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A new approach to apply crystalline titania hydrosols onto a polyester cloth

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A new procedure was developed to attach titania hydrosols to polyester fabrics, providing processed fibers with self-cleaning properties.

Titania-based coatings with a high specific surface area and a narrow pore size distribution are useful in solar energy conversion, photocatalysis and water and air cleaning and processing as self-cleaning,[1–4] photochromic,[5] conductive[6] and superhydrophobic/hydrophilic coatings.[7,8] A promising direction in materials technology is the production of textile materials possessing dirt- and oil-repellent, hydrophobic, bactericidal, heat- and acid-resistant properties. The development of 'smart textiles' exhibiting both bactericidal and self-cleaning properties is also of interest.

Low temperature sol-gel processed photocatalytic titania coatings on cotton fabrics provide antibacterial properties and a UV-blocking effect.[9] The photocatalytic self-cleaning properties of modified cotton textiles were demonstrated by TiO_2 clusters attached with chemical spacers *via* removing the organic stains produced by wine, coffee and make-up.[10] TiO_2 species can be produced with acceptable photoactivity on non-heat-resistant materials.[11] The method is based on using crystalline titania sols, which can be obtained in an aqueous medium at temperatures higher than 80 °C. Processing polyester and other hydrophobic fibers with systems of this kind to uniformly coat an active layer is practically impossible because of low wettability of the surface, which leads to a non-uniform coating on a fiber and, as a consequence, to a decrease in the self-cleaning effect.[12] Titania thin films can be formed on polymers such as polystyrene, poly(ethylene terephthalate), polyamide 66, poly(methyl methacrylate), polyethylene and polyethersulfone by the hydrolysis of a titanium fluoro complex in an aqueous solution.[13] Other studies were devoted to cross-linking by titania based on the initial surface modification of a polyester fiber by plasma-chemical processing.[14] These methods, as a rule, require hi-tech equipment or expensive precursors for the uniform distribution and reliable fixation of titania onto the surface of a polyester fiber.

Here, we report the preparation of nanocrystalline titania sols, the attachment of TiO_2 nanoparticles to a polyester fiber based on codissolution using isopropanol and chloroform as solvents and the self-cleaning properties of a modified polyester fiber.

The self-cleaning properties of TiO_2-processed polyester fibers were assessed by the rate of decomposition of Rhodamine B under UV irradiation (365 nm)[15] from a high-pressure 250 W mercury lamp. The 4 cm^2 samples of the processed and raw polyester fibers were spotted with 10 μl of a Rhodamine B solution (0.04 g dm^{-3}), dried and subjected to UV irradiation for 60 min.

The durability of TiO_2 layers on polyester fibers was evaluated by repeatedly washing at 50 °C for 45 min, which was equivalent to home washing repeated five times. The self-cleaning performance of the washed samples was examined as described in the assessment of decomposition activities of the colorant above. The difference in the cloth coloring intensity before and after UV irradiation is an appropriate value to determine the photocatalytic effect of TiO_2 on the decomposition of dye stains.

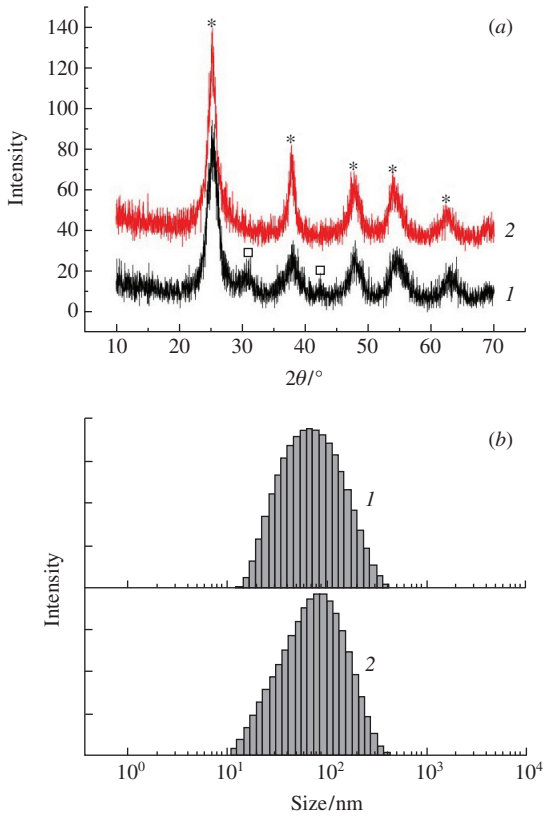

Figure 1 (*a*) XRD patterns of as-synthesized titania hydrosols prepared by methods (*1*) I and (*2*) II and (*b*) their hydrodynamic diameter distribution: (∗) anatase and (□) brookite.

Figure 1(*a*) shows the results of the XRD analysis of crystalline titania hydrosols. The titania prepared using method I[†] was characterized by the presence of crystalline anatase (ICDD no. 021-1272) and brookite (ICDD no. 29-1360) phases with average crystallite sizes of 4.7 and 3.9 nm, respectively. The produced titania was an anatase–brookite polymorph containing 58% anatase and 42% brookite. The sample prepared using

[†] The synthesis of nanostructured titania (method I) was carried out in a single stage using a solution prepared by mixing 12 ml of isopropanol (Aldrich) and 16 ml of titanium isopropoxide $Ti(OPr^i)_4$ (98%). The peptizing solution containing 100 ml of twice-distilled H_2O and 0.7 ml of concentrated HNO_3 was heated to 80 °C and added dropwise to the above solution after stirring for 2 h. As a result, the aggregated amorphous precipitate upon peptization and long-term heat exposure (at 80 °C for 8 h) was dissolved in a colloidal solution of the TiO_2 sol, which was used for the treatment of polyester fibers. The surface area of the dried sample was 149 m^2 g^{-1}, the pore volume was 0.086 cm^3 g^{-1}, and the average pore size was ~2.2 nm.

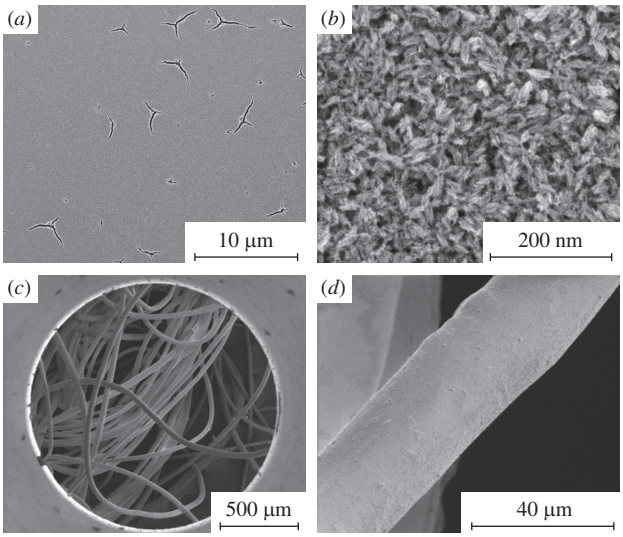

Figure 2 SEM images of (*a*),(*b*) pure TiO_2 nanoparticles prepared by method II and (*c*),(*d*) polyester fibers treated by this hydrosol.

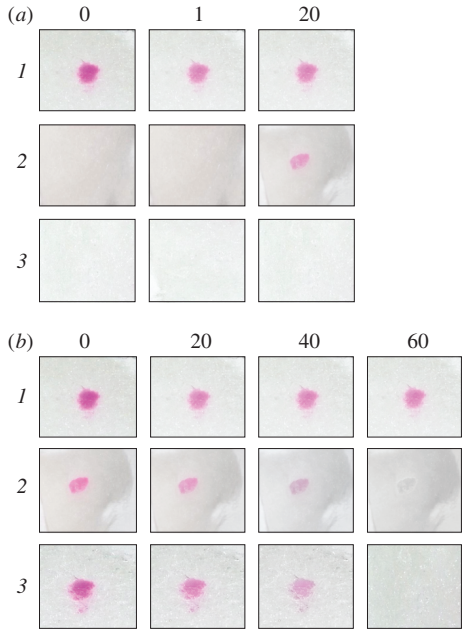

Figure 3 Self-cleaning test using Rhodamine B *vs.* (*a*) the number of washing cycles and (*b*) UV irradiation time (min). The images shown are the exposed sides of (*1*) only polyester substrates, (*2*) titania-coated (method I) original polyester substrates, and (*3*) titania-coated (method II) polyester substrates.

method II‡ was characterized by the presence of only crystalline phase of anatase with the average crystallite size of 4.9 nm.

Figure 1(*b*) exhibits the hydrodynamic diameter size distribution of TiO_2 hydrosol nanoparticles, which is defined by the ionic strength of a medium. It was 70 or 80 nm for titania produced by method I or II, respectively; thus, the agglomerates formed during hydrolysis were peptized by nitric or acetic acid to form a stable sol consisting of nanoparticles.

Figure 2 shows the scanning electron microscopy images of the pure titania (method II) and polyester fibers treated by this hydrosol. The titania nanocrystallites form a dense film [Figure 2(*a*)] consisting of anisotropic nanorods with diameters of 1–2 nm and lengths of 10–15 nm [Figure 2(*b*)]. When applying TiO_2 to polyester textile products that may likely be subject to frequent washing, it is necessary to improve the adhesion between TiO_2 and polyester, which is not good because of the lack of chemical bonding. To improve the adhesion, surface treatments for altering chemical and physical properties of the polyester surface may be needed. The processing of polyester fibers performed in this work is based on a codissolution technology. By dispersing the obtained crystalline titania sols first in isopropanol and then in chloroform, it is possible to achieve a homogeneous distribution of nanoparticles on a fiber surface [Figure 2(*c*),(*d*)] and to substantially increase their adhesion.

The self-cleaning properties of a cloth without washing and after 20 washing cycles were assessed by the degree of decomposition of the model dye Rhodamine B [Figure 3(*a*)] under UV irradiation. The rate of photodestruction was determined by a change in the intensity of a stain coloring in due course [Figure 3(*b*)].

Several washing stages were applied to remove loose titania nanoparticles and to estimate the performance characteristics of the composites. Degradation of the organic dye on a polyester fiber under UV irradiation was almost not observed due to its high stability [Figure 3(*a*), row *1*]. At the same time, upon processing a polyester fiber with titania nanoparticles, an efficient photocatalyst, this process can intensify. The overall performance of such a composite depends on many factors, including the quantity of the reactive centers, the degree of crystallinity and the presence of a highly developed porous structure. The degree of interaction upon joining these nanoparticles and the fiber surface together is also important. As a rule, nanocrystalline titania hydrosols hardly moisten the surface of a polyester fiber, which leads to a nonuniform surface distribution of particles possessing low adhesion to the substrate. As a result, the quantity of the reactive centers sharply decreases leading to a loss in the photoactivity of the final composite. As found experimentally, an amplification of cross-linking of titania nanoparticles and polyester fibers can be reached by applying a codissolution method. In our case, a polyester fiber processed with chloroform containing titania hydrosol showed high photoactivity even after 20 washing cycles since titania nanoparticles were intercalated into the surface layer of a polyester fiber. This process occurs because chloroform partially dissolves the polyester, which provides the penetration and fixation of titania nanoparticles to the surface layer of a fiber after drying. According to Figure 3(*a*), coating a polyester fiber with titania nanoparticles obtained by method II shows the greatest stability since it keeps the initial level of its activity even after 20 washing cycles. The reason is a special morphological form (rodlike) of the generated aggregates [Figure 2(*b*)] which apparently possess higher penetrating ability, despite their greater hydrodynamic radius of aggregates in a solution as compared to TiO_2 nanoparticles produced by method I. Photocatalytic activity in the photodestruction of the model dye on the surface of a polyester fiber modified with titania sol in both cases reveals similar changes. It can be explained by the quantitative similarity of key factors responsible for the number of free hydroxo radicals formed during irradiation, namely the degree of crystallinity and the specific surface area.

Thus, we described an original method of modifying polyester fibers with titania. The titania nanoparticles with different crys-

‡ For the room-temperature synthesis of a crystalline titania hydrosol (method II), 5 ml of titanium isopropoxide was added dropwise to 100 ml of deionized water containing 10 ml of acetic acid with vigorous stirring at room temperature for 24 h. The freshly prepared sample was kept without stirring at room temperature and atmospheric pressure. It became transparent in 10 days. The surface area of the dried sample was 108 $m^2\ g^{-1}$, the pore volume was 0.069 $cm^3\ g^{-1}$, and the average pore size was ~3.8 nm.

The impregnating solution was obtained by the consecutive mixing of 1 ml (method I) or 3 ml (method II) of a titania hydrosol, 10 ml of isopropanol and 20 ml of chloroform. The polyester fibers were processed with the freshly prepared impregnating solution at 50 °C for 1 h, dried at 60 °C for 2 h and washed with twice-distilled water to remove non-bonded titania and organic solvents.

talline forms were produced employing a low-temperature sol-gel method with nitric or acetic acid as a peptizing agent. Upon the partial dissolution of a polyester fiber surface, the nanoparticles penetrate into the surface layer of the fiber, and they are firmly fixed. The processed polyester fibers exhibit high self-cleaning properties and retain them even after 20 washing cycles.

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