Electronic Supplementary Material

Boosting the effectiveness of UV filters and sunscreen formulations using photostable, non-toxic inorganic platelets

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Contents

1. Experimental section

1.1 Materials

Sodium hydroxide, sodium carbonate, magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), and aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were purchased from Sigma-Aldrich. The UV filters, including Tinosorb®S Lite Aqua, Uvinul® T 150 and Uvinul® A Plus Granular were obtained from BASF. The sunscreens were purchased from NIVEA. All chemicals and materials were used without purification.

1.2 Synthesis of Mg_2Al-LDH nanoplatelet

The metal precursor solution (50 mL) of 8.552 g $Mg(NO_3)_2{\cdot}6H_2O$ (33.4 mmol) and 6.25 g $Al(NO_3)_3{\cdot}9H_2O$ (16.67 mmol) were added quickly into the mixing solution (200 mL) of 3.5298 g Na_2CO_3 (33.4 mmol) and 4 g NaOH (100 mmol) under a 1000 rpm stirring at room temperature. The suspension was continuously stirring for 30 mins at room temperature. The mixture was then divided into 5 tubes for centrifugation and washed by DI water for three times. Following redispersion the solid product of each tube in 50 mL DI water, these suspensions were the aged at 25, 50, 100, 150 and 200 ℃ for 18 h, respectively. The obtained Mg_2Al-LDHs were denoted as Mg_2Al-LDH-25, Mg_2Al-LDH-50, Mg_2Al-LDH-100, Mg_2Al-LDH-150 and Mg_2Al-LDH-200. The wet form of Mg_2Al-LDHs was used for UV absorption and light scattering measurements after density confirmation. The solid powder of Mg_2Al-LDHs was used for the XRD and TEM characterization.

1.3 Optical measurements

Optical measurement was conducted by using the UV-Vis-NIR spectrophotometer (PerkinElmer lambda 1050+). Both UV/vis properties of scattering and adsorption of well-dispersed LDH samples were measured by using a 150 mm diameter integrating sphere and 1 cm quartz cuvettes.

To investigate UV/vis scattering properties, different modes were used (**Fig. S1**). Forward scattering (FS) measures all the scattered light propagating to the forward direction, and the cuvette is positioned in the front of the integrating sphere. Backward scattering (BS) counts for all the scattered light propagating to the backward direction, and the cuvette is attached to the backside of the integrating sphere. Total scattering (TS) is all the scattered light in all directions, and the cuvette is put inside the integrating sphere. Side scattering (SS) can be calculated as:

SS = TS – FS – BS

To get the portion of the absorption, we need to know all the light that is scattered, directly reflected and directly transmitted. In the STR (the sum of scattering, transmittance and reflectance) mode as shown in **Fig. S1**, all the lights that scattered in all directions, directly transmitted and directly reflected are all collected by the integrating sphere; therefore, the UV absorption (A_{UV}) can be calculated as below:

A_{UV} = 1 – STR

The boosting effect was conducted by comparing the UV absorption (A_{UV}) with and without adding Mg_2Al-LDHs to the UV absorbers. Both commercial, skin contact-approved UV filters and commercial sunscreens were used as UV absorbers. For Tinosorb®S Lite Aqua, the solid content of 0.0003% was applied for the boosting effect investigations. To get the boosting effect of Mg_2Al-LDHs, the UV absorption (A_{UV}) with and without Mg_2Al-LDH in 0.0003% Tinosorb®S Lite Aqua were measured, which were denoted as $A_{UV\text{-}w/LDH}$ and $A_{UV\text{-}0/w\ LDH}$, respectively (the A_{UV} is usually obtained at the representative wavelength, such as 340 nm for Tinosorb®S Lite Aqua). The boosting effect ($E_{boosting}$) was calculated as followings:

$E_{boosting} = A_{UV\text{-}w/LDH} / A_{UV\text{-}0/w\ LDH}$

Similar measurements were used for other UV absorbers. All measurements would be repeated three times at least for each sample.

The photostability studies were conducted by measuring the UV absorption (A_{UV}) of the mixture of 0.1 wt% Mg_2Al-LDH-150 and commercial sunscreen before and after 2-h UV radiation by using the portable UV light. The portable UV light has two outputs, one is 365 nm in the UVA range and the other one is 254 nm in the UVC range. The stability was evaluated by the variation of the UV absorption (A_{UV}) over time (240 h) with the mixture of 0.1 wt% Mg_2Al-LDH-150 and a commercial sunscreen, this mixture was kept in the dark without exposure to light during the stability test. All these measurements are repeated three times for each sample.

1.4 Sun Protection Factor (SPF) measurement

The SPF values of prepared sunscreens were measured by the UV-2000s ultraviolet transmittance analyser (Labsphere, USA). 50 mg sunscreen samples were evenly transferred to the surface of polymethyl methacrylate (PMMA) plate (50 × 50 mm) using a disposable syringe, then coated as soon as possible by a covered finger. After being dried in the dark room for 15 min, and the tests were conducted. Every test was repeated for five times for each sample.

1.5 Characterisation

X-ray diffraction (XRD) measurements were recorded on Bruker D8 diffractometer (40 kV and 30 mA) with Cu K_α radiation (λ_1 = 1.544 Å and λ_2 = 1.541 Å). LDH samples were mounted on PMMA sample holders.

Transmission electron microscopy (TEM) images were gained by a JEOL 2100 microscope with an accelerating voltage of 200 kV using a single tilt specimen at DCCEM within the Department of Materials, University of Oxford. LDH nanoplatelets were dispersed in ethanol with sonication and then casted onto copper grids.

The particle diameter distribution of LDHs was obtained by randomly measuring ~150 nanoparticles by TEM, following the calculation of their average particle diameter (d) according to the equation of $d = \sum d_i/n$ (d_i is the diameter of particle, i is the index of the summation, and n is the upper limit of summation) and the standard deviation.

2. Supporting figures

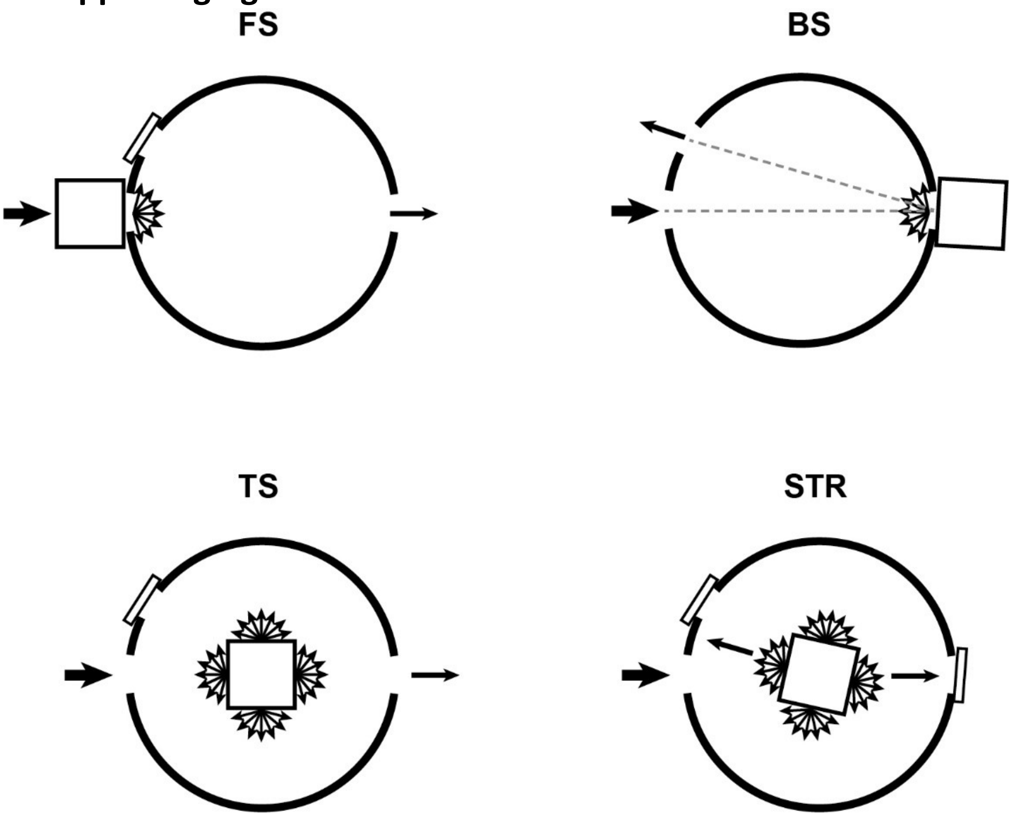

Figure S1. Schematic of four optical measurement modes, namely FS, BS, TS and STR using an integrating sphere measurement system and the samples in a 1 cm quartz cuvette with DI water as solvent.

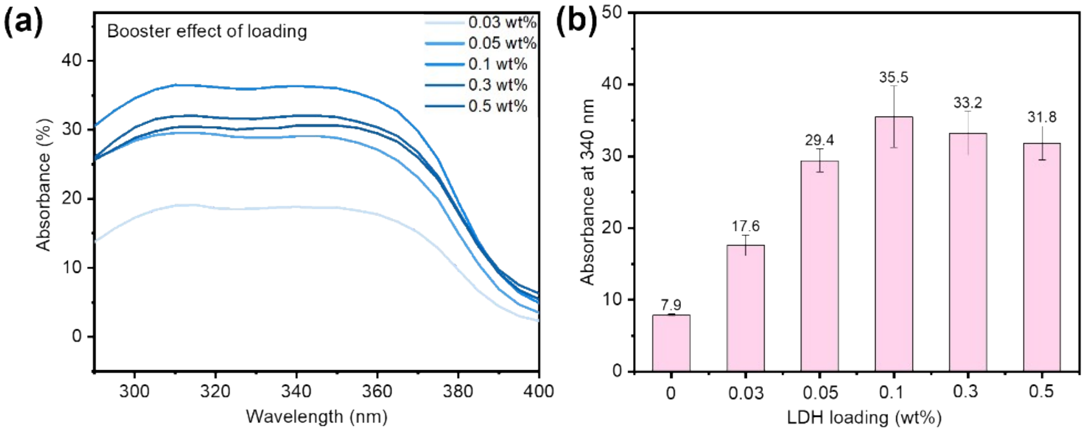

Figure S2. The absorbance of the mixture with a different solid content of Mg_2Al-LDH-150 and 0.0003% Tinosorb S Lite Aqua (a) and its summary of the absorbance at 340 nm (b).

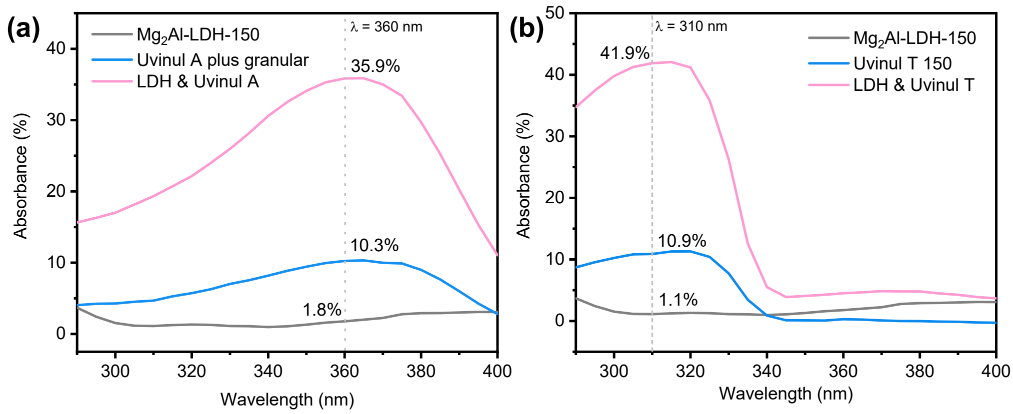

Figure S3. Boosting effect of Mg_2Al-LDH-150 on (a) Uvinul® A Plus Granular; (b) Uvinul® T 150 (The loading of all LDHs is fixed at 0.1 wt%).

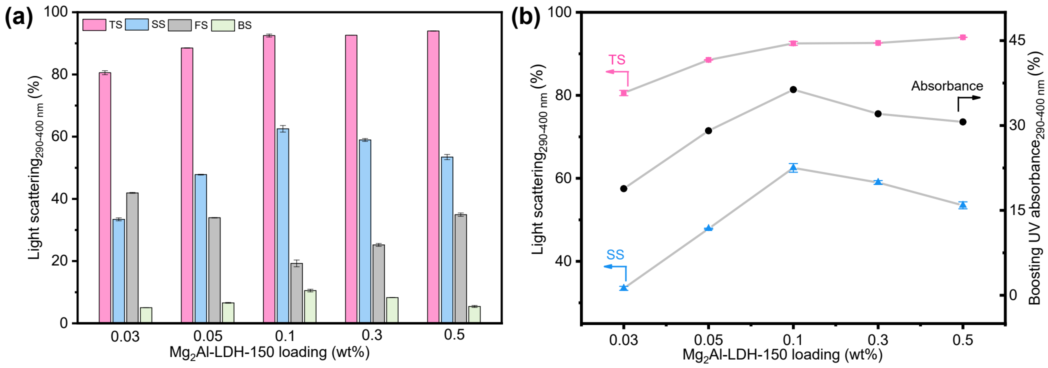

Figure S4. (a) Mg_2Al-LDH-150 platelet loading-dependence light scattering. (b) The comparison of the loading-dependence total scattering, side scattering and absorbance to the loading-dependence boost effect. The error bar represents the standard error from the repeated experiments. Average (mean) from 290 nm to 340 nm UV range

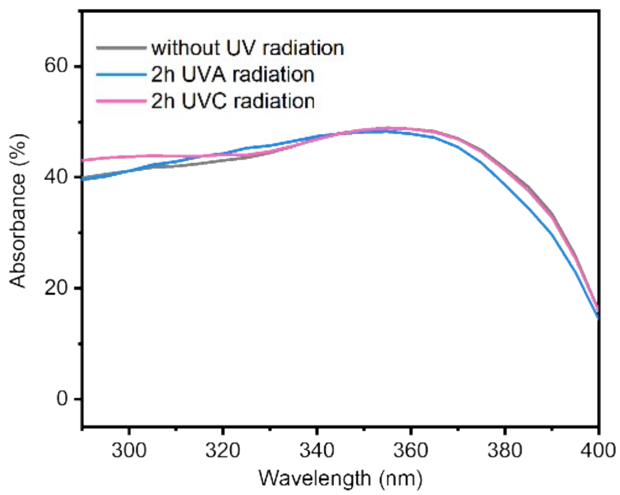

Figure S5. The photostability of Mg_2Al-LDH-150 platelet by 2-h UV radiation.

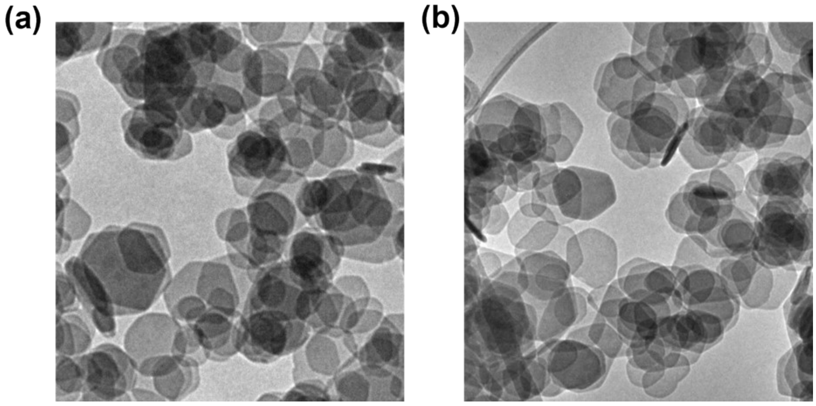

Fig. S6. The TEM images of Mg_2Al-LDH nanoplatelet before (**a**) and after (**b**) the photostability study.

3. Supporting tables

Table S1. The summary of the particle size dependence of light scattering. Average (mean) between 290–340 nm.

	Average particle diameter (nm)	Total scattering (%)	Side scattering (%)	Forward scattering (%)	Backward scattering (%)
Mg_2Al-LDH-25	18 ± 3	66.9±1.3	10.6±0.8	52±0.5	4.4±0.01
Mg_2Al-LDH-50	27 ± 5	72.8±0.7	20.0±0.5	47.6±0.2	5.3±0.01
Mg_2Al-LDH-100	81 ± 19	89.1±2.3	54.4±1.7	23.6±0.6	11.1±0.05
Mg_2Al-LDH-150	280 ± 55	92.5±0.5	62.6±1.1	19.3±1.1	10.6±0.4
Mg_2Al-LDH-200	376 ± 73	91.4±0.9	58.0±1.6	24.7±1.9	9.6±0.6

Table S2. The summary of the solid content dependence of light scattering. Average (mean) between 290–340 nm.

Sold content of Mg_2Al-LDH-150 (wt%)	Total scattering (%)	Side scattering (%)	Forward scattering (%)	Backward scattering (%)
0.03	80.6±0.6	33.5±0.5	42.0±0.1	5.1±0.02
0.05	88.5±0.04	47.9±0.1	34.0±0.06	6.7±0.1
0.1	92.5±0.5	62.6±1.05	19.3±1.1	10.6±0.4
0.3	92.6±0.02	59.0±0.5	25.3±0.5	8.3±0.01
0.5	94.0±0.02	53.5±0.8	35.0±0.5	5.5±0.3

Table S3. The summary of the SPF boosters reported in boosting the SPF value.

SPF Booster	Loading	Boosting effect	reference
Mg_2Al-LDH	3 wt%	206%	This work
SunSpheres™ (styrene/acrylate polymer)	5 wt%	173%	[1]
Sunhancer™ (Wax from plant)	5 wt%	189%	[2]
Silica microparticles	10 %	140%	[3]
Hollow Polydopamine (h-PDA_St10_DA1.2)	5 wt%	234%	[4]
Na-lignosulfonate	5 wt%	125~172%	[5]
Bacillus Lysate	3.5 %	133%	[6]
Calcium phosphates (Cap-N)	9 wt%	199%	[7]

Reference

[1] SunSpheres^{TM} SPF booster in Daily Wear Applications. (https://www.dow.com/documents/324/324-06420-01-sunspheres-spf-booster-in-daily-wear-applications.pdf?iframe=true)

[2] Sunhancer^{TM} Eco SPF booster. Protects from the sun. Respects the planet. (https://www.lubrizol.com/Personal-Care/Products/Sunhancer-Eco-SPF-booster)

[3] J. Lademann, S. Schanzer, U. Jacobi, H. Schaefer, F. Pflücker, H. Driller, J. Beck, M. Meinke, A. Roggan and W. Sterry, *J. biomedi. opt.*, 2005, **10**, 014008.

[4] Y. Wongngam, G. Supanakorn, R. Thiramanas and D. Polpanich, *ACS Biomater. Sci. Engineer.*, 2021, **7**, 3114-3122.

[5] F. Lorquin, J. Lorquin, M. Claeys-Bruno, M. Rollet, M. Robin, C. Di Giorgio and P. Piccerelle, *Sustain. Chem. Pharm.*, 2021, **24**, 100539.

[6] K.S. Landry, E. Young, T.S. Avery and J. Gropman, *Cosmetics*, 2023, **10**, 138.

[7] A. Adamiano, F. Carella, L. Degli Esposti, C. Piccirillo, and M. Iafisco, *ACS Biomater. Sci. Engineer.*, 2022, **8**, 4987-4995.