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COMMUNICATION

Surfactant-Free bottom-up synthesis of Ultrathin MOFs Nanosheets for the Oxidation of Isoeugenol to Vanillin

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The direct synthesis of the ultrathin MOF nanosheets are extremely challenging. Plenty of methods have been developed for the fabrication of MOF nanosheets; although, it suffers from structural deterioration, aggregation, morphological fragmentation, and low yield. So, the direct synthesis of MOF nanosheets are more desirable but relies on our ability for the facile, controllable, synthesis of nanosheets yet it remains a challenging task. Herein, we report the direct bottom-up synthesis of MOF nanosheets comprising and assemblies of a single layer with high crystallinity, surfactant-free low-cost MOF nanosheets with high yield.

Metal Organic Frameworks (MOFs) are the most fascinating field in Chemistry and Material science,[1-10] They are made of metal ion or cluster with an organic molecule, its high surface area and tunable functionality provide lots of application in the field of catalysis. [11-15]due to their ultrahigh porosity large surface area and tunable structures and functions. The MOF nanosheet as a new member of the 2D nanomaterial family, it provides fundamental studies and quite interesting applications due to their highly exposed active sites. [16-21] More importantly, like other 2D materials, the ultrathin thickness and large lateral size also make them promising in surface active applications. Direct synthesis of the ultrathin MOF nanosheets is extremely challenging. Unfortunately, such a MOF nanosheets with higher yield and crystallinity is extremely difficult. MOF nanosheets can be fabricated by two approaches. The top-down approach involves delamination of layered MOF precursors via methods such as sonication and chemical intercalation. however, it suffers from low yield and the structural deterioration and morphological fragmentation during exfoliation.[22, 23] so the direct bottom-up synthesis of MOF nanosheets is more desirable but relies on our ability to direct crystal growth to form high-aspect-ratio nanosheets at reasonable yield. Apart from a few recent reports, there are only two series of MOFs that could be directly synthesized as ultrathin nanosheets dispersible in solvents. Rodenas et al. reported a three-layer synthesis method for M-BDC (M = Cu, Co, BDC = 1,4-benzenedicarboxylate) nanosheets by modulating the growth kinetics of MOF crystals. Moreover, this approach often a low yield and does not offer good control over the morphology of nanosheets. Later Zhao et al. introduced a PVP as a surfactant in the synthesis of M-TCPP (M = Zn, Cu, Cd, Co, TCPP = tetrakis (4-carboxyphenyl) porphyrin) nanosheets. However, to utilize properly the exposed active surface of nanosheets, the PVP surfactant should probably have to be removed. Here we report the direct synthesis of nanosheets with high crystallinity comprising assemblies of a single layer. the direct synthesis of ultrathin Cobalt MOF $Co(Hoba)_2$. $2H_2O$ Hoba = 4,4-oxybis (benzoic acid) was originally reported in the form of bulk materials,[24] With the direct synthesis method reported here, ultrathin Cobalt nanosheets are produced by surfactant-free and without morphological fragmentation, deterioration, aggregation, and low cost, high yield.

The fabrication of Cobalt MOF nanosheets was accomplished by the direct bottom-up method. Firstly, we screen the fabrication by considering several parameters like variation of solvents, temperature, time, without base, with the different mole ratio of reactant. Based on the screening, we have fabricated the ultrathin cobalt nanosheets with optimized reaction condition via Co $(NO_3)_2{\cdot}6H_2O$ (0.4 mmol) and H_2Oba (0.8 mmol) were mixed in 5 mL of distilled water, 20µl of TEA were added into the solution to adjust the pH value to ~7.00. The solution was kept in a 20 mL Teflon-lined stainless-steel autoclave heated at 120 °C for 12h, followed by cooling to room temperature. Centrifuge and washed with ethanol several times and dried at 60°C under vacuum oven for 12h. finally collected the pink colored MOF with a 60 % yield.

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† Footnotes relating to the title and/or authors should appear here.
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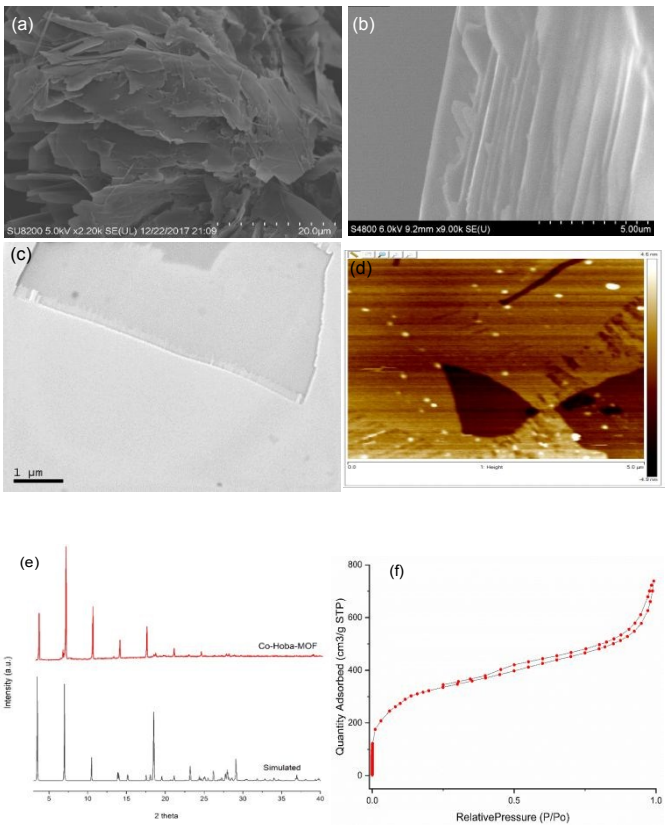

Figure 1 (a, b) SEM image (c) TEM image (d) AFM image (e) PXRD (f) N_2 adsorption-desorption isotherms of synthesized Co-Hoba MOF.

Figure 1 depicted the successful fabrication of ultrathin Cobalt MOF nanosheets. SEM image shows the layered structure of cobalt MOF nanosheets. TEM image further exhibited the layered structure. In order to further study the crystal structure of nanosheets, X-ray diffraction (XRD) measurements were performed. The powder X-ray diffraction pattern confirmed that the synthesized MOF nanosheets highly crystalline. Atomic force microscopy was used to further gain insight into their thickness. The AFM image revealed that the sheets with an average thickness of ~10 nm. The Brunauer-Emmett-Teller (BET) surface area obtained 1189 m^2 g^{-1}

The fabrication of Nickel MOF nanosheets was accomplished by the direct bottom-up method. Firstly, we screen the fabrication by considering several parameters like variation of solvents, temperature, time, without base, with the different mole ratio of reactant. Based on the screening, we have fabricated the ultrathin cobalt nanosheets with optimized reaction condition via $Ni(NO_3)_2{\cdot}6H_2O$ (0.4 mmol) and H_2Oba (0.8 mmol) were mixed in 5 mL of distilled water, 20µl of TEA were added into the solution to adjust the pH value to ~7.00. The solution was kept in a 20 mL Teflon-lined stainless-steel autoclave heated at 120 °C for 12h, followed by cooling to room temperature. Centrifuge and washed with ethanol several times and dried at 60 °C for 12h. Finally collected the greenish colored MOF with a 56 % yield.

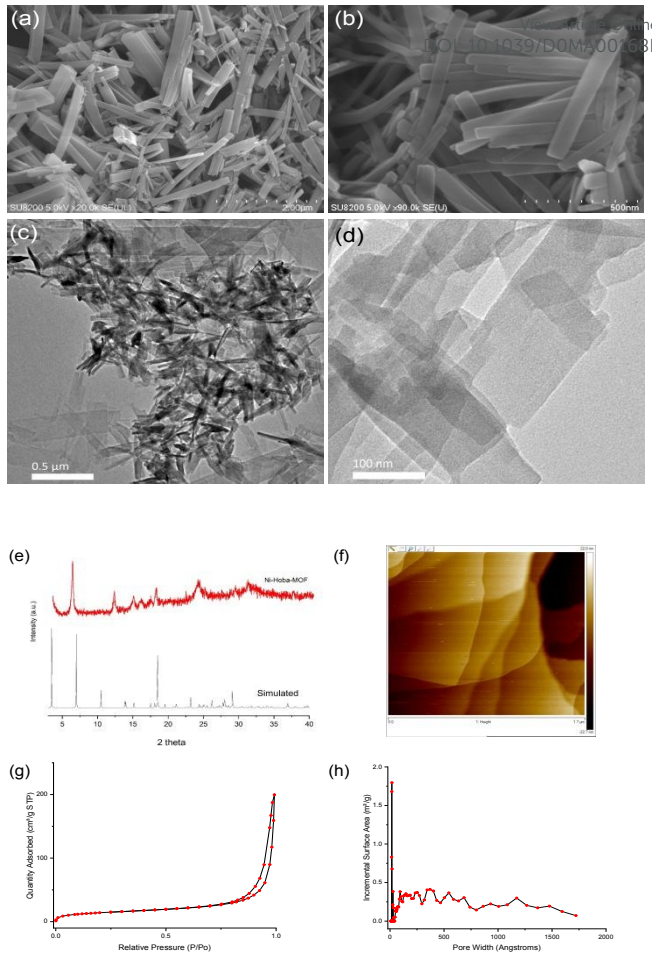

Figure 2 (a, b) SEM image (c, d) TEM image (e) PXRD (f) AFM image (g) N_2 adsorption-desorption isotherms (h) Pore size distribution of synthesized Ni-Hoba MOF.

Figure 2 depicted the successful fabrication of ultrathin Nickel MOF nanosheets. SEM image shows the layered structure of cobalt MOF nanosheets. TEM image further exhibited the layered structure. In order to further study the crystal structure of nanosheets, X-ray diffraction (XRD) measurements were performed. The powder X-ray diffraction pattern confirmed that the synthesized MOF nanosheets highly crystalline. Atomic force microscopy was used to further gain insight into their thickness. The AFM image revealed that the sheets with an average thickness of ~15 nm. The Brunauer-Emmett-Teller (BET) surface area obtained 52 m^2 g^{-1}

Vanillin is one of the most commonly used natural products.[25] Its a vital chemical in the aroma industry, due to its abundantly used in pharmaceutical, food, cosmetic, and chemical industries. so, lots of research has been done for the improvement of its production. which can also be produced from. The chemical synthesis of vanillin is well-established in large-scale production from lignin-derived feedstocks. These classical synthetic routes are not environment-friendly and the vanillin produced by these methods is considered to be of lower quality because it does not contain some trace components that

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contribute to the natural vanilla flavor. These compounds are easily derived from lignin and have the common structural unit with that of vanillin, being potentially useful for vanillin production via simple oxidation pathways. Another problem related to the slow reaction rates, unsuitable for commercial production. As a result, chemical oxidation pathways were also followed. To achieve faster kinetics and better selectivity of vanillin. To overcome this problem, lignin-derived monomers (such as eugenol, isoeugenol, ferulic acid, etc.) have been used in the last few years. However, selective and efficient production of vanillin from these feedstocks still remains an issue to replace the existing process.

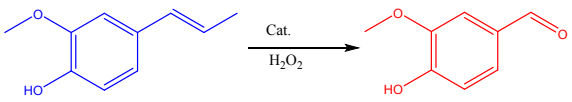

Table 1 Synthesis of Vanillin with various catalysts under standard Conditions

No	catalyst	Conversion (%)	Selectivity (%)
1	Co-Hoba	18%	90
2	Ni-Hoba	23%	92
3	Cu-Hoba	10%	82

[a] Reaction condition: 0.5ml Isoeugenol, cat: 20mg, H_2O_2 - 2ml, rt, 24h.

First, we screened the reaction to evaluate different parameters, like the oxidant, solvent, and catalyst. From the screening tests, we conclude that the synthesis of vanillin from isoeugenol could occur with H_2O_2 as an oxidant and acetonitrile as a solvent, catalyzed by the Ni-Hoba MOF.

We have fabricated a facile bottom-up synthesis of MOF nanosheets assemblies of a single layer. Which is surfactant-free and without any morphological fragmentation, deterioration, aggregation. Furthermore, it's an indeed simple, efficient and high yield method. It believed that our facile direct bottom-up synthetic method can be used to synthesize other ultrathin MOF nanosheets, which might have promising applications in vanillin synthesis. We achieved moderate conversion with good selectivity**.**

Conflicts of interest

There are no conflicts to declare.

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