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Photocatalytic self-cleaning keratins: A feasibility study

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Abstract

Anatase nanocrystals were successfully synthesized and deposited on protein keratin-type wool fibers with good compatibility and significant photocatalytic self-cleaning activity using the sol–gel process. Due to the low chemical resistance and liability to photo-degradation of protein materials, the effect of the acid catalyst used in the sol synthesis was studied. The sols were prepared using oxidizing and non-oxidizing catalysts, nitric acid and hydrochloric acid, respectively, for the hydrolysis and condensation reactions of the titanium dioxide precursor. The size distribution and crystallinity of the sols were characterized by X-ray diffraction spectroscopy and photon correlation spectroscopy. The compatibility of sol formulations and wool is thoroughly compared and discussed by analyzing fibers photo-degradation, surface morphology and self-cleaning properties including stain degradation and colorant decomposition. The UV absorption and mechanical properties of wool fibers before and after coating are also discussed.

Keywords: Titanium dioxide; Photocatalysis; Self-cleaning; Acid catalysis; Nanocoating

1. Introduction

Keratins, a family of natural fibrous-structured proteins, are the main constitute of corneous epidermal tissues of animals found in skin, hair, nails, and animal fibers. Keratins are composed of 19 amino acids constituted by five elements: carbon, hydrogen, oxygen, nitrogen, and sulfur, and linked together in ladder-like polypeptide chains by peptide bonds. Of the 19 amino acids composing keratins, sulfur-containing amino acid, cystine, is the major component. Cystine confers great rigidity and thermal stability to keratin by creating strong and rigid helix shape fibrous matrix through the cross-linked disulfide bridges formed from closely aligned cysteine, where the helical and fibrous keratin molecules eventually twist together, forming insoluble elongated strand as intermediate filament. Apart from the above-mentioned chemical properties, keratins offer important physical properties including insulating ability, durability, practicability and biodegradability. Hence, keratins are an important class of fibrous materials in a wide range of applications such as insulation, tires, strong fibers and textiles [1,2].

Since the discovery of photocatalytic water splitting on TiO_2 electrodes in the late 1960s [3–5], great scientific attention has been given to TiO_2, particularly, in exploring its functions of purification, sterilization and deodorization [6–12]. Owing to its impressive physical and chemical properties such as efficient photocatalytic activities, facilitated by its particle size to diffuse the excited electrons and holes towards the surface before recombination [13], high oxidizing ability, high stability, non-toxicity, and low-cost, TiO_2 has been regarded as an ideal photocatalyst [3]. Among all preparation techniques for producing TiO_2 [14–15], the sol–gel method is the most widely used due to its ability to nucleate anatase at relatively low temperatures [16–17], which makes it suitable for application in materials with low thermal resistance such as plastics and biomaterials.

Self-cleaning treatment technology of fibers by incorporation of titanium dioxide nanoparticles is a new concept that has been introduced in recent years [18–19]. With the fast-growing demand towards functional fibers, where

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fibers not only have the basic characteristics such as maintaining thermal insulation, air permeability and elasticity, but also possessing extra functionality such as self-cleaning, anti-bacterial, environmental friendly, and anti-pollution [4–12,18–22]. It is anticipated that self-cleaning fibrous materials would have significant potential in the global commercial market. Therefore, this novel concept continues to open up exciting opportunities for further research and development.

Protein keratin fibers such as silk and wool are luxurious, delicate, have low thermal and chemical resistance with poor photo-stability in presence of UV-containing light sources, difficult to maintain and care for, and more liable to attack by microorganisms as compared to cellulosic fibers such as cotton and flax. Therefore, it is essentially significant for protein fibers to possess self-cleaning property. Although much work has been conducted on cellulosic fibers such as cotton [23–30], due to the low chemical and thermal resistance and liability to photo-degradation of protein materials [31–33], a tailor-made anatase colloid should be devised wherein the effect of the acid catalyst is taken into account.

It is believed that the development of self-cleaning protein fibers may lead to new possibilities of self-cleaning materials. In this contribution, a systematic investigation was performed in order to study the feasibility of the application process, the impact on wool's intrinsic characteristics, and the efficiency and stability of the introduced self-cleaning properties.

2. Materials and methods

2.1. Sol–gel preparation and surface coating

The sols were prepared by hydrolysis and condensation of 5% titanium tetraisopropoxide (Yizheng City Tianyang Chemical Plant, 97%) in aqueous acidic medium containing 5% glacial acetic acid (Lab-Scan, 99.8%) and either 1% nitric acid (Lab-Scan, 70%) or 1.4% hydrochloric acid (Lab-Scan, 37%). The mixtures were heated at 60 °C under vigorous stirring for 16 h. The sol produced with nitric acid is termed N-sol (pH 1) and that with hydrochloric acid is termed H-sol (pH 1). Fibers were first cleaned by non-ionic detergent (Kieralon OL) at 45 °C for 30 min to remove impurities prior to modification. The dried samples were dipped in the sol at room temperature for 1 min, dried at 60 °C for 5 min, and cured at 120 °C for 3 min [17,33].

2.2. Chemical characterization of sol–gel formulation

The crystallinity of solid powder extracted from the sol was studied by X-ray diffraction spectroscopy (Philips Xpert XR System) with detector scan mode operating at 40 kV and 30 mA in the region of $2\theta = 20$–$50°$. The grain size of the titanium dioxide nanoparticles was calculated according to the Scherrer equation shown in Eq. (1). The particle size distribution was also measured in dilute aqueous sols by particle size analyzer (Zeta Sizer HS 3000) using photon correlation spectroscopy (PCS) and laser diffraction.

$$0.9\lambda \times 180/\mathrm{FWHM} \times 3.14 \times \cos(\theta) \quad (1)$$

2.3. Photo-degradation effect

The photo-degradation, also known as photo-yellowing effect, of the samples induced by the sol coating was studied after exposure to simulated terrestrial solar irradiation for 20 h by means of a solar simulator with irradiance of 45–95 mW cm^{-2} (Xenotest® Alpha LM Light Exposure and Weathering Test Instrument) equipped with Xenochrome 320 filter. The CIE (International Commission on Illumination) Whiteness was then evaluated after converting the reflectance spectra from the equations of CIE Whiteness system (Eq. (2)) in accordance with the standard of AATCC 110-2005, using the parameters of D_{65} daylight illuminant.

$$Y + 800(x_n - x) + 1700(y_n - y) \quad (2)$$

where $x_n = 0.31138$, $y_n = 0.3309$.

2.4. Surface morphology

SEM images were obtained using field emission scanning electron microscopy (JOEL JSM-6635F). Given that wool fibers can be easily damaged by the high-energy electron beam during SEM observation, the equipment was operated at 3.0 kV of accelerating voltage at a maximum of 10,000 magnification.

2.5. UV protection property

The UV transmission of the fibers was compared before and after coating according to the Australia/New Zealand Standard AS/NZS 4399:1996 using Varian Cary 300 UV–visible spectrometer in a wavelength range of 280–400 nm. The ultraviolet protection factor (UPF) value was automatically recorded and calculated according to the standard using data collected from the spectrometer.

2.6. Photocatalytic self-cleaning activity

The static solid-state photocatalytic effectiveness of food stain degradation was assessed using Suntest solar simulator (Xenotest® Alpha LM Light Exposure and Weathering Test Instrument) with irradiance of 45–95 mW cm^{-2} for 8 and 20 h. The dynamic wet-state photocatalytic effectiveness was evaluated following the decomposition of colorant by immersing 2.5 g samples of 1 cm^2 size in 50 ml aqueous 3,7-bis(dimethylamino)phenazathionium chloride (methylene blue) solution with 10 mg l^{-1} concentration (pH 6) under vigorous shaking, followed by UV irradiation (Philip 15 W UV lamps) operating at 20 V with irradiance of 1.2–1.3 mW cm^{-2}. The UV–vis absorption spectra of the

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