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# Suppression of the photocatalytic activity of $TiO_2$ nanoparticles encapsulated by chitosan through a spray-drying method with potential for use in sunblocking applications

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ABSTRACT

Solar exposure, in particular to UVA and UVB radiation, is a major carcinogen through direct DNA damage and the production of reactive oxygen species (ROS). Inorganic UV filters present in sunscreening agents, such as titanium dioxide ($TiO_2$), are commonly employed for protection however, due to their photocatalytic nature, they have been shown to instigate the production of ROS when irradiated with UV radiation, which in turn can lead to the degradation of the sunscreening formulation and subsequent damage to the skin. In this work, chitosan/$TiO_2$ nanocomposite particles were produced via a spray-drying method, in a single step, directly through aqueous solution for the purpose of reducing the photocatalytic activity of commercially available $TiO_2$ nanoparticles. The photocatalytic activity of the nanocomposite materials were assessed using the organic dye, crystal violet, as the degradation target and irradiating in a UV reactor. It was found that the photoactivity of the chitosan encapsulated nanoparticles were greatly reduced compared to that of the pristine $TiO_2$ nanoparticles, from 95% degradation after 120 min for pristine $TiO_2$ to 39.5% for the chitosan/$TiO_2$ spray dried particles, highlighting the potential for this simple coating process and chitosan material for application as an inactive protective coating for sunblocking applications.



## 1. Introduction

Solar UV radiation exposure, particularly to wavelengths in the UVA (320–400 nm) and UVB (290–320 nm) regions, is a known cause of skin cancers and has been proven to cause DNA damage both directly and indirectly through the production of reactive oxygen species (ROS) and induction of oxidative stress [1]. The use of UV filtering products such as sunscreens is the primary means of protection employed. These products contain organic and inorganic compounds, which can protect the skin against UV radiation through modes of absorption, scattering or reflection. Titanium dioxide ($TiO_2$) is extensively used in sunscreen products as an inorganic UV filter due to its broadband protection across the UVA and UVB regions, as well as its ability to produce high sun protection factor (SPF) products. Additionally, modern sunscreen products may now contain this material in the form of nanoparticles, not only due to the increased transparency in formulation, but also due to the increased absorbance of UV radiation they display comparatively to larger particles as a result of size quantization [2]. $TiO_2$ is a semiconducting material which, when illuminated by electromagnetic radiation of energy equal to or greater than its band gap ($E_g$), can result in the production of photoexcited electron ($e^-$)/hole ($h^+$) pairs. In the context of a biological system, these photoexcited species can interact with molecules adsorbed to the surface of these particles such as water ($H_2O$), a major constituent of human cells, producing ROS, which can go on to cause cellular and potentially mutagenic damage. Some of these ROS include hydroxyl (OH•) and superoxide ($O^{2-}$•) radicals and are due to interfacial redox reactions between the $e^-/h^+$ pairs and adsorbed $H_2O$ molecules. One study on the photoxidative ability of these photocatalysts involved the investigation of various sunscreen products containing $TiO_2$ and the effect when applied to steel sheets pre-painted with highly durable coatings such as fluoropolymer coating types [3]. After performing a series of "accelerated weathering" experiments, it was found that formulations containing these inorganic components resulted in severe degradation of the panels in terms of gloss and surface roughness. In addition, it was found through X-ray diffraction that, for a particular cream, the active UV filtering $TiO_2$ ingredient shared a similar mixed anatase/rutile crystal structure to that of the known commercial photocatalyst $TiO_2$ powder (P25). This commercial powder has been extensively studied for use in applications such as dye-sensitized solar

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cells, self-cleaning glass and water purification owing to its photocatalytic nature and ability to generate free-radicals [4–6]. As such, despite the inherent benefits of nanoparticles in sunscreen products, there has been concern as to the potential of these materials to penetrate past the skin and to induce oxidative stress due to their known photocatalytic activity. In a review on the safety of nanoparticles in sunscreens [7], it was concluded that the weight of evidence suggests that these nanoparticles remain on the surface of the skin and the outer layer of the stratum corneum, where they can only interact with non-viable cells, however there is conclusive in vitro evidence that, whilst in the presence of UV radiation, these materials are able to produce ROS, which can potentially lead to the damaging of cells. Furthermore, it has been suggested by the Scientific Committee on Consumer safety (SCCS) that highly photoactive or easily inhalable spray or cream products containing $TiO_2$ nanoparticle should not be used [8]. As such, there has been an emphasis on developing and investigating alternative materials for potential use as UV filtering additives in sunscreen products. Some potential candidates include cerium oxide $CeO_2$, iron oxide ($Fe_2O_3$) and tin oxide ($SnO_2$) [9–11]. Developing methods for reducing the production of ROS and thus reducing the photocatalytic activity of $TiO_2$ is an additional approach being explored and include methods of doping with foreign elements and coating/encapsulating with ceramic or polymeric materials. Wakefield et al. synthesized manganese (Mn) doped $TiO_2$ nanoparticles through a sol gel method with increased UVA attenuation [12]. Additionally, the free radical production was observed to be inhibited and was attributed to a free radical scavenging effect. Commonly used coating materials include wide Eg metal oxides, such as silica ($SiO_2$) [13] and alumina ($Al_2O_3$) [14] however, conflicting reports have shown that such composites could in fact enhance the photoactivity [15], thus alternative materials such as polymers have also been investigated [16]. One promising coating/encapsulating material is the natural polymer chitosan. Chitosan is a non-toxic, biocompatible and biodegradable polysaccharide that has gained interest for use in biomedical applications such as drug delivery, artificial skin and wound dressing [17–19]. Studies involving chitosan as a coating material have also been reported and have yielded promising results in the context of UV filtration. For example, an investigation into the photocatalytic activity of chitosan/ZnO composite nanoparticles synthesized through ionotropic gelation had been investigated and reported to exhibit a quenching effect on the free radical production of ZnO [20] highlighting its potential suitability for use as a UV filtering additive in cosmetic products. Work on the development of chitosan/$TiO_2$ composites has been reported but such findings generally involve chitosan as a form of scaffolding for the $TiO_2$ usually for tissue engineering [21] and ultrafiltration [22] applications. In this study, nanocomposite chitosan/$TiO_2$ particles were processed by spray drying, in a single step, and an investigation into the optical, thermal and morphological properties of the composite materials was carried out. Additionally, the effect of chitosan as a coating on the photocatalytic activity of the $TiO_2$ core nanoparticles was assessed through the photodegradation of an organic dye, crystal violet (CV), in the presence of the synthesized materials.

## 2. Materials and methods

### 2.1. Synthesis of chitosan and chitosan/$TiO_2$ particles

For the preparation of the chitosan and chitosan/$TiO_2$ (denoted CHI and CHI/$TiO_2$ here forth) nanocomposite materials, desired quantities of chitosan powder (from Shrimp shells, ≥75% deacetylated, Sigma-Aldrich) and commercial photocatalyst $TiO_2$ powder (P25, Degussa Evonik) were weighed and transferred to a beaker containing a solution of 3% v/v aqueous acetic acid ($CH_3COOH$, Sigma-Aldrich) in deionized water such that the theoretical weight ratios of chitosan to $TiO_2$ were 2:1, 1:1 and 1:0 (in the case of the purely chitosan sample). The solution was left to stir overnight so as to ensure homogeneity before being spray-dried through a 0.7 mm spray drying nozzle using a home-made spray dryer system at a flow rate of 100 mL $h^{-1}$ with an inlet temperature of 120 °C and outlet temperature of 40 °C. The resultant CHI and CHI/$TiO_2$ nanocomposite particles were cross-linked via a vapour phase process using a heated vacuum desiccator system (JP Selecta S.A.) set at 25 °C and in the presence of glutaraldehyde ($OHC(CH_2)_3CHO$, 50% in $H_2O$, Sigma-Aldrich) for 48 h.

### 2.2. Materials characterization

Scanning electron microscopy was performed on the CHI and CHI/$TiO_2$ nanocomposite particles by initially immobilizing on an SEM stage using double-sided carbon tape and coated with platinum before being analysed using an JSM-7500FA field emission electron microscope with a Bruker X-Flash 4010 10 $mm^2$ X-ray detector for energy dispersive X-ray mapping images. The average diameter and distribution of the nanocomposite particles were calculated over approximately 50 particles using the Image-J software. In addition, transmission electron micrographs were obtained using a JEM-2010 transmission electron microscope (JEOL) on low concentration samples drop cast onto lacey/carbon 200 meshes. X-ray diffraction patterns for the pristine chitosan, $TiO_2$ and nanocomposite particles were obtained using a MAC Science X-ray diffractometer scanning between $2\theta = 4–60°$ at a scan speed of 1.5° $min^{-1}$ and step size of 0.020. Thermo-gravimetric analysis (TGA) was performed using a Mettler-Toledo TGA/DSC in the temperature range of 40–800 °C at varying heating rates (between 10 and 40 °C $min^{-1}$) under regular atmospheric air. Fourier transform infrared spectra (FTIR) were collected with a Shimadzu IRAffinity-1 FTIR coupled with a Miracle 10 total reflection attachment (Shimadzu Scientific Instruments) scanning between the wavelengths of 600–4000 $cm^{-1}$ at a resolution of 2 $cm^{-1}$. Diffuse reflectance spectra were collected on the powdered samples using a UV-3600 Spectrophotometer (Shimadzu) coupled with an integrating sphere attachment (Shimadzu ISR-3100) scanning in the range of 300–800 nm.

### 2.3. Assessment of photocatalytic activity towards degradation of crystal violet

The photocatalytic activity of the composite samples were evaluated using the water soluble dye, crystal violet (CV, dye content ≥90%, Sigma-Aldrich), as a decomposition target. A RPR-200 Photochemical Reactor (Rayonet) lined with 300 nm (8×, 21 W) and 350 nm (8×, 24 W) phosphor-coated lamps were used as the irradiation source. A 100 mL suspension of the composite particles (5 mg $L^{-1}$) in a solution of the dye (5 mg $L^{-1}$) was created and transferred to a quartz beaker and left to stir under darkness in the photoreactor for 30 min. The mixture was then irradiated for a period of 2 h and 10 mL aliquots collected periodically every 20 min. The resultant degradation was assessed via UV–Vis spectroscopy using a UV-1800 Spectrophotometer (Shimadzu) by measuring the changes in the major absorption peak of the dye at $\lambda = 590$ nm.

## 3. Results and discussion

### 3.1. Synthesis setup and microstructural analysis

The setup used for the spray drying system is represented in Fig. 1. Briefly, the solution is fed to the nozzle with the aid of a peristaltic pump. The nozzle is connected to an air pump system that atomizes the solution, whilst a hot air stream is applied in co-current flow, leading to the drying of the polymer nanocomposite droplets, and subsequently to the solid particle formation.

SEM/TEM micrographs of the chitosan/$TiO_2$ composites were obtained so as to ascertain the morphological profile of the spray dried particles and to assess the loading effects on the particle sizes obtained. As highlighted from SEM (Fig. 2) and TEM (Fig. S1), the $TiO_2$ loading amount has an impact on the particle morphology and particle sizes of