

Supplementary information

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S1. Do smaller particles indeed filter UV light more efficiently?

Physical sunscreens filter UV light with a combination of scattering and absorption. In the case of TiO₂ the absorption mechanism is clearly dominant (app. 70 % of the incident UV light is absorbed, whereas the remaining part is elastically scattered). Here we give a theoretical justification that in such a case (dominant absorption) the UV-filtering ability is improved if particle size is reduced. For the sake of generality, however, we consider a suspension of spherical particles that include both filtering mechanisms at arbitrary weighting. Let a thin slice of suspension with thickness δL be illuminated by a beam with intensity I as depicted in figure S1.

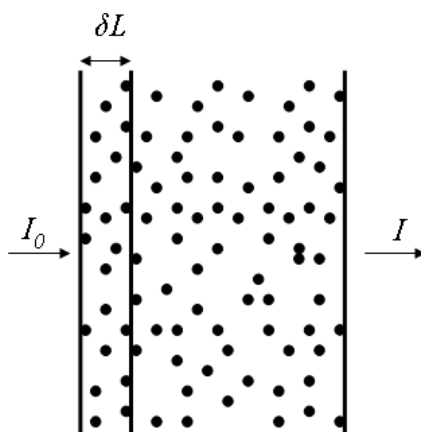


Figure S1: Schematic representation of a sample of suspended UV-filter particles.

If the total beam area is A , the volume of the illuminated sample is $A\delta L$. The number density of suspended particles will be denoted as ρ_N , thus the total number of particles in the illuminated sample is $\rho_N A\delta L$. For the moment we treat separately scattering and absorption and focus first on the former.

Each particle scatters a certain amount of light energy corresponding to that in an area C of the incident beam, called the *scattering cross-section*. If each of those particles effectively blocks an area C , then the fractional area of the beam from which light is removed due to scattering is $\rho_N C A\delta L / A = \rho_N C \delta L$. This can be interpreted as the fraction of light removed from the beam due to scattering.

By contrast, in the case of absorption we first consider the total area of the beam from which the light can be removed by absorption, that is, the sum of crosssections of the beam and the particles (see fig. S2).

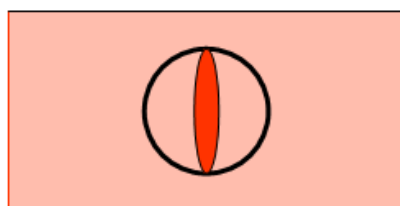


Figure S2: The total effective interaction area of a light beam and an absorber particle.

From this total area, hereafter termed »efficient« area, the fraction of light removed depends only on the absorption coefficient of absorber particles and the number of absorber molecules in the particle. If we denote the absorption coefficient of the absorber molecules as ϵ_l , then we can define the absorption coefficient per unit volume of the particle as $\epsilon_V = \epsilon_l N_p / V_l$ where N_p is the number of molecules in the particle and V_l the volume of the particle.

We are now interested in the intensity of a light beam which illuminates an area of sample A after passing through a layer of absorber particles of diameter d . The absorption coefficient

per unit volume ε_V is proportional to the number of particles ($\rho_N A \delta L$) times the fractional area of the beam which interacts with one particle times the fraction of light removed by the total volume of the particles ($\varepsilon_V V_p = N \varepsilon_V \pi d^3 / 6$ where V_p is the total volume of all the particles in the slice), thus $\rho_N A (A_I/A) \varepsilon_V V_I \delta L = \rho_N A_I \varepsilon_V V_I \delta L$.

In the last argument we assumed that light reaches the particles only directly and not by scattering from other particles (which is an obvious but not crucial simplification). The total differential change of intensity when the light passes through a slice of suspension of thickness δL is therefore given by

$$\frac{dI}{I} = -\rho_N (C + A_I V_p \varepsilon_V) dL \quad (\text{S1})$$

We now assume that each layer removes the same fraction of light incident, thus ignoring secondary scattering and absorption of the already scattered light. Upon integration and rearrangement of terms an equation of the Beer-Lambert form is obtained:

$$I = I_0 \exp(-\rho_N (C + A_I V_p \varepsilon_V) L) \quad (\text{S2})$$

where I_0 represents the intensity of the incident beam (corresponding to $L=0$). We first focus on scattering. Intuitively, we can assume that the scattering cross-section depends in some manner on the geometrical cross-sectional area. If we define the scattering coefficient Q_s as the ratio »scattering cross-section/geometrical cross-sectional area«, we get for a sphere

$$C = \pi d^2 Q_s \quad (\text{S3})$$

A particle can scatter very much less or much more light than incident on it (thus C can vary from close to 0 to more 1). We can rewrite (2) in terms of 'turbidity' for UV light, by defining the turbidity as $\tau = \rho_N C$. Then we obtain

$$I = I_0 \exp(-(\tau + \rho_N A_I V_p \varepsilon_V) L) \quad (\text{S4})$$

Furthermore if the particles are small compared to the wavelength of incident light, we can use the Rayleigh approach to estimate the scattering cross-section C , according to which all

the light scattered from a particle is in phase. The scattering coefficient for a spherical particle in the Rayleigh approximation is given by

$$Q = \frac{8}{3} \alpha^4 \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (\text{S5})$$

where α represents a dimensionless size parameter given by $\alpha = \pi d / \lambda$. Since the volume of a particle is given by $\pi d^3 / 6$ the total volume fraction of particles (thus the total volume of particles per unit volume of suspension) is $\varphi = \rho_N \pi d^3 / 6$. We can now define the specific turbidity (the turbidity normalized by the particle volume concentration) as

$$\frac{\tau}{\varphi} = \frac{4\pi^3 \alpha^3}{\lambda} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (\text{S6})$$

Let us now compare the difference of intensities of transmitted light through samples of suspensions of equal thickness containing particles of the same kind but of diameters d_1 and d_2 with volume fractions φ_1 and φ_2 , respectively. We get

$$\ln \frac{I_1}{I_2} = \left[\rho_N^2 (C^2 + A_1^2 V_{tot}^2 \epsilon_V) - \rho_N^1 (C^1 + A_1^1 V_{tot}^1 \epsilon_V) \right] L \quad (\text{S7})$$

or in terms of turbidities

$$\ln \frac{I_1}{I_2} = \left[(\tau_2 + \rho_N^2 A_1^2 V_{tot}^2 \epsilon_V) - (\tau_1 + \rho_N^1 A_1^1 V_{tot}^1 \epsilon_V) \right] L \quad (\text{S8})$$

Using eq.(S7) and assuming that the relative refractive index is independent of particle size we can express on of the τ 's with the help of the other ($\tau_1 = \tau_2 (\varphi_1 / \varphi_2) (d_1 / d_2)^3$) and the product of total volume of the particles and the number density in terms of the volume fraction of particles times the number of particles, thus eq. (S8) becomes

$$\ln \frac{I_1}{I_2} = \left[\tau_2 \left(1 - \frac{\varphi_1}{\varphi_2} \left(\frac{d_1}{d_2} \right)^3 \right) + \frac{\pi \epsilon_V}{4} (N_2 \varphi_2 d_2^2 - N_1 \varphi_1 d_1^2) \right] L \quad (\text{S9})$$

From here, the ratio of transmitted intensities as a function of volume fractions and particle diameters becomes

$$\frac{I_1}{I_2} = \exp \left[\tau_2 \left(1 - \frac{\varphi_1 \left(\frac{d_1}{d_2} \right)^3}{\varphi_2} \right) + \frac{\pi \varepsilon_V}{4} (N_2 \varphi_2 d_2^2 - N_1 \varphi_1 d_1^2) \right] L \quad (\text{S10})$$

We now decide to compare the ratio of transmittances of suspensions with equal volume fractions of particles, but different particle sizes. We rewrite eq.(10) as

$$\frac{I_1}{I_2} = \exp \left[\tau_2 \left(1 - \left(\frac{d_1}{d_2} \right)^3 \right) + \frac{\pi \varepsilon_V \varphi N_2 d_2^2}{4} \left(1 - \left(\frac{d_2}{d_1} \right) \right) \right] L \quad (\text{S11})$$

We first consider the two limiting cases, namely the one where scattering dominates (in the case of weakly absorbing systems) and the other one where absorption dominates (in the case of strongly absorbing systems). It can be directly observed from eq. (S11) that the effect of variation of particle size affects scattering and absorption in an opposite manner. Let us now rewrite (S11) for both limiting cases

$$\begin{aligned} \frac{I_1}{I_2} &\approx \exp \left[L \tau_2 \left(1 - \left(\frac{d_1}{d_2} \right)^3 \right) \right] \\ \frac{I_1}{I_2} &\approx \exp \left[\frac{L \pi \varepsilon_V \varphi N_2 d_2^2}{4} \left(1 - \left(\frac{d_2}{d_1} \right) \right) \right] \end{aligned} \quad (\text{S12})$$

First we look at the simplest case, in which d_2 is such that we get $L\tau_2$ equal to 1, thus

$$d_2 = \frac{1}{\pi} \left(\frac{\lambda}{4L\varphi} \left(\frac{n^2+2}{n^2-1} \right)^2 \right)^{\frac{1}{3}} \quad (\text{S13})$$

In the second case we choose the following equality

$$d_2 = \frac{2}{(L\pi\varepsilon_V\varphi N_2)^{\frac{1}{2}}} \quad (\text{S14})$$

The results of eqns (S13) and (S14) are shown in fig 3A.

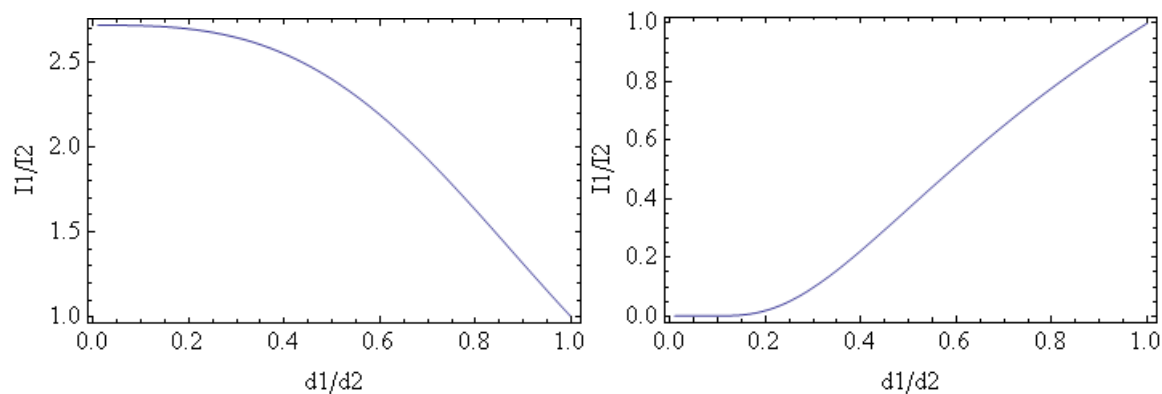


Figure S3: Relative transmittances given by eqns. (S12) using eqns. (S13) and (S14) respectively. The left diagram corresponds to elastic scattering only, the right to absorption only.

We now look at the influence of specific values parameters in eqns. (S12) by defining dimensionless parameters

$$X = L\tau_2 = \frac{4L\phi\pi^3\alpha^3}{\lambda} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2$$

$$Y = \frac{L\pi\varepsilon_v\phi N_2 d_2^2}{4} \quad (\text{S15})$$

Figure S4 shows the ratio of transmittances of two suspensions as a function of the ratio of particle diameters in case of scattering only for values of X equal to (from the bottom up) 0.1, 0.25, 0.5, 1, 1.5 and 2.

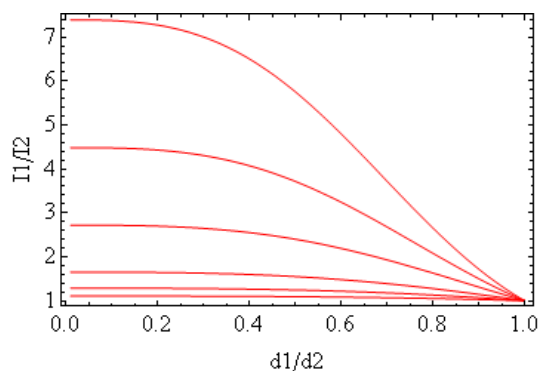


Figure S4: Ratio of transmittances as a function of the ratio of particle diameters in the case of scattering only for values of X equal to (from the bottom up) 0.1, 0.25, 0.5, 1, 1.5 and 2.

Figure S5 shows the ratio of transmittances of two suspensions as a function of the ratio of particle diameters in case of absorption only for values of Y equal to (from the top down) 0.1, 0.25, 0.5, 1, 2, 5 and 10.

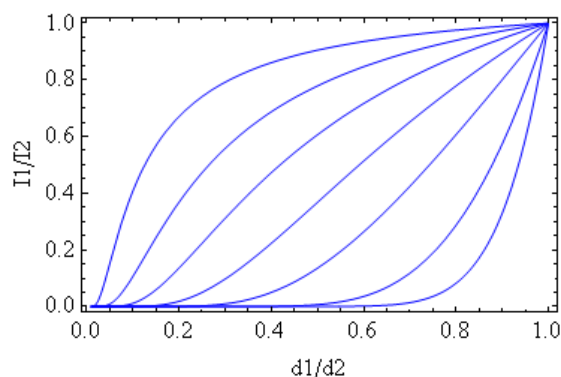


Figure S5: Ratio of transmittances of two suspensions as a function of the ratio of particle diameters in case of absorption only for values of Y equal to (from the top down) 0.1, 0.25, 0.5, 1, 2, 5 and 10.

To assess the influence of reduction of particle size on the ratio of intensities in the case where both mechanisms are present (scattering and absorption) we rewrite eq. (S11) using eq. (S15):

$$\frac{I_1}{I_2} = \exp \left[1 - \left(\frac{d_1}{d_2} \right)^3 + K \left(1 - \left(\frac{d_2}{d_1} \right) \right) \right] \quad (\text{S16})$$

where K is a measure of the relative contribution to the filtering, i.e. $K=0$ if only scattering is present and $K>1$ means the dominance of absorption. By using this *ansatz* we actually set X equal to 1 and define Y relative to X . The result of eq.(S16) for values of K ranging from 0 to 10 are shown in figure S6.

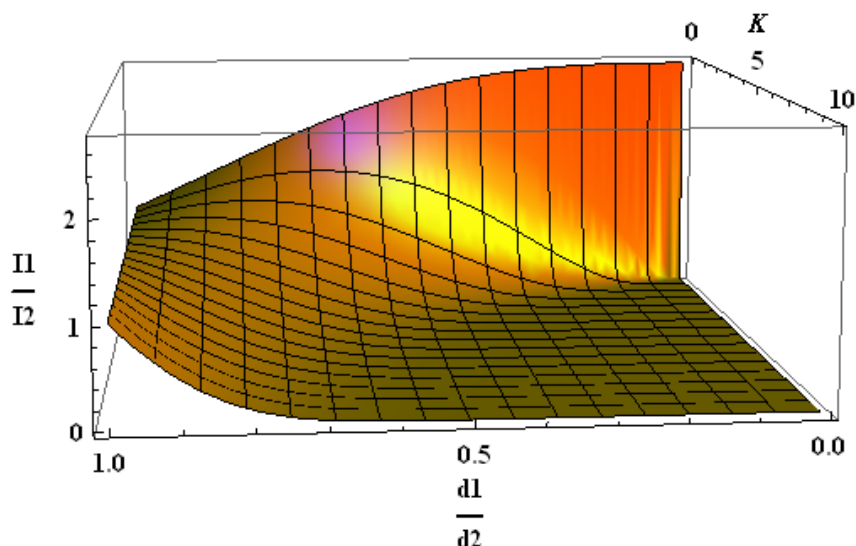


Figure S6: The result of eq.(S16) for values of K ranging from 0 to 10.

From fig. S6 it is observed that for K values lower than approximately 2 the ratio of transmittances is not a monotonous function of the ratio of particle diameters but first increases and then drops again for very low d_1/d_2 ratios (this only occurs if there is some absorption present). From the above analysis we can deduce that if the absorption mechanism is sufficiently expressed, that is if the particles possess significant absorption ability, the particle size reduction will always result in an improved filtering ability.

SI2. Additional analysis of selected features observed in Fig. 6a (see main text)

The second endothermic event between 200 and 280 °C is due to the removal of unreacted ethoxy groups and additional polymerization of Si-OH and Ti-OH groups to Si-O-Si and Ti-O-Ti bridges.^[30] The corresponding weight loss is observed in the TG curves (Fig. S7). The difference in the remaining mass after this event is app. 0.53 %. This increase is expected since both samples are supposed to have the same fraction of unreacted EtO-Si groups with respect to the total amount of surface groups (Si-OH, Si-O-Si and Si-OEt and Si-O-LA). Thus

if the total mass fraction of BTSE coating in case of TiO₂-BTSE-LA is lower (due to LA) the corresponding weight loss is also smaller.

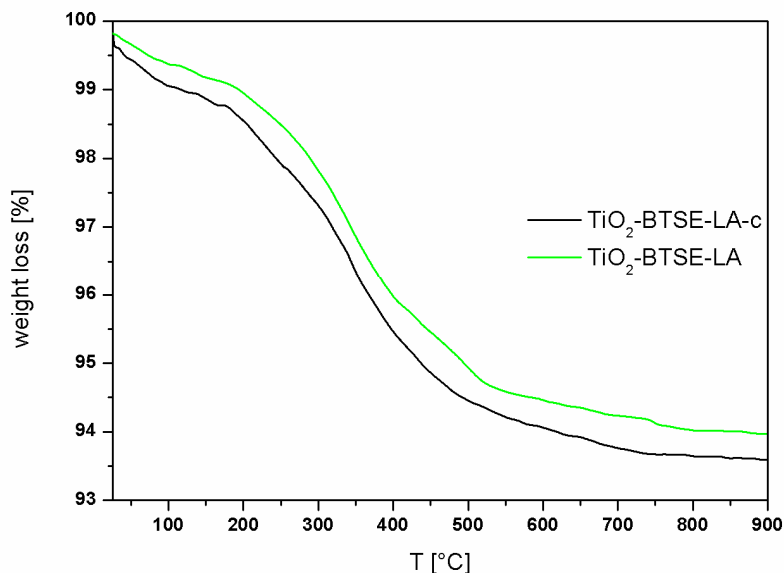


Fig. S7. TG curves corresponding to DTA curves shown in Fig. 6a (main article).

The weight loss between 300 and 450 °C is somewhat larger in the case of TiO₂-BTSE-LA which is expected due to the larger BTSE mass fraction and agrees well with the DTA data where the peak area is also slightly larger. The difference in the remaining mass at 330 °C is app. 0.48 %. Thus, a drop in the difference is observed probably due to the first stage of combustion of LA at 320 °C which means that the total mass fraction of the coating increases slightly, and this difference increases again to app. 0.51 % at 450 °C (due to complete combustion of ethylene groups so that total mass fraction of the coating decreases again thus increasing the difference in remaining mass). In the interval 450 and 550 °C the difference in mass first increases to app. 0.58 % and afterwards decreases to app. 0.36 % (see magnification in fig. 6a; DTA and TG events in this temperature interval are in good agreement) which is the same as at 200°C. After that, there are further small oscillations of the difference in remaining mass which at 900 °C again approaches 0.36 %. Because this difference is the

same as after the evaporation of residual water and ethanol, one could deduce that it is entirely due the difference of the content of those solvents.