



Multifunctional flexible composite aerogels constructed through in-situ growth of metal-organic framework nanoparticles on bacterial cellulose



Xiaoting Ma^{a,1}, Yue Lou^{a,1}, Xiao-Bo Chen^{a,b}, Zhan Shi^{a,*}, Yan Xu^{a,*}

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

^b School of Engineering, RMIT University, Carlton, VIC 3053, Australia

HIGHLIGHTS

- MOF nanoparticles are assembled on the bacterial cellulose by weak interaction.
- MOF aerogels with hierarchical structures are flexible and lightweight.
- BC@ZIF-8 demonstrates an excellent adsorption performance of heavy metal ions.
- BC@UiO-66@PDA interlayer can improve the performance of Li-S batteries.

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ABSTRACT

Flexible metal-organic framework (MOF) aerogels with practical macroscopic shapeability and hierarchical porosity were prepared through in-situ growth of MOF nanoparticles, i.e. zeolitic imidazolate framework-8 (ZIF-8) and University of Oslo-66 (UiO-66), on bacteria cellulose (BC). The yielded composite aerogels inherit high porosities from feedstock MOFs and mechanical flexibility from BC template. BC template offers high porosity, mechanical flexibility to the composite aerogels, which significantly suppresses the aggregation of individual MOF nanoparticles. Owing to the structural characteristics of MOF and BC, BC@ZIF-8 composite aerogel sponges exhibit a low density below 0.03 g cm^{-3} , hierarchical porosity, large surface area, high mass transfer efficiency and superior adsorption performance of heavy metal ions. After 24 h adsorption in simulated industrial wastewaters, removal efficiency of the composite aerogels reaches up to 81% with respect to Pb^{2+} ion pollutants, which is 1.2 times higher than that of original ZIF-8 nanoparticle counterparts. BC@UiO-66 composite aerogel film, as a flexible lithium-sulfur battery interlayer, demonstrates a high reversible capacity of 631 mAh g^{-1} at 0.5C over 100 cycles, which is attributed to its selectivity for Li^+ ions and efficient inhibition to the soluble polysulfide ions. In addition, the presence of polydopamine (PDA) coating on BC@UiO-66 nanofibers in BC@UiO-66@PDA composite aerogel films increases reversible capacity up to 739 mAh g^{-1} at 0.5 C over 100 cycles. This work provides a feasible solution to process MOF powders into a flexible and tailorable form, and holds a new promise to rational design and manufacturing of MOF monoliths with a great structural diversity as advanced multifunctional materials.

1. Introduction

Metal-organic frameworks (MOFs) stand for a great variety of highly porous crystalline materials with tunable structures and diverse functionalities, and are commonly prepared by combining inorganic metal ions or ion clusters with organic ligands through covalent coordination linkage [1,2]. Engineering applications of MOFs have been seen in various fields, spanning from gas storage and separation, catalysis,

sensing, drug delivery, water treatment, to energy storage and conversion [3–8]. The common forms of synthetic MOFs include bulk powders and colloidal crystals. However, the intrinsic fragility of MOFs is a key challenge for retaining their desired structural integrity during service life, which significantly retards the practical employment of MOFs [9]. Therefore, it is of great significance to prepare a shapeable MOF monolith with high mechanical durability and flexibility. A prevalent processing option is extrusion of MOFs under high pressure,

* Corresponding authors.

E-mail addresses: zshi@mail.jlu.edu.cn (Z. Shi), yanxu@jlu.edu.cn (Y. Xu).

¹ Xiaoting Ma and Yue Lou contributed equally to this work.

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however, extrusion is detrimental to porosity and catalytic activity of MOF monolith yields [10–12].

To tackle such a technical issue, a number of alternative methods for introducing both macroscopic shapeability and hierarchical porosity into MOFs have been reported [13–16]. A representative bottom-up method for manufacturing MOFs with desired 3D architectures usually involves in-situ growth on porous substrate with aid of seeding growth, layer-by-layer deposition or hydrothermal treatment [14,15,17–20]. However, size and loading rate of MOF nanoparticles are constrained by surface roughness and charged properties. Surface modification is required to increase physical and chemical compatibility between MOFs and substrates [21]. On the other hand, post-treatment processing is commonly employed for combining MOFs with additives through sol-gel casting, surfactant-assisted dip-coating, freeze-drying, and so on [22–24]. In both fabrications, high stability of both substrate and additives is key to the success of MOF preparation. Although these strategies could overcome some disadvantages of preparing shaping MOFs, MOF-based composites are mechanically unstable and an unsatisfactory load rate of MOFs. Hence, a feasible technique for fabricating flexible MOF monoliths with a low density and a high MOF loading rate is highly needed.

Cellulose is the most widely distributed and abundant polysaccharide in nature, which attracts considerable attention due to its inherent renewability, low density, biodegradability, low cost and non-toxic [25]. In recent years, nanocellulose demonstrate a great potential as supporting host or scaffolding template for immobilization of guest materials [26–28]. Due to its super-toughness, it can be used as mechanical support to prepare composites with flexibility, shapeability and hierarchical porosity. In recent years, metal-organic framework/cellulose composites have gradually attracted the attention of scientists [13,29]. Kitaoka and co-workers reported a densely packed barrier film with low oxygen permeability obtained by in-situ growth of MOF on cellulose nanofibers (CNF) for high-performance gas-separation [30]. But the barrier films adhere tightly to commercial filter paper, which cannot be removed during analysis characterization and gas separation test. Recently, a pioneering study of combining MOFs and cellulose nanocrystal (CNC) to prepare hierarchical aerogels through sol-gel process, followed by freeze-drying was proposed [31]. However, this strategy requires modification of CNC to induce crosslinking ability. Meanwhile, addition of flexible carboxymethyl celluloses is also essential to yield robust mechanical behavior to address cracking issues. As a cost-effective, lightweight and commercially available porous material, BC is an excellent host and template for immobilizing guest materials, such as polymers, metal nanoparticles, conductive materials and fluorescent molecules [32–37]. We thus postulate that use of flexible BC aerogels as scaffolding template could facilitate the nucleation and growth of MOFs and homogenous distribution of MOF particles on BC through offering copious reaction sites from its abundant hydroxyl group terminals. The presence of abundant hydrogen bonds between BC nanofibers in the resulting MOF aerogels is an advantage to withstand large-strain deformation.

Herein, we attempt to validate such hypothesis through developing a rapid and straightforward in-situ growth method for combining MOFs and BC into a composite aerogel with hierarchical structures to tackle the longstanding challenge of processing MOFs into a flexible and tailorable monolith. BC offers high porosity, mechanical flexibility for the composite aerogels and decreases the aggregation of individual MOF nanoparticles. The composite aerogels not only maintain the high porosity of original MOFs, but also shapeability, flexibility, hierarchical porosities and low density (below 0.03 g cm^{-3}) from BC. Tailorability of the BC aerogels and functionality of MOFs allow us to design and synthesize composite materials for different applications. Typically, the preparation of composite aerogels involves two principle steps, a simple immersion of pristine BC aerogels in an inorganic metal ion solution and nucleation growth of MOFs. In this research work, two types of MOF materials including ZIF-8 and UiO-66 and the corresponding

composite aerogels are prepared and characterized for two key engineering applications, i.e. water purification and intermediate layer for high-performance lithium-sulfur (Li-S) battery. Adsorption measurements indicate that BC@ZIF-8 composite aerogel sponge plays a vital absorbent role in purifying Pb^{2+} or Cd^{2+} ions containing solutions, which is attributed to its large surface area, high porosity and excellent pore accessibility. It is promising that BC@ZIF-8 composite aerogel sponges are easy to be separated from solution, which could avoid secondary pollution. In terms of battery application, highly porous BC@UiO-66 and BC@UiO-66@PDA flexible composite aerogel films are used as interlayer in Li-S battery to isolate the commercial polypropylene separator (Celgard 2500) from cathode, which can entrap active materials and prevent polysulfide shuttle. Electrochemical measurements confirm that the Li-S battery with a composite aerogel interlayer possesses a low capacity-fading rate, which is derived from the addition of thin film for effectively suppressing the transfer of polysulfides from electrolyte to anode side.

2. Experimental

2.1. Materials

Anhydrous ethanol (> 99.7%), anhydrous acetic acid, sodium hydroxide and tert-butanol (99%) were obtained from Beijing Chemicals Co., China. D-glucose anhydrous was purchased from AMRESCO. Yeast extract was purchased from OXOID. Peptone was purchased from Beijing Aoboxing Biotechnology. Bacterial strain *Acetobacter Xylinum* HN001 was provided by Tianjin University, China. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-methylimidazole was purchased from Energy Chemical. Tris(hydroxymethyl)aminomethane and dopamine hydrochloride were obtained from Aladdin. Terephthalic acid and zirconium chloride (ZrCl_4) were obtained from Alfa Aesar. Lead acetate trihydrate ($\text{Pb}(\text{COOH})_2 \cdot 3\text{H}_2\text{O}$) was obtained from Xilong Scientific Co. Ltd. CMK-3 was purchased from XFNANO. All reagents were used as received without further purification.

2.2. Preparation

2.2.1. BC aerogel

BC aerogels were synthesized according to the procedures as reported previously [38]. In a typical process, 25 g D-glucose, 7.5 g yeast, 10 g peptone and 10 g disodium hydrogen phosphate were dissolved in 950 ml deionized water under stirring. pH of the solution was adjusted to 5.0 with dropwise addition of anhydrous acetic acid, followed by addition of deionized water to make 1 L clear solution. After inoculation of *acetobacter xylinum* HN001, culture medium was shaken at a rotation rate of 200 rpm using an incubator shaker at 30 °C until flocculent bacterial cellulose was generated. Then, a bacterial cellulose pellicle was formed after static cultivation in an incubator at 30 °C for 1–4 days. Bacterial cellulose was purified using 1 M sodium hydroxide solution for 1 h at 60 °C, and then washed by deionized water and ethanol for several times to neutral. The as-cultured BC hydrogels were solvent-exchanged in tert-butanol at 30 °C for 6–7 h under gentle agitation for 3 times. Next, BC aerogels can be obtained by freeze-dried in a freeze-dryer to liberate the solvent. The aerogels can be cut into rectangular or circles.

2.2.2. BC@ZIF-8 composite aerogel

In a typical experiment, 0.08 g BC aerogels were immersed in $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /ethanol solution (100 mM) by stirring at room temperature until fully swelling. Then 2-methylimidazole/ethanol solution (800 mM) was added dropwisely under magnetic stirring, followed by sonicating for 2 h. The as-synthesized composites were washed by ethanol for three times and freeze-dried to obtain white composite

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