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Full Paper

Tunable Nanoparticles

Size and Optically Tunable Ethyl Cellulose Nanoparticles as Carriers for Organic UV Filters

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Abstract: Optically active nanoparticles (NPs) are potential building blocks for bottom-up functional technology in applications such as displays, sensors, and sunscreens. For sunscreens in particular, NPs can be used as delivery systems for organic UV filters in order to minimise skin exposure to these molecules. Here, we investigate the synthesis of size-tunable ethyl cellulose NPs (ECNPs) and their application as carriers for multiple organic UV filters. We prepared ECNPs with sizes of 50 to 165 nm via an antisolvent precipitation technique and investigate the incorporation of three commonplace organic UV filters – oxybenzone, avobenzone, and octinoxate – into the ECNPs. We found the particle loading varied greatly with each UV filter. Photodegradation of the UV filters remained unchanged upon incorporation into ECNPs and was not affected by co-encapsulating the antioxidant α-tocopherol. These results can significantly advance the development of environmentally friendly functionalized nanoparticles and UV-protective coatings.

Introduction

Nanoparticles are becoming increasingly popular as building blocks for novel functional materials via a bottom-up approach. Adding functionality to nanoparticles allows for specialization for particular applications, and this functionality is most often achieved either via surface modification or incorporation of materials into the nanoparticles. The incorporation of optically active molecules into nanoparticles, in particular, has significant importance in applications such as displays,[1,2] sensors,[1,3] pigments,[4] and sunscreens.[5–8]

Sunscreens can potentially utilize nanoparticles to address the issues surrounding possible direct skin contact with the organic UV filtering compounds. These organic UV filters – for example oxybenzone, avobenzone, octinoxate, padimate-O, and octocrylene – are often highly conjugated aromatic molecules and work by absorbing UV radiation, therefore filtering the amount that reaches the substrate (i.e. skin) which they are protecting. Despite providing vital protection against harmful UV light, there are many adverse health effects associated with the direct contact of skin with organic UV filters. Multiple studies have raised concern that organic UV filters can penetrate through the skin and enter the blood stream[7,9]. Some such UV filters, oxybenzone in particular, have also been identified as potential endocrine disruptors and potent skin allergens.[5,10–14] Moreover, many organic UV filters are also well-known for their photo-instability resulting in the production of carcinogenic reactive oxygen species (ROS) upon solar irradiation.[15–18] One prospective method to improve the stability of organic UV filters whilst also minimizing skin contact is to incorporate them into nanoparticles.

The incorporation of individual organic UV filters into nanoparticles has been demonstrated with nanoparticles designed from materials such as: silica,[8,19–21] solid-lipid nanoparticles,[22] poly-lactide particles,[7,23] gelatin,[24] cyclodextrins,[25] and ethyl cellulose[26] (EC). Nanoparticles from EC, in particular, are very appealing as carriers for organic UV filters because: i) they are biobased and biocompatible, ii) the particles can be prepared in a simple precipitation process using acceptable solvents, and iii) they are suitable for use in various solvent systems thus multiple sunscreen formulation types i.e. emulsion, oil based and even formulations containing ethanol – EC is soluble only in pure ethanol and EC nanoparticles are perfectly stable in 25% v/v ethanol.[26] Although EC nanoparticles (ECNPs) are promising carriers for UV filters in sunscreen applications, their synthesis and optical properties are not well studied.[27] In this study, we investigate the size and optical tunability of ECNPs.

Herein, we initially explore the preparation of ECNP dispersions using a simple antisolvent precipitation method and explore the range of particle sizes that can be prepared. Thereafter, we encapsulate three commercial organic UV filters (oxybenzone, avobenzone, and octinoxate) into the ECNPs and determine the maximum particle loadings for each UV filter. We then investigate the incorporation of the UV filters into the ECNPs – the particle morphological changes upon incorporation, the effect of incorporating UV filters on the ECNP

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dispersion stability, and the physical state (amorphous or crystalline) of the UV filters when incorporated. Finally, we explore the photostability of the UV filters upon encapsulation when exposed to artificial sunlight. We compare the photodegradation of the UV filters before and after encapsulation into the ECNPs, and furthermore investigate whether the photodegradation can be suppressed by co-encapsulating an antioxidant photostabilizer.

Our results provide a vital insight into the preparation of ECNPs and the incorporation of organic molecules into ECNPs to give optically functionalized nanoparticles.

Results and Discussion

Preparation of ECNPs and Investigation of the Particle Size Tunability

We investigated the size range that we could prepare ECNPs using a modified antisolvent precipitation method from literature.[28] The ability to prepare particles of very small sizes (< 100 nm) is advantageous for use in sunscreens to enhance cosmetic appeal – sunscreen formulations appear transparent when applied on skin due to the reduced scattering of visible light. We found that we could easily tune the average size of the ECNPs between 50 nm and 165 nm in diameter by varying the amount of EC used in the synthesis (see dynamic light scattering (DLS) measurements in Figure 1(a–h) and Figure 1i).

Attempts to prepare particles smaller than 50 nm by using lower concentrations of EC resulted in dispersions where the particle concentration was too low to be measured by DLS. We therefore did not probe lower concentrations than 1.6×10^{-3} g mL^{-1} of EC in ethanol. Aqueous dispersions of ECNPs of smaller sizes (42 nm) have actually been reported in literature by using lower EC concentrations and a different solvent system (isopropyl alcohol instead of ethanol).[29] Attempts to prepare particles greater in size than 165 nm resulted in bimodal, very polydisperse distributions of particle sizes (Figure S1). Moreover, there was a large amount of macroscopic aggregates formed during the precipitation. We actually found this in general, that greater amounts of macroscopic aggregates of precipitated EC formed during the antisolvent precipitation as a function of greater initial EC concentrations in ethanol. This can be explained by the decrease in the yield of particles upon increasing concentrations of EC (Figure S2, raw data in Table S1). Smaller particles were prepared with very high yields – close to 100% – but the larger particles (> 100 nm) had lower yields. Although we expect that the yield of larger particles could be enhanced by introducing a steric stabilizer, we did not use one because we wanted to keep the formulation as simple as possible.

The ECNP size shows an almost perfect linear dependence on the initial concentration of EC in ethanol Figure 1i, raw data in Table S1), a phenomenon which has previously been reported with other materials using an antisolvent precipitation method.[30–32] TEM and SEM imaging showed particle sizes consistent with the DLS measurements (Figure 2).

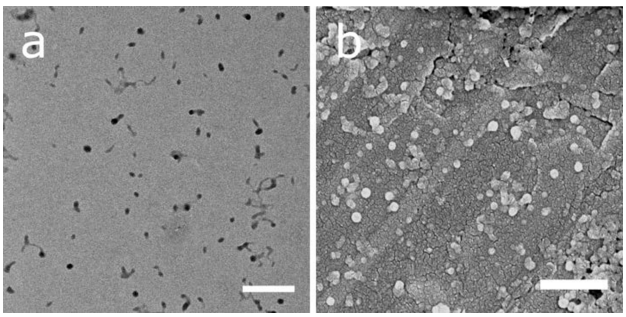

Figure 2. TEM (a) and SEM (b) image of ECNPs. Scale bars 500 nm.

We have therefore demonstrated tunability of particle sizes in the range very appealing for sunscreen applications (< 100 nm), where these very small sizes are particularly interesting because such formulations appear transparent when applied on skin.

Loading of UV Filters into ECNPs and Investigation of the Maximum Particle Loadings

We chose to investigate the ECNPs with size 71 nm (corresponding to the dispersion in Figure 1d) because these are the

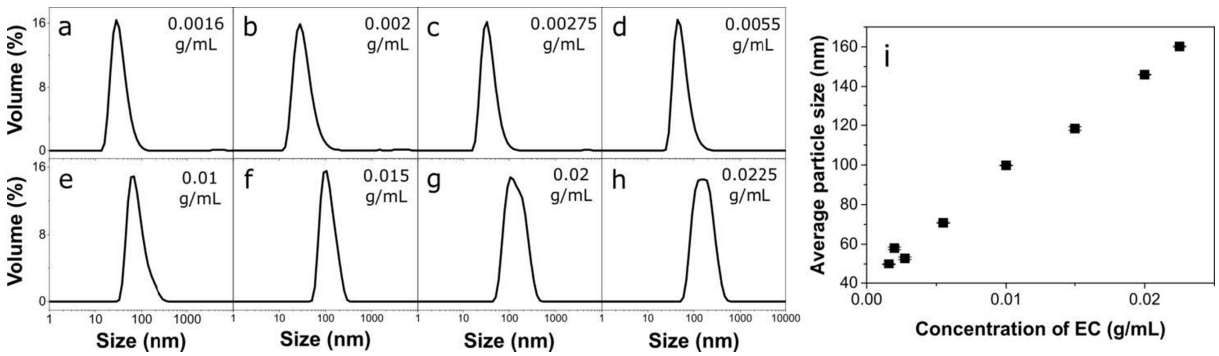

Figure 1. (a–h) Size distributions determined by DLS for ECNPs at various EC concentrations in ethanol. (i) Average particle size (values from the DLS measurements) as a function of the concentration of EC used in the antisolvent precipitation.

largest ECNPs that can be prepared with a very high yield (> 80%) (Figure S2). We then explored the optical tunability in terms of the maximum possible loadings of UV filters into the ECNPs. UV filters can be incorporated into ECNPs by performing the antisolvent precipitation with both EC and UV filter dissolved together in ethanol before pouring into water.[26] The antisolvent precipitation procedure results in aqueous dispersions of nanoparticles with incorporated UV filters, because of the coprecipitation of hydrophobic EC along with the hydrophobic UV filters. We chose to investigate the three UV filters oxybenzone, avobenzone, and octinoxate, because they are commonplace in sunscreen formulations and because of their solubility properties (soluble in ethanol and insoluble in water).

We found that all UV filters could be encapsulated efficiently and that more UV filter used in the synthesis generally resulted in more incorporated (Figure 3, data in Table S3). Interestingly, the UV filter octinoxate was efficiently incorporated to very high maximum particle loadings (54.5 wt%), whereas the UV filters avobenzone and oxybenzone show lower maximum particle loadings of 7.8 wt% and 13.8 wt% respectively. To put these loading values into context, similarly-sized ECNPs (< 100 nm) have been explored as drug carriers, showing maximum particle loadings of 17 wt% for the drug Repaglinide[33]. As an experimental observation, this lower encapsulation efficiency of oxybenzone and avobenzone is evident during the synthesis because larger amounts of macroscopic precipitate are observed after the antisolvent precipitation when larger amounts of UV filter are used. Although the exact reason for this large discrepancy in loading between the UV filters is not known, we hypothesise that this may be a result of a higher solubility of octinoxate in EC (thus a greater partition coefficient) compared with oxybenzone and avobenzone, analogous to the loading of SLNs with lypophilic drugs[34] and polycarbonate NPs with highly hydrophobic drugs.[35] Avobenzone and oxybenzone apparently have a lower solubility limit in the EC than octinoxate and therefore the ECNPs are saturated at lower loadings.

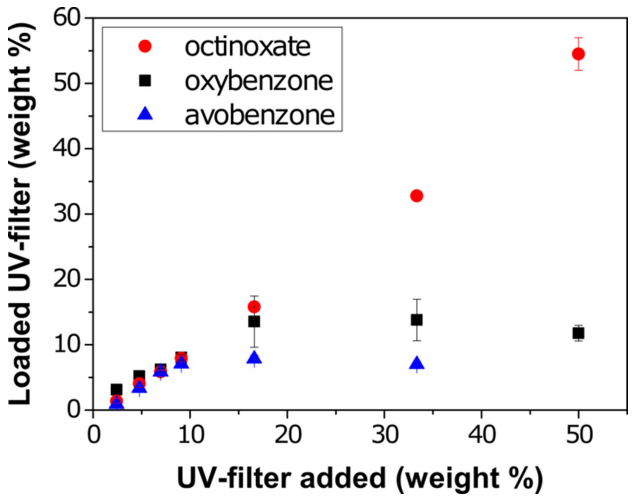

Figure 3. Amount of UV filter loaded into the ECNPs as a function of the amount of UV filter dissolved in the solvent phase in the synthesis. Actual values are reported in Table S3.

Despite the increasing amounts of precipitating material between dispersions, the loadings were still relatively low which meant that the particle sizes mostly did not change upon encapsulation of the UV filters and remained constant (~70 nm) for all dispersions except for the ECNP dispersion containing the highest loading of octinoxate (54.5 wt%), where the average particle size increased to ~90 nm (see Figure S3).

Attempting additions of large amounts of avobenzone (50 wt%) resulted in the formation of a bimodal particle distribution where micron sized particles were also observed along with the smaller ECNPs (Figure S4). This is why there is no data point in Figure 3 for avobenzone at 50 wt%. These micron sized particles are either pure avobenzone particles or avobenzone particles stabilized with some EC at the interface: similarly-sized particles form when the antisolvent precipitation procedure is carried out with an equal amount of *only* UV filter (no EC, Figure S5). The addition of very large amounts of octinoxate (> 50 wt%) also resulted in a bimodal particle distribution of micron-sized particles observed along with the smaller ECNPs (Figure S6) – similar to what we witnessed previously with large amounts of avobenzone. Similar to the case with avobenzone, we hypothesize that the larger micron-sized particles were pure octinoxate particles or octinoxate particles stabilized with some EC at the interface: similarly-sized particles form when the antisolvent precipitation procedure is carried out with an equal amount of *only* UV filter (no EC, Figure S7). The larger micron-sized particles form along with the ECNPs only when there is enough UV filter added. We hypothesize that these larger micron-sized particles only form beyond a critical point when there is enough excess unencapsulated UV filter to form stable particles.

Insight into the ECNPs with Incorporated UV Filters

We gained an insight into the incorporation of UV filters into the ECNPs with TEM imaging, zeta potential measurements, and powder X-Ray diffraction measurements.

To explore whether the particle morphology changed upon the incorporation of UV filters, TEM imaging was performed on the ECNPs from the dispersions with the highest loadings of the UV filters (13.8 wt% for oxybenzone, 54.5 wt% for octinoxate, 7.8 wt% for avobenzone). In Figure 4 we see that the ECNPs remain roughly spherical upon incorporation of the UV filters and that the particle size of the ECNPs remains consistent with the DLS measurements.

Using the zeta potential measurements we investigated two factors associated with the incorporation of UV filters into ECNPs: i) whether the dispersion was made more/less colloidally stable (and therefore prone to particle aggregation) by the encapsulation of UV filters, and ii) whether the UV filters exist surface bound, inside the ECNPs, or both upon encapsulation. With respect to the former point, Figure 5a shows that the zeta potential gets more negative as a function of greater loadings for all UV filters, which is desirable as it indicates improved

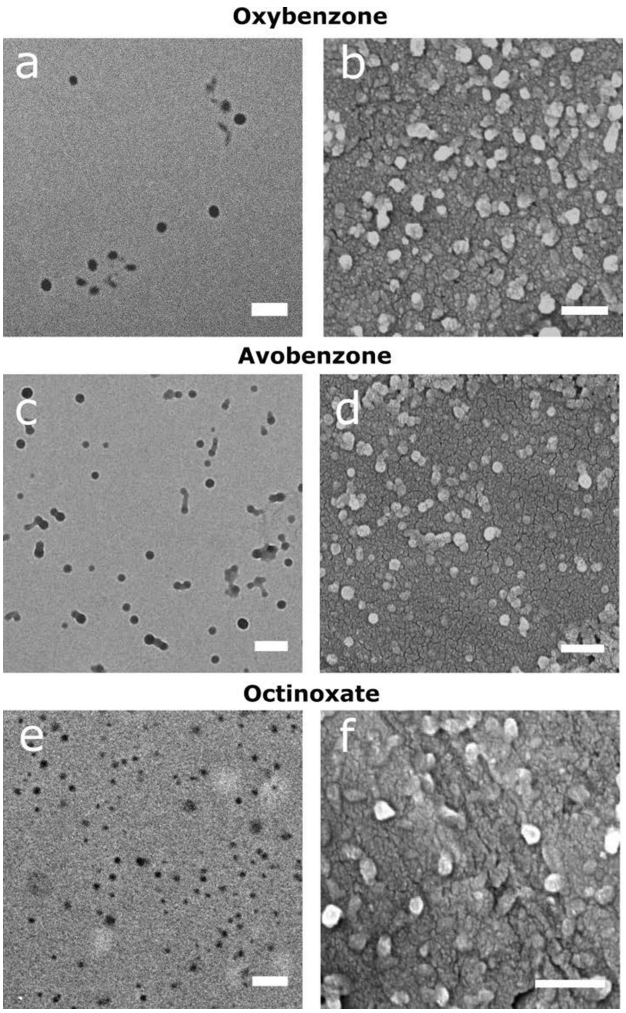

Figure 4. TEM/SEM images of ECNPs with encapsulated oxybenzone (a–b), encapsulated avobenzone (c–d), encapsulated octinoxate (e-f). All scale bars 200 nm.

stability. This could be considered a surprising result because the UV filters are all neutral molecules and therefore should have little effect on the surface charge, however, it is known that even nonpolar surfaces can acquire a considerable negative potential by adsorption of hydroxide ions released by the self-dissociation equilibrium of water.[36] A similar charging mechanism is also commonly seen with emulsions and particles stabilized by non-ionic surfactants.[32,37] With respect to the second point, it is desirable that UV filters are *less* surface bound because the intended application is for cosmetic UV protection – therefore skin contact is minimized. The change in zeta potential as a function of particle loading in Figure 5a indicates that all the three UV filters are likely present on the ECNP surface, and that higher loadings result in greater surface presence. Despite this, the UV filters are likely not *exclusively* present on the ECNP surface, and this hypothesis is supported by our findings in Figure S10 which show that the maximum loadings of the UV filters into larger ECNPs is considerably greater than would be expected if the UV filters were exclusively incorporated on the particle surface.

We gained further insight into the incorporation of the UV filter into the ECNPs using X-Ray diffraction measurements. Upon encapsulation, it is necessary that the UV filters are distributed evenly and amorphously amongst the ECNPs and therefore do not exist in crystalline clusters. Crystalline clusters would hypothetically result in an uneven distribution of UV filter across a coating prepared from these ECNPs, which is obviously undesirable. We performed the X-Ray diffraction measurements on the dried particles from the dispersions which contained the largest amount of encapsulated UV filter (13.8 wt% for oxybenzone, 7.8 wt% for avobenzone). In Figure 5b we see the crystalline nature of both UV filters oxybenzone and avobenzone in their pure form (octinoxate is a liquid and therefore was not measured) before incorporation into the ECNPs and how this crystalline nature is no longer exhibited when incorporated. These UV filters therefore exist in

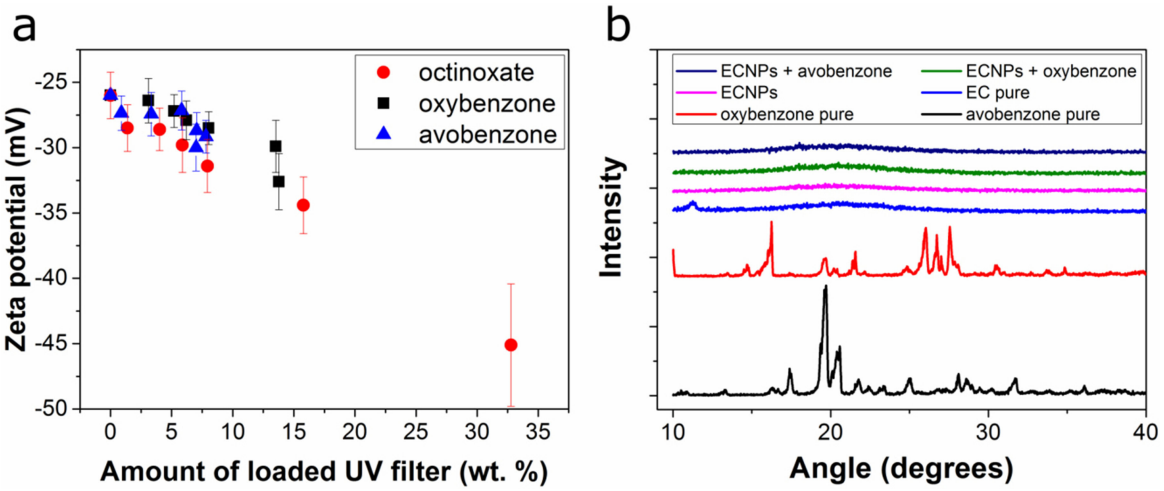

Figure 5. (a) Zeta potential as a function of the amount of the loaded UV filter for oxybenzone, octinoxate, and avobenzone. (b) X-Ray diffraction measurements for: dried ECNPs with encapsulated avobenzone (ECNPs contained 13.8 wt% avobenzone), dried ECNPs with encapsulated oxybenzone (ECNPs contained 7.8 wt% oxybenzone), pure ECNPs, pure ethyl cellulose, pure oxybenzone, and pure avobenzone.

the desired state inside the ECNPs for coating applications such as sunscreens.

Photodegradation Studies of UV Filters in ECNPs and the Effect of Co-Encapsulation with an Antioxidant Photostabilizer

Finally, an effective nanoparticle carrier for UV filters must allow the UV filters to remain photostable, where 'photostability' is quantified by the extent of the degradation of absorption of UV radiation as a function of time when irradiated by sunlight (a.k.a. photodegradation). Therefore, the ECNPs should preferably have little effect on the ability of the UV filters to absorb UV radiation as a function of time. Nanoparticles prepared from certain materials, such as poly-D,L-lactide-co-glycolide, have even been reported to actually provide a stabilizing effect on UV filters resulting in reduced photodegradation[23].

In order to investigate the photodegradation of the three UV filters (oxybenzone, octinoxate, and avobenzone) encapsulated into our ECNPs, we irradiated diluted aqueous dispersions of ECNPs with encapsulated UV filters (loading 8.0 wt%, 7.9 wt% and 7.8 wt% for oxybenzone, octinoxate, and avobenzone respectively) by artificial sunlight and measured the absorption profiles at hourly intervals for three hours in total. We found that the photodegradation of the UV filters is identical when incorporated into the ECNPs to when dissolved in ethanol (Figure 6 farthest left column compared with the middle column, no significant difference is observed in the degradation profiles). It is noteworthy that octinoxate shows a large degradation after the first hour. This is because octinoxate initially exists primarily of the high-absorbing cis isomer and irradiation of sunlight causes an isomerism of the octinoxate molecule to a racemic mixture.[38] The identical photodegradation profiles of the UV filters when both incorporated and not incorporated therefore show that ECNPs fulfill the requirement of allowing the UV filters to remain photostable when incorporated.

The photostability of UV filters is known to be influenced by the presence of antioxidants, which are commonly added to sunscreen formulations for this reason. The antioxidants – in particular α-tocopherol – are primarily known to neutralize the degradation products generated as a result of irradiation by sunlight.[39–41] Some studies, although less common, have also

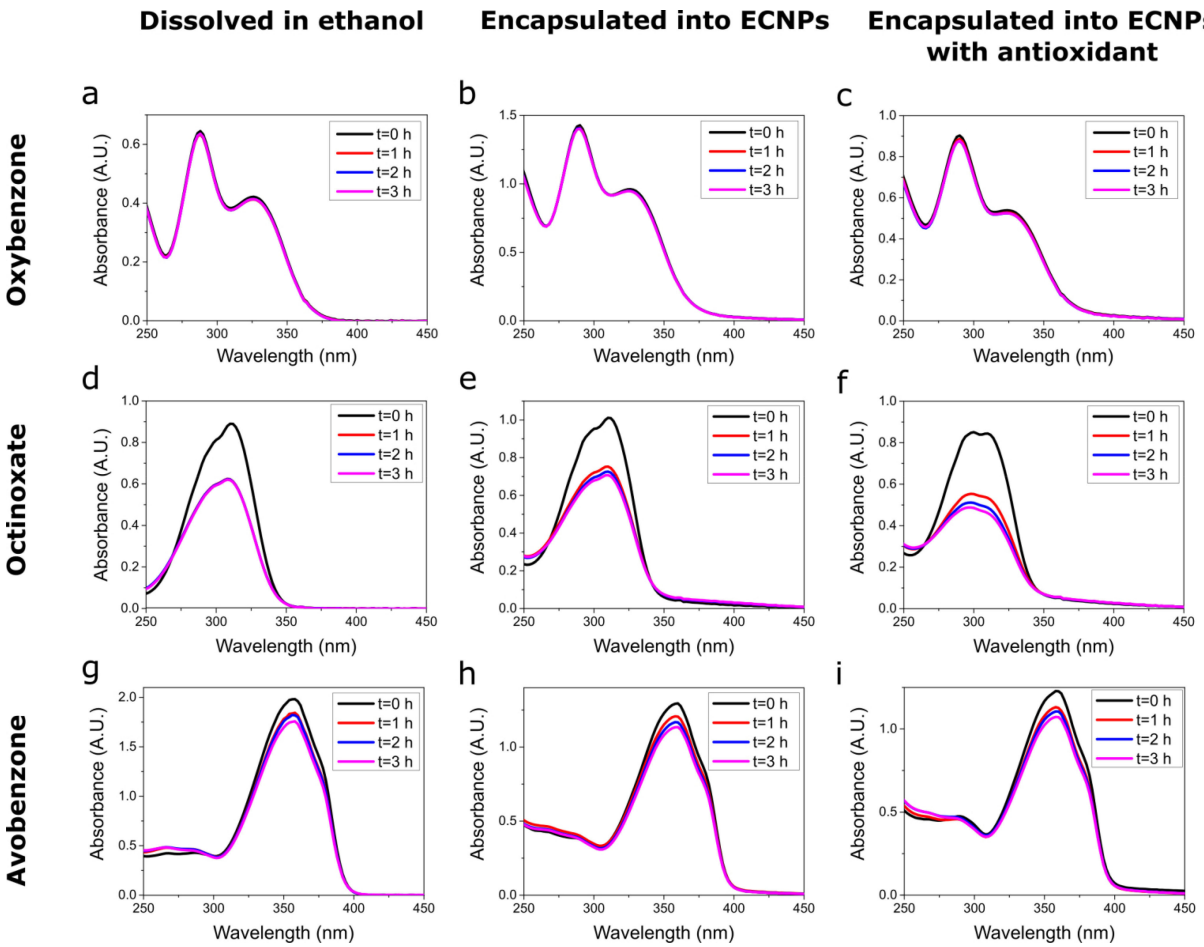

Figure 6. Absorbance measurements of the three UV filters (octinoxate, avobenzone, and oxybenzone) taken at hourly intervals when irradiated by artificial sunlight. (a, b, c) correspond to oxybenzone, (d, e, f) correspond to octinoxate, (g, h, i) correspond to avobenzone. (a, d, g) The UV filters are dissolved in ethanol, (b, e, h) the UV filters are encapsulated into ECNPs, (c, f, i) the UV filters are encapsulated into ECNPs along with an antioxidant which is co-encapsulated (mass ratio 1 : 1).

reported α-tocopherol to provide a beneficial effect towards-suppressing the photodegradation of UV filters.[41,42] We therefore investigated whether co-encapsulating α-tocopherol along with UV filters in ECNPs would suppress the photodegradation of the UV filters.

In previous work, we observed that the incorporation of octinoxate and α-tocopherol in a 1:1 ratio into ECNPs results in a significant suppression of the reactive oxygen species produced upon irradiation by artificial sunlight.[26] Here, we therefore prepared three ECNP dispersions with this same 1:1 ratio of UV filter to antioxidant but this time investigated the effect of the antioxidant α-tocopherol on the *photodegradation* of the three UV filters oxybenzone, avobenzone, and octinoxate. Dispersion 1 consisted of ECNPs with oxybenzone and α-tocopherol incorporated, dispersion 2 consisted of ECNPs with octinoxate and α-tocopherol incorporated, and dispersion 3 consisted of ECNPs with avobenzone and α-tocopherol incorporated. The incorporation of the α-tocopherol is evident from the slightly increased absorbance peak at $\lambda = 288$ nm (see Figure S11 for absorption spectrum of ECNPs with *only* α-tocopherol incorporated), as can be seen in Figure 6 (most noticeable when comparing Figure 6h with Figure 6i). The dispersions were stable and the particles were sized ~70 nm.

Interestingly, we observed no photo-stabilizing effect of the antioxidant α-tocopherol on any of the three UV filters. This can be seen in Figure 6, in which the photodegradation profiles where an antioxidant is co-encapsulated with the UV filter (in the farthest-right column) show no lesser photodegradation than when no antioxidant is incorporated (middle column). In fact, we found that the photodegradation of octinoxate was actually marginally greater in the presence of the antioxidant α-tocopherol (Figure 6f shows a marginally greater degradation than Figure 6e). It is conceivable that this marginally greater degradation is not actually the octinoxate photodegrading faster, but the α-tocopherol – which absorbs in the same region as octinoxate and is known to photodegrade[43] – also photodegrading. These results imply that the antioxidant α-tocopherol does *not* suppress photodegradation of UV filters, and thus the antioxidant's stabilizing effect comes only in neutralizing the skin-damaging decomposition products which we have shown in previous work.[26]

Conclusions

We demonstrated the preparation of ECNPs with tunable size (50–165 nm) via an upscalable antisolvent precipitation technique. We then investigated the loading of ECNPs with the three commonplace commercial UV filters: oxybenzone, avobenzone, and octinoxate.

We found that the maximum loadings varied strongly depending on the encapsulated UV filter (avobenzone 7.8 wt%, oxybenzone 13.8 wt%. octinoxate 54.5 wt%). TEM imaging showed the composite particles remained spherical with no significant morphological changes upon incorporation of the UV filters. The incorporation of greater amounts of UV filters resulted in moderate (avobenzone, oxybenzone) to strong (octinoxate) increases in the zeta potential. X-Ray diffraction measurements showed that the UV filters exist in an amorphous state upon incorporation into the ECNPs. Photostability of the UV filters was not affected after incorporation into the ECNPs. Moreover, the addition of an antioxidant didn't result in better maintenance of absorbance by the UV filters, contrary to some other studies.[41,42]

Here, we studied the incorporation of three commonplace UV filters into ECNPs and conclude that ECNPs have great potential in photoprotection applications because of their simple size and optical tunability, upscalable potential and biobased nature. UV-absorbing ECNPs can significantly advance the utilisation of biobased functionalized nanoparticles for many industrial applications where photoprotection is required, but further studies are needed for this to become a commercial reality, such as the extent of leakage, the incorporation of biobased UV filters and photostabilisers, and tests on the compatibility of ECNPs with other formulation components.

Experimental Section

Materials

Ethyl cellulose (EC) degree of substitution 2.1–2.6 (100 cP, lot number MKBT0521V), oxybenzone (98%, solubility in water 69 mg/L at 25 °C (PubChem database)), avobenzone (≥99%, solubility in water 2.2 mg/L at 25 °C (PubChem database)), octinoxate (98%, solubility in water 0.4 mg/L at 24 °C (PubChem database)), antioxidant α-tocopherol (≥95%) were all purchased from Sigma Aldrich. Ethanol (100%) was purchased from Interchema and pure water was used from a Millipore system.

Preparation of ECNPs

ECNPs were prepared via a modified 'antisolvent precipitation' technique from literature[28]. We prepared a series of various sizes of ECNPs by dissolving various masses of EC (0.08 g, 0.1 g, 0.1375 g, 0.275 g, 0.5 g, 0.75 g, 1 g, 1.125 g, 1.25 g) in ethanol (50 mL) before pouring into the antisolvent water (150 mL, pH 5–6) under fast magnetic stirring, resulting in the spontaneous formation of ECNPs. Rotary evaporation removed the ethanol and some water until the dispersion was 50 mL. If too much was evaporated, the dispersions were topped up to 50 mL with water to keep particle concentrations constant. The dispersions were then passed through a 1.2 μm filter to remove any large aggregates that formed. The dispersions were prepared two-fold.

Loading of UV Filters into ECNPs

UV filters were encapsulated into ECNPs via a coprecipitation in the same antisolvent synthesis described above. We prepared a series of various amounts of encapsulated UV filter in ECNPs, where each series contained six dispersions for each UV filter oxybenzone, avobenzone, and octinoxate. Here, EC (0.275 g) *and* UV filter (6.9×10^{-3} g, 0.014 g, 0.021 g, 0.028 g, 0.055 g, 0.14 g, see full data in Table S2) were both dissolved in ethanol (50 mL) before pouring into antisolvent water (150 mL). The same antisolvent precipitation procedure was then followed (evaporation, top up to 50 mL, pass through a filter) resulting in 50 mL aqueous dispersions of ECNPs with encapsulated UV filters.

Determination of Particle Loadings

Loadings of UV filter in ECNPs were determined via a spectrophotometric method. Here, approximately 40 mL of the ECNPs with encapsulated UV filter dispersions was dried in a glass 100 mL beaker with magnetic stirrer at 80 °C overnight. The following morning, the dried solid was removed from the beaker and weighed. This known mass of ECNPs with encapsulated UV filter was then completely dissolved in ethanol (10 mL) in a small glass vial sealed with a cap. Once completely dissolved, a certain amount of this solution was diluted by a known amount (usually 100 times further – 0.1 mL solution made up to 10 mL with water) and the absorption spectrum was measured using a HP 8452a spectrophotometer. The absorbance value at the peak in the spectrum was compared with a pre-prepared calibration curve comprised of multiple concentrations of UV filter dissolved in ethanol. The measurements were performed in triplicate.

Particle Size Characterisation

ECNPs were characterised with TEM (Philips TECNAI12 electron microscope) in which the samples were prepared by pipetting a drop of the ECNP dispersion onto a Butvar-coated TEM grid, SEM (FEI XL30FEG), and DLS (Malvern Zetasizer Nano ZS, particle size distributions were obtained by using a CONTIN fitting).

Powder X-Ray Diffraction Measurements

Powder X-Ray Diffraction measurements were performed with PW 1729 Philips diffractometer, equipped with a Cu Kα X-ray source ($\lambda = 1.5418$ Å), by drying the dispersions overnight at 80 °C under stirring and taking the resultant solid material for the XRD measurements.

Zeta potential Measurements

Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS, at equal particle concentrations, equal dilutions, and in the presence of a background salt (10 mM NaCl). The pH was also kept constant (that of milliQ water, pH 5–6). Keeping the pH constant therefore allowed us to directly compare the particles from dispersion to dispersion. Typically, a sample of the ECNP dispersion was taken and this was diluted 40 times (i.e. 0.1 mL dispersion topped up to 4 mL with water which contained 10 mM dissolved NaCl). All measurements were performed one day after preparation of the ECNP dispersion.

Photodegradation Studies of UV Filters in ECNPs and the Effect of Co-Encapsulation with an Antioxidant Photostabilizer

ECNPs with encapsulated UV filters were prepared as described above. Encapsulating an antioxidant was also done in the same manner, where EC (0.275 g), antioxidant α-tocopherol (0.028 g) and UV filter (0.028 g) (therefore mass ratio 1:1) were dissolved in ethanol before performing the antisolvent precipitation as described above.

In order to quantify the photodegradation, the dispersions were diluted with water 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 three hours. The total UV dose was thus 324 kJ m^{-2}; equivalent to 1 hour 48 minutes of summer sunlight in Nice at noon[44].

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: antioxidants · UV filters · nanoparticles · photoprotection · sunscreens

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