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# UV-stable paper coated with APTES-modified P25 $TiO_2$ nanoparticles

Fei Cheng[a], Seyed Mani Sajedin[a], Stephen M. Kelly[a,*], Adam F. Lee[b], Andreas Kornherr[c]

[a] Department of Chemistry, University of Hull, Cottingham Road, Hull HU6 7RX, UK
[b] European Bioenergy Research Institute, Aston University, Aston Triangle, Birmingham B4 7ET, UK
[c] Mondi Uncoated Fine Paper, Haidmuehlstrasse 2-4, A-3363 Ulmerfeld-Hausmening, Austria

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ABSTRACT

In order to inhibit the photocatalytic degradation of organic material supports induced by small titania ($TiO_2$) nanoparticles, highly photocatalytically active, commercially available P25-$TiO_2$ nanoparticles were first modified with a thin layer of (3-aminopropyl)triethoxysilane (APTES), which were then deposited and fixed onto the surface of paper samples via a simple, dip-coating process in water at room temperature. The resultant APTES-modified P25 $TiO_2$ nanoparticle-coated paper samples exhibit much greater stability to UV-illumination than uncoated blank reference paper. Very little, or no, photodegradation in terms of brightness and whiteness, respectively, of the P25-$TiO_2$-nanoparticle-treated paper is observed. There are many other potential applications for this Green Chemistry approach to protect cellulosic fibres from UV-bleaching in sunlight and to protect their whiteness and maintain their brightness.



## 1. Introduction

Titanium dioxide ($TiO_2$) is a very important industrial material. It has been widely used, for example, in pigments, paints, cosmetics, photocatalysis and photocatalyst supports (Chen, Wang, & Chiu, 2007; Gesenhues, 2001; Fernandez-Garcia, Martinez-Arias, Hanson, & Rodriguez, 2004; Hebeish, Abdelhady, & Youssef, 2013; Youssef, Kamel, & El-Samahy, 2013). Titanium dioxide has also been used for anti-reflection and optical coatings as well as beam splitters due to its large dielectric constant and high refractive index (Samuel, Pasricha, & Ravi, 2005). Titanium dioxide naturally exists in three crystalline polymorphs, i.e., anatase, rutile and brookite of which the most commonly used forms are anatase and rutile (Pelton, Geng, & Brook, 2006; Wold, 1993). Both the anatase and rutile $TiO_2$ polymorphs are in photocatalysis, for example, whereby the anatase $TiO_2$ polymorph shows the higher photocatalytic activity (Linsebigler, Lu, & Yates, 1995). P25 is a commercial $TiO_2$ powder (EVONIK), which consists of 80% of the anatase phase and 20% of the rutile phase of titanium dioxide. These commercial titania nanoparticles have been widely used as photocatalysts in photochemical reactions due to their very high photocatalytic activity (Ryu & Choi, 2008). Unfortunately, the high redox activity of titania can lead to photodegradation of any organic substrate, support, functional material, etc., which limits the application of titania nanoparticles in the paper, textile, paint and plastic film industries, for example. The use of rutile titania nanoparticles with a large diameter ($d > 200$ nm), and core/shell $TiO_2/SiO_2$ nanoparticles are the most common approaches adopted to inhibit the photocatalytic effect of $TiO_2$ nanoparticles and thereby to inhibit the degradation of the catalyst support (Furusawa, Honda, Ukaji, Sato, & Suzuki, 2008).

3-Aminopropyltriethoxysilane (APTES) is frequently used as a coupling agent for attaching organic molecules to hydroxylated silicon oxide or metal oxide substrates, due to the presence of the terminal amine group on the propyl chain, (Kim, Cho, Seidler, Kurland, & Yadavalli, 2010; Pasternack, Amy, & Chabal, 2008) for example, APTES has been used to link proteins to $TiO_2$ surfaces or to promote cell adhesion to $TiO_2$ surfaces (Balasundaram, Sato, & Webster, 2006; Filippini et al., 2001). Adsorption of APTES-modified organic dyes onto $TiO_2$ surfaces has also been reported using APTES as the coupling agent (Andrzejewska, Krysztafkiewicz, & Jesionowski, 2004). Although in many cases APTES has been used for many applications, the nature of the dominant conformation or chemical form of APTES at interfaces is often open to doubt and conjecture, because these factors depend not only on the reaction conditions, but also on the crystal structure of the $TiO_2$ substrate (Song, Hildebrand, & Schmuki, 2010; Chen & Yakovlev, 2010; Ukaji, Furusawa, Sato, & Suzuki, 2007). APTES has not, to the authors' best

* Corresponding authors. Tel.: +44 1482 466347.
*E-mail addresses:* cheng_f@hotmail.com (F. Cheng), s.m.kelly@hull.ac.uk (S.M. Kelly).

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knowledge, been used so far to deposit and bind $TiO_2$ nanoparticles to the surface of cellulose or to that of its many diverse derivatives.

Cellulose is the most abundant, widespread and naturally occurring biopolymer in nature. Alongside its traditional applications in paper and cotton textiles, cellulose is also a very important environmental friendly, biocompatible and cost-effective, carbon-based resource for the development of novel advanced functional materials (Habibi, Lucia, & Rojas, 2010). Cellulose is a high-molecular-weight, linear, mainchain carbohydrate polymer consisting of repeating β-D-glucopyranose moieties, which are linked covalently through acetal functions between the equatorial OH groups. The presence of a large number of hydrophilic hydroxyl groups (Klemm, Heublein, Fink, & Bohn, 2005; Roy, Semsarilar, Guthrie, & Perrier, 2009) in cellulose and its derivatives can promote the nucleation and growth of inorganic phases at the cellulose fibre surface and thus facilitate the production of organic/inorganic nanocomposites (Pinto, Marques, Barros-Timmons, Trindade, & Neto, 2008; Li et al., 2009; Iguchi, Ichiura, Kitaoka, & Tanaka, 2003).

The protection of cellulosic textiles against different kinds of degradation and the creation of new functionalised cellulose derivatives can be realised by coating the textiles with silica sols with a nanoparticle diameter smaller than 50 nm (Mahltig, Haufe, & Bottcher, 2005). The surface of vegetable cellulose fibres has been modified, for example, with a nanoparticle-functionalised siloxane coating, first using the hydrolysis of tetraethoxysilane (TEOS), octyltrimethoxysilane (OTMS) or polydimethylsiloxane (PTMS), followed then by layer-by-layer deposition of previously synthesized titanium dioxide nanoparticles (Goncalves, Marques, Pinto, Trindade, & Neto, 2009). Morphologically well-defined silica nanoparticles have been successfully deposited onto cellulose fibre surfaces via a polyelectrolytes layer-by-layer approach (Pinto et al., 2008).

In this report, commercially available, highly photochemically active and strongly UV-absorbing P25 $TiO_2$ nanoparticles (EVONIK) have been modified to form a strongly UV-absorbing, but non-photo-catalytically active, coating on the surface of cellulose paper in order to significantly improve its resistance to UV-degradation in terms of maintaining the original brightness and whiteness of paper samples under standard, commercial UV-illumination test conditions. In a simple, two-step process, the surface of small, photo-active titania nanoparticles was first modified with a thin coating of APTES to produce deactivated, APTES-coated $TiO_2$ nanoparticles, which were then deposited and fixed on the surface of paper simply using a very simple, water-based dip-coating procedure at room temperature. The APTES-modified $TiO_2$ nanoparticles protect the paper from photochemical bleaching as far as possible under standard UV-illumination test conditions. No impact or spray coating techniques, chemical binders, surfactants, dispersants or a post-treatment curing step are required in this two-step process. The presence of additional amine and silane groups present in the APTES coating covering the surface of the APTES-modified $TiO_2$ nanoparticles should promote attachment and fixation to the many hydroxyl-groups present on the surface of the cellulose fibres. The APTES-modified $TiO_2$ nanoparticles are prepared in a simple fashion at a relatively low reaction temperature. The structural and mechanical properties of the cellulose fibres will not be impaired by the presence of the APTES-modified $TiO_2$ nanoparticles, whose presence just on the outer surface, not in the core, of the fibre will ensure a high effective absorption of UV-light. A much lower loading of nanoparticles is required using this surface-based approach than dispersing nanoparticles in the bulk fibre mixtures used to prepare paper, fabrics, textiles, etc., which is advantageous in terms of minimising contamination of the environment with nanoparticles.

## 2. Experimental

### 2.1. Materials and characterisation methods

The $TiO_2$ P25 nanoparticles were sourced from EVONIK. (3-Aminopropyl)triethoxysilane [APTES, $(C_2H_5O)_3Si(CH_2)_3NH_2$] and xylene were supplied by Aldrich and used as received. The paper samples, which are 1 mm thick and which do not possess a surface coating, such calcium carbonate or china clay, were provided by Mondi Uncoated Fine Paper, Austria. Acetone was sourced from Fisher Scientific, UK, and used as received.

Fourier transform infrared spectra were recorded on a Nicolet Magna-500 FTIR spectrometer. X-ray powder diffraction (XRD) analyses were performed on a SIEMENS D5000 Instrument. Scanning electron microscopy (SEM) images were obtained using a Carl Zeiss SMT 'EVO60' SEM microscope operating at 20 kV and EDX data were obtained using an Oxford Instruments 'INCA' energy dispersive X-ray spectrometer. Transmission electron microscopy (TEM) was collected using a Jeol 2010 TEM running at 200 kV. TEM images were obtained with a Gatan Ultrascan 4000 digital camera. Solid samples were prepared by suspension in distilled water and 5 μL aliquots of a suitable dilution dropped onto carbon-coated copper grids. The BET surface area and pore size diameter of the various titania powders were calculated from nitrogen adsorption/desorption isotherms at 77 K using a Micromeritics three star 3000 instrument. The whiteness of the standard paper samples and the APTES-modified $TiO_2$ nanoparticle paper samples was measured using a standard whiteness tester (Lorentzen&Wettre, Elrepho). The brightness of these samples was determined, before and after the suntest (Suntest $XLS_+$; ATLAS Material Testing Solutions). The suntester allows irradiation of paper samples with a xenon lamp under accurate, repeatable conditions (i.e. 90 min, 500 W, and 2700 kJ/m$^2$). XPS was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutraliser and magnetic focusing lens employing Al $K_\alpha$ monochromatic radiation (1486.7 eV). Surface elemental analysis was undertaken on Shirley background-subtracted spectra applying the appropriate instrument- and element-specific response factors. Spectral fitting was conducted using CasaXPS, version 2.3.14, with binding energies corrected to the C 1s peak at 284.5 eV and with the high-resolution C 1s, O 1s, N 1s, Si 2p and Ti 2p XP spectra fitted using a common Gaussian/Lorentzian peak shape. Errors were estimated by varying the Shirley background subtraction procedure across reasonable limits and re-calculating fits. The photocatalytic activity of the P25 $TiO_2$ and APTES-modified $TiO_2$ was evaluated in terms of the degradation of Rhodamine B (Ren, Chen, Zhang, & Wu, 2010). P25 $TiO_2$ or APTES-modified $TiO_2$-powder (10 mg) was suspended in 10 mL of water and then 10 mL of Rhodamine B solution (20 mg/L) was added to the suspension solution. The UV irradiation was carried out under a UV light at 365 nm for 30 min. The suspension solutions were centrifuged at 10,000 rpm for 15 min. The Rhodamine B content in the solutions was determined by UV–vis analysis in the range between 300 and 700 nm using a Perkin Elmer Lambda 25 spectrometer.

### 2.2. Modification of $TiO_2$ surfaces with APTES ($TiO_2$-APTES)

APTES (1.5 mL) was added to a stirred suspension of P25 $TiO_2$ nanoparticles (0.5 g) in xylene (50 mL). After allowing the reaction mixture to react at 50 °C for 10 h, a white powder was obtained by centrifugation of the cooled reaction mixture, which was then washed with xylene and then twice with acetone followed by drying under vacuum overnight.