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Synthesis of zeolitic imidazolate framework nanocrystals

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ABSTRACT

For the first time, three kinds of ZIF (zeolitic imidazolate framework) nanocrystals were synthesized with narrow size distribution under additive-free hydrothermal and solvothermal conditions. The crystal size was ca. 60, 75 and 220 nm for ZIF-71-EIM, ZIF-93 and ZIF-8-MCIM, respectively. The N_2 adsorption isotherms and TG analysis indicate that the nanocrystals possess permanent microporous structure and good thermal stability. These new ZIF nanocrystals hold promising potentials for the applications in the fields of nanotechnology devices and nanocomposite membranes. Q2

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) [1], a subfamily of metal–organic frameworks (MOFs), have attracted considerable attention over the past few years for energy [2–4], environment [5] and sensor [6] applications. Yaghi and others systematically explored the rich zeolitic chemistry of ZIFs with tetrahedral networks, which possess more than 100 ZIF members [1]. However, ZIFs in the form of bulk crystalline materials do not always fulfill all specific needs for their applications. Nanoscale ZIFs are mandatorily required in many areas, e.g. nanotechnology devices [6], heterogeneous catalysts [3], nanocomposite membranes [7–10] and adsorbents [11,12]. To the best of our knowledge, until now, only several kinds of ZIF nanocrystals were reported, such as ZIF-7 [13,14], ZIF-8 [15–18], ZIF-67 [19], ZIF-71 [20] and ZIF-90 [21].

In this work, for the first time, three kinds of ZIF nanocrystals were synthesized under additive-free hydrothermal and solvothermal conditions, i.e. ZIF-71-EIM (isoreticular to ZIF-71 [22], RHO topology, Zn(2-ethylimidazolate)$_2$) [23], ZIF-93 (RHO topology, Zn(4-methylimidazolate-5-carbaldehyde)$_2$) [22] and ZIF-8-MCIM (isoreticular to ZIF-8 [24,25], SOD topology, Zn(4-methylimidazolate-5-carbaldehyde)$_2$) [26] (Fig. 1). The N_2 adsorption isotherms and TG analysis were performed, indicative of their permanent microporous structure and good thermal stability.

2. Experimental

ZIF-71-EIM nanocrystals were solvothermally synthesized at room temperature (25 ± 2 °C). A solution of $Zn(NO_3)_2 \cdot 6H_2O$ in DMF was rapidly poured into a solution of EIM in DMF under stirring with a molar ratio of Zn^{2+}/EIM/DMF = 1:8:1000. The mixture slowly turned milky. After stirring for 2 d, the resulting nanocrystals were isolated and thoroughly washed (6 times) using MeOH with assistance of centrifuge and ultrasonic bath. The yield is about 45% based on zinc.

A facile hydrothermal procedure was employed to prepare ZIF-93 nanocrystals. A $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution was rapidly poured into a MCIM aqueous solution (molar ratio Zn^{2+}/MCIM/H_2O = 1:8:1000) at room temperature(25 ± 2 °C). The mixture turned milky immediately. After stirring for 5 min, the resulting nanocrystals were isolated and thoroughly washed (6 times) using MeOH with assistance of centrifuge and ultrasonic bath. The yield is about 45% based on zinc.

ZIF-8-MCIM nanocrystals were solvothermally synthesized at 85 °C. A solution of $Zn(NO_3)_2 \cdot 6H_2O$ in DMF was rapidly poured into a solution of MCIM in DMF (molar ratio of Zn^{2+}/MCIM/DMF = 1:4:1000). After mixing, the thus obtained solution was sealed in a Teflon-lined autoclave and placed in a pre-heated convection oven at 85 °C for 42 h under static condition. After cooling to room temperature, the resulting nanocrystals were isolated and thoroughly washed (6 times) using MeOH with assistance of centrifuge and ultrasonic bath. The yield is about 40% based on zinc.

XRD patterns of the activated nanocrystals were recorded on a Rigaku D/MAX 2500/PC. The SEM images were performed on a

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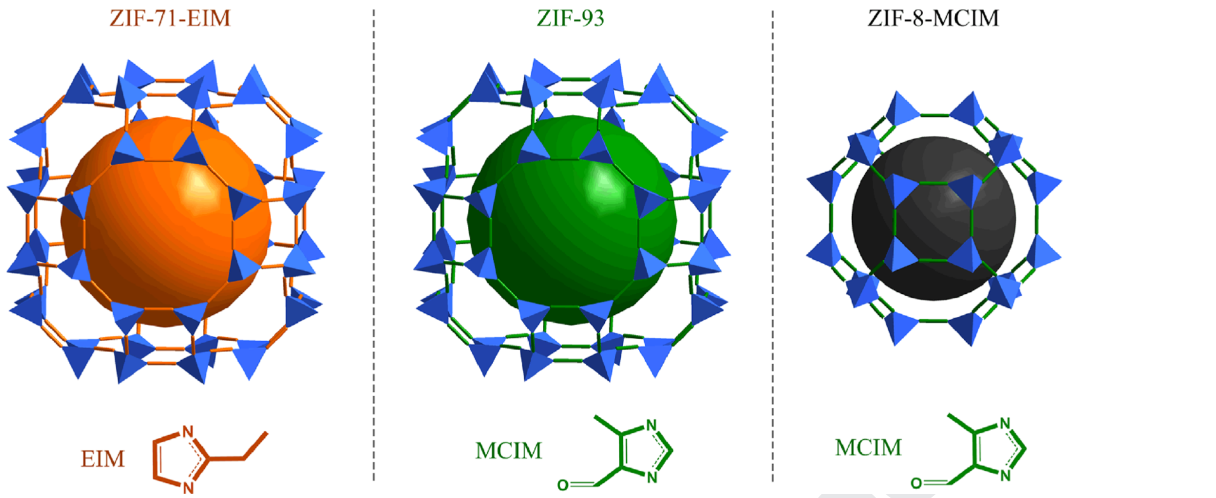

Fig. 1. The structure of one cage that is linked together to make the structures of ZIF-71-EIM, ZIF-93 and ZIF-8-MCIM, and the structural formula of their ligands. The balls within the cages, tetrahedra on the frameworks and line segments connecting tetrahedra represent the free spaces, zincs and ligands, respectively.

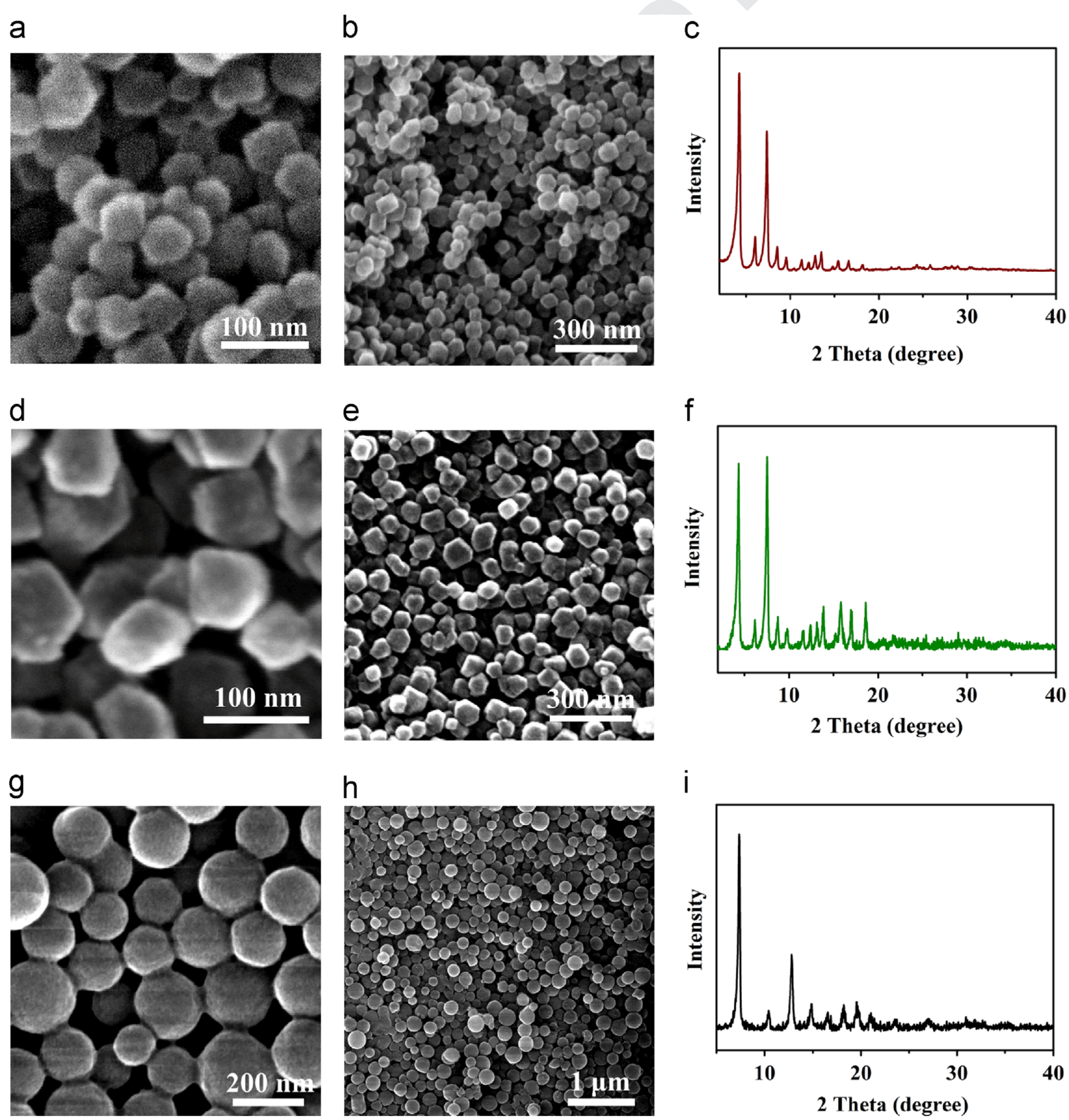

Fig. 2. High and low magnification SEM images and XRD patterns for ZIF-71-EIM (a–c), ZIF-93 (d–f) and ZIF-8-MCIM (g–i) nanocrystals.

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