Alteration of skin light-scattering and absorption properties by application of sunscreen nanoparticles: a Monte Carlo study

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We report about alteration of optical properties of the superficial layer of human skin at two UV range wavelengths (310 and 400 nm) by application of 35–200 nm –sized particles of titanium dioxide (TiO_2), silicon (Si) and zinc oxide (ZnO). The study, based on combination of the Mie theory and Monte Carlo simulations, reveals the optimal sizes of the nanoparticles minimizing the transmittance of the layer for the considered wavelengths.

INTRODUCTION

Skin located on the body surface is in direct contact with the environment. It protects the inner cells and tissues from such types of hazards as mechanical, chemical, thermal, optical, etc. The skin thickness depends on the body region and varies between 1.5 and 4 mm. The comprising layers are epidermis, dermis and a layer of subcutaneous fat. The uppermost part of epidermis is known for its dead cells without nuclei and is referred to as stratum corneum or horny layer. The data about stratum corneum thickness differ in different sources: 6 – 40 μm on such common sites as the abdomen, flexor forearm, thigh, and back; however, on the palms of hands and soles of feet it is 5–10 times thicker.

Ultraviolet (UV) radiation, being a part of the solar spectrum, covers a range of 100 – 400 nm and it is usually divided into three sub-ranges: UVC (100 – 280 nm), UVB (280 – 315 nm) and UVA (315 – 400 nm). UVC is completely absorbed by the atmospheric ozone layer located at a height of 18 – 40 km above the sea level. UVB and UVA penetrate the atmosphere and affect humans. The UVB fraction is responsible for sunburn and increases the risk of basal cell and squamous cell carcinoma due to direct DNA damage. The UVA fraction causes sun tanning, photoaging, and provokes malignant melanoma by indirect DNA damage (via free radical generation). Moderate sun tanning can prevent sunburn due to increased production of melanin, a natural UV protector.

Improvement of UV protecting functions of the stratum corneum is achieved with chemical and physical compounds of sunscreens [1], i.e. light-absorbing organic chemical substances and light-scattering and light-absorbing TiO_2 and ZnO nanoparticles [2-3].

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Recently, Si nanoparticles were suggested for use in sunscreens [4]. In order to suppress the generation of free radicals by the particles in the presence of UV light, they are covered [5] with silica and alumina. Nanoparticles have a tendency to form aggregates and agglomerates in emulsions resulting in changes of their optical properties that are hard to estimate. Nevertheless, in recent years new methods were designed to produce particles with diameters of 25 nm, deviation of 15 – 20% from the mean value and agglomeration-free.

In this paper, we theoretically investigate how optical properties of skin in the UV spectral range can be modified to reduce the light transmittance by imbedding TiO_2, ZnO, and Si nanoparticels. Performed calculations are based on the Mie theory and Monte Carlo simulations.

MATERIALS AND METHODS

According to our earlier study [6], nanoparticles in sunscreens even after multiple applications are located mostly within the uppermost part (1 – 2 μm from the surface) of the stratum corneum. A mathematical model for Monte Carlo simulations developed by us is represented by an infinitely wide plane layer mimicking stratum corneum (20-μm-thick) containing nanoparticles in its uppermost part (1-μm-thick). Particle diameters were varied between 35 and 200 nm; however, all of them were of the same size for each calculation. Light scattering in this upper part is described by a linear combination (hybrid) of Mie and Henyey-Greenstein phase functions describing scattering by spherical nanoparticles and cells. For the wavelengths used in the simulations, the scattering (μ_s) and absorption (μ_a) coefficients of the stratum corneum (without nanoparticles) are the following: 1) for 310 nm light: $\mu_s = 240$ mm^{-1}, $\mu_a = 60$ mm^{-1}; 2) for 400 nm light: $\mu_s = 200$ mm^{-1}, $\mu_a = 23$ mm^{-1}; refractive index is equal to $n = 1.53$ and anisotropy factor $g = 0.9$ are the same for the both wavelengths. The above-mentioned wavelengths were chosen because the 310 nm value corresponds to the erythemal peak and 400 nm is at the end of the UV spectrum. Total thickness of stratum corneum was 20 μm.

Optical properties of nanoparticles were accounted for according to [7, 8]. Free software MieTab 7.23 was utilized to calculate scattering and absorption cross-sections and a *g*-factor of the particles. Using the obtained values, scattering and absorption coefficients of particle suspensions with a volume fraction of particles of 1 % were further calculated according to the earlier obtained formulas [9, 10].

In all simulations, one million photons were launched into the medium. This amount ensured sufficient statistical precision of the calculations with an error not exceeding 3 %. Based on the amount of photons absorbed, reflected and transmitted through the stratum corneum (depending on the particle size and material) the optimal particle sizes minimizing the light transmittance were calculated.

RESULTS

As an example, calculated transmittance curves for TiO_2 and Si particles for the considered wavelengths are depicted in Fig. 1. For the shorter wavelength (310 nm) the attenuation effect of both types of particles is comparable, while for the longer one (400 nm) the Si particles clearly outperform TiO_2. The sizes of the most attenuating particles are the following: 56 and 70 nm for Si (for 310 and 400 nm light, respectively) and 62 and 122 nm for TiO_2 particles (for 310 and 400 nm light, respectively). The mechanisms behind these affects are the absorption of the UV radiation of the shorter wavelength for both types of particles; scattering for TiO_2 and absorption and, to a lesser extent, scattering for Si nanoparticles.

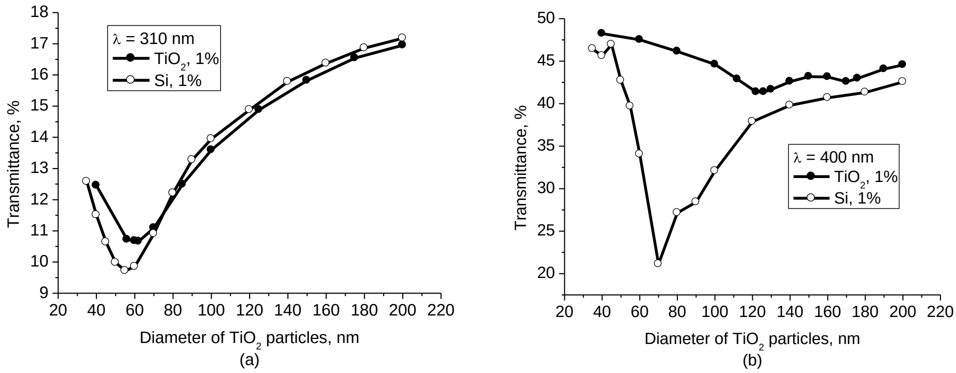

Figure 1. Transmittance of 310- (a) and 400-nm (b) light through the whole stratum corneum in presence of TiO_2 and Si nanoparticles of different sizes within its uppermost 1-μm-thick part.

Comparing the TiO_2 and Si nanoparticels as UV protectors we show that the Si particles are considerably more effective for attenuation of the longer wavelength (400 nm) radiation, while for 310 nm light the efficacy of the particles of both types are more or less at the same level. Results are compared to those for the ZnO particles.

REFERENCES

[1] U. Jacobi, H.-J. Weigmann, M. Baumann, A.-I. Reiche, W. Sterry, and J. Lademann. Lateral spreading of topically applied UV filter substances investigated by tape stripping. Skin Pharmacol. Physiol. **17** (2004).

[2] J. Lademann, H.-J. Weigmann, C. Rickmeyer, H. Barthelmes, H. Schaefer, G. Mueller, and W. Sterry. Penetration of titanium dioxide microparticles in a sunscreen formulation into the horny layer and the follicular orifice. Skin Pharmacol. Appl. Skin Physiol. **12** (1999).

[3] J. Lademann, S. Schanzer, U. Jacobi, H. Schaefer, F. Pflücker, H. Driller, J. Beck, M. Meinke, A. Roggan, and W. Sterry. Synergy effects between organic and inorganic UV filters in sunscreens. J. Biomed. Opt. **10** (2005).

[4] A.I. Rybaltovsky, V.N. Bagratashvili, A.I. Belogorokhov, V.V. Koltashev, V.G. Plotnichenko, A.P. Popov, A.V. Priezzhev, A.A. Ishchenko, A.A. Sviridova, K.V. Zaitseva,

and I.A. Tutorsky. Spectral features of water-emulsion composite media containing silicon nanoparticles. Optics and Spectroscopy **101** (2006).

[5] J. Lademann, H.-J. Weigmann, H. Schaefer, G. Mueller, and W. Sterry. Investigation of the stability of coated titanium microparticles used in sunscreens. Skin Pharmacol. Appl. Skin Physiol. **13** (2000).

[6] A.P. Popov, A.V. Priezzhev, J. Lademann, and R. Myllylä. TiO2 nanoparticles as an effective UV-B radiation skin-protective compound in sunscreens. J. Phys. D: Appl. Phys. **38** (2005).

[7] E.D. Palik. *Handbook of Optical Constants of Solids*. Academic Press, Orlando (1985).

[8] S.M. Al-Hilli and M. Willander. Optical properties of zinc oxide nano-particles embedded in dielectric medium for UV region: Numerical simulation. J. Nanoparticle Research **8** (2006).

[9] A.P. Popov, A.V. Priezzhev, J. Lademann, and R. Myllylä. The effect of nanometer particles of titanium oxide on the protective properties of skin in the UV region. J. Opt. Technol. **73** (2006).

[10] A.P. Popov, A.V. Priezzhev, J. Lademann, and R. Myllylä. Effect of multiple scattering of light by titanium dioxide nanoparticles implanted into a superficial skin layer on radiation transmission in different wavelength ranges. Quantum. Electron. **37** (2007).