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Abstract

© 2020, Springer Science+Business Media, LLC, part of Springer Nature. The use of TiO₂ nanoparticles in sunscreen products has raised concern over their oxidative potential and adverse health effects brought about by their propensity to produce free radicals when exposed to UV radiation. In this study, an investigation into industry-scalable methods for synthesizing rutile TiO₂ nanorods with controllable morphological characteristics was carried out. The effects of hydrothermal reaction temperature and nitric acid concentration on the crystal phase, composition and morphology were explored to assess the most suitable conditions for reproduction. Optimal reaction conditions for obtaining purely rutile TiO₂ nanorods occurred when treating the titania precursor at 150 °C for 24 h with 16 M nitric acid. Here, these rutile nanorods are decorated with CeO₂ nanoparticles, as a means of producing a material with high UV attenuation and low photocatalytic activity. The nanocomposite materials are prepared using facile hydrothermal and precipitation methods and showed selective UV absorption whilst also demonstrating a reduction in photocatalytic activity compared to bare rutile TiO₂ nanorods of up to 88% and 77% when exposed to UV and solar simulated light. The results suggest CeO₂/TiO₂ could be safely applied as an 'active' inorganic UV absorber in sunscreen products.

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**Hydrothermal Synthesis of Rutile TiO₂ Nanorods and their Decoration with CeO₂
Nanoparticles as Low-Photocatalytic Active Ingredients in UV Filtering Applications**

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Abstract

The use of TiO₂ nanoparticles in sunscreen products has raised concern over their oxidative potential and adverse health effects brought about by their propensity to produce free radicals when exposed to UV radiation. In this study, an investigation into industry scalable methods for synthesizing rutile TiO₂ nanorods with controllable morphological characteristics was carried out. The effects of hydrothermal reaction temperature and nitric acid concentration on the crystal phase, composition and morphology were explored to assess the most suitable conditions for reproduction. Optimal reaction conditions for obtaining purely rutile TiO₂ nanorods occurred when treating the titania precursor at 150°C for 24 hr in 16 M nitric acid. Here, these rutile nanorods are decorated with CeO₂ nanoparticles, as a means of producing a material with high UV attenuation and low photocatalytic activity. The nanocomposite materials are prepared using facile hydrothermal and precipitation methods and showed selective UV absorption whilst also demonstrating a reduction in photocatalytic activity compared to bare rutile TiO₂ nanorods of up to 88 % and 77 % when exposed to UV and solar simulated light. The results suggest CeO₂/TiO₂ could be safely applied as an 'active' inorganic UV absorber in sunscreen products.

Keywords: photocatalysis, nanocomposite, sunscreens, surface modification, nanorods

1. Introduction

Titanium dioxide (TiO_2) has long been used as an inorganic based ultraviolet (UV) filtering ingredient in many sunscreen products. Modern formulations often contain TiO_2 in the form of nanoparticles due to the enhanced absorption provided across the UVA (320 – 400 nm) and UVB (290 – 320 nm) wavelength bands, as well as the increased transparency in the visible light region (400 – 700 nm)[1]. However, there is concern associated with the enhanced photocatalytic activity of this material at this size range and their role in the formation of reactive oxygen species (ROS) such as the highly reactive hydroxyl radical ($\text{OH}\cdot$)[2]. TiO_2 nanoparticles have also been shown to induce genotoxic and cytotoxic effects on human cell lines, particularly after exposure to UV radiation, which leads to the production of ROS[3,4]. ROS production can also affect other active ingredients present in sunscreen formulations. Degradation of these ingredients can lead to a loss of sunscreen efficacy and lowering of the labelled sun protection factor (SPF). The extent of ROS production and the photocatalytic activity of TiO_2 can be modified by manipulating certain material parameters such as the crystal phase, particle size and the surface coating.

The two main crystal phases linked with TiO_2 use in photocatalysis are anatase and rutile. Often, the anatase phase is associated with higher photocatalytic activity, however, there is also substantial evidence to suggest certain compositions of anatase-rutile mixtures can outperform either single phase[5,6]. One such proprietary mixture, AEROXIDE® TiO_2 P25 (also known as Degussa P25), is a popular IUPAC reference material used in photocatalysis research, and is a TiO_2 nanopowder with an anatase-rutile ratio of 4:1[7]. This same ratio of anatase-rutile has also been found in certain sunscreen products containing TiO_2 which were shown to cause accelerated damage to organic surface coatings used in outdoor roofing applications[8]. As such, an essential parameter for improving the safety of nanoparticulate TiO_2 in sunscreens is to ensure the use of rutile TiO_2 . Although lower in activity, the rutile crystal phase can still exhibit

substantial photocatalytic properties, leading to the need for additional modification. Surface coatings have been utilized as a means of mitigating the photocatalytic effect of nanoparticulate TiO₂. Different types of coating materials can be used and are often based upon silicon or aluminium oxides, hydroxides or polymers[9]. The principle mechanism behind this process is that the photo-inactive coating helps promote recombination of photo-excited electron/hole (e⁻/h⁺) pairs in the core TiO₂ material, by presenting an insulating layer with an increased band gap, thus reducing the probability of ROS production. However, such methods are not entirely foolproof as evidenced by the incorporation of additional antioxidant compounds in many sunscreen formulations to counteract remnant ROS produced[2]. Complex coating materials can also require lengthy synthesis processes hence increase the price of production. We have previously investigated the surface modification of TiO₂ nanoparticles with bismuth subcarbonate ((BiO)₂CO₃) and achieved a product with lower photocatalytic activity, relative to bare TiO₂, whilst still maintaining adequate UV protection[4]. However, the core TiO₂ nanoparticles used were the aforementioned highly photoactive P25 TiO₂, and so, the composite produced was not directly suitable for UV filtering applications. Cerium oxide (CeO₂) is a wide-band gap semiconducting material that has also been previously investigated as an alternative coating material due to its ability to absorb UV radiation and act as a free-radical scavenger by cycling of surface Ce sites through the 3⁺/4⁺ oxidation states[10]. Combined with *in vitro* and *in vivo* evidence of its superoxide dismutase mimetic activity in human cells exposed to radiation, CeO₂ nanoparticles could be the solution to countering the photocatalytic activity of TiO₂ used in sunscreens[11-13]. In addition to the reduced photocatalytic activity, certain criteria outlined by governing health and cosmetic regulatory organisations, such as the European Union Scientific Committee on Consumer Safety (SCCS) need to be considered when developing cosmetically used TiO₂[14]. These include the purity, crystal phase composition, aspect ratio and surface area of the core TiO₂ nanoparticles and the stability of the coating material.

In this work, we describe the preparation of rutile TiO_2 nanorods and a $\text{CeO}_2/\text{TiO}_2$ nanocomposite material, by facile hydrothermal and precipitation routes and describe the potential application of these nanoparticles for use in UV filtering applications, with emphasis on controlled TiO_2 particle morphology and reduced ROS generation in the nanocomposite material. Rutile TiO_2 nanorods were prepared by treating an amorphous TiO_2 precursor under mild hydrothermal conditions. Subsequently, the TiO_2 nanorods were decorated with CeO_2 nanoparticles through a simple chemical precipitation method. An investigation into the optical and morphological properties of the materials was carried out. Furthermore, the photocatalytic activity of the composite and pristine materials were assessed through the irradiation of the water soluble dye, crystal violet (CV) with UV radiation and solar simulated light. The performance of these synthesized materials were also compared to two commercial TiO_2 products, namely, AEROXIDE® TiO_2 P25 (Evonik, DP25) and rutile TiO_2 nanoparticles (Sigma Aldrich, SR). Finally, the new materials are benchmarked against the SCCS criteria mentioned above and the suitability of these materials for application as inorganic UV absorbers are also assessed.

2. Experimental Section

2.1 Synthesis of rutile TiO_2 nanorods

The rutile TiO_2 nanoparticles were synthesized through a two-step process based upon a similar procedure previously outlined by Bu *et al* [15]. The first step involves the generation of amorphous TiO_2 from the precursor source, titanium butoxide (TBT, 97%, Sigma Aldrich). Typically, 10 mL of TBT was dissolved in 40 mL of warmed ethanol (EtOH). Separately, a solution of 0.5 M ammonium hydroxide (NH_4OH , 28 – 30% NH_3 basis, Sigma Aldrich) was prepared. To the dissolved TBT, 75 mL of the 0.5M NH_4OH was added drop-wise under vigorous stirring. The resultant suspension was stirred a further 30 min before being collected via centrifugation and washed multiple times with deionized (DI) water and EtOH. The

precipitant obtained was then dried at 90°C for 12 hrs then ground into a powder with a mortar and pestle. The second step of the synthesis involves the hydrothermal synthesis of the rutile TiO₂ nanoparticles from acidic media. A suspension of the amorphous TiO₂ was prepared in 10 mL of nitric acid (HNO₃, 70%, Sigma Aldrich) at various concentrations and sonicated for an hour. The concentration of acid used was adjusted through 3 – 16 M by diluting in DI water. After sonicating, the suspension was transferred to a 45 mL Teflon cup and sealed in an acid digestion vessel (Parr Instruments, USA). The vessel was then transferred to an oven and heated for 24 hrs at either 150°C or 180°C so as to assess the temperature effects on the resultant material. After cooling back to room temperature, a white precipitate was obtained. The suspended precipitate was carefully diluted in DI water to reduce the acid concentration before being separated via centrifugation. The separated solid was further diluted with DI water and EtOH before being dried in air at 100°C for 12 hrs. A fine powder was obtained after crushing the dried product with a mortar and pestle.

2.2 Synthesis of the CeO₂/TiO₂ nanocomposite

A suspension of the rutile TiO₂ nanorods (HTIO₂, Table 1, 0.5g) was prepared in 50 mL of DI water. To the suspension, an amount of cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99%, Sigma Aldrich) was added so as to give a relative weight percentage of Ce/Ti of 7.5 wt. %. The suspension was then heated to 60°C before the addition of, firstly, 1 mL of concentrated NH₄OH and 1 mL of hydrogen peroxide (H₂O₂, 30 wt. % in H₂O, Sigma Aldrich) with rapid stirring. The resulting precipitate was collected and washed several times with DI water and EtOH before being dried at 100°C overnight. The final nanocomposite was obtained by grinding the dried product into a fine powder.

2.3 Materials Characterization

X-ray diffraction patterns were collected (XRD, Enhanced Mini-Materials Analyser X-Ray Diffractometer, GBC Scientific) using Cu K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 25 mA to assess sample crystal phase composition. Further examination of the crystal phase composition of the samples were assessed via Raman spectra (LabRAM HR Evolution, Horiba). Morphological information was obtained using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images (JSM-7500FA field emission electron microscope, JEOL) were obtained on platinum (Pt) coated specimens attached to sticky carbon tape on aluminium stubs (Al). TEM images (JEM-ARM200F, JEOL) were collected on specimens drop-cast in EtOH on carbon-coated copper grids. Particle size measurements were performed using the TEM images obtained and the software program Image-J. Additionally, electron-energy loss (EELS) spectra were obtained from the same TEM equipped with an EELS spectrometer (Quantum 963 SE image filter, Gatan) to investigate the crystal phase composition of the samples and distribution of Ce throughout the composite sample. Brunauer-Emmett-Teller (BET) specific surface area values were obtained using a Tristar II 3020 gas adsorption analyser (Micromeritics). The adsorbate used was nitrogen gas (N₂) and measurements run at liquid nitrogen temperature. Prior to measurement, samples were degassed overnight at 100°C.

2.4 UV-Vis Spectroscopy

Absorption spectra were obtained using a UV-1800 spectrophotometer (Shimadzu). Samples were dispersed in EtOH at a concentration of 30 mg/L and suspended using a sonication bath (Branson 3800, Ultrasonics Corp) for an hour prior to analysis. Spectra were collected over the range of 200 – 800 nm and slit width of 1 nm. Diffuse reflectance spectra were obtained on powder samples using a UV-3600 spectrophotometer (Shimadzu) coupled with an integrating sphere attachment (ISR-3100, Shimadzu) scanning between 200 – 800 nm. The optical band gaps (E_g) for samples were calculated from Tauc plots which follow the general expression:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

Where α , h (eVs), ν (s^{-1}), A and E_g (eV) are the absorption coefficient, Planck constant, light frequency, a constant and the optical band gap, respectively. The value of the exponent, n , changes depending on the nature of the transition from the conduction to valence band in a semiconducting material and can take on values varying between 0.5 and 3.

2.5 Evaluation of Photocatalytic Activity

The photocatalytic activities of the prepared samples were evaluated using the aqueous dye crystal violet (CV, dye content $\geq 90\%$, Sigma Aldrich) as the decomposition target. The photoactivity of the materials tested were assessed using two different lights sources. A Rayonet photocatalytic reactor lined with 350 nm and 300 nm, 12 W phosphor-coated lamps provided a UVA/UVB light source. Solar simulated light was provided by a halogen lamp (50 W) calibrated to AM 1.5 G one sun (100 mW cm^{-2}). For both light exposure tests, a solution containing 5 mg L^{-1} of CV and 5 mg L^{-1} of the test material was prepared. The solution was thoroughly sonicated and allowed to stir in the dark for 60 min to establish the adsorption-desorption equilibrium between the dye and the tested nanoparticles. Following this, the solution was irradiated for 60 min, when exposed to simply UV radiation and 300 min, when exposed to solar simulated light. Aliquots of the solution were periodically collected and the absorbance of CV at $\lambda = 590 \text{ nm}$ recorded using a UV-Vis spectrometer (UV-1800, Shimadzu).

3. Results and Discussion

3.1. Establishment of synthesis conditions for obtaining TiO₂ rutile phase

The initial conditions for preparing the rutile TiO₂ nanoparticles were established through a series of hydrothermal experiments, cycling through various HNO₃ concentrations and adjusting the autoclaving temperature. Fig. 1 highlights the XRD patterns and Ti L_{2,3} main edge spectra obtained for the samples prepared under differing acid and temperature conditions. Online Resource 1 highlights the amorphous nature of the precipitated powder obtained prior to hydrothermal treatment, which suggests that any induced crystallinity seen post-hydrothermal treatment is a result of the treatment process. In Fig. 1(a), modification of the HNO₃ concentration resulted in a progressive transition in crystal phase, starting from a mixture of the anatase (PDF card 96-101-943), rutile (PDF card 96-900-7532) and brookite (PDF card 96-900-4138) crystal phases before transitioning to purely the rutile phase at higher concentrations of acid. The presence of brookite in the samples prepared in 3M and 6M HNO₃ (H3M and H6M) coincides with previously reported findings when preparing TiO₂ nanoparticles through precipitation in acidic media and low temperatures[16,17]. It has also been suggested that brookite nuclei may play a major role in facilitating the phase transformation of the initial precursor powder to the rutile phase during hydrothermal treatment[18].

Fig. 1 Variation of the crystal phase of the synthesized TiO₂ as influenced by the (a) concentration of HNO₃ (when treated at 180°C) and (b) autoclaving temperature (when treated with 16M HNO₃). (c) EELS line profiles obtained for sample H6M. EELS profiling location shown in Online Resource 1

The distinction between the mixed phase and pure phase samples is also evident when comparing their respective Raman spectra (Online Resource 2). A number of Raman active peaks featured for the H3M and H6M samples whilst four distinct features were seen for both samples prepared in 16M HNO₃ but at differing treatment temperatures (H16M and HTiO₂, respectively). From experimental evidence and computational studies, the number of Raman active modes typically seen for the common TiO₂ crystal phases are 4, 6 and 36 corresponding to the rutile, anatase and brookite phases[19-22]. Brookite bands present for the H3M sample were assigned in accordance with reported peak positions and are attributed to the A_{1g} (126, 152, 194, 247, 413, 452, 544 and 636 cm⁻¹), B_{1g} (213, 286, 322, 501 cm⁻¹), B_{2g} (366, 460 and 583 cm⁻¹) and B_{3g} (171 cm⁻¹) symmetries[23,21]. Similarly for the H6M sample, brookite peak assignments are given for the A_{1g} (126, 152, 195, 247 and 545 cm⁻¹), B_{1g} (214, 284, 320 and 500 cm⁻¹), B_{2g} (367 cm⁻¹) and B_{3g} (172 cm⁻¹) symmetries. It is also possible that some of these peak assignments could be due anatase vibrational modes as there is substantial overlap between certain anatase/brookite Raman active transitions. Such modes include the anatase E_g (152 and 172 cm⁻¹) and A_{1g} (500 cm⁻¹) vibrational modes. The four major peaks observed at

approximately 143, 446 and 609 cm^{-1} for both the H16M and HTIO2 samples are assigned to the B_{1g} , E_g and A_{1g} Raman active modes for the rutile crystal phase. These also appear prominently in the H6M sample spectrum, corroborating with the higher rutile phase content observed from XRD. The broad feature centred at 235 cm^{-1} has been previously attributed to crystal lattice disorder or second-order scattering[24,25]. No evidence of brookite or anatase Raman active modes for the two 16M HNO_3 synthesized samples again corroborates with the XRD data, highlighting the rutile phase purity of the samples.

Fig. 2 SEM and TEM (inset) micrographs of the hydrothermally synthesized TiO_2 samples.

(a) H3M, (b) H6M, (c) H16M and (d) HTIO2

Fig. 2 highlights SEM and TEM images obtained for the H3M, H6M and H16M samples prepared at 180°C and the HTIO2 sample prepared at 150°C. A mixture of particle morphologies were observed for both the H3M and H6M samples (Fig. 2(a) and (b)), varying from smaller spheroidal particles to larger, elongated rod-like particles which can be attributed to the mixed crystal phase composition for these samples. These differences in morphology for particles in the same sample are thought to arise due the mixed crystal phase composition of the sample and was further investigated through EELS. Fig. 1(c) compares the EELS profiles for the Ti $L_{2,3}$ edges taken from different particles observed through TEM analysis of the H6M sample. The line profile obtained for the spectra labelled rutile was collected from a rod-like particle (Online Resource 3), similar to those present in the H16M and HTIO2 samples. The splitting and shape of the L_3 edge peak centered at 459.6 eV is in agreement with previously reported findings for the rutile TiO_2 crystal phase and is attributed to electron transitions from the $2p_{3/2}$ state to e_g state of the Ti 3d orbital produced by crystal field splitting[26,27]. Variation in shape of this transition between TiO_2 crystal phases is due to the differences in the coordination of oxygen around titanium and can be used as a method for studying the crystal structure of individual particles. As can be seen, the line shape of this peak varies when obtained from the more spheroidal particles, giving shapes consistent with previously reported EELS spectra for the anatase and brookite crystal phases[28,29]. The identification of all three main TiO_2 crystal phases is also consistent with the XRD and Raman data obtained. Both the H16M (Fig. 2(c)) and HTIO2 (Fig. 2(d)) samples displayed elongated particles of varying length. The rod-like morphology formed is indicative of rutile particle growth along the [001] orientation and has been previously ascribed to rapid rutile chain growth along the c axis of the TiO_6 octahedra due to corner sharing on opposite ends in the (001) plane[15,30]. Employing an acid-based solvent during hydrothermal synthesis of TiO_2 nanoparticles has also been previously shown to influence the crystal phase formed[31-33]. A high concentration of NO_3^- has been suggested to facilitate and promote corner shared bonding, as in the case of the rutile crystal

phase, and could explain the crystal phase transformation observed at higher concentrations of HNO_3 treatment[34,35]. There is also a significant difference in the length and size of the rod-like particles formed when hydrothermally treated at different temperatures. Particles obtained at 180°C (H16M $\bar{x}$ (width) = 50 ± 10 nm) are notably larger than those obtained at 150°C (HTIO_2 $\bar{x}$ (width) = 16 ± 3 nm) and treated for the same period of time (24 hr). This is expected considering particle growth is strongly governed and facilitated by the temperatures and pressures employed during synthesis.

One of the proponents for a commercially “acceptable” UV filter, and subsequent sunscreen formulation, is transparency. Inorganic based UV filters, such as TiO_2 , have long suffered issues with this due to their inherently high refractive index and large particle size (aggregates in the μm range), contributing to substantial visible light scattering and opaqueness. Reducing the primary particle size can help improve the ‘transparency’ of such particulate filters by enhancing UV absorption mediated by a higher percentage of surface atoms compared to bulk TiO_2 and a reduction in visible light scattering governed by Mie theory[2,36]. It is also an important criterion outlined by the SCCS to ensure that the particle size fits with the number size distribution of 30 – 100 nm. As such, for the remainder of this work, the hydrothermally synthesized rutile TiO_2 discussed is that prepared at 150°C using 16M HNO_3 owing to its smaller particle size relative to the 180°C treated sample. Furthermore, in accordance with SCCS criteria for cosmetic TiO_2 nanoparticles, the 150°C , 16M HNO_3 hydrothermally prepared sample addresses the crystal phase criteria by being composed solely of the rutile crystal phase. In addition, the morphology and aspect ratio of these particles are in line with variants included in the criteria ie being of lanceolate/needle shape and aspect ratio between 1.0 to 4.5 (calculated aspect ratio of 6 ± 2 falls within this range based upon length and width measurements as shown in Table 1).

Table 1: Experimental results obtained relating to crystallite/particle size; surface area; optical band gap and photocatalytic activity for the as-prepared and commercial samples. The errors shown are taken as the standard deviation between triplicate measurements

Sample	Mean Crystallite Size ^a (nm) (XRD)	Mean Particle Size (nm) (TEM)	Surface Area (m ² g ⁻¹)	Band Gap (eV)	Rate Constant k (min ⁻¹)($\times 10^{-3}$)	
					UV	AM1.5G
DP25	37	40 $\pm$ 20	59 $\pm$ 2	3.37	40 $\pm$ 1	12.3 $\pm$ 0.4
HTIO2	25	L: 90 $\pm$ 20 W: 16 $\pm$ 3	44.0 $\pm$ 0.8	3.04	10.1 $\pm$ 0.3	3.63 $\pm$ 0.05
SR	54	60 $\pm$ 20	22.4 $\pm$ 0.3	2.94	7.4 $\pm$ 0.1	4.22 $\pm$ 0.08
CTIO2	-	1.8 $\pm$ 0.4 ^b	75 $\pm$ 2	2.95	0.88 $\pm$ 0.07	0.55 $\pm$ 0.01

^a Mean crystallite sizes calculated using the Scherrer equation for the most intense peak in each XRD pattern. ^b This measurement is for the size of the CeO₂ nanoparticles decorating the rutile TiO₂ nanorods.

3.2 Comparative performance of hydrothermally synthesized rutile TiO₂ and composite CeO₂/TiO₂ compared to commercial products as a potential UV filter

Fig. 3 depicts the XRD patterns for the commercial TiO₂ powders, DP25 and SR, as well as the as-prepared HTIO2 and CeO₂/TiO₂ (CTIO2) nanoparticles. Of the samples tested, the SR, HTIO2 and CTIO2 samples displayed single phase reflections, indexed to the rutile crystal phase as expected. DP25 exhibited a mixed phase composition consisting of approximately 80% anatase to 20% rutile, which corroborates with previously published findings for the material[37,38]. The lack of reflections due to a CeO₂ impurity phase in the CTIO2 sample could be a result of a lack of crystallinity but also due to the very low loading of CeO₂ expected. In fact, the weight loading percentage (wt%) of Ce relative to Ti was determined to be 7 $\pm$ 4 wt% as calculated through EDS (Online Resources 4 and 5). The associated mean crystallite sizes and BET specific surface area values are listed in Table 1.

Fig. 3 XRD patterns for the commercial TiO₂ and hydrothermally synthesized powders tested

A comparison of the particle morphologies and sizes between the synthesised and commercial samples is shown in Fig. 4. The DP25 sample (Fig. 4(a)) consisted of a relatively inhomogeneous mixture of spherical, ellipsoidal and cubic particles with a mean particle size of 40 ± 20 nm. Similarly, the other commercial product, SR (Fig. 4(c)), also displayed particles of varying morphology albeit with a larger mean particle size of 60 ± 20 nm. The larger particle size of SR is also consistent with the smaller specific surface area calculated as compared to DP25 (22.4 ± 0.3 compared to 59 ± 2 m² g⁻¹). HTIO2 and CTIO2 (Fig. 4(a) and (d)) both consist primarily of the hydrothermally synthesized rutile TiO₂ nanorods as shown previously in Fig. 3. The mean widths and lengths for these rod-like particles were determined to be 16 ± 3 and 90 ± 20 nm, respectively. The specific surface area for HTIO2 was calculated to be 44.0 ± 0.8 m² g⁻¹, lower than that of DP25, which could be again attributed to differences in particle dimensions, but also the synthesis and treatment methods involved in preparing either sample.

Fig. 4. SEM and TEM (inset) micrographs of (a) DP25, (b) HTiO₂, (c) SR and (d) CTiO₂.

Interestingly, the CTiO₂ sample was found to have a specific surface area of $75 \pm 2 \text{ m}^2 \text{ g}^{-1}$, approximately 21% larger than that of DP25, despite being primarily based upon the same rutile TiO₂ as those in the HTiO₂ sample. A possible reason for the increased surface area could be due to the presence of extremely fine CeO₂ nanoparticles at the surface of the rutile rods in CTiO₂. As depicted in Fig. 5, the CeO₂ nanoparticles appear deposited, not as a uniform coating of complete coverage, but as small aggregates or even as individual particles along the surface of the core TiO₂ rods (Fig. 5(b) and (c)). The addition of these extremely fine particles ($\bar{x} = 1.8 \pm 0.4 \text{ nm}$) along the surface of the TiO₂ rods could be providing additional sites for gas sorption, leading to an overall increase in the specific surface area. HAADF of these fine CeO₂ nanoparticles (Fig. 5(c)) suggest these particles are crystalline as evidenced by the uniformity

of lattice fringes, which further suggests that the lack of a CeO₂ impurity phase from XRD of CTiO₂ is due to the low loading of CeO₂ relative to the core TiO₂.

Fig. 5 (a) High-angle annular dark-field (HAADF) image of the CTiO₂ composite sample. (b) EELS map detailing the distribution of Ti and Ce for the particles shown in (a) in the form of heat map. (c) High resolution HAADF of the particles shown in (a), highlighting the presence of a CeO₂ nanoparticle at the surface of the rutile TiO₂

The ultraviolet filtering properties of the commercial and synthesized samples were assessed through dilute UV-Vis spectroscopy. Fig. 6 highlights the absorption spectra obtained for each sample in ethanol. DP25 displayed the highest absorbance, with peak absorbance occurring in the UVB wavelength region, coinciding with its use as a UVB filtering agent in suncreening products. The optical band gap for DP25 was calculated to be 3.37 eV, which is in close agreement with previously reported findings[39]. The commercial rutile sample, SR, showed significantly less absorbance, with peak absorbance centred within the UVA region. Band gap values of 3.04, 2.94 and 2.95 eV were calculated for the HTiO₂, SR and CTiO₂ samples. The narrowing of these band gap values is a reflection of the rutile crystal phase composition of these samples relative to DP25, which consists of a mixed anatase/rutile crystal composition. Although the absorbance properties of the HTiO₂ and CTiO₂ samples are less than that of

DP25, substantial absorbance across both the UVA and UVB wavelength regions highlights their suitability as UV protective agents.

Fig. 6 UV-Vis absorption spectra recorded for the commercial and as-prepared TiO₂ samples for 30 mg L⁻¹ suspensions prepared in ethanol. The absorbance spectra for a sample of CeO₂ nanoparticles (30 mg L⁻¹) prepared through the same precipitation process used for the CTiO₂ nanocomposite is also shown for reference.

The photocatalytic activities were evaluated through the photo-mediated catalytic decomposition of CV. Such degradation has previously been ascribed to follow a pseudo first order rate mechanism, namely, the Langmuir-Hinshelwood model[40]. The rate of dye-degradation can be expressed as follows:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (2)$$

Where t is the irradiation time (min), C_0 and C the initial and instantaneous dye concentration (mg L⁻¹) and k the apparent rate constant (min⁻¹). Fig. 7 displays the relative decrease in CV absorbance over time and the respective kinetics plots when exposed to UV radiation (Fig. 7(a)) and solar simulated light (Fig. 7(b)). The apparent rate constants, k , for each tested sample were calculated and are listed in Table 1. For both light sources, DP25 exhibited the highest performance of degradation with k values of 40 ± 1 and 12.3 ± 0.4 ($\times 10^{-3}$ min⁻¹). This was

expected since, not only is it manufactured and used as a reference photocatalyst, but also when considering the materials properties. Coupled with its already very high UV absorbance, relative to the other samples, DP25 is also a mixture of the anatase and rutile crystal phases. The anatase TiO_2 crystal phase is often cited as having greater photocatalytic activity than the rutile phase, particularly in relation to the degradation of organic compounds under aerated conditions[41]. It has also been reported that mixed phase TiO_2 displays even greater photocatalytic activity relative to either of the single phases, depending on the composition[42]. Sunscreen products in the past that have used micronized TiO_2 previously have been shown to contain particles of a similar crystal phase composition to that of DP25. In fact, a study investigating the discolouration of coated steel panels linked the usage of sunscreen products containing DP25-like TiO_2 by workers installing the panels to the early onset of degradation[8,43]. The reason for this discolouration was attributed to the photocatalysed production of ROS or, more specifically, $\text{OH}^\cdot$. As such, it is desirable to modify sunscreen based TiO_2 in a manner that mitigates this free radical production whilst also maintaining adequate protection from UV radiation. Samples HTIO2 and SR both displayed reduced UV and solar simulated light photocatalytic activities, as compared to DP25. A number of factors may be in play to explain the observed results. To begin, both HTIO2 and SR are purely rutile which, as previously mentioned, is often found to be less active than that of the anatase crystal phase. Another factor involved, is the reduced absorbance by these samples across the UVA and UVB bands relative to DP25. This means that the production of ROS will likely be reduced due to the decreased excitation of the catalysing material through UV photon absorption. Yet another factor to consider is the lower specific surface areas of HTIO2 and SR as compared to DP25. In this instance, the reduced surface area means that there are fewer surface active sites for the CV dye and free water based species (H_2O , OH^- , H_3O^+) to adsorb to. This impairs the ability for the catalysing material to directly degrade the dye or indirectly degrade it through the production of ROS, thus leading to a decrease in photocatalytic activity. Although lower in

UV absorbance performance, taking into account the reduced photocatalytic activity seen and the physical parameters in line with SCCS criteria, the HTIO₂ sample also, on its own, appears an ideal platform for conducting future investigations into the surface modifications of sunscreen based TiO₂ UV filters. In the case of the CTIO₂ sample, yet a further reduction in photocatalytic activity whilst under either UV or solar simulated light was observed. As with HTIO₂ and SR, CTIO₂ also has weaker absorbance across the UV region as compared to DP25, however, the surface area calculated for CTIO₂ is much larger, which would suggest some other factor is involved. Furthermore, a comparison of the UV absorptive properties of the CTIO₂ nanocomposite as compared to pristine CeO₂ nanoparticles (Fig. 6) at the same concentration (30 mg L⁻¹) reveals that the CeO₂ imparts minimal additional UV absorbance benefits. This is particularly apparent as the actual loading of CeO₂ in the CTIO₂ nanocomposite (7±4 wt%) is significantly lower than the amount of CeO₂ present in the UV-Vis absorbance measurements of the CeO₂ nanoparticles. As such, the contribution of the CeO₂ nanoparticles in the CTIO₂ sample towards the decreased photocatalytic activity observed due UV 'blocking' is relatively small. Instead, deposition of CeO₂ nanoparticles on the surface of the rutile TiO₂ rods in CTIO₂ could be providing a means of inhibiting free radical production or scavenging free radicals before degradation may occur. Indeed, CeO₂ nanoparticles have been reported to behave as an antioxidant as a result of a large number of surface defect sites. These defect sites enable the reversible oxidation/reduction of the cerium cation by interaction with surface adsorbed molecules, enabling scavenging of free radical species[44]. It has also been suggested that the size of the CeO₂ nanoparticles can impact this free-radical scavenging ability, whereby, as the particle size decreases, the antioxidant activity increases[10,45]. The presence of CeO₂ in CTIO₂ is thus enabling free radical scavenging of photogenerated ROS whilst also blocking surface active sites on the core rutile TiO₂ particles for adsorption of other molecules. This scavenging and blocking interplay is not perfect however, as evidenced by the small degradation that still occurs under both light sources, but is certainly much improved compared

to DP25, HTiO₂ and SR. Combined with its absorbance across the UVA and UVB regions, the material shows great potential as a new active sunscreens ingredient. The very low photocatalytic activity observed for the CTiO₂ sample also addresses another important SCCS criteria in relation to TiO₂ nanoparticle cosmetic use. Ideally, new TiO₂ based UV filters should have no photocatalytic activity, however, the SCCS considers up to 10% activity relative to a standard or corresponding un-coated/un-doped reference to be acceptable. In this instance, CTiO₂ displays up to 2% (UV light) and 4% (solar simulated light) of the photocatalytic activity of DP25, a material with a crystal phase composition exact to that of a previously used commercial TiO₂ UV filter (these percentages are based upon the calculated rate constants listed in Table 1)[8]. Compared to the uncoated form, HTiO₂, the composite sample is also substantially low in activity (9% and 15% under UV and solar simulated light), further emphasizing its applicability as a potential UV filter in sunscreens products.

Fig. 7 Photodegradation plots for the commercial and as-prepared TiO₂ samples highlighting the relative absorbance change of the crystal violet dye (left) and the degradation kinetics (right) when exposed to (a) UV radiation and (b) simulated solar radiation

4. Conclusion

In this work, we developed a low photocatalytic nanocomposite material based upon rutile TiO₂ nanorods decorated with CeO₂ nanoparticles for use as an ‘active’ ingredient in sunscreen products. The rutile TiO₂ nanorods with controlled morphology were produced using a facile hydrothermal method and exhibited physical characteristics in line with cosmetic regulatory guidelines for use of TiO₂ in cosmetic products. We demonstrated that deposition of a small

CeO₂ loading (Ce/Ti weight percentage equal to 7±4 wt%) at the surface of the TiO₂ nanorods can greatly reduce photocatalytic activity of the bare material as well as other commercial variants of TiO₂ nanoparticles under both UV and solar simulated light exposure. The reduction in photocatalytic activity and maintaining of the UV filtering properties of this nanocomposite material highlights its potential for application in sunscreen products.

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Conflicts of Interest

The authors have no conflicts of interest to state.

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