Metal-Organic Frameworks (MOFs)-Graphene Composites: Growth and Characterization of HKUST-1 on functionalized graphene layers for gas storage applications.

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Over the last twenty years Metal-Organic Frameworks (MOFs) have catalyzed the interest of many research groups around the world and, currently, they are well known as a new class of functional solid materials. MOFs are characterized by: *i*) highly crystalline 1-, 2- or 3-dimensional coordination networks; *ii*) porous structures with extremely high surface area and with tunable pore size dimensions; *iii*) network topologies that can be easily functionalized with different chemical groups; *iv*) many different technological fields of applications that range from gas storage/separation and catalysis to drug delivery and to many others [1]. One of the next challenges in this research area is the preparation of MOF composites in order to improve the properties of the component materials in a synergistic way [2]. MOF composites of graphite oxide (GO) [3] and functionalized reduced graphite oxide (rGO) have been recently reported in the literature. An increase in the CO_2 uptake as well has the ability to remove toxic gases, such as H_2S, NH_3 and NO_2, have been documented for some of these materials. More challenging is the obtainment of graphene/MOF composites due to the lack of functional groups on graphene layers that help the growth of MOF on the sp^2 carbon layers. The work presented here has the aim to develop new graphene/MOF composites to be used in methane storage technologies. MOFs are characterized by very low thermal conductivity and the preparation of composites with a good thermal conductor, such as graphene, should give the opportunity to develop more energy efficient adsorbing materials.

For the preparation of graphene/MOF composites, among all the MOFs prepared so far, we selected HKUST-1 [5] or $[Cu_3(BTC)_2(H_2O)_3]_n$ (H_3BTC = benzene-1,3,5-tricarboxylic acid) for at least two reasons: its synthesis is simple, employ commercial reagents and has been widely investigated under different experimental conditions; recently it has been identified as one of the best porous MOF for methane storage [6]. To facilitate the preparation of the composites we used a benzoic acid functionalized reduced graphite oxide (BFG) that was prepared according to literature procedures [4]. HKUST-1 was synthetized with different methods in the presence of variable amounts of BFG and the obtained materials were characterized by spectroscopic methods, X-Ray diffraction, SEM, TEM (Figure 1) and nitrogen adsorption isotherms. Preliminary results indicate the formation of MOF/BFG composites. In particular, HKUST-1 grows on BFG layers without evident structural modifications even in the presence of large amounts of carbon materials; the morphology and size of HKUST-1 crystallites are affected by the presence of BFG; nitrogen adsorption isotherms on the composites materials show hysteresis not evident in the case of pure HKUST-1 samples [7].

References

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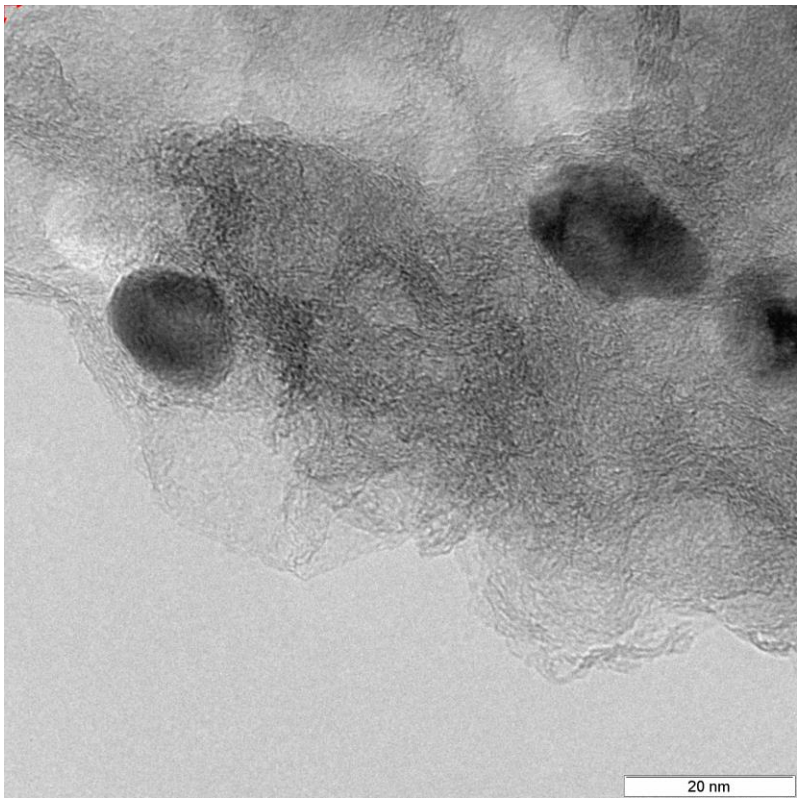

Figure 1: TEM image of a composite sample prepared at room temperature under stirring with 50% of BFG.