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Preparation of amphiphilic nano-sized NaA/glass films and powders using layer-by-layer in-situ sol–gel method

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ABSTRACT

Nano-sized NaA/glass films were prepared by a layer-by-layer in-situ sol–gel method combined with the steam-assisted conversion technique. Consequently, nano-sized zeolite NaA powders were obtained by scraping the films and treating the resultant powders with a 0.6% acetic acid solution. The films and the powders were characterized by XRD, FT-IR, SEM, TEM, and AFM, and their hydrophilicity and antimicrobial activity after Ag^+-exchange were examined. The preparation conditions such as the reaction time and the amount of water prefilled in the autoclave were examined. The NaA crystals on the films are about 50–100 nm in size and they are aggregated together. Their particle sizes can be further reduced to 40–80 nm and they can be changed from aggregated to highly dispersed particles after treated in the acid solution. The amount of water during the synthesis is quite important for successful synthesis of well-crystallized nano-sized zeolite NaA on the glass. And dispersed 40–50 nm zeolite NaA particles can be obtained when suitable amount of water is used. The nano-sized NaA/glass film exhibits superhydrophilicity and oleophilicity. After ion-exchange with Ag^+, the NaA/glass film shows high antimicrobial activity, better than the nano-sized NaA powders and other NaA films or coatings reported in literature.

1. Introduction

Zeolite films have attracted considerable attention in the last twenty years because they can be widely used in many areas such as separation membranes, structured catalysts, chemical sensors, ion-exchange electrodes, low-dielectric-constant films, nonlinear optical materials, anti-reflection coating, anti-corrosion coatings, anti-microbial coatings and so on [1–4]. Among these applications, anti-microbial zeolite coatings and films have been paid special attention since 2003 as the ability of antimicrobials broadens the application of zeolites [5]. Since then, a variety of zeolite films including MFI, AEL, LTA, FAU type zeolite, are thus prepared on alumina alloy, stainless steel, silica rubber for anti-microbial purposes [5–9]. They have been shown to inactivate virus and bacteria with high efficiency. When these films are highly hydrophilic, their antimicrobial property is expected to be improved as cells can adhere to the films easily and strongly, because the hydrophilicity may have allowed microbes to adhere to the film instead of being transferred to the buffer solution [9]. Furthermore, combination of both hydrophilicity and antimicrobiality of zeolite films enables them to be promising for use in space applications [3].

Hydrophilicity of zeolite films depends on the nature of the zeolite type and the surface structure of the zeolite film. Naturally, zeolite NaA is hydrophilic and zeolite silicalite-1 is hydrophobic. Thus, zeolite NaA is usually used to prepare zeolite films with hydrophilicity. Moreover, zeolite NaA has good ion-exchange capacity. After ion-exchange with Ag^+, the silver-exchanged zeolite A show good antimicrobial activity as it can kill a large number of cells over a short amount of time [10]. Therefore, zeolite NaA films are good candidate of antimicrobial coatings. On the other hand, the surface structure of the zeolite film is based on the preparation method. However, the preparation methods are limited to mainly in-situ crystallization, secondary growth method and vapor phase transport method. And zeolite crystals with particle sizes in the range of 0.5–7 μm are produced [11–17]. Zeolite films composed of nano-sized crystals have advantages not only in their unique optical

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and sensitive properties due to the unique pore structure and the short pathway from film surface to substrate, but also in determining the surface structure by roughness, which is quite important in determining their hydrophilicity. Up to now, the types of nano-sized zeolite films are limited in high silica zeolite silicalite-1, silicalite-2, ZSM-5, TS-1 and β [18–23]. Secondary growth method is the main technique to prepare them because the seeding procedure can reduce the crystallization time and better control of the growth. Although zeolite A films show good hydrophilicity as well as ion-exchange capacity, to the best of our knowledge, there is no report on preparation of nano-sized zeolite NaA films. This can be ascribed to the difficulty in the synthesis of nano-sized NaA particles.

Nano-sized NaA particles are mainly prepared by adding organic templates [24–26], mostly tetraethyl ammonium hydroxide (TMAOH) in the hydrogels for the synthesis [24]. But removal of these organic templates by calcination often leads to irreversible aggregation of the nanocrystals or slightly change of the Si/Al ratio and pore size [27]. Furthermore, a confined space method has been developed for synthesis of zeolite A nanocrystals by conducting the synthesis in the pores of porous carbon [28], in microemulsion [29], and in thermoreversible polymer hydrogels [30] or in microdroplets [31,32] without adding organic templates. The resultant zeolite NaA nanoparticles can be adjustable in the particle sizes from 50 to 300 nm. However, this method cannot be used to prepare nano-sized zeolite NaA films. Recently, Sharma et al. [33] and Ghasemi et al. [34] report that optimization of the synthesis conditions and physical synthesis parameters are effective to prepare nano-sized NaA zeolite by promoting the nucleation rate in the hydrogels, thus resulting in a smaller particle size. Zeolite A with particle sizes in the range of 70–150 nm and 50–120 nm are produced by using high concentration synthesis solution (The SiO_2/H_2O molar ratio is 1/19) [33] and through high alkalinity (The Na_2O/H_2O molar ratio is 3/50) [34], respectively. However, there still contain a large amount of zeolite particles larger than 100 nm in the products and most of the particles are aggregated. In addition, the feasibility of this method in the preparation of nano-sized zeolite NaA film is not known.

Based on the strong demand for the zeolite NaA films with strong hydrophilicity and simple methods to prepare nano-sized zeolite NaA crystals, we develop a layer-by-layer in-situ sol–gel method combined with the steam-assisted conversion technique to prepare nano-sized zeolite NaA/glass films in this paper. The aim is to prepare highly hydrophilic zeolite NaA films for antimicrobial purpose as well as nano-sized zeolite NaA crystals with all the particles smaller than 100 nm by a simple route. The method is conducted by alternatively dipping a glass slide in a silica solution and an alumina solution, thus loading high concentration precursors on the glass support, followed by steam-assisted crystallization to transform the precursors to nano-sized NaA crystals. Glass slides are used as nano-sized zeolite NaA crystals cannot be formed on other substrates (Supporting Information Fig. S2). We find that the NaA/glass film shows both superhydrophilic and oleophilic properties. We examine the antimicrobial property of the NaA/glass film after ion-exchanged with Ag^+, demonstrating high antimicrobial efficacy. We can further obtain dispersed zeolite nanoparticles by scraping the zeolite film and treat them with a weak acid solution. All the zeolite NaA particles are less than 100 nm in sizes with good dispersity. No organic templates are used in the synthesis. This approach is very efficient and economical, which provides a new and an effective way to synthesize both nano-sized NaA films and dispersed particles. To the best of our knowledge, there is no report on zeolite films with superhydrophilicity, which, combined with high antimicrobial efficacy, may have potential applications in the fields of antimicrobial.

2. Experimental

2.1. Materials

Sodium silicate ($Na_2SiO_3 \cdot 9H_2O$), sodium aluminum ($NaAlO_2$), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) were used as received from Sinopharm Chemical Reagent Co. Ltd. Acetic acid (HOAc) and silver nitrate ($AgNO_3$) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd and Shanghai Shenbo Chemical Co. Ltd, respectively. Before the preparation, glass slides (25.4 mm × 38.1 mm × 1 mm) were pretreated by first washing with detergent to remove organic residues on their surface, followed by immersing in a piranha solution (70% volume of concentrated sulfuric acid (H_2SO_4, Shanghai Lingfeng Chemical Reagent Co. Ltd.) and 30% volume of H_2O_2) with ultrasonic treatment for 30 min. Afterward, they were washed with deionized water for several times and dried at 50 °C.

2.2. Preparation of nano-sized NaA/glass film and NaA particles

The nano-sized NaA/glass film was prepared by a layer-by-layer in-situ sol–gel process. First, a silica solution and an alumina solution were, respectively, prepared by mixing 5.888 g of $Na_2SiO_3 \cdot 9H_2O$, 1.3 g of NaOH in 40 mL water and mixing 2.676 g of $NaAlO_2$, 1.3 g of NaOH in 40 mL of H_2O. Then, the glass slide was dipped in the silica solution for 5 min. It was slowly pulled out and dried in a desiccator for 3 min. Afterward, it was quickly dipped in the alumina solution and pulled out immediately, followed by drying in a desiccator for 3 min. The alternative dipping in the silica and alumina solutions was repeated for 2 cycles before the coated glass slide was installed vertically in an autoclave prefilled with 10 g of water. Finally, the autoclave was put in a 90 °C oven for 36 h. The glass slide was taken out, washed with water and dried to obtain the nano-sized NaA/glass film. The nano-sized NaA particles were obtained by scraping the nano-sized NaA/glass film with a utility knife with moderate strength, followed by dispersing into a 0.6% HOAc solution with ultrasound treatment for 2.5 h.

For comparison, preparation of zeolite NaA/glass film was also attempted by in-situ hydrothermal synthesis using the synthesis solution by mixing the above silica solution and the alumina solution. The molar composition is 6.33 NaOH:2 $NaAlO_2$:1.926 SiO_2:256 H_2O. The piranha-pretreated glass was vertically placed in the solution and the synthesis was conducted at 90 °C for 36 h. On the other hand, preparation of zeolite NaA/glass film was further attempted by dipping the piranha-pretreated glass slide in the synthesis solution for 5 min, followed by slowly pulling out, drying in a desiccator for 3 min, and treating with the steam-assisted conversion method at 90 °C for 36 h.

2.3. Ion exchange with silver ions and antimicrobial testing

The silver ion-exchange was performed by inserting the NaA/glass film in a 0.01 M solution of $AgNO_3$ in a polypropylene bottle at room temperature for 2 h with gently agitation. Then the film was taken out of the solution, washed with deionized water for several times, and soaked in deionized water for 1 h before it was used for antimicrobial testing.

The antimicrobial testing of the film was performed as follows. Individual colonies of *Escherichia coli* grown on Luria–Bertani (LB) plates were transferred with steriled toothpicks to sterile test tubes containing LB broth and incubated at 37 °C overnight with shaking. The Ag^+-exchanged NaA/glass film was exposed to ultraviolet light for 20 min to ensure sterility prior to biocidal testing. Then it was placed into the conical flask and 0.5 mL of the *E. coli* suspension containing greater than 1×10^6 colony-forming units (CFU) was