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One-pot template-free fabrication of hollow mesoporous sodalite nanospheres for drug release

Shixiang Zuo [a,b], Wenjie Liu [a], Chao Yao [a,c,*], Xiazhang Li [a,c], Shiping Luo [a], Fengqin Wu [a,d], Yong Kong [a], Xiaoheng Liu [b,**]

[a] School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China
[b] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[c] R&D Center of Xuyi Attapulgite Applied Technology, Changzhou University, Xuyi 211700, China
[d] Changzhou Aotena New Materials S&T Co. Ltd., Changzhou 213164, China

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ABSTRACT

Hollow mesoporous sodalite nanospheres (HMSN) were facilely fabricated by a one-pot template-free hydrothermal route using natural halloysite as a silicon–aluminum source. The obtained products were characterized by X-ray diffraction, Fourier transform infrared spectrum, transmission electron microscope, field emission scanning electron microscope and N_2 adsorption–desorption isotherm. Well-defined HMSN with a mesopore structure were successfully obtained when the hydrothermal temperature was 180 °C, the reaction time was 9 h and the NaOH concentration was 3 mol/L. The products began to gradually transform from HMSN to micro-nepheline hydrate when the time was extended to 12 h. The drug release results indicate that the modified HMSN have outstanding drug release performance. The capacity for aspirin loading can reach as high as 20.8% and its cumulative release can reach 65% when release time is ~50 h.

1. Introduction

Hollow mesoporous nanospheres (HMN) with penetrating porous matrix wall or shell geometries, which are considered to be one of the best effective carriers, have captured increasing interests due to their conspicuous features of low density, high specific surface, large void space fraction, and high chemical stability (Feng et al., 2008; Zhang et al., 2012). All these characteristics make them more suitable candidates for many potential applications in catalysis, separation/adsorption, and drug delivery *etc.* Some HMN, such as carbon, SiO_2, SnO_2 and Fe_xO_y, have been extensively studied by many researchers (Ding et al., 2011; Jin et al., 2012; Dai et al., 2014; Xin et al., 2014). Template-assisted synthesis has been one of the most common approaches to fabricate HMN due to its unique advantages against the shell thickness of a hollow sphere and its morphology, which can be effectively controlled using different templates and raw materials. For instance, SiO_2-HMN are generally synthesized with various templates including inorganic colloids, surfactant/vesicle templates, emulsion templates and polymeric micelle templates (Liu et al., 2010; Sasidharan et al., 2013). However, the removal of the templates is expensive and time consuming. Therefore, it is urgent to find straightforward and economic routes to obtain HMN. Template-free hydrothermal synthesis has been considered to be an effective methodology. It can be described as follows, firstly, the insoluble matters can redissolve under the circumstance of high temperature and high pressure without templates, and then the dissolved matters renucleate and grow at certain supersaturation.

As a traditional zeolite, sodalite has been intensively investigated due to a wide range of applications including catalyst support, gas sorption, and hydrogen separation (Shanbhag et al., 2009; Zheng et al., 2009; Wang et al., 2014). Currently, micro-nano sized sodalite crystals with a solid structure can be synthesized by the hydrothermal process (Wei et al., 2008; Jiang et al., 2012). A few hollow sodalite nanospheres have been reported previously. Ji et al. (2011) fabricated hollow sodalite micro-spheres with a hole on the shell in a first-closed then-open system from the synthesis gels aged under ultrahigh nitrogen pressures. Firstly, the synthesis gels were transferred into a sealed autoclave with adjustable pressure, and then the pressure in the autoclave was slowly released by opening this valve. Although some templates are not used in a previous report, the above synthetic methods have some drawbacks in terms of complicated technology, high cost and long periodicity. As a naturally engineered aluminosilicate clay with a nanotube structure and a 1:1 Al:Si ratio (Yah et al., 2012a,b), halloysite has been universally used in functional materials (Zhou, 2011; Zhou and Keeling, 2013). Herein, a one-pot template-free strategy was adopted to obtain hollow mesoporous sodalite nanospheres (HMSN) using

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* Correspondence to: C. Yao, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.
** Corresponding author.
E-mail address: yaochao420@163.com (C. Yao).

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halloysite as a Si–Al source because of its advantages compared with previous work: (a) the raw material-halloysite is abundant and economical, and the tube-like and special crystal structure of which are efficiently utilized; (b) as a unique molecular sieve, HMSN have more excellent performance in the above applications compared to the other HMN. To date, there has been no report on the hydrothermal fabrication of HMSN. Due to their environmental friendliness and biocompatible nature, HMSN are expected to play a significant role in the drug loading and release.

2. Experimental

100 mL of HCl solution (1.0 mol/L) was poured into 200 mL of dispersion containing 9.6 g of halloysite. After stirring for 3 h at 80 °C, the obtained dispersion was filtered and washed using deionized water until neutral, and the acid–halloysite was dried at 80 °C for further use. 4.0 g of acid–halloysite was dispersed into 100 mL of NaOH solution (3.0 mol/L), and then transferred into a Teflon-sealed autoclave. The autoclaves were maintained respectively at different temperatures for different times. The products were separated by filtration, followed by washing with deionized water, and finally dried at 80 °C. Fourier transform infrared (FT-IR) spectrum was performed by a Nicolet Avatar 370 (Thermo Corporation, USA) from 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on a D/Max 2500 PC X-ray diffractometer (Rigaku Corporation, Japan) with CuKα radiation of the X-ray wavelength of 0.15418 nm over a 2θ range (5–80°). The N_2 adsorption–desorption isotherms and pore distribution (Brunauer–Emmett–Teller, BET method) were determined by a Micromeritics Corporation ASAP2010C surface area and porosimetry system. The morphologies of the as-obtained samples were observed by a JEOL Corporation (Japan) JEM-2100 transmission electron microscope (TEM) and a Carl Zeiss Corporation (Germany) SUPRA-55 field emission scanning electron microscope (FE-SEM).

First of all, the sodalite was modified with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KH792) under similar technological conditions (Zuo et al., 2013). Subsequently, 0.5 g of sodalite was impregnated in 20 mL of ethanolic solution containing 0.24 g of aspirin (ASP) at room temperature for 48 h. Afterwards, the above dispersion was filtrated and washed with ethanol several times. Finally, 0.1 g of ASP-sodalite was added into 50 mL of phosphate buffered solution (PBS; pH = 7.5) with constant rotation at 37 °C, and the effect of release time on the cumulative release of ASP was studied in detail. For comparison, halloysite was also investigated under the same technological conditions. The loading content of the drug and the cumulative release were determined according to the methods as reported by Liang (2012).

3. Results and discussion

3.1. XRD and FT-IR analysis

To ascertain the structures of the products, the XRD patterns are shown in Fig. 1. As can be generally confirmed, the sodalite crystals have been mainly harvested at 180 °C for 3–9 h. The XRD reflections of halloysite appear at 2θ = 12.1°, 19.9° and 24.8° in accordance with reflection planes (001), (020), (110) and (002), respectively (JCPDS no. 74-1022) (Liu et al., 2013). However, the above reflections disappear after a hydrothermal reaction, and the new reflections can be observed clearly. The tiny new reflection at 2θ = 10.8° can be clearly found when the hydrothermal time reaches 12 h, suggesting that a very small

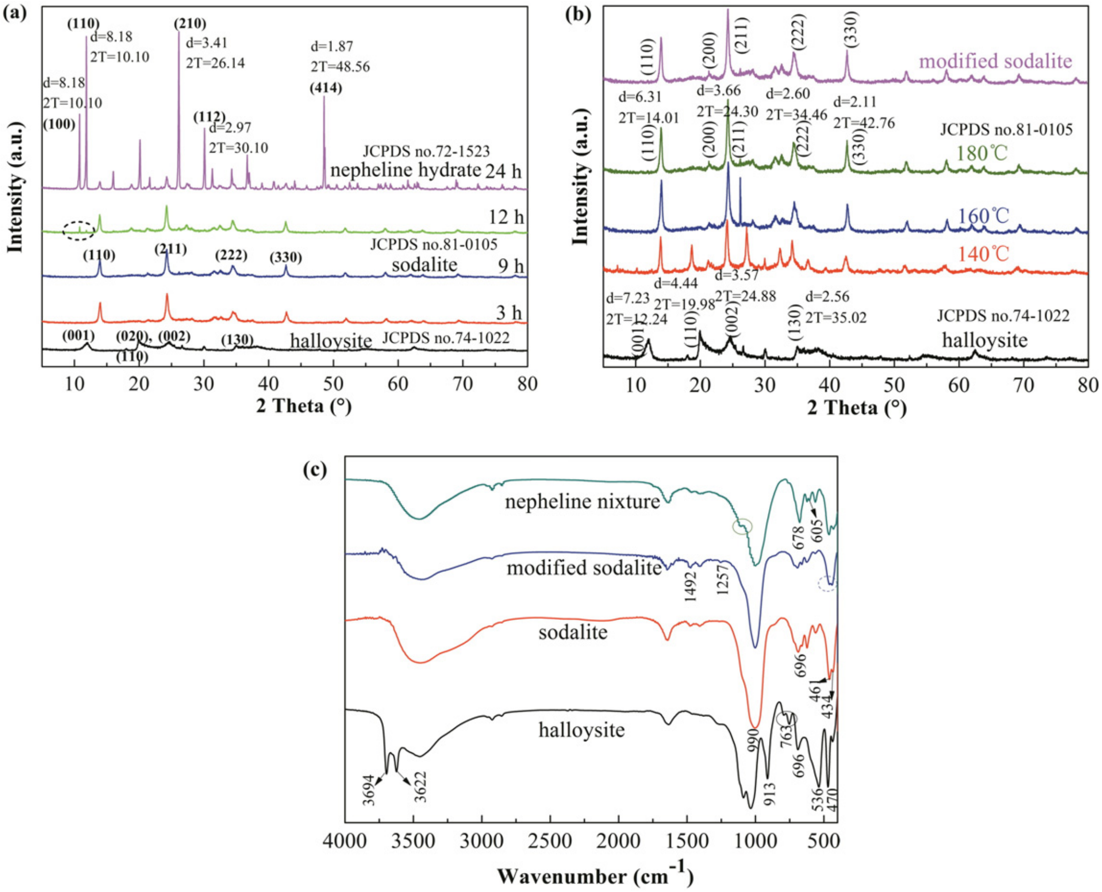

Fig. 1. (a) XRD patterns of products at 180 °C for different times; (b) XRD patterns of products at different temperatures for 9 h, and modified sodalite; (c) FT-IR spectra of products and modified sodalite.