodium hydroxide were of laboratory grade chemicals.

2.2. Methods

2.2.1. Synthesis of TiO_2 nanowires

0.2 g of titanium nanoparticles (P_{25}) in strong alkaline aqueous solution of NaOH (10 M, 40 ml) was placed into a Teflon-lined autoclave. The mixture was stirred to form a milky suspension, sealed and hydrothermally treated at 230–250 °C for three days. The precipitate formed was separated by filtration and washed with de-ionized water until a pH value near 8 was reached. Up to this stage, the precipitate denoted hydrogen form $Na_xH_{2-x}Ti_3O_7$ (x = 0.75) (Haroun & Youssef, 2011). The suspensions were then filtered, washed several times with sodium chloride solution to replace Na instead of H to form sodium form ($Na_2Ti_3O_7$) of TiO_2 nanowires, and oven-dried at 70 °C for more than 8 h.

2.2.2. Synthesis of TiO_2 nanowires/TiO_2 nanoparticles doped silver

In typical method Ag doped TiO_2 nanoparticles and/or TiO_2 nanowires were prepared via photo-reducing Ag^+ ions to Ag metal on theTiO_2 nanoparticle or TiO_2 nanowire surface as per the following technique (Vamathevan, Amal, Beydoun, Low, & McEvoy, 2002). First pH of the TiO_2 nanoparticle or nanowire suspension was adjusted to 3.5 proceeding to reaction using perchloric acid. Aliquots of various amounts of Ag^+ ions, prepared by dissolving silver nitrate salt ($AgNO_3$) in deionized water, were added into the suspension of TiO_2 such that the Ag^+ concentration was 5% in relation to TiO_2 nanoparticles or nanowires. Then, the mixtures were exposed to irradiation using UV light by four mercury lamps (8 W) for 6 h with continuous air supply. The suspensions were then filtered, washed and dried to give Ag doped TiO_2 and Ag doped TiO_2 nanowires.

2.2.3. Treatment of cotton fabric with PVP

Bleached cotton fabric was immersed in two different aqueous solutions of PVP 1% and 3% (w/v). The treated samples were then padded in two dips and nips to a wet pick-up of 80–85%. Treated samples were dried at 85 °C for 5 min and then washed twice with hot water at 50 °C for 15 min. Finally the samples were dried at an ambient condition.

2.2.4. Coating of TiO_2 nanowires/TiO_2 nanoparticles/TiO_2 nanowires doped silver/TiO_2 nanoparticles doped silver on cotton fabric

Bleached untreated cotton fabric and PVP treated cotton fabrics were coated with nano solutions using pad-dry-cure method. 2% (w/v) suspended solutions of nanoparticles were prepared and sonicated for 10 min. Fabrics were immersed in presuspended solutions and kept for 5 min. The samples were then padded in two dips and nips to a wet pick-up of 100%. After padding the cotton fabrics were dried at 80 °C for 5 min and cured at 130 °C for 3 min. Finally the samples were washed with distilled water and finally dried at ambient conditions.

2.3. Testing and analysis

2.3.1. Characterization of synthesized nanoparticles

The nanoparticles were characterized using the following techniques:

2.3.1.1. X-ray diffraction (XRD). XRD patterns recorded on a Philips PW 3050/10 model. The samples were recorded on a Philips X-Pert MMP diffractometer. The diffractometer was controlled and operated by a PC with the programs P Rofit and used a MoK source with wavelength 0.70930 Å, operating with Mo-tube radiation at 50 kV and 40 mA.

2.3.1.2. Transmission electron microscopy (TEM). The nanostructure of different samples was elucidated by JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of TiO_2 nanowires and silver nanoparticles doped TiO_2 nanoparticles and/or nanowires were prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air.

2.3.1.3. Scanning electron micrograph SEM/EDX analysis. Samples for SEM/EDX were taken using FEI INSPECTS Company, Philips, Holland environmental scanning without coating. Elemental micro-probe and elemental distribution mapping techniques were used for analyzing the elemental constitution of solid samples. An elemental analysis of the particles was implemented by a SEM equipped with an energy dispersive spectroscope (EDX), which can provide a rapid qualitative and quantitative analysis of the elemental composition.

2.3.2. Characterization of coated cotton fabric

2.3.2.1. Evaluation of antibacterial activity. Antibacterial activity of treated cotton fabrics was evaluated using Agar Plate Method (AATCC Test Method 147-1988). The coated fabrics were performed to Gram positive bacteria (*S. aureus* and *Bacillus cereus*), Gram negative bacteria (*E. coli* and *P. aeruginosa*) and fungi (*Candida albicans*).

2.3.2.2. Photocatalytic studies.

2.3.2.2.1. Evaluation of photocatalytic degradation of methylene blue (MB). Degradation of adsorbed MB on cotton fabric coated with TiO_2 nanoparticles, TiO_2 nanowires, TiO_2 nanoparticles doped Ag and TiO_2 nanowires doped Ag has been investigated. Also degradation of MB on PVP treated cotton fabric coated with the prepared nanoparticles has been investigated. In detail, eight pieces of treated cotton fabric (0.5 g) were placed in four 100 ml beakers containing 50 ml of aqueous solutions of MB (10 mg/l). The beakers were then exposed to normal laboratory environmental conditions

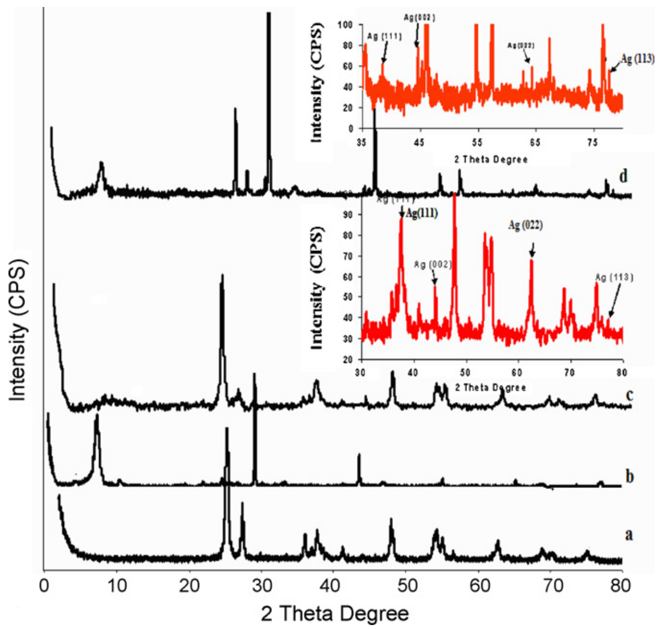


Fig. 1. XRD pattern of (a) TiO_2 nanoparticles, (b) TiO_2 nanowires, (c) TiO_2 nanoparticles doped by Ag nanoparticles and (d) TiO_2 nanowires doped by Ag nanoparticles.

for 2 h and 10 h under shaking. The rate of decolorization of colorant solutions was recorded to the change in the intensity of absorption peak of MB in visible region. UV–vis absorption spectra of the colorant solutions treated cotton fabric were recorded using Perkin Elmer Lambda 3B UV–vis spectrometer. For comparison the same test was also performed using untreated cotton fabric.

2.3.2.2.2. Evaluation of photocatalytic degradation of MB coated cotton fabric. Photocatalytic activity of treated cotton fabric with TiO_2 nanoparticles, TiO_2 nanowires, TiO_2 nanoparticles doped Ag and TiO_2 nanowires doped Ag was also investigated through the fabric self cleaning of MB dye stains. Self cleaning takes place at the surface of cotton fabric exposed to direct sunlight for 2 h and 12 h.

2.3.3. Mechanical properties of treated cotton fabric

2.3.3.1. Tensile strength and elongation at break. Tensile strength and elongation at break were determined by the strip method according to ASTM D1682-64.

2.3.3.2. Surface roughness. Surface roughness was monitored according to JIS 94 standard, using surface roughness measuring instrument, SE 1700α made in Japan.

2.3.3.3. Tear strength. Tear strength was measured according to ASTM D2261-96.

3. Results and discussion

3.1. X-ray diffraction

The TiO_2 nanoparticles and white crystalline nanowires of Na-titanate were premeditated first by means of XRD. This is because the titanate ($Na_2Ti_3O_7$) nanowire possesses a clay-like layered crystal lattice. The XRD pattern (Fig. 1a) shows the *d*-space diffraction peak (3.5 Å, or 0.35 nm) for the titanium nanoparticles, and (Fig. 1b) demonstrates the formation of Na-titanate after hydrothermal process of nanoparticles and washing by sodium hydroxide until the pH 8 which suggests a uniformity of the crystal phase. The washing in NaCl solution has greatly discouraged the ion exchange by proton (H^+) in the de-ionized water, otherwise a smaller *d*-space corresponding to the smaller interlayer-proton should be seen. This NaCl-washing is crucial, simply because the smaller interlayer space can hinder the intercalation of large organic cation. The *d*-spacing of Na-titanate increases to 7 Å (or 0.7 nm) due to the intercalation of Na^+ cation between the interlayer spacing of titanium nanowires.

XRD was also used to determine the phase structure of the samples. Fig. 1c and d shows XRD pattern of TiO_2 nanoparticles and TiO_2 nanowires doped by silver nanoparticles respectively. The XRD pattern shows that all peaks in the pattern can be allocated to the diffraction of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of face centered cubic (fcc) silver, which are marked with Ag in Fig. 1c and d. Also, this pattern demonstrates that additional peaks appear, which can be attributed to the anatase phase of TiO_2 suggesting that the samples c and d contain anatase TiO_2 and metal Ag two phases, and this is reliable with the following SEM and TEM observations.

3.2. TEM

TEM studies were done for investigating detailed structural and surface information on the nanowires. Fig. 2b suggests that the bundled Na-nanowires mostly stay in a stacked and twisted form owing to an interfacial bonding that holds all the nanowires together in a bundle, and the recognizable space in-between the nanowires in the bundles is due to the interfacial bonding as weak as, likely, a H-bonding. However, transmission electron microscopic analysis provides information on the size and shape of primary particles and state of agglomeration (Fig. 2a). The general morphology of the TiO_2 nanoparticles doped Ag is observed in Fig. 2c. It is clear that the primary particles have diameters <15 nm, small weak agglomerates are formed that increase with increasing Ag content. To get more information about the structure of TiO_2 nanowires doped Ag, it was further investigated in Fig. 2d which provides a typical TEM image of TiO_2 nanowires doped Ag, thus confirming further the core–shell structure of TiO_2 doped Ag. The TEM image shows that the TiO_2 nanowires are coated by a layer of Ag nanoparticles. This close interconnection between Ag shells and TiO_2 cores is believed to favor the transfer and separation of photogenerated electrons from TiO_2 cores to the silver shells (Zhang et al., 2003).

3.3. SEM and EDX

Most recently, one-dimensional (1D) TiO_2 nanostructures (e.g. nanowires and nanotubes) have been synthesized to possess various sizes and morphologies in nanoscale. As another family of relatively new nanomaterials, single-crystal TiO_2 nanowire, typically in a diameter below 100 nm and length up to cm level, which can be prepared from the TiO_2 nanoparticles via a simple hydrothermal synthesis (Adachi, Okada, Ngamsinlapasathian, Murata, & Yoshikawa, 2002) reported to show novel properties for advancing a wide range of important technologies.

The Na-titanate nanowire's morphology was characterized by the SEM. In Fig. 3a, the SEM photograph demonstrates well-grown TiO_2 nanowires; it can be seen that the surface of TiO_2 nanowires is very smooth, each with an average length >10 μm and an average diameter 30–50 nm. Most of the Na-titanate nanowires are well-separated singles even though some in aggregated bundles, all of which nonetheless possess a smooth surface typical for single crystalline in structure, which highly supports the data of Fig. 3a. The SEM pictures of pure TiO_2 nanoparticles and Ag doped TiO_2 are also shown in Fig. 3b and d. Fig. 3b depicts that the size of titanium dioxide particle is mostly uniform. But in Fig. 3d the distribution of

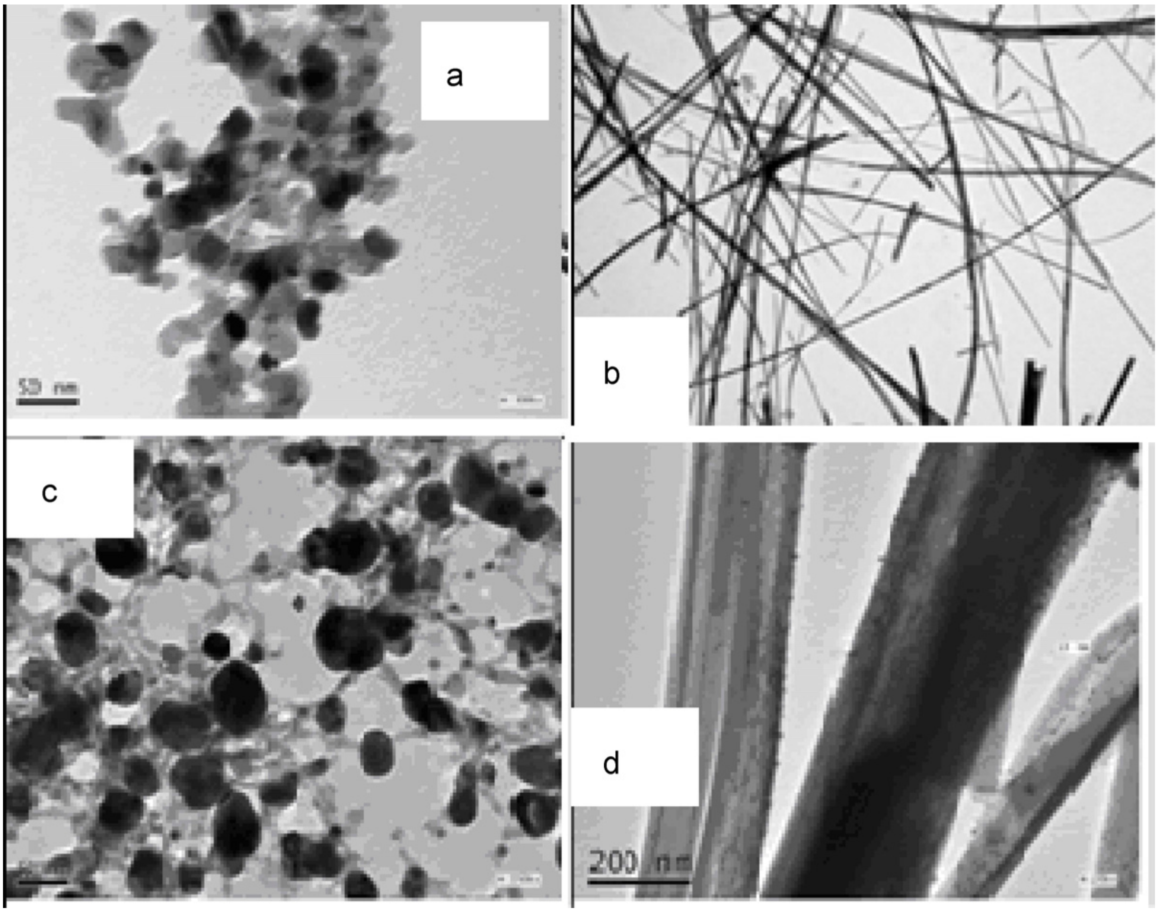


Fig. 2. TEM images of (a) TiO_2 nanoparticles, (b) TiO_2 nanowires, (c) TiO_2 nanoparticles doped Ag, and (d) TiO_2 nanowires doped Ag.

silver on the surface of TiO_2 nanoparticles is not uniform and contains unequal shaped particles which are the aggregation of tiny crystals. While, in case of TiO_2 nanowires doped Ag (Fig. 3c), the Ag doped TiO_2 nanowires display very rough surface morphologies, and a layer of tiny Ag nanoparticles is uniformly deposited on the surface of TiO_2 nanowires. On the other hand, Fig. 3e represents the SEM image of untreated cotton fabric in which surface of the fabric appears smooth in comparison with Fig. 3f in which thin layer of TiO_2 doped Ag is deposited on its surface and distributed uniformally without any aggregation at higher magnification of images. Fig. 3g shows the distribution of TiO_2 nanowires doped Ag on surface of cotton fabric which appears porous and rough at higher magnification. EDX analysis of coated cotton fabric is also shown in Fig. 3f and g. Titania and silver contents on the cotton fabric were identified by EDX spectrum. On the basis of the results, the higher peaks of titania observed in Fig. 3f related to higher amount of nano TiO_2 adsorbed on the surface of the fabric. But the higher peak of silver observed in Fig. 3g related to higher amount of doping in case of TiO_2 nanowires which are adsorbed on the fabric.

3.4. Antibacterial activity

The originality of this work is the synthesis of two nano forms of TiO_2, their doping with silver nanoparticles and determination of their antimicrobial properties when intercalated with PVP. Coating the cotton fabrics that is, TiO_2 in the form of nanoparticles as well as in the form of nanowires along with their corresponding mates doped by Ag nanoparticles inserted in PVP gives rise to nanocomposites. By virtue of its application to the fabrics before the nanocomposite formation, nanocomposites coat the fabric. Results of antimicrobial activity are summarized in Table 1 and Fig. 4. Results of table reveal that:

(1) At zero concentration of PVP, all cotton fabrics treated with nanomaterials under investigation exhibit noticeable antimicrobial activity as indicated by the clear inhibition zones against Gram positive bacteria, Gram negative bacteria and fungi. Nevertheless the antimicrobial efficiency relies on nano form of TiO_2 used. Killing mechanism of the microorganisms originally involves degradation of the cell wall and cytoplasmic membrane under the influence of reactive oxygen species such as hydroxyl radicals and hydrogen peroxide produced by TiO_2. This initially leads to leakage of cellular contents e.g. cations, RNA and protein, then cell lysis and may be followed by complete mineralization of the organism (Matsunaga, Tomoda, Nakajima, Nakamura, & Komine, 1988; Matsunaga, Tomoda, Nakajima, & Wake, 1985).

(2) An excellent antimicrobial effect as evidenced by the higher increase in the values of inhibition zones could be achieved when samples were treated with nano TiO_2 (particles or wires) doped silver. This could be attributed to the fact that silver nanoparticles can interact with sulfur-containing proteins from cell membrane and phosphorus containing compounds in cells,

attacking the respiratory chain, with cell division leading to cell death (Rai, Yadav, & Gade, 2009; Zhang & Chen, 2009).

It is as well to emphasize that Ag nanoparticles can also enhance photocatalysis by enhancing charge separation at the surface of the TiO_2 (Kubacka, Ferrer, Martínez-Arias, & Fernández-García, 2008; Musil et al., 2009). Ag^+ is antimicrobial and can enhance generation of reactive oxygen species (Eqs. (1)–(3)).

$$Ag^{+} + O_2{}^{\bullet -} \rightarrow Ag^{0} + O_2 \quad (1)$$

$$Ag^{0} + O_2{}^{\bullet -} \rightarrow Ag^{+} + O_2{}^{2-} \quad (2)$$

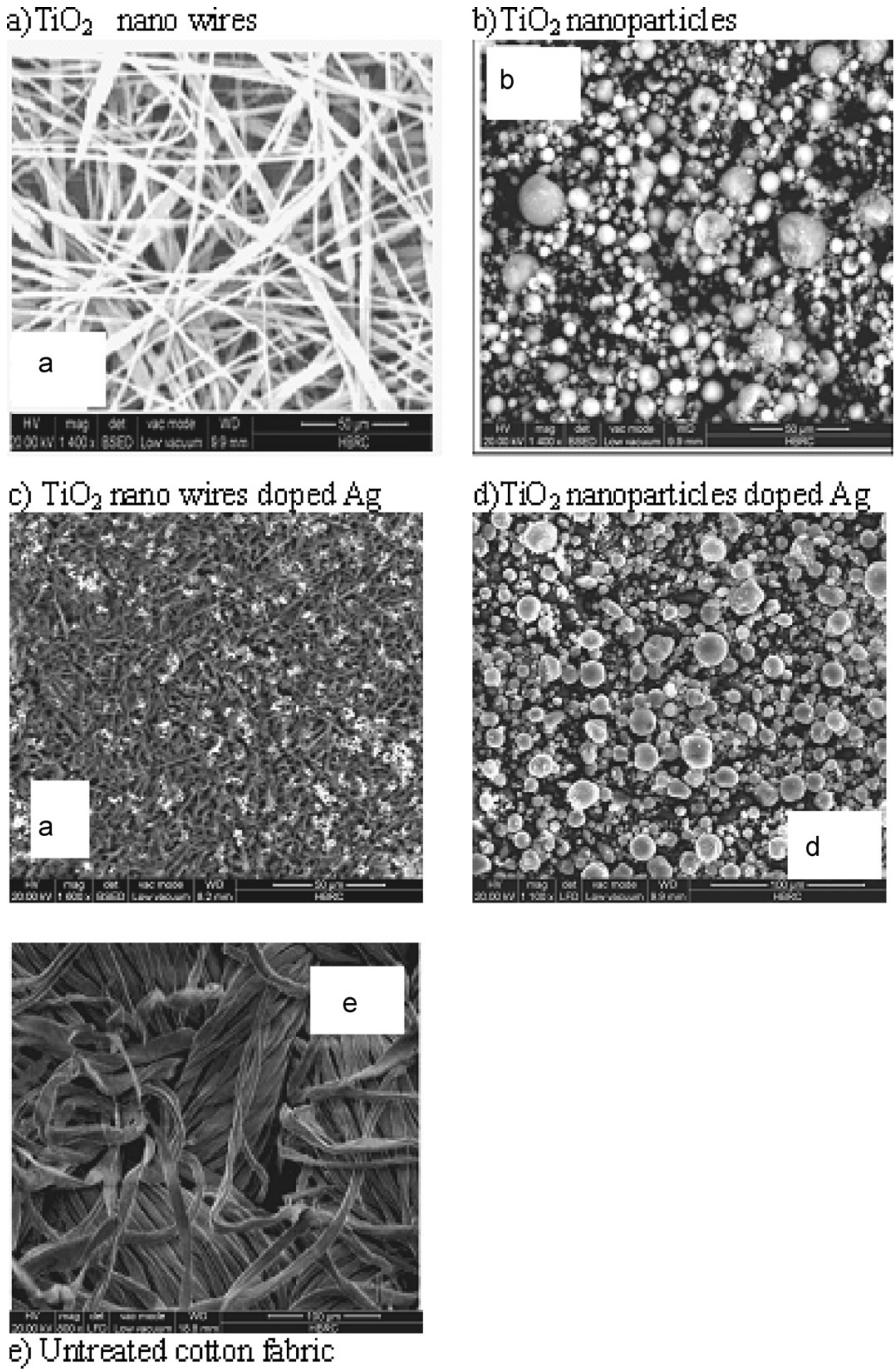
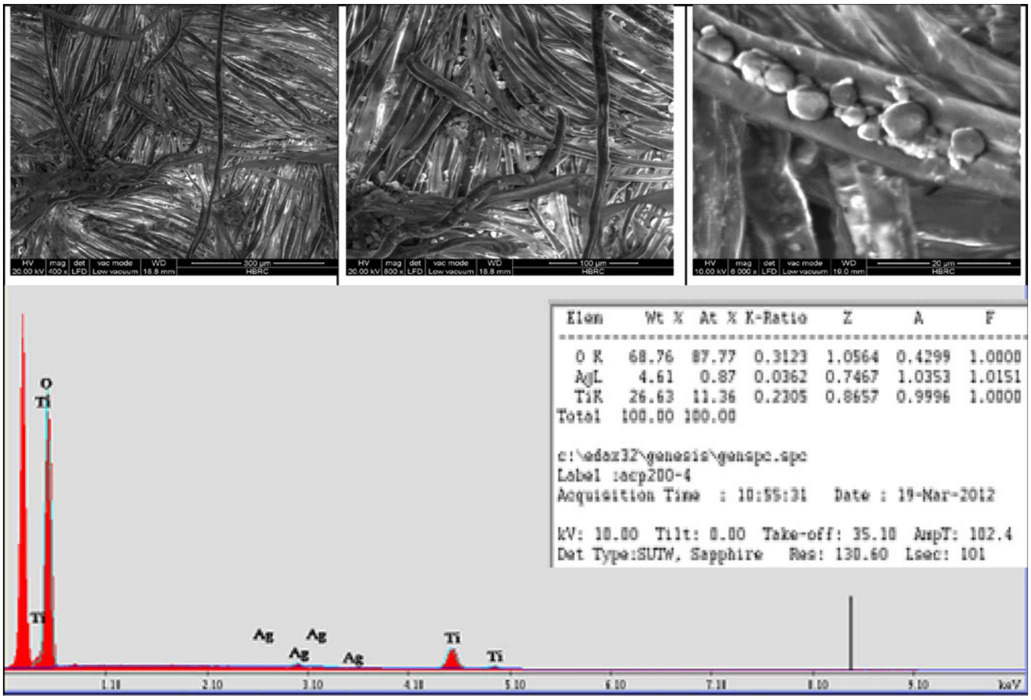


Fig. 3. SEM and EDX analysis of cotton fabric coated with nano TiO_2 (particles and wires) and its doping with Ag.



f) PVP treated cotton fabric coated with TiO_2 nanoparticles doped Ag

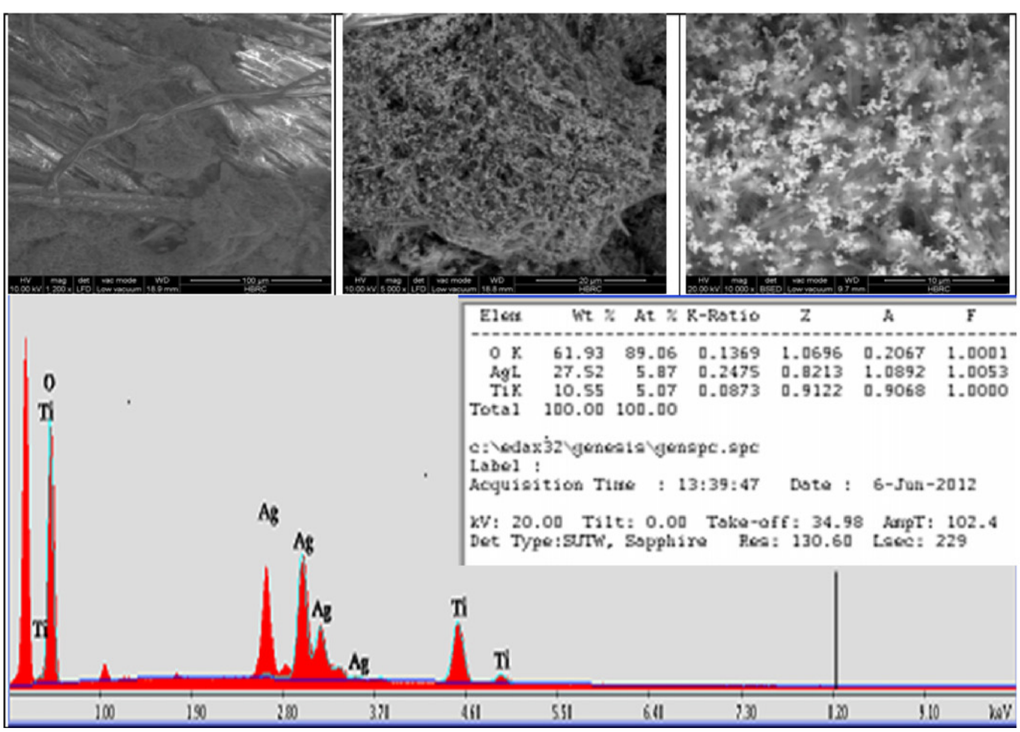


Fig. 3. (*Continued*)

$$H_2O_2 + Ag^0 \rightarrow HO^- + {}^\bullet OH + Ag^+ \quad (3)$$

(3) Increasing the concentration of PVP to 1% (w/v) is accompanied by higher enhancement in value of inhibition zones against all the organisms studied. This could be ascribed to the point that the PVP used in coating fabric acts as dispersing as well as stabilizing agent and prevents the aggregation of nano TiO_2 on cotton fabric coated with nanocomposites (Gupta, Jassal, & Agrawal, 2008). Different values of clear inhibition zones could be associated with the differences in cell wall

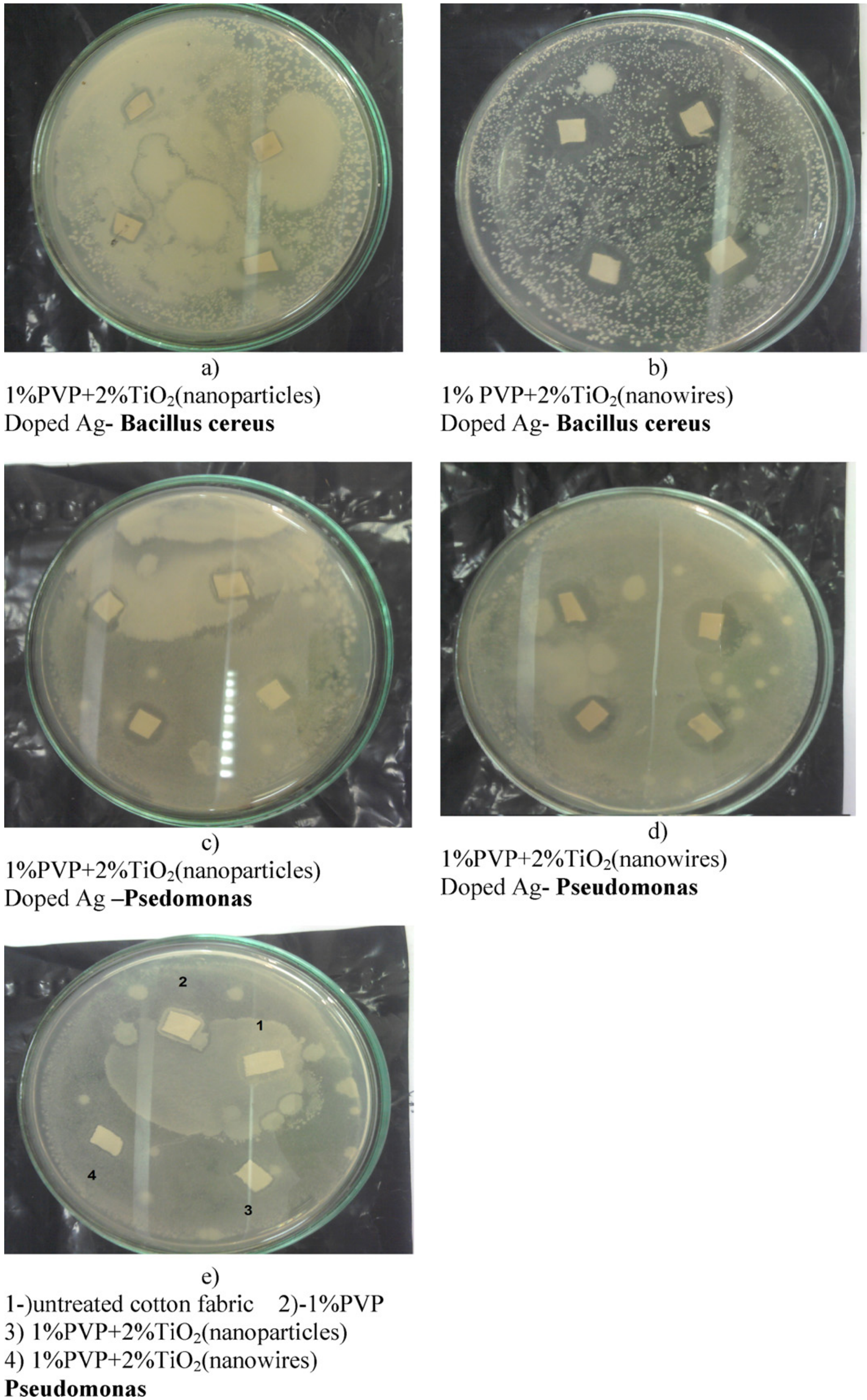


Fig. 4. Photographs of inhibition zones against *Bacillus cereus* and *Pseudomonas* for the treated cotton fabric.

Table 1
Effect of concentration of PVP on antimicrobial properties of treated cotton fabric.

Treatment of cotton fabric	Inhibition zone (mm/1 cm sample)				
	Pseudomonas aeruginosa (G−)	*Staphylococcus aureus* (G+)	*Escherichia coli* (G−)	*Bacillus cereus* (G+)	*Candida albicans*
Blank cotton fabric	0	0	0	0	0
0% PVP					
2% TiO_2 (nanoparticles)	11	11	11	11	0
2% TiO_2 (nanowires)	12	11	11	11	0
2% TiO_2 (nanoparticles) doped Ag	14	13	14	13	11
2% TiO_2 (nanowires) doped Ag	18	15	15	19	11
1% PVP					
2% TiO_2 (nanoparticles)	11	11	12	11	11
2% TiO_2 (nanowires)	12	12	12	13	12
2% TiO_2 (nanoparticles) doped Ag	18	15	17	15	13
2% TiO_2 (nanowires) doped Ag	23	17	18	23	15
3% PVP					
2% TiO_2 (nanoparticles)	13	12	13	11	12
2% TiO_2 (nanowires)	13	13	12	12	13
2% TiO_2 (nanoparticles) doped Ag	19	15	17	15	13
2% TiO_2 (nanowires) doped Ag	24	18	19	24	16

structures. Further increase in concentration of PVP 3% (w/v) causes insignificant effect on antimicrobial efficiency of cotton fabric coated with nanocomposite.

Based on the above results, it is clear that 1% PVP constitutes an optimal concentration for PVP coating. The latter refers to TiO_2 and TiO_2 doped Ag-PVP nanocomposites. This coating imparts antimicrobial activity to cotton fabric (TiO_2 nanowires) and its doping with silver nanoparticles of treated cotton fabrics.

3.5. Photocatalytic studies

3.5.1. Photocatalytic degradation of methylene blue (MB)

The spectral changes brought about by degradation of MB adsorbed cotton fabric, MB/TiO_2 (nanoparticles)/cotton

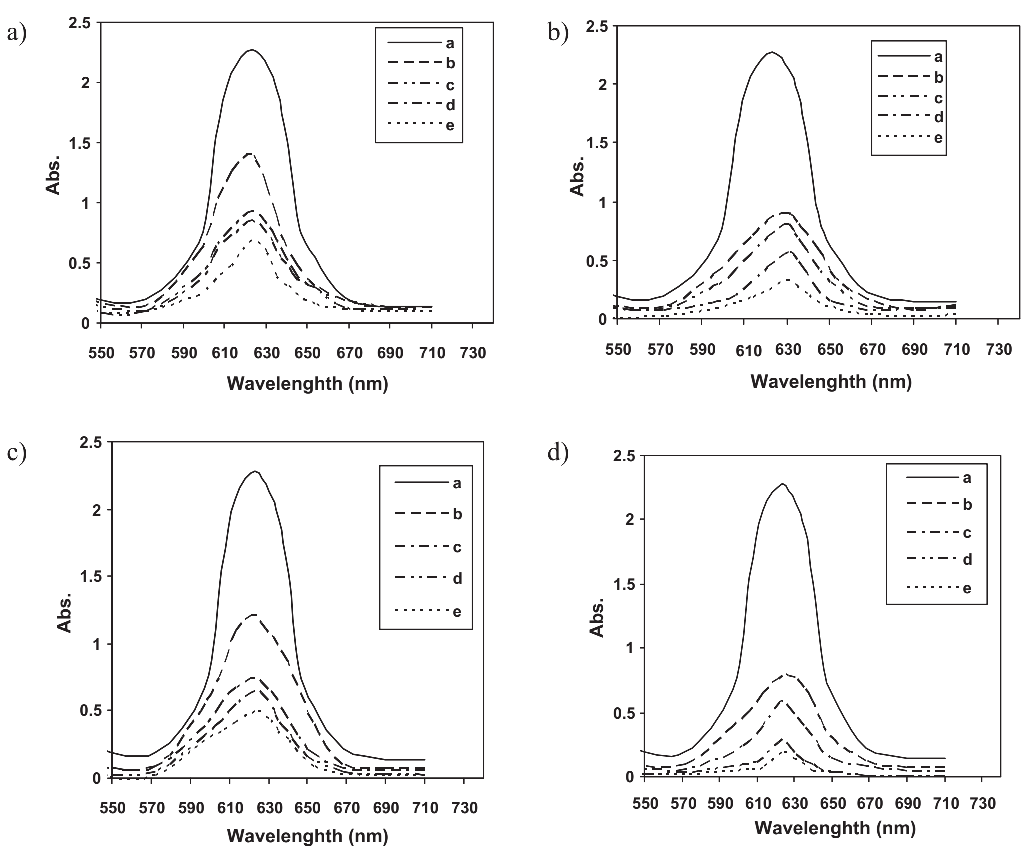


Fig. 5. UV–vis absorption spectra of degradation of methylene blue (MB) under normal laboratory environment. Photodegradation of MB on the TiO_2 nanoparticles treated cotton fabric when time of exposure is (A) 2 h and (B) 12 h: (a) MB/untreated cotton fabric, (b) MB/TiO_2 (nanoparticles)/cotton fabric, (c) MB/TiO_2 (nanoparticles)/PVP treated cotton, (d) MB/TiO_2 (nanoparticles) doped Ag/cotton fabric and (e) MB/TiO_2 (nanoparticles) doped Ag/PVP treated cotton fabric. Photodegradation of MB on the TiO_2 nanowires treated cotton fabric when time of exposure is (C) 2 h and (D) 12 h: (a) MB/untreated cotton fabric, (b) MB/TiO_2 (nanowires)/cotton fabric, (c) MB/TiO_2 (nanowires)/PVP treated cotton, (d) MB/TiO_2 (nanowires) doped Ag/cotton fabric and (e) MB/TiO_2 (nanowires) doped Ag/PVP treated cotton fabric.

fabric, MB/TiO_2 (nanoparticles) doped Ag/cotton fabric, MB/TiO_2 (nanoparticles)/1% PVP treated cotton fabric and MB/TiO_2 (nanoparticles) doped Ag/1% PVP treated cotton fabric are shown in Fig. 5A and B. As is evident reaction of TiO_2 (through the reactive oxygen species on its surface) with MB dye causes changes in the rate of degradation of the latter. The rate of degradation is recorded with respect to the change in the intensity of absorption peak in visible region. The major peak is observed at 623 nm. In Fig. 5A (for a given time of exposure of 2 h) the observed peak decreases gradually. Increasing time of exposure to 12 h (Fig. 5B) enhances the rate of photocatalytic degradation of MB dye and follows the order:

MB/TiO_2 (nanoparticles) doped Ag/1% PVP treated cotton fabric > MB/TiO_2 (nanoparticles) doped Ag/cotton fabric > MB/TiO_2 (nanoparticles)/1%PVP treated cotton > MB/TiO_2 (nanoparticles)/cotton fabric > MB adsorbed cotton fabric.

The photocatalytic process involved several numbers of possible reactions. TiO_2 is a semiconductor. The adsorption of a photon with sufficient energy by TiO_2 promotes electrons from the valence band (e_{vb}^-) to the conduction band (e_{cb}^-), leaving a positively charged hole in the valence band (h_{vb}^+; Eq. (4)). The band gap energy (energy required to promote an electron) of anatase is approx. 3.2 eV, which effectively means that photocatalysis can be activated by photons with a wavelength of below approximately 385 nm (i.e. UVA). The electrons are then free to migrate within the conduction band and the holes may be filled by an electron from an adjacent molecule. This process can be repeated. Thus, holes are also mobile. Electrons and holes may recombine (bulk recombination) a non-productive reaction, or, when they reach the surface, react to give reactive oxygen species (ROS) such as $O_2^{\bullet-}$ (Eq. (5)) and $^\bullet OH$ (Eq. (6)). These in solution can react to give H_2O_2 (Eq. (7)), further hydroxyl (Eq. (8)) and hydroperoxyl (Eq. (9)) radicals. Reaction of the radicals with organic compounds results in mineralization (Eq. (10)) (Howard, Foster, Sajnu, & Alex, 2011).

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \quad (4)$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \quad (5)$$

$$h_{vb}^+ + H_2O \rightarrow {}^\bullet OH + H^+(aq) \quad (6)$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad (7)$$

$$O_2^{\bullet-} + H_2O \rightarrow {}^\bullet OH + OH^- + O_2 \quad (8)$$

$$O_2^{\bullet-} + H^+ \rightarrow {}^\bullet OOH \quad (9)$$

$${}^\bullet OH + \text{organic} + O_2 \rightarrow CO_2 + H_2O \quad (10)$$

It is observed from the above results that TiO_2 doped Ag is more efficient in enhancing photocatalytic degradation of MB adsorbed on cotton fabric than pure TiO_2. This may be explained as follows. Ag nanoparticles deposited on the nano TiO_2 surface can act as electron–hole separation centers (Henglein, 1979; Herrmann, Disdier, & Pichat, 1986). The electron transfer from the TiO_2 conduction band to metallic silver particles at the interface is thermodynamically possible because the Fermi level of TiO_2 is higher than that of silver metals (Sclafani & Herrmann, 1998). This results in the formation of Schottky barrier at the metal–semiconductor contact region, which improves the charge separation and thus enhances the photocatalytic activity of TiO_2.

It is also clear from the previous order that inclusion of TiO_2 (nanoparticles) doped Ag in PVP treated cotton fabric causes the highest photodegradation of MB dye as compared with all other treated samples. This could be associated with the role of PVP in enhancing the efficiency of photodegradation of adsorbed dye by increasing the transportation of photo-induced electrons and holes in the photocatalyst (Wang, Gu, & Jin, 2003).

Table 2
Effect of concentration of PVP/nano TiO_2 doped Ag on mechanical properties of coated cotton fabric.

Treatment of substrate	Concentration of PVP (%)											
	0				1				3			
	Roughness (μm)	Tear strength (kg f)	Tensile strength (kg f)	Elongation at break (%)	Roughness (μm)	Tear strength (kg f)	Tensile strength (kg f)	Elongation at break (%)	Roughness (μm)	Tear strength (kg f)	Tensile strength (kg f)	Elongation at break (%)
Cotton fabric (control)	13.58	3.4	74	9	13.60	3.3	73	10	13.60	3.1	72	12
2% TiO_2 (nanoparticles)	14.74	3.2	74	10	14.00	3.3	73	11	14.00	3	71	13
2% TiO_2 (nanowires)	15.24	3.2	74	10	14.65	3.3	73	11	14.20	3	71	13
2% TiO_2 (nanoparticles) doped Ag	15.00	3.1	73	11	14.60	3.2	72	12	14.3	3	71	11
2% TiO_2 (nanowires) doped Ag	15.60	3.1	73	11	15.00	3.2	72	12	14.79	3	70	14

Conditions used: wet pick up, 80%; PVP molecular weight, 40,000 Da; drying at 80 °C for 5 min; curing at 130 °C for 3 min.

Fig. 5C and D shows the spectral changes due to degradation of MB adsorbed on cotton fabric, MB/TiO_2 (nanowires)/cotton fabric, MB/TiO_2 (nanowires) doped Ag/cotton fabric, MB/TiO_2 (nanowires)/1% PVP treated cotton fabric and MB/TiO_2 (nanowires) doped Ag/1% PVP treated cotton fabric at time of exposure of 2 h and 12 h. it is observed (Fig. 5C and D) that the rate of degradation of the adsorbed MB dye increases by increasing the time of exposure and the treated samples follow the order:

MB/TiO_2 (nanowires) doped Ag/PVP treated cotton fabric > MB/TiO_2 (nanowires) doped Ag/cotton fabric > MB/TiO_2 (nanowires)/PVP treated cotton > MB/TiO_2 (nanowires)/cotton fabric > MB adsorbed on cotton fabric.

It is worthy to note that TiO_2 (nanowires) is more efficient in photodegradation than TiO_2 (nanoparticles). It is also observed that TiO_2 (nanowires) doped Ag is more efficient in photodegradation than TiO_2 (nanoparticles) doped Ag nanoparticles. This could be interpreted in terms of relatively large surface area of TiO_2 (nanowires) and hence the dye adsorption increases leading to higher photodegradation of dye.

3.5.2. *Photocatalytic degradation of MB dye coated cotton fabric*

Cotton fabric coated with nano TiO_2 (particles or wires) doped Ag was also evaluated through monitoring the fabric self-cleaning of MB dye stains. Self-cleaning takes place at the cotton fabric surface under direct sunlight for 2 h and 12 h as shown in Fig. 5A and B. Fig. 5A shows the self-cleaning and degradation of the dye on the blank and treated cotton fabric stained with MB dye (10 g/l) when subjected to direct sunlight for 2 h. An insignificant degradation of MB dye can be observed. On the other hand, prolonging the exposure time to 12 h (Fig. 5B) is accompanied by enhanced degradation and decolorization of the dye on the fabric surface, since under direct sunlight (UV light) more possible reactions occur between TiO_2 surface and MB dye. Fig. 5 illustrates that MB dye stain on sample 10 (PVP treated cotton fabric coated with TiO_2 nanowires doped Ag nanoparticles) is completely degraded after 12 h exposure to direct sunlight.

3.6. *Mechanical properties of coated cotton fabric*

Table 2 shows the effect of concentration of PVP on major chemical properties of the cotton fabrics coated with PVP at different concentrations before and after they were injected with nano TiO_2 (particles and wires) and their doping with silver. It is obvious that at zero concentration of PVP and under the different treatments employed, insignificant change in tear strength and tensile strength along with an increase in both roughness and elongation at break is observed. This could be associated with deposition of nano TiO_2 and TiO_2 doped Ag nanoparticles on the surface of treated fabrics. Increasing the PVP concentrations to 1% and 3% has practically no effect on roughness, tear strength and tensile strength. On the other hand, the elongation at break tends to be higher at higher PVP concentrations (i.e. 3%).

4. Conclusion

The TiO_2 nanowires were effectively prepared through hydrothermal method by strong alkaline medium using TiO_2 nanoparticles as precursor. Also TiO_2 nanowires doped Ag and TiO_2 nanoparticles doped Ag were successfully synthesized using photo-reducing Ag^+ ions to Ag metal. The XRD, SEM, and TEM confirmed the formation of nanomaterials. Cotton fabrics were coated with TiO_2 nanowires and TiO_2 nanowires doped Ag-PVP nanocomposites. Coated cotton fabrics show high efficiency in MB photodegradation, thus suggesting high photocatalytic self cleaning properties under normal laboratory environmental conditions and direct sunlight. Also treated cotton fabric modified by nanomaterials recognized good antimicrobial activity against Gram positive bacteria, Gram negative bacteria and fungi. Based on the above results, coated cotton fabrics could be promising for possible medical and industrial applications.

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