Synthesis of Single Layered Hybrid Materials Based on 1D Associated Metalorganic Nanoribbons for Controlled Release of Chemicals

José María Moreno,[a] Ismael Navarro,[b] Urbano Díaz,[a] Jaime Primo,[b] Avelino Corma*[a]

Abstract:
New family of stable layered organic-inorganic materials have been prepared, in one-step solvothermal process. They are based on ordered associated nickel clusters-type nanoribbons separated by specific alkyl (heptyl- or dodecyl-) acrylic mono-carboxylate moieties acting as molecular spacers, perpendicularly located to 1D inorganic chains. These organic spacers contain hydrocarbon tails with different length which control the separation level between inorganic 1D sub-units, inhibiting the 3D growth of conventional DUT-8-type MOFs. The lamellar nature of the materials formed was studied and confirmed by different characterization techniques, showing the structural location of individual organic and inorganic builders. They have been successfully used as a long lasting biodegradable and water proof materials for controlled release of chemicals such as pheromones for sustainable treatment of plagues.

Nanometric sheets are fundamental builders to obtain novel families of versatile lamellar materials, being their preparation, study and applicability a true challenge in materials science. They are useful since it is possible to take advantage of their capacity to be modified and used as integral part of new hybrid nanocomposite solids. Inorganic sheets, based on metallic oxides, are essential structural units which are conforming different types of lamellar solids with several long-order topologies, spatial arrangement and physico-chemical characteristics.[1-3] It is known the capacity of these layered materials to be modified by the spatial alteration of individual layers through swelling, intercalation or exfoliation processes to obtain more accessible solids,[4-6] being possible to incorporate additional functions during post-synthesis treatments.[7-9] In the case of metalorganic structures, MOF-type, it is not frequent the formation of modifiable layered precursors, and 3D structures based on the coordination binding between metallic nodes and rigid bi-carboxylate linkers are normally obtained.[10,11] Preparation of modifiable layered metalorganic precursors formed by individual organic-inorganic layers obtained by direct synthesis, is a matter of interest, prior studied in well-known 2D coordination polymers.[12,13] Incipient studies related with the formation of MOF nanosheets by modulation of growth kinetics have also been reported.[14] Nevertheless, the existence of 3D conventional MOFs which exhibited lamellar structural tendency in the spatial distribution of their structural building units, could be indicative of the possibility to obtain lamellar metalorganic structures.[15-21]

Taking the above into account, we have succeeded here in the preparation of different layered organic-inorganic materials, in one-step process. The materials are based on ordered associated nickel clusters-type nanoribbons, similar to sub-networks detectable in 3D DUT-8 materials, separated by specific alkyl acrylic mono-carboxylate moieties acting as molecular spacers, and which are perpendicularly located to inorganic clusters. These specific organic spacers contain hydrocarbon tails with different length that control the separation between 1D inorganic sub-units, inhibiting the 3D growth of conventional DUT-8-type MOFs. The nature of these lamellar hybrid materials appeared to us as solid micelles and directed to investigate them as containers for controlling release of non-polar active principles (semiochemicals), offering a real possibility for field applications as an alternative to the massive use of pesticides.[22-26]

The methodology was based on the use of organic spacers with only one carboxylate reactive point that interacts with inorganic metallic nodes through stable coordination bonds. In our case, alkyl benzene monocarboxylate compounds with hydrocarbon chains of different length (ethyl (EB), heptyl (HB) and dodecyl (DB)), in all cases located in para conformation, were used as molecular spacers (Scheme S1 in the Supporting Information). These organic spacers were employed instead of conventional rigid acrylic dicarboxylate linkers. Solvothermal processes facilitated the preparation of ordered lamellar hybrid materials based on associated 1D Ni-metalorganic nanoribbons.
separated by the alkyl benzene monocarboxylate spacers, perpendicularly located to inorganic nodes. When desired, a post-synthesis treatment of layered structures with no-polar solvents allowed the expansion, dispersion and exfoliation of the metalorganic 1D subunits (Scheme 1). Representation of individual organic-inorganic nanoribbons is drawn in Scheme S2 in the Supporting Information, highlighting the different basal space obtained between the associated formed layers, as a function of the organic spacers’ length which would act as effective growing inhibitors of the 3D metalorganic structure. As observed in the cartoon, individual 1D organic-inorganic subunits could be formed by consecutive edge-sharing NiO₆(ОH)₂ octahedral, conforming inorganic chains, which are separated by alkyl benzene monocarboxylate ligands, located in both sides of metallic nodes.

Scheme 1. Synthesis routes to obtain layered hybrid materials: Ni-ITQ-HB or Ni-ITQ-DB and exfoliated solids.

The XRD patterns of the hybrid materials showed that lamellar organization was achieved when longer alkyl benzene monocarboxylate linkers (HB and DB) are used, being detectable the (100) low angle diffraction peak, which is characteristic of layered solids formed by individual sheets perpendicularly disposed to a axis (Figure 1). The presence of further peaks, assigned to (200) and (300) diffraction orders, would confirm that a high regularity in the separation observed between the successive piled organic-inorganic sheets was achieved (Scheme 1). When a shorter alkyl aryllic spacer (EB) was used, the material obtained (Ni-ITQ-EB) exhibited poor crystallinity and lamellar structuration was not achieved. On the contrary, regular lamellar materials were obtained with heptyl- (HB) and dodecyl- (DB) benzene monocarboxylic acids, named as Ni-ITQ-HB and Ni-ITQ-DB solids. They show one intense low angle (100) diffraction peak centred at ~3.1 and ~2.0 2θ degrees, corresponding to basal spaces of ~28 Å and ~44 Å, respectively.

Considering that the used organic spacers – HB and DB – exhibited molecular lengths of 13.8 Å and 20.0 Å, respectively, and that they were probably perpendicularly located in both sides of 1D inorganic NiO₆(ОH)₂ chains, it would be possible to estimate that the thickness of each individual 1D nickel-chain was close to ~4-5 Å (Scheme 1). This result would imply the formation of lamellar hybrid materials based on ordered associated 1D nanoribbons of [NiO₆] octahedral separated by long alkyl aryllic spacers. XRD peaks observed at higher than 20 2θ degrees, in the Ni-ITQ-DB pattern, were assigned to nickel oxyhydroxide species present in the 1D inorganic chains.

Figure 1. XRD patterns of layered hybrid materials compared with 3D Ni-MOF: (a) DUT-8(Ni), (b) Ni-ITQ-EB, (c) Ni-ITQ-HB and (d) Ni-ITQ-DB. Inset figure shows XRD patterns of Ni-ITQ-HB and Ni-ITQ-DB materials at lower 2θ angles.

The lamellar morphology of Ni-ITQ-HB and Ni-ITQ-DB materials was confirmed by HRTEM micrographs (Figure 2). The ordered distribution of piled sheets with basal spaces around 30 Å and 44 Å, respectively, can be observed, which are similar to those obtained from X-ray diffractograms. Remarkable differences were observed between the layered hybrid materials and the standard 3D DUT-8(Ni) by means of SEM and AFM micrographs. Specifically, the latter was formed by dense elongated prism-type crystals, while the bi-dimensional character together with a homogenous distribution of ordered layers were detectable in the lamellar hybrid structures, being observable the presence of little plate-type crystallites assembled as bigger flower-like crystals (Figure S1 and Figure S2 in the Supporting Information). Post-synthesis treatments
with non-polar solvents allowed the expansion and exfoliation of previously obtained ordered lamellar hybrid materials. Lasting and stable colloidal solutions with isolated short ribbons of approximately 5 Å of thickness were identified from HRTEM micrographs (Figure 3). In fact, the observable disordered nanowires probably are the inorganic counterpart of each individual metalorganic nanoribbon, i.e., 1D chains based on associated [NiO\(_6\)] octahedral (Scheme 1). This behaviour showed the expandable capacity of this type of lamellar metalorganic solids and the possibility to obtain individual short Ni-based-ribbons.

![Figure 2. HRTEM images of Ni-ITQ-HB sample where organized nanosheets are observed. In the inset, two consecutive nanosheets with their corresponding basal space are highlighted.](image)

![Figure 3. HRTEM images of stable solution derived of post-synthesis treatment of Ni-ITQ-HB sample with dichloromethane.](image)

From elemental CHNS analysis and thermogravimmetrical curves showed in Table S1 and Figure S3 in the Supporting Information, it was estimated that the organic content was more elevated in the layered materials than in the standard 3D DUT-8(Ni), being the stability of the hybrid metalorganic materials close to 300-350ºC because decomposition of para-alkyl benzene monocarboxylate molecules, used as spacers, and NiO\(_4\)(OH)\(_2\) units present in the 1D inorganic Ni-chains was observed at this temperature range. Furthermore, the chemical analysis allowed estimating the composition of Ni-ITQ-HB and Ni-ITQ-DB materials that exhibited C/Ni molar ratios between 1.5 and 2. This result implies that the organic linkers were located in both sides of octahedral NiO\(_4\)(OH)\(_2\) units (Scheme 1). \(^{13}\)C CP/MAS NMR and IR spectra of 3D DUT-8(Ni) and lamellar metalorganic materials confirmed the total integrity of the structural linkers (NDC and DABCO) or organic spacers (HB and DB) (Figure S4, Figure S5 and Figure S6 in the Supporting Information).

The hybrid lamellar materials were used as long lasting biodegradable dispensers for controlled release of chemicals, and more specifically sexual pheromones, for sustainable management of plagues. The active principle used was 3-(S)-methyl-6-(R,S)-isopropenyl-9-decenyl acetate, i.e. the sex pheromone emitted by the females of the armored scale Aonidiella aurantii (Maskell) (California red scale), one of the most damaging pests of citrus (Scheme S3 in the Supporting Information). In preliminary experiments, a load of 25 wt% (pheromone / matrix) was estimated as the maximum amount of volatile held by direct adsorption in the materials. Specifically, Ni-ITQ-HB material, as matrix for controlled release, was compared with the same layered material based on aluminum (see experimental part in Supporting Information), while conventional and inexpensive mesoporous silica M41S-type was used as reference matrix.

Kinetic data showed a very different behavior among the three compared materials. As inferred from Figure 4a, the standard mesoporous material is not suitable for controlled release due to its high retention level of pheromone (aprox. 50 %). Both metalorganic layered materials show a release of the volatile compound, but only the nickel based material has an acceptable residual pheromone level, around 10 % of the initial load, after sixty days of aeration. Probably, the reason of the high residual level in the aluminum layered hybrid material (aprox. 50 %) compared to nickel is the higher Lewis acidity showed by aluminum, which results in a stronger interaction between the ester moiety of the pheromone and the matrix. Despite the good residual level showed by the Ni-ITQ-HB material, the kinetic results were far from fitting the desirable zero-order, being closer to an exponential desorption rate expression. Since the high level of pheromone initially loaded (25 wt%) can influence the emission behavior, the total amount of the volatile loaded was reduced up to 10 wt% in the adsorbed
Ni-ITQ-HB material to be comparable with the afore-described prism-type 3D DUT-8(Ni) material.

Kinetic results showed that the lower organic content achieved by the prism-type 3D-DUT-8 material, together with its higher free porous volume, probably promoted the high residual level (with an asymptote at approx. 50% of content) when compared with the layered material (Figure 4b). After losing the external surface adsorbed pheromone during the first week of aeration, the release profile of the Ni-layered hybrid material fits a desired zero-order kinetics ($R^2 = 0.99$), being therefore appropriate for controlled pheromone release. The amount of pheromone released required is specific for each pest and technique, ranging from 60 to 3000 micrograms per device and day, and could be easily adjusted by scaling up the emitters.

Taking into account the low residual level of pheromone previously achieved with the Ni-ITQ-HB material (< 10%) and the well-established comparison between the forced conditions set in the aeration chamber and field conditions, longer dispenser lifespan fitting zero order kinetics for controlled release of pheromones should be achieved with this material in field applications.\[29\]

In conclusion, a novel family of layered organic-inorganic materials, based on ordered associated nickel clusters-type nanoribbons, has been prepared in a one-step synthesis. Post-synthesis treatments with different non-polar solvents allowed their easy expansion, being possible the generation of exfoliated materials formed by disordered 1D short inorganic chains. This fact opens the possibilities for these lamellar hybrid materials to be used as builder precursors to form novel nanocomposites with potential applications in catalysis, adsorption or separation processes, exploiting their hydrophilic-hydrophobic nature. The excellent kinetic showed in controlling the release of the *A. aurantii* sex pheromone makes these materials suitable for controlled liberation of semiochemicals.

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**Figure 4.** Residual pheromone loading in samples with different initial adsorbed pheromone content: (a) 25 wt% and (b) 10 wt%.

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Layered organic-inorganic materials, based on ordered associated nickel-nanoribbons separated by alkyl aryllic mono-carboxylate spacers perpendicularly located to 1D inorganic chains, as matrix for controlling release of active principles (sexual pheromones) in environmentally friendly pest management.

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