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Zeolitic imidazole Framework-8 (ZIF-8) fibers by gas-phase conversion of electroblown zinc oxide and aluminum doped zinc oxide fibers

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ABSTRACT

Electroblowing was used to prepare ZnO and aluminum doped zinc oxide (AZO, 1–3 cation-% of Al) fibers. The as-blown fibers were calcined at 500 °C to obtain the target material. The average fiber diameters ranged from 240 ± 60 nm for ZnO fibers to 330 ± 80 nm for AZO with 3% Al. Smaller crystallite size was measured with x-ray diffraction for the Al doped fibers. Electroblowing was found out be an effective method to increase the fiber productivity over electrospinning and other methods reported in literature to prepare AZO fibers as a high production rate of 0.32 g/h was achieved. The ZnO and AZO fibers could be converted to zeolitic imidazole framework-8 [ZIF-8, zinc(2-methylimidazolate)$_2$] by a solvent free thermal treatment in an autoclave under 2-methylimidazole (HmIM) vapor at 150 and 200 °C while preserving the fibrous structure. The conversion process to ZIF-8 occurred faster at higher temperatures and on fibers with smaller crystallite size. Depending on the conversion treatment time either ZnO/ZIF-8 and AZO/ZIF-8 core/shell fibers or ZIF-8 fibers could be obtained. At best the prepared ZIF-8 fibers had a very high BET specific surface area of 1340 m^2/g.

1. Introduction

Metal organic frameworks (MOFs) are hybrid materials consisting of metal ions or clusters connected by organic linker molecules. Owing to their inherent nanoporous network structure, MOFs have applications in areas such as gas sensing, gas storage and catalysis [1,2]. Recently they have been studied also for a wide variety of electronic and optoelectronic applications in the form of patterned structures, which has sparked demand for new conformal synthesis methods down to the nanoscale [3,4]. Nanofibers as interconnected fibrous networks have great interest for such applications where a large and readily accessible surface area is required. For example, porous nanofibers with large surface to volume ratio combined with high specific surface area are promising as energy storage materials for lithium ion batteries and supercapacitors [5].

Zeolite imidazole framework-8 (ZIF-8, zinc(2-methylimidazolate)$_2$) is a MOF material that comprises of tetrahedrally coordinated zinc ions connected by 2-methylimidazolate linkers in a zeolite-like topology [6]. Most commonly ZIF-8 is prepared via solvothermal synthesis methods, but preparing patterned structures through these routes is difficult [4,7]. Recently a new method for ZIF-8 synthesis has emerged that relies on the conversion of ZnO to ZIF-8 via a reaction between solid ZnO and 2-methylimidazole (HmIM) vapor [8,9]. This gas phase conversion enables the preparation of conformal ZIF-8 coatings with a uniform thickness, controlled at a much more accurate level compared to the more commonly used solvothermal preparation methods. Thus far this gas phase conversion of ZnO to ZIF-8 has been restricted to thin films.

To the authors' knowledge there are no reports on preparation of ZIF-8 fibers, nor any other MOF material in the bare fiber form, but ZIF-8 has been incorporated as particles within fiber matrices and as a coating on fibers. Electrospinning is the most well-known and most used method to prepare long continuous polymer nanofibers and, via calcination of polymer fibers containing additional precursors, also ceramic fibers [10–12]. Composites consisting of polymer fibers loaded with ZIF-8 particles have also been prepared by electrospinning [13–15]. An atomic layer deposited ZnO thin film on electrospun polyacrylonitrile fibers has been solvothermally converted to a ZIF-8 coating [16]. Tellurium nanowires [17] and polymer fibers [18,19] have been directly coated with ZIF-8 by crystallization of ZIF-8 from a solution onto the fiber surfaces. Similarly TiO_2 nanofibers have been coated with ZIF-8 by sonochemical crystallization from a ZIF-8 precursor solution [20], and recently also ZnO nanowires and electrospun ZnO fibers have been solvothermally coated with ZIF-8 for gas sensing applications [21,22].

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ZnO in itself is an interesting semiconductor material with optical and electrical properties that can be tuned for various applications by doping with different elements. For example Al or Ga doped ZnO provides a cheaper and less toxic alternative to the commonly used indium tin oxide (ITO) transparent thin film electrodes for solar cells [23–26]. ZnO and doped ZnO fibers are especially interesting for gas sensing and optoelectronic applications due to their high surface to volume ratio. There are several reports in the literature on electrospinning of ZnO, doped ZnO and various metal oxide/zinc oxide composites [27–45]. Al doping has been used to improve the conductivity of ZnO [41–45]. Fibers of bare ZnO [29,30], ZnO doped with cobalt [31], copper [32], cerium [33] and cadminum [34], and ZnO/SnO2 [35,36] and ZnO/In_2O_3 [37] composites have been used as gas sensors. ZnO/SnO_2 [38,39] and ZnO/NiO [40] have been studied as high capacity anodes for lithium ion batteries.

Although the excellent controllability of fiber properties and the wide range of attainable materials have made electrospinning the most popular nanofiber preparation method, its industrial applicability is limited due to its modest production rate [46]. Conventionally fibers have been spun from a single needle in which case typical solution flow rates are in the range of 0.1–2 ml/h and fiber productivity around 0.1 g/h and even less in the case of ceramic fibers. Upscaling via multiplication of needles is complicated because the electric fields at the needle tips are altered by the nearby needles significantly affecting the spinning process [47]. Needleless designs relying on self-formation of Taylor cones on polymer solution surfaces have shown improved upscalability, but typically have somewhat less control on the fiber properties [48–52].

Solution blow spinning has recently emerged as a new straightforward method for improving fiber productivity [53–55]. It relies on a high velocity gas flow to draw a polymer solution into fibers. The method has gained significant interest especially in the preparation of nanofibers for biomedical applications. As compared to the needle electrospinning substantially higher solution feed rates can be used and thus productivity is significantly increased. Electroblowing is a combined method of both the conventional needle electrospinning and solution blow spinning, i.e. both high voltage and high velocity gas flow are used to form fibers from a solution [56–58]. The main jet drawing force is the high velocity gas flow and thus high production rates comparable to solution blow spinning can be obtained. Similarly to electrospinning the repulsion between the charges in the polymer jets in electroblowing results in a randomly oriented fiber network with less bundling of fibers as compared to the solution blow spinning [59,60].

Significantly less materials have been prepared by solution blow spinning and electroblowing as compared to electrospinning. Especially reports on preparation of inorganic fibers are scarce. Solution blow spinning has been used to prepare ZnO [61] and via pyrolysis of solution blown zinc acetate/polyacrylonitrile also ZnO encapsulated carbon [62] nanofibers. Alumina fibers have also been solution blow spun and electroblown, though only with relatively large average fiber diameters of 4.12 and 2.75 μm, respectively [58].

In this study we used electroblowing to prepare ZnO and conductive aluminum doped zinc oxide (AZO) nanofibers. To the authors' knowledge there are no prior reports on electroblowing of these materials in the literature. Further on we used the prepared fibers as templates for the preparation of ZIF-8 fibers. The ZnO and AZO fibers were converted to ZIF-8 by thermal treatment under HmIM vapor in an autoclave at 150 and 200 °C. Depending of the conversion parameters core/shell or bare ZIF-8 fibers were obtained. This is to the best of our knowledge also the first report on the preparation of bare ZIF-8 or any other kind of metal-organic framework fibers.

2. Experimental

The electroblowing solutions were prepared by dissolving of Zn$(NO_3)_2{\cdot}4H_2O$ (Merck, 98.5%) and Al$(NO_3)_3{\cdot}9H_2O$ (J.T. Baker, 98.6%) in appropriate amounts of deionized water followed by addition of DMF (Sigma-Aldrich, 99.9%) and a beforehand prepared 18 wt % PVP (Aldrich, M_w = 1 300 000) in EtOH (VWR Chemicals, 96%) solution (Table 1). The aluminum content varied from 0 to 3 mol. % in respect to the Zn and Al in the solution [Al/(Al + Zn)]. Additionally some experiments were performed on electroblowing of ZnO with solutions where either H_2O or DMF was fully replaced with the other one in the solvent (Supporting information, Table S1).

Table 1
The electroblowing solutions.

Solution	Zn$(NO_3)_2{\cdot}4H_2O$ (g)	Al$(NO_3)_3{\cdot}9H_2O$ (g)	H_2O (ml)	DMF (ml)	18 wt % PVP/EtOH (ml)
ZnO	1.0	–	2	4.5	7.5
AZO-1	1.0	0.014	2	4.5	7.5
AZO-2	1.0	0.029	2	4.5	7.5
AZO-3	1.0	0.044	2	4.5	7.5

A self-made apparatus was used to blow the solutions into fibers. Compressed air was delivered through a custom made 3 mm metal nozzle at a rate of 30 Nl/min. A 27G needle was pushed through the nozzle and placed at the center of the gas flow protruding ~2 mm from the aperture. The needle was connected to a 10 ml syringe and the solution was pushed through the needle at rate of 15 ml/h with a syringe pump (KDS Legato™). The needle and nozzle were set to 15 kV with a high voltage power source. The solution jet ejected from the needle tip was collected as fibers on grounded metal grid collectors. A cylindrical collector with a diameter of 50 cm and a planar back collector 80 cm from the nozzle were used similarly to our previous study [63]. The collectors were enclosed in a box with an additional drying gas flow (40 Nl/min) for efficient solvent vapor removal from the box through the holes located behind the back collector. The relative humidity within the box during the experiments remained below 15%. The as-blown fibers were calcined to the target material in an ashing furnace at 500 °C in air for 4 h, unless otherwise noted in the text. Some ZnO samples were calcined at 400 and 600 °C for 4 h. When necessary for comparative purposes the calcination temperatures used to prepare the ZnO fibers are indicated as ZnO@400 °C, ZnO@500 °C and ZnO@600 °C. Regardless of the calcination temperature a heating rate of 1 °C/min was always used.

The ZnO and AZO fibers were converted to zeolitic imidazole framework-8 (ZIF-8) by thermal treatment in 2-methylimidazole (HmIM) vapor in an autoclave (Parr 4744). First 0.5 g of HmIM was placed at the bottom of the autoclave. Next approximately 0.05 g of fibers were placed inside a glass vial that was inserted in the autoclave. The autoclave was closed and placed in an oven at 150 °C or 200 °C for variable time periods. After the treatment the autoclave was let to cool and the fibers were removed and placed in an oven at 150 °C for at least 2 h to remove any residual HmIM from the samples.

The prepared fibers were imaged with scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) in a Hitachi S-4800 field emission SEM. Prior to SEM characterization 4 nm of Au/Pd was sputtered onto the fibers to enhance image quality. Image J software was used to determine the average fiber diameters from measurements of 100 individual fibers in each sample. The crystal structures were analyzed with a PANalytical X'Pert Pro MPD X-ray diffractometer using CuKα-radiation. The crystallinity and phase compositions were analyzed with a PANalytical X'Pert Pro MPD X-ray diffractometer using CuKα-radiation and parallel beam optics. The apparent crystallite sizes and the ZIF-8 to ZnO phase ratios were determined from the XRD data by Rietveld refinement using the MAUD software [64,65]. Thermogravimetric analyses (TGA) were conducted with a Mettler Toledo Star^e system equipped with a TGA 850 thermobalance using a heating rate of 10 °C/min between 25 and 800 °C in air and N_2. The BET specific surface areas and pore size distributions were