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In situ growth of microporous ZIF-8 nanocrystals on a macroporous phyllosilicate mineral

Trung Tuyen Bui [a], Nguyen Duc Cuong [a], Yong Shin Kim [b,*], Hyungphil Chun [b,*]

[a] Department of Bionano Engineering, Hanyang University, Ansan 426-791, Republic of Korea
[b] Graduate School of Applied Chemistry, Hanyang University, Ansan 426-791, Republic of Korea

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ABSTRACT

Microporous zeolitic imidazolate frameworks (ZIFs) have shown great potential in many application fields. However, the small dimensions of ZIF nanoparticles make them difficult to employ in practical systems. To overcome this problem, a novel and efficient strategy has been developed to immobilize ZIF crystals on a macroporous phyllosilicate mineral. As an example, water-stable ZIF-8 nanocrystals were synthesized and assembled on the dopamine-modified surface of expanded vermiculite using the sequential addition of methanol solutions of $Zn(NO_3)_2{\cdot}6H_2O$ and 2-methylimidazole. The ZIF-8 nanoparticle-decorated mineral exhibited a dense growth of microporous ZIF-8 nanocrystals of 80 ± 10 nm, resulting in 9.8 wt% of ZIF-8 loading and a BET surface area of 120 m^2/g.

1. Introduction

A type of metal-organic framework (MOF) known as zeolitic imidazolate frameworks (ZIFs) have attracted a great deal of attention since their initial discovery [1,2]. They possess highly desirable material properties such as crystallinity, microporosity, a large surface area, and active metal centers, which can be useful for various applications including CO_2 capture [3], gas separation [4], chemical sensing [5], and heterogeneous catalysis [6]. Furthermore, several ZIFs exhibit exceptional chemical resistance to hydrolysis in aqueous solutions [1,7]; thus, they have potential to be applied to adsorptive removal of pollutants from wastewater. Among these materials, ZIF-8 nanocrystals have been extensively investigated due to their facile synthesis, large surface area of 1810 m^2/g, and polar bonding characteristics between Zn and the 2-methylimidazole (Hmin) ligand [8–10]. These studies reported high adsorption capacities for various pollutants. However, the need for laborious and inconvenient separation, generally using centrifugation, hampers the practical use of this adsorbent. To overcome this problem, Zhao et al. synthesized a magnetic MOF composite of core-shell Fe_3O_4@$Cu_3(btc)_2$ that could be simply separated with a strong magnet [11]. Another approach to the problem is to immobilize the microporous MOF crystals on a supporting matrix. Recently, ultrathin and conformal coatings of ZIF-8 nanocrystals on porous polymer supports were attained [12,13]. Nevertheless, the immobilization of MOF nanocrystals on chemically inert, granule-like supports that can be employed in continuous reactors under harsh conditions remains a challenge.

Vermiculite is a low-price phyllosilicate mineral formed by hydrothermal alternation of mica, having excellent chemical stability. Its flakes can be exfoliated using thermal or chemical treatments, resulting in concertina-shaped granules with macroporosity [14]. Expanded vermiculite (EV) and its chemically modified types have been utilized as a cheap and durable supporting matrix in the adsorption applications despite a relatively low surface area of 1–10 m^2/g [15].

Herein, we prepared ZIF-8 nanocrystal-decorated expanded vermiculite particles (EV@ZIF-8) with a core-shell structure for easy handling and reliable utilization of the promising MOF nanoparticles. To the best of our knowledge, this work presents the first synthesis of hybrid material combining microporous nanocrystals on the surface of a macroporous mineral, thus providing an opportunity to realize MOF-containing hybrid materials in a cost-effective and environment-friendly manner.

2. Experimental

Crude vermiculite flakes (Palabora, size = 0.84 mm) were exfoliated at 1000 °C to obtain expanded products as described previously [16]. The surface of 1.0 g EV was modified for 12 h in a

* Corresponding authors.
E-mail addresses: yongshin@hanyang.ac.kr (Y.S. Kim), hchun@hanyang.ac.kr (H. Chun).

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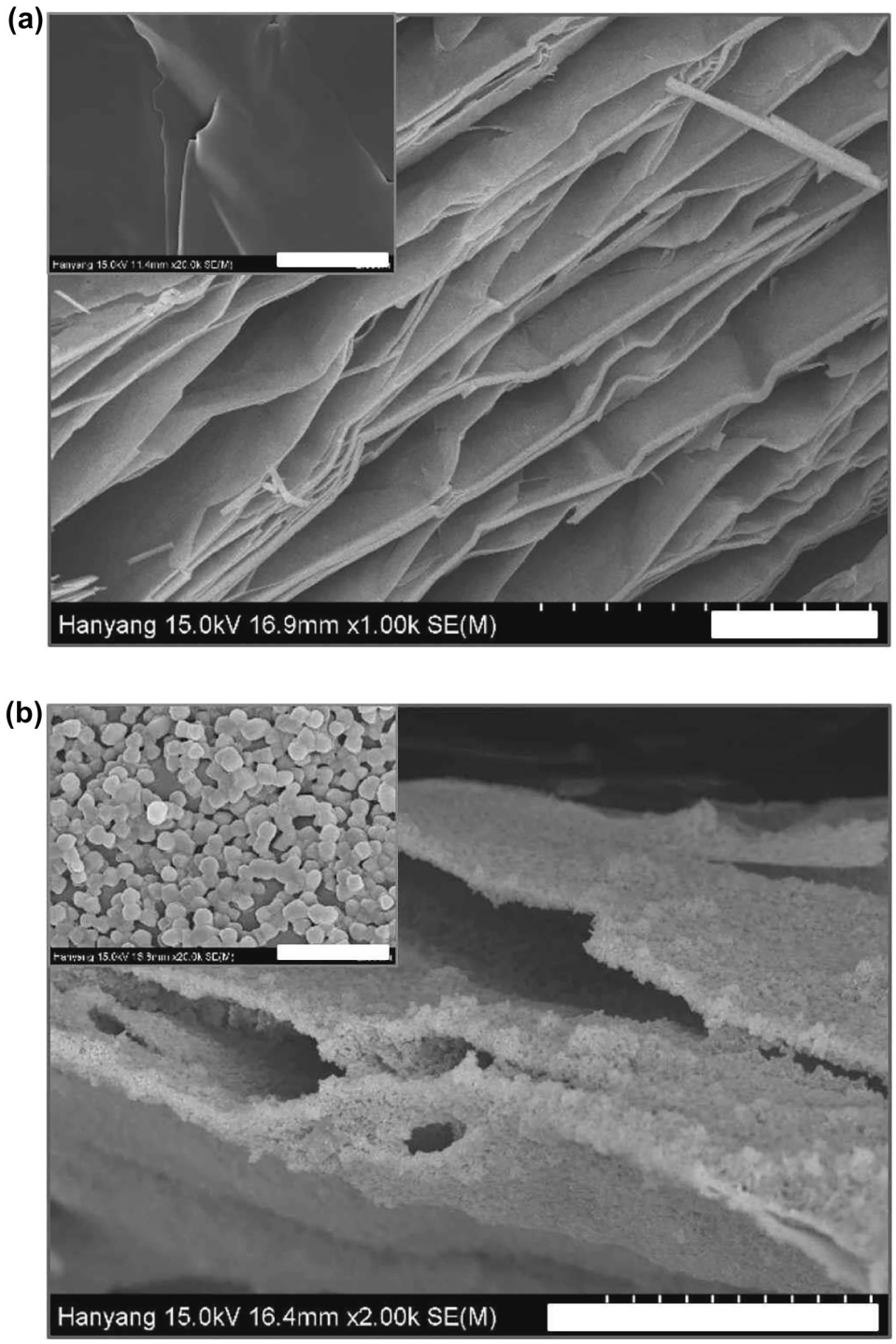

Fig. 1. SEM images of (A) EV and (B) EV@ZIF-8 hybrid material. The scale bars are 25 μm and 2 μm in inset.

15 mL aqueous buffer solution (pH = 8.5) containing 20 mM dopamine hydrochloride, which created black polydopamine-coated expanded vermiculite (PD-EV). The product was collected on filter paper, washed three times with deionized water, and dried in an oven at 60 °C. To grow ZIF-8 crystals on the PD-EV surface, 0.9 mL of 0.25 M $Zn(NO_3)_2{\cdot}6H_2O$ solution in methanol was first added into a vial containing 0.15 g of PD-EV, and the mixture was kept in a 60 °C oven for 12 h without a cap. Next, 0.9 mL of a ligand solution (2 M Hmin in MeOH) was added into the vial, and the mixture was kept at room temperature for 12 h. The hybrid EV@ZIF-8 was filtered, washed with methanol, and then dried at 60 °C.

Various characterizations of the hybrid materials were performed using scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), nitrogen sorption, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Samples for PXRD, TGA, FTIR and XPS analyses were pulverized by a ball mill. N_2 sorption and TGA analyses used samples heat-treated at 150 °C.