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Photocatalytic solution discoloration and self-cleaning by polyester fabric functionalized with ZnO nanorods

Munir Ashraf¹, Philippe Champagne^{2,3}, Anne Perwuelz^{2,4}, Christine Campagne^{2,4} and Anne Leriche^{2,3}

Abstract

Polyester fabric was functionalized with ZnO nanorods grown by hydrothermal method. The ZnO seeds were deposited on fabric which provided the sites for growth of nanorods. The functionalized fabric showed self-cleaning by degrading color stains and solution discoloration under the effect of ultraviolet (UV) light which was studied using two azo and one triphenylmethene dye. The stained fabric was exposed to UV light and K/S (K = absorption coefficient, S = scattering coefficient) values were measured by spectrophotometer. Most of the stains were degraded in first 300 min and they disappeared completely after 24 h. The solution discoloration was studied by using different concentrations of dyes and was characterized by measuring absorbance. The rubbing and washing durabilities of the functionalized fabric were also investigated.

Keywords

ZnO nanorods, photocatalytic self-cleaning, stain degradation, solution discoloration, functionalized textiles

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Introduction

During the recent years, the semiconductors have been used to functionalize different textiles to impart photocatalytic self-cleaning properties. These functionalized fabrics have the ability to oxidize the coloring substances in the form of solutions and stains [1,2]. Under the effect of UV light, the electrons present in valence band jump to the conduction band and the positive holes are produced. The electrons react with oxygen to produce $\bullet\text{O}_2^-$, on the other hand, the positive holes react with adsorbed water to produce free hydroxyl radicals [3]. These free radicals are highly oxidative with very high redox potential ($E^0 = +3.06\text{ V}$) and cause mineralization of several organic species [4].

Mostly, the nanoparticles of TiO_2 prepared by sol-gel [1,2,5] and hydrothermal methods [6] have been used to generate self-cleaning textiles [7,8]. Another semiconductor which appears to be an alternative to TiO_2 is zinc oxide (ZnO). It has also been reported that ZnO has better photocatalytic properties than TiO_2 [9] and it absorbs larger fraction of the solar spectrum [10]. Recently, a few attempts have also been made to functionalize textiles with ZnO to generate self-cleaning properties. For this, the nanoparticles of ZnO were deposited on cotton which degraded methylene blue solution [11]. ZnO in powder form has been extensively used for photocatalytic degradation of dyes present in effluent [9,12]. However, the usage of powdered ZnO has problem of recovery after degradation, because some of ZnO powder is lost while draining the solutions. This can be overcome by attaching ZnO to a substrate particularly textiles because they offer the highest surface area. These ZnO functionalized textiles can be used for effluent treatment as well as self-cleaning.

For this purpose, various kinds of nanostructures of ZnO like nanofilms [13], nano flower like structures [14–17], nano-dumbbell [18], nanobelts [19], nano-cages [20] and nanorods [21–23] can be grown to functionalize textile surfaces. Among all the above mentioned nanostructures, the nanorods have attracted lot of attention because of their facile synthesis by hydrothermal method. In this method, the substrate is first coated with ZnO seeds on which the nanorods are grown [24–26]. Recently, Athauda et al. have reported the growth of nanorods and nanowire on cotton and nylon [27,28].

The objectives of the present work is to study the self-cleaning and solution discoloration by the immobilized ZnO nanorods grown on polyester (PET) fabric and to check the possibility for its re-use. To carry out this study, C.I. reactive orange 13 (RO), C.I. reactive violet 5 (RV) and C.I. acid blue 9 (AB) have been used. The dyes RO and RV are azo while dye AB is triphenylmethylenes. These dyes are extensively used for dyeing of cotton and wool fabrics as well as coloration of food stuff. Also, they form the biggest part of textile effluent and can also stain the fabric during usage and handling. Therefore, they were used as representative of azo and triphenylmethylenes dyes.

Experimental procedure

Materials

American Chemical Society (ACS) reagent grade zinc acetate dihydrate, zinc nitrate hexahydrate, hexamethylenetetramine (HMT) and sodium hydroxide were bought from Sigma Aldrich. Methanol of 99.6% was bought from Carlo Erba, France. C.I. acid blue 9, C.I. reactive orange 13 and C.I. reactive violet 5 were supplied by Dystar.

Functionalization of PET fabric

The plasma treated plain woven PET fabric made up of microfilaments (9–10 μm , 1 denier) was functionalized with ZnO nanorods according to our recently published work [29] see supplementary information for details. The atmospheric air plasma device used in this study was the “Coating Star” Systems. Dielectric barrier discharge (DBD) was created in air at atmospheric pressure. The following machine parameters were used: speed of $2\text{ m}\cdot\text{min}^{-1}$, electrical power of 750 W and frequencies of 26 kHz. Each sample was treated twice on each side. This plasma treated fabric was functionalized with ZnO nanorods in two steps by using hydrothermal method. The first step consists of preparation and application of ZnO seeds on fabric. The ZnO seeds were prepared by adding 75 mM solution of sodium hydroxide slowly to 90 mM solution of zinc acetate dihydrate in methanol with continuous stirring by using magnetic stirrer at 100 r/min. The mixture was refluxed at 60°C and a transparent ZnO seed solution was obtained after 3 h. The fabric was immersed in it for 5 min, then padded at pick up of $70 \pm 5\%$ (for each padding cycle) and dried at 120°C for 2 min. This process was repeated five times to ensure uniform application of seeds on each filament. Finally, seeded fabric was cured at 170°C for 8 min.

The seeded PET fabric was held vertically in AHIBA TURBOCOLOUR type TU 1000 dyeing machine and 800 mL each of 100 mM solution of zinc nitrate hexahydrate and 100 mM solution of HMT were added. The mixture was agitated at 25% agitation at 90°C for 4 h. Then, the sample was washed five times in distilled water and dried at 120°C for 10 min.

Characterization

Nanorods: The morphologies of ZnO nanorods grown on PET fabric were characterized by HITACHI S-3500N scanning electron microscope (SEM). To get high resolution images, the samples were coated with ultrathin layer of gold. FEI Tecnai G2 20 transmission electron microscope (TEM) was used to check the size of nanorod. PANalytical's X'Pert PRO Materials Research Diffraction system operating at 45 kV and 40 mA was used to characterize crystal structures and their orientation. The wavelengths of tube Cu were $K\alpha_1 = 1.540593 \text{ \AA}$, $K\alpha_2 = 1.54442 \text{ \AA}$ and $K\alpha_3 = 1.54187 \text{ \AA}$.

The amount of zinc present on fabric in the form of ZnO nanorods was determined by using Atomic Absorption Spectroscopy (PERKIN ELMER 1100 B). A piece of functionalized textile (1 g) was conditioned at 65% relative humidity and 25°C for 5 h then it was stirred in 1 M hydrochloric acid by using magnetic stirrer at 100 r/min for 1 h. The diluted solution was injected into the instrument and absorption peak for zinc (Zn) was determined. An average amount of Zn%w/w was calculated from five different samples. The amount of ZnO was determined by using stoichiometric calculations.

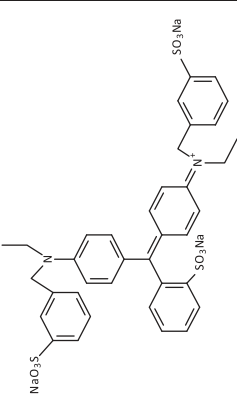
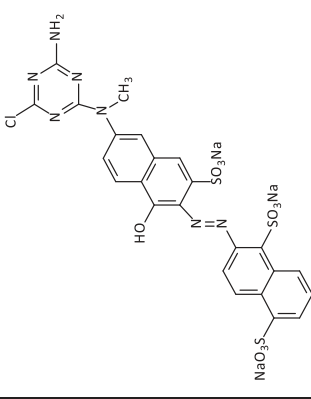
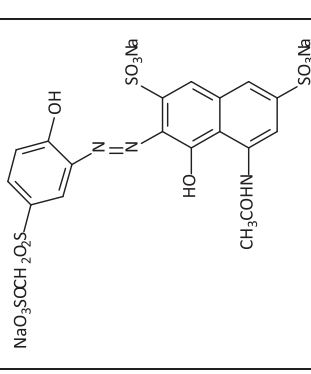
Self-cleaning and solution discoloration: The structures of dyes used for self-cleaning and solutions discoloration are presented in Table 1.

For the solution discoloration, a circular piece of functionalized fabric with 2.8 cm diameter was placed in each beaker containing 6 mL solution of dye and exposed to a Sylvania F20T12BLB backlight 20 W UV (UV = 315–400 nm with maximum emission at 368 nm) at a distance of 18 cm below the light source. One milliliter aliquot of the solution was removed periodically after each hour and was poured back in beaker after measuring the absorbance in visible region by using JASCO UV/VIS spectrophotometer V-530. The adsorption of dyes by the control fabric (with and without plasma treatment) as well as nanorods functionalized fabric was also studied in dark. It was found that either the adsorption was so small that it could not be detected by spectrophotometer with absorbance accuracy 0.001 or the dyes have no affinity for control and functionalized fabrics.

To study the stain degradation, the functionalized samples (3 cm × 2 cm) were dipped in solution of each dye for 3–5 s for staining (pickup $120 \pm 5\%$), then dried and conditioned for 15 min. These samples were exposed to UV by placing them below the light source at a distance of 18 cm. The K/S values as function of time were measured with the help of DATA COLOR spectrophotometer SPECTRA FLASH SF 600 PLUS using illuminant D65 excluding UV at band width of 10 nm. The aperture size was 2°. According to Kubelka-Munk equation, $K/S = (1 - R)^2 / 2R$. Where K = absorption coefficient, S = scattering coefficient and R = reflectance. The K/S represents the color strength on a surface and is directly proportional to the amount of dye present on it. The decrease in K/S values shows that the stains are disappearing.

Durability of functionalized samples: The washing and abrasion tests were carried out to determine the durability of samples. For washing durability, ISO 105 C10:2007 tests were carried out. In these tests, the samples were washed by using WASHTEC P at 40°C and 60°C for 30 min. These washing tests are equivalent to one washing cycle at 40°C and 60°C. The abrasion durability was determined by rubbing the samples against cotton abrasents at 7.5 oz and in continuously changing directions for 100 and 500 cycles using M235 Martindale Abrasion Tester (ASTMD-4970). The stain degradation was studied before and after these tests. The ability of functionalized fabric to degrade dye stains and decolorize the solutions more than once was determined by carrying out the successive discolorations with dye

Table 1. Structures of dyes used for stain degradation and solution discoloration.

<p>C.I. Acid blue 9(AB)</p> 	<p>C.I. Reactive orange 13(RO)</p> 	<p>C.I. Reactive violet 5(RV)</p> 
<p>$\lambda_{\text{max}} = 628\text{nm}$</p>	<p>$\lambda_{\text{max}} = 488\text{nm}$</p>	<p>$\lambda_{\text{max}} = 554\text{nm}$</p>

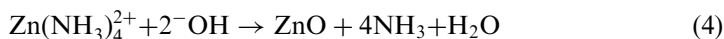
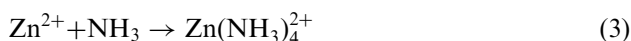
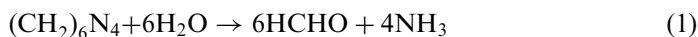
AB. For this, the sample was stained, dried and exposed to UV light. After degradation, it was re-stained on the same place. This process was repeated five times and a comparison was made using K/S values measured during UV irradiation for each stain degradation. Similarly, five successive discolorations of solution were carried out. The functionalized fabric was placed in dye AB solution and exposed to UV light as described for solution discoloration. After complete discoloration, the solution was drained and new dye solution was added in the beaker containing same piece of functionalized fabric. This process was repeated five times.

Results and discussions

Nanorods

The micrographs a, b, c and d in Figure 1 show the morphologies of untreated, seeded and nanorods functionalized PET fabric, respectively. The nanorods grow as an array of forest on seeded fabric which is highly oriented and perpendicular to fiber surface. The plasma treatment was carried out to make the fabric hydrophilic by generation of polar groups. These polar groups attach the seeds which are responsible for uniform growth of nanorods [19]. Figure 1(e) shows TEM micrograph of single nanorod. The nanorod is about $1\ \mu\text{m}$ long and $50\ \text{nm}$ thick at the top.

Under the hydrothermal conditions, HMT decomposes to produce ammonia which reacts with water and Zn^{++} according to following reactions [30].



The ZnO precipitates on seeds which provide the site for growth of nanorods. There are some nanorods which grew in solution and deposited on the fabric in the form of aggregates and remained there due to inadequate washing of treated fabric (Figure 1b). The functionalized fabric contains around $5.60 \pm 0.06\ \text{wt}\%$ Zn which corresponds to $7\ \text{wt}\%$ ZnO present in the form of nanorods.

As PET fibers consist of both amorphous and crystalline regions, the intense diffraction peaks at $2\theta = 17.9^\circ$, 23.0° and 26.3° are due to the (010), (-110) and (100) reflection planes of PET, respectively. Similar spectra is obtained on seeded fabric which indicates that deposited seeds are either non crystalline or their amount is too low but the typical diffraction peaks at $2\theta = 32^\circ$ (100), 34.6° (002), 36.4° (101), 48° (102), 57° (110), 63° (103) and 68.5° (112) which correspond to Figure 2 suggest that the nanorods are assigned to hexagonal zincite as pure ZnO (JCPDS Card no.

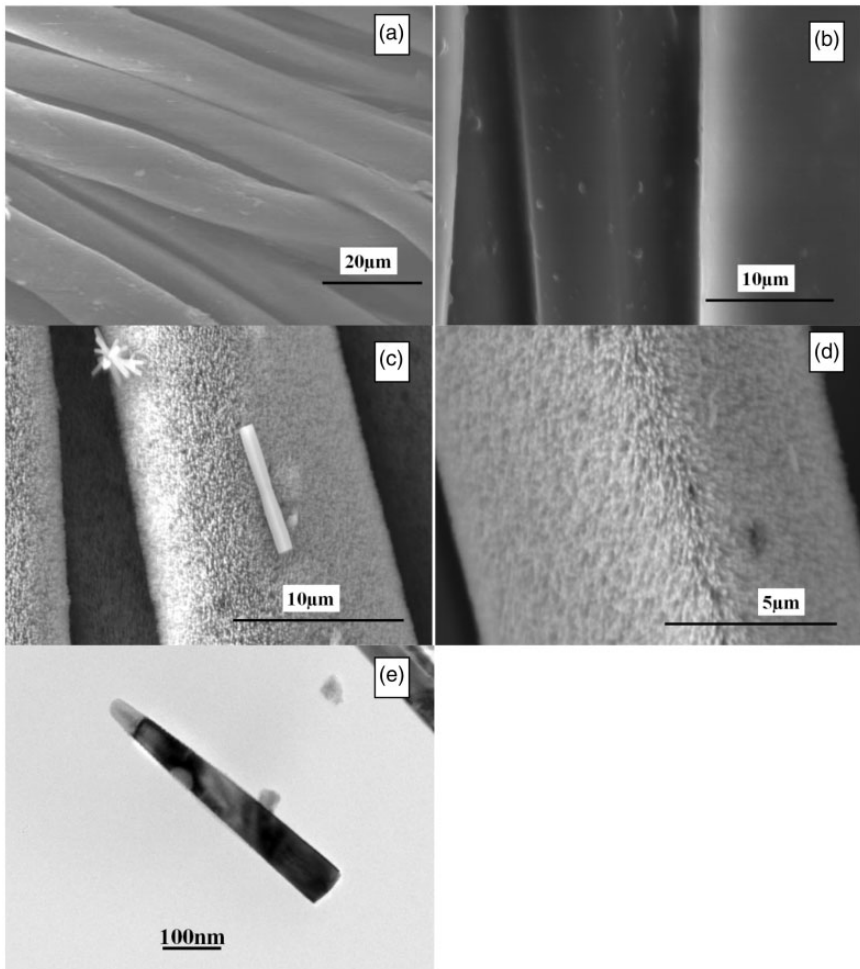


Figure 1. Scanning electron microscope (SEM) micrographs of (a) untreated polyester (PET) fabric, (b) fabric treated with ZnO seeds, (c) nanorods grown on seeded PET fabric, (d) high magnification micrograph of nanorods functionalized fabric and (e) TEM micrograph of nanorod scraped from fabric.

36-1451). The diffraction peaks at $2\theta = 38.5^\circ$, 45° , 65° and 78° for all three samples (untreated, seeded and nanorods functionalized fabrics) are attributed to the (111), (200), (220) and (311) planes of the face-centered cubic Al (JCPDS Card no.04-0787), respectively. These peaks are caused by the tested Al plate.

Solution discoloration

Figure 3 represents the evolution of solution absorbance as a function of time during discoloration by functionalized fabric under the effect of UV. As absorption

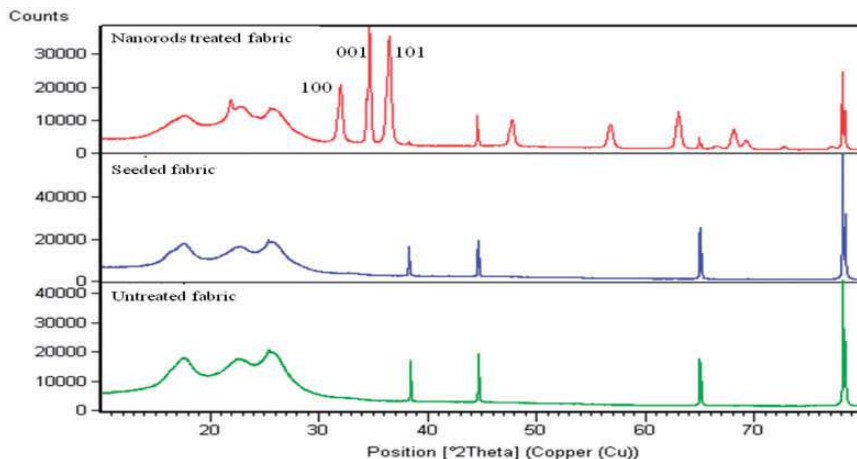


Figure 2. X-ray diffraction (XRD) analysis at 2θ on untreated, seeded and nanorods functionalized samples.

of the solution is directly proportional to concentration of dye in solution, the decrease in absorption shows the decrease in dye concentration. After 4 h of UV irradiation, most of the dyes are decolorized. The absorbance of dyes solutions containing untreated PET fabric does not change with the passage of time which shows that they have good UV fastness and the discoloration takes place only due to photocatalytic effect of nanorods.

The discoloration of solution is quick at the beginning but it slows down with the passage of time. At the beginning, only dye molecules adsorb on the active sites and the degradation takes place but once the reaction proceeds, the degraded products compete for adsorption with the dye molecules. This slows down the adsorption of the molecules and their subsequent degradation.

With the increase in initial concentration of dyes, the discoloration slows down. It is possibly because of two reasons. Due to increase in concentration, the more and more molecules adsorb on active sites which causes their blockage [20]. The second important reason is shielding effect of dyes. At low concentrations, the UV light can easily reach to zinc oxide to activate it but with the increase in initial concentration, the absorbance of dyes is also increased which acts as a shield against UV and prevents it from reaching to ZnO. Therefore, the rate of degradation decreases.

Figure 4 shows the absorbance evolution of five successive discoloration of dye AB solution as function of time. There is no change in photocatalytic effect of functionalized fabric during successive discoloration. Even after five discolorations, the sample does not lose its activity. This shows that it can be re-used for several times.

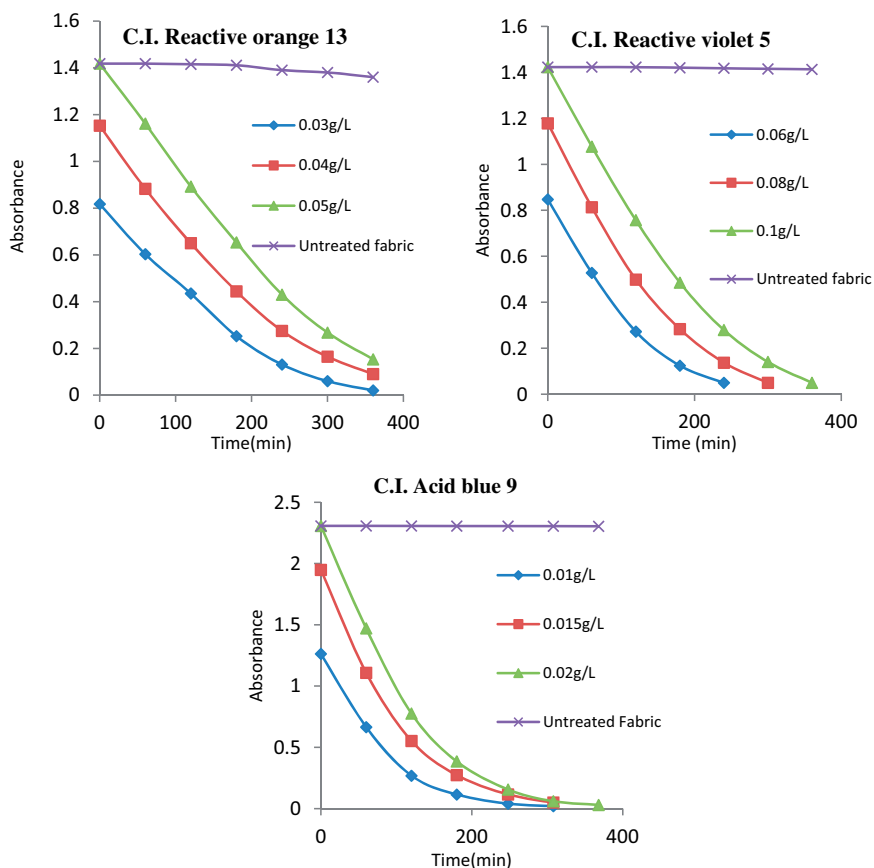


Figure 3. Evolution of absorbance of C.I. acid blue 9, C.I. reactive orange 13 and C.I. reactive violet 5 solutions in contact with functionalized and untreated fabrics as function of time during UV irradiation.

Self-cleaning

Figure 5 shows the stains of all three dyes on functionalized fabric at the beginning, after 300 min and 24 h of UV irradiation. Most of the stains disappear within 300 min and the samples become approximately white.

Figure 6 shows the K/S values of stained samples measured at different times. At the beginning, the stain degradation is very fast, but it slows down afterward. For instance, the color strength of dye AB stains decrease by 50% during initial 20 min of exposure in all three concentrations which means that half of dye stains are degraded, while the rest of 35% disappear in the following 4 h and the remaining 15% take 20 h for degradation. Approximately similar behavior is observed for the other two stains. The reason for decrease in stain degradation rate is entirely

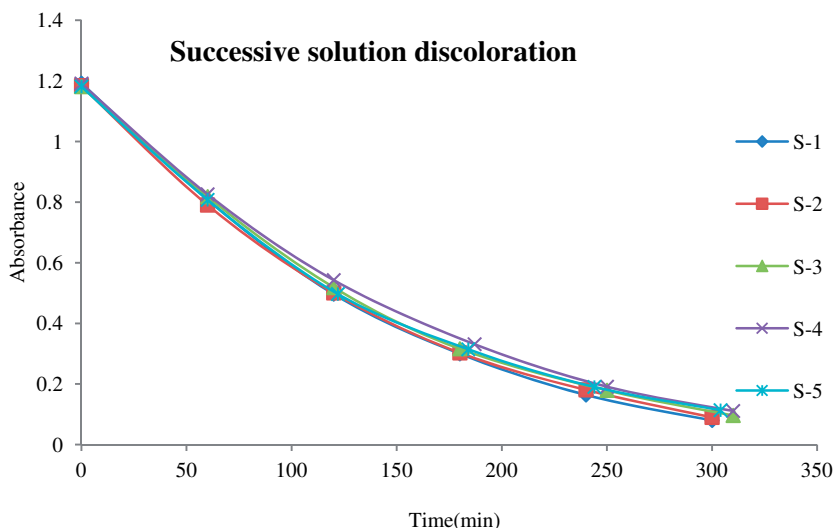


Figure 4. Five successive solution discolorations by the functionalized fabric (S-1 = first discoloration, S-2 = second discoloration and so on).

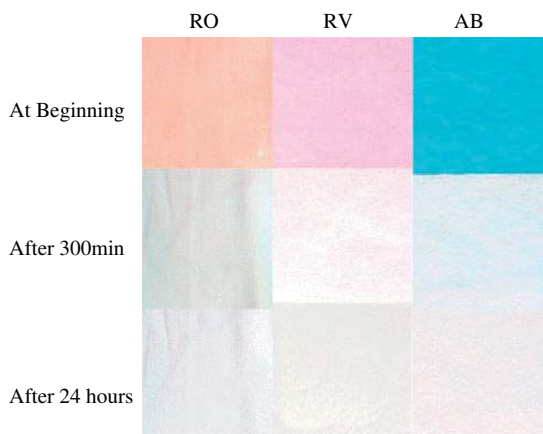


Figure 5. Stains of C.I. reactive orange 13, C.I. reactive violet 5 and C.I. acid blue 9 before, after 300 min and 24 h of exposure to UV light.

different than solution discoloration. As the dye stain is deposited on nanorods, the part of it which is on top of nanorods degrades quickly because it is completely exposed to UV whereas the dye deposited on the sides of nanorods takes more time. With the increase in initial concentration of dye stains, their degradation slows down. This is due to the same reason described for solution discoloration (shielding effect).

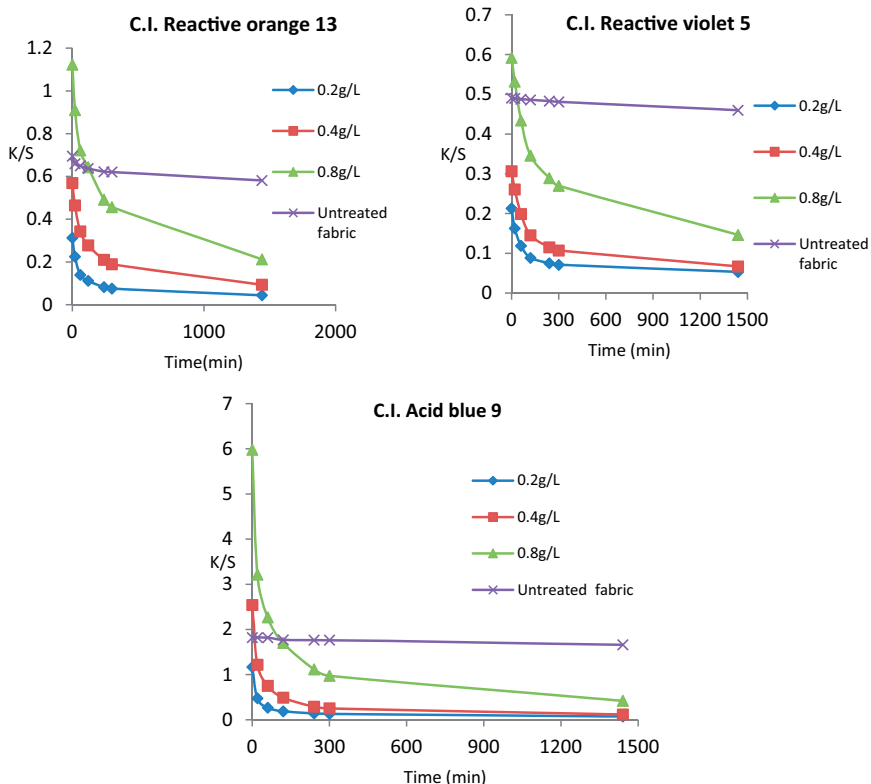


Figure 6. Evolution of K/S values as function of time during UV irradiation of samples stained with C.I. acid blue 9, C.I. reactive orange 13 and C.I. reactive violet 5.

To check the light sensitivity of dyes, the blank experiments were also carried out. For this, untreated PET fabric was stained with each dye solution and exposed to UV light under the same conditions. It was found that there was no significant decrease in K/S values even after 24 h exposure to UV (Figure 6). Therefore, all three dyes have good light durability. Although the concentrations used for blank experiments were highest (0.8 g/L), the depths of stains were lower than the ones on nanorods functionalized samples. This is due to low absorbency of PET even after plasma treatment which becomes superhydrophilic on functionalization with nanorods.

The functionalized fabric is capable of degrading dye stains more than once. Figure 7 shows the results of five successive stain degradations without intermediate washing. Apparently, the ability to degrade stains decreases with successive degradations. Due to UV activation during first degradation, the hydrophilicity of ZnO is increased [21] which leads to absorption of more dye and the depth of stain is higher than the previous one. This prevents the UV light from reaching to ZnO (shielding effect). Therefore, the degradation of S-2 is relatively slower than S-1.

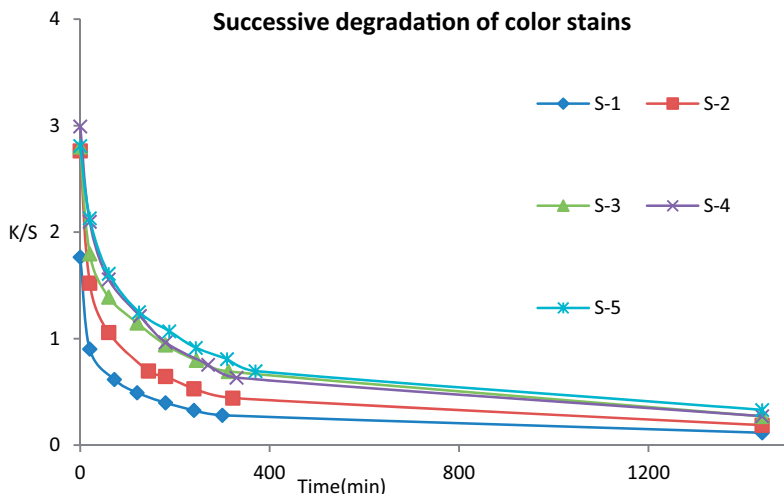


Figure 7. Successive stain degradations by functionalized fabric (S-1 = first stain degradation, S-2 = second degradation and so on).

In the three successive degradations, the depth of stains are the same however, their degradations take more time. This is due to the presence of the degraded products of previous stains on the nanorods. These products mask the ZnO rods and reduce its photocatalytic activity.

If we compare successive solution discolorations and stain degradations, the functionalized fabric retains its photocatalytic effect even after five solution discolorations but its stain degradability decreases successively. In the solution discoloration, once the solution is decolorized, it is drained and new dye solution is added. Therefore, all the degraded products are removed and they do not interfere in next discoloration process. However, in the stain degradation, the stain is in dry state. Once it is decolorized, the fabric is stained once again by dipping in dye solution without washing the degraded products of previous stain. These products continue to accumulate on fabric after every stain causing a decrease in degradation rate.

Durability of treated samples

The functionalized fabric has excellent washing durability. It withstands washing tests conducted at 40°C and 60°C. The stain degradation before and after these tests does not show any loss of photocatalytic activity which means that the nanorods treated sample has very good water durability (Figure 8a). Contrary to this, the stain degradations before and after Martindale rubbing tests at 100 and 500 cycles show that there is small decrease in the ability of fabric to degrade color stains. After 100 cycles, the loss in stain degradability is about 6% which increases to 13% after 500 cycles (Figure 8b). Due to rubbing, the nanorods are peeled off from

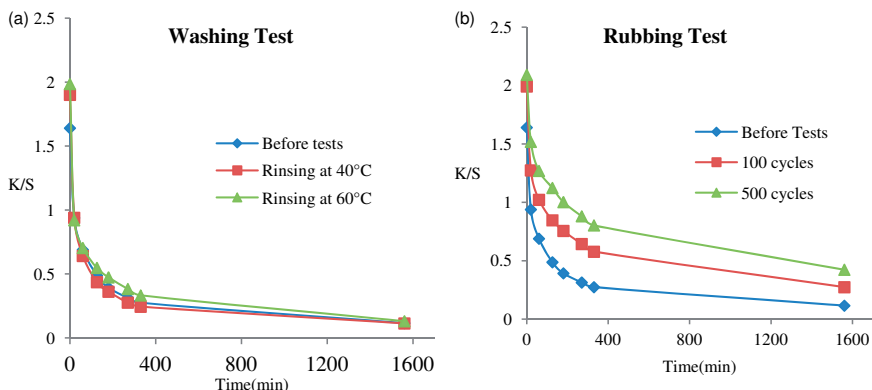


Figure 8. (a) Stain degradation carried out on samples before and after washing tests conducted at 40°C and 60°C for 30 min. (b) Stain degradation carried out on samples before and after Martindale rubbing test at 100 cycles and 500 cycles.

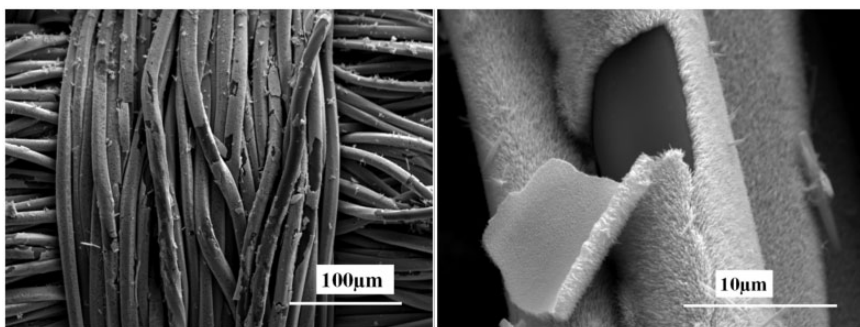


Figure 9. Scanning electron microscope (SEM) micrographs of nanorods functionalized fabric showing the removal of nanorods after 100 cycles on Martindale.

fabric surface as shown in Figure 9 which causes the reduction in stain degradability.

Conclusion

By using hydrothermal method, the ZnO nanorods have been grown on PET fabric, which are single crystalline wurtzite. The fabric contains around 7%w/w ZnO present in the form of nanorods. The functionalized fabric degrades the stains and decolorizes the solution due to photocatalytic effect of ZnO. The fabric sustains the repetitive usage for solution discoloration but its stain degradability decreases after each degradation. The functionalized fabric has excellent washing fastness but fairly good rubbing durability.

The kinetics of self-cleaning and solution discoloration by nanorods functionalized fabric will be studied in the future.

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