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

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We have studied the size-dependent optical scattering of aqueous suspensions containing Mg<sub>2</sub>Al-LDH platelets, which exhibit high total- and side-scatterings. By incorporating 3 wt% Mg<sub>2</sub>Al-LDH platelets (280 nm) in a commercial sunscreen formulation, we achieved a twofold Sun Protection Factor boost, providing a promising, high-efficient and non-toxic strategy to enhance sunscreen effectiveness.

Overexposure to UV radiation can lead to considerable harm to humans, including sunburn, erythema, premature skin aging, and the risk of skin cancers.<sup>1,2</sup> To safeguard against UV radiation, sunscreens have been developed since 1928. In 2022 the global sun care product market size was valued at \$13.97 billion. Projections indicate an anticipated growth from \$14.40 billion in 2023 to \$19.65 billion by 2030.<sup>3,4</sup> The active ingredient in sunscreen is the UV filter, which can be classified as either physical or chemical UV filters. Typical physical UV filters are inorganic compounds (e.g., TiO<sub>2</sub> and ZnO) which can protect the skin by both reflecting and absorbing the UV radiation. Chemical UV filters are usually organic compounds, such as triazines, avobenzenes and ensulizoles, known for their ability to absorb light and release it as heat or light.<sup>5</sup> However, it has recently become evident that both inorganic and organic UV filters have unfavourable safety impacts on both human health and the environment.<sup>6–10</sup> For example, UV absorption by these filters increases their photoactivity, resulting in the generation of

harmful radicals.<sup>9,10</sup> A number of commonly used organic UV filters (e.g., ethylhexyl triazone) have been found in several aquatic organisms, raising concerns on their potential environmental impacts.<sup>7</sup> Therefore, a key challenge has arisen in minimising the quantities of UV filters used in sunscreen formulations while still ensuring high sun protection efficacy.

The incorporation of a sun protection factor (SPF) booster into sunscreen formulations has been considered as an effective strategy to reduce the proportion of the active UV filter but still offering a high level of skin protection.<sup>11</sup> SPF boosters do not act as active optical absorbers. Instead, they should meet specific requirements as an ingredient in sunscreen, possessing several key attributes: (i) negligible UV radiation absorption; (ii) safe for both human use and the environment; (iii) compatibility with a wide variety of sunscreen formulations. Significant effort has been focused on the development of SPF boosters from natural sources, such as green coffee oil, spruce bark stilbenes, and lignin-based substances (e.g., lignosulfonates).<sup>12–17</sup> Another type of SPF boosters is synthetic polymer-based materials, such as polydopamines and styrene/acrylates copolymers.<sup>18,19</sup> Some of them have been commercialised. Sunhance<sup>TM</sup> (made from plant sources by Lubrizol) and SunSpheres<sup>TM</sup> (a copolymer from Dow Chemicals) are two examples of SPF boosters in the current market. Although these SPF boosters are biocompatible, they both usually contain organic components with UV absorption. This may lead to poor photostability or require restricted cosmetic application due to the strict audit process concerning both legal and safety use considerations.<sup>20</sup> Some attempts have been made to use inorganic materials as SPF boosters, such as TiO<sub>2</sub>, ZnO, silica and alumina. Typically, inorganic materials can enhance the UV absorption efficiency of the organic UV filter. For instance, the incorporation of 10% spherical silica can boost the UV absorbance of Evans blue by a factor of 1.8.<sup>21</sup> However, other potential inorganic boosters (e.g., TiO<sub>2</sub>) exhibit photocatalytic activity, which can result in the photodegradation of organic UV filter component or generation of harmful radicals. Some inorganic SPF boosters, such as ZnO and TiO<sub>2</sub>, have been

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approved as UV filters, leading to their use as SPF boosters in sunscreen restricted and limited by regulation.<sup>22</sup> Hence, there is an urgent need to develop biocompatible, safe and effective inorganic SPF boosters to enhance both the efficacy and safety of sunscreen formulations.

Layered double hydroxides (LDHs) are a large class of anion exchangeable inorganic materials that are described by the formula  $[M_{1-x}M'_x(OH)_2]^{a+}[(A^{n-})_{a/n}] \cdot bH_2O$  (M and M' are divalent and trivalent metal cations respectively, A is charge balancing anion, and  $0 < x < 1$ ). The first naturally occurring LDH was named hydrotalcite,  $[Mg_{0.75}Al_{0.25}(OH)_2][CO_3]_{0.125} \cdot 0.5H_2O$ . In general,  $[Mg_{1-x}Al_x(OH)_2][CO_3]_{x/2} \cdot bH_2O$  (noted as  $(Mg_{(1-x)/x}Al$  LDHs)) are proven to be biocompatible and non-toxic materials. MgAl-LDHs have been generally recognized as safe (GRAS) by the US Food and Drug Administration (FDA) (UNII:17432CG1KU)<sup>23</sup> and it also has EU approval as an antacid medicine and as a food contact safe material (GRAS) (PM/REF: 34690 & 60080).<sup>24</sup> Additionally, LDHs have been shown to induce low cell cytotoxicity in a number of studies.<sup>25–27</sup> Furthermore, a related zinc layered hydroxide has been commercialised as an active ingredient in a face brightening cosmetic (Vitabrid C<sup>12™</sup>).<sup>28</sup> In addition to the known safety data for  $Mg_{(1-x)/x}Al$ -LDHs, there are potentially significant additional advantages for its use as an effective booster in sunscreen formulations: (i) its white appearance; (ii) thermal and UV stability; and (iii) low photocatalytic activity; (iv) existing commercial good manufacturing practice (GMP) production capacity. In earlier studies, the research mainly focused on the use of LDHs as UV filters by designing and synthesizing molecular UV absorbers intercalated within LDHs structure. However, LDHs in those cases were functioned as UV absorbers rather than SPF boosters.<sup>29</sup> Herein, we have exploited size-dependent particle scattering as a SPF boost mechanism to enhance the optical absorbance of an absorber formulation.<sup>30</sup> Although the scattering of UV radiation by  $Mg_{(1-x)/x}Al$ -LDH particles has been reported,<sup>31</sup> their use as tailor-made SPF booster to enhance SPF in sunscreen formulations has not been reported.

In this work, we have systematically studied the platelet diameter-dependence of the optical scatterings of  $Mg_2Al$ -LDH 2D platelets in aqueous suspensions using an integrating sphere measurement system (Fig. S1, ESI†). We have discovered a size-optimised  $Mg_2Al$ -LDH platelet for boosting the UV absorption performance of skin contact approved broad spectrum UV absorbers.

We prepared five  $Mg_2Al$ -LDH 2D platelet samples with the platelet diameter distribution covering the range 18–376 nm. To enable platelet diameter control, we created instantaneous nucleation of the  $Mg_2Al$ -LDH platelets by rapidly mixing the metal precursors with a mixture of sodium carbonate and sodium hydroxide solution. The as-formed wet solid was then dispersed in deionised (DI) water for subsequent aging process at the various temperatures between 25–200 °C to control the final particle diameters of  $Mg_2Al$ -LDH platelets.  $Mg_2Al$ -LDHs prepared after aging for 18 h at 25, 50, 100, 150 and 200 °C, are denoted as  $Mg_2Al$ -LDH-T (T is the temperature. *e.g.*,  $Mg_2Al$ -

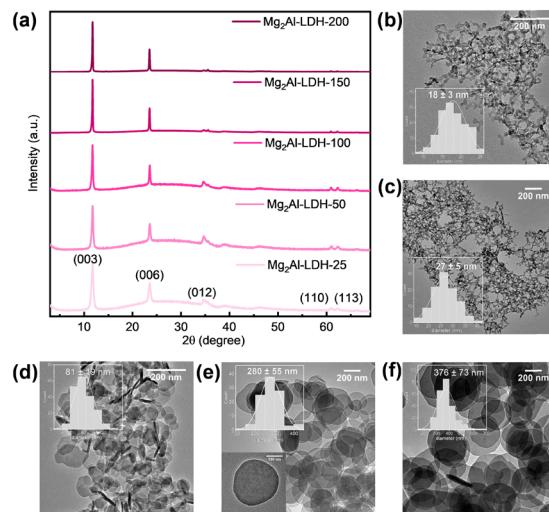


Fig. 1 (a) XRD patterns for  $Mg_2Al$ -LDH-T platelets; TEM images for (b)  $Mg_2Al$ -LDH-25, (c)  $Mg_2Al$ -LDH-50, (d)  $Mg_2Al$ -LDH-100, (e)  $Mg_2Al$ -LDH-150 and (f)  $Mg_2Al$ -LDH-200. Insets are the particle diameter distributions measured from TEM images.

LDH-150 is the sample that was obtained at 150 °C). Full synthesis details were given in the ESI.† The powder X-ray diffraction (XRD) data for all samples are shown in Fig. 1a. They are typical patterns expected for carbonate intercalated  $Mg_2Al$ -LDHs with characteristic Bragg reflections (003), (006), (012), (110) and (113). The relative intensity of (012), (110) and (113) compared to the (003) Bragg reflections decreased with increasing aging temperature during the synthesis. This may be attributed to an increase in the preferred orientation of the larger diameter platelets on the XRD sample plate holder. In addition, the TEM images show that the average particle diameters of  $Mg_2Al$ -LDH samples increased with increasing the aging temperature, ranging from 18–376 nm (Fig. 1b–f). The smaller platelets are more uniform in diameter with standard deviations between ±3 and ±19 nm. The nucleation and aging growth mechanism means that the larger diameter platelets exhibit a larger standard deviation, *i.e.* ±55 nm for  $Mg_2Al$ -LDH-150.

The  $Mg_2Al$ -LDH-T platelets all exhibit negligible UV absorption, especially in the UVA and UVB ranges (UVA: 320–400 nm; UVB: 290–320 nm) (Fig. 2a), indicating that  $Mg_2Al$ -LDHs have low photoactivity as expected for a material with a quoted optical band gap of 3.12 eV.<sup>32</sup> The UV/vis absorption of Tinosorb®S Lite Aqua (bis-ethylhexyloxyphenol methoxyphenyl triazine and acrylates/C12-22 alkyl methacrylate copolymer), a commercial, skin contact approved broad spectrum UV filter, is shown in Fig. 2b. An aqueous solution containing 0.0003 wt% Tinosorb®S Lite Aqua exhibits a 7.9% UV absorbance at 340 nm. The UV absorbance dramatically increased up to 36.2% after adding 0.1 wt%  $Mg_2Al$ -LDH-150 platelets to the Tinosorb®S Lite Aqua solution. The performance of other sized  $Mg_2Al$ -LDH-T platelet/Tinosorb®S Lite Aqua suspensions were measured to investigate the particle size dependence on the total optical absorption as shown in Fig. 2c. Fig. 2d summarises



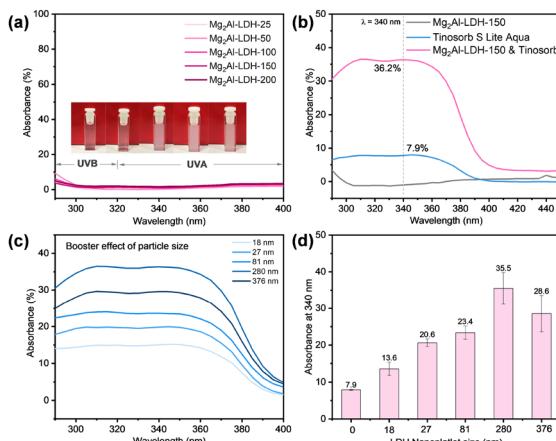


Fig. 2 (a) UV absorbance of Mg<sub>2</sub>Al-LDH platelet aqueous dispersions. The inset images are the dispersion of 0.1 wt% Mg<sub>2</sub>Al-LDH in DI water, from left to right are Mg<sub>2</sub>Al-LDH-25, Mg<sub>2</sub>Al-LDH-50, Mg<sub>2</sub>Al-LDH-100, Mg<sub>2</sub>Al-LDH-150 and Mg<sub>2</sub>Al-LDH-200, respectively; (b) boosting the UV absorbance of UV filter Tinosorb S Lite Aqua by Mg<sub>2</sub>Al-LDH-150; (c) the boosting effect of LDH platelet sizes on Tinosorb S Lite Aqua and (d) their summary of the absorbance at 340 nm. The loading of all LDHs is fixed at 0.1 wt% and Tinosorb S Lite Aqua at A 0.0003 wt%. Error bar represents the standard error from repeated experiments.

the enhancement of the UV absorbance resulting from the addition of the Mg<sub>2</sub>Al-LDH-T platelets, indicating that all Mg<sub>2</sub>Al-LDH-T platelets have a positive impact on the overall absorption in the UV range. There is a 1.7-4.5-fold enhancement on the UV absorption of Tinosorb<sup>®</sup>S Lite Aqua. The greatest enhancement (*ca.* 4.5 times) in the UV absorbance was observed when using Mg<sub>2</sub>Al-LDH-150 platelets with an average platelet diameter of 280 nm.

The UV boosting effect of Mg<sub>2</sub>Al-LDH-150 platelet loading in 0.003 wt% Tinosorb<sup>®</sup>S Lite Aqua solution was investigated. The UV spectra (Fig. S2, ESI<sup>†</sup>) show that the UV absorption increases with an increase in the platelet loading and reaches the highest UV absorbance boosting effect at 0.1 wt% loading. It is even more significant, from a commercial perspective, the boosting effect still has about 3.4 times with less loading (only 0.05 wt%). Other commercial, skin contact-approved UV filters, including UVB filters (Uvinul<sup>®</sup> T 150: ethylhexyl triazone) and UVA filters (Uvinul<sup>®</sup> A Plus: diethylamino hydroxybenzoyl hexyl benzoate) were also used in this study. The absorbances of these filters are significantly enhanced by addition of 0.1 wt% Mg<sub>2</sub>Al-LDH-150 with a 3.5-fold enhancement at 360 nm for Uvinul<sup>®</sup> A Plus Granular (Fig. S3a, ESI<sup>†</sup>) and 3.8-fold enhancement at 310 nm for Uvinul<sup>®</sup> T 150 (Fig. S3b, ESI<sup>†</sup>).

The origin of the optical boosting was investigated by performing detailed studies of the optical scatterings (290–400 nm) from aqueous dispersions of the Mg<sub>2</sub>Al-LDH-T platelets. The impacts of LDH particle diameter and loading on the light scatterings are shown in Fig. 3 and Fig. S4 (ESI<sup>†</sup>), respectively. A high total scattering (TS) of up to 92.5% (Fig. 3a) was observed in the dispersions of LDH platelets. Upon increasing the particle diameter, the total scattering increased, reaching a plateau at the particle diameter larger

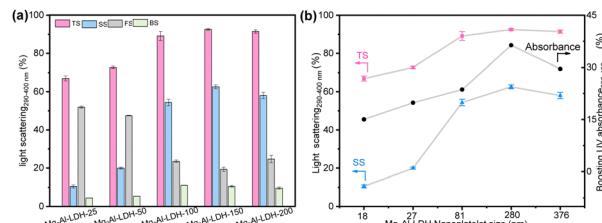


Fig. 3 (a) Mg<sub>2</sub>Al-LDH-150 platelet size-dependence light scattering; (b) the comparison of the size-dependence total scattering, side scattering and absorbance to the size-dependence boost effect. Error bar represents the standard error from repeated experiments.

than 280 nm (Mg<sub>2</sub>Al-LDH-150). The side scattering (SS) increased with particle diameter from 18 to 280 nm, and then slightly decreased. A slight difference in optical scatterings between Mg<sub>2</sub>Al-LDH-150 and Mg<sub>2</sub>Al-LDH-200 might be due to a partial overlap in the particle sizes, as also evidenced by a corresponding overlap in the UV boosting effect in Fig. 2d. The highest proportion of side scattering was found to be 63% for the dispersion of Mg<sub>2</sub>Al-LDH-150 platelets with the particle diameter of 280 nm. High forward scattering (~50%) was found for smaller particle diameters, whereas low forward scattering (~20%) for larger platelets (Table S1, ESI<sup>†</sup>). In general, all Mg<sub>2</sub>Al-LDH-T samples exhibited very low backward scattering (~10%). The optical scattering dependence on the LDH solid content are shown in Fig. S4 and Table S2 (ESI<sup>†</sup>). It is surprising to find that, even at a low solid content of 0.03 wt%, the Mg<sub>2</sub>Al-LDH-150 platelets still exhibit a high total scattering of up to 81% (Fig. S4a, ESI<sup>†</sup>). The total scattering increased with increasing the solid content reaching a plateau (~92.5%) when solid content is higher than 0.1 wt%. The highest proportion (63%) of side scattering was observed at a solid content of 0.1 wt%. The low backward scattering was obtained over all solid content fractions studied. The diameter-dependence of both total scattering and side scattering was plotted alongside the diameter-dependence of the boosting effect (Fig. 3b). The data indicates that the boosting effect is strongly correlated to the side scattering of LDH platelets. The same correlation was also found in the solid content data (Fig. S4b, ESI<sup>†</sup>).

The SPF values of a commercial sunscreen containing 0–7 wt% Mg<sub>2</sub>Al-LDH-150 were measured by a specialised UV-2000s ultraviolet transmittance analyser (Labsphere, USA) (Fig. 4). We found that the SPF values of these commercial sunscreen formulations increased with the addition of Mg<sub>2</sub>Al-LDH-150 platelets. Promisingly, up to a 2-fold increase in SPF was observed at a Mg<sub>2</sub>Al-LDH loading of 3 wt%. This boosting effect (206%) ranks top among the reported SPF boosters as summarized in the Table S3 (ESI<sup>†</sup>). The stability of 0.1 wt% Mg<sub>2</sub>Al-LDH-150 platelets in a sunscreen suspension was studied, revealing that the optical absorbance remained constant after 240 h in the dark (Fig. 4b).

The photostability was also measured by comparing the absorbance of a mixture before and after 2-h UV radiation. A negligible difference was found in the absorbance curves (Fig. S5, ESI<sup>†</sup>). TEM image confirmed that the morphology of



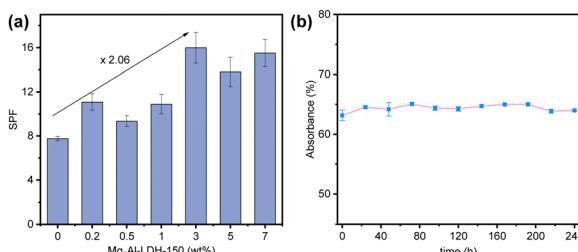


Fig. 4 (a) SPF values of a commercial sunscreen with different loadings of Mg<sub>2</sub>Al-LDH-150. (b) The stability of the UV absorbance of commercial sunscreen and 0.1 wt% Mg<sub>2</sub>Al-LDH-150 platelet mixture. Error bar represents the standard error from the repeated experiments.

Mg<sub>2</sub>Al-LDH-150 remains the same after 2 h UVA radiation (Fig. S6, ESI<sup>†</sup>). These findings demonstrate that Mg<sub>2</sub>Al-LDH platelets have neither chemical nor photo-induced interactions with the sunscreen ingredients that may affect its UV absorbance performance, this will encourage further studies of these materials in commercial UV blocking/cosmetic products.

In summary, size dependent optical scatterings of aqueous dispersions containing Mg<sub>2</sub>Al-LDH platelets with diameters ranging from 18 to 376 nm have been studied. These platelets show negligible optical absorbance across the UV/vis spectrum. Instead, they present high total and side scattering. The total scattering/ side scattering increases with increasing the particle size and/or loading, reaching maximum when the platelet diameter is 280 nm. We find that the UV absorbance boosting of these platelets is highly correlated to their side scattering performance. The Mg<sub>2</sub>Al-LDH-150 sample (280 nm at 0.1 wt%) produces the largest boost (3.5–4.5-fold) in the UVA and UVB absorbance when mixed with widely used, commercial sunscreen adsorbers. In a commercial sunscreen, the SPF can be boosted by 2.06-fold using Mg<sub>2</sub>Al-LDH-150. These biocompatible, non-toxic, safe, and effective LDH platelets provide a promising option for boosting the effectiveness of UV filter formulations.

Lina Chen and Junxin Wang performed the synthetic and experimental work; Claire T. Coulthard assisted with the electron microscopy studies; Xuwen Wu and Yong Qian conducted the SPF measurement; Chunping Chen supervised the work; and Dermot O'Hare conceptualised the research and acquired funding.

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## Conflicts of interest

The authors declare no competing financial interests.

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