Scientific paper

Surface Treated Titanium Dioxide Nanoparticles as Inorganic UV Filters in Sunscreen Products

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Abstract

TiO_2 nanoparticles were used in this research as an inorganic UV absorber for preparation of a sunscreen that ensures optically transparent films with adequate SPF. TiO_2 nanoparticles in rutile crystal form, produced in Cinkarna Celje, were used in this research. The elementary principle of the nanograde TiO_2 production is the sulphate synthesis process, which is upgraded for the synthesis of final nano product. TiO_2 nanoparticles were subsequently surface modified by coating with sodium silicate as the source of silica. The resulting silica coated TiO_2 nanoparticles were examined by scanning (SEM) and transmission electron microscopy (TEM). Uniform particles distribution and homogeneous amorphous coatings, formed in heterogeneous nucleation of silica molecules on the surface of TiO_2 nanoparticles, were observed. Sun-protection factor (SPF) of 28 was determined for sunscreen with incorporated 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica according to the "Method for the In Vitro Determination of UVA Protection Provided by Sunscreen Products".

Keywords: Nano titanium dioxide; Surface treatment; Silica; Sunscreen

1. Introduction

Most of the sunscreens on the market have inorganic and organic UV filters in their formulations. UV filters are able to transform, disperse or absorb the ultraviolet (UV) radiation. UV radiation in the solar spectrum at the Earth's surface is in the 290–400 nm band and is conventionally divided into UVB (290–320 nm) and UVA (320–400 nm), whereby the latter is further divided into UVAI (340–400 nm) and UVAII (320–340 nm) on the basis of their biological activity.[1] When looking for a sunscreen with lower allergenic potential the best UV filters are the inorganic ones which, however, are more difficult to incorporate.[2] The most frequently used inorganic UV filters are the titanium dioxide (TiO_2) and zinc oxide (ZnO). These oxides have been prepared as nanometric particles which demonstrate the least reflection of visible radiation, thus producing less effect of white coloration when applied to the skin, and also have special properties from the viewpoint of photo protective efficacy.[2]

TiO_2 is of potential interest as an UV radiation blocking material in personal care products because of its excellent UV light absorption properties, cost effectiveness and inertness. Its chemical and physiological inertness makes it ideal for formulating mild or hypoallergenic sun care products, especially for children and people with sensitive skin.[3] TiO_2 is known to exist in three crystal forms: anatase, brookite and rutile. The rutile phase is generally used as a component in sunscreen cosmetics because of its higher UV absorption.[4] Its high photocatalytic activity, however, facilitates the generation of reactive oxygen species.[5–8] Consequently, high photocatalytic activity of TiO_2 causes the decomposition of the cosmetic formulation and facilitates the generation of reactive oxygen species, thus raising safety concerns. The covering of the TiO_2 surface with nonactive oxides is a key point in its development for wide spectra application in cosmetics by preventing the escaping of radicals produced by the reaction of oxygen and/or water with the electron–hole pair. For that reason special surface treatments with silica (SiO_2), dimethicone ($(C_2H_6OSi)_n$) or alumina (Al_2O_3) are required to suppress TiO_2 inherent photoactivity.[9–13] Coating the particles is accomplished by precipitating white hydrated oxides onto the particle surface. These precipitation processes can be strongly influenced by the conditions during treatment. Thus optimum treatment conditions need to be determined after the surface treatment chemicals have been selected.

It is also important to properly formulate and disperse inorganic sunscreens so that they are effective; the inorganics remain effective as long as the particles remain on the skin because they are photo stable.[3] When incorporated in a suitable vehicle, they reflect or disperse sunlight. The first generations of sun filters containing microparticles of ZnO and TiO_2 were opaque and whitish when applied to the skin. These problems practically disappeared with the use of the same metal oxides as nanoparticles, whose chemical, mechanical, electrical and optical properties differ substantially compared to microparticles.[1,14] Since TiO_2 nanoparticles do not penetrate the skin, inorganic filters are considered safer than organic filters.[1,15]

1. 1. Regulation of Sunscreen Ingredients

Sunscreens are regulated in all developed countries. Each country has a list of authorized ingredients and their maximum allowable concentrations in final products, which are classified as cosmetics or over-the-counter drugs.[16] In the EU, sun products are classified as cosmetics, in line with the directives of the Council of Europe, ratified by all member states and converted into laws containing lists of allowed ingredients. The lists are updated on the basis of scientific research and approved by The European Cosmetics Association, a body that liaises with the European Commission. TiO_2 is included on the EU list of permitted UV filters that cosmetic products may contain and is declared safe in concentrations up to 25.0% of the formulation by weight.[1]

2. Experimental

2. 1. Materials

TiO_2 nanoparticles in rutile crystal form, produced in Cinkarna Celje, were used in this research. The elementary principle of nano grade TiO_2 production is the sulphate process, which is upgraded for the synthesis of final nano product. Cinkarna Celje decided for strategic orientation towards the production of nano grade TiO_2 explicitly in suspension form. For that reason, Cinkarna has already developed the synthesis methods for rutile nanoparticles obtained in suspension form without any intermediate powder phase. The decision is based on mastering the fine particles that stay in the suspension and care for the healthy working conditions of the employees and the users of the product. Suspension of TiO_2 nanoparticles in rutile crystalline form, used in this research, contained approximately 30.0 wt. % solid material.

Rutile was subsequently surface treated with hydrated amorphous silica. Silica coated TiO_2 nanoparticles were prepared starting from Na-silicate (c = 200 g/L SiO_2) by the chemical liquid deposition method. Surface treatment began after a precursor addition to TiO_2 suspension. Precipitation of oxide particles from precursor started with a gradual adjustment of the pH. The initial hydroxide gel resulted from the reaction of Na-silicate with an acid. During the precipitation process silica hydroxides bind on the surface of TiO_2. After successful surface treatment process the surface of the particles was entirety surrounded by silica layer.

TiO_2 nanoparticles, surface treated with 5.0 wt. % SiO_2 were used for sunscreen formation. 5.0 wt. % SiO_2 was selected based on results obtained by UV light absorption determination in previous research.[17] The results indicated that that type of TiO_2 nanoparticles ensure the highest protection against harmful UV radiation.

Surface-treated rutile was incorporated into lotion emulsion. 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica were incorporated into emulsion under stirring and prepared for the testing. Emulsion contained inorganic UV filter only.

2. 2. Methods

2. 2. 1. Surface Morphology Determination by SEM and (S)TEM

The morphology of surface treated TiO_2 nanoparticles can be identified directly only with the utilization of electron microscopy, e.g. scanning (SEM) and transmission (TEM) microscope.

A drop of TiO_2 suspension was dropped on the adhesive carbon band on brass holders for the observation on a Zeiss SIGMA VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany), with a maximum resolution of up to 1.5 nm at 20 kV. STEM images were collected and elaborated according to standard procedures.

In addition, morphology analysis of surface treated TiO_2 nanoparticles was performed using transmission electron microscope (TEM, JEOL 2100F, Japan). For the analysis, a drop of suspension was dropped on Cu-grid.

The morphology of surface treated TiO_2 nanoparticles was observed at different magnifications.

The presence of silica was verified by semi-quantitative elemental analysis (EDS).

2. 2. 2. Electrochemical Properties Determination

Mütek™ PCD-04 Particle Charge Detector (BTG Instruments GmbH, Germany) was used for determination of isoelectric point (IEP) of aqueous samples. The IEP is the pH-dependent point of zero charge (PZC) of a particle. By adding a titrant (acid/ base) drop by drop, the sample's pH is shifted until the IEP (streaming potential = 0 mV) is reached. Cationic samples are titrated with a base and anionic samples with an acid up to the point of 0 mV.

PZC, in physical chemistry, is a concept relating to the phenomenon of , and it describes the condition where the electrical charge density on a surface is zero. The isoelectric point (IEP) is the at which a particular or surface carries no net . The PZC is the same as the IEP if there is no of other ions than the potential determining H+/OH- at the surface. In the presence of specific adsorption, PZC and IEP generally have different values.[18–21]

2. 2. 3. UV-protection Determination

For UV-protection and transparency determination, transparent film with incorporated 0.6 wt. % TiO_2 nanoparticles was prepared from acrylic stain. Cary 100 UV–Vis spectrophotometer with integrating sphere (Varian Inc., USA) was utilized for UV-protection determination. Transmittance versus wave length of films was determined.

2. 2. 4. Sun Protection Factor (SPF) Determination

UVA protection of sunscreen was determined according to the "Method for the in vitro determination of UVA protection provided by sunscreen products" (COLIPA, 2011) by Derma Consult GmbH. The "In Vitro Method for the Determination of the UVA Protection Factor and žCritical Wavelength Values of Sunscreen Products" (COLIPA, 2011) are based upon the absorbance of UV light by its passage through roughened polymethyl acrylate (PMA) coated with a sunscreen product, taking the declared in-vivo SPF into account and exposing the sample with a dose of UV radiation related to its UVA protective capacity. Determination was done using UV Transmittance Analyzer UV-2000 (labsphere Inc., North Hutton, USA) and Suntest CPS+ (ATLAS Material Testing Technology GmbH, Linsengericht, Germany) as an UV-Source.

2. 2. 5. Visual Test

Visual test for the estimation of the appearance of applied sunscreen on the skin was performed. As the prepared sunscreen was applied on the skin the transparency of the applied layer was observed.

3. Results with Discussion

3. 1. Surface Morphology

In Fig. 1A and 1B, SEM and TEM images demonstrate surface morphology of rutile nanoparticles before surface modification. Nanoparticles are non-spherical in shape, with approximately 80 nm in length and 25 nm in width. Crystal lattice fringes for rutile TiO_2 can be seen. Sharp edges in the case of untreated TiO_2 nanoparticles can be seen in Fig. 1B, while homogeneous amorphous coatings formed in heterogeneous nucleation of silica molecules on the surface of TiO_2 nanoparticles (Fig. 2B). Therefore, the surface of rutile TiO_2 nanoparticles became rougher due to amorphous silica precipitation. Another important observation is a uniform particles distribution. Figure 2A shows SEM image of evenly distributed surface-treated TiO_2 nanoparticles. No agglomerates can be seen, which proves that individual particles were effecti-

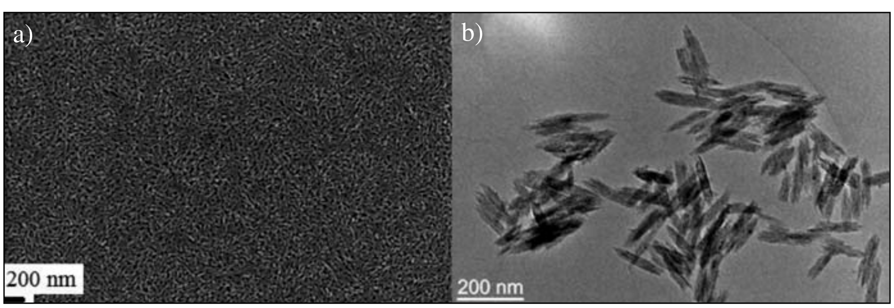

Figure 1: SEM (A) and TEM (B) images of untreated TiO_2 nanoparticles.

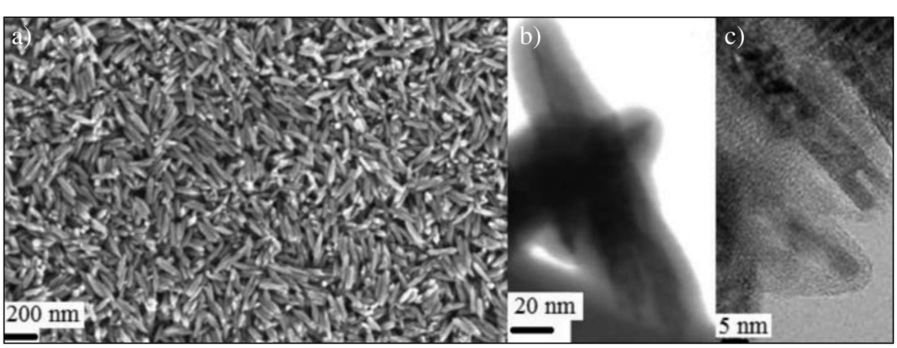

Figure 2: SEM (A), STEM (B) and TEM (C) images of silica surface treated TiO_2 nanoparticles.

vely kept separated during the surface treatment. Prevention of agglomeration presented the greatest challenge due to the fact that TiO_2 tend to agglomerate. However, the use of proper synthesis conditions yielded efficiently surface-treated TiO_2 nanoparticles.

It's evident from the semi-quantitive elemental analysis (EDS) results that element Si (Si) was present in the surface treated TiO_2 nanoparticles (Fig. 3).

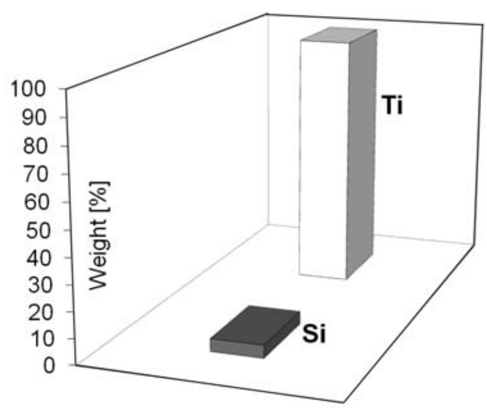

Figure 3: EDS analysis of TiO_2 surface treated with 5 wt. % silica.

3. 2. Electrokinetic Properties

One of the most significant properties of an insoluble oxide like TiO_2 and SiO_2 is the IEP. In our research PZCs of untreated and silica surface treated rutile TiO_2 nanoparticles were determined. The results of streaming potential (*U*) as a function of pH value are graphically presented in Figure 4. PZC of TiO_2 nanoparticles occurred when the solution pH was ~ 5.5, which is in accordance with the literature.[22] In the meantime, the precipitation of silica on TiO_2 surface resulted in the shift of PZC. 5.0 wt % of silica loading caused the PZC of coated nanoparticles to shift to lower pH values (pH ~ 2). Coated nanoparticles altered the electrokinetic behaviour similar to the silica nanoparticles, which suggested that complete silica coating layers formed on TiO_2 nanoparticles. The results are in agreement with literature.[9,13, 22–24]

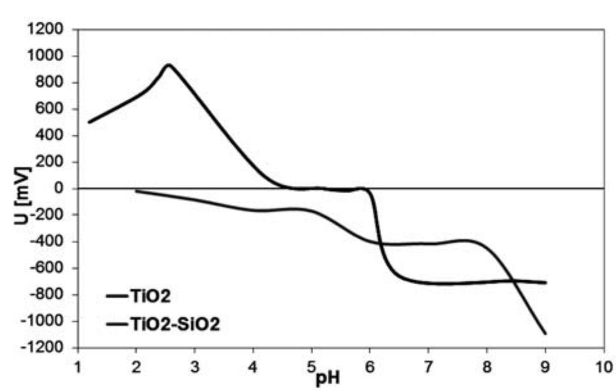

Figure 4: Streaming potential (*U*) as a function of pH value.

3. 3. UV-protection

While the visible range of the spectra (400–800 nm) is not harmful, high-energy ultraviolet (UV) radiation of shorter wavelengths affects human skin. According to the literature[1] skin damage caused by UV radiation, especially skin cancer is mainly due to UVB (290–320 nm) and partly to UVAII (320–340 nm). This assumption influenced photoprotective strategy, which for a long time aimed at producing sun filters that mostly blocked UVB radiation. For that reason, it was attempted to prepare sunscreens with incorporated silica surface treated TiO_2 nanoparticles, which would enable maximum efficiency by the means of transparency and UV protection. TiO_2 nanoparticles surface treated with 5.0 wt. % silica improved UV protection. The results in Fig. 5 show that TiO_2 nanoparticles, surface treated with 5.0 wt. % silica filter UV light entirely up to 380 nm.

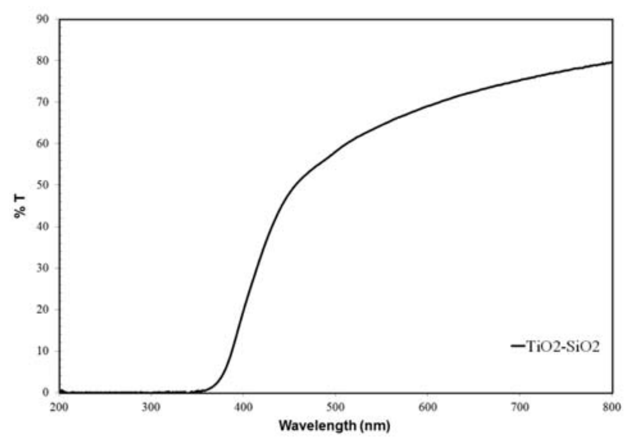

Figure 5: UV-Vis transmittance versus wavelength of coating with incorporated 0.6 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica.

3. 4. Sun Protection Factor (SPF) Determination

For sunscreen with incorporated 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica SPF 28 was determined according to the "Method for the In Vitro Determination of UVA Protection Provided by Sunscreen Products" (COLIPA, 2011). The ratios of SPF/UVAPF and the reciprocal ration UVAPF/SPF (EU criterion: UVA protection1/3 of SPF) were calculated for the mean UVAPF determined.

3. 5. Visual Test

Visual test for the estimation of the appearance of applied sunscreen on the skin was performed. As prepared sunscreen (Fig. 6) was applied on the skin the transparency of the applied layer was observed. Fig. 7 shows 4 different deposits of sunscreens with various formulations (with incorporated pigmentary TiO_2 and TiO_2 nanoparticles). Deposit within a white border was obtained by application of a cream with incorporated 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica. Neutral pH of sunscreen with incorporated silica surface treated TiO_2 nanoparticles was determined, which indicates that prepared cream is appropriate for use in sunscreen cosmetics.

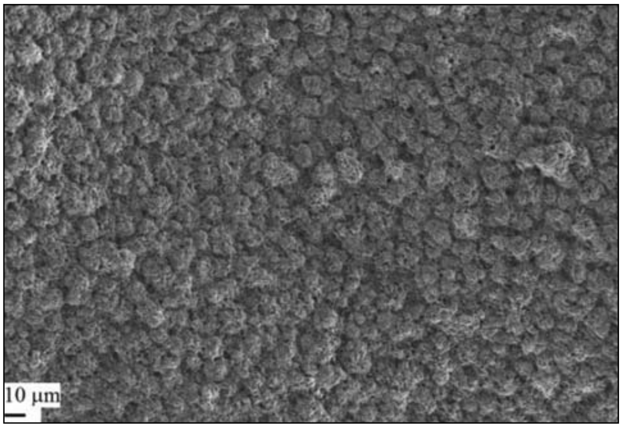

Figure 6: SEM image of sunscreen with incorporated 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica.

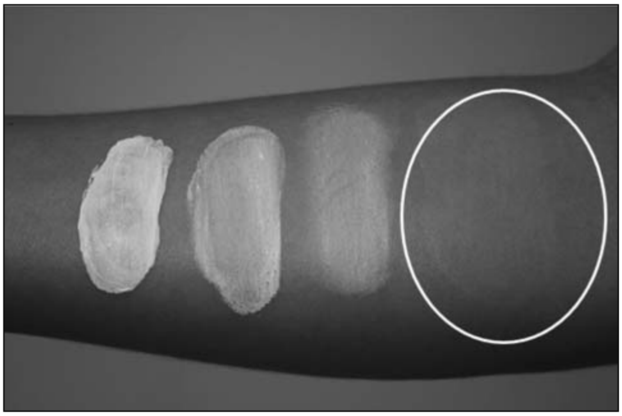

Figure 7: Transparent layer of UV protective sunscreen.

In addition, chemical element composition was determined by instrumental neutron activation analysis using the k_0 method (k_0INAA) by Slovenian accredited laboratory, Department for Environmental Sciences at Institute Jožef Stefan (Ljubljana, Slovenia). According to the results, the material is appropriate for use as a sunscreen ingredient.

4. Conclusion

In the presented work we were successful in synthesizing stable suspension of silica surface treated TiO_2 nanoparticles with desired properties. After incorporation of TiO_2 nanoparticles in an emulsion, the resulting sunscreen demonstrated satisfying SPF factor. For sunscreen with incorporated 9.0 wt. % TiO_2 nanoparticles, surface treated with 5.0 wt. % silica SPF of 28 was determined according to the “Method for the In Vitro Determination of UVA Protection Provided by Sunscreen Products” (COLIPA, 2011).

5. References

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Povzetek

V raziskavi so bili za pripravo sončne kreme, ki zagotavlja optično prosojne nanose z ustreznim zaščitnim faktorjem, uporabljeni kot anorganski UV absorber nanodelci TiO_2. Uporabljeni nanodelci TiO_2 so bili v kristalni strukturi rutil. Osnovni princip proizvodnje nanodelcev TiO_2 je sulfatni postopek, ki je nadgrajen za sintezo končnega izdelka v nano obliki. Nanodelci TiO_2 so bili nato površinsko modificirani s plastjo amorfnega silicijevega hidroksida. Kot vir silicijevega hidroksida je bil uporabljen prekurzor natrijev silikat. Površinsko obdelani nanodelci TiO_2 so bili analizirani z uporabo vrstične (SEM) in presevne elektronske mikroskopije (TEM). Ugotovljena je bila enakomerna porazdelitev delcev in homogeni amorfni plaščki, nastali v heterogeni nukleaciji molekul silicijevega hidroksida na površini nanodelcev TiO_2. Zaščita pred soncem (SPF) se je določala v skladu z metodo za »in vitro« določanje UVA zaščite, ki jo zagotavljajo produkti za zaščito pred soncem. Sončna krema z vključenimi 9,0 ut. % nanodelci TiO_2, površinsko obdelanimi s 5,0 ut. % silicijevega hidroksida je izkazovala SPF 28.