Multicomponent polymer coating to block photocatalytic activity of TiO_2 nanoparticles†‡

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Chemical grafting of anti-oxidant molecules with an additional hydrophobic polymer coating directly onto TiO_2 particle surfaces, using sonochemistry, is found to eliminate photocatalytic degradation enabling highly effective screening against UV radiation.

It is well recognized that UV light in the range 280–400 nm is responsible for the majority of photodamage to the skin. UV light from the sun can be characterized in three ranges: UVA, 320 to 400 nm, UVB, 280 to 320 nm, and UVC, 200 to 280 nm. UVC is the most energetic and hence can cause the highest amount of damage. On the other hand, it is also absorbed by the atmospheric ozone, and hence is not a factor near sea level. UVB is mostly stopped within the epidermis and causes the inflammation known as "sunburn". UVA is the longest wavelength component and hence can penetrate into the dermis where melanoma originates.[1,2]

Inorganic particles have been introduced in sunscreen formulations in order to reflect the UV radiation and reduce the amount of the organic molecules required in order to achieve the designated SPF factors. Recently, these inorganic materials have been shown to be an imperfect solution. Wu *et al.*[3] showed that photodegradation of squarylium cyanine dyes was accelerated when TiO_2 particles were dispersed in the aqueous medium, prior to illumination.

It is well known that when TiO_2 is illuminated with UV light, the energy is greater than its band gap which promotes electrons from the valence to the conduction band. These electrons then migrate quickly to the particle's surface and react with oxygen to form superoxide and hydroxyl radicals. Dunford *et al.*[4] showed that when plasmid DNA was exposed to simulated sunlight-UVA and UVB rays, in the presence of TiO_2 particles, the hydroxyl radicals were instrumental in accelerating the breakage of the chains. Data from *in vivo* study of skin penetration is scarce, and inconclusive, since the experiments have been performed on intact skin and without controlled UV exposure.[5,6] The interactions of the particles with whole tissue physiology is complex and outside the scope of this paper. However, in order to understand it, we must first begin by isolating the interaction of the particles with individual components. Here we focus on the production of free radicals and their interaction with DNA. Work is currently in progress on the interactions of these particles with different types of cells.[7]

Since the photocatalytic activity is the culprit in all the damage scenarios, we propose to eliminate the photocatalytic activity simply by effectively blocking the emission of the surface electrons. Here, we demonstrate that this could be accomplished by chemical grafting of anti-oxidant molecules directly onto the TiO_2 particle surface, using sonochemistry. This would minimize free radical formation, while still providing protection against UV irradiation. Furthermore, we show that grafting an additional hydrophobic polymer coating, can stabilize the anti-oxidant without increasing the local pH of the solution, thereby allowing these particles to be further tested in tissue culture.

Ultrafine rutile TiO_2 (US Cosmetics) nanoparticles were used in the coating process. The average size of the particles was measured by transmission electron microscopy and found to have a mean diameter of 30.2 ± 6.9 nm. Antioxidant formed from grape seed extracts (Oligomeric Proanthocyanidins)[8] and anionic polymer poly[methyl vinyl ether/maleic acid] were mixed in a 1 : 1 ratio and dissolved in a 22 : 1 water–denatured ethanol solution using a lightening mixer at 25 °C. After the solution became homogeneous, a new mixture was prepared composed of 30 wt% of the antioxidant/anionic polymer solution, 22 wt% DI water, 43 wt% titanium dioxide and 5% hydrophobic polymer (triethoxysilylethyl polydimethylsiloxyethyl dimethicone, Shin-Etu Chemical Co., Ltd). The entire slurry was then sonicated for 30 min with medium intensity at 25 °C using an ultrasonic probe (Sonicor Instrument Co.) at 20 kHz. This last step was performed in order to encapsulate the anionic/antioxidant molecules and prevent them from desorbing, dissociating, or lowering the pH of the solution. In order to precipitate the particles and remove the excess polymers, the resultant mixture, which was a thick colloidal suspension, was then centrifuged for 15 min at 9000 rpm and washed with DI water. The washing procedure was then repeated three times in order to ensure that all unattached materials were removed. The product was then dried at 110 °C under vacuum for 16–20 h.

In order to determine the amount of the polymer coating the particles, we performed thermal gravimetric analysis (TGA) on both the coated and uncoated particles, where the heating rate was set at 10 °C min^{-1}. We found that the coating decomposed in the region of 300–500 °C, from which we found that the total mass fraction of coating was approximately 12%. The density of the

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† The HTML version of this article has been enhanced with colour images.
‡ Electronic supplementary information (ESI) available: Scheme 1: Proposed mechanism for binding the antioxidant, anionic polymer and the dimethicone derivative polymers to the TiO_2 nanoparticles. Table 1: Characteristic parameters of the polymers and TiO_2 particles used. See DOI: 10.1039/b709449c

particles was measured using a pycnometer and found it to decrease from 4.23 to 0.986 g cm^{-3} after coating.

The thickness of the polymer shell could then be derived from the measured parameters using the relationship; $\alpha = \beta(r_1 + r_s)^3/r_1^3$, where $\alpha = \rho_1/\rho_2$, = 4.32 is the ratio of the densities of the bare TiO_2 particles, ρ_1, and the functionalized particles, ρ_2, and $\beta = M_1/M_2$ where M_1 and M_2 are the masses of the bare and functionalized TiO_2 particles, respectively. The mass ratio of the functionalized particles can be obtained from the TGA measurements, while the mean mass of the bare particles can be estimated from the mean particle radii, r_1 = 15 nm, and the density to obtain, β = 0.88. Substituting into the previous relation, we find the radius of the shell, r_s = 11 nm. Then calculating the mass of the shell, $m = 6.8 \times 10^{-17}$ g, dividing by the mass per chain and the mean area of the bare TiO_2 particle core, we obtain a grafting density of $\sigma \approx 0.5$ chains nm^{-2}. This value is nearly the size of the intermolecular spacing; hence the chains in the coating are fully stretched.

In order for these particles to maintain their initial function, we also tested whether the functionalization process affects their ability to screen against UV radiation.

The relative intensity of the transmitted light, as measured with a spectrophotometer is marked on each sample. Coated and uncoated particles were suspended in a silicone/ester oil phase emulsion, similar to the base of suntan lotion and spread on a slide at a concentration of 2.0 mg cm^{-3}.[9] The material was dried for 15 min and the SPF factor was calculated from the absorption curve, as measured using a UV spectrophotometer, in the wavelength region 280 to 320 nm. A value of SPF = 22 was found for both types of particles, indicating that no degradation of UV screening occurred upon coating. In order to determine whether the coating was effective in reducing the electron emission form the particles upon exposure to UV light, an auxiliary test was performed where the florescence of disodium 2′,4′,5′,7′-tetrabromo-4,5,6,7-tetrachlorofluorescein (also known as Red Dye 28), was measured. 0.15 g of either coated or uncoated TiO_2 particles were added to a cuvette containing solutions of the dye and the samples were illuminated under a solar simulator with 5.42 μW cm^{-2} in the wavelength region 280–400 nm. The cuvettes are shown as an inset to Fig. 1 after exposure for 27 h. From the figure, in the cuvette with TiO_2 particles most of the dye is removed after irradiation, while the color in the cuvette containing the coated TiO_2 particles is identical to the color of the unexposed control sample. Since the degradation of the dye fluorescence is known to result from the electron emission from the TiO_2 particles surface, these results indicate that even though the coating does not effect the SPF value, or the UV absorption, it is very efficient at preventing the emission of the electrons in the solution surrounding the particles and producing free radicals. Hence the coating could also prevent discoloration commonly observed in formulations using TiO_2 particles blended with polymers or colloidal suspensions.[10]

A more dramatic consequence of the free radical production has been shown by Serpone *et al.*[11] to result in damage of DNA. We therefore prepared a solution of λ-phage DNA (48,502 bp) at a concentration of 50 μg ml^{-1} in 1 × TBE buffer, and added 2 mg ml^{-1} of either nano-TiO_2 (rutile) or surface-modified nano-TiO_2. We placed each sample 3 cm from UVA, UVB or UVC sources. The exposure times ranged from 1 to 4 h for different

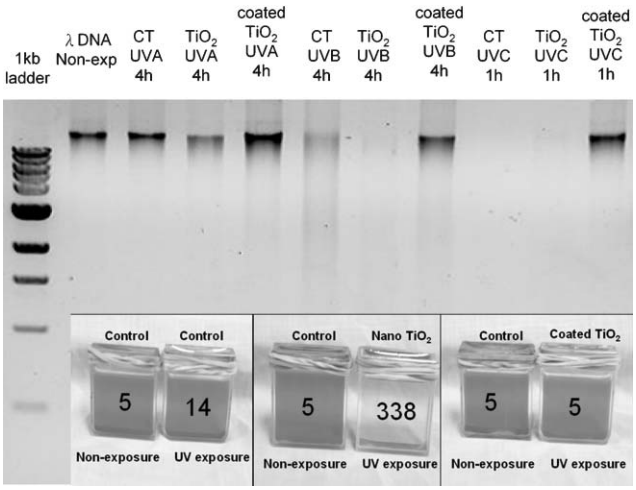

Fig. 1 λ DNA gel electrophoresis for the control (no UV exposure), after exposure to UVA, UVB or UVC with TiO_2 or with coated TiO_2. Inset: Red 28 dye (1.2×10^{-4} M) assay for photodegradation where the sample on the left, in each panel, was exposed to simulated solar rays for 27 h. The control sample consists of DI water and ethanol. The test samples contain uncoated TiO_2 (middle) and coated TiO_2 (left) nanoparticles.

wavelengths. The gel electrophoresis was prepared with 0.8% (w/v) agarose in 1 × TAE buffer and a 5 V cm^{-1} electric field was applied for 30 min. The results are shown in Fig. 1(a). The left-most column is a control run consisting of a 1-kb ladder which shows reasonable separation of the digested DNA fragments. The first column corresponds to λ DNA which was not exposed. λ DNA is too large to elute through the gel and all the intensity remains at the input of the channel. Exposure of the λ DNA to UVA for 4 h does not seem to reduce the intensity of the signal. A significant reduction is observed after exposure for 4 h in the presence of TiO_2 uncoated particles, followed by a diffuse tail. This indicates that the DNA was broken forming short fragments which were eluted rapidly in the channel. No change is observed in the channel containing the coated TiO_2 particles.

Exposure to UVB radiation for 4 h produced significant breakage in the column containing DNA and in the column containing DNA and uncoated TiO_2 particles, no DNA remains. Similarly exposure to UVC for 1 h completely destroys DNA with and without the presence of TiO_2 particles. On the other hand, it is remarkable that the intensity of signal from the DNA remains nearly unchanged in the column where the coated TiO_2 particles were added prior to irradiation.

In order to confirm that the absence of intensity in the UVC column is the result of chain scission, we also checked these results by performing surface electrophoresis. This is a new technique that has been described previously[12] where a droplet of DNA is deposited upon a silicon wafer and the migration time of individual chains is measured at a fixed distance from the injection point. Since this technique does not use a sieving medium, it has the advantage that it could detect simultaneously DNA chains that vary by more than six orders of magnitude in the number of base pairs.[12] The results of the measurements corresponding to the samples irradiated with UVC are shown in Fig 2(a)–(d). Here we see that a single peak is eluted in the control sample, which is not exposed to UV radiation. The peak position is similar to that

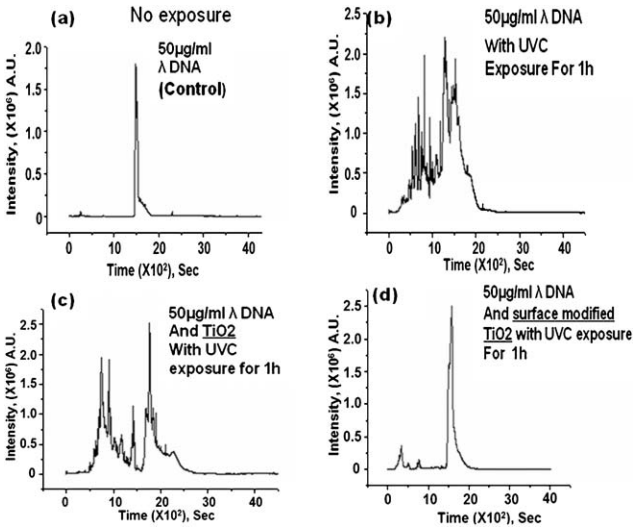

Fig. 2 Surface electrophoresis of λ DNA, florescence intensity plotted as a function of time. (a) Control, unexposed sample. (b) λ DNA exposed to UVC for 1 h, (c) λ DNA with TiO_2 nanoparticles after exposure to UVC for 1 h. In this case also, we can observe DNA breakage with many fragments. (d) λ DNA with coated TiO_2 nanoparticles after exposure to UVC for 1 h.

reported in the literature, corresponding to λ DNA.[12] Exposure with and without uncoated TiO_2 nanoparticles results in a complex spectrum with multiple peaks eluting faster than the central λ peak, which correspond to short broken fragments. On the other hand, a large single peak, arriving at the same time as that in the unexposed control sample, is observed for the DNA where the coated TiO_2 particles were added prior to exposure, confirming the electrophoresis results which do not show breakage of the λ DNA. In addition, the fact that the mobility of the chains is unaltered also indicates that no detectable hydrolysis of the chains occurs with the coated particles. The mobility of the DNA chains on the surface is not only a function of the chain length, but also the interaction of the chains with the substrate, and the chain rigidity. Hence if the DNA became hydrolyzed, as a result of the irradiation, even in the absence of chain scission, the surface mobility and interactions would have been altered.

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