Advanced Visible-Light-Driven Self-Cleaning Cotton by Au/TiO₂/SiO₂ Photocatalysts

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ABSTRACT A facile process to prepare porous Au/TiO₂/SiO₂ nanocrystallites was presented. The novel nanocrystallites synthesized were characterized by FESEM, HRTEM, XRD, UV-blocking, and visible light self-cleaning properties. The ultraviolet protection factor of the sample results before and after 30 wash fastness tests have revealed that the treated samples are rateable according to the Australia/New Zealand Standard AS/NZS 4399: 1996. The durable visible light self-cleaning properties were initially conducted and achieved after 20 washes with 20 h simulated visible light irradiation. The Au/TiO₂/SiO₂ nanocomposites have shown more significant visible light self-cleaning performance than that of TiO₂ treated only and represent a remarkable step forward in visible-light-driven self-cleaning treatment for flexible materials with a high potential for commercialization.

KEYWORDS: visible light • self-cleaning • UV-blocking • stain removal • wash fastness • Au/titania/silica • durability

1. INTRODUCTION

To date, the prospect of self-cleaning fibers, yarns, and fabrics might be getting closer, since textile scientists have initially invented efficient ways to fabricate nanoscale ZnO (1−5) and tiny particles of TiO₂ (6−19) on natural or artificial fibers. These nanoparticles are photocatalysts that help to break down carbon-based molecules and require only photoactivating sunlight to trigger the reaction (7, 15, 17). An exponential growth of research activities has been seen in sunlight or visible light self-cleaning cotton (7, 17, 20, 21), wool (32, 22, 23), polyester (18, 23), and plasma-modified cotton (18, 23−25) in recent years. Therefore, the development of efficient visible-light-induced photocatalysts is indispensable for making use of solar energy. Recently, various possible strategies toward TiO₂'s intrinsic limitation, including doping TiO₂ with metal or nonmetal elements such as SiO₂ (16, 26, 27), Au (29), Ag (29, 30), S (31), and N (31) or a bonding spacer (32) or photosensitizing TiO₂ with inorganic or organic compounds, were often efficient but unstable (33). The object of this work is to strengthen the visible light self-cleaning properties of TiO₂, and to improve the durability of the surface of the treated fibers, yarns, and fabrics.

Here, it is reported that a highly active Au/TiO₂/SiO₂ photocatalyst can be obtained by embedding Au and Si species using sol–gel nanotechnology. The as-prepared composites are porous nanoparticles with a size of less than 30 nm. A hydrophilic surface was achieved. The treated fabrics did not change their appearance color in comparison to the control even after several months. The durable UV-blocking properties were observed even after 30 wash fastness tests. The outstanding self-cleaning durability was evidenced from the wash-fastness effect on decoloration of red wine and coffee stained cotton samples.

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals were used as received. The cellulosic substrates (knitted or woven cotton fabrics pretreated) were scoured with nonionic detergent to remove wax, grease, and other chemical residues from fabrics before coating. The scouring process was performed at 80 °C for 30 min.

2.2. Synthesis of 2 wt % TiO₂ Nanosol. The 2 wt % TiO₂ was synthesized according to our previous approach (16, 17). Titanium tetraisopropoxide (Aldrich, 97%) was added dropwise into acidic water (0.7% nitric acid) and acetic acid (Aldrich, 97%) at 60 °C with vigorous stirring. Then the mixtures were stirred for 16 h.

2.3. Synthesis of Au/TiO₂/SiO₂ Nanosol. Au/TiO₂/SiO₂ nanosols with different concentrations were synthesized as follows. In a typical procedure, a predetermined amount of $AuCl_3 \cdot HCl \cdot 4H_2O$ aqueous solution (9.55×10^{-4} mol L^{-1}, International Laboratory), and 0.5 mL of tetraethyl orthosilicate (TEOS, International Laboratory) were added dropwise into 200 mL of as-prepared 2 wt % TiO₂ aqueous solution with vigorous stirring at about 60 °C for 10 min. Different amounts of $AuCl_3 \cdot HCl \cdot 4H_2O$ aqueous solution, 0.1, 0.2, and 0.5 mL, were used for samples 1−3, respectively. Then the flask was moved to a self-made UV light source chamber under UV irradiation (the UV intensity is around 12 W/m²) at ambient temperature for 15 min.

2.4. Coating Processes. The as-prepared sol could be applied onto the substrate by various techniques as follows: dip-pad-cure, dip-coating, and spraying processes. In our study, the dip-pad-dry-cure process was employed to form a durable layer. The cleaned substrates were dipped in the Au/TiO₂/SiO₂ nanosol for ¹/₂ min and then padded with an automatic padder (Rapid Labortex Co., Ltd., Taipei, Taiwan) at a nip pressure of 2.75 kg/cm². The padded substrates were air-dried for 30 min at 100 °C and finally cured at 150 °C for 2 min in a preheated curing oven (Memmert ULE800 Universal Oven) to ensure particle adhesion to the substrate surface.

2.5. Instruments and Characterization. The products were structurally characterized by powder X-ray diffraction (XRD, Philips X'pert diffractometer in θ−2θ configuration). The morphologies were investigated using field emission scanning electron microscopy (FESEM, Leica Stereoscan 440, operating

at 20 kV; JSM-6335F at 3.0 kV, JEOL, Tokyo, Japan). The lattice spaces were determined by employing high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2010 operated at 200 kV).

The UV protection factor (UPF) was measured by a Varian Cary 300 UV spectrophotometer according to the Australia/New Zealand Standard AS/NZS 4399: 1996. Wash fastness was evaluated with reference to the Technic Manual of the American Association of Textile Chemists and Colorists (AATCC). Washing was performed using a laundering machine (AATCC Standard Instrumental Atlas Launder-Ometer LEF, Atlas Electric Devices Co., Chicago, IL) at 49 °C in a 1.2 L stainless steel lever lock canister with details following AATCC Test Method 61-1996 Test No. 2A. The substrates were then rinsed thoroughly with water and dried at room temperature prior to further investigations.

Irradiations of all samples were carried out with Xenotest Alpha LM light exposure and a weathering test instrument (air-cooled xenon arc lamp, irradiance 45−95 W/m^2; Xenotest Alpha LM, Heraeus Industrietechnik, Hanau, Germany). The 3 M PR07 UV-blocking films (the UV blocking range of this film is greater than 99% of UV rays in the 250−340 nm range) were used to conduct the visible light self-cleaning experiments. The fabric samples were cut into 5 × 15 cm pieces. The red wine and coffee stained cotton fabrics were irradiated for 20 h.

3. RESULTS AND DISCUSSION

3.1. UV-Blocking Properties of Fabrics.
UPF is based on an in vitro method; it is a ranking of the sun protective abilities of a textile. It is the ratio of the average effective UV radiation (UV-R) irradiation calculated for unprotected skin to the average effective UV-R irradiance calculated for skin protected by the test fabric. A UPF rating of less than 15, between 15 and 50, and more than 50 (50+) are generally classified as nonratable, good to very good, and excellent UV-blocking properties for fabrics, respectively. A low UPF (less than 15) of cotton fabric is inadequate protection for outdoor wearers; therefore, clothing with a greater UPF should be worn outdoors.

In Figure 1, it can be seen that pristine woven cotton fabrics cannot be worn, due to its low UPF of just around 4 before or after washes. The treated samples have shown wearable UV-blocking properties before washing (the upper) and after 30 wash tests (the bottom). Excellent wash fastness after 30 home launderings was achieved for the treated samples used in this study, as a thin layer of nanocrystallites was formed on the cotton fabrics. The TiO$_2$-coated sample demonstrated more durable UPF in comparison to other nanocomposite-treated samples. This might be caused by the hydrophilic modification of the SiO$_2$ layer. TiO$_2$/SiO$_2$- and Au/TiO$_2$/SiO$_2$-treated samples also demonstrated wearable UPF after 30 wash fastness tests. The increment of gold dosage decreased the wash fastness ability due to the formation of larger size nanoparticles.

3.2. Visible Light Self-Cleaning Properties.
The removal of stains such as coffee and red wine is a key test to evaluate the self-cleaning activities of the coatings on fibers or fabrics. Figure 2 presents the decoloration results of a red wine stain and a concentrated coffee stain, respectively, on control cellulosic fabrics, TiO$_2$-treated cellulosic fabrics, and Au/TiO$_2$/SiO$_2$ sample 3 coated white cellulosic
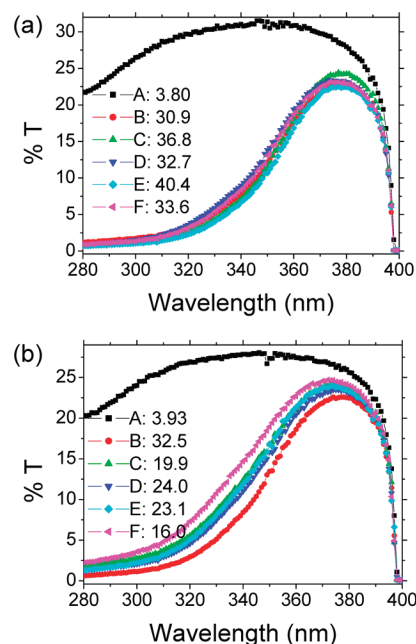

FIGURE 1. UPF of the samples before washing (a) and after 30 washes (b): (A) control, pristine cellulosic fabric; (B) TiO$_2$-coated sample; (C) TiO$_2$/SiO$_2$-coated sample; (D) Au/TiO$_2$/SiO$_2$ sample 1; (E) Au/TiO$_2$/SiO$_2$ sample 2; (F) Au/TiO$_2$/SiO$_2$ sample 3.

FIGURE 2. Degradation results of a red wine stain and a concentrated coffee stain, respectively, on control (pristine cellulosic fabrics), TiO$_2$-treated cellulosic fabrics, and Au/TiO$_2$/SiO$_2$ sample 3 coated cellulosic fabrics before and after 20 h visible light irradiation using a Suntest solar simulator with a light intensity of 6460 lx.

fabrics under visible light irradiation using a Suntest solar simulator with a light intensity of 6460 lx.

In Figure 2, it can be observed that the decoloration of red wine stain in Au/TiO$_2$/SiO$_2$ sample 3 was more significant after 20 h of irradiation in comparison with the TiO$_2$-treated woven cotton fabrics. The stain in pristine cellulosic fabrics cannot be removed even after 50 h of irradiation. The results showed that cotton fabrics treated only with TiO$_2$ might not provide enough visible light self-cleaning ability for red wine stains.

Both TiO$_2$- and Au/TiO$_2$/SiO$_2$-coated woven cotton fabrics have shown significant decoloration of concentrated coffee stains after 20 h of visible light irradiation. As for red wine stains, coffee stains cannot be self-cleaned on the pristine cellulosic fabrics even after 50 h of irradiation.

3.3. Durability of Visible Light Self-Cleaning Properties.
The self-cleaning durability of the as-treated substrates is of importance for potential applications. The implication of the visible-light-driven self-cleaning is that the
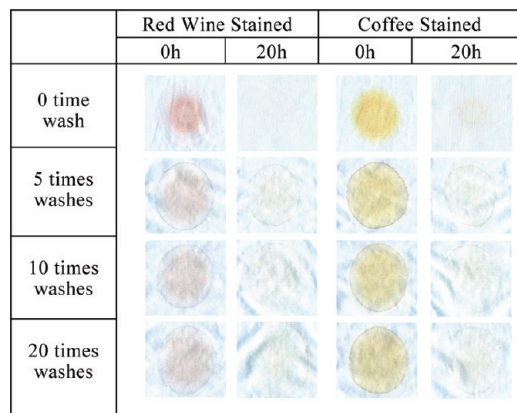
FIGURE 3. Wash-fastness effect on degradation results of a red wine stain and a concentrated coffee stain, respectively, on Au/TiO$_2$/SiO$_2$ sample 3 coated cellulosic fabrics before and after 20 h of visible light irradiation using a Suntest solar simulator with a light intensity of 6460 lx.

reaction center is localized on the semiconducting surface durably attached to the substrate. To the best of our knowledge, self-cleaning durability has been seldom reported. Fabrics are a rather ideal substrate to conduct the durable experiments of the self-cleaning properties according to AATCC Test Method 61-1996 Test No. 2A, as shown in Figure 3. This figure demonstrates the wash-fastness effect on degradation results of a red wine stain and a concentrated coffee stain, respectively, on Au/TiO$_2$/SiO$_2$ sample 3 coated cellulosic fabrics before and after 20 h of visible light irradiation using a Suntest solar simulator with a light intensity of 6460 lx. The wash fastness tests were achieved after 0, 5, 10, and 20 washes, respectively. It can be seen that the Au/TiO$_2$/SiO$_2$ sample 3 treated samples have shown significant decoloration in comparison to the control before and after washes.

The durability improvement might be due to the low polycondensation levels of AuTiO$_2$/SiO$_2$ nanosols, low calcination temperatures, and the chemical bonding of hydroxyl groups between cotton fabrics and nanosols during the curing step at around 150 °C. The origin of visible-light-driven activity of Au/TiO$_2$/SiO$_2$ can be attributed to the strengthened adsorption in the near-UV-A and visible light region and the improvement of UV−vis vacancies, quantum efficiencies, and red shift in the adsorption edge. Au species may improve the rate of electron transfer to oxygen, thus decreasing the rate of recombination between excited electron/hole pairs.

3.4. SEM Observations.
SEM observations in Figure 4 revealed that the TiO$_2$, SiO$_2$/TiO$_2$, and Au/TiO$_2$/SiO$_2$ were porous structural nanoparticles with dimensions of less than 30 nm. In Figure 4B,C, TiO$_2$ and Au/TiO$_2$ were modified by a SiO$_2$ layer. The apparent porous structure is demonstrated in Figure 4C, mainly due to the fabrication of Au nanoparticles doped on the TiO$_2$/SiO$_2$ surface.

3.5. X-ray Diffraction Properties of Au/TiO$_2$/SiO$_2$ Nanomaterials.
SiO$_2$ and Au peaks were not observed, due to the lower dosage (33). Both anatase and rutile phases were observed in the as-prepared composites, as presented in Figure 5; the main characteristic peaks of
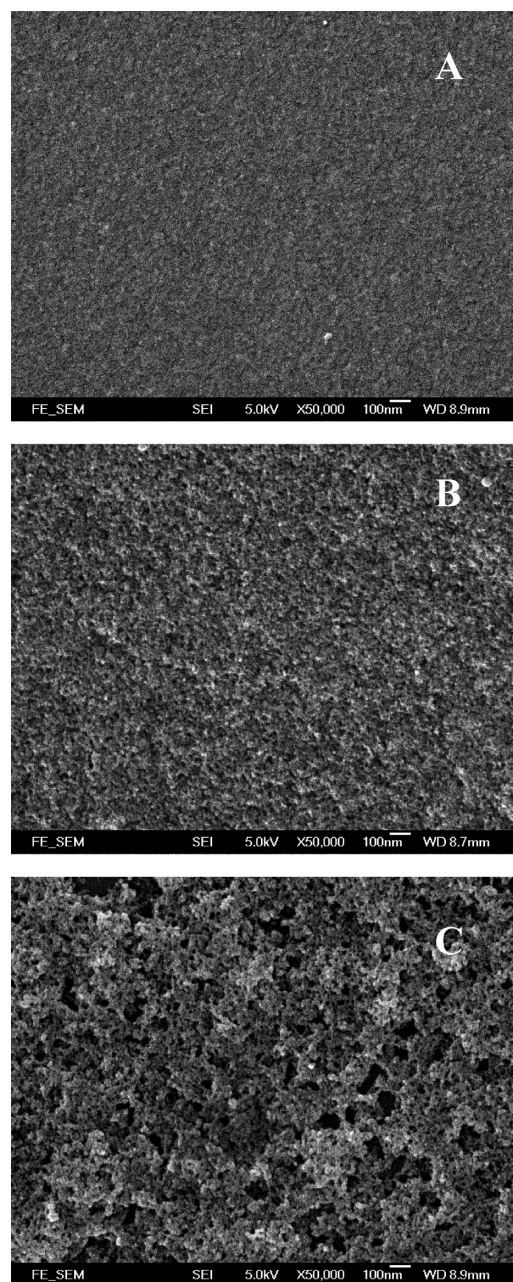

FIGURE 4. Typical FESEM images of TiO$_2$ nanosols (A), TiO$_2$/SiO$_2$ nanocrystallites (B), and Au/TiO$_2$/SiO$_2$ sample 3 nanocrystallites (C).

anatase TiO$_2$ were shown at 48.0° etc., while the main characteristic peaks of rutile TiO$_2$ are observed at 37.0, 63.0°, etc.

3.6. Transmission Electronic Microscopy Analysis.
The nanoparticles are highly crystallized, as evidenced from the well-resolved Au(111) (0.25 nm) and TiO$_2$(101) (0.36 nm) crystalline lattices shown in Figure 6. The dimension and size of the nanocomposites were further confirmed by high-resolution TEM observations. SiO$_2$ is amorphous, and no typical crystallites were observed (17). The Au species were scaled around 10 nm. The size of the Au/TiO$_2$/SiO$_2$ sample 3 nanocomposite was measured as 20−30 nm.
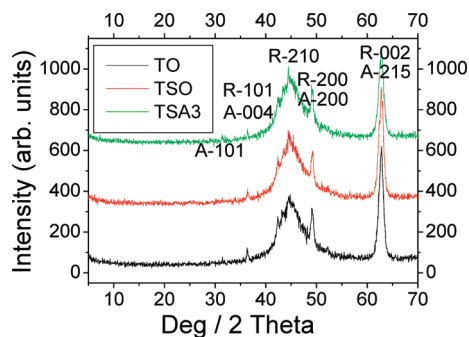
FIGURE 5. XRD patterns of the Au/TiO$_2$/SiO$_2$ nanocomposites: TO, TiO$_2$ only; TSO, TiO$_2$/SiO$_2$ only; TSA3, Au/TiO$_2$/SiO$_2$ sample 3.
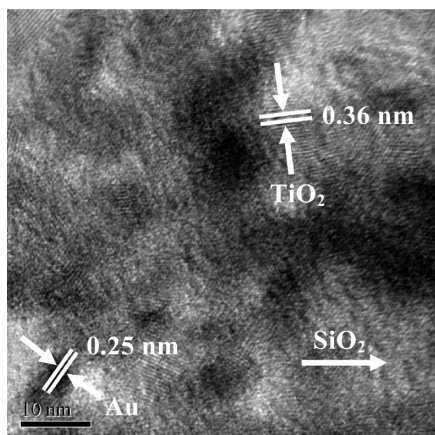

FIGURE 6. HRTEM image of the Au/TiO$_2$/SiO$_2$ sample 3 nanocomposites.

4. CONCLUSIONS AND SUMMARIES

The Au/TiO$_2$/SiO$_2$ nanocomposites were prepared by a sol−gel approach to reduce the negative effect of TiO$_2$ and improve the visible light self-cleaning performance. The hydrophilic properties of TiO$_2$/SiO$_2$ and Au/TiO$_2$/SiO$_2$ were achieved in comparison to TiO$_2$ only. The visible light self-cleaning properties of TiO$_2$ were strengthened after the modification. Studies of the UPF of the sample results before and after 30 washes have revealed that the samples are rateable after the treatments according to the Australian/New Zealand Standard AS/NZS 4399: 1996. The visible light self-cleaning properties were achieved after 20 washes with 20 h of simulated visible light irradiation when the samples were covered by 3 M PR07 UV-blocking films. The Au/TiO$_2$/SiO$_2$ nanocomposites have shown significant visible light self-cleaning performance in comparison to that of TiO$_2$-only treatment. The durability of the self-cleaning properties was initially highlighted in this study. The durability improvement might be due to the low polycondensation levels of AuTiO$_2$/SiO$_2$ nanosols, low calcination temperatures, and the chemical bonding of hydroxyl groups between cotton fabrics and nanosols during the curing step at around 150 °C. The origin of visible-light-driven activity of Au/TiO$_2$/SiO$_2$ can be attributed to the strengthened adsorption in the near UV-A and visible light region, the improvement of UV−vis vacancies, quantum efficiencies, and a red shift in the adsorption edge. Au species may improve the rate of electron transfer to oxygen and thus decrease the rate of recombination between excited electron/hole pairs. Therefore, the as-prepared structural material demonstrated a remarkable step forward in visible light self-cleaning treatment for flexible substrates and has a high potential for commercialization.

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