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Self-Cleaning Keratins

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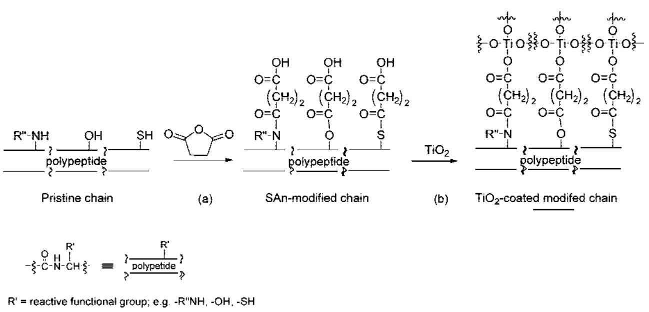
Keratins, a class of biologically fibrous proteins, are tough and insoluble due to the formation of adjacent peptide bond that allow close alignment of the sulfur-containing amino acid constituent, cysteine, enabling the formation of disulfide bridges, cross-links, that confer rigidity and thermal stability to keratinous materials, which make them an important class of fibrous materials. Keratins are a type of natural protein and the main structural constituents of animal tissues. Keratinous protein fibers such as wool, silk, hemp, and spider silk find numerous applications such as insulation, tires, and strong fibers in addition to textiles.[1,2] Although, protein fibers offer excellent physical and processing properties, as biological materials, they lack the minimally required thermal and chemical resistance and intrinsic reactivity of their constituting polypeptide chains to enable modification or fine-tuning of their properties. They are also subject to photodegradation in presence of UV containing light such as solar and indoor lighting. These special characteristics have hindered further functionalization of proteinic materials and limited their full utilization despite their abundance, practicability and biodegradability. Proteinic fibers, capable of converting incident light to self-cleaning power to decompose its stains, dirt, and harmful microorganisms in a process of photocatalytic purification, are very interesting materials for various applications. In this contribution, self-cleaning keratin fibers have been realized following a bottom-up nanotechnology approach in which anatase nanocrystals of titanium dioxide are formulated and carefully applied to the fibers via a near room temperature sol–gel process in order to maintain their intrinsic properties while conferring self-cleaning properties and self-protection against UV degradation. This may enable wider utilization of these natural fibers. Colloids of anatase titanium dioxide, a highly efficient photocatalyst, have recently been prepared via a near room temperature process.[3,4] This synthetic innovation implies that the application of anatase nanocrystals can be extended to low thermal resistance materials such as biomaterials.[5–9] However, due to additional low chemical and thermal resistance and liability to photodegradation of protein fibers, a tailor-made anatase colloid should be devised that suits the target application. It was found that a synthetic formulation of an acidic aqueous colloid of titanium dioxide using hydrochloric acid produces single-phase anatase nanocrystals (4–5 nm), which is applicable to a keratin fiber representative, wool, without affecting its intrinsic properties. Although these functionalized fibers were found to possess excellent self-cleaning and UV-protection properties, these properties may not be stable. TiO_2 has high affinity toward hydroxyl and carboxylic groups,[7,10–13] especially the latter. However, keratin fibers contain less than 50% of those functional groups. Therefore, it is necessary for these fibers to undergo a chemical modification to their backbone chains to enable stable bonding with the anatase nanocrystals. Acylation of fibers by acid anhydride allows for enrichment of carboxylic groups. Other functional groups on the amino acid residues such as amino, hydroxyl, phenol and thiol groups are also potent reactive sites.[14–18] Following the introduction of additional carboxylic groups into the fiber, the change of the binding ability toward metal ions have been studied.[14,18]

Scheme 1. Succinylation of Keratins and the Binding Action of TiO_2 toward Modifying Agent



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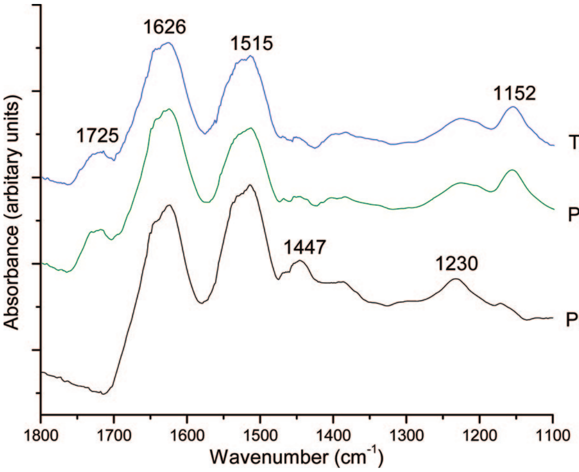

Figure 1. ATR-IR spectra of pristine PO, succinic anhydride modified PS, and T60-coated modified TS fibers.

Succinic anhydride is a nontoxic and mild acylating agent. On the basis of the observed properties of the modified fibers, it was found that the acylation reaction allows for increasing functionality and reactivity toward anatase nanocrystals which in turn resulted in enhanced self-cleaning functionality. This finding may open up new applications and extendibility to other proteinic materials.

Succinylation of fibers was carried out in DMF at 60 °C as shown in Scheme 1. Details of the succinylation reaction are given in the Supporting Information. This reaction introduces additional carboxylic groups to proteinic fibers which are potential reactive functional groups. ATR-IR spectroscopy was applied to verify the reaction of the anhydride with the fibers through the changes in the spectral regions and the characteristic absorptions of the ring-opened anhydride molecules (Figure 1). The spectrum of succinylated fiber **PS** showed spectral changes in the regions 1750–1700 and 1152 cm^{-1}. The band at 1750–1700 cm^{-1} is ascribed to the carboxylic groups that arise from the opening of the anhydride ring and the spectral absorption at 1152 cm^{-1} corresponds to the C−O−C stretching which could arise from the formation of ester bonds by the acylation of hydroxyl groups on the amino acid residue. After modification, the fibers were treated with nanosized TiO_2 colloid T60 by a dip coating process. Attempts were made to examine the chelating effect between titanium atom and carboxylate groups of modified fibers by ATR-IR technique, however the absorption band at 1530 cm^{-1} assigned to the coordination of oxygen atoms of carboxylic groups toward titanium atoms[11–13] cannot be easily observed in the spectrum of T60-coated modified sample **TS** because of the overlapping with bands corresponding to other functional groups of the fibers.

The surface morphology of pristine **PO**, succinic anhydride modified **PS**, T60-coated unmodified **TO** and T60-coated modified **TS** samples was examined by FESEM. Figure 2b shows no significant change in surface structure when compared with **PO** (Figure 2a) as well as some fine particles of the anhydride adhered to the **PS** surface. The major difference was observed in the surface features of **TO** and **TS** (images c and d in Figure 2, respectively). Figure 2c shows uneven distribution of TiO_2 deposit on the surface of **TO** with accumulation at the edge of the scales. In sharp contrast, smooth and uniform deposition of TiO_2 on the modified **TS** was observed in Figure 2d. Possibly, the introduction of more carboxylic groups by the treatment with succinic anhydride resulted in effective binding ability to TiO_2, thus a more uniform T60 coating was observed. Apart from the surface smoothness, it is also evident that the structure of **TS** has not been damaged by the modification.

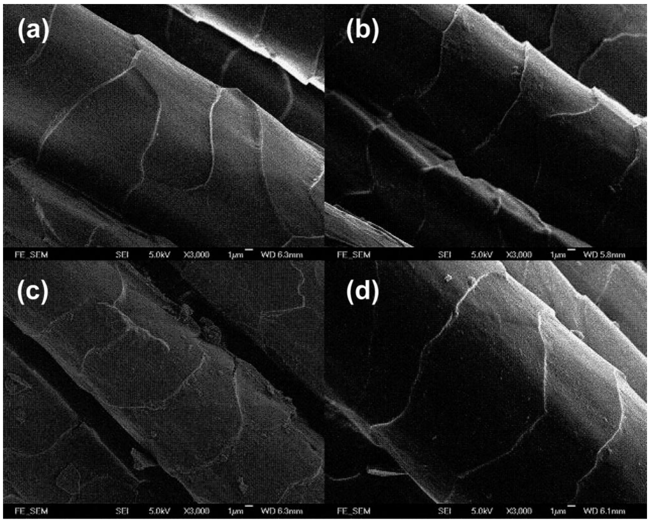

Figure 2. FESEM images of (a) pristine wool fiber PO, (b) modified wool fiber PS, (c) T60-coated wool fiber TO, (d) T60-coated modified wool fiber TS.

Table 1. Surface Elemental Composition of Samples

	chemical composition %					atomic ratio	
sample	C	N	O	S	Ti	Ti/C	Ti/N
PO	73.0	15.8	8.7	2.5	0.0		
TO	59.9	4.6	34.0	1.6	5.7	0.09	1.24
TS	47.2	4.9	37.8	0.5	9.6	0.20	1.94

XPS surface analysis was used to quantify the amount of titanium present on the near surface region. Information of the surface elemental composition of T60-coated samples is shown in Table 1. The titanium content increased significantly by approximately 70% after succinylation. Besides, the ratios of Ti/C and Ti/N of the modified fibers are larger than that of unmodified ones. These results indicate that the density of the TiO_2 deposited on the fiber surface is enhanced by the introduction of free carboxylic groups after succinylation.

The photocatalytic self-cleaning properties of the T60-coated samples were investigated by the decomposition of colorant and degradation of food stains. The results are shown in Figures 3 and 4 in which data of unmodified and modified fibers are compared. Figure 3 illustrates the discoloration of red wine on pristine **PO**, T60-coated **TO**, and T60-coated modified **TS** samples before and after light irradiation with simulated sun light from a Suntest solar simulator with light intensity of 45 mW cm^{-2}, which simulates real life conditions under exposure to solar light. A significant discoloration of red wine stains on both **TO** and **TS** samples can be observed after light irradiation (Figure 3). On the other hand, no discoloration of red wine was observed from the pristine keratin sample **PO** even after prolonged light irradiation demonstrating the pho-

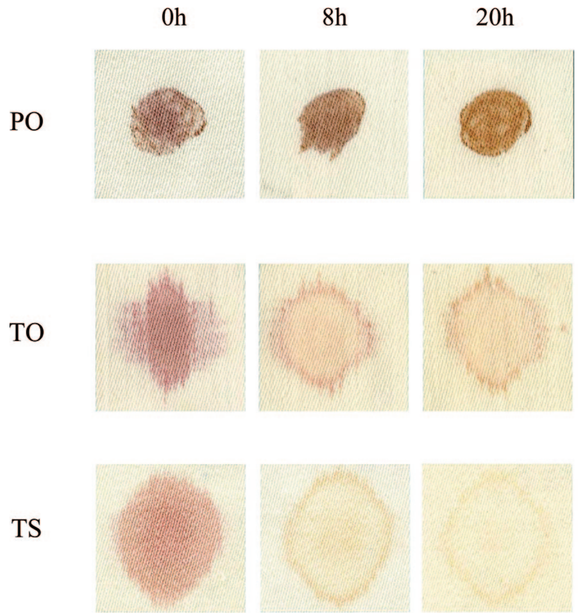

Figure 3. Degradation of red wine stains on pristine PO, T60-coated TO, and T60-coated modified TS samples after 0, 8, and 20 h of light irradiation by a solar light simulator with light intensity of 45 mW cm^{-2}.

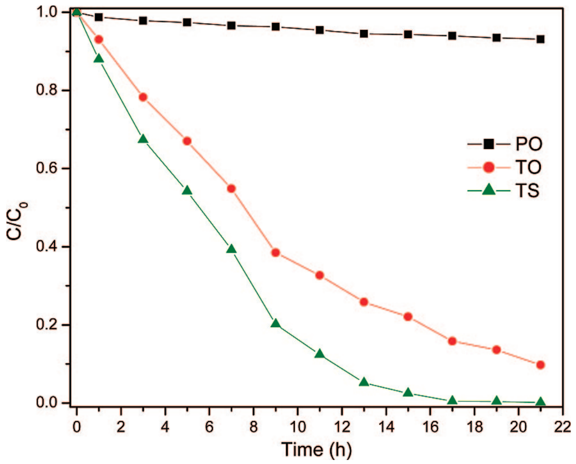

Figure 4. Degradation of methylene blue by pristine PO, T60-coated TO, and T60-coated modified TS samples under UV irradiation.

todegradation ability of the TiO_2 coatings in **TO** and **TS** against red wine stains. In comparing the photodegradation effectiveness between **TO** and **TS**, it is clear that **TS** shows greater activity compared to that of **TO**. Almost complete elimination of the red stain on the **TS** sample (Figure 3) was observed after 20 h of simulated solar light irradiation, which could be attributed to the enhancement of TiO_2 deposition on the modified sample. Figure 4 reveals that the **TS** sample presents a significantly faster degradation rate of methylene blue under UV irradiation by approximately 33% compared to **TO**, whereas dye decomposition was scarcely observed from the **PO** samples due to the absence of TiO_2 (Figure 4). These results confirm that the introduction of additional carboxylic groups to the keratin fibers by succinylation allowed for efficient binding of TiO_2 on the fiber surface which resulted in an enhancement of the self-cleaning properties.

This study shows that self-cleaning fibrous proteins such as wool can be produced by a simple coating process with anatase TiO_2 under mild conditions. A modification of these fibrous proteins with succinic anhydride introduces additional carboxylic groups by acylation which allows for enhanced bonding between TiO_2 and the fibers that in turn results in more effective self-cleaning properties. The chemical modification and anatase coating processes do not employ toxic reagents or solvents and the procedures are carried out under mild conditions favorable for keratinous materials. The observed results from this study could pave the way for further functionalization and thus widen the utilization of these naturally occurring biodegradable keratinous materials.

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Supporting Information Available: Experimental details of the preparation; attenuated total internal reflectance Fourier Transform Infrared spectroscopy, scanning electron microscopy; X-ray photoelectron spectroscopy characterizations; and the photocatalytic study (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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