

Application of Ce-based Metal–Organic Framework (MOF) for Efficient Uranium Extraction from Seawater (UES)

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1. Introduction

Nuclear energy is a clean, eco-friendly, and stable energy source in contrast to conventional fossil fuels as well as intermittent renewable energy sources. Nuclear energy is projected as a potential future energy source owing to its enduring sustainability and key contribution to addressing global challenges such as climate change and fossil fuels depletion [1]. The global demand of uranium as nuclear fuel source has increased manifold, leading to exhaustion of non-renewable land-based reserves at an alarming rate. Fortunately, seawater preserved a vast uranium reserve (~4.5 billion tons) compared to terrestrial resources [2]. Nevertheless, the ultralow concentration of uranium (~3.3 ppb), excessive salt content, multitude of competing ions, alkaline pH, and marine biofouling make it extremely challenging to extract uranium selectively and efficiently from seawater [3]. Over recent decades, among various utilized approaches for uranium recovery, physicochemical adsorption has emerged as the most efficient and practical approach [4]. Several adsorbents have been developed so far, including porous materials, clays, zeolites, composite, hybrid material, and gels [5]. However, these materials typically exhibited numerous limitations owing to complex seawater environment, inefficient uranium extraction, poor selectivity, inadequate regenerability and susceptible to degradation.

Metal organic frameworks (MOFs) built by metal ions and organic linkers provide a robust framework with high surface area. These porous crystalline structures with tunable functionality offer easy access to the active sorption sites. More specifically, hierarchically porous MOFs have garnered significant attention due to their rapid mass transfer, enabling an efficient extraction of target ion from solution [6]. The polymeric templating strategy is among the widely employed approaches used to tailor the porosity of a range of materials [7]. This study aims to boost the uranium extraction efficiency from seawater by fabricating a superstructure and highly porous Ce-based MOF (Ce-UiO-66) utilizing a soft template, triblock copolymer Pluronic F-127.

2. Materials and methods

2.1 Materials

The reagents and solvents employed in this study consist of Cerium(IV) ammonium nitrate ((NH₄)₂Ce(NO₃)₆) 99%, Sodium perchlorate monohydrate (NaClO₄·H₂O), Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆), Terephthalic acid (H₂BDC), acetic acid (AA), ethanol (EtOH), N,N-dimethylformamide (DMF), purchased from Sigma Aldrich Co., Ltd and Samchun chemicals Co., Ltd. All the purchased reagents were of analytical grade and used without further purification.

2.2 Characterization

The Powder X-ray diffraction pattern of synthesized Ce-based MOF was recorded on a Rigaku MiniFlex 600 X-ray diffractometer equipped with a copper K α radiation at an accelerating voltage and current of 40 kV and 15 mA, respectively. Scanning electron microscopy (SEM) images were captured by an HR-FESEM-II, JSM 7800F Prime with Dual EDS. Fourier transform infrared (FT-IR) data of the synthesized MOF was acquired using a Thermo Fisher Smart iTR diamond ATR instrument over the range of 550 - 4000 cm⁻¹. Inductively Coupled Plasma Mass Spectrometry (ICP-MS, PerkinElmer NexION 300D), was utilized to quantify the uranium concentration during batch UES experiment.

2.3 Synthesis of Ce-UiO-66 MOF

The MOF was synthesized following the literature reported procedure [8] with some modification. About 100 mg of F127 was dissolved in 6 mL of deionized water. Following this, 5.1 mmol of AA and 3.5 mmol of NaClO₄·H₂O were added to the mixture. After stirring to obtain a homogeneous solution, 1 mmol of each (NH₄)₂Ce(NO₃)₆ and BDC were sequentially introduced. Subsequently, the mixture was stirred for 30 minutes at 60 °C, and then subjected to centrifugation and washed twice with DI water and DMF. To remove the template, the obtained solid was immersed in ethanol for two days at 60 °C, with daily renewal of ethanol. Finally, the product was obtained by drying the ethanol washed solid at 60 °C under vacuum overnight.

3. Results and discussion

The crystalline pattern of synthesized MOF was examined by the X-ray diffraction (XRD) as shown in Fig. 1. Three prominent peaks were observed at 2θ values of 7.24° , 8.36° , and 24.9° consistent with the lattice planes (111), (200), and (600), respectively [9]. This confirms the well-defined crystallinity and purity of synthesized MOF. Notably, the XRD patterns of synthesized MOF exhibited a remarkable concordance with the simulated diffraction patterns, validating the successful formation of Ce-based MOF [10].

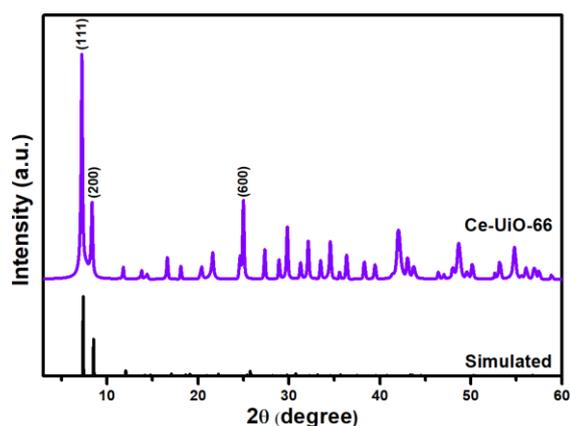


Fig. 1. X-ray diffraction patterns of Ce-UiO-66.

The Fourier transform infrared spectroscopy (FTIR) was employed to identify the various function groups present in the synthesized MOF (Fig. 2). The IR band observed at 3250 cm^{-1} was mainly attributed to the O-H stretching vibration, suggesting the formation of hydrogen bonding between the hydroxyl groups of intercrystalline water and carboxyl groups located on the MOF surface [11].

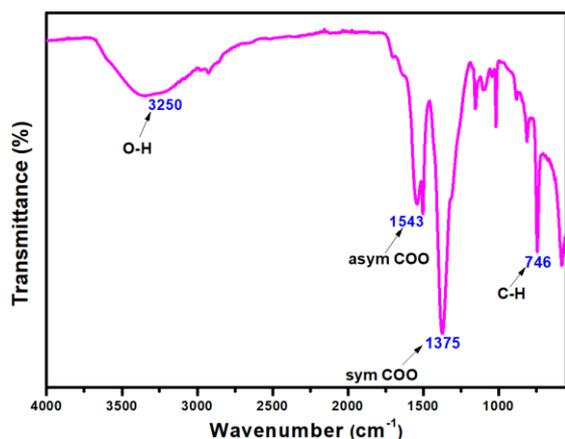


Fig. 2. FTIR spectra of Ce-UiO-66.

The IR vibrational bands observed at 1543 cm^{-1} and 1375 cm^{-1} were designated to the COO asymmetric and symmetric stretching, respectively, indicating the presence of carboxylate group attributed by organic ligands (H_2BDC) [12]. Additionally, a small band at 746

cm^{-1} was ascribed to the C-H stretching of ligand (H_2BDC) [13].

The scanning electron microscopy (SEM) was utilized to reveal the microstructure and morphology of synthesized MOF. SEM images disclose a distinct homogeneity and a well-defined morphology of truncated octahedron with particle size ranging from $0.9\text{--}1.2\text{ }\mu\text{m}$ (Fig. 3a and 3b). Moreover, energy dispersive spectroscopy (EDS) elucidates the uniform distribution of Ce and O, confirming their successful incorporation in synthesized MOF framework (Fig. 3c and 3d).

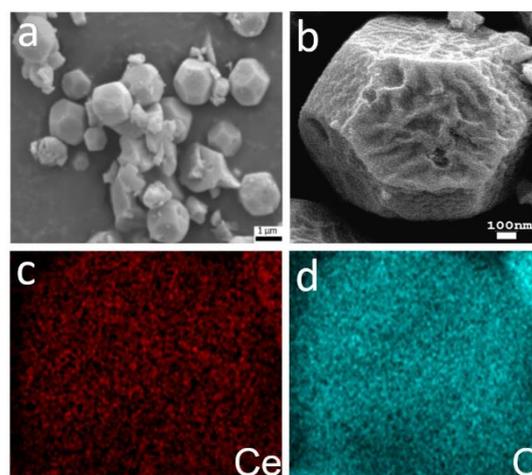


Fig. 3. Morphology and elemental mapping of Ce-UiO-66. SEM images (a and b), and EDS analysis (c and d).

4. Conclusion

A superstructure and uniform Ce-UiO-66 MOF was synthesized by employing a soft templating strategy. The successful synthesis of the targeted MOF, Ce-UiO-66 was validated by XRD and FTIR. SEM analysis revealed a superstructure MOF ($0.9\text{--}1.2\text{ }\mu\text{m}$) with a definite homogeneity and octahedrons morphology. Considering the remarkable potential of synthesized MOF for a robust mass transfer owing to highly porous structure (pore size analysis is ongoing) equipped with uranium trapping functional groups (carboxylate), uranium extraction should be achieved with an optimum uranium adsorption capacity for efficient UES.

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