Solvent-induced Delamination of a Multifunctional Two Dimensional Coordination Polymer

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Abstract

Low dimensional carbon structures have attracted great attention in the last years due to their amazing properties and low dimensionality [1]. However, while many of the extraordinary properties of these carbon-based materials are due to its restricted chemistry and structural simplicity, in many cases this is not an advantage but a limitation. For applications where more complex structures are required alternative materials are mandatory.

Thus, a new revolution can be envisioned in materials science by extending this successful dimensional variability of carbon allotropes to other compounds with higher structural capabilities and a broad panel of properties. A good example of this tendency can be coordination polymers (CPs), and their subclass metal-organic frameworks (MOFs) [2]. CP can be defined by an organometallic polymer structure containing metal cation centers linked by ligands. Although little has been done so far regarding 2D forms of CP [3], up to now most works reported ultrasound assisted exfoliation of laminar 3D materials (top-down approach) or vacuum deposition of organic molecules on metal ions to generate MOFs (bottom-up approach). However, chemical or solvent exfoliation (without the use of other external forces) of 3D-layered materials is very little described.

In this work, solvent-assisted delamination of multifunctional 2D MOF $[Cu(\mu\text{-}pym_2S_2)(\mu\text{-}Cl)]_n{\cdot}X$ (X = MeOH or H_2O) is reported. Molecular thick layer of this compound with large lateral sizes and good structural integrity are isolated just by immersion of the laminar crystals in water. We determine that this unprecedented behavior is a direct consequence of its structure, characterized by interlayer cavities that can be filled by different solvent molecules producing delamination in a simple and reproducible way. DFT calculations confirm the tendency of the solvents to induce delamination of the compound.

We have evaluated the macroscopic effect of the solvent on the monocrystals by means of Scanning Electron Microscopy (SEM) and the material incorporated to the suspension as a function of time by Atomic Force Microscopy (AFM). According to AFM and XPS data, the isolated layers reach an atomic thickness and structure consistent with the starting bulk material, confirming structural integrity.

We have been able to measure optical properties of the isolated single/few-layers. The electrical characterization of the single layers is currently under evaluation. Preliminary experiments carried out by EFM on layers adsorbed on SiO_2 suggest electrical conductivity.

Therefore we conclude that multifunctional laminar coordination polymers with suitable structurally design can be considered as a source of multifunctional 2D-materials with high potential applications alternatives to graphene.

References

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[2] Carne, A.; Carbonell, C.; Imaz, I.; Maspoch, D. Chemical Society Reviews, **40** (2011) 291.
[3] Amo-Ochoa, P.; Welte, L.; González-Prieto, R.; Sanz Miguel, P. J; Gómez-García, C. J.; Delgado, S.; Gómez-Herrero, J.; Zamora, F.; Chemical Communications, **19** (2010) 3262.

Figures

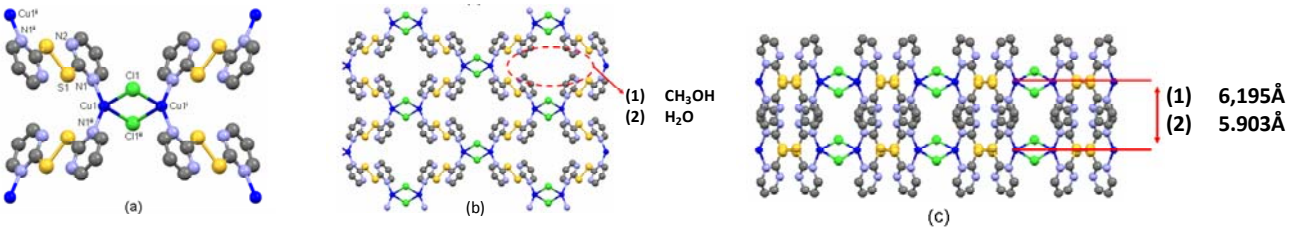

Figure1. Compounds $[Cu(\mu\text{-}pym_2S_2)(\mu\text{-}Cl)]_n \cdot X$ (X ≡ MeOH or H_2O) are isostructural **(a)** A fragment of the crystal structure. **(b)** Perpendicular view of the sheets and **(c)** side view showing pile up of two sheets.

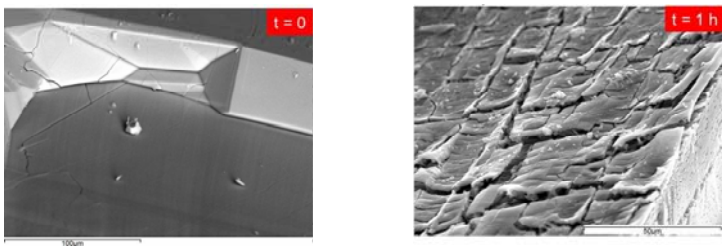

Figure 2. Scanning electron microscopy micrographies of the time evolution of crystals immersed in water. The image of the crystal surface before immersion is characterized by a flat surface. After 1 h in water, the crystal surface shows a significant evolution characterized by formation of a rough crystal surface with scale-like structures on the surface.

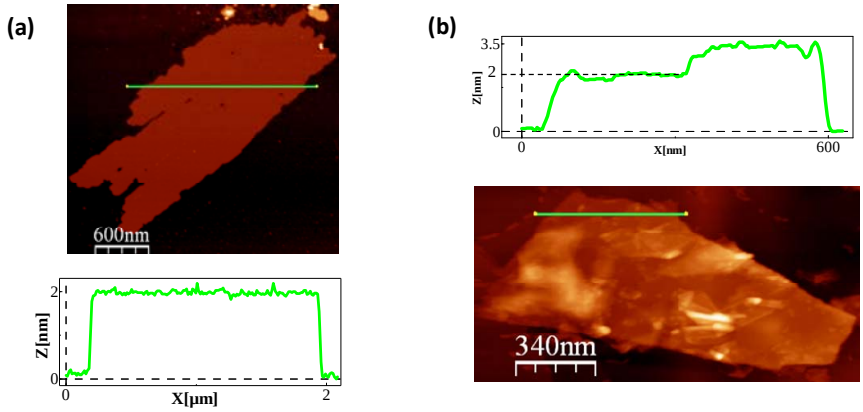

Figure 3. AFM topographies and heights profiles obtained upon drop-casting adsorption on (a) mica and (b) HOPG of the suspensions formed by treatment crystals with water at 4 days.

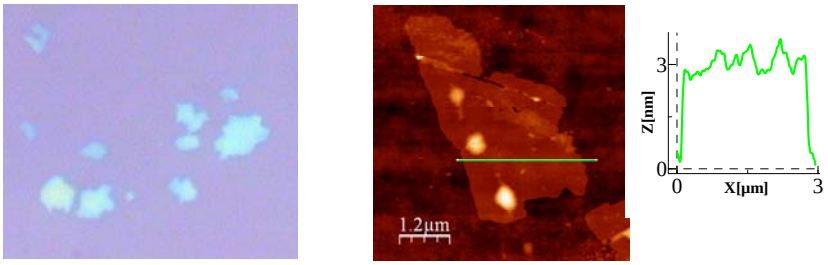

Figure 4. Fluorescence image of isolated flakes on SiO_2 and AFM topography of one of these with its height profile.