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Functional Modification with TiO_2 Nanoparticles and Simultaneously Dyeing of Wool Fibres in a One-pot Hydrothermal Process

Hui Zhang,[1*] Hongyan Yan,[1] and Ningtao Mao[1,2]
[1]School of Textile & Materials, Xi′an Polytechnic University, Xi′an, Shaanxi Province 710048, China
[2]School of Design, University of Leeds, Leeds, LS2 9JT, United Kingdom

ABSTRACT: Wool fibres are treated with titanate tetrabutyl in the presence of C. I. Reactive Blue 69 dye in one-pot process under hydrothermal conditions. The structural changes of wool fibres before and after treatments as well as the remaining particles are characterized by small-spot Micro X-ray fluorescence (μ-XRF), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) techniques. The properties of percentage of exhaustion, K/S value, colour fastness to light, tension, photocatalytic activity, and diffuse reflectance spectrum (DRS) are also investigated. The experimental results indicate that after treatment with titanate tetrabutyl and C. I. Reactive Blue 69, wool fibres are evenly immobilized with a thin layer of anatase phase TiO_2 nanoparticles with an average grain size of less than 10 nm. The TiO_2 nanocrystals are synthesized and simultaneously grafted onto wool fibres via the C-Ti^{4+}, S-Ti^{4+}(Ti^{2+}), and N-Ti^{4+} bonds. The thermal stability of wool fibres changes a little. The capability of wool fibres to protect against ultraviolet radiation is improved. The tensile properties decrease to some degree. The photocatalytic activity to decolourize methylene blue dye is endowed. A high degree of percentage of exhaustion and K/S value are obtained by adding a certain amount of acetic acid in the precursor solution, which can well be matched with the custom dip dyeing technique.

KEYWORDS: wool fibres; TiO_2 nanoparticles; modification; dyeing; one-pot process

1. INTRODUCTION

Titanium dioxide (TiO_2) has attracted increasing attention because of its unique characteristics, such as inexpensive, non-toxicity, stable, and high catalytic efficiency.[1] When exposed to ultraviolet (UV) light, the photon energy generates an electron hole pair on the surface of TiO_2. The hole in the valence band can react with hydroxyl ions (OH^{-1}) adsorbed on the surface to produce hydroxyl radicals (·OH), and the electron in the conduction band can reduce oxygen to produce peroxide ions ($O_2^{\cdot -}$). Both hydroxyl radicals and peroxide ions are extremely reactive species, and they can decompose organic compounds upon contact with them.[2] It is found that the photocatalytic activities of TiO_2 are greatly dependent upon crystallinity, crystallite size, morphology, phase, and the porosity of the coating of TiO_2 particles.[3–5] and such unique photocatalytic properties of TiO_2 particles, especially nanocrystalline TiO_2 particles, enable TiO_2 nanoparticles to have been widely used to enhance the properties of fibre, yarns, and fabrics in the textile industry.[6]

Nanocrystalline TiO_2 can effectively reduce the rate of photoyellowing by inhibiting free radical generation in TiO_2-doped wool mixtures, which acts primarily as a UV absorber on wool in dry conditions and not as a photocatalyst.[7] Generally, the surfaces of both wool fibres and TiO_2 nanoparticles are modified by using various chemical or physical methods in order to enhance the binding strength between them. One of the frequently used methods is to use carboxylic acids as acylation and cross-link agents to modify the surfaces of wool fibres, and those carboxylic acids include succinic, citric and butane tetracarboxylic acids. In one example, wool fibres are pretreated with succinic anhydride under mild conditions and then treated with the anatase TiO_2 nanosol by a simple coating process.[8] During this process, additional carboxylic groups are introduced on wool fibre surface by acylation, which result in enhanced bonding between TiO_2 particles and the modified wool fibres[8] due to the compatibility between the anatase TiO_2 sols and wool fibres;[9] Wool fabrics are reported to be treated with citric acid as the cross-linking agent and bonded either with different concentrations of nano TiO_2 to improve its photostability[10] or with TiO_2/Ag nanocomposites to improve self-cleaning properties.[11] The surfaces of nanoparticles are frequently modified by using chemical or physical modification. For instance, in order to obtain coated nano-TiO_2 particles having greater surface activity and higher light absorption capacity, PET/wool fabric is first treated with proteases and lipases enzymes, and then dipped into an ultrasound bath containing nano TiO_2 and butane tetracarboxylic acid, and finally cured. The adsorption and stabilization of nanoparticles coated on fabric surface are greatly improved.[12]

While TiO_2 nanoparticles can be obtained by using various techniques, hydrothermal method for the preparation of TiO_2 nanoparticle has some intrinsic advantages over other methods in producing TiO_2 nanoparticle of high degree of crystallinity, desired sizes and shapes with homogeneity in composition.[13] It favors a decrease in agglomeration among particles, narrow particle size distribution, phase homogeneity, and controlled particle morphology.[14] In a recent research, it is found that wool fabrics modified with TiO_2 nanoparticles on the surface then subsequently dyed with C. I. Reactive Blue 69 have both improved anti-felting property and better colour fastness to light.[15]

In this study, we will investigate if it is feasible to treat textiles with nanoscaled TiO_2 particles and simultaneously to dye the textile substrates with reactive dyes in one step method; the property changes of Merino wool fibres before and after being treated, as well as dyeing efficiencies (percentage of exhaustion and K/S value), in one-pot process under low temperature hydrothermal conditions by using titanate tetrabutyl together with C. I. Reactive Blue 69 dye are systematically examined and compared with wool fibres being solely dyed using the same dye in similar conditions by employing thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) techniques. The microstructures of the resultant Ti nanoparticles coated on wool fibres and remained in the dyeing bath after dyeing process are characterized by means of small-spot Micro X-ray fluorescence (μ-XRF), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) with high resolution TEM (HRTEM), and selected area electron diffraction (SAED) analyses; the chemical bonding between wool fibre and nanoparticle is also studied by using Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Some important physical properties of wool fibres including colour fastness to light, tensile properties, photocatalytic activity, and diffuse reflectance spectrum (DRS) are also analyzed.

2. EXPERIMENTAL SECTION

2.1. Materials

The merino wool fibres having an average diameter around 20μm, as well as nonionic surfactant W900, were provided by the local textile mill. The reagent-grade chemicals, including titanate tetrabutyl ($Ti(OC_4H_9)_4$), sodium carbonate (Na_2CO_3), ammonium sulfate ($(NH_4)_2SO_4$), sodium sulfate (Na_2SO_4), methylene blue (MB) dye, glacial acetic acid, acetone, and anhydrous ethanol, were used without further treatment. Deionized water was used throughout the experiment. The C. I. Reactive Blue 69 dye ($C_{23}H_{14}BrN_3Na_2O_9S_2$) and levelling agent Abegal B were obtained from Ciba Specialty Chemicals Inc.

2.2. Hydrothermal Treatment of Wool Fibres

Raw wool cleaning: About 3.0 g of wool fibres was scoured in 200 mL of mixed solution containing 2.0 g/L of sodium carbonate and 0.5% of nonionic surfactant W900 at 50°C for 15 min, then degreased with a 100 mL of acetone and anhydrous ethanol solution at 50°C for 10 min, respectively, and then washed thrice in deionized water at room temperature for 10 min and dried at 60°C for 8 h.

Scheme one (solely dyeing process): The wool fibres cleaned as above were dyed using C. I. Reactive Blue 69 with a dip dyeing process in the lab. The dyes were applied at 0.2%, 0.5%, 1.0%, 1.5%, and 2.0% owf at a liquor-to-goods ratio of 20:1. About 0.3 g of pretreated fibre samples was immersed in the dye bath at 50°C. After 5 min, 4% owf of ammonium sulfate, 10% owf of sodium sulfate, and 1.0% owf of Albegal B were added into the same bath with continuous stirring and kept for 5 min under the same condition. The pH of liquor was maintained at about 6.5 by adding a certain amount of acetic acid. The C. I. Reactive Blue 69 was then added into the dye bath with stirring and kept for 5 min. The liquor was subsequently heated to 95°C at a speed of 1.5°C/min and kept for 60 min. After this treatment, the dye bath was cooled down naturally. The dyed fibre samples were washed in an aqueous solution containing soap 2 g/L and sodium carbonate 2 g/L at 80°C at a liquor-to-goods ratio of 50:1 for 15 min. The fibre samples were finally washed with cold water and dried under ambient conditions.

Scheme two (hydrothermal treatment process): About 0.5 mL of titanate tetrabutyl was added dropwise into 10 mL of 95% ethanol solution under vigorous stirring at room temperature. The solution was then diluted with 70 mL of deionized water. A certain amount of C. I. Reactive Blue 69 (0.2%, 0.5%, 1.0%, 1.5%, and 2.0% owf), Abegal B (1% owf), and acetic acid (0.2%, 0.5%, 1.0%, 1.5%, and 2.0% owf) as well as without acetic acid were then added respectively. About 0.3 g of pretreated fibre samples were subsequently dipped in the above suspension for 15 min, and then transferred to a PTFE sealed can with a capacity of 100 ml, which was put into the stainless steel autoclave. The autoclave was placed in a furnace and run at a speed of 30 r/min. The temperature was raised to 110°C at a heating rate of 2.5°C/min. After 2 h, the autoclave was cooled down naturally and the as-prepared wool fibres were taken out and washed with the above soaping process as described in scheme one. The fibre samples were successively washed with the acetone, ethanol, and deionized water at room temperature for 10 min, respectively, and finally dried at 50°C. The remaining particles were separated from the solution by centrifugation, and repeatedly washed with acetone, anhydrous ethanol, and deionized water, respectively, and dried in an oven at 120°C for 10 h. The wool fibres were preconditioned before testing in a standard environment in accordance with to ISO 139:2005.

2.3. Measurement of Wool Fibre Properties and the Efficiencies of Its Dyeing Process

Dyeing efficiencies were characterized by using both percentage of exhaustion and K/S value. The colour yield of wool fibres was characterized by K/S value and calculated according to equation 1.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

Where K is the absorption coefficient, depending on the concentration of the colourant; S is the scattering coefficient, caused by the dyed substrate; and R is the reflectance of the coloured wool samples. The higher the K/S value, the greater the uptake of dye and a better colour yield. K/S values of dyed wool fibres at the maximum absorption wavelength (610 nm) within the visible spectrum were measured at a circular measuring area of 63.6 mm^2 under D65/10° illuminant by using a SF300 Plus colourimeter (Datacolour Inc.). The colourimeter was calibrated before testing against a standard white board.

The percentage of dyeing exhaustion E (%) was obtained through the measurement of the absorbance of dyeing liquor at the wavelength of 610 nm on a VIS-7220N spectrophotometer (Beijing Rayleigh Analytical Instrument Corp.).[16] The percentage of exhaustion E (%) was calculated by equation 2.

$$E(\%) = \left(1 - \frac{D_2 \times n_2}{D_1 \times n_1}\right) \times 100\% \qquad (2)$$

Where D_1 is the absorbance of raw dyeing liquor without adding the sample; D_2 is the absorbance of residual dyeing liquor after dyeing the sample; n_0 and n_1 are the dilution multiples of raw and residual dyeing liquors, respectively. The samples were measured three times and the average of the measurements was given.

The colour fastness to artificial light (Xenon arc fading lamp test) of dyed wool fibres was measured in line with ISO 105−B02:1994. The change of colour yield at the wavelength of 610 nm was also recorded every 12 h using the above colourimeter.

The tensile properties of wool fibres were measured on an YG001N electromechanical testing machine according to GB/T 13835.5−2009 at standard conditions. The gauge length was 10 mm and the constant extension rate was 10 mm/min. More than 300 wool fibres were measured to ensure a 95% confidence level.

The photocatalytic activity of wool fibres was carried out by the photodecolourization of MB at room temperature under UV lights. About 0.3 g of fibre sample was immersed in 30 mg/L of 35 mL MB aqueous solution. After 2 h in the dark to reach the adsorption and desorption equilibrium, the reaction solution containing the sample was irradiated by a Philips 30 W UV lamp with a main wavelength of 254 nm at a distance of 10 cm. The absorbance of MB at the maximum absorption wavelength (665 nm) was monitored using the VIS-7220N spectrophotometer every other hour. The decolourization rate, D, was determined by equation 3.

$$D = (1 - \frac{A_t}{A_0}) \times 100\% \qquad (3)$$

Where A_0 is the initial absorbance of MB solution which reaches the absorption equilibrium, and A_t is the absorbance of MB solution at time t.

The optical properties of wool fibres were determined using diffuse reflectance spectroscopy (DRS). The U-3010 spectrophotometer was equipped with an integrating sphere (ø150 mm) and $BaSO_4$ was used as the reference. The spectra were recorded at ambient temperature in 200-800 nm range at a scanning speed of 600 nm/min.

2.4. Characterization of the Microstructures of Wool Fibres and Resultant Ti Particles

The X-ray diffraction (XRD) pattern of the as-obtained particles was obtained by using Cu $K\alpha_1$ radiation

(λ=0.154056 nm), using a 7000S diffractometer at 40 kV and 40 mA with the angle of 2θ from 10° to 80° at a scan speed of 8 deg/min. The crystallite size of the remaining particles was determined by the Scherrer equation $D=K\lambda/\beta\cos\theta$, where D is the diameter of the particle; λ is the X-ray wavelength; β is the full width at half maximum (FWHM) of the diffraction line; θ is the diffraction angle; and K is a constant 0.89.

The microstructure of the as-obtained particles was characterized by transmission electron microscopy (TEM, JEOL3010, 200 keV).

The information on composition and 2D element distribution of the TiO_2-coated and dyed wool fibres was analyzed using the M4 TORNADO small-spot Micro X-ray Fluorescence (μ-XRF) analysis system.

The surface morphologies of wool fibres before and after treatments were examined using field emission scanning electron microscope (FESEM, JEOL JSM-6700).

The thermal properties of wool fibres, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were performed in a NETZSCH STA 449F3 instrument at a heating rate of 10 K/min with a nitrogen flush rate of 20 mL/min over the range of 40-550°C. The initial decomposition temperature, peak decomposition temperature, and reaction enthalpy were determined.

Functional groups of untreated and treated wool fibres were analyzed by using Fourier transform infrared spectroscopy (FT-IR) measurements on a FTIR 7600 spectrophotometer (Lambda Scientific Systems, Inc.). The spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellets.

The composition and chemical states of the fibre samples were studied using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (XPS) system. The fibre samples were analyzed with Al Kα monochromatic X-ray source (1486.68 eV, 12 kV, 6 mA) and the vacuum of the analysis chamber was less than 8×10^{-6} Pa. All binding energies were calibrated relative to the C_{1s} peak (284.6 eV) from hydrocarbons absorbed on the surface of the samples. The XPS peak areas and peak decomposition were determined. The spectrum was first smoothed by using the Savitsky-Golay algorithm (autoapply changes). The peak background was then processed by using the smart algorithm. The peak was fitted by using the Gauss-Lorentz mixed algorithm.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Resultant Titanate Oxidant Particles

The crystal structures of the resultant solid particles obtained in scheme two in hydrothermal process are characterized and identified by using XRD, TEM, HRTEM, and SAED analyses.

3.1.1. XRD Analysis

Both the crystalline structure and particle sizes of the resultant titanate oxidant particles from experiment of scheme two are characterized by using XRD pattern of the as-obtained particles as shown in Figure 1. The crystalline structure of the as-obtained solid particles is indexed by comparing the standard peaks of anatase phase TiO_2 with no other peaks of impurities detected. It is noted that a series of characteristic peaks of the solid particles at 25°(101), 38°(004), 48°(200), 54°(105), 56°(211), 63°(204), 68°(116), 70°(220), and 75°(215) are in agreement with the data list in JCPDS card no. 21-1272.[17] The crystallite size of TiO_2 particles obtained is determined by measuring the full width at half maximum (FWHM) of (101), (004), and (200) reflections based on Scherrer's equation. The average crystallite size is calculated to be 10.0 nm.

3.1.2. TEM, HRTEM, and SAED Analyses

The detailed structure of the as-obtained powder is further characterized by TEM, HRTEM and SAED, as shown in Figure 2. The typical TEM image of the TiO_2 particles implies the particles have the spherical features assembled by nanoparticles. Some nanoparticles are coated with a very thin transparent film. The size of TiO_2 particles, synthesized by taking $Ti(OC_4H_9)_4$ as the precursor in the presence of dye, is observed to be less than 10 nm (Figure 2a), which is agreement with the particle size measured in XRD analysis. It is also indicated in HRTEM image that the resolved lattice spacing is of 0.347 nm (Figure 2b), which is closely matched with the (101) crystal plane (0.35 nm). A series of diffraction rings shown in the SAED pattern are indexed as (101), (004), (200), (105), (211), and (204) crystal planes of anatase TiO_2 (Figure 2c),[18] which is corresponding to the index of crystal planes identified in XRD analysis.

3.2. Dyeing Efficiencies: Percentage of Exhaustion and K/S Values

The effects of dyeing concentration on the percentage of exhaustion and K/S value of wool fibres prepared by both scheme one and scheme two but without any addition of acetic acid are shown in Figure 3a. It is found that most of dyes (nearly 96%) has been absorbed/deposited on wool fibres in solely dyeing process (scheme one) while only a proportion of dyes (60%~96%) is absorbed by wool fibres in hydrothermal process (scheme two without acetic acid) when dyeing concentration is less 1.5%. It is apparent that the dyeing concentration in solely dyeing process has little influence on the percentage of exhaustion which is constantly larger than 96%. But in scheme two without adding acetic acid, the percentage of exhaustion decreases sharply with the increase of dyeing concentration up to 1.5%. It is also found that, while the corresponding K/S values in both experimental schemes increase with the increases of dyeing concentrations, the increase rate of colour yield with the increase of dyeing concentrations in scheme one (9 K/S value per 1% owf increase of dyeing concentration) is much more rapidly than that in scheme two without addition of acetic acid (4 K/S value per 1% owf increase of dyeing concentration). Based on the above conclusions, the dyeing concentration of 1.0% owf is used to dye wool fibres with the addition of different amounts of acetic acid in hydrothermal process. It is clear that the addition of acetic acid has great impacts on both percentage of exhaustion and K/S value, as illustrated in Figure 3b. Both percentage of exhaustion and K/S value increase significantly with the increase of the concentration of acetic acid up to 1.0%. The high dye affinity to wool fibres is thought to be ascribed to the protonated acetic acid, which can efficiently absorb the anionic dye by electrostatic attraction.[19]

3.3. Physical Properties of the Resultant Wool Fibres Coated with TiO_2 Nanoparticles

3.3.1. Colour Fastness to Artificial Light

When the dyed wool fibres are exposed to simulated solar light in light fastness tests, the effects of irradiation time on the K/S value of dyed wool fibres from both experimental schemes are obtained and shown in Figure 4. It is evident that the K/S values of the wool fibres obtained from both of the experimental schemes decrease gradually with the increase of irradiation time. However, it is noticed that the K/S value of the TiO_2-coated and dyed wool fibres obtained from scheme two is much greater than the fibres solely being dyed in scheme one. It is anticipated that the macromolecular dyes are penetrated through the scales and absorbed by the matrix of wool fibres from both schemes. For the dyed wool fibres obtained from scheme one, because there is no a film of TiO_2 nanoparticles on wool fibres, the simulated solar irradiation (especially UV rays) can directly irradiate on the dyed wool fibres inducing the photodegradation of organic dyes. But for the TiO_2-coated and dyed wool fibres obtained from scheme two, the coating of TiO_2 deposited onto wool fibres can efficiently block most of the UV irradiation.[20] In addition, C. I. Reactive Blue 69 dye absorbed by the matrix of wool cannot contact closely with the TiO_2 nanoparticles, thus the photocatalytic degradation of the dye can be avoided to a great extent. Therefore, the decrease rate of K/S value with the increase of irradiation time in scheme one is much faster than that in scheme two. After the wool fibres being irradiated for 84 h, their K/S values drop about 25.6% for scheme one and 19.8% for scheme two, respectively. That is, the one-pot hydrothermal treatment of wool fibres (scheme two) can significantly improve the colour fastness to artificial light in comparison with solely dyeing process of wool fibres.

3.3.2. Tensile Properties

The tensile properties of wool fibres before and after the two dyeing processes are shown in Table 1. In comparison with untreated wool fibres, the average breaking stresses of treated wool fibres are reduced about 10.6% for scheme one and 8.6% for scheme two, and their corresponding elongations at break decrease about 5.1% and 7.8%, respectively. In those two dyeing processes, the dye liquor of high temperature causes damages to wool fibres immersed in it for a long time. Although the wool fibres degrade slightly greater under the hydrothermal processing conditions, the differences of tensile properties of the wool fibres resultant from those two processes are not significant.

3.3.3. Photocatalytic Activity

The change of the decolourization rate of the MB aqueous solution against the irradiation time is shown in Figure 5. It is obvious that the dyed wool fibres (scheme one) have no the capability to degrade the MB dye. A slight increase in the rate of decolourization of MB is attributed to the UV irradiation. But for the TiO_2-coated and dyed wool fibres (scheme two), the decolourization rate increases distinctly with the increase of irradiation time. After 5 h of UV irradiation, the decolourization rate reaches to 93%. The photocatalytic activity of the TiO_2-coated and dyed wool fibres is due to the TiO_2 coating. The MB dye in the solution can be adsorbed onto the surface of TiO_2 film, which is irradiated by a UV lamp. The irradiation energy leads to an excitation of electron from valence band into conduction band while the positive hole is left behind. These photo-generated electrons and holes migrate to the particle surface inducing the charge transfer to adsorbed MB dye molecules. Some of electrons and holes on their way to the particle surface get trapped at the surface or bulk trapping sites. The charges trapped at the TiO_2 surface react with electron acceptors or donors adsorbed at the particle surface.[21] Thus, the reactions between free conduction electrons, trapped electrons at the particle surface or valence band positive holes, H_2O and O_2 result in generation of extremely reactive species like $OH\cdot$ and $O_2\cdot^-$, which further decompose the MB dye.

3.3.4. Optical Properties

It is shown that the existence of TiO_2 particles coated on the surface of wool fibres has little influence of the optical properties of dyed wool fibres. The diffuse reflectance spectra of untreated wool fibres, wool fibres dyed with nano TiO_2 particles and without TiO_2 particles (scheme one and scheme two) are shown in Figure 6. When wool fibres are dyed solely with C. I. Reactive Blue 69, the diffuse reflectance spectrum is totally dominated by the photophysical absorption characteristic of C. I. Reactive Blue 69, which has a broad absorption band around 610 nm. The diffuse reflectance spectrum of the TiO_2-coated and dyed wool fibres is nearly overlapped with that of dyed wool fibres. Therefore, the optical property of TiO_2-coated and dyed wool fibres is mainly determined by the chemical structure of dye molecules rather than the TiO_2 particles.

3.3.5. μ-XRF Analysis of Elements Distribution

The composition and homogeneity analysis of wool fibres resultant from scheme two are performed on M4 Tornado standard instrument, as depicted in Figure 7. Individual woo fibres are clearly seen in the optical image (Figure 7a). The key elements including Ti, Fe, S, and Si are usually distributed homogeneously in the examined area except the concentration of Fe and Si in one particular location in the area (Figure 7b and 7c). A comparison of the spectra of all those elements is shown in Figure 7d. The proportions of each main element in the whole examined area are given in Table 2. It is noticed that only Fe differs in intensity from other elements. The elements of Fe and Si become more intense in comparison with Ti and S elements.

The reason need to be clarified in future. Therefore, all other selected elements have a lower relative mass concentration.

3.3.6. Changes of Surface Morphology of Wool Fibres Observed in FESEM Images

The FESEM images of the surface morphology of wool fibres before and after treatments are shown in Figure 8. The surfaces of both untreated wool fibres (Figure 8a) and wool fibres treated in scheme one (Figure 8b) are free of any solid particles. However, there are many small solid particles, whose sizes ranges from nanometers to micrometers, homogenously distributed on the surface of wool fibres (Figure 8c) after treatment with $Ti(OC_4H_9)_4$ and dye. These particles are constituted of nanoparticles with a diameter less than 100 nm and are closely adhered onto fibre surfaces (Figure 8d). Even when the TiO_2-coated and dyed wool fibres are successively washed for 20 times with acetone, anhydrous ethanol and deionized water at 60°C for 15 min, there are still some glue-like substances firmly adhered onto wool fibres (Figure 8e).

3.3.7. Thermal Properties

The thermal properties of wool fibres before and after treatments are examined by using TGA and DSC methods and are shown in Figure 9. It is seen from the TGA curves that the onset decomposition temperature increases slightly from 263.3°C to 268.3°C when wool fibres are solely dyed with C. I. Reactive Blue 69. The remaining mass decreases from 36.7% to 33.0% at a temperature of 550°C. After treatment with $Ti(OC_4H_9)_4$ and being dyed simultaneously, the onset decomposition temperature for the wool fibres obtained from scheme two decreases from 263.3°C to 253.4°C. The remaining mass is 34.0% (Figure 9a). It is clear from the DSC curves that the initial endothermic peak increases from 81.2°C in untreated wool fibres to 85.1°C in the solely dyed wool fibres, and the major endothermic peak at 277.4°C increases slightly to 277.7°C. The corresponding reaction enthalpy in this case increases from 741.5 J/g to 1002.0 J/g. In contrast, the initial endothermic peak for the wool fibres obtained from scheme two (81.6°C) has little change in comparison with that of the untreated wool (81.2°C), and its major endothermal peak decreases from 277.4°C to 274.4°C. The corresponding reaction enthalpy decreases from 741.5°C to 638.5 J/g. Apparently, such change in thermal properties of TiO_2-coated and dyed wool fibres is not due to the dye molecules bonded into the wool fibres, we thus believe that it is likely to be due to the TiO_2 coating (Figure 9b).

3.4. Chemical Bonding between Wool Fibres Coated with the Resultant TiO_2 Nanoparticles

3.4.1. FT-IR Analysis

Functional groups of wool fibres before and after treatments as well as the TiO_2 powder are investigated by using FT-IR spectra analysis as shown in Figure 10. When wool fibres are solely dyed with C. I. Reactive Blue 69, the bands at 2961 cm^{-1} (CH_3 asymmetric stretching), 2932 cm^{-1} (CH_2 asymmetric stretching), 2877 cm^{-1} (CH_3 symmetric stretching), and 1708 cm^{-1} (carbonyl group) cm^{-1} in untreated wool fibres are slightly shifted to 2958 cm^{-1}, 2925 cm^{-1}, 2874 cm^{-1}, and 1714 cm^{-1}, respectively in solely dyed wool fibres. Also, the amide I band at 1636 cm^{-1} (C=O stretching) is shifted to 1629 cm^{-1}; the bands at 933 cm^{-1} (C-O stretching) and 568 cm^{-1} (N-H bending) are shifted to 937 cm^{-1} and 580 cm^{-1}, respectively. So, it can be deduced that C. I. Reactive Blue 69 dyes react with the wool fibres. In the wool fibres after treatment with $Ti(OC_4H_9)_4$ and dyed with C. I. Reactive Blue 69 in hydrothermal process in scheme two, the N-H band decreases from 3425 cm^{-1} to 3407 cm^{-1}, and this band shift is attributed to the surface absorbed-water induced by TiO_2 nanoparticles; The bands at both 2932 cm^{-1} and 1708 cm^{-1} are shifted to 2928 cm^{-1} and 1711 cm^{-1}, respectively. The amide I and III bands are reduced from 1636 cm^{-1} and 1234 cm^{-1} (C-N stretching) to 1638 cm^{-1} and 1229 cm^{-1}, respectively; also, the band at 933 cm^{-1} decreases to 928 cm^{-1}. In addition, influenced by the broad Ti-O band of TiO_2 ranging from 486 cm^{-1} to 547 cm^{-1}, the N-H band at 568 cm^{-1} increases to 577 cm^{-1}.[22] It is thus concluded that TiO_2 nanoparticles are immobilized onto wool fibres by chemical grafting.

3.4.2. XPS Analysis

To further study the binding mechanism between TiO_2 nanoparticles and wool fibres, XPS technique is used for the characterization of wool fibre surfaces. The survey spectra and core level single spectra of the bonding partners (C_{1s}, O_{1s}, S_{2p}, N_{1s}, and Ti_{2p}) of the untreated, TiO_2-coated and dyed wool fibres are shown in Figure 11 and the quantitative XPS data are given in Table 3.

The element of titanium is found for the TiO_2-coated and dyed wool fibres. Compared with the C_{1s} XPS spectra of the untreated fibres, the subpeaks of C-C/C-H, C-N/C-O, and C=O/C(O)N for scheme two are shifted from 284.54 eV, 286.23 eV, and 287.61 eV to 284.45 eV, 285.90 eV, and 288.15 eV, respectively.[23,24] Meanwhile, two new subpeaks at the binding energies of 279.87 eV ($C\text{-}Ti^{3+}$) and 282.86 eV ($C\text{-}Ti^{4+}$) are identified.[25] These are ascribed to C atoms of wool fibres bound to Ti of TiO_2. Also, after the hydrothermal treatment with $Ti(OC_4H_9)_4$, the O_{1s} peak of the untreated fibres is deconvoluted into two sub-peaks; the subpeaks at 531.42 eV (O=C) and 532.39 eV (O-C) are shifted to 530.86 eV and 532.80 eV, respectively. In addition, two new subpeaks at both 529.0 eV and 526.38 eV are formed. The subpeak at 529.0 eV is assigned to O atoms bound to Ti of TiO_2 ($O\text{-}Ti^{4+}$), and the subpeak at 526.38 eV is attributed to O atoms of wool fibres bound to Ti of TiO_2 ($O\text{-}Ti^{3+}$).[26]

With respect to the S_{2p} XPS spectra of the untreated fibres, the subpeaks at 163.42 eV (S-S) and 164.67 eV (S-H) are shifted to 163.01 eV and 165.79 eV, respectively. Moreover, a shoulder at lower binding energy of 157.88 eV is observed, and this has been assigned to a new formed by S atoms of wool fibres bound to Ti of TiO_2 ($S\text{-}Ti^{3+}$).[27] However, it has been reported that the peak of a binding energy between 163~164 eV is assigned to element sulphur or TiS,[28] and that TiS_2 nanoparticles is formed by sol-gel process.[29,30] therefore, there might be the new bindings of $S\text{-}Ti^{4+}$, $S\text{-}Ti^{3+}$, and $S\text{-}Ti^{2+}$ formed between wool fibres and TiO_2 nanoparticles in the hydrothermal process.

For the N_{1s} XPS spectra of wool fibres, the subpeaks at 398.62 eV and 400.08 eV are shifted to 397.96 eV and 400.14 eV respectively after treatment. At the same time, a new sub-peak at 394.74 eV is formed, which may be attributed to the nitrogen replacing the oxygen in the crystal lattice of TiO_2,[31] and the N atoms of wool fibres might thus be bound to Ti of TiO_2 ($N\text{-}Ti^{4+}/N\text{-}Ti^{3+}$).

The Ti_{2p} XPS spectrum consists of four distinct subpeaks, which is consistent with the XPS spectra of C_{1s}, O_{1s}, S_{2p}, and N_{1s}. The sub-peaks at 464.86 eV and 459.03 eV represent $C\text{-}Ti^{4+}/O\text{-}Ti^{4+}/S\text{-}Ti^{4+}/N\text{-}Ti^{4+}{}_{2p1/2}$ and $C\text{-}Ti^{4+}/O\text{-}Ti^{4+}/S\text{-}Ti^{4+}/N\text{-}Ti^{4+}{}_{2p3/2}$, respectively. The subpeaks at 462.79 eV and 456.81 eV are correspond to $C\text{-}Ti^{3+}/O\text{-}Ti^{3+}/S\text{-}Ti^{3+}/N\text{-}Ti^{3+}{}_{2p1/2}$ and $C\text{-}Ti^{3+}/O\text{-}Ti^{3+}/S\text{-}Ti^{3+}/N\text{-}Ti^{3+}{}_{2p3/2}$, respectively. Thus, the results confirm that the new bindings of $C\text{-}Ti^{4+}(Ti^{3+})$, $O\text{-}Ti^{3+}$, $S\text{-}Ti^{4+}(Ti^{3+}, Ti^{2+})$, and $N\text{-}Ti^{4+}(Ti^{3+})$ are formed in the lattice of the TiO_2 crystal during the hydrothermal processing, implying TiO_2 nanoparticles are grafted onto fibre surfaces.

While it is known that titanium trivalent (Ti^{3+}) on the surface of TiO_2 particles is very reactive[32] and plays an essential role in photocatalytic process over TiO_2 photocatalyst,[33] and that it can be generated by using UV irradiation and thermal annealing on the surface of anatase TiO_2 particles, we thus propose that the stable bonding between TiO_2 particles and wool fibres are $C\text{-}Ti^{4+}$, $S\text{-}Ti^{4+}(Ti^{2+})$, and $N\text{-}Ti^{4+}$. As a summary of the discussion above, the possible technical route and reaction mechanism between TiO_2 nanoparticles and wool fibres are proposed and shown in Figure 12 and 13, respectively.

4. CONCLUSIONS

The TiO_2-coated and simultaneously dyed wool fibres are fabricated using titanate tetrabutyl and C. I. Reactive Blue 69 in one-step process under hydrothermal conditions, this indicates that it is feasible for functional treatment of textile fibres or fabrics with nanoparticle treatment with fibres or fabrics dyeing simultaneously, and this technology is worth to be exploited further in the textile industrial production of functional fibres or fabrics. It is found that a thin film of anatase TiO_2 with particle size of less than 10 nm is uniformly distributed and chemically bonded on the surfaces of woo fibres after treated with titanate tetrabutyl and dyed with C. I. Reactive Blue 69. The TiO_2 nanoparticles are bond to the fibre surfaces via the functional groups of C-Ti^{4+}, S-Ti^{4+}(Ti^{2+}), and N-Ti^{4+}. For the resultant wool fibres coated with TiO_2 nanoparticles and dyed with C. I. Reactive Blue 69, its performance in blocking UV rays is prominently enhanced. The photocatalytic activity of the TiO_2-coated and dyed wool fibres for the degradation of MB dye under UV lights is obtained. The breaking stress and elongation at break of the resultant wool fibres decrease slightly; its thermal properties of the fibres appear some changes due to the TiO_2 coating; its major endothermal peak decreases from 277.4°C to 274.4°C. The corresponding reaction enthalpy decreases from 741.5 J/g to 638.5 J/g. The use of acetic acid during the hydrothermal process can effectively improve the percentage of exhaustion and colour yield (K/S value) of the as-prepared wool fibres.

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Figure captions:

Figure 1 XRD pattern of the as-obtained solid particles resultant from scheme two
Figure 2 TEM (a) and HRTEM (b) images and (c) SAED pattern of the as-obtained solid particles resultant from scheme two
Figure 3 Effects of dyeing concentration (a) and concentration of acetic acid (b) on the percentage of exhaustion and K/S value of dyed wool fibres
Figure 4 Effects of irradiation time on the K/S values of dyed wool fibres exposed to artificial light
Figure 5 Effects of irradiation time on the decolourization rates of MB solution
Figure 6 Diffuse reflectance spectra of wool fibres
Figure 7 The composition and homogeneity analysis of the TiO_2-coated and dyed wool fibres
Figure 8 FESEM images of wool fibres: (a) 1000× untreated; (b) 1000× for scheme one; (c) 1000× and (d) 10000× for scheme two; (e) 1000× after being washed for 20 times for scheme two
Figure 9 TGA (a) and DSC (b) curves of wool fibres before and after treatments
Figure 10 FT-IR spectra of wool fibres before and after treatments
Figure 11 XPS spectra of wool fibres before and after treatments with $Ti(OC_4H_9)_4$ and dye
(a) Survey spectra; (b) Ti_{2p} spectrum; (c) before and (d) after treatment of C_{1s} spectra; (e) before and (f) after treatment of O_{1s} spectra; (g) before and (h) after treatment of S_{2p} spectra; (i) before and (j) after treatment of N_{1s} spectra
Figure 12 The technical route for the treatment of wool fibres
Figure 13 The suggested reaction mechanism between TiO_2 nanoparticles and wool fibres

Table titles:

Table 1 The results of tensile properties of wool fibres
Table 2 The proposed components of wool fibres obtained from scheme two
Table 3 XPS data of wool fibres before and after treatments with $Ti(OC_4H_9)_4$ and dye