

Supporting Information

Bio-based nanoparticles for broadband UV protection with photo-stabilized UV-filters

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1. Preparation of ECNPs

ECNPs were synthesised via a modified anti-solvent technique as reported by Bizmark *et al.*¹ A 5.35 g L⁻¹ solution of ethyl cellulose (Sigma Aldrich, code: 247499-100G) in ethanol (100%, Interchema) was prepared and decanted into three times as much water (Millipore system). Rotary evaporation removed ethanol and some water resulting in a 5.35 g L⁻¹ aqueous dispersion of ECNPs. This was then passed through a 2 µm filter to remove any aggregate. DLS measurements (Figure S1a) showed a monodal size distribution with z-average 50 nm. TEM (Figure S1b) imaging was consistent with this observation, however, the ECNPs appeared deformed probably because they are soft. For this reason, cryo-TEM imaging was performed to capture a snapshot of the particles as they would exist in dispersion and not flattened on a surface (Figure S1c). The cryo-TEM images were also consistent with the size measurements from the DLS.

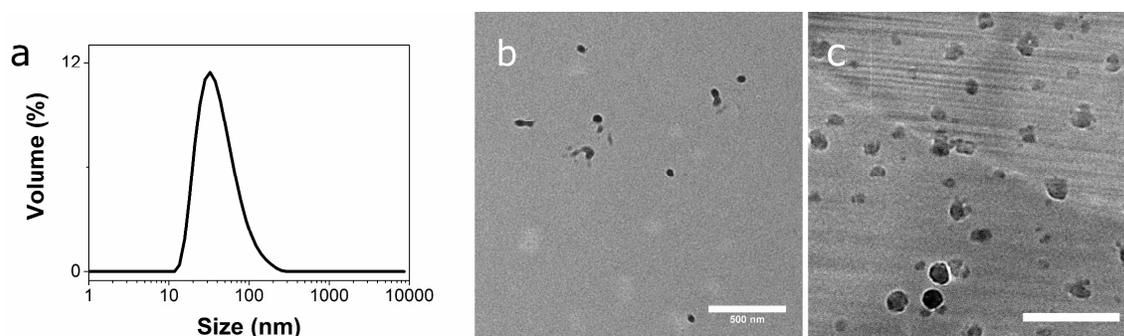


Figure S1. (a) DLS measurement of the aqueous dispersion of ECNPs, (b) TEM image of the ECNPs. Scale bar 500 nm. (c) cryo-TEM image of the ECNPs. Scale bar 200 nm.

2. Encapsulation of UV-filters and an antioxidant

The UV-filters oxybenzone (Sigma Aldrich, 98%), avobenzone (Sigma Aldrich ≥99%), octinoxate (Sigma Aldrich, 98%) and the antioxidant α -tocopherol (Sigma Aldrich, ≥95%) were encapsulated by dissolving them into the original ethanol solution with ethyl cellulose, before repeating the anti-solvent precipitation procedure.

3. Effect of antioxidant on reduction of ROS in ECNPs

ENCNPs with encapsulated: DPA (Sigma Aldrich, 97%), DPA and UV-filter, DPA and UV-filter and antioxidant, were all prepared via the anti-solvent precipitation as described above. The dispersions were diluted and added to a quartz cuvette sealed with a Teflon stopper. The cuvette was subjected to irradiation by a 75 W Xenon lamp at a distance of 20 cm (a flux of 3 mW cm⁻² between 300 and 400 nm). The absorbance was measured hourly for four hours. The total UV dose was thus 432 kJ m⁻²; equivalent to 2 hours 24 minutes of summer sunlight in Nice at noon.²

4. Photostability measurements of ECNPs with encapsulated UV-filters and antioxidant

ENCNPs with encapsulated UV-filters and antioxidant (oxybenzone, avobenzone, octinoxate, α -tocopherol, (1:1:1:1 mass ratio)) were irradiated by artificial sunlight in a identical way as described above. The absorbance does degrade slightly but only by 20% (measured from the degradation at 292 nm, Figure S2) after 4 hours of irradiation under artificial sunlight (equivalent to 2 hours 24 minutes of summer sunlight in Nice at noon²).

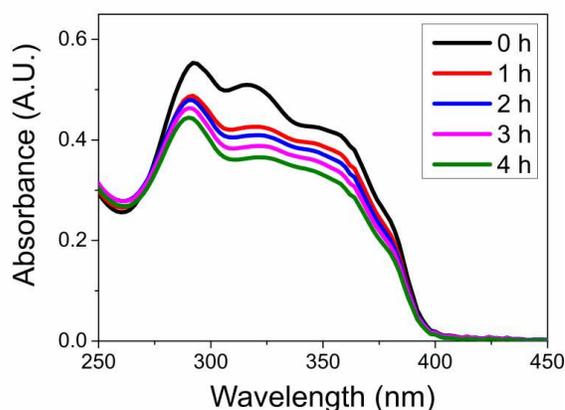


Figure S2. Absorption spectrum showing the degradation of the absorbance of the three UV-filters and antioxidant encapsulated together into ECNPs as a function of time when irradiated by artificial sunlight.

5. Preparation of UV-protective coatings

A concentrated dispersion (42 g L^{-1}) of the ECNPs containing encapsulated avobenzone was spin-coated onto plasma-cleaned glass microscope cover slips (No. 1) at 1500 rpm for one minute. Coating thickness was determined by breaking the coated cover slip in half and imaging the broken slide placed vertically in the SEM.

6. Analysis of coating thickness

Concentrated dispersions of ECNPs (42 g L^{-1}) were spin coated onto circular microscope cover slips (22 mm). Additional layers were spin coated onto the original coating layer to increase the coating thickness. The thickness of the coating was measured via SEM imaging. To achieve this, a coated microscope slide was broken in half and the broken edge was imaged from directly above. The edge of the glass was visible and a small coating layer upon it (Figure S3a). Figure S3b and S3c show the surface of the broken coated microscope slide at greater magnification and a small coating layer is visible. The thickness of the layer was determined by ten measurements at different points across the layer using ImageJ. Figure S3d is an image of the surface of the coated microscope slide. At this magnification some artefacts become apparent but to the human eye the coating is uniform.

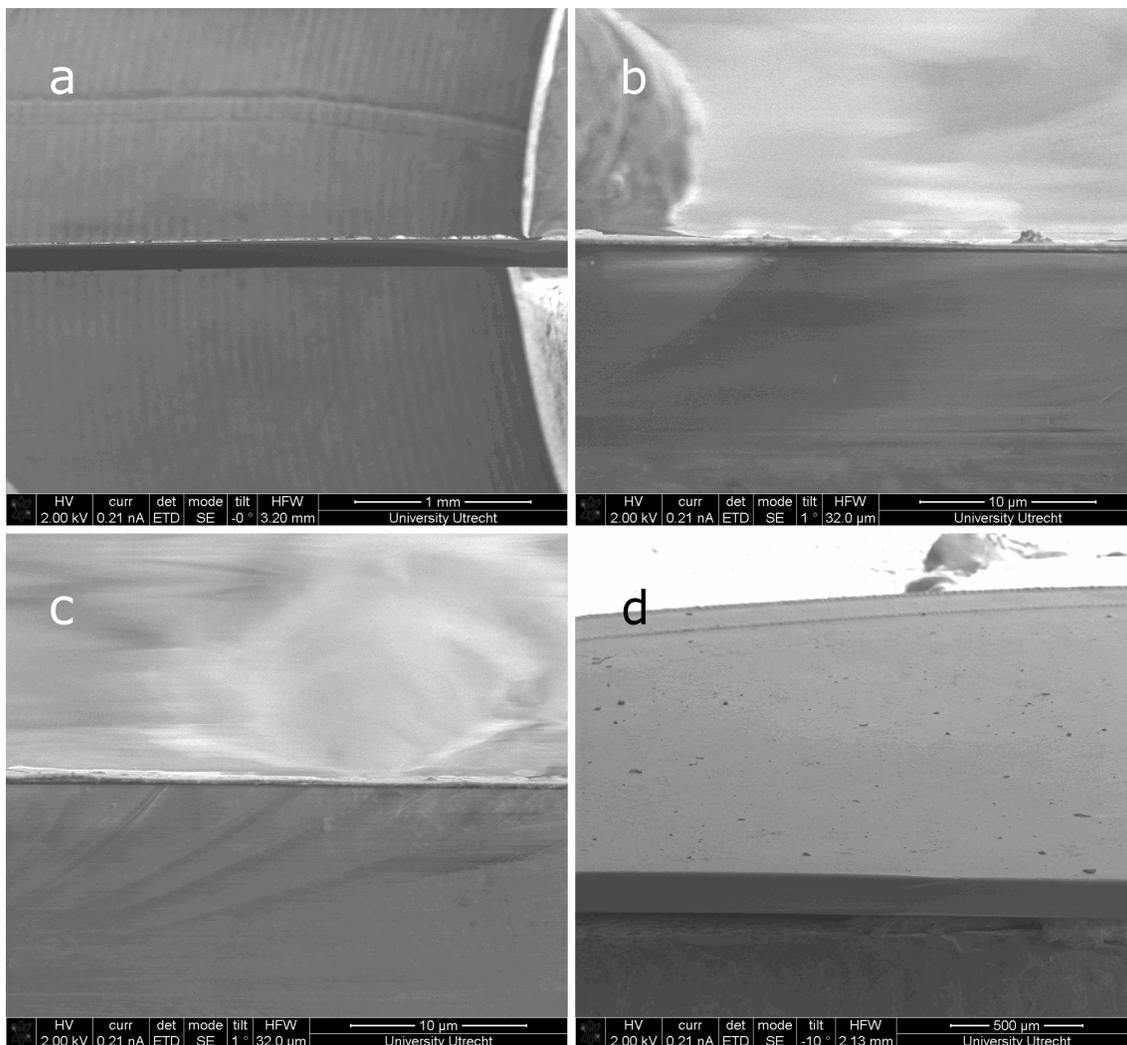


Figure S3. SEM images of the microscope slide with ECNP coating broken in half in which the coating thickness was determined. (a) The broken edge of the microscope slide is imaged from directly above at low magnification. (b) The edge is imaged at higher magnification and a thin coating layer is present. (c) The edge at a different area along the broken slide edge is imaged at high magnification. (d) The surface of the coating is imaged at low magnification and appears uniform despite some artifacts.

7. Measurements and characterizations

Aqueous ECNP dispersions were characterized by: TEM (Philips TECNAI12 electron microscope), spectrophotometry (HP 8452a), SEM (FEI XL30FEG) and DLS (Zetasizer Nano ZS, Malvern). Coatings were prepared with a spin-coater (SCS P6700) and the coating thickness images were analyzed with ImageJ. Photographs of fluorescent squares were taken

using a DigiEye (VeriVide). The photographs of the cover slips with transparent and flexible coatings were taken with a Nikon D70.

8. References

- (1) Bizmark, N.; Ioannidis, M. a.; Henneke, D. E. Irreversible Adsorption-Driven Assembly of Nanoparticles at Fluid Interfaces Revealed by a Dynamic Surface Tension Probe. *Langmuir* **2014**, *30* (3), 710–717.
- (2) Séite, S.; Moyal, D.; Richard, S.; De Rigal, J.; Lévêque, J. L.; Hourseau, C.; Fourtanier, A. Mexoryl® SX: A Broad Absorption UVA Filter Protects Human Skin from the Effects of Repeated Suberythemal Doses of UVA. *J. Photochem. Photobiol. B Biol.* **1998**, *44*, 69–76.