Response letter to reviewer #2

Title: “Stearic acid/layered double hydroxides composite thin films deposited by combined laser techniques”
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We thank the reviewers for their valuable evaluation of the manuscript, as well as for their comments, which helped us strengthen the presentation of our results.

We would like to emphasize that the aim of this paper is to study stearic acid-layered double hydroxide (LDH) composite films, with controlled wettability capabilities, deposited by a combined pulsed laser deposition (PLD) - matrix assisted pulsed laser evaporation (MAPLE) system. We believe that these results are very promising for a variety of applications, in particular for using them as protective coating.

We have modified the text to respond to all the issues and have elaborated the responses below. We hope that the revised manuscript fulfils all requirements for being published in Molecules, section Physical Chemistry, issue Surfaces, Interfaces, Coatings and Nanostructures of Molecular and Soft Materials.

Please find enclosed the list with the required modifications.

The reviewer’s comments are marked with the letter Q.
The answers of the authors are marked with the letter A.
In the manuscript text we have added in red the modifications.
We have also checked the manuscript to eliminate grammatical and typing errors.

Q1: Authors need to detail more about their research originality.
Is the process they used unique? How so? The use of PLD process to fabricate thin films is extensive, therefore authors need to clarify the originality of their work.
A: We have entirely modified the abstract and the conclusions, emphasizing the advantage of the employed deposition system. Different deposition parameters (wavelength, laser fluence, repetition rate) can be used for each material, depending on its physico-chemical properties.
The deposition of the stearic acid via MAPLE and of the LDH via PLD occurred simultaneously thus the resulting composite films consist in stearic aggregated embedded between the LDH layers. Such films exhibiting long-term stability and enhancement of their hydrophobicity are good candidates to be used as protective coatings. The combined PLD-MAPLE setup displays a large versatility in terms of ability of producing composite complex films or organic-inorganic heterostructures and sandwiches without opening the deposition chamber and by this, reducing the contamination.

Q2: Did the authors analyze the cross sections of the fabricated composite films?
A: We have not checked the deposited films in cross section, but we have previously published a paper (Hybrid layered double hydroxides-curcumin thin films deposited via Matrix Assisted Pulsed Laser Evaporation-MAPLE with photoluminescence properties, F.Andrei, A.Vlad, R.Birjega, T.Tozar, M.Secu, I.Urzica, M.Dinescu, R.Zavoianu, Applied Surface Science, 478, 2019, 754-761, https://doi.org/10.1016/j.apsusc.2019.02.011) where we have studied the side view of composite organic/LDH thin films. The present study is part of a research in the framework of a larger project. The outcomes were some sort unexpected and at the beginning, we did not consider cross sections on the freshly films. However we are not sure we could discriminate between the organic and the inorganic components as they are deposited simultaneously. For the hybrid curcumin/Zn,Al-LDH films mentioned above we have used the side view only to estimate the thickness of the films.

We will have in mind this observation for further studies. Thank you.
Q3: Figure 5 shows the contact angle property variation of the made films. What is the significance of the shown data?

A: Details on the contact angles significance has been introduced in the manuscript. The next paragraph has been introduced:

Coatings preserving their hydrophobic properties after long-time storage are of great interest for their protective function especially for metallic surfaces. There are several papers reported on the transformation of micro-nanostructured metal and metal/oxides from initially hydrophilic to hydrophobic and even super-hydrophobic by air exposure without any other chemical modifications [28-34]. The explanations are quite diverse. Xiao et.al claimed that after one month storage a dense oxide film is formed on Co substrates lowering their surface energy [28]. The transition from super-hydrophilic to super-hydrophobic of a Ni micro-nano cones array surface were attributed by Geng et al. to the formation of NiO during the two weeks storage [29]. For Wang et. al [30] the increase of the contact angle to super-hydrophobicity of nanostructured CuO film during three weeks air exposure might be caused by the physical adsorption of oxygen molecules on the surface. S. Korsand et. al [31-33] attributed the wettability transition from a super hydrophilic nature to a super-hydrophobic one of Ni films and Ni-Co films mainly to their very particular hierarchically micro-nano structure which, by allowing air to be trapped in rough surfaces during the two weeks exposure to air, will form convex surface between the interface of liquid and air. For the Ni-Co alloy coatings the surface adsorption of air-borne hydrocarbons [32-33] is also considered similar to Li et al. for several metal, Cu, Ni, Au etc. as a cause of increased super-hydrophobicity by their effect of reducing the surface free energy [34]. After reaching super-hydrophobicity the Ni-Co alloy coatings exhibit long time durability, the coatings being air exposed more than 4 months [32]. Mg2.5AlPLD(266 nm) film exhibiting higher roughness (RMS) and alike morphological appearance as the composite SIMAPLE(266 nm)/Mg2.5AlPLD(266 nm) (Table 2 and Figure 4) undergoes no increase of CA in 36 months storage, while the composite film becomes hydrophobic. In the same time the other composite sample SIMAPLE(266 nm)/Mg2.5AlPLD(1064 nm) with smaller roughness and different morphological aspect (Table 2, Figure 4) reveals a similar transition to hydrophobicity after long-time storage. The deposition of the stearic acid via MAPLE and of the Mg2.5AI-LDH occurred simultaneously thus the resulting composite films consist more likely in very disperse SA small aggregated embedded between the LDH layers.

Q4: Figure 6 is poorly constructed with inadequate cations.

A: The caption for figure 6 has been modified, and details of the images have been added.

Figure 6. FT-IR spectra of as deposited films, of the stearic acid deposited via MAPLE and of the composite films deposited via a combined MAPLE-PLD deposition. The FT-IR spectrum of the solid NIST (National Institute of Standards and Technology-US) is included. In the right column the detailed spectra from 3000-2700 cm-1 wavenumbers are exposed, emphasizing the νCH2 to the νCH3 bands
Q5: What is the conclusion of this work? Composite LDH can be made? This conclusion is too brief, it merely states the feasibility of the experiment tool the authors have used, it appears to be a brief research report conclusion.

A: We have entirely changed the conclusions, as follows:

Composite organic-inorganic (stearic acid/Mg,Al-LDH) films were obtained by using a set-up combining the standard PLD and MAPLE. A MAPLE deposition system was adapted to provide the possibility of irradiating two concentric targets, with two different laser beams. The composite films exhibit long-term behavior different from the inorganic LDH films deposited by PLD and the stearic acid film deposited by MAPLE. A shift to hydrophobicity after 36 months of storage was observed for both composite films although they display different morphologies and roughness. The result was explained, based on FT-IR measurements, on the reorientation in time of the alkyl chains of the highly dispersed stearic-acid aggregates embedded between LDH oriented layers. This particular structure is due to the simultaneous deposition of both the inorganic and the organic component. Such films exhibiting long-term stability and enhancement of their hydrophobicity are good candidates to be used as protective coatings. The combined PLD-MAPLE setup displays a large versatility in terms of ability of producing composite complex films or organic-inorganic heterostructures and sandwiches without opening the deposition chamber and by this, reducing the contamination.