Safer-by-design hybrid nanostructures: An alternative to titanium dioxide UV filters in skin care products

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Supplementary Information

1. Dispersion

In figure S1, we show the observations of preliminary dispersion tests of Hyb0.7 in three different media: Water, Alcohol (Ethanol) and Oil (Hexadecane, Coco-Caprylate and Isopropyl Palmitate resp.). The Hyb0.7 concentration in each suspension is equal to 2 wt%. Except in oils, the hybrid nanostructures disperse completely in water and ethanol, as demonstrated by completely opaque white color with no suspended lump. Even after strong centrifugation (10 000 rot/min at 10 °C for 15 min), no precipitation was observed.

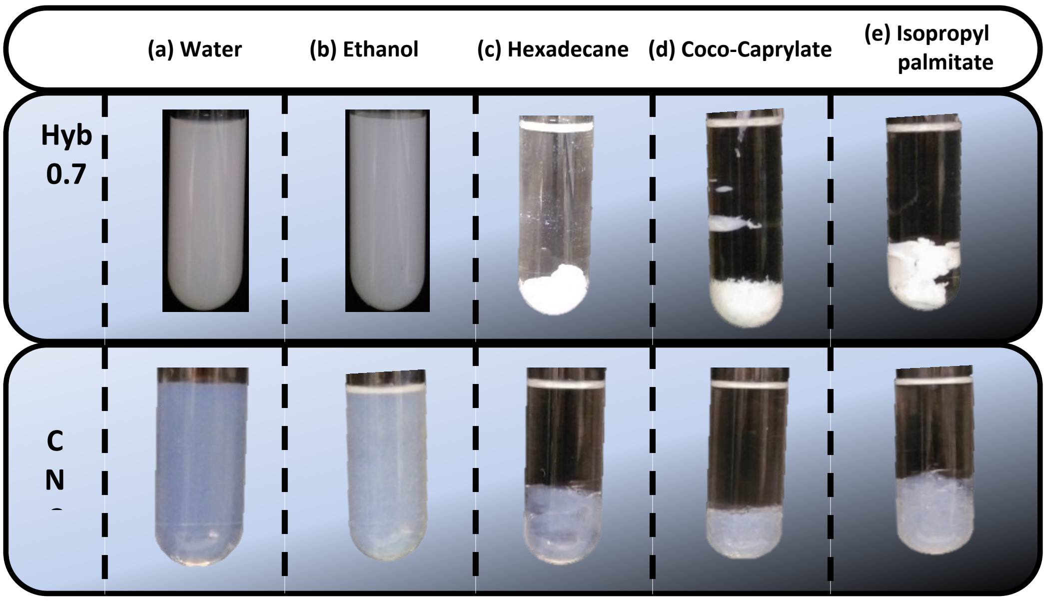

Figure S1: Visual observations of Hyb0.7 and CNC suspensions in **(a)** water **(b)** ethanol **(c)** Hexadecane **(d)** Coco-Caprylate **(e)** Isopropyl palmitate

To compare, the corresponding suspensions of CNC were also prepared with exactly same concentrations. Their visual observations are also shown in figure S1. CNC is fully dispersible in water. Some small CNC lumps were visible though in the ethanol suspension (not visible in the figure) which couldn't be reduced even after sonication. This type of *partial dispersion* in the ethanol wasn't observed in the case of Hyb0.7. The nucleation of TiO_2 NP renders CNC dispersible in ethanol. For the three oils, CNC too remains indispersible.

2. Pickering emulsions

Figure S2 illustrates the ability of Hyb0.7 to stabilize emulsions prepared using two different oils: Coco-caprylate and Isopropyl Palmitate. These two oils are widely used in the cosmetics industry for the products formulation. Clearly, stable oil droplets formation can be observed for both oil types which reduce in size when the concentration of Hyb0.7 is increased from 0.12 g/l to 0.36 g/l. At 0.12 g/l of Hyb0.7 in emulsion, the mean oil droplets size= 22 µm for Coco-caprylate. However, for Isopropyl Palmitate, the mean oil droplets size is almost double i.e. 42 µm. The same variation in the oil droplets size can be observed when the concentration of Hyb0.7 is increased to 0.36 g/l. The corresponding cases are also shown for Hexadecane to compare the results.

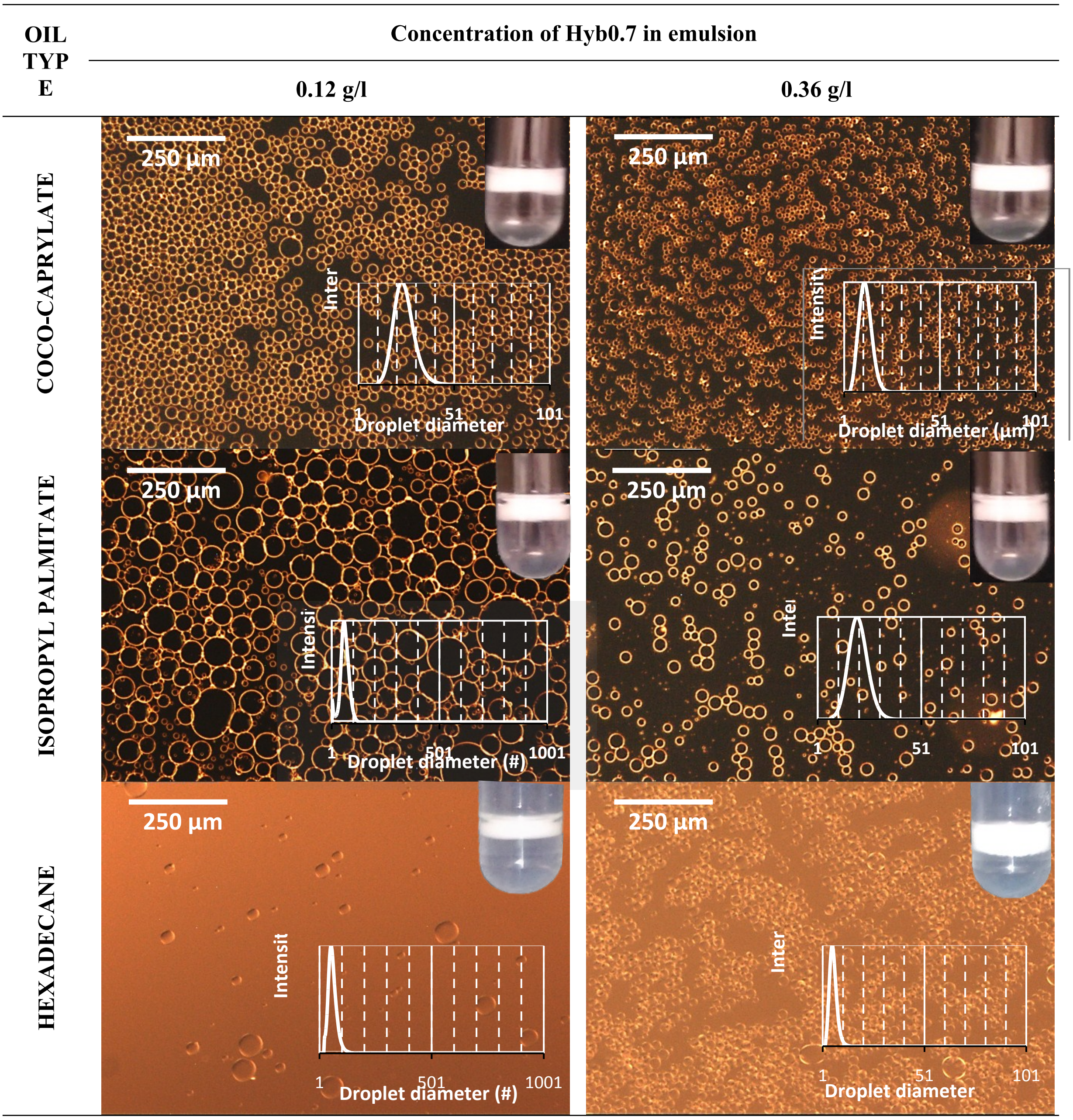

Figure S2: Oil droplets size measurement in the emulsions prepared using Coco-caprylate, Isopropyl Palmitate and Hexadecane respectively at two different concentrations of Hyb0.7 in emulsion

3. Calculation of hybrid samples mass for UV absorbance and Photostability tests

For the hybrid samples, aqueous suspensions of 10 ml, with 0.046 g/l of TiO_2 concentration in each suspension, were prepared. As revealed by TGA, in Hyb0.1, TiO_2 mass content is equal to 18%. Therefore, 2.3 mg {= 100/20 x 0.46 mg} of Hyb0.1 was added in 10 ml of de-ionized water. Similarly, for Hyb0.3, Hyb0.7 and Hyb0.9, TiO_2 mass content is equal to 33% and thus 1.4 mg {= 100/33 x 0.46 mg} of these three hybrid samples was added in 10 ml of de-ionized water respectively. However, for the commercial grade TiO_2 NP, the TiO_2 mass content is equal to 83% and it is completely hydrophobic in nature. Therefore, 0.6 mg {= 100/83 x 0.46 mg} of these commercial NP were suspended in 10 ml of analytical grade ethanol.

4. Photostability

The respective photostabilities of Hyb0.7 and commercial TiO_2 NP *i.e.* their ability to resist to any change or breaking down under the influence of UV light energy was measured by observing the variations in their absorbance levels. For this, the suspensions with TiO_2 concentration of 0.046 g/l were prepared and exposed to 4500 mW/cm^2 intensity (at 365 nm) of UV rays for different durations (t=0 to 120 min). This was the maximum permissible irradiance value that could be achieved as the worst case scenario. The results are shown in figure S3. Clearly, there is no significant variation in the absorbance levels of the two suspensions. The same holds true for the CNC suspension with same CNC concentration, although its absorbance level is insignificant.

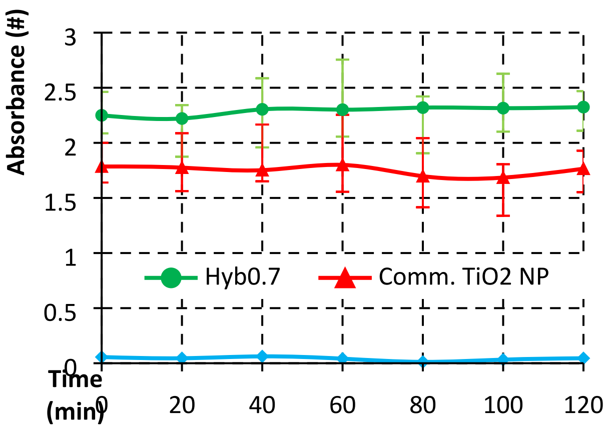

Figure S3: Variation of the UV absorbance with exposure radiation duration for the aqueous suspension of Hyb0.7 and ethanol suspension of commercial Eusolex® TS TiO_2 NP

Therefore, both Hyb0.7 and commercial TiO_2 NP show complete photostability against the tested UV irradiance levels. One must note that it is the photostability which is among the very properties that makes the use of minerals like TiO_2 and ZnO favorable in the commercial sunscreens.

5. UV absorbance Improvement Factor (IF) calculation for Hybrid nanostructure

IF can be defined as the factor by which the hybrid nanostructure becomes more efficient to absorb UV rays than its commercial counterpart. In other words, for a given UV wavelength, it can be expressed as:

$$IF = \frac{Concentration\ of\ rutile\ TiO_2\ in\ commercial\ product\ to\ absorb\ certain\ fraction\ of\ UV\ rays}{Concentration\ of\ rutile\ TiO_2\ in\ hybrid\ nanostructure\ to\ absorb\ same\ fraction\ of\ UV\ rays}$$