Variable morphologies of self-assembled metal-complexed lauroyl-glycylglycine in the presence of montmorillonite-silica nanowires

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Synthesis of cobalt (II) and Ni (II) complexes of lauroyl-glycylglycine in the presence of montmorillonite-silica nanowires was followed in terms of variable morphologies induced by self-assembling phenomena. The interactions between different metal complexes and the montmorillonite-silica nanowires segments were observed by FTIR, TGA, DSC and SEM results. These interactions induced variable morphologies (sheet-like, ribbon-like, tube-like and fiber-like). Variable morphologies, physical and chemical nature and the thermal stability recommend this new class of hybrids in catalysis applications.

1. Introduction

Surfactants are molecules that are able to self-assemble in water in a variety of morphological structures, due to their amphiphilic structure. They possess a polar head group (hydrophilic) and a nonpolar tail (hydrophobic), presenting in the same time attraction and repulsion for many solvents, especially water. In aqueous solutions surfactants comply with the law of diluted solutions until reaching critical micelle concentration. Above that concentration begins a process of association of surfactant molecules to form aggregates entropic favoured, due to insoluble groups that tend to associate in such a way that a minimum surface contact is created against the phase for which it has no affinity. As a result surfactants self-assemble into micelles, followed by the formation of highly organised structures, such as vesicles, fibers, helices, tubes [1]. A relationship between the shape of the aggregates and the structure of the surfactant was developed by Israelachvili on the basis of packing parameter [2].

The self-assembly of the surfactants is triggered by several factors, among which are mentioned: geometry and size of the molecule, intermolecular interactions, external parameters such as electrolytes, polar / non-polar solvents, pH, temperature, metal ions, stirring, sonication [3-7].

Metal-complexed surfactants exhibit an organized interface of metal ions, and the most common metal ions that can promote the self-assembly phenomena in surfactant self-assembly are the transition metal ions [8-11]. Self-assembled metal-complexed surfactants show an increasingly higher interest due to their potential uses in drug delivery systems, templates to produce metal oxide nanotubes, photocatalytic nanotubes [12, 13].

In particular, researchers have studied nanostructures by complexing metal ions with amphiphilic amino acids or peptides. For example, by complexing the copper ions to a long chain histidine derivative, boomerang shape aggregates were obtained [14]. Dicarboxylic valylvaline bolaamphiphiles form complexes in water with transition metals, which upon self-assembly led to the formation of nanofibers of 15-20 nm wide. [15]. In the same way oligoglycine-based lipids form a variety of nanostructures in the presence of transition metal cations, from sheet-like structures (complexes with Co^{2+}, Zn^{2+}, Ag^+, La^{3+}) to nanotubes (complexes with Mn^{2+}, Fe^{3+}, and Cu^{2+}) and nanofibers (complex with Ni^{2+}) [12].

Silica nanowires obtained on montmorillonite nanolayers [16] is a new class of structures which are combining the 1D with 2D architecture with perspectives in a wide area of applications were some critical properties are involved: mechanical reinforcing, thermal stabilizer, sensing or photocatalytic activity.

In this work we report the synthesis of Co^{2+} and Ni^{2+} complexes with lauroyl-glycylglycine in presence of montmorillonite-silica nanowires. By this approach the thermal stability of the final system drastically increase by selective interaction (i.e. Co complex case) between partners. Silica domains can act in the nucleation step of the metal complexes assembling (Ni complex case) in organized superstructures with clear influence in the morphology. Silica wire-like morphology is able to act like a hard template for initiating the metal complex morphology in sheet-like or fiber- like form. The new class

of hybrids could be of much interest in photocatalysis since both structures are having by nature low optical losses.

2. Experimental

2.1 Lauroyl-glycylglycine synthesis

Lauroyl-glycylglycine (LGG) was synthesized according to modified Schotten-Baumann reaction [17]. To 0.1 moles glycylglycine (Merck) dissolved in solvent mixture (water/acetone 2.4/1 v/v) mixture and brought to pH 11 was added 0.1 moles lauroyl chloride (Merck) and maintained at 50^0C until the aminic nitrogen content no longer decreases. Aminic nitrogen content was established by Sorensen method. The conversion of glycylglycine into lauroyl-glycylglycine was 98%. The reaction mixture was acidified to pH 1.5 by adding 35 % hydrochloric acid. The lauroyl-glycylglycine precipitated and it was vacuum filtered and washed with distilled water. The filtered product was then oven-dried at a temperature lower than 50 °C in order to avoid colouring.

2.2 Synthesis of cobalt (II) and nickel (II) complexes with lauroyl-glycylglycine (LGGCo, LGGNi)

In order to form complexes with transition metals, LGG should be in a deprotonated state [12] so prior to complexation it was performed the neutralisation of LGG with 25% NaOH solution and the product was oven-dried. For the synthesis of the complexes 0.2 mmoles of sodium lauroyl-glycylglycinate were dissolved in 10 mL distilled water. 0.1 mmoles of the cobalt acetate tetrahydrate, respectively nickel acetate tetrahydrate were dissolved in 5 mL distilled water and added to the solution of sodium lauroyl-glycylglycinate and maintained under stirring 10 minutes at room temperature. The cobalt and nickel complexes of lauroyl-glycylglycine were filtered off, washed with distilled water and dried in air.

2.3 Synthesis of cobalt (II) and nickel (II) complexes with lauroyl-glycylglycine in the presence of montmorillonite - silica nanowires

Montmorillonite-silica nanowires (SiNW) were synthesized by a sol gel process on montmorillonite layers as described in literature [16]. 0.1 g SiNW was dispersed using an ultrasonic device in 10 mL distilled water. 0.2 mmoles of sodium lauroyl-glycylglycinate were added to the dispersion. Then 0.1 mmoles of the cobalt acetate tetrahydrate, respectively nickel acetate tetrahydrate were dissolved in 5 mL distilled water and mixed under stirring with the first solution for 10 minute at room temperature, and then filtered off, washed with distilled water and dried in air.

2.4. Analyses

Elemental analysis of sodium lauroyl-glycylglycinate and cobalt (II) and nickel (II) complexes with lauroyl-glycylglycine for C, H and N was carried out on a Perkin Elmer analyser.

Elemental analysis data for lauroyl – glycylglycine with the formula $C_{16}H_{30}N_2O_4$ (M= 314.44) were as follows: Calculated (%): C 61.12; H 9.62; N 8.90. Found (%): C 61.31; H 10.23; N 8.53. The results of elemental analysis for cobalt (II) complex with lauroyl-glycylglycine with the formula $C_{32}H_{58}N_4O_8Co$ (M=685.76) were: Calculated (%): C 55.99; H 8.45; N 8.17. Found (%): C 56.21; H 8.59; N 8.05. For nickel (II) complex with lauroyl-glycylglycine, having the formula $C_{32}H_{58}N_4O_8Ni$ (M=685.52) the elemental data were as follows: Calculated (%): C 56.01; H 8.46; N 8.17. Found (%): C 56.19; H 8.57; N 8.05.

The Co (II) and Ni (II) content from the effluent by filtration of metal complexes was determined by complexonometric titration with EDTA, in buffer solution using Murexid as indicator. At a molar ratio ligand: Me^{2+} of 2:1, the cation concentration in effluent was zero, confirming the complexation of cations with sodium lauroyl- glycylglycinate.

Fourier transform infrared spectroscopy (FTIR) spectra were registered with a Brucker TENSOR 37 instrument in ATR module.

Environmental scanning electron microscopy (ESEM) images were obtained using a FEI-Quanta 200 instrument.

Thermal analysis have been performed on a Mettler Toledo Thermo-gravimetric Analyzer TGA / SDTA 823^e, in the range of temperature 25 °C to 900 °C, in dynamic air, with 60 ml/min, at a heating rate of 20 °C/min, in alumina crucible, for all the samples, of 6 mg to 10 mg. DSC was performed on a Metter-Toledo Instrument DSC 823^e. Samples (6-10 mg) were loaded into sealed aluminum pans with lids and heated to up to 800 °C at a heating rate of 20 °C/min. in oxygen flux (80 ml/min.). The empty aluminum pan was used as reference and the heat flow between the sample and reference pans was recorded.

3. Results and discussion

Metal complexes formation in the presence of SiNW was firstly observed by the optical appearance of the samples (Fig. 1). The colour occurrence was almost instantaneous indicating the fast reaction involved in the obtaining of neat LGG metal complexes [12]. The reaction mixtures showed homogenous colloidal dispersions of LGG metal complexes/SiNW in both cases. In the case of LGGNi/SiNW a particular phenomenon occurred, by a transition of the colloidal dispersion towards a translucent compact gel phase in the entire mass (without phase segregation). The driven vector for this phenomenon was later found in the structural FTIR and SEM section by favourable interaction between LGGNi and SiNW which had as result the increase in fiber-like density in the bulk

phase and increase of fiber dimensions. Therefore the interconnected fibre networks of the LGGNi/SiNW are forming almost a continuous phase in the initial bulk dispersion which finally induced the gel formation.

After the optical evidence of metal complexes formation (as a result of self-assembling) FTIR spectra confirmed by structural evidence the complex formation (Figs. 2 and 3). The vibration absorbance of the specific carboxylate anions showed the vC=O asymmetrical peaks in 1540-1650 cm^{-1} region indicating the metal complexation. The symmetrical 1602 and 1587 cm^{-1} for the protonated form (LGG) turns in an asymmetrical one and the 1602 cm^{-1} position almost vanishes for neat LGGCo. In the case of LGGCo/SiNW both peaks are drastically reduced (barely observable) indicating an even better complexation between LGG and Co cations in presence of SiNW. This could be explained by the higher availability of SiNW nanolayers to interact with the organo-complex, rather then with cations or organic molecules alone (this aspect will be resumed again in the morphological section).

Fig. 1. Appearances indicating the metal complex formation in presence (absence) of SiNW particles (homogenous dispersions and gel-like for LGGNi/SiNW).

The bands assignable to amide (I) (from the C=O stretching) at 1634 cm^{-1} and amide (II) 1587 cm^{-1} in the case of LGGCo/SiNW are found (by contrast with neat LGGCo) in symmetrical position. This aspect is an argument for different packaging conformations of the glycylglycine segments in hydrogen bond networks [12, 15]. Other evidences on a different assembling in LGGCo/SiNW can be found by small shifts: in OH stretching mode (from 3491 to 3486 cm^{-1}); 3320 to 3316 cm^{-1} (NH -stretching mode, sustaining again a different packaging mode of the LGGCo in SiNW presence) [15]. In the case of LGGNi, the interaction on the SiNW nanolayers is apparently weaker in comparison with LGGCo complexes since no significant modifications were found on carboxyl anions bands in presence of SiNW. The same shifts (but weaker in comparison with

LGGCo/SiNW) were found in OH stretching, NH-streching, NH deformation (amide II) modes. But there are two major structural changes occurred in LGGNi/SiNW in comparison with neat LGGNi. The confinement of the organic network (by C-C skeletal vibration) changes in presence of SiNW (1028 cm^{-1} in LGGNi to 1038 cm^{-1} in LGGNi/SiNW, respectively from 678 cm^{-1} to 673 cm^{-1} rocking vibration) [12, 15]. All these aspects are suggesting changes in the metal complexes assembling in presence of SiNW.

SiNW are thermally stable structures during programmed heating by TGA analysis (up to 800 °C). Their weight loss (of less then 5% wt.) occurs mainly because of the water molecules elimination (free water up to 100 °C, bonded water between 100 and 200 °C, and hydroxyl loss over 450 °C) (Figs. 4 and 5).
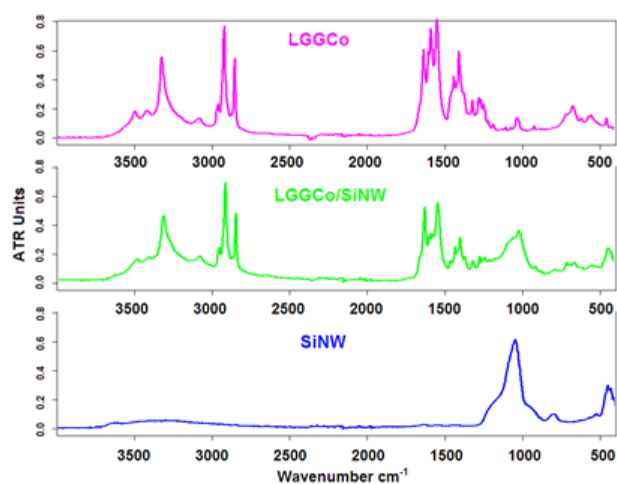

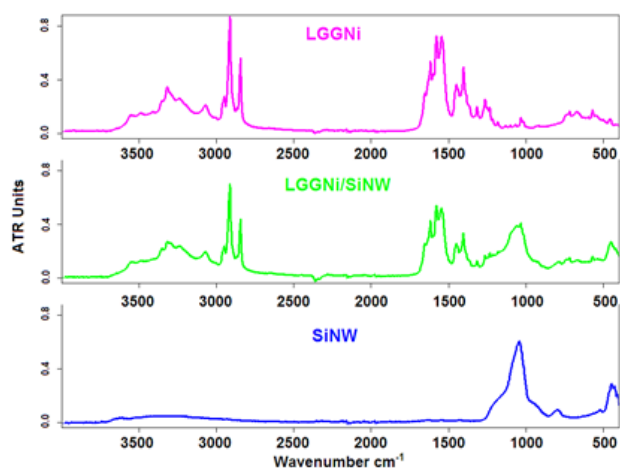*Fig. 2. FTIR spectra modification in LGGCo/SiNW self-assembling system.*

Fig. 3. FTIR spectra modification in LGGNi/SiNW self-assembling system.

LGGCo showed smaller amounts of free water and larger ones of bonded water (100-200 °C), in comparison

with neat SiNW (Fig. 4). The decomposition [18, 19] of the organic chain present in LGG complex starts immediately after 200 °C by the C-NH-C elimination from the LGG units. The decarboxylation stage starts over 300 °C up to 400 °C followed by the remains of the alkyl chain up to 500 °C. Over 500 °C bonded hydroxyls on carbonaceous residue is lost.

LGGCo obtained in the presence of SiNW showed an important improvement of the overall thermal stability profile in comparison with LGGCo alone. The increasing in thermal stability was found in all decomposition stages. The interaction between LGGCo and SiNW involved a smaller amount of the bonded water (with several wt. percents in 100-200 °C stage). The decrease of bonded water could be explained by two directions: i) the increase in hydrophobic content of the resulted structures and ii) the restriction of water molecules assembling on both SiNNW and LGGCo as consequence of the Co complex interaction with montmorillonite layers found in SiNW. The argument for confirming the second direction as main phenomena is brought by the stabilization effect found in the next decomposition stages and is also confirmed by the above FTIR data. The interaction [20] between Co ions is much more improved in metal complex combinations. LGGCo/SiNW thermal stability drastically increases in comparison with LGGCo. The increase stability is notable in both decomposition temperature value and amount of loss (reduction in comparison with the wt. ratio LGGCo/SiNW used for synthesis). The decomposition profile turns more to a linear shape, indicating the stabilizing effect as continuous one over the entire stage of the organic phase decomposition.
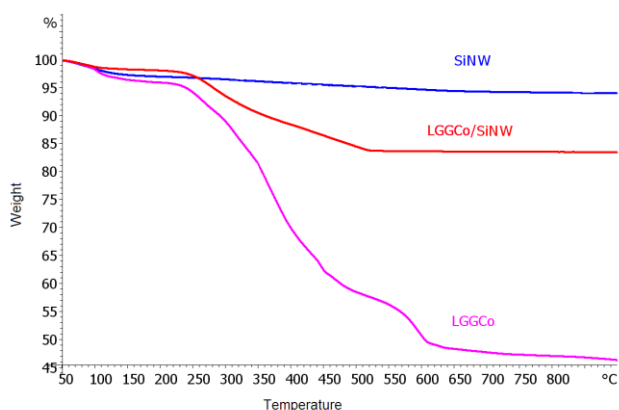

Fig. 4. TGA profiles of LGGCo complexes obtained in presence of SiNW.

LGGNi/SiNW thermal stability showed a totally different profile in comparison with LGGCo/SiNW (Fig. 5). The interaction between montmorillonite layers found in SiNW and Ni complex was proven less active, turning in a less stable system in comparison with LGGNi alone. The overall stability up to 650 °C decreases in terms of both decomposition temperature and weight loss (larger amounts of decomposed organic phase). Judging on the

SiNW large specific surface one can notice a certain catalytic effect on LGGNi decomposition. SiNW hydroxyl groups could be involved also in the faster decomposition of the LGGNi organic network.

LGGCo/SiNW and LGGNi/SiNW complexes showed only endothermic effects on DSC profiles (Figs. 6 and 7). Looking back to TGA profiles (Figs. 4 and 5) we can state that all the decompositions were endothermic in nature. DSC enthalpic events are shifting also towards higher temperatures like in TGA profiles. Over 300 °C all the enthalpic processes are reduced for LGGCo/SiNW in comparison with LGGCo alone. DSC curves are confirming also the stabilization effect of the SiNW induced in LGGCo/SiNW hybrids.
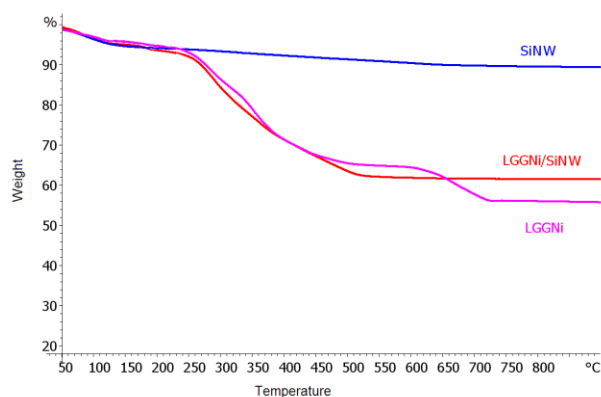

Fig. 5. TGA profiles of LGGNi complexes obtained in presence of SiNW.

Turning to 50-200 °C interval, the interaction between SiNW can be quantified also by the sum of the enthalpic transitions, which is around 94 J/g in LGGCo versus 57 J/g in LGGCo/SiNW. The existence of a confined LGGCo phase in SiNW layers can be confirmed also by a small transition (grey highlighted in Fig. 6) at 73 °C (possible to lipid bilayered structures melting) which overlaps on the water desorption process.
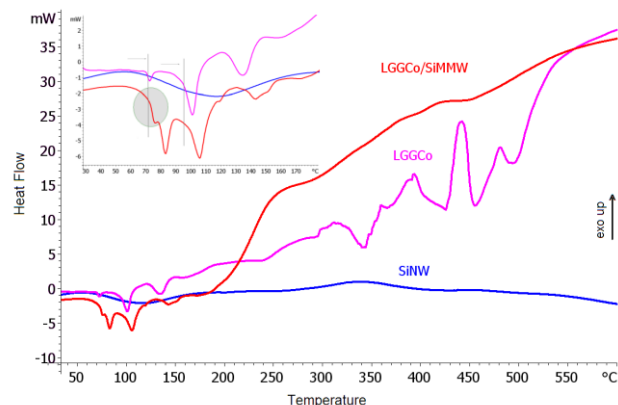

Fig. 6. DSC profiles of LGGCo complexes obtained in presence of SiNW.

In LGGNi/SiNW hybrids the assistance of SiNW to LGGNi decomposition is less cooperative judging after the DSC profiles comparison (with LGGCo) (Figs. 5 and 6). Only a few transitions are restricted over 300 °C, clear endothermic peaks were found around 400 °C, 520 and 580 °C. This behaviour proofs that a certain confinement of the C-C chain could be involved in the interaction with SiNW.

LGGCo metal complexes are restricted to assemble in the specific [12] uniform sheet shape in presence of SiNW (Fig. 8). SiNW provide a large surface in the reaction media before complex formation. Even if the large SiNW interface for polar interaction (negatively charged) is present in the system the Co and Ni complexes are formed almost instantaneous showing a coloured dense phase and occupying the entire colloidal dispersion.
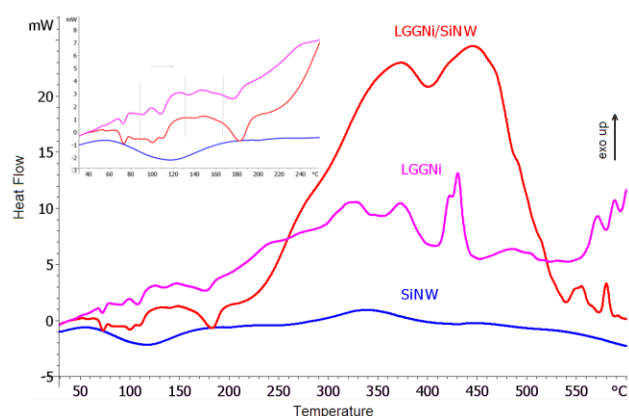

Fig. 8. SEM images with sheet-like morphology of LGGCo complexes obtained in presence of SiNW.

Fig. 7. DSC profiles of LGGNi complexes obtained in presence of SiNW.

Fig. 9. SEM images with fiber-like morphology of LGGNi complexes obtained in presence of SiNW.

The silica domains as seen in the SEM images were distributed quite uniform on the LGG-metal complexes phase. SiNW are promoting the different sheet-like assembling of the LGGCo complexes. The uniform sheet-like morphology [12] present in LGGCo alone turns in to a bended (and twisted) mode specific in ribbon-like morphology (Fig. 8). Moreover tubular shapes were found as well, but in low percentage. This conformational switching indicates a possible interaction between Co ions and montmorillonite sites present on SiNW structure [20]. This interaction is enhanced by the presence of the organic chain in the metal-complex structure [20].
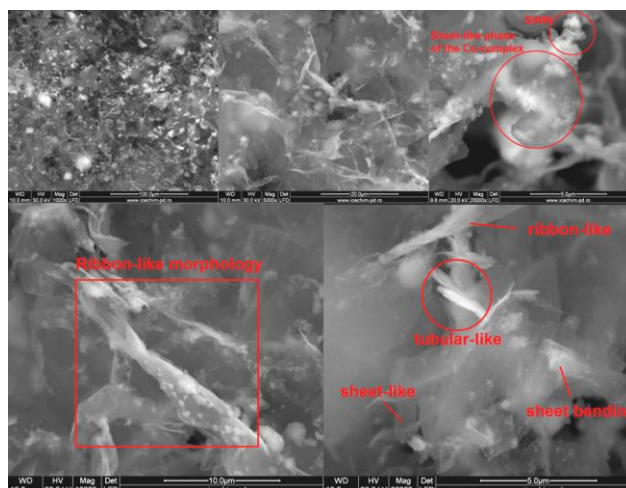
Ni complexes are known for weaker interaction with montmorillonite sites in literature [20]. Therefore LGGNi complexes obtained in the presence of SiNW are showing in contrast with their Co analogues a pronounced tendency of assembling in fiber-like structures (Fig. 9). Moreover the density of fibers excide in appearance the one observed in literature [12]. SiNW presence could induce a certain nucleating tendency favourable to LGGNi fiber morphology. Even if a clear interaction could not be seen, FTIR results showed the confinement of the C-C chain is different in presence of SiNW (since several small band shifts are present).

4. Conclusions

The influence of montmorillonite - silica nanowires on the morphology of self-assembled cobalt (II) and nickel (II) complexes with lauroyl-glycylglycine acted on several directions. The use of montmorillonite - silica nanowires as a hard template initiated changes in the sheet-like or fiber-like form morphology of the complexes. These changes are

a consequence of the interactions between LGG metal complexes and SiNW nanolayers. The thermal analysis confirmed the stabilising effect of SiNW over LGGCo for the entire stage of the organic phase decomposition, as consequence of Co complex interaction with montmorillonite layers found in SiNW. SEM imagines showed apart from sheet-like structures produced by LGGCo complexes, bended forms specific in ribbon-like morphology and tubular shapes, promoted by SiNW. In the case of LGGNi complexes obtained in presence of SiNW, the system was thermally less stable in comparison with LGGNi alone, due to a less active interaction between nanolayers layers found in SiNW and Ni complex. However FTIR and SEM results showed a pronounced tendency of assembling in fiber-like structures and with higher network density than for LGGNi alone, indicating the nucleating effect of SiNW favourable to LGGNi fiber morphology. In future studies the investigations of this new class of hybrids could be of much interest in catalysis.

Acknowledgements

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