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In situ sonosynthesis of nano TiO_2 on cotton fabric

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ABSTRACT

Here, titanium dioxide nanoparticles (NPs) were sonosynthesized and loaded simultaneously onto the cotton fabric. Titanium tetra isopropoxide (TTIP) was used as precursor and ultrasonic irradiation was utilized as a tool for synthesis of TiO_2 in low temperature with anatase structure and loading nanoparticles onto the cotton fabric. TiO_2 loaded cotton fabric was characterized by XRD, FE-SEM, EDS, and XRF. Moreover, several properties of the treated cotton fabrics such as self-cleaning, UV protection, washing durability, and tensile strength were studied. The effect of variables, including TTIP concentration and sonication time, was investigated based on central composite design (CCD) and response surface methodology (RSM). The results confirmed formation of anatase TiO_2 nanoparticles with 3–6 nm crystalline size loaded onto the cotton fabric at low temperature (75 °C) that led to good self-cleaning and UV-protection properties. The excellent UV-protection rating of the treated fabric maintained even after 25 home launderings indicating an excellent washing durability. Interestingly, sonochemical method had no negative influence on the cotton fabric structure. The statistical analysis indicated significant effect of both TTIP concentration and sonication time on the content of the loaded TiO_2 on the fiber and self-cleaning properties of the fabric.

1. Introduction

TiO_2 nanoparticles (NPs) have created a new approach for remarkable applications as an attractive multifunctional material [1,2]. TiO_2 NPs have been used to achieve antibacterial [3–5], self-cleaning [4–8], UV protection [4,5,9,10], flame retardant [5,11], hydrophobic [12] or hydrophilic [5,13] properties, dye degradation in textile effluent [14], and free carrier dyeing of polyester fabric [15]. In addition, the nanoparticles can be used as a nano photo scouring and nano photo bleaching of cotton [16] and wool [17], and nano catalyst for cross-linking cellulose with poly carboxylic acids [6,12,18,19].

The application of ultrasound in nanocrystalline synthesis has recently become an important method [20]. It is well-known that physical and chemical effects of ultrasound arise from acoustic cavitation phenomena: the rapid formation, growth, and the collapse of bubbles in liquid [21,22]. The collapse conditions depend on the intensity and frequency of the ultrasound as well as liquid physical properties and temperature of the liquid [23]. The extremely high local temperature (>5000 K), pressure (>20 MPa) and very high cooling rates (>10^{10} K s^{-1}) confer sonicated solutions unique properties that can reduce metal ions to metal or metal oxide nanoparticles [21]. The major advantage of this method, apart from its fast quenching rate and operation at ambient conditions, is simplicity and energy efficient process [21]. Abundant groups led by Gedanken published numerous papers dealing with sonochemical synthesis of nanomaterials [24,26]. Their major works were focused on the application of ultrasonic irradiation for preparing diverse nanometer scale materials.

Moreover, sonochemical irradiation has been proven as an effective technique for the synthesis of nanocrystalline TiO_2 at low temperature [20,24,25]. Huang et al. [24] introduced a simple and efficient method for the selective synthesis of anatase and rutile as well as their mixture with various precursors, including titanium tetra isopropoxide (TTIP) and titanium tetrachloride, using ultrasonic irradiation. Guo et al. [25] synthesized TiO_2 NPs under high intensity ultrasonic irradiation at 90 °C. Ghows and Enterazi [20] synthesized titania NPs by hydrolysis of TTIP under ultrasonic irradiation at low intensity and relatively low temperature (75 °C) in a short time. Furthermore, synthesis of nano structured TiO_2 *via* an ultrasound assisted sol–gel method has been reported by Prasad et al. [27,28]. They have been found that the temperature of the phase transformation of anatase-to-rutile and crystallite size reduced with ultrasonic irradiation [27].

Recently, ultrasonic irradiation has been used to deposit metals or metal oxides nanoparticles on different types of fabrics. For instance, silver nanoparticles were synthesized and deposited on

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different types of fabrics [29,30], silver chloride nanoparticles were achieved on silk yarn [31], ZnO nanoparticles [32], CuO nanoparticles [33], and TiO_2 nanoparticles [34] were synthesized and deposited on the surface of the cotton fabrics.

During the past years, many efforts have been made to immobilize TiO_2 NPs onto textile materials; however a few investigations have so far dealt with in situ sonosynthesis of TiO_2 NPs on textiles. This method can be used not only for reducing finishing processes, but also for improving washing durability. However, sol–gel method has been used for synthesis and deposition of TiO_2 NPs on the cotton fabric. Daoud and Xin [35–37] reported the successful nucleation and growth of anatase crystallite on the cotton fabrics at low temperature. They suggested that coating with titania imparted UV protection, antibacterial performances, and self-cleaning properties to the cotton fabric [35–37]. Uddin et al. [38] deposited and grafted TiO_2 NPs on the cotton fabric by using sol–gel method at low temperature created self-cleaning and UV protection properties on the treated cotton fabric. These methods involved two-step processes, which were started with synthesis of TiO_2 NPs and followed by coating process [35–38]. Pereleshtein et al. [34] synthesized and deposited TiO_2 NPs in two forms of anatase and rutile on the cotton fabric in one-step process. They declared that sonochemical irradiation led to formation of the crystalline phase of titania without requiring subsequent heating [34].

To the best our knowledge, the only research in this field involved using high intensity ultrasonic horn (20 kHz, 750 W) [34], however in this paper, ultrasonic bath was utilized for sonosynthesis of TiO_2 on the cotton fabric. This study was set out to investigate the synergistic role of sonosynthesis of TiO_2 onto the cotton fabric, and to elucidate the impacts of the process on self-cleaning, UV protection, and tensile properties of the treated fabrics. For the first time, experimental parameters including TTIP concentration and sonication time were optimized accurately by using statistical analysis in order to achieve the optimal synthesis conditions and self-cleaning property.

2. Materials and methods

2.1. Materials

100% bleached cotton fabric with mass of 118 g/m^2 and warp and weft yarn density of 25 and 30 yarns/cm, respectively was used. Titanium tetra isopropoxide (TTIP), glacial acetic acid 100%, and methylene blue (C.I. Basic Blue 9) were supplied by Merck Co. (Germany). All chemical reagents were used without any purification. Non-ionic detergent (Rucogen DEN) based on fatty alcohol ethoxylated was purchased from Rudolf Chemie Co. (Tehran, Iran). Distilled water was used in all preparations.

2.2. Methods

2.2.1. Scouring

The cotton samples were washed in a bath containing 1 g/L nonionic detergent (Rucogen DEN) with L:G = 40:1 (liquor to good ratio) at 60 °C for 15 min. Next, it was rinsed with distilled water and dried at 70 °C for 15 min.

2.2.2. In situ sonosynthesis of TiO_2 NPs onto the cotton

Nanocrystalline TiO_2 was synthesized and loaded onto the cotton simultaneously by hydrolysis of titanium tetra isopropoxide (TTIP) in the presence of distilled water, acetic acid as a dispersant, and the cotton fabric under ultrasonic irradiation (50 kHz, 50 w). The preparation procedure for in situ sonosynthesis of nano TiO_2 on the cotton fabric is illustrated in Fig. 1a. In typical synthesis, 100 mL distilled water was mixed with 0.2 mL acetic acid under vigorous stirring (250 rpm) in 250 mL glass beaker for 5 min. A piece of the cotton fabric (10 × 10 cm) was then immersed in prepared solution (total volume of 100.2 mL) and sonicated in an ultrasonic bath with dimensions of 0.24 × 0.14 × 0.14 m for 5 min. The beaker was kept in the bath for sonication as shown in Fig. 1b. 9 mL TTIP was then poured drop-wise into the working solution during sonication. The mixture was sonicated for 4 h under ambient condition (25 ± 3 °C). The ultrasonic bath was equipped with digital heating control system. To find proper initial and final temperature of process as well as appropriate sonication time for formation of anatase phase, preliminary experiments were carried out as reported in Appendix A. Supplementary data. Based on the preliminary results, the temperature was adjusted to 25 °C that was then increased to 75 °C during 2 h and hold to the end of the procedure by introducing a flow of fresh water to the ultrasound bath. However, the fabric color had not changed at the end of the procedure. The treated fabric was remained for 24 h under ambient air (25 ± 3 °C); eventually, the product was washed thoroughly with distilled water and dried at 70 °C for 15 min.

In order to accentuate the crucial influence of ultrasound, similar sample was prepared by conventional stirring method that 4 mL TTIP was added to mixture solution including 100 mL distilled water, 0.2 mL acetic acid, and the cotton fabric (10 × 10 cm) under vigorous stirring condition (250 rpm). The temperature was set exactly similar to the sonochemical method, although a hotplate was used as a heating source. In present paper this sample will be hereafter designated as sample S.

2.2.3. Solid powder extraction

The obtained solution (section 2.2.2) was centrifuged for 20 min (15,000 rpm) in order to remove TiO_2 powder. The white resultant powder was then washed with distilled water and dried at 70 °C for 4 h.

2.2.4. The experimental design

Table 1 shows the experiments designed with different TTIP concentration and sonication time using central composite design (CCD) as well as blank sample (pristine cotton) and sample S. The influence of the variables on the results including: Y_1: the relative amount of synthesized and loaded TiO_2 onto or into the cotton fabric, Y_2: self-cleaning after 10 h daylight irradiation (ΔRGB_{10}), and Y_3: self-cleaning after 20 h daylight irradiation (ΔRGB_{20}) was adjusted by using second polynomial function according to Eq. (1):

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 \; i \geq j \; i,j = 1,2,3. \qquad (1)$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i are regression coefficients that explain the influence of the variables in their linear form, b_{ij} are regression coefficients of the interaction terms between variables, and c_i are the coefficients of quadratic form of variables [11,19].

2.3. Test methods

2.3.1. Characterization

The surface morphologies of the samples were observed by a Hitachi S4160 field emission scanning electron microscope (FE-SEM) equipped with Oxford Energy Dispersive spectroscopic (EDS) analysis system. EDS analysis was also performed to verify the elemental composition of the loaded materials on the fiber surfaces. The TiO_2 content of the samples was estimated using X-ray fluorescence (XRF) microanalyzer (Unisantis XMF-104, Germany) with 40 kV, 300 mA and Mo radiation. XRD patterns were collected by means of Inel EQUINOX 3000X-ray diffractometer to identify the crystal phase and structure. Cu Kα radiation (λ = 1.5406 Å)