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Self-cleaning cotton textiles surfaces modified by photoactive SiO_2/TiO_2 coating

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Abstract

The photocatalytic activity of TiO_2–SiO_2-coated cotton textiles was investigated through the self-cleaning of red wine stains. It was shown that a TiO_2–SiO_2 species could be produced at temperatures of 100 °C with acceptable photo-activity on non-heat resistant materials. The most suitable Ti-content of the coating was found to be 5.8% and for SiO_2, the content was 3.9% (w/w). The discoloration of red wine led to CO_2 evolution that was more efficient for TiO_2–SiO_2-coated cotton for samples than of TiO_2-coated ones. The reasons for these results are discussed. The textile surface did not show any change after several consecutive light-induced discoloration cycles of a red wine stain. By high-resolution transmission electron microscopy (HRTEM), the TiO_2–SiO_2 layer thickness on the cotton fibers was detected to 20–30 nm. The TiO_2 and SiO_2 were both observed to have particle sizes between 4 and 8 nm. Further electron microscopy work coupled with energy dispersive spectroscopy (EDS) showed that the Ti-particles were always surrounded by amorphous SiO_2 and never alone by themselves. Infrared spectroscopy revealed that no modification of the cotton could be detected after photo-discoloration processes with TiO_2–SiO_2, taking a wine stain as model compound. The mixed TiO_2 and SiO_2 colloids lead during the dip-coating and subsequent thermal treatment on cotton to an organized structure of highly dispersed TiO_2 particles always surrounded by amorphous silica.

Keywords: Self-cleaning; Cotton textiles; Wine stains; TiO_2–SiO_2 coating; Photocatalysis

1. Introduction

The development of permanent self-cleaning cotton textiles with a life cycle of 25–50 washings or more is an objective sought by the textile industry in the framework of new products classified as intelligent textiles [1,2]. Such a product could have applications in the EU market of about 14 million meters of textiles/year. The cost saving on cleaning using these fabrics, presenting a total or partial self-cleaning properties, is one benefit. The other is to prolong the lifetime of the textile due to the continuous self-cleaning taking place at the fabric surface under daylight irradiation. Such an innovation comprises TiO_2 nano-clusters thin films deposited on the textile surface, in our case, a cotton textile. TiO_2 was shown in the last decade to be the best candidate for a photocatalytic applications [3–5]. Nano-sized TiO_2 particles show high photocatalytic activity because they have a relatively large surface area per unit mass and volume, which facilitates the diffusion of the surface, generated charge carriers under light irradiation [6,7]. Sol–gel TiO_2-based thin layers require a high temperature treatment >300 °C treatment to produce thin films with a defined crystallographic phase. This limits the possibility of achieving well-crystallized TiO_2 films, to supports with reasonable thermal stability such as glass or ceramics [1–6].

We have found only three prior reports on TiO_2 thin films prepared from sol–gel TiO_2 at relatively low temperatures. The first report discussed deposited TiO_2 films on silicon wafers between 60 and 180 °C by film autoclaving under water pressure [7]. The second report was related to TiO_2 deposition on polymer PMMA and polycarbonate from TiO_2 sol–gel [8]. The third and last report involved the production of TiO_2 films of alcoxides at temperatures of 100 °C [9]. Out of our laboratories, we have recently reported the coating of synthetic fabrics with

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TiO_2 by physical and chemical methods at temperatures higher than 100 °C [10–13].

The first objective of this study was to optimize the parameters intervening in the preparation of photoactive transparent thin films of TiO_2–SiO_2 on cotton knowing that this substrate has a poor heat resistance. The maximum exposure that cotton can take without being damaged is 180 °C for 10 min and somewhat lower temperatures for longer time periods. The experimental conditions were screened for the preparation of photocatalytic active TiO_2–SiO_2 layers in the thermal range compatible with the cotton heat stability. The photocatalytic activity of TiO_2 strongly depends on the size, specific surface BET area, porosity and structure of the layers deposited on the textile surface. The specific surface area of the TiO_2 coating is favored by low temperature preparation. No sintering of the TiO_2 occurs decreasing the porosity of the film, as is the case for TiO_2 films calcined on heat-resistant substrates at a few hundred degrees. The second objective is to report in detail the SiO_2–TiO_2 morphology, responsible for the observed photoactivity, by HRTEM and EDS. The third objective of this study was to characterize and assess the surface changes on the cotton textile during the self-cleaning process by elemental analysis (EA), X-ray diffraction (XRD) and infrared spectroscopy (ATR-IR).

SiO_2 was selected as a binder since it does not decompose due to the strong photocatalytic action of TiO_2. The composite layer of TiO_2–SiO_2 should avoid as much as possible the attack on the cotton by the h^+_{vb} generated by the TiO_2 under daylight irradiation. Experiments are reported, which evaluate quantitatively the effect of the corrosion of the cotton upper layers by the action of TiO_2 under light.

2. Experimental

2.1. Materials and reagents

The cotton bleached fabrics were a gift from Cilander AG, 9100 Herisau (Ar), Switzerland. The titanium tetra-isopropoxide (TTIP), acetic acid and nitric acid were Fluka p.a. reagents and used as received. Triply distilled water was used in all experiments. The colloidal silica solution Ludox SM-30 (ex-Dupont) was used for the preparation of the mixed TiO_2–SiO_2 colloids and was a gift of Grace GmbH, 4153 Rheinach, Switzerland. These colloid particles were negatively charged having Na as a stabilizing counter-ion. The colloid contained 30 wt.% SiO_2 (specific surface area 360 m^2/g) in solutions with pH 6.9. It is widely used in industry to increase the strength and abrasion resistance of treated textiles.

2.2. Preparation of TiO_2–SiO_2 colloids and coating of the cotton fabrics

After a long series of preliminary experiments, the most efficient discoloration of red wine on the cotton was observed with a TiO_2–SiO_2 layer colloid prepared as follows. The TiO_2 solution prepared from 25 ml titanium tetra-isopropoxide (TTIP), and 5 ml acetic acid were added to 500 ml of tri-distilled water. Subsequently, 3.5 ml HNO_3 was added under stirring, and the mixture was heated to 80 °C for 30 min. The resulting TiO_2 colloid was kept under stirring for 2 h. The TiO_2–SiO_2 layers on the cotton were deposited by immersing the cotton in a 1:1 volume mixture made up of the TiO_2 colloid and SiO_2 Ludox SM-30. Subsequently, the sample was dried in air and treated at 100 °C for 1 h. The process of preparing and loading TiO_2–SiO_2 on cotton textiles is schematically shown in Fig. 1.

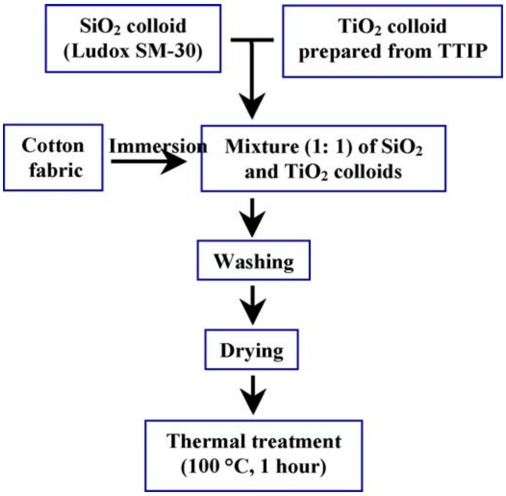

Fig. 1. Scheme of the colloid preparation and cotton loading with TiO_2- and SiO_2-colloidal mixture.

During the preparation of diverse colloidal mixtures, the solution parameters that varied were: (a) the nature of the colloidal solutions of SiO_2, (b) the ratio of SiO_2 to TiO_2, (c) the drying temperature of the colloid on the cotton, (d) the drying time of the colloid on the cotton, (e) the dip-coating conditions of the cotton into the colloidal mixture and (f) the pH and concentrations of the mixed colloids. Preliminary discoloration experiments of wine spots showed that mixed colloids of SiO_2 and TiO_2 presented a better performance than when TiO_2 colloids were used alone for the photo-discoloration of wine stains. Also, when the SiO_2 colloid was added first to the cotton and then dried followed by the TiO_2 colloid in order to protect the textile with a layer of inert SiO_2, the photo-discoloration effect was much reduced.

When TiO_2 and SiO_2 colloids are mixed, a mixing at the molecular level is observed [14] that on heating will crosslink and gellate leading to the formation of a 3-D network. In contact with the textile surface, the condensation of the mixed colloid is higher than the crystallization rate leading to separate TiO_2 and SiO_2 loosely bound particles with a specific structure as described in Section 2.5 by HRTEM and EDS experiments.

2.3. Irradiation procedure and evaluation of the textile cleaning action

The photochemical reactor consisted of 80 ml cylindrical Pyrex flasks each containing a strip of textile of 48 cm^2 positioned immediately against the wall of the reactor. Irradiation of the samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany), air-cooled at 45 °C. The Suntest lamp emitted 5–6% of the photons in the 290 and