Self-Exfoliated Metal-Organic Nanosheets through Hydrolytic Unfolding of Metal-Organic Polyhedra

Bikash Garai,[a, b] Arijit Mallick,[a, b] Anuja Das,[c] Rabibrata Mukherjee,[c] and Rahul Banerjee*[a, b]

Abstract: Few-layers thick metal-organic nanosheets have been synthesized using water-assisted solid-state transformation through a combined top-down and bottom-up approach. The metal-organic polyhedra (MOPs) convert into metal-organic frameworks (MOFs) which subsequently self-exfoliate into few-layered metal-organic nanosheets. These MOP crystals experience a hydrophobicity gradient with the inner surface during contact with water because of the existence of hydrophobic spikes on their outer surface. When the amount of water available for interaction is higher, the resultant layers are not stacked to form bulk materials; instead few-layered nanosheets with high uniformity were obtained in high yield. The phenomenon has resulted in high yield production of uniformly distributed layered metal-organic nanosheets from three different MOPs, showing its general adaptability.

Introduction

Two-dimensional layered nanostructured materials have recently gained attention because of their potential for applications in various emerging fields such as optoelectronics, energy storage, ultrafiltration, semiconductors, supercapacitors, and photovoltaic cells.[1] In general, two-dimensional layered bulk structures are grown by deposition of individual layers one by one through non-covalent interactions like hydrogen bonding, π–π stacking, van der Waals, and dipole-dipole interactions.[2] Although these interactions are weak in comparison to the covalent bonding between atoms, the energy required to separate these layers into mono- or few-layered stacks is significant.[3] Traditionally, the required energy for such delamination is supplied in the form of mechanical grinding, mechanical shearing, ultrasonication, and intercalation assisted peeling.[3] In all these cases, the bulk materials are separated into discrete layers and thus these methods have been categorized as a top-down approach.[4] Such few-layered nanostructures could also be synthesized through a bottom-up approach, where the deposition of subsequent layers is restricted after the formation of the 1st layer.[5] These approaches include chemical vapor deposition, templated growth, and interfacial growth.[6] In recent years, research on delaminated layered metal-organic framework (MOF) structures[7] has gained attention because of their promising use in gas separation, molecular sieving, and isotope separation.[8] The performance of these materials in terms of separation efficiency and catalysis on active surfaces increases drastically when the separated layers are used over the bulk materials.[9] Routes utilized to obtain such MOF nanosheets include both top-down and bottom-up approaches but both these processes have their individual limitations.[10] In the top-down approach, the nanosheets are obtained with a good yield but it is difficult to control their thickness and therefore the generated nanostructures are non-uniform. On the other hand, nanosheets with uniform and controllable thickness are generated through bottom-up approaches, but the processes, in general, require difficult experimental set up. Thus, the synthesis of metal-organic nanosheets in high yield with uniform and controllable thickness in an efficient way requires a combination of both top-down and bottom-up approaches. However, because of their divergent nature, to date it has not been possible to combine both these approaches into a single unified approach. Herein, we have made an effort to combine both these approaches under one synthetic domain to convert metal-organic polyhedra (MOPs)[11] directly into two-dimensional metal-organic nanosheets with a few nanometers thickness in high yield and with a uniform morphological dispersion.[12]


Results and Discussion

Blue-colored crystals of the MOPs (MOP-MIA, MOP-EIA, MOP-PrIA) are readily synthesized from the solvothermal reaction between copper (II) nitrate and the corresponding organic linkers, 5-methoxy isophthalic acid (5-MIA), 5-ethoxy isophthalic acid (5-EIA) and 5-(n-propyloxy) isophthalic acid (5-PrIA), respectively, in mixed DMF solvent at 90 °C (Figure 1). MOP-MIA is obtained as orthorhombic crystals while MOP-EIA and MOP-PrIA are separated as polycrystalline crystals after 48 h (for full synthetic details, see Supporting Information). The polyhedral architecture in all these MOPs is constructed from the co-ordination between metal ions and the organic linkers through the formation of a Cu–Cu paddle wheel secondary building unit (SBU). These MOP units exist discretely, describing their discrete nature. Each MOP unit has been represented by individual color and the interstitial cavities are marked with white boxes.

Figure 1. (a) Chemical structure of the isophthalic acid based linkers used for the synthesis of MOPs. ORTEP diagram for (b) MOP-MIA, (c) MOP-EIA, and (d) MOP-PrIA; packing of the individual MOP units (e–g) showing their discrete nature. Each MOP unit has been represented by individual color and the interstitial cavities are marked with white boxes.

When these polyhedral MOP crystals are treated with a measured amount of water (50 μL mg⁻¹), small-sized [0.2×0.2×0.1 mm] MOP crystals start forming after 10 min. The as-synthesized crystals of the MOPs turn opaque after the initial contact with water. With time, the opacity of the MOP crystals increases and they finally split into crystals of the corresponding bulk MOF materials (Figure 2). This conversion proceeds through an amorphous phase (Figure 2a–c) observed during the opacity loss of the parent MOP crystals. Notably, this whole conversion occurs through an all-solid-state pathway, where no component of the starting materials dissolves in water, as evidenced from the UV/Vis spectra of the collected filtrate (Figure S13 in Supporting Information). As the amount of water added to the system is increased, the thickness of the resulting MOF crystals starts decreasing and beyond a certain water concentration (1.5 mL mg⁻¹), no solid particles are visually observed. However, the Tyndall effect (Figure 4b) from the obtained liquid indicates the presence of solid particles as a dispersion in the aqueous medium. Although the nanometer size of these particles makes their structural characterization challenging, the respective successor MOF crystals were analyzed structurally through single crystal X-ray diffraction. MOF-MIA crystallizes in the P4/n space group generating square-shaped pores [8×8 Å], whereas MOP-EIA and MOP-PrIA crystallize in the P321 and P3 space group, respectively. For the case of MOF-EIA and MOF-PrIA, two types of pores were found in their structure; the pore with bigger aperture [11.3×4.1 Å] has hexagonal geometry and contains all the alkyloxy groups pointed towards the pore center. The other set of pores are triangular [5.2×5.1 Å] and contain only coordinated water molecules from the paddle wheel SBUs. All these MOFs have two dimensional layered structures and the stacking of the molecular layers generate channels in their extended form (Figures S1–S3 in Supporting Information).

The phase purity of all the as-synthesized MOPs and the resultant MOF crystals has been confirmed by matching the experimentally observed PXRD patterns with the corresponding simulated patterns (Figures S4 and S5). Some peaks in the observed MOP PXRD pattern remain unindexed because of higher thermal disorder of the alkyloxy groups and the non-coordinated solvent molecules.[13] FTIR spectra of the as-synthesized MOP crystals reveal that the carboxylic O−H signal centered at 2900 cm⁻¹ disappears because of the co-ordination with metal ions. This co-ordination also causes a red-shift of the carboxylic acid C=O peak by 60 cm⁻¹. No additional signal is observed in the FTIR spectra after the conversion of the MOPs into the MOFs (Figures S7–S10). This phenomenon indicates the similarity in the chemical environment and bonding in the MOPs and the corresponding MOFs. Retention of the peaks for the alkyloxy O−C bond at 1054 and 1375 cm⁻¹ also suggests that the alkyloxy groups do not get fragmented during the conversion. All these MOPs are found to be thermally stable up to 300 °C with removal of trapped and coordinated solvent molecules (Figure S11). However, the thermal stability gets enhanced to 450 °C for the case of bulk MOFs (Figure S12). Thermal removal of the solvent molecules from the MOP core results in the gain of readily accessible surfaces.
and pores for incoming guest and other molecules. Adsorption of N$_2$ by MOP-EIA shows an availability of 450 m$^2$ g$^{-1}$ surface area as per the BET equation; one of the highest values reported to date for discrete MOPs (Figure 3). The available surface areas for the other two MOPs are less and this variation of the surface area results from the stability of the MOP units that originated from their crystal packing. MOP-EIA has a closely packed structure where the distance between adjacent MOP units is minimal [8.5 Å]. Similar spacing boxes bear dimensions of 8.4 x 12.9 x 21.0 and 11.0 x 9.0 x 8.6 Å for MOP-MIA and MOP-PrIA, respectively (Figure 1e–g). This close packing reduces the interstitial voids and minimizes the possibility of structural collapse during removal of solvent.

As evidenced from the structure of MOPs, the hydrophobic alkyl functionalities located on the outer surface of the MOPs are in a disfavored situation as they directly face the incoming water molecules. On the other hand, for the less hydrophobic inner surface, water contact should be a favorable situation. Thus, a strain gets developed between the two surfaces and in order to minimize this strain, the system tries to equally distribute the hydrophobic groups among the two surfaces. This equalization is achieved through the mechanism explained in Figure 2d. Thus, from each MOP crystal, several layers of MOFs are formed and are arranged in parallel as per their packing along the corresponding crystal planes.

It is evident from Figure 4a that MOP units from the bulk crystals first unfold to minimize the surface strain upon interaction with water through the combination of hydrophobic repulsion and hydration pressure to generate an amorphous

![Figure 2. Monitoring of the hydrolytic conversion through time dependent PXRD for (a) MOP-MIA, (b) MOP-EIA, and (c) MOP-PrIA. (d) The mechanism for the conversion of alkyl decorated MOPs into MOFs. Scanning electron microscopic images for monitoring the conversion of (e) MOP-MIA, (f) MOP-EIA, and (g) MOP-PrIA.](image1)

![Figure 3. N$_2$ adsorption isotherm for MOP-EIA. The available surface area as per the BET equation is 450 m$^2$ g$^{-1}$.](image2)
phase. The neighboring MOP units join along the crystallographic axes through unfolding of the closed structures and cause the generation of extended nanosheets. When the amount of water present in the system is limited, the conversion occurs at controlled rate because of the slower diffusion of water. This results in the generation of properly grown MOF layers, well stacked to produce micrometer sized single crystals. However, when the water content is higher, the excess amount of water does not allow the layers to stack up to the full extent which is required for the growth of the single crystals of the MOFs. As a result, the metal-organic nanosheets remain dispersed in water forming an aqueous suspension. The absence of stacking in their extended form causes the diminishing of the PXRD peak at 2θ = 5°, corresponding to the 100 plane (Figure S6 in Supporting Information). However, their chemical bonding and the chemical environment around each functional moiety remains intact, as evidenced from the similar FTIR spectra as that of the corresponding bulk MOFs. SEM images of the nanostructures clearly indicate their hexagonal morphology and that with time these structures are getting peeled-off from the bulk MOP materials and finally form the 2-dimensional sheets with nanometers scale thickness (Figure 2e–g). TEM imaging provides an input about their lateral dimension and the nanosheets are found to have aspects of 1.7×1.7 μm for MIA-NS, 2.0×2.0 μm for EIA-NS, and 1.8×1.8 μm for PrIA-NS (Figure 4c–e). The statistical variation in the dimension of the nanosheets has been determined using an AFM, by scanning several samples derived from each of the sources. The average height of the features are found to be 15.3±1.2, 17.2±1.1, and 11.8±0.6 nm for sheets obtained from MOP-MIA, -EIA and -PrIA, respectively. The error bar corresponds to the standard deviation of the data over all the samples. The aspects of the features were also verified from the AFM, by taking the average over many samples, and their values were found to be rather close to that obtained from TEM analysis (Aspect: 1.63±0.21 μm for MIA-NS, 1.96±0.16 μm for EIA-NS, and 1.82±0.13 μm for PrIA-NS) shown in Figure 4c–e. The molecular thickness of each layer has been calculated as 2.0 nm from the crystal structure. Hence we could clearly say that each of these nanosheets contain around 6–8 stacks of the molecular layers. While Figure 4f–h shows the detailed AFM image of a single sheet, an image of larger scan area indeed verifies that the sheets are of uniform thickness. One such image showing uniform size and thickness dispersion of PrIA nanosheets has been shown in Figure S19 in the Supporting Information. The size of the nanosheets has again been measured from particle size analysis with a dynamic light scattering (DLS) experiment where the effective diameters of the nanosheets were found to be 2.1, 1.7, and 3.3 μm for MIA-NS, EIA-NS, and PrIA-NS, respectively (see Supporting Information).

PXRD patterns collected during the hydrolytic conversion of the MOPs indicate that an amorphous phase is first attained because of the interaction with water. This amorphous phase
is responsible for conversion into metal-organic nanosheets as per the postulated mechanism. And thus, transformation of the crystalline MOP units into the amorphous phase is an instance of the top-down approach for nanosheet synthesis. This amorphous form is then transformed into the nanosheets following the bottom-up approach. Additionally, for the top-down segment of the conversion pathway, no energy needed to be supplied in terms of ultrasonication or mechanical shear- ing. Rather, the nanosheets were separated from the bulk amorphous phase by themselves utilizing the interaction with a pool of water molecules. Hence, the generation of the nanosheets is best-described as self-exfoliation. The benefit of this method has been tested by comparing with the nanomaterials obtained from two paths of top-down approach, mechanical grinding and ultrasound treatment to the bulk MOF crystals (Figure S17). In both these cases, the obtained materials do not possess the regular morphology required to be termed as nanosheets.

The chemical stability of the obtained nanosheets was tested through checking their chemical integrity as well as sus- pension stability. It has been seen from the UV/Vis spectra for the aqueous suspension of the nanosheets (Figure S14) that they do not disintegrate into CuI in presence of water after more than 30 days. The DLS particle size analysis for the aqueous suspension of the nanosheets also concludes that the effective diameter of the nanosheets does not change for the period of 30 days (See Supporting Information).

Conclusion

In conclusion, for the first time, we have been able to combine top-down and bottom-up approaches for synthesizing metal-organic nanosheets. By controlling the amount of water present in the contact media of MOPs during their hydrolytic conversion into MOFs, control of their growth has been achieved. Thus, metal-organic nanosheets with uniform size and thickness were obtained at high yield in a single conversion step. Additionally, no external energy was supplied for the separa- tion of the nanosheets from the bulk materials, revealing true self-exfoliation.

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Conflict of interest

The authors declare no conflict of interest.

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