

Preparation of cerium-based UiO-66 metal-organic framework (MOF) without addition of solvent for developing its sustainable synthesis

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Abstract. UiO-66(Ce) metal-organic framework (MOF) has been a promising material for broad applications, including gas adsorption, photocatalysis, water treatment and reaction catalysis. For its usual preparation, a large amount of solvent is required and added during its fabrication process. This solvent is harmful to the environment most of the time. It is neither recyclable nor reusable, indicating the difficulty in waste disposal after MOF fabrication and the challenges for its scaling-up production. Given this, a solvent-free way of synthesizing the UiO-66 MOF to develop its sustainable synthesis was reported here. The MOF can be obtained by mechanically grinding the cerium (IV) ammonium nitrate (CAN) and terephthalic acid (BDC) using mortar and pestle without the addition of any solvent. Then the mixture was transferred into an autoclave and heated at 100 °C for one day. In this work, UiO-66(Ce) MOF samples with varying Ce to BDC molar ratios were successfully fabricated using the solvent-free method, supported by the XRD, SEM, EDX and FT-IR analysis results. By looking at their XRD patterns, two characteristic peaks for UiO-66(Ce) MOF were observed at 8.4° and 9.1°. The SEM images revealed the spherical crystalline morphology of UiO-66 MOF. At the same time, the EDX analysis result found the elemental composition of UiO-66 MOF was coherent with the reactants used, suggesting the excellent purity of MOF product formed in this work. As verified by the thermal stability test, the UiO-66 MOF produced here is thermally stable up to 250 °C in the air atmosphere.

1. Introduction

Metal-organic Framework (MOF) is an organic-inorganic hybrid material built from metal ions interconnected with the organic ligand molecules to form a systematic and uniform framework structure [1]. This material has gained a lot of interest over the years and is still capturing the attention of

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researchers nowadays since it offers wide advantages, including high thermal and chemical stability, high porosity, flexible and tunable frameworks [2-3].

UiO-66 is one of the critical subclasses for MOFs. The University of Oslo introduced the first zirconium based UiO-66 MOF in early 2008 [4]. It demonstrated exceptional thermal and chemical stability compared to the other known MOFs [5]. Later in 2015, the cerium-based UiO-66 MOF was firstly reported by Lammert and his co-workers. This UiO-66(Ce) MOF was found to be isostructural to the zirconium-based UiO-66 MOF, with enhanced stability and potential in fields of redox and catalysis reaction [6]. UiO-66(Ce) MOF has promised potential applications in gas adsorption, photocatalysis, water treatment and redox catalysis. Because of this, it has been of great interest for the synthesis of UiO-66(Ce) MOF.

In general, the preparations of MOFs were accomplished by the hydrothermal/solvothermal method, requiring a large amount of solvent and a long synthesis duration. The large amount of non-recyclable or non-reusable solvents added during the synthesis process makes the scaling-up process challenging, burdens the waste disposal process, and leads to environmental problems [7-8]. Several studies reported on the synthesis of UiO-66(Ce) MOF employing solvent methods. For example, Dalapati and co-workers synthesized the dimethyl-functionalized UiO-66(Ce) MOF by dissolving the CAN metal precursor and organic linker in DMF solvent and heated at 100 °C using an oil bath under magnetic stirring [9]. While in 2019, UiO-66(Ce) solid was obtained by dissolving the CAN in DI water, whereas the BDC was dissolved in DMF to have a homogenous mixture solution to be heated at 110 °C in a dryer [10]. The lack of an eco-economic synthetic route for UiO-66(Ce) hinders its real-life application.

Hence, a solvent-free or green synthetic route for UiO-66(Ce) MOF is strongly desired. Recently, a near solvent-free synthetic way for this UiO-66(Ce) MOF was proposed by Campanelli and co-workers. They obtained the MOFs by grinding the CAN and BDC with the addition of a small amount of acetic acid as a modulator and then heated the mixture at 120 °C for one day [5]. To further develop the sustainable synthesis for UiO-66(Ce) MOF, an utterly solvent-free synthesis route was reported here. UiO-66(Ce) can be prepared without adding any solvent during its synthesis process, and it has been confirmed to be successfully formed with varying Ce to BDC molar ratios from 0.5:1 to 2:1 in this work.

2. Materials and methodology

2.1. Fabrication of UiO-66(Ce) MOF

The chemicals used in this work include cerium (IV) ammonium nitrate (CAN) (99%, Acros Organics), terephthalic acid (BDC) (99%, Acros Organics), dimethylformamide (99.5%, Fisher Chemical) and acetone (99.8%, Merck), they are all commercially available and used without further processing. UiO-66(Ce) MOF was obtained here without the addition of solvent. Firstly, the metal precursor: cerium ammonium nitrate and the organic linker: terephthalate, were mixed and ground using mortar and pestle for around 10 minutes. Then, the well-grinded mixture was transferred into a Teflon-lined autoclave and to be heated at 100 °C for 12 hours. After it had been naturally cooled down to room temperature, the obtained off-white UiO-66 product was washed with DMF and acetone separately (X 5,500 rpm) for 15 minutes to remove any unreacted reactants. The preparation steps for UiO-66(Ce) were illustrated in figure 1. There was a total of four cerium based UiO-66 samples being fabricated under this study with varying cerium metal to organic linker ratios, and they were named according to table 1.

Table 1. Naming of UiO-66(Ce) samples fabricated in this work.

Sample Name	Ce to BDC Molar Ratio
C0.5	0.5:1
C1	1:1
C1.5	1.5:1
C2	2:1

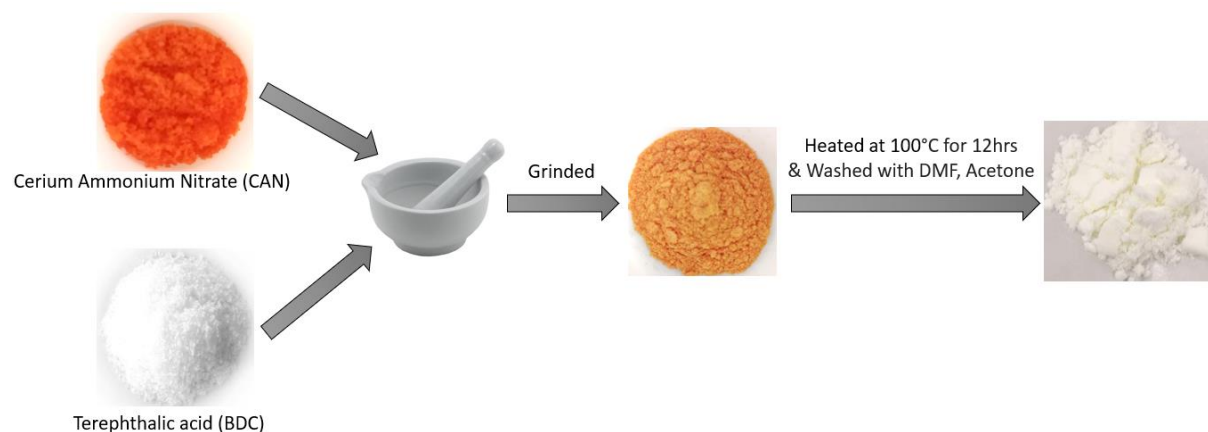


Figure 1. Illustration of the UiO-66(Ce) MOF preparation.

2.2. Sample characterization

A diffractometer (Shimadzu 6000) was employed to obtain the XRD patterns of samples fabricated in this work with a 2θ angle ranging from 5° to 40° with a scanning speed of 1.2° in one minute. While the samples' SEM micrographs, together with surface elemental composition, were acquired and determined from a Hitachi-S-3400N scanning electron microscope (SEM) coupled with energy-dispersive x-ray spectroscopy (EDX). Before the SEM analysis, each sample surface was coated with a thin layer of conductive gold/platinum material to improve its quality in imaging.

The samples prepared were also scanned by a Thermo Nicolet iS10 FT-IR spectrometer from an infrared range of 400 to 4000 cm^{-1} to obtain their respective transmission spectra. Additionally, the samples fabricated in this work were examined on thermal stability. Hence, they were placed into the Perkin Elmer STA 8000 thermogravimetric analyzer (TGA) and exposed to high temperature up to 600°C in airflow. Around 15 mg of sample was placed into the TGA in each thermal stability test with the airflow rate, and heating rate held constant at 20 mL/min and 10°C/min , respectively.

3. Results and discussion

3.1. XRD graphs analysis

The diffraction patterns for UiO-66(Ce) MOFs fabricated in this work, including the C0.5, C1, C1.5 and C2, are shown in figure 2. Their XRD patterns are identical in terms of the shape and location of peaks. They all displayed characteristics peaks for UiO-66(Ce) MOF at around 8.4° and 9.1° , which are well-agree with the reported XRD patterns of UiO-66 MOF fabricated with solvent [10-12]. Hence, the successful formation of UiO-66(Ce) MOF is proven using the solvent-free method reported here. By comparing the peak intensities, it can be predicted that the crystallinity level of C2 is the highest, followed by C1, C0.5 and C1.5.

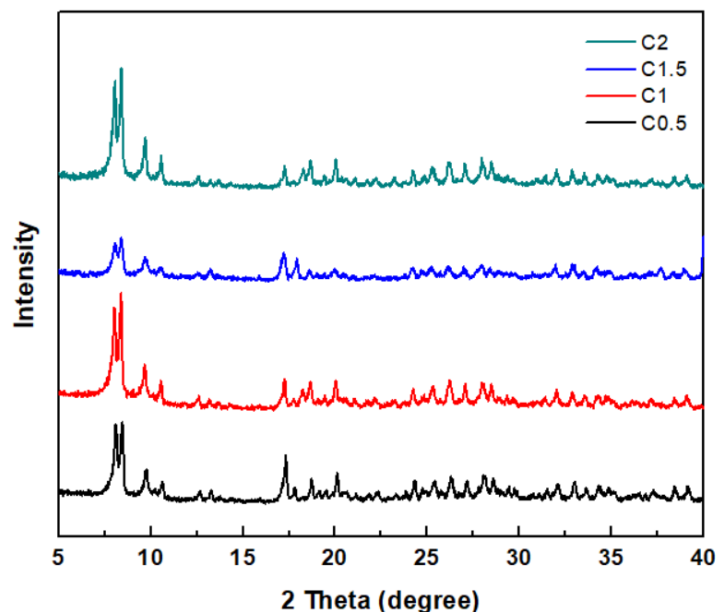


Figure 2. XRD graphs of C0.5, C1, C1.5 and C2.

3.2. EDX result

The elemental composition for the cerium based UiO-66 samples obtained here are listed in table 2. For ensuring the accuracy of EDX results obtained, three readings were acquired from the different spots for each sample. And only three elements were detected for the composition of UiO-66(Ce) samples; they are cerium sourced from the CAN metal precursor and both carbon and oxygen that originated from the BDC organic linker [13], indicating the purity of cerium based UiO-66 MOF formed here. Based on this EDX analysis result, it is noted that the cerium element weight percentage increases while both oxygen and carbon compounds decrease as the Ce to BDC mole ratio increases and vice versa. Therefore, the weight percentage of cerium elements in C2 is the highest, followed by C1.5, C1 and C0.5.

Table 2. Elemental composition of UiO-66(Ce) samples fabricated in this work.

Sample Name	C Element (wt%)	O Element (wt%)	Ce Element (wt%)
C0.5	45.52	25.32	29.16
C1	34.93	30.42	34.65
C1.5	24.67	31.54	43.79
C2	18.61	30.33	51.06

3.3. SEM micrographs

The SEM micrographs of UiO-66(Ce) samples synthesized in this work were captured at a magnification of 10 K and are well displayed in figure 3. Their SEM micrographs shown in figure 3 show agglomeration of spherical crystalline particle, which is similar to the morphology of UiO-66 MOF reported by previous literature works [5-6]. Based on the SEM images and XRD patterns obtained, it is therefore confirmed that the cerium based UiO-66 MOF were successfully formed with Ce to BDC molar ratios of 0.5:1, 1:1, 1.5:1 and 2:1 using the solvent-free method reported here.

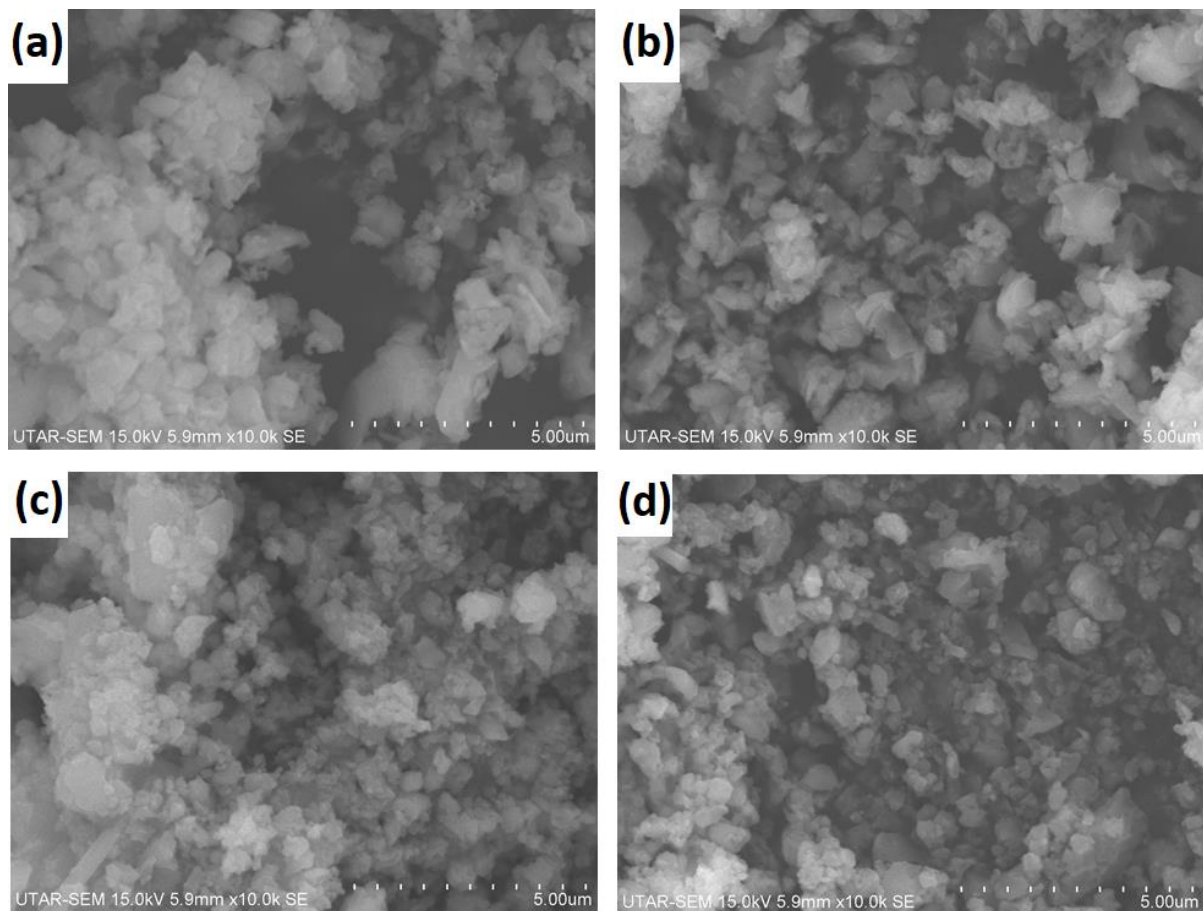


Figure 3. SEM micrographs of (a) C0.5, (b) C1, (c) C1.5 and (d) C2.

3.4. FT-IR spectrum analysis

Figure 4 shows the FT-IR spectra of UiO-66(Ce) MOFs synthesized in this work. Based on the FT-IR spectra, characteristic peaks for Ce-O vibration are found at 560 cm^{-1} for all samples [14]. Also, symmetric carboxylate groups stretching are observed near the wavenumbers of 1370 cm^{-1} and 1430 cm^{-1} , while its asymmetric stretching bonds are discovered at 1555 cm^{-1} in their spectra [13]. The absorption band can denote the existence of moisture within the sample itself at 3400 cm^{-1} and the peak near 1610 cm^{-1} [9].

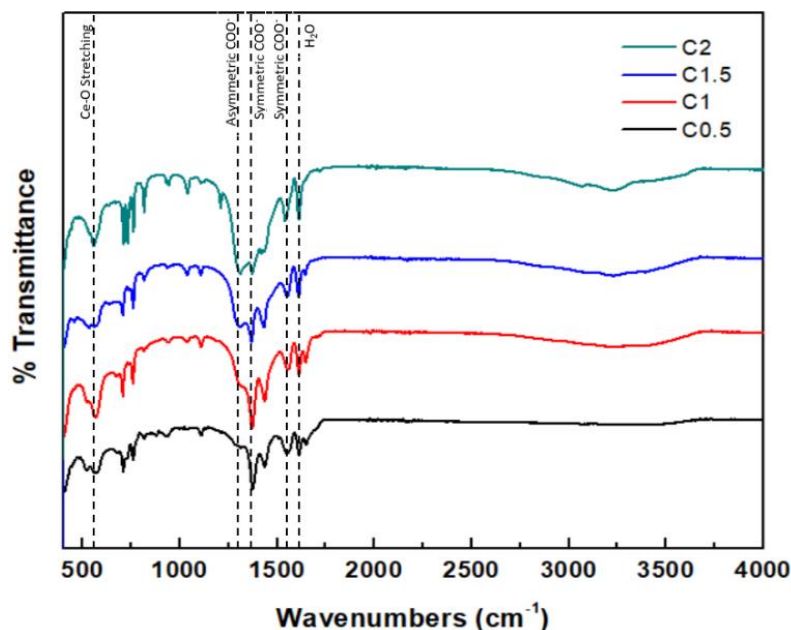


Figure 4. FT-IR spectra of C0.5, C1, C1.5 and C2 samples.

3.5. Thermal stability result

The thermal stability curves for C0.5, C1, C1.5 and C2 are depicted in figure 5. The UiO-66(Ce) MOF samples have three stages of weight loss when exposed to temperatures ranging from 50 °C to 600 °C. The first stage of weight loss happened from 50 °C to 120 °C, accounting for approximately 4 wt% of the drop due to the elimination of water molecules embedded within the samples [11]. The second stage of weight loss was ascribed to removing chemical residuals [9,15]. The decomposition of frameworks for C0.5 and C1 started at around 220 °C. While for the more robust samples, C1.5 and C2, they began to decompose at 250 °C, evidenced by a steep decrease in their weight [13]. After the decomposition process, the sample weight percentage of the UiO-66 samples fabricated in this work remained at approximately 38 to 42 %.

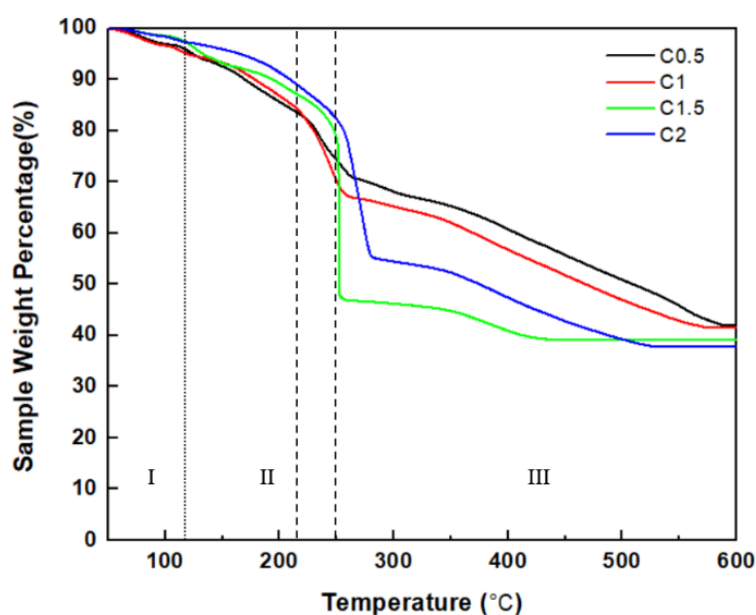


Figure 5. TGA curves of C0.5, C1, C1.5 and C2 samples.

4. Conclusions

Solvent-free preparation of cerium-based UiO-66 MOF was demonstrated in this work. A combination of characterization tests, including XRD, SEM, EDX, and FT-IR had confirmed the formation of UiO-66(Ce) MOF by employing the solvent-free method with varying Ce to BDC molar ratios from 0.5:1 to 2:1. The thermal stability test result revealed that the UiO-66(Ce) synthesized here could maintain their UiO-66 MOF structure at a temperature of at least 200 °C.

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