Photocatalytic Degradation of Synthesized Colorant Stains on Cotton Fabric Coated with Nano TiO_2

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Abstract: Optimization of cured cotton textiles through self-cleaning property constructs the main goal of present investigation. Cotton textiles with 0.1, 0.3, 0.5, 1 and 1.5 wt% were cured by Nano-titanium dioxide (P25 Degussa) with and without using cross-link method. Stability of the TiO_2 coatings is a particular requirement for textiles because they are subject to frequent washing hence use of a suitable coating condition is necessary. During this study sucsinic acid was used as spacers to attach TiO_2 to cotton. Viscosity degree of titania particles to cotton fabrics is studied by burning method by determining the percentage of titania coated. Further, following experiments were conducted: thermal behaviour of curing samples with TGA, self-cleaning degree of curing cotton fabrics and stained samples with Dark green BN green 6 and Reactive orange V-2G dyes under irradiation of 20 & 400 W UV lamps using reflectance spectrophotometer, structure and morphology of titania coated cotton fabric through scanning electron microscopy (SEM) and crystallinity of titania coatings by X-ray diffraction (XRD). Tearing strength of cured cotton fabrics was investigated before and after employing irradiation process. Results show that stability of Nano TiO_2 coating and degree of self-cleaning cured with cross-link method is extremely higher than in non cross-link operation and cotton cellulosic chains are not decomposed by photocatalytic activity of titania.

Keywords: Self-cleaning, titania, photocatalytic, cotton, cross-linking, irradiation.

1. Introduction

In the late 1960s, Akira Fujishima, Tokyo University alumnus, started his investigation about reaction of semiconductors against light. At that time, photocurrent reaction of zinc oxide semiconductor electrode on aqueous solution was studied. In 1977, when Frank and Bard tested for the first time the possibility of cyanide decomposition with TiO_2 in water, an ideal photocatalytic property was observed and it was shown that environmentally-friendly applications gained an optimal trend [1]. In recent years more attention is paid to the application of semiconductors like ZnO, Fe_2O_3, and CdS as photocatalysts to degrade organic contaminations. As a popular photocatalyst, titania has been widely used because of its various merits, such as optical and electronic properties, low cost, high photocatalytic activity, chemical stability and non-toxicity [2,3]. Some particle characters affecting photocatalytic activity are particle size, crystal structure, hydroxylated level, absolute crystallinity, intensity of light irradiation, surface absorption of contaminants, pH of the solution, and the preparation method. When TiO_2 particles' size is reduced to nano scale, photocatalytic activity increases firstly as a result of expansion of light band-gap for quantum size and secondly due to enhancement of effective surface area [4-8]. TiO_2 is used for self-cleaning surfaces and has now emerged in commercial products ranging from kitchen and bathroom ceramic tiles, and fabrics, to indoor air filters, and window glass section [9]. When TiO_2 catalysts are subjected to irradiation with photons of energy equal to or higher than their band gap, the generated electron-hole pairs can induce the formation of reactive oxygen species, such as hydroxyl radical and superoxide radical that are directly involved in the oxidation processes leading to the degradation of both contaminants and microorganisms [10]. Titanium dioxide exists in three crystalline phases: Rutile, anatase, and brookite. Among these three forms, rutile is more sustainable than the other two forms. Anatase and brookite, on the influence of heat, would change to rutile. Structure of rutile and anatase is tetragonal while brookite structure is orthorhombic [11]. Although some applications such as normal solution filtering do not require crystalline membranes, crystallinity is essential when biocompatible, photocatalytic, or semiconducting properties are desired.

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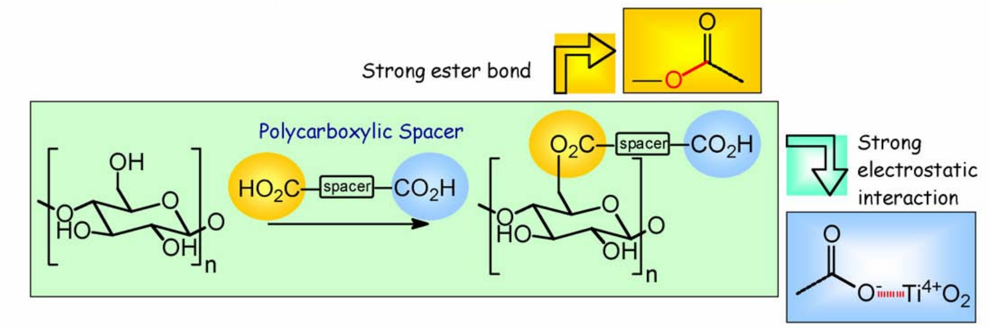

Scheme 1 Connection of spacer to cotton and TiO_2 using cross-link method.

For example, anatase phase titania is preferred in dye sensitized solar cells and catalysis, whereas rutile is mostly used in the area of dielectrics and high temperature oxygen gas [12]. Reports reveal that anatase TiO_2 basically produces hydrogen peroxide, while rutile TiO_2 produced superoxide radical from oxygen. This difference was explained by the higher photocatalytic activity of anatase TiO_2 and by the difference in the surface conditions of their crystalline structures. Since rutile TiO_2 has lower activity than anatase TiO_2 in general, a synergy effect was reported for the high photocatalytic activity by mixing rutile TiO_2 into anatase TiO_2 [13]. Both anatase and rutile have accessible band-gaps, their photoactive nature means that radical species are produced at their surfaces in the presence of sunlight and water. The incorporation of titania nanoparticles with cellulose or cotton surfaces has been reported to create a self-cleaning phenomenon [14]. 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. Such a product could have applications in the EU market of about 14 million meters of textiles/year [15]. Cellulose is the most abundant and widespread biopolymer on Earth. Owing to its abundance, biodegradability, and specific properties ,cellulose is a very important renewable resource for the development of environment friendly, biocompatible, and functional materials, quite apart from its traditional and massive use in papermaking and cotton textiles. Cellulose fibres present a polar surface associated to the hydroxylated nature of the constituting anhydroglucose units. Such feature is responsible for the high hydrophilicity of cellulose, enabling the establishment of strong hydrogen bonding between fibres and the formation of three dimensional fibre-based structures. On the other hand, the presence of these hydrophilic groups can promote the nucleation and growth of inorganic phases, such as TiO_2, at the cellulose fibre surfaces and thus allowing production of nanocomposites [16]. One way to graft nano TiO_2 on cotton fabrics is achieved using cross-link method. This spacer needs to have at least two free carboxylic groups to be able to bind both the cotton and the TiO_2. The spacer should also have an acceptable chemical and thermal stability. Cotton-cellulose is a polysaccharide with many free hydroxyl groups on the surface. The spacer will be introduced by formation of a covalent ester-bond. This indicates esterification of a spacer carboxylic group through cellulose carboxylic group. This implies esterification of one carboxylic group of the spacer by a hydroxyl group of cellulose. The second spacer carboxylic group is meant to anchor TiO_2 by electrostatic interaction. Previous work shows that TiO_2 presents a strong electrostatic interaction with carboxylic groups (Scheme 1) [17,18].

2. Experimental

2.1 Materials

The white cotton fabric bleached with H_2O_2 supplied by Yazdbaf, Iran. sodium hypo-phosphate (NaH_2PO_2) from Fluka as catalyst, succinic acid ($C_4H_6O_4$) as cross-link agent from Merck, Nano dioxide titanium powder from Degussa (P25, Germany), having 21 nm particle size and BET area $55m^2/g$, were prepared.

2.2 Coating process

Two methods of (not) using cross-link were used to coat cotton fabrics with titania. Cross-link method was performed in 7 stages as follows:

1-Cotton fabric was washed with distilled water at 80°C for an hour to remove wax and extra materials.

2-Samples of Washed cotton were immersed in an aqueous solution with succinic acid as cross-link agent (6%, w/w) in the presence of sodium hypo-phosphate as catalyst (4%, w/w) for 1 h.