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Dendrimer-based preparation of mesoporous alumina nanofibers by electrospinning and their application in dye adsorption

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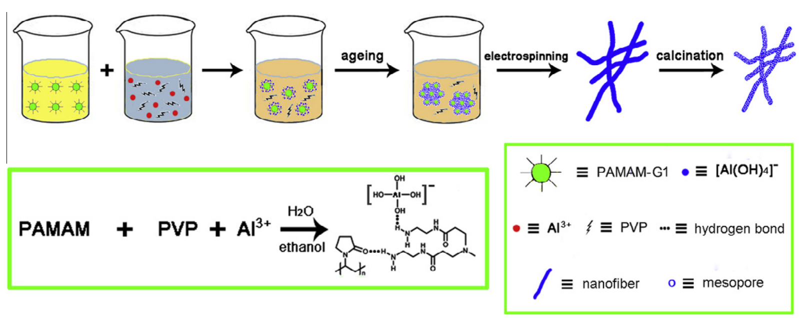
HIGHLIGHTS

- Mesoporous alumina nanofibers are obtained by electrospinning and calcination.
- Dendrimer polyamidoamine plays a crucial role in the formation of mesopores.
- Hydrogen bonds drive the self-assembly of alumina–dendrimer–polymer composites.
- The mesoporous alumina nanofibers have a high surface area and a large pore volume.
- The product is efficient in adsorbing Methyl Orange dye from aqueous solutions.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous alumina nanofibers were obtained by a combined method including three steps, as the sol–gel process, electrospinning and calcination. Dendrimer polyamidoamine was employed as the structure directing agent to form the mesoporous structures. The electrospinning process was applied to providing the alumina with a fibrous morphology and a flexible property, which were fixed during calcination. Products with different crystal structures and physicochemical properties were obtained at different calcination temperatures. The typical mesoporous alumina nanofibers showed a surface area of 417.7 m^2/g according to the Brunauer–Emmett–Teller method and a total pore volume of 0.40 cm^3/g on the basis of the Barrett–Joyner–Halenda model when the calcination temperature was set as 450 °C. The possible formation mechanism of the mesoporous structures was analyzed. The typical product was applied to the adsorption of Methyl Orange from aqueous solutions. The influence of system pH on adsorption, the adsorption isotherm feature, the kinetics and the reuse performance were investigated.

1. Introduction

Along with the development of nanoscience, the position of commercial activated alumina may be gradually replaced by the corresponding substitute, the mesoporous alumina molecular sieves, which are one of the most widely studied non-silica mesoporous materials [1–4]. Due to favorable physicochemical properties (such as high surface area, large pore volume and uniform pore size) and good availability, mesoporous aluminas have been regarded as a promising material for industrial catalysis (as catalysts or catalyst carriers) and environmental purification (as adsorbents). Currently, main challenges in the field of mesoporous alumina preparation and application include two aspects:

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One is to explore more efficient structure directing agents to obtain mesoporous alumina products with better physicochemical properties (such as higher surface area and larger pore volume), which is crucial to their practical performance on guest molecule adsorption. According to the general preparation laws of mesoporous materials, it usually needs a structure directing agent, or a "template" (such as surfactants), to form the porous structures of alumina. The dendrimer polyamidoamine has been employed as a series of structure directing agents in the biomimetic synthesis of mesoporous materials [5–8]. The one-generation polyamidoamine (PAMAM-G1) is simple in structure in this dendrimer family; however, its application has not been fully developed [9,10]. One PAMAM-G1 molecule contains eight amino groups and twelve imino groups, which make it a potential candidate for the template in the self-assembly of mesoporous alumina materials driven by hydrogen bonds.

The other is to precisely control the external morphology of mesoporous alumina products in order to make them adapt to the standard of practical applications. Up to now various mesoporous alumina materials have been obtained with great differences on external morphology. Typical mesoporous alumina materials include nanoparticles [11,12], nanorods [13,14] and nanofibers [15,16]. However, amazing morphologies do not always lead to great practicality, as green chemical processes aim to save any unnecessary costs. Concerning the adsorption/catalysis field, people usually focus on improving the recoverability of adsorbents/catalysts. Thus, the powder state of conventional nanoparticles has been regarded as a crucial defect, inhibiting their wider application. One solution is to prepare these materials *via* electrospinning, which is a versatile process for preparing nanofibrous membranes [17], providing people with a novel choice to obtain membrane-like products. Compared with conventional powder-like nanomaterials, the nanofibrous membranes behave better in regeneration/recycling processes because they are easier to be removed from liquid phases, saving the recycling costs, which is beneficial to practical engineering processes. The preparation of inorganic mesoporous nanofibers such as SiO_2 [18,19], TiO_2 [18,20] and $ZnO–SnO_2$ [18,21] has been reported *via* this process using hydrophilic polymers as assistants for improving system viscosity. The products show fibrous morphology at the microscale and membrane shape at the macroscale, which is desirable in industrial processes. Mesoporous alumina nanofibers have also been obtained *via* electrospinning using an amphiphilic triblock copolymer as the template [16]. Yet the biomimetic synthesis of mesoporous alumina nanofibers *via* electrospinning using dendrimer PAMAM as the template has not been reported. Meanwhile, aluminum alkoxide (such as aluminum isopropoxide) was usually employed as the precursor of alumina in previous researches [16,22], which leads to a higher complexity of preparation and a higher cost.

Mesoporous alumina materials have been used in environmental purification as adsorbents, especially for removing inorganic arsenic [11,23] and dyes [12,24]. Printing and dyeing wastewater consists of complex components, which are usually of high chroma and high toxicity. Since dye contaminants are widespread around the world and lead to high environmental risk, new treatment methods of higher efficiency, better environmental friendly characteristic and lower cost are worth studying. Adsorption is superior to other processes like chemical oxidation and coagulation because no secondary contaminant is introduced to the system. Also, other than the processes based on chemical reactions, adsorption can be applied to dye removal without regarding the specific chemical properties of dyes. Among the commercial dyes, Methyl Orange (MO) is common, which is widely used as an indicator and a stain for cells in laboratory, as well as a dye for textiles in industry. MO is also generally used as a model in environmental research [25,26] because it is a typical azo dye of simple molecular structure and high chemical stability.

In this work, the synthesis of mesoporous alumina nanofibers *via* the combination of sol–gel, electrospinning and calcination is reported. The core of this synthesis is electrospinning, which is employed to obtain membrane-like products made up of nanofibers. Concerning the application prospect, the nanofibrous membranes are superior to conventional ultrafine powders due to their highly recyclable property. Common aluminum nitrate was used as the precursor instead of aluminum alkoxide. Dendrimer PAMAM-G1 was used as the structure directing agent to form mesoporous structures on alumina nanofibers for the first time. The typical product was applied to removing MO dye from aqueous solutions *via* adsorption. The dendrimer-based electrospun mesoporous alumina nanofibers can be a favorable candidate for dye adsorbents in environmental purification field. Also, it may be introduced into other fields such as arsenic removal and industrial catalysis, exhibiting a versatile characteristic and a great potential to be applied to various chemical engineering and environmental engineering processes.

2. Experimental section

2.1. Chemicals

Polyvinylpyrrolidone (PVP, M_w ~1,300,000) and PAMAM-G1 (20% solution in methanol) were supplied by Sigma–Aldrich. Aluminum nitrate nonahydrate (99.0%), ethanol (99.7%), Methyl Orange, hydrochloric acid (37.0%) and sodium hydroxide (96.0%) were provided by Sinopharm Chemical Reagent Co., China. Before use, PAMAM-G1 was treated by removing methanol solvent using vacuum distillation. Other reagents were used without further purification. Deionized water was used throughout this work.

2.2. Preparation of alumina precursor sol

Magnetic stirring was applied throughout this part. In a typical process in this work, 0.034 g of PAMAM-G1 was dropped into 12 mL of ethanol to obtain a dendrimer solution. Meanwhile, 1.6 g of PVP was added to a mixed solvent containing 10 mL of ethanol and 4 mL of water. After the polymer has dissolved completely, a total content of 0.54 g of $Al(NO_3)_3{\cdot}9H_2O$ was added to the solution. When the aluminum salt has mixed evenly with the polymer solution, the mixture was dropped slowly into the dendrimer solution prepared above. The reaction system was stirred for another 30 min. Then, the alumina precursor sol was obtained. The whole preparation process was performed at room temperature.

2.3. Preparation of PVP/alumina nanofibers

The composite sol was moved to a plastic syringe equipped with a metallic nozzle. During electrospinning, a high voltage (18 kV) was applied to the nozzle. The sol was continuously pushed out the syringe at a constant rate of 0.8 mL/h. The deformed drops converted to ultrathin fibers when they touched the high voltage. The fibers were collected on the counter electrode covered with an aluminum foil. After dried under vacuum at 60 °C for 24 h, the PVP/alumina nanofibers were obtained.

2.4. Preparation of mesoporous alumina nanofibers

The as-prepared PVP/alumina nanofibers were calcined in air through the following procedures. First, the temperature was raised from 20 °C to 450 °C (or 550 °C, 700 °C, 800 °C) at a ramping