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Skin protection against UV radiation using thin films of cerium oxide

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Abstract – In this work, we evaluated the efficiency of cerium oxide as sunscreen using titanium oxide as standard comparison material. Geant4 software was used to perform numerical simulation, we calculated the radiation dose that ultraviolet radiation deposits in a skin sample as a function of thin film thickness of the sunscreens. We found that in the interval between 5 and 15 nm of the thin film thickness and for wavelengths between 160 and 400 nm, cerium oxide has the potential to reduce the radiation dose more than 10% with respect to the same thickness band of titanium oxide. Using thin films of cerium oxide and titanium oxide with same thicknesses and greater than 45 nm, the difference in the attenuation of the radiation dose for both materials is less than 1%. The results lead us to propose cerium oxide as an alternative material to titanium oxide for the manufacture of sunscreens.

Keywords: UV radiation / cerium oxide / sunscreen

1 Introduction

The interactions between nanoparticles and cells are a crucial issue with regard to two fields: nanomedicine and nanotoxicology. Respect to the last field, one major concern with nanoparticles lies in their size, high reactivity and large surface area that allow them to interact with cell components, to interfere with the cell machinery, potentially triggering side effects and toxicity (Forest *et al.*, 2015).

Titanium dioxide (TiO_2) is a natural oxide of the element titanium with low toxicity; the classification as bio-inert material has given the possibility to normal-sized (> 100 nm) TiO_2 particles to be extensively used in food products and as ingredients in a wide range of pharmaceutical products and cosmetics, such as sunscreens and toothpastes (Grande and Tucci, 2016). The photocatalytic function and its ability to absorb UV radiation lead to its use as solar filter in sunscreens (Jiménez Reinosa *et al.*, 2016).

Human exposure to the TiO_2 may occur through ingestion and dermal penetration, or through inhalation route during both the manufacturing process and use. The biological effects and the cellular response mechanisms are still not completely elucidated, mechanistic toxicological studies show that TiO_2 nanoparticles predominantly cause adverse effects *via* induction of oxidative stress resulting in cell damage, genotoxicity, inflammation, immune response, metabolic change and potentially carcinogenesis (Skocaj *et al.*, 2011; Grande and Tucci, 2016).

Cerium oxide (CeO_2) nanoparticles have a great potential application as nanofiller due to its high surface area and quick transformation between $Ce^{+3} \leftrightarrow Ce^{+4}$ which enhance its antioxidant properties (Krishnamoorthy *et al.*, 2014). Chigurupati *et al.* (2013) report that topical application of water soluble CeO_2 nanoparticles accelerates the healing of full-thickness dermal wounds in mice by a mechanism that involves enhancement of the proliferation and migration of fibroblasts, keratinocytes and vascular endothelial cells. Other works, *e.g.* (Thill *et al.*, 2006; Fang *et al.*, 2010; Pelletier *et al.*, 2010) have shown the antibacterial activity of CeO_2.

The impact of the CeO_2 nanoparticles on human health and on the environment is not fully elucidated; Forest *et al.* (2017) showed that *in vitro* toxicity depends on the morphology of the CeO_2 nanoparticles, they found that, unlike cubic/octahedral nanoparticles, rod-like nanoparticles significantly and dose-dependently enhanced pro-inflammatory and cytotoxicity responses.

The ultraviolet (UV) spectrum has been conveniently divided in UVC with wavelengths from approximately 200 to 280 nm, UVB covers the spectrum from 280 to 315 nm and

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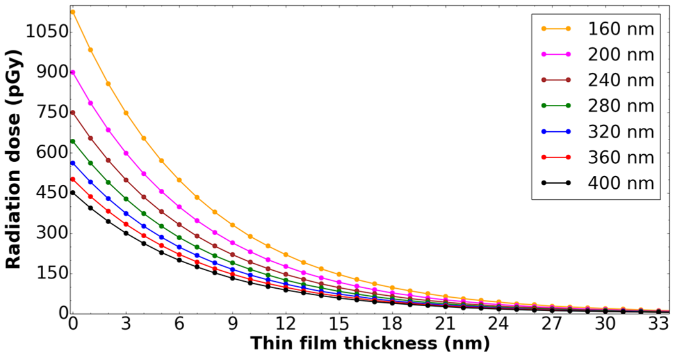

Fig. 1. Radiation dose deposited by UV radiation with different energies as a function of thin film thickness of CeO_2, the circles show the calculated values. For more information see text.

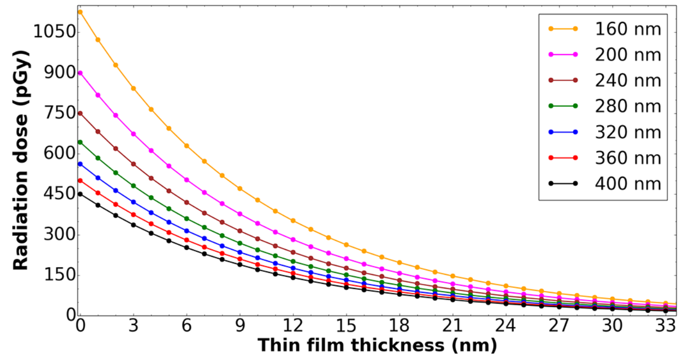

Fig. 2. Radiation dose deposited by UV radiation with different energies as a function of thin film thickness of TiO_2, the circles show the calculated values. For more information see text.

UVA from 315 to 400 nm (MacKie, 2000). The beneficial effects of human exposure to UV radiation are relatively few. The best proven is the necessity for UVB radiation to promote the synthesis in the skin of pro-vitamin D obtained in the diet, to vitamin D. Potentially damaging effects of UV radiation in human include effects on the skin, on the immune system and on the eyes.

When healthy cells are exposed to radiation, they ameliorate the damaging effect of free radicals by the release of innate protective molecules such as superoxide dismutase, glutathione, and metallothionine, which increase and intensify DNA repair mechanisms. Nonetheless, although these protective and repair mechanisms for cells are efficient, they are not capable of blocking all of the damage, which ultimately leads to the death of normal tissue (Colon *et al.*, 2009).

A number of pre-malignant cutaneous conditions are well established as being associated with an excess of UV radiation exposure. The three main types of cutaneous malignancy are basal cell carcinoma, squamous cell carcinoma and malignant melanoma. All of these types of malignancy are associated with excess exposure to ultraviolet radiation, commonly in the form of natural sunlight (MacKie, 2000). UV radiation in sunlight is the most prominent and ubiquitous physical skin carcinogen in our natural environment (Gruijl, 1999).

The potential negative effects of UV radiation on human health, discussed in the previous paragraphs, are the motivation to carry out the present work, this involves evaluating thin films of CeO_2 as a plausible sunscreen. With this aim, we developed a numerical simulation using Geant4 software, with which, we calculated the radiation dose that UV radiation fluxes with different energies deposited in the skin as a function of thin films thickness of CeO_2 and TiO_2.

2 Setup of the simulation

Geant4 software is a toolkit for the simulation of the passage of particles through matter. It is used for a variety of applications domains, including high energy physics, astro-physics and space science, medical physics and radiation protection (Allison *et al.*, 2016). Geant4 is used extensively in medical physics applications such as particles beam therapy, microdosimetry and radioprotection. The basic extensibility of the toolkit has facilitated its expansion into new user domains, such as biochemistry, material science and non-destructive scanning.

For this work, we used a skin sample (G4_SKIN_ICRP) from Geant4 material's database, with a cross section of $10 \times 10\,cm^2$ and with a thickness of 1 mm. G4_SKIN_ICRP is the skin tissue equivalent slab reported in the International Commission on Radiological Protection (ICRP) to calculate the localised skin dose conversion coefficients was adopted into the Monte Carlo transport code Geant4 (Zhang *et al.*, 2013). The ICRP is the primary body in protection againt ionising radiation, it is a registered charity and is thus an independent non-governmental organisation created by the 1928 International Congress of Radiology to advance for the public benefit the science of radiological protection (ICRP Publication 119, 2012).

We also used thin films of CeO_2 and TiO_2 as sunscreens; the thicknesses of the sunscreens used were from 1 to 44 nm, with increments of 1 in 1 nm. As UV radiation source, we used fluxes of 10^7 photons with wavelength of 160, 200, 240, 280, 320, 360 and 400 nm.

In this simulation, with the help of Geant4, we calculated the radiation dose that UV radiation with different wavelength deposited in a skin sample as a function of thin film thickness. The photons were injected perpendicularly to the cross section of the skin, with a uniform distribution.

3 Results

When calculating the radiation dose (RD) under the conditions mentioned in the previous section, we obtained that the statistical error is less than 0.2% for each calculated value. Since statistical errors are relatively small, we decided not to point them out in the figures that we present in this section.

In Figures 1 and 2, we show the RD that UV radiation deposits in the skin sample as a function of thin film thickness used as sunscreens, they are made of CeO_2 and TiO_2 respectively.

The typical RD deposited without sunscreen in the skin sample by different energies is shown on the ordinate axis corresponding to a thin film thickness of 0 nm; here, we can see that the UV radiation with higher wavelength deposits a lower RD in the skin sample, while the UV radiation with lower wavelength deposits a higher RD.

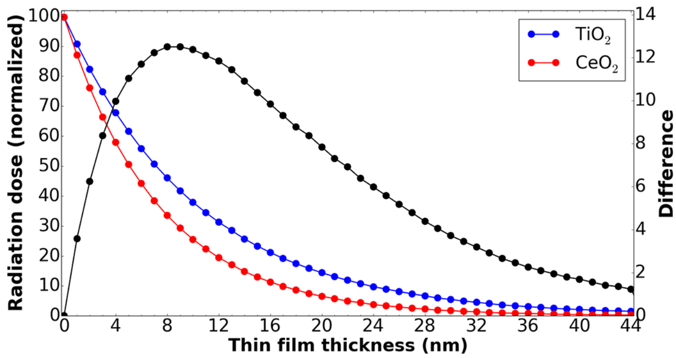

Fig. 3. On the left ordinate axis the percentage attenuation of the radiation dose deposited by UV radiation with wavelength between 160 and 400 nm in a skin sample as a function of thin film thickness made of CeO_2 (red line) and TiO_2 (blue line) is shown. On the right ordinate axis we present the percentage difference between the attenuation curves (black line). The circles show the calculated values.

In Figures 1 and 2, we can see that the RD curves show an abrupt decrease for thin film ticknesses from 0 to ~12 nm, for greater thicknesses the decrease is less pronounced.

We found that the attenuation rate of the RD curves for all wavelengths used in this work is statistically equal for every one of the materials employed as sunscreen. To reduce the RD deposited in the skin sample to 50, 10 and 1% by any wavelength, it is necessary to use thin films of CeO_2 with a thickness of 5, 17 and 34 nm, respectively; while to reduce to the same percentages the RD using thin films of TiO_2 7, 24 and 46 nm are necessary, respectively.

In Figure 3, we can see that: 1) when CeO_2 is used as sunscreen the attenuation the curve shows a greater decrease with respect to the attenuation curve obtained with TiO_2; 2) in the interval between 5 and 15 nm of the thin film thickness and a wavelength band between 160 and 400 nm, CeO_2 has the potential to reduce the RD more than 10% with respect to the same thickness band of TiO_2; 3) the maximum percentage difference (12.5%) between the attenuation curves is given at a thickness of 8 nm; 4) the percentage difference is ~1% for the thin films thickness of 44 nm and; 5) for thicknesses greater than 45 nm the percentage difference is less than 1%.

4 Conclusions

The development and evaluation of sunscreens is of vital importance due to the potential damages that sunlight over exposure may cause to human health.

In this work, we evaluated the efficiency of CeO_2 and TiO_2 as sunscreens, for this, and with the help of Geant4 software, we calculated the radiation dose that UV radiation deposits in a skin sample as a function of thin film thickness of the sunscreens.

For UV radiation with wavelength between 160 and 400 nm deposited in the skin, we found that a thin film of CeO_2 with thickness 5, 17 or 34 nm is able to reduce the radiation dose to 50, 10 and 1%, respectively, as compared to that received without sunscreen; in the case of a film of TiO_2, the thicknesses required for the same percentages reduction would be 7, 24 and 46 nm.

We also found that in the interval between 5 and 15 nm of the thin film thickness and for a wavelength between 160 and 400 nm, CeO_2 has the potential to reduce the radiation dose more than 10% with respect to the same thickness band of TiO_2. Using thin films of CeO_2 and TiO_2 with same thicknesses and greater than 45 nm, the difference in the attenuation of the radiation dose for both materials is less than 1%. The foregoing leads us to propose to CeO_2 as an alternative material to TiO_2 for the manufacture of sunscreens.

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