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Mesoporous Material Nanofibers by Electrospinning

Sh. Sohrabnezhad, A. Jafarzadeh

***Abstract*—**In this paper, MCM-41 mesoporous material nanofibers were synthesized by an electrospinning technique. The nanofibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), and nitrogen adsorption–desorption measurement. Tetraethyl orthosilicate (TEOS) and polyvinyl alcohol (PVA) were used as a silica source and fiber forming source, respectively. TEM and SEM images showed synthesis of MCM-41 nanofibers with a diameter of 200 nm. The pore diameter and surface area of calcined MCM-41 nanofibers was 2.2 nm and 970 m^2/g, respectively. The morphology of the MCM-41 nanofibers depended on spinning voltages.

***Keywords*—**Electrospinning, electron microscopy, fiber technology, porous materials, X-ray techniques.

I. Introduction

THE mesoporous molecular sieves of the M41S family were designated MCMs, an acronym for Mobil's Composition of Matter, were respectively MCM-41 (hexagonal), MCM-48 (cubic) as well as MCM-50 (lamellar). The hexagonal structure, MCM-41, is the most studied member of the family of mesoporous materials. MCM-41 combines a myriad of attractive properties including highly ordered pore systems with tunable pore diameters (in the range 2-10 nm), large pore volumes, high hydrocarbon sorption capacities, high BET surface areas and thermal stability, as well as a high density of surface silanols. Mesoporous silica materials are synthesized from the surfactant micellar template addition of an inorganic silica source [1]. By changing the inorganic precursors and synthesis conditions, mesoporous thin films [2], spheres [3], tubes [4], fibers [5], and monoliths [6] have been prepared. Catalysis, separations, sensors, optical waveguides, lasers and drug delivery are just a few areas that could benefit from a fibrous configuration. There are several papers about the synthesis of mesoporous fibers by different methods such as sol-gel process [7], spray-drying method 38], laser deposition [9], solvent evaporation techniques [10], and emulsion methods [7]. But, these methods had complex process and sometimes the length of fibers is limited by the fibrous template. Therefore, a practicable and simple method is needed to prepare ultrafine and long molecular sieve fibers. Eelectrospinning is the simplest and flexible way to fabricate continuous fibers in micro and nanoscale. In electrospinning process, a viscous solution is pumped to a high electric field [11]. Usually, high viscosity and voltage are used for fabricating [12]. Several works focus on fabricating mesoporous fibers such as SBA-15 [13], silicalite-1 [14], DAM-1 (Dallas Amorphous Materials -1) [15] and SiO_2 fibers (hexagonal and cubic) [16]. The number of papers about the synthesis of MCM-41 fibers by electrospinning method is low. The original work on the preparation of MCM-41 fiber and MCM-41 ribbons by electrospinning was reported by [14] and [17]. But, the spinning conditions were not optimized, and MCM-41 fibers were not uniform. In this work, we report for the first time synthesis of MCM-41 mesoporous material nanofibers from the solution containing of polyvinyl alcohol (PVA) as the polymeric gelator, cetyltrimethylammonium bromide (CTAB) as the template source and tetraethyl orthosilicate (TEOS) as the silica source, by electrospinning technique. In this study, the employed polymer was polyvinyl alcohol (PVA, $M_W \sim 72000$) that had a molecular weight less than other polymers.

Sh. Sohrabnezhad is with Department of Chemistry, Faculty of Science, University of Guilan, P.O.Box 1914 Rasht Iran (corresponding author, phone: +981333367262; fax: +981333367262; e-mail: sohrabnezhad@ guilan.ac.ir).

A. Jafarzadeh, Department of Chemistry, Faculty of Science, University of Guilan, P.O.Box 1914 Rasht (e-mail: ajafarzadeh@gmail.com).

II. Procedure

All chemicals (tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), hydrochloric acid, polyvinyl alcohol (PVA, $M_W \sim 72000$), absolute ethanol, and sodium hydroxide) were analytical grade. Deionized water was used throughout this work. Cetyltrimethylammonium bromide (CTAB, 0.43 g) was added into 1.93 g absolute ethanol under stirring. After stirring for 20 min, 2.08 g TEOS and then 0.41 ml HCl 0.12 M was slowly added to the resulting mixture. The molar ratio of the composition was TEOS: 0.12 CTAB: 0.005 HCl: 4.2 EtOH: 7H2O: 0.1PVA (repeat unit). The reaction mixture was transferred in a glass vial. The closed vial was placed in an oven at 80 °C for 2 h, and thereafter left open at 25 °C for two days (low temperature promotes condensation between silica oligomers and increases calcination stability of the mesostructured phase). After two days a 4 wt.% aqueous solution of polyvinyl alcohol (PVA, $M_W \sim 72000$) was added to the mixture under vigorous stirring until a clear, homogeneous, viscous, and spinnable solution was obtained and used as the feeding solution for electrospinning.

The electrospinning was set up horizontally. The spinnable feeding sol was poured into the plastic syringe equipped with a gauge needle made of stainless steel, which was connected to a high-voltage DC supplier. During the electrospinning process, the feeding sol was pressurized by the tracing injection device. The driven voltage applied was in range 8-25 kV, and the distance between the needle and the flat aluminum foil collector was 10-14 cm and finally, the electrospinning process was conducted under ambient temperature, and then nanofibers were air-dried at 110 °C for 10 h. After that the sample was calcined at 600 °C at a rate of 3 °C min^{-1} for 3 h. The electrospun sample was white color after calcinations.

With temperature and calcinations, the nanofibers become brittle.

Powder X-ray diffraction patterns of the samples were recorded using an X-ray diffractometer (Bruker D8 Advance) with Co Kα radiation (λ = 1.789 A˚). UV–Vis absorption spectra were recorded using a Shimadzu 1600 PC in the spectral range of 190-900 nm. The infrared spectra were measured on a Bruek spectrophotometer using KBr pellets. The transmission electron micrographs (TEM) were recorded with a Philips CM10 microscope, working at a 100 kV accelerating voltage.

III. Results and Discussion

The powder X-ray diffraction patterns of the electrospun sample from TEOS are shown in Fig. 1. The electrospun sample before calcination showed reflections at 2θ = 2.26° (100), 3.92° (110), 4.53° (200), and 5.95° (210) that corresponds to a hexagonal structure of MCM-41 mesoporous material. Although only the three reflections were observed for the calcined sample at 2θ = 2.45°, 4.28° and 4.95° [8]. The increase in peak intensity after calcination is due to the greater scattering density contrast and reduced X-ray absorbance after surfactant and polymer removal. Furthermore, the d-value related to (100) reflection decreased from 39 to 36 A° on calcination, corresponding to a moderate contraction in the mesoporous structure.

Fig. 2 (A) shows the SEM images of the calcined electrospun MCM-41 nanofibers were synthesized by TEOS at different magnifications. The MCM-41 nanofibers indicated average uniform diameter of 200 nm. The TEM images displayed that the nanofibers obtained after calcination had both porous and rough surfaces. Dependence of morphology of the MCM-41nanofibers on spinning voltages are showed in Fig. 3. Increasing the voltage to 20 kV, diameter of nanofibers decreased. The broken and short MCM-41 nanofibers were observed in higher voltage (>20 kV).

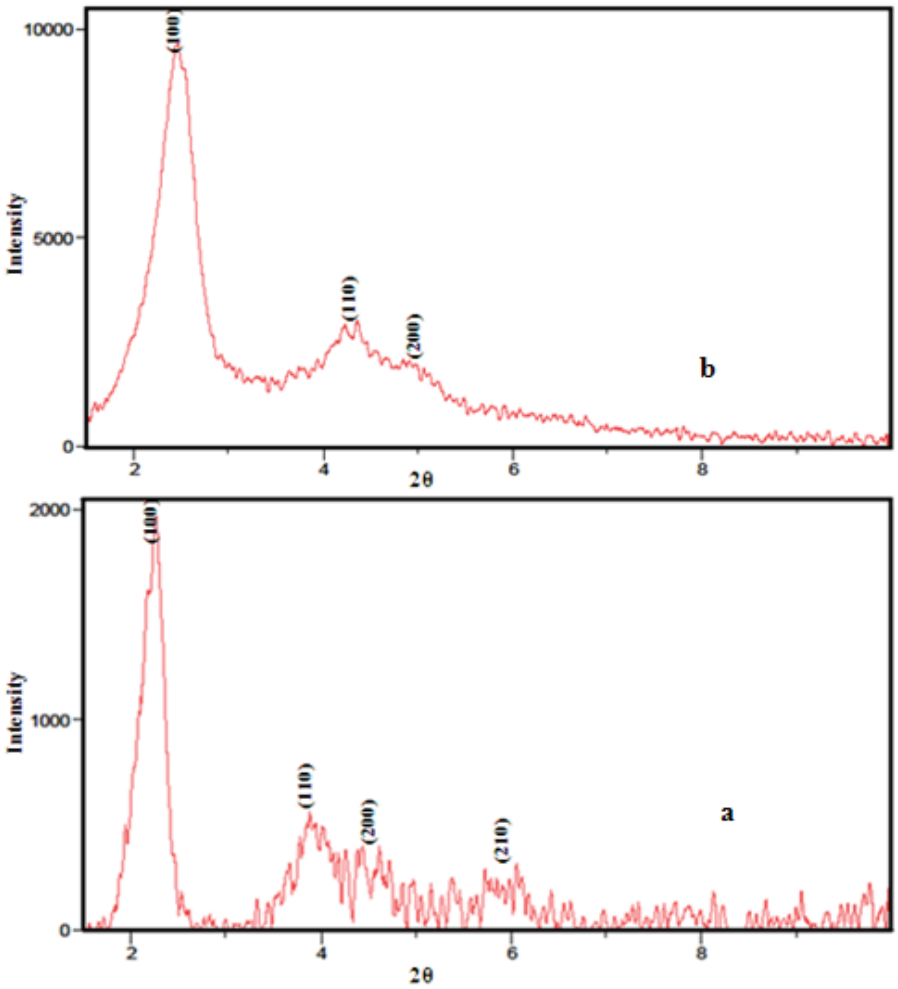

Fig. 1 XRD patterns of electrospun sample from TEOS (a) before (b) after calcinations. Spinning voltage 12 kV and distance 10 cm

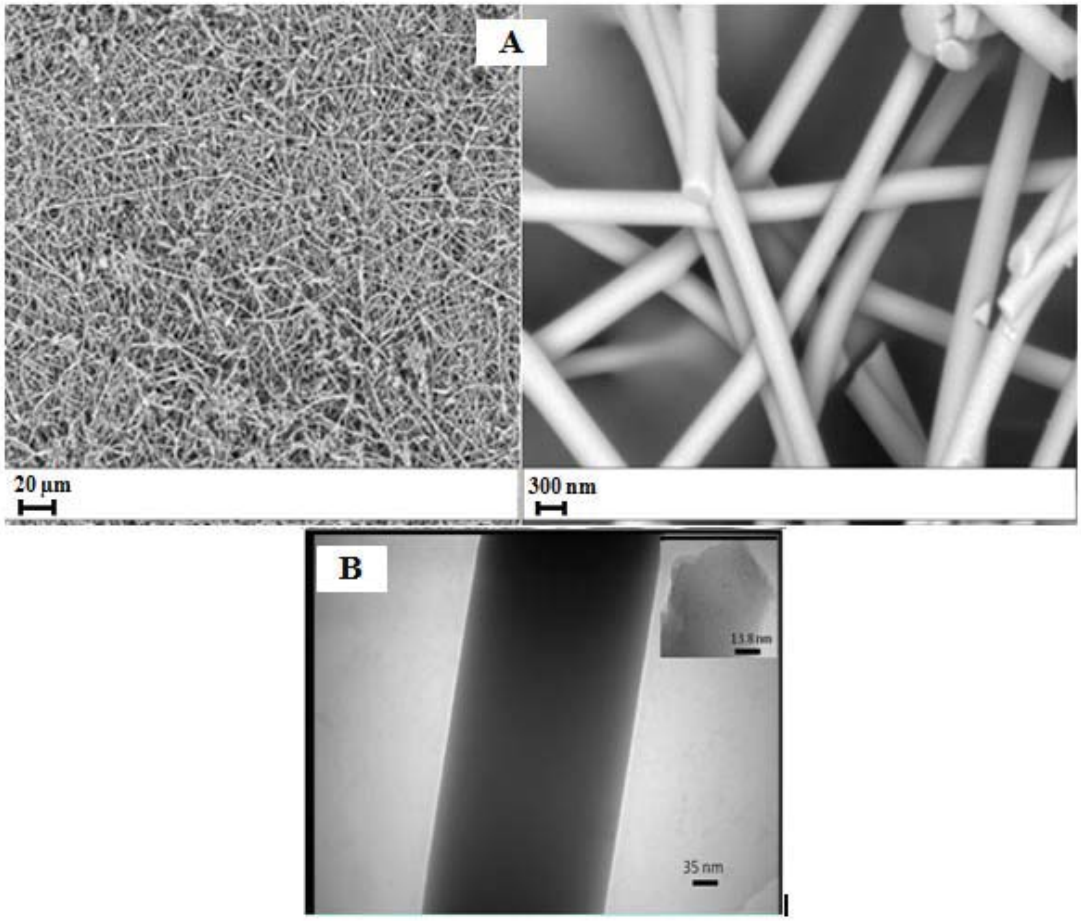

Fig. 2 (A) SEM and (B) TEM images of MCM-41 nanofibers from TEOS after calcination at different magnifications. Spinning at voltage of 12 kV and distance 10 cm

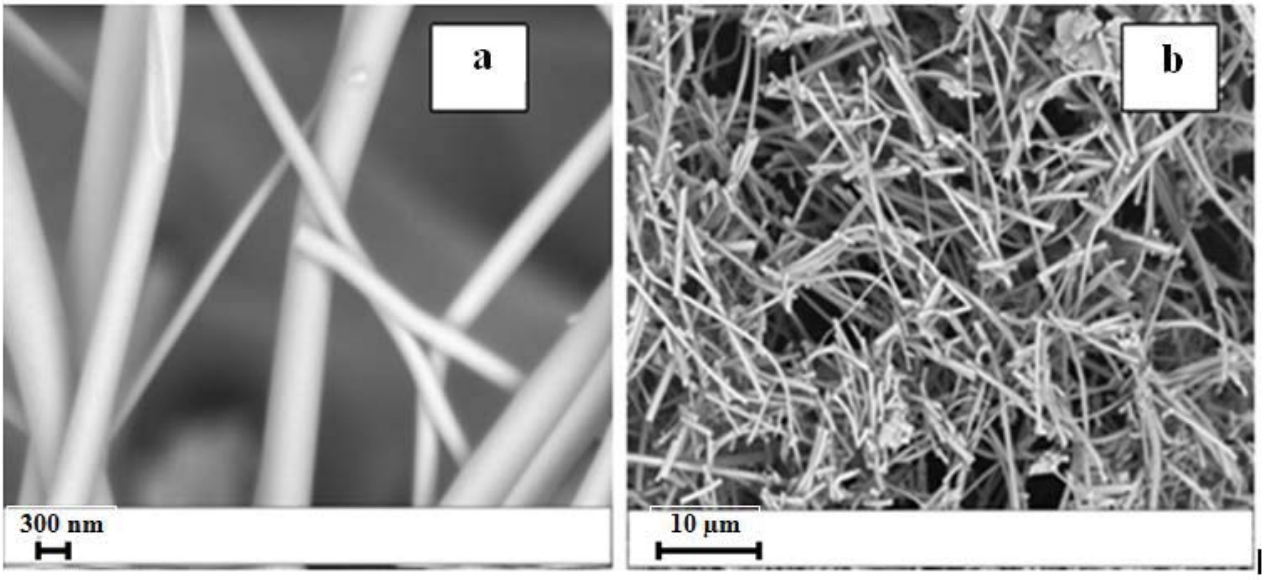

Fig. 3 SEM images of MCM-41 nanofibers from TEOS after calcination at spinning voltages of (a) 16 kV (b) 25 kV Spinning distance of 10 cm

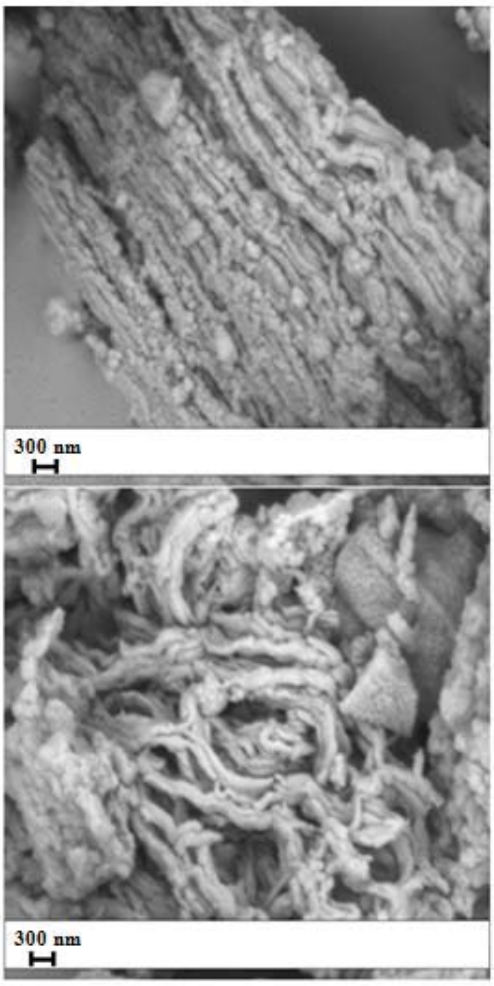

Fig. 4 SEM images of MCM-41ropes after calcination at spinning voltage of (a) 12 kV Spinning distance of 10 cm with different views

The results showed that MCM-41 ropes were produced when the molar ratio of the composition became TEOS: 0.24 CTAB: 0.005 NaOH: 4.2 EtOH: 2000H2O: 0.1PVA (Fig. 4).

It is seen by SEM that the MCM-41 ropes are almost at the nanometer scale. The length is uniform. Mou et al. synthesized MCm-41 ropes in 1999 at the millimeter scale, but the length was not uniform [18].

The nitrogen absorption/desorption isotherms for the calcined MCM-41 nanofibers are shown in Fig. 5 (A). These correspond to Type IV isotherms with a steep increase in the nitrogen uptake around P/P0 ~ 0.37, which is associated with capillary condensation in cylindrical pores and has been observed in MCM-41 molecular sieves hydrothermally synthesized with the aid of CTAB [19]. The Barrett–Joyner–Halenda (BJH) model was used to calculate the pore size distribution and pore volume (Fig. 5 (B)). The specific surface area was measured by using the Brunauer–Emmett–Teller (BET) method. By nitrogen adsorption/desorption analysis, the mesoporous nanofibers have a BET surface area of 970 m^2/g and a 2.2 nm pore diameter.

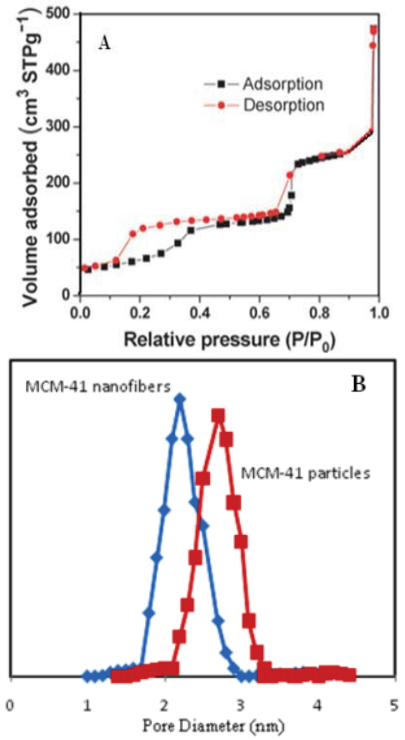

Fig. 5 (A) Nitrogen adsorption–desorption loops for the MCM-41 nanofibers and (B) BJH pore size distribution analysis for MCM-41 nanofibers

IV. Conclusions

In summary, for the first time fabrication of nanofibers of MCM-41 mesoporous material was reported by electrospinning technique. The MCM-41 nanofibers were observed, when TEOS was used as silica source. For the spinning voltages in the range 8–20 kV, MCM-41 nanofibers were obtained. The soft and length MCM-41 nanofibers were observed in voltages less than 20 kV. MCM-41 ropes were synthesized in bases media, and TEOS to CTAB ratio equals 4.

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