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Self-cleaning and superhydrophilic wool by TiO_2/SiO_2 nanocomposite

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ABSTRACT

Wool fabrics were functionalised using TiO_2 and TiO_2/SiO_2 nanocomposites through a low-temperature sol–gel method. Titanium terta isopropoxide (TTIP) and tetra ethylorthosilicate (TEOS) were employed as precursors of TiO_2 and SiO_2, respectively. Nanocomposite sols were devised based on three molar ratio percentages of TiO_2/SiO_2 70:30, 50:50, and 30:70 to investigate the role of each component. The self-cleaning and hydrophilicity of wool fabrics were analysed based on the removal of coffee stain under UV and water droplet contact angle measurements, respectively. It was observed that applying TiO_2/SiO_2 50:50 and 30:70 sols to wool rendered the fabric superhydrophilic. Fabrics functionalised with TiO_2/SiO_2 30:70 showed the highest efficiency in stain removal, followed by samples functionalised with TiO_2/SiO_2 50:50.

1. Introduction

Among various types of natural fibres, wool has been the subject of numerous scientific research in order to modify its intrinsic features using nanotechnology [1]. Dwindling the photo-degradation and shrinkage of wool, and imparting new features such as self-cleaning and antimicrobial activity to wool have attracted a great deal of attention [1,2]. Wool is well known for its outstanding resilience, breathability and softness, which have made it a superior fibre [3]. Wool has a composite structure consisting of fibrils with α-keratin structure embedded into an intermacrofibrillar matrix [4,5]. The outer layer of wool with a thickness of 2.5 nm is called epicuticle and is covered with a fatty acid layer [4]. This covalently bonded layer protects the interior parts of the fibre against alkali and oxidising media as well as proteolytic enzymes [3,4]. The scales which cover the outmost layer of wool play the main role in quality of some features such as friction, hand feel, shrinkage, dyeability and water uptake of fibre [6]. The hydrophobicity of textiles can result in unfavourable static charge on garments and outfits, causing discomfort to consumers [4]. Also, this feature can be an obstacle for an effective wet textile chemical processing such as dyeing and anti-shrinkage finishing [7].

Titanium dioxide, thanks to its photocatalytic properties, has been used in functionalising textiles [8]. UV illumination plays the main role in triggering the photocatalytic activities of titanium dioxide. Titanium dioxide is excited under UV ray with energy equal to or greater than its band gap (3.2 eV anatase TiO_2) [9]. Subsequently, pairs of negative electrons and positive holes are generated in conduction and valence bands of titanium dioxide, respectively [10,11]. These active species in turn react with water and oxygen molecules producing hydroxyl radicals and super oxide anions. Contaminants adsorbed on the photocatalyst surface undertake some reactions with the generated active species forming water and carbon dioxide as the main by-products of this process [2]. Although the functionality of pure titanium dioxide on textiles has been proved, integrating silica as a metal oxide into the surface coating formulation has been put forth to augment the efficacy of titanium dioxide photocatalyst [12,13]. The presence of silica plays dual main roles of increasing the surface area in the vicinity of titanium dioxide and surface acidity of the photocatalyst [12,13].

Self-cleaning cotton was introduced through the growth of anatase nano titanium dioxide crystallite onto the fabric surface by Daoud and Xin [14]. Based on their approach, cotton and wool fabrics were treated with nano titanium dioxide colloids through a low temperature sol–gel method [10,15,16]. Stain removal capability of cotton and wool fabrics treated with titanium dioxide was assessed based on the colour fading of stains such as coffee and red-wine after UV illumination [15–17]. Similarly, Montazer and Pakdel treated wool fabrics with nano titanium dioxide powder (Degussa P-25) sonicating in an aqueous solution in the presence of cross-linking agents namely butane tetra carboxylic acid (BTCA)

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and citric acid (CA) [18]. It was confirmed that nanoparticles were anchored to the functional groups such as $-NH_2$, $-COOH$ and $-SH$ on the surface of wool. The self-cleaning function was assessed based on the colour degradation amount of fruit juice and Acid Blue 113 under UV [18]. There are other reports on the self-cleaning function of nano titanium dioxide [15,19–22]. Along with pure TiO_2 application, TiO_2/SiO_2 has also shown some promising results in functionalising the textiles. Enhanced UV-blocking and self-cleaning functions have been reported after applying the TiO_2/SiO_2 systems to textiles [23–25]. Pakdel and Daoud have successfully enhanced the self-cleaning function of nano titanium dioxide on cotton fabrics through integrating the silica nanoparticles into the coating system [26].

Changing the water absorption characteristics of various substrates using nanotechnology has also been an attractive research arena for scientists. Fujishima et al. demonstrated that the contact angle on TiO_2 surface could be reduced to zero after UV illumination [27]. Adding the hydrophilicity function to some natural textiles such as wool would bring about increased comfort for end users [28]. Montazer et al. treated wool fabrics with titanium dioxide nanoparticles to improve its hydrophilicity with UV illumination [29]. Likewise, antimicrobial and superhydrophilic wool was reported after a mixture of silica and silver nanoparticles was applied to wool fabrics [30]. Hydrophilicity of TiO_2/SiO_2 systems on some substrates such as glass and tile has also been studied [31,32]. Corona discharge and enzymatic treatment have also been reported to increase the water absorption capability of wool [33]. Removing the fatty acid layer of wool cuticle by helium plasma treatment, wool fabrics became more hydrophilic [34,35].

In this investigation, wool fabrics were treated with colloids of TiO_2/SiO_2 through a low temperature sol–gel method using the dip-pad-dry-cure process. This study was set out to investigate the synergistic role of silica in enhancing the functionality of TiO_2 on wool fabric, and to elucidate the impacts of silica addition on self-cleaning and hydrophilicity of wool fabrics. Wool fabrics were stained with coffee and exposed to UV to assess the self-cleaning property. The water absorption behaviour of treated samples was analysed based on the water droplet contact angle.

2. Experimental

2.1. Materials and apparatuses

A 100% wool fabric with a mass of 225.2 g/m^2, woven by the Sunshine Group, China, was used as substrate. Tetraethylorthosilicate (TEOS) and titanium tetraisopropoxide (TTIP 97%) were purchased from Sigma–Aldrich as the precursors of SiO_2 and TiO_2, respectively. Hydrochloric acid 37% (Ajax Finechem, Australia) and glacial acetic acid (Rowe Scientific, Australia) were employed as other components for sol preparation. The surface morphology of wool fabrics was analysed via scanning electron microscopy (SEM) images taken by KYKY-EM3200 (China). The anatase crystalline structure of synthesised photocatalysts was proved by X-ray diffractometer X'Pert PRO MRD XL (PANalytical). Water contact angle metre (KSV CAM101) was employed to investigate the hydrophilicity of fabrics. The synthesised nanocomposites were characterised through FTIR spectrum (Varian 1000, Australia). This instrument was equipped with an ATR attachment with a diamond crystal to study the fabrics chemistry before and after the treatment.

2.2. Preparing the sols

Titania sol was prepared by vigorous stirring of TTIP, acetic acid, distilled water and hydrochloric acid mixture for 2 h at 60 °C. Silica sol was prepared through hydrolysis and condensation of TEOS in water and in the presence of hydrochloric acid (pH = 3). This mixture was stirred for 2 h and then kept overnight for 16 h. TiO_2/SiO_2 composite sols were prepared through mixing the TiO_2 and SiO_2 sols together based on three different Ti/Si molar percentage ratios of 70:30, 50:50 and 30:70 and stirring for 1 h.

2.3. Scouring

Scouring was performed to remove the surface impurities of wool fabrics, in a bath containing 2 g/L of colourless nonionic detergent (Kieralon F-OL-B) with a liquid to fabric ratio of 50:1 at 40 °C for 20 min. Then the samples were rinsed thoroughly with water.

2.4. TiO_2/SiO_2 treatment

Prepared sols were applied to the surface of wool fabrics using the dip-pad-dry-cure process. The excessive uptake of sols was removed from the fabrics by an automatic horizontal padding machine with a nip pressure of 2.75 kg cm^{-2} and rotating speed of 7.5 rpm. The fabrics were dried in an oven at 80 °C for 5 min and subsequently cured at 120 °C for 2 min.

2.5. Self-cleaning test on fabrics

Functionalised wool fabrics were stained with 20 μl of 12 g/L coffee solution and exposed to UV radiation with an intensity of 0.98 mW cm^{-2}. The self-cleaning property was evaluated based on the colour removal of coffee stains on fabrics.

2.6. Solid extraction

Immediately after adding sodium carbonate solution into the TiO_2/SiO_2 sols, the suspended nanoparticles formed a precipitate at the bottom of the beaker. The precipitate was separated from the liquid phase through centrifugation. The pH of nanoparticles was lowered to neutral through washing with distilled water and subsequent centrifugation. The extraction process was finalised through drying the product at 70 °C for 12 h.

3. Results and discussion

3.1. Characterisation of synthesised catalysts

3.1.1. X-ray diffraction (XRD)

The crystallite structure of TiO_2/SiO_2 nanoparticles was assessed through X-ray diffraction (XRD) of synthesised catalysts. There is a broad peak at $2\theta = 25.31°$, corresponding to the anatase crystalline structure of titanium dioxide. It was observed that synthesising the titanium dioxide nanoparticles through this method at 60 °C led to the formation of anatase structure (Fig. 1). These results are consistent with previous findings [36]. The addition of silica into the titania sol did not have an impact on the crystalline structure of titanium dioxide.

3.1.2. Fourier transform infrared spectroscopy (FTIR)

To analyse the established bonding between the oxides in the nanocomposites, the FTIR spectrum of TiO_2/SiO_2 50:50 powder using KBr background was obtained (Fig. 2). FTIR was used to confirm the existence of Ti—O—Si and Si—O—Si bonds. The peaks around 1100 cm^{-1} and 800 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of Si—O—Si bonds, respectively [37]. Another peak at 450 cm^{-1} is related to the bending mode of Si—O—Si [37]. A small peak related to Ti—O—Si linkages appeared at 960 cm^{-1} affirming the bonding between Ti and Si [38]. The wide OH stretching peak can be seen at around 3400 cm^{-1}. This is likely from the presence of moisture related hydroxyl groups inside the fibre.

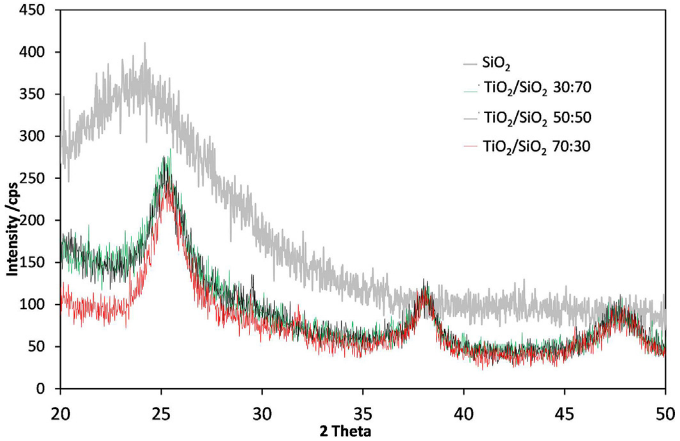

Fig. 1. XRD patterns of extracted powders.

3.2. *Characterisation of functionalised fabrics*

3.2.1. *Attenuated total reflectance (ATR)*

In order to investigate the binding between the fibres and coating layer, ATR analysis was performed on wool samples in the 600–4000 cm^{-1} region. The functional groups on wool surface that are potential reaction sites for binding with nanoparticles are carboxyl (—COOH), amino (—NH_2) and hydroxyl (—OH) groups [16,18,39]. High affinity of nano titanium dioxide particles to negatively charged hydroxyl and carboxyl groups has already been proved [16,40,41]. For this reason, introducing additional hydroxyl and carboxyl groups onto the substrates was reported helpful to stabilise the nanoparticles on fabric [40]. Nevertheless, in this study, the wool fabrics did not undergo any pre-treatment before being functionalised. Therefore, the probable binding reactions would have occurred between the titanium dioxide particles and functional groups that naturally exist in wool structure. Fig. 3 displays the ATR spectra of pristine wool and the sample treated with

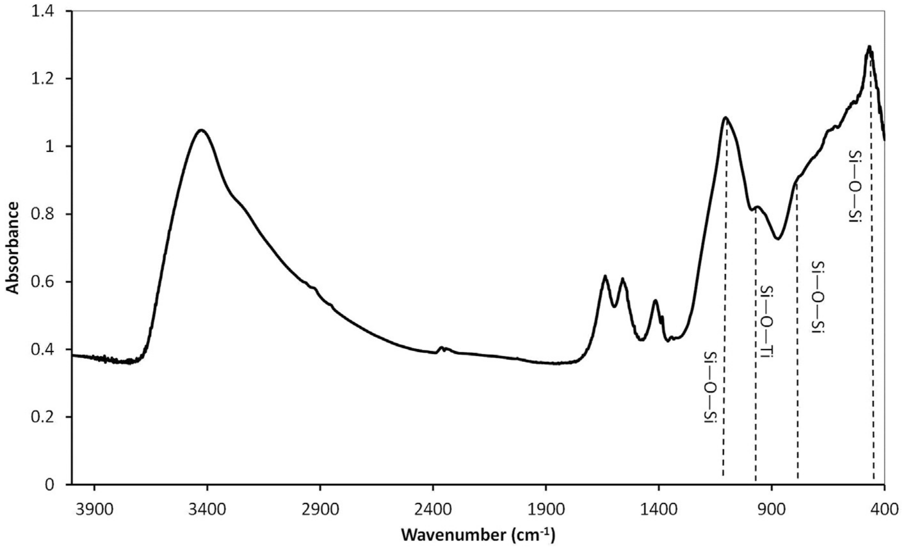

Fig. 2. FTIR spectrum of synthesised powder of TiO_2/SiO_2 50:50 over 400–4000 cm^{-1}.

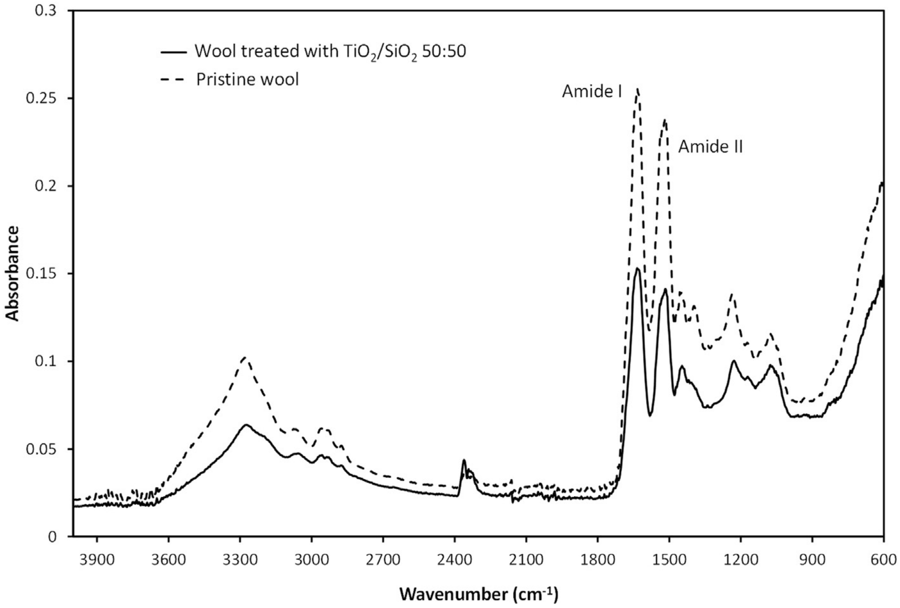

Fig. 3. The ATR spectra of pristine wool and wool treated with TiO_2/SiO_2 50:50.

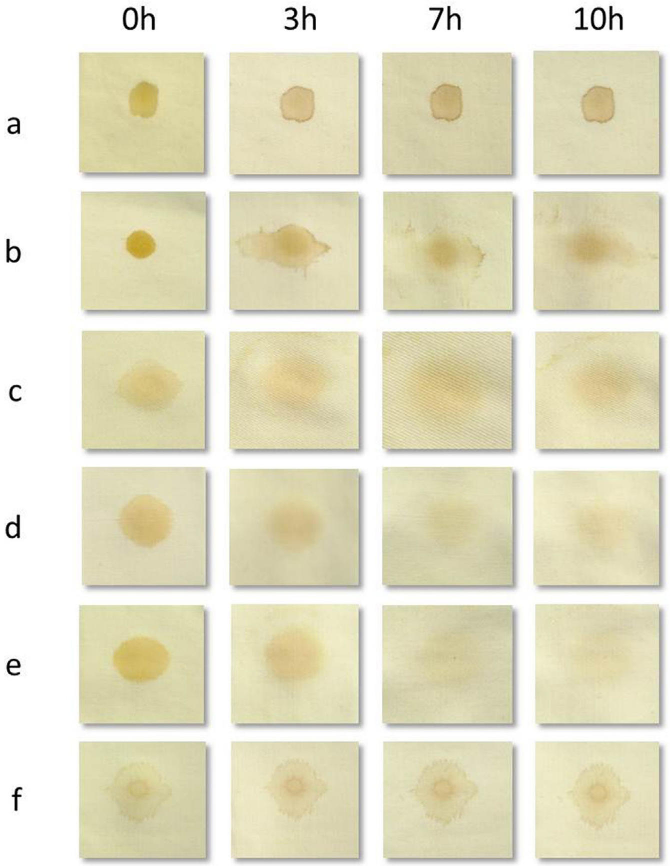

Fig. 4. Coffee stain removal of wool samples: (a) pristine wool; fabric treated with (b) TiO_2, (c) TiO_2/SiO_2 70:30, (d) TiO_2/SiO_2 50:50, (e) TiO_2/SiO_2 30:70, and (f) SiO_2.

TiO_2/SiO_2 50:50 sol. The characteristic peaks of amines I and II appeared at 1640 cm^{-1} and 1550 cm, respectively [42]. The peak at 1640–1650 cm^{-1} would correspond to the stretching vibration of C═O of CONH unit in polypeptide chain [43]. The peaks at 1700–1750 cm^{-1} would be ascribed to the interactions between the surface carboxyl groups of wool and titanium [16]. These peaks are not very obvious due to overlapping with peaks related to the functional groups of wool [16]. It seems that after treating the wool samples with acidic colloidals of nanoparticles, the intensity of peaks related to amide I and amide II decreased.

3.2.2. Self-cleaning function

The self-cleaning function was compared through monitoring the removal of coffee stain on fabrics at different intervals of UV illumination. The energy of UV was employed to trigger the photocatalytic decomposition of stains by titanium dioxide particles. Through exposing the stained samples to UV, the photocatalytic properties of titanium dioxide altered the molecular configuration of stains turning them into colourless products [18]. Fig. 4 depicts that the coffee spots on pristine wool and SiO_2 treated samples have not faded away during the UV illumination, highlighting the fundamental role of nano titanium dioxide particles. Three different molar percentages of Ti/Si including 70:30, 50:50 and 30:70 were used to devise the TiO_2/SiO_2 sols and then applied to fabrics. It can be seen that the self-cleaning feature of samples treated with TiO_2/SiO_2 50:50 and 30:70 was obviously higher than TiO_2 treated samples. This could be justified by the role of silica in increasing the surface area in the surroundings of titanium dioxide particles. At this condition, there would be more accessible sites for the adsorption of stains on the photocatalyst, which in turn increases the potential interactions between active species generated by TiO_2 and coffee stains. The presence of silica can increase the surface acidity of the photocatalyst resulting in a higher concentration of hydroxyl groups involved in photocatalytic reactions [44]. These two factors played a significant part in enhancing the self-cleaning function on TiO_2/SiO_2 treated wool samples. The establishment of connection between Ti and Si results in a charge imbalance producing positive charge in photocatalyst. At this condition, a higher amount of hydroxyl groups is attracted to the surface of photocatalyst [44]. This in turn increases the generated active species during the photocatalytic process of TiO_2. As mentioned earlier, titanium dioxide generates active species which could react with the stain molecules producing colourless products. With silica in the vicinity of titanium dioxide particles, the interactions between active species like superoxide anion and hydroxyl radicals with dye molecules would be stronger. This causes a higher decomposition rate of stain molecules hence a better self-cleaning function. As for surface acidity, it is noteworthy that due to the presence of higher amount of hydroxyl groups on the surface of nanocomposite, the photocatalytic activity is intensified resulting in a higher decomposition rate of coffee stains.

Based on the results in Fig. 4, 10 h of UV irradiation of wool samples treated with TiO_2/SiO_2 50:50 and particularly 30:70 could be enough to decompose the coffee stains. We had already demonstrated that the self-cleaning property of titanium dioxide on cotton fabric could be augmented through the incorporation of silica nanoparticles [26]. Based on the shape of coffee stains on the

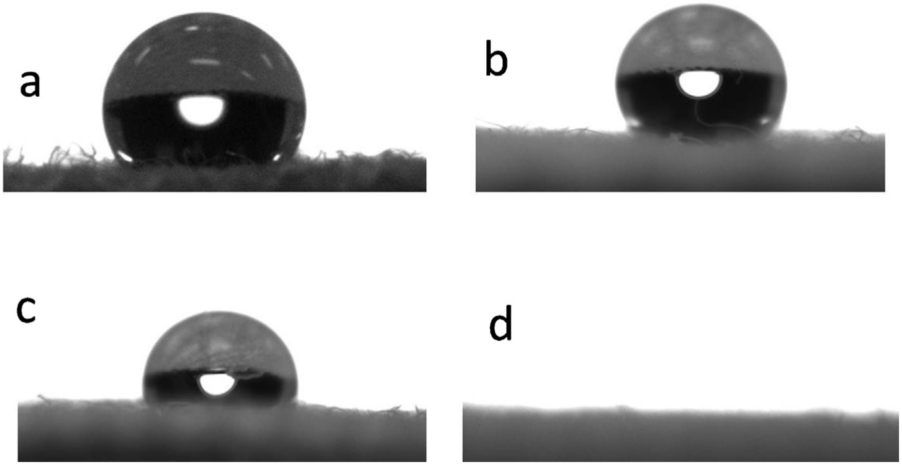

Fig. 5. Water droplets on wool samples: (a) pristine wool; wool treated with (b) TiO_2, (c) TiO_2/SiO_2 70:30, (d) TiO_2/SiO_2 50:50 or 30:70.

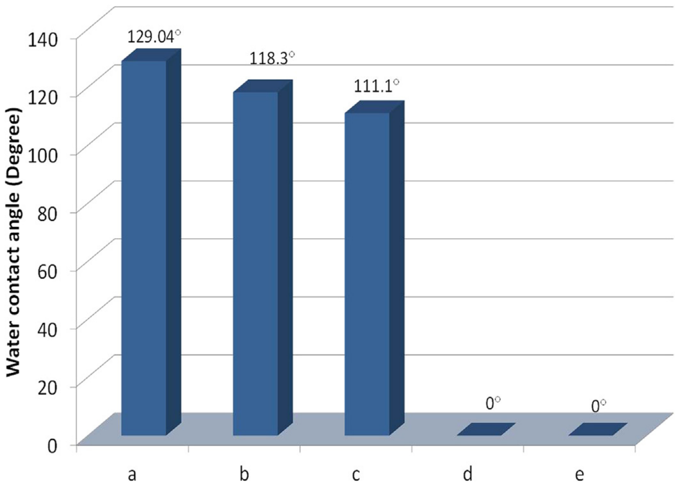

Fig. 6. Water contact angle on wool samples: (a) pristine wool; fabrics treated with (b) TiO_2, (c) TiO_2/SiO_2 70:30, (d) TiO_2/SiO_2 50:50, and (e) TiO_2/SiO_2 30:70.

surface of wool, it can be implied that the fabrics treated with TiO_2/SiO_2 composites have higher hydrophilicity. Moreover, the extent of stains on samples treated with TiO_2/SiO_2 systems is less than on TiO_2 treated sample. This can be related to higher amount of water molecules adsorbed on the surface of coated wool [32].

3.2.3. *Water contact angle*

In this study, the water contact angle on coated samples was measured. It was observed that through the addition of silica, the hydrophilicity increased. While TiO_2/SiO_2 70:30 application slightly reduced the water droplet contact angle with wool, TiO_2/SiO_2 50:50 and 30:70 nanocomposites rendered the wool fabric superhydrophilic. The contact angle measurement was performed on fabrics without any UV illumination. It was observed that the water contact angle decreased dramatically to zero after applying TiO_2/SiO_2 50:50 and 30:70 sols to wool samples bringing about rapid water absorption. As soon as the water droplet was placed on the fabrics, which were treated with TiO_2/SiO_2 50:50 and 30:70 sols, the droplets dispersed completely. Fig. 5 shows the water droplets on pristine and treated wool surfaces. Due to the instant water absorption on samples treated with TiO_2/SiO_2 50:50 and 30:70 sols, the images of water droplets before absorption could not be taken.

The hydrophilicity of samples was compared based on the average water contact angle for 0.6 s after locating the water droplet on the surface of wool. Fig. 6 shows the water contact angle variation on different wool samples. The water contact angle on pristine wool was 129.04° which was decreased to 118.3° after applying the TiO_2 sol to fabric. It can be seen that water contact angle on wool fabric treated TiO_2/SiO_2 70:30 sols is 111.1°. While the water contact angle on samples treated with TiO_2/SiO_2 50:50 and 30:70 was 0° showing the superhydrophilicity function of treated fabrics. Applying the sols to wool fabrics led to an increase in the surface energy of wool fabrics hence bringing about a higher wettability [3,45]. Essentially, the surface energy of solids in general and fabric in particular depends largely on the surface area and the intermolecular forces which exist on the surface [45]. The obtained superhydrophilicity on wool samples in the presence of silica can be justified by the higher surface acidity providing a higher concentration of hydroxyl groups. Higher content of hydroxyl groups was resulted from the presence of Ti—O—Si linkages [44]. This causes charge imbalance which provides Lewis acid sites thus absorbing more hydroxyl groups on the surface of photocatalyst [44].

3.2.4. *Scanning electron microscopy (SEM)*

Surface morphology of wool samples was analysed through the SEM images (Fig. 7). The pristine wool sample showed clear and clean scales on the fibre surface. After the application of nano TiO_2 sol to the fabrics, an even coating layer on the surface of fibres was

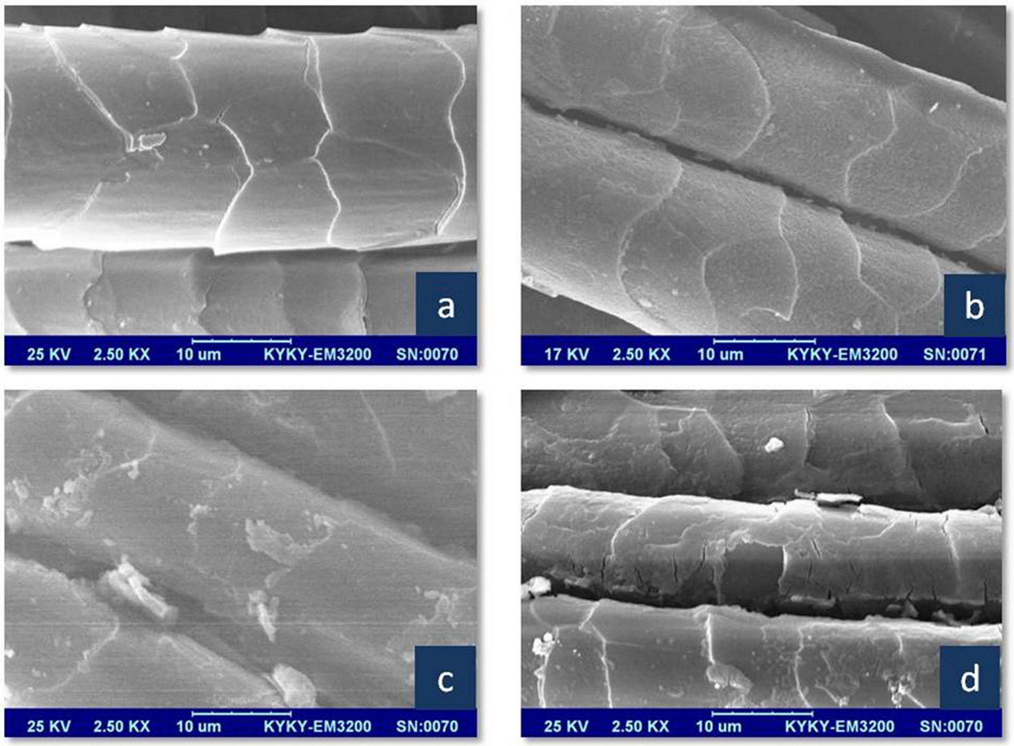

Fig. 7. SEM images of wool samples: (a) pristine wool; fibres coated with (b) TiO_2, (c) TiO_2/SiO_2 50:50, and (d) TiO_2/SiO_2 30:70.

obtained. With the addition of silica into the TiO_2 sol, a thicker layer of nanoparticles was deposited onto the wool surface. Although some small aggregations in TiO_2/SiO_2 nanoparticles are observed, the addition of silica into the TiO_2 sol increased the self-cleaning function on fabrics.

4. Conclusion

Self-cleaning function and hydrophilicity of wool fabrics were successfully improved through the integration of silica in the TiO_2/SiO_2 nanocomposites. Increasing the concentration of silica, the TiO_2/SiO_2 nanocomposite showed more capability in decomposing the stains. This was confirmed through monitoring the discolouring rate of coffee stains on pristine and treated wool samples. Providing a higher surface area in the vicinity of TiO_2 and also increasing the surface acidity of the photocatalyst, silica could enhance the functionality of the self-cleaning coating layer on wool fabric. After applying TiO_2/SiO_2 50:50 and 30:70 onto a wool fabric, a superhydrophilic surface was obtained even in the absence of UV irradiation. Establishing Ti—O—Si and Si—O—Si linkages in the synthesised nanocomposite was demonstrated using the FTIR pattern. Furthermore, the presence of anatase crystalline structure in synthesised nanoparticles was confirmed using the XRD patterns. SEM images showed a relatively even layer of TiO_2 and TiO_2/SiO_2 nanoparticles on the surface of wool. Further work is still required to examine other important aspects of the treated wool fabric, such as durability in washing and abrasion.

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