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FABRICATION OF POROUS SILICA FIBERS BY ELECTROSPINNING FOR SOUND ABSORBING MATERIALS

Macroporous silica fibers having spherical cavities were fabricated by electrospinning using the spinning solution prepared from the mixed dispersion of tetraethylorthosilicate (TEOS) and polystyrene nanospheres as precursor and sacrificial templates, respectively, by injection through metallic nozzle. By applying electric field, the electro-spun fibers obtained by evaporation-driven self-assembly were collected on flat substrate or rotating drum, followed by the removal of the templates by calcination. The sound absorption coefficient of the porous fibers was measured by impedance tube, and the measured value was larger than 0.9 at high frequency region of incident waves. The surface of the resulting fibers was modified using fluorine-containing silane coupling agent to produce superhydrophobic fibrous materials to prevent the infiltration of humidity.

Keywords: Electrospinning, Porous Silica Fiber, Thermal Insulator, Sound Absorption

1. Introduction

Fibrous materials with complex network structures and high porosity have attracted much attention for the applications of filters, adsorbents, catalytic supports, and biological scaffolds for tissue engineering [1-4]. Among various fabrication methods of fiber materials, electrospinning is widely adopted, since the process variables such as applied voltage, injection rate, the composition of spinning solution, and the gap distance between tip and collector can be adjusted to control the morphologies, size, and compositions of fibers [5].

Thus far, fibrous structures have been fabricated using various materials such as polymers, metals, ceramics, and composites by electrospinning. Since thermal resistance of porous fibers at high temperature is important in many applications including construction engineering, the ceramic fibers with a number of macropores can be considered as advantageous material rather than conventional polymeric fibers.

Since the noise generated from roads and buildings has been a serious problem due to deterioration of the quality of human life, it is essential to develop the techniques to absorb sound waves by efficient manner. Although porous materials have been applied to absorb sound waves effectively, researches on novel sound absorbing materials are still necessary since excellent sound absorbing property should be guaranteed with light weight and sufficient thermal resistance [6]. Among various ceramics with excellent thermal resistance, silica can be a promising candidate for sound absorbing material, since it can be prepared by sol-gel reaction with controllable reaction rate using relatively cheap precursors such as TEOS or water glass.

In the present article, the fabrication of macroporous silica fibers by electrospinning was studied to apply sound absorbing materials. For excellent sound absorption property, the synthesis of porous structure in fibrous material is key factor to prepare abundant air voids for the attenuation of incident sound energy. For this purpose, the self-assembly of polystyrene nanospheres and silica precursor in spinning solution was conducted during electrospinning to form organic-inorganic composite fibers, followed by the removal of the polymeric templates for porous silica fibers by thermal decomposition.

2. Experimental

2.1. Materials

Ethanol (99.9%) as reaction medium for dispersion polymerization was purchased from Daejung Chemicals. For the synthesis of polystyrene nanospheres, the monomer such as styrene (99%) was purchased from Daejung Chemicals. 2-(methacryloyloxy) ethyltrimethylammonium chloride (MTC) as cationic comonomer was bought from Aldrich Chemicals. The initiator, α, α'-azobis(isobutyronitrile) (AIBN, 99 %) and the stabilizer, polyvinylpyrrolidone (PVP k30, M.W. = 40,000 g/mol) were bought from Junsei Chemicals and Sigma-Aldrich, respectively.

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For the fabrication of porous silica fibers, tetraethyl orthosilicate (TEOS, 99.9%) as ceramic precursor was purchased from Sigma-Aldrich. Hydrochloric acid (0.1 N) for gelation of precursor was bought from Sigma-Aldrich. For electro-spinning, PVP360 (M.W. = 360,000 g/mol) was used to adjust the viscosity of the feed solution.

2.2. The synthesis of monodisperse polystyrene nanospheres

Polystyrene nanospheres were synthesized by dispersion polymerization, and used as templating materials for porous silica fibers. The particle stabilizer, PVP k30, was dissolved in ethanol and styrene was poured into the polymerization reactor containing the reaction medium under mild stirring. Comonomer (MTC) was added to the reactor, and nitrogen was purged for 1.5 hours to remove oxygen. Finally, the initiator (AIBN) was added to form particles at elevated temperature. After 20 hours, the polymerization was terminated and the particle suspension was filtered to remove aggregates. The detailed reaction conditions can be found elsewhere [7].

2.4. Fabrication of macroporous silica fibers by electrospinning for sound absorbing material

The spinning solution was prepared by mixing the polystyrene beads dispersed in ethanol and PVP 360. TEOS and aqueous HCl were added to the solution under vigorous stirring, which was injected through metallic nozzle with constant speed at 10 to 30 μl/min under the external electric field of 10 to 12 kV using power supply (NNC-HV60, Nano NC). The spinnerets were collected on flat-type or drum collector, and calcination was performed using box furnace (Hantech, M13P) at 500°C to convert the resulting organic-inorganic fibers to porous silica fibers. The sound absorption coefficient of the fibrous materials was measured by impedance tube (BSWA Tech, SW466) [8].

2.5. Fabrication of superhydrophobic surfaces

The fibrous materials composed of porous silica fibers were treated with fluorine-containing silane coupling agent, HDFTHDTS, (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) triethoxysilane, 97%, Aldrich). After the dipping the fibers into the methanol solution containing HDFTHDTS (2 vol. %) for 2 hours, the silica fibers were dried at room temperature to form superhydrophobic surfaces.

3. Results and discussion

Before electrospinning process, the spinning solution was prepared using silica precursor such as TEOS and aqueous HCl solution. The sacrificial templates such as PS nanospheres were also added to the spinning solution, followed by aging the sol-gel precursor during stirring. Then, electrospinning was performed to prepare the composite fibers of organic-inorganic materials by elongating the spinning solution from the metal nozzle under strong electric field. During spinning of the fibers, the solvent contained in the spinneret was evaporated rapidly, and

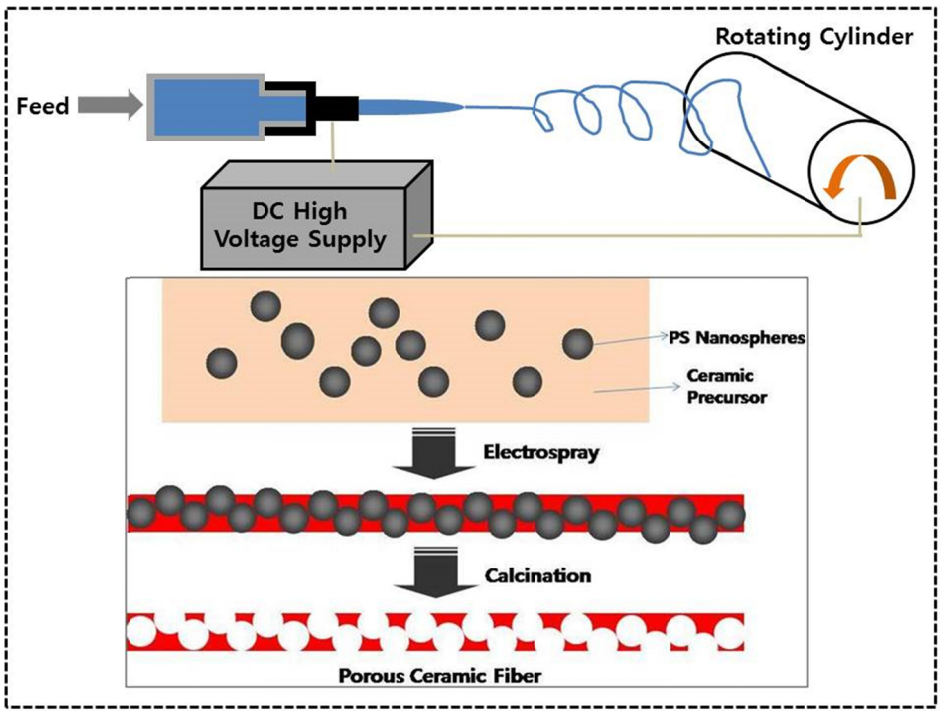

Fig. 1. Schematic figure of electrospinning process for the fabrication of macroporous silica fibers for sound absorbing materials by rotating drum as fiber collector

the precursors were self-assembled to form fibrous materials. Then, the polymeric templates were removed from the composite fibers by calcination to form macroporous silica fibers, as depicted schematically in Fig. 1. To enhance the production yield of the macroporous silica fibers, rotating drum was adopted as collector instead of the flat SUS sheet during the colloidal templating process.

Fig. 2 contains the SEM images of the macroporous silica fibers fabricated by electrospinning using PS nanospheres with 700 nm in diameter. Before electrospinning, the aging time was adjusted as 0.5 to 1 hour, and the resulting morphologies are displayed in Fig. 2(a) and 2(b). However, the fibrous structure could not be maintained, and the morphology of the sample was fragment of the fiber-cut when the aging time was 2 hours, as displayed in Fig. 2(c), implying that prolonged aging induced the gelation and hardening of the spinning solution. Thus, one hour was adopted as aging time to form porous silica fibers.

Since the flat-type collector should be replaced as new one periodically, the rotating drum can be an efficient alternative during continuous production of the fibrous materials for industrial applications. In this study, the injection rate of the spinning solution was maintained as 30 μl/min, and the SEM images of the resulting porous silica fibers fabricated at 90 and 130 rpm are displayed in Fig. 3(a) and 3(b), respectively. When the rotation speed of the drum was slow enough, the porous silica fibers having a number of spherical cavities could be successfully fabricated as displayed in Fig. 3.

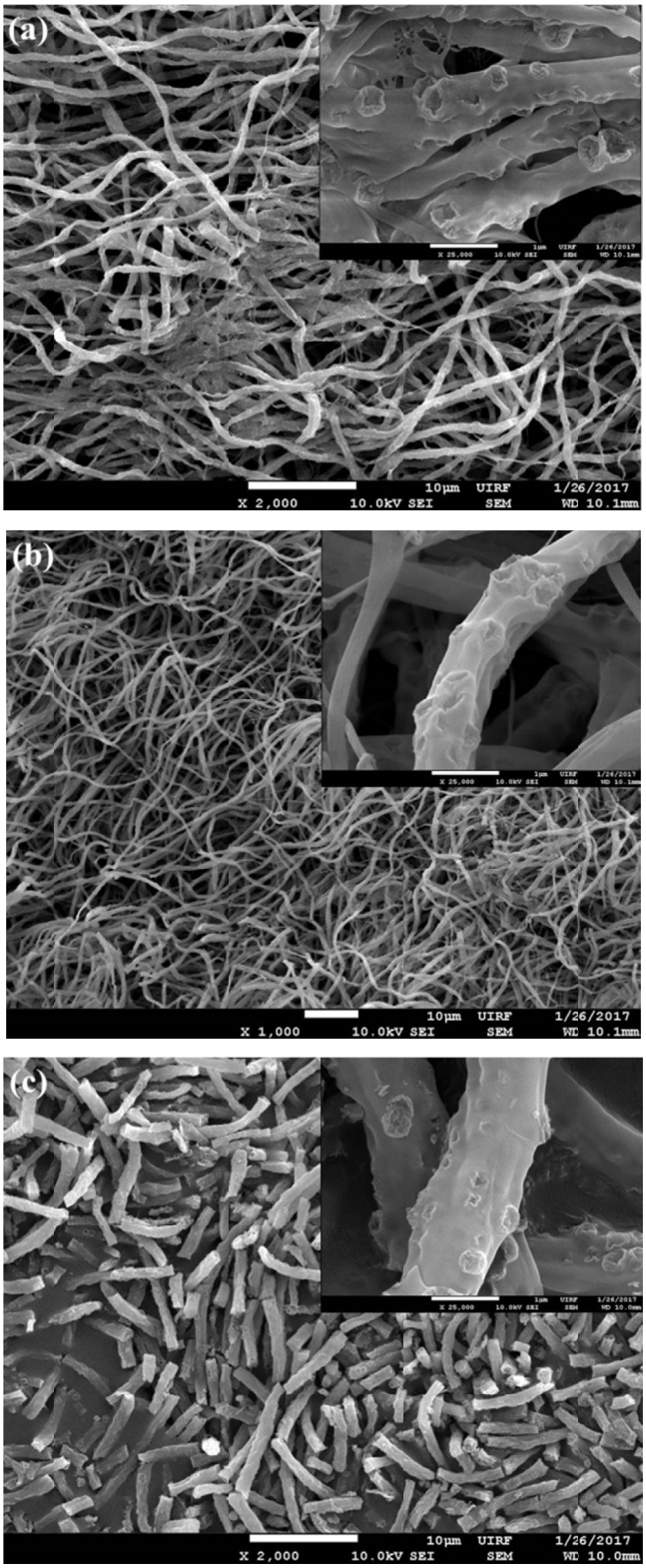

Fig. 2. SEM images of macroporous silica fibers fabricated by electrospinning method using polystyrene nanospheres with 700 nm in diameter as templating materials. The aging time of the spinning solution was a) 0.5, b) 1, and c) 2 hours

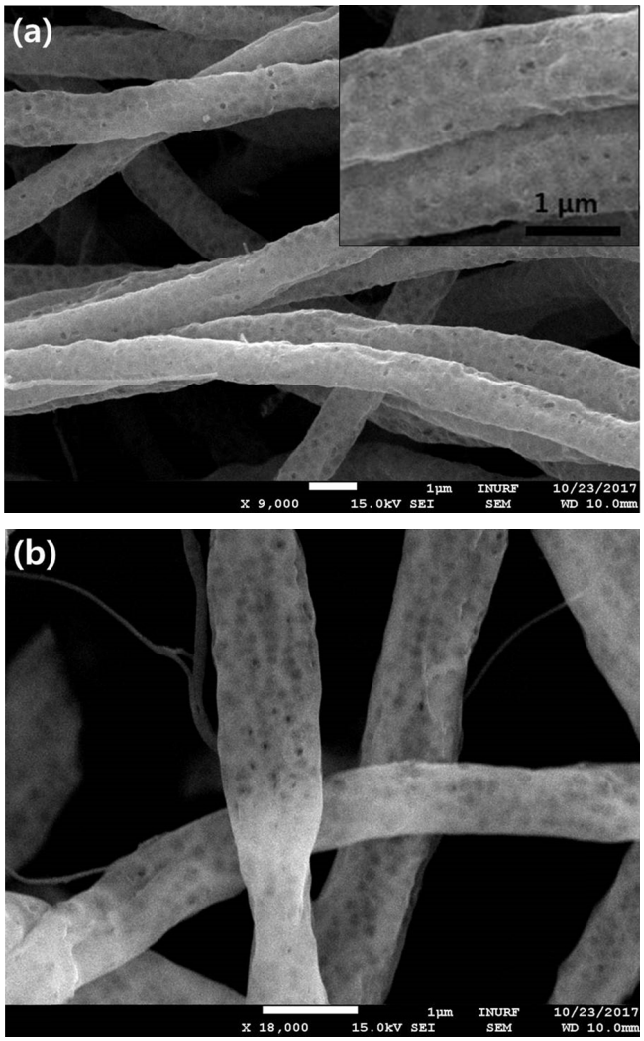

Fig. 3. SEM images of macroporous silica fibers using the rotation speed of drum collector at (a) 90 and (b) 130 rpm

The change of composition of fibrous materials was analyzed by FT-IR spectrometer before and after calcination, as shown in Fig. 4(a). Several characteristic peaks derived from PVP could be detected before calcination, whereas only a few peaks remained after heat treatment, indicating that amorphous silica was formed by removing PVP and PS nanospheres. In addition to FT-IR data, TGA result was also obtained for electro-spun fibers, as displayed in the inset graph of Fig. 4(a). During heating, the mass of electro-spun fibers reduced significantly, indicating that the density of porous silica would be extremely low due to the removal of PVP and PS nanospheres.

Since the preparation of PVP spinning solution is relatively simple and the polymeric fibers have sufficient sound absorption property, the sound absorption coefficient of PVP fibers was

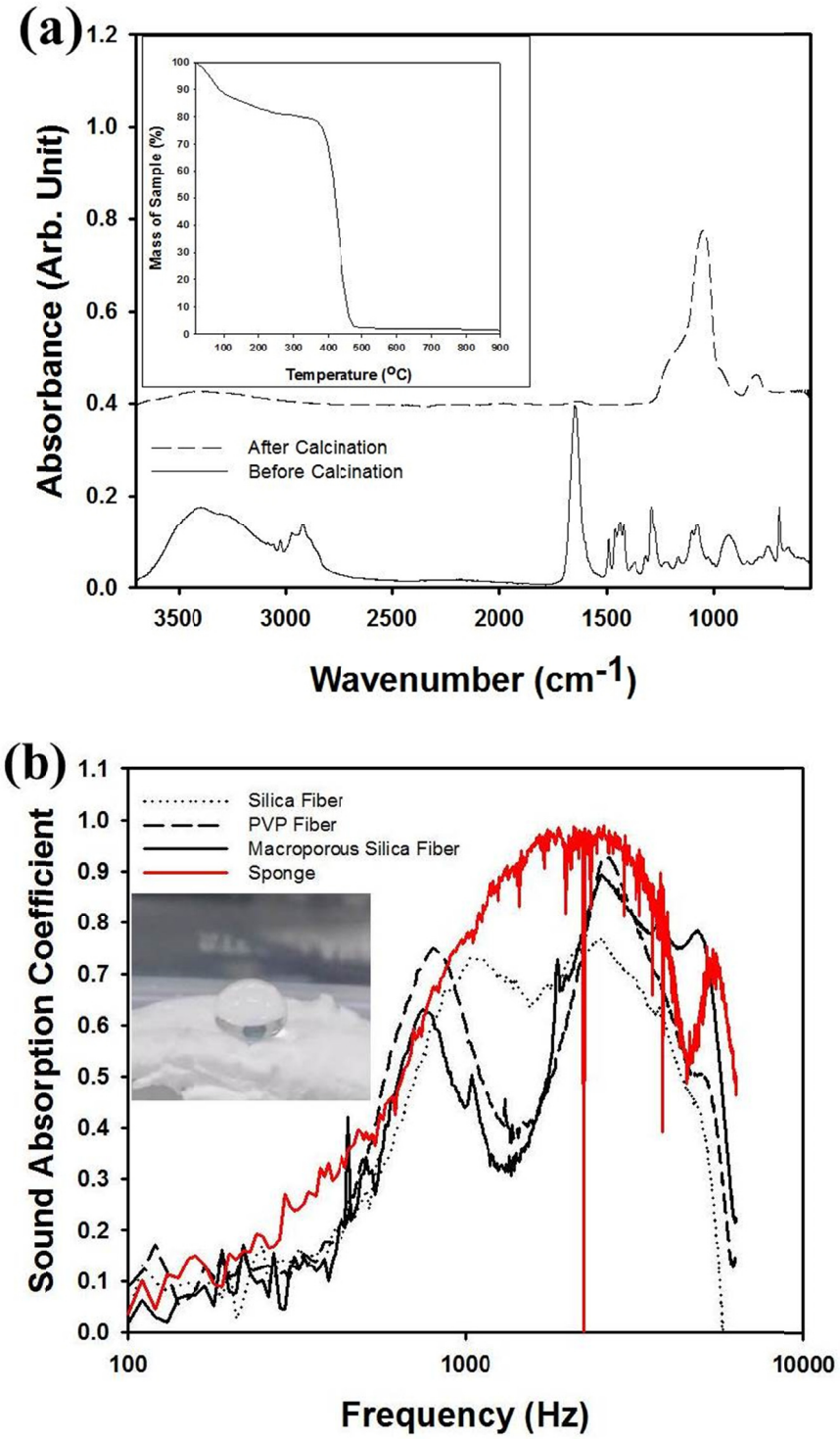

Fig. 4. (a) FT-IR analysis results of fibrous materials before and after calcination at 500°C. The inset figure presents the TGA result of electro-spun fibers. (b) The sound absorption coefficient of PVP fibers, silica fibers without macropores, macroporous silica fibers having macropores with 700 nm in diameter, and commercial sponge as a function of the frequency of incident acoustic wave. The inset figure presents the photograph of water droplet on macroporous silica fibers having macropores with 700 nm in diameter. The fibrous materials were treated with fluorine-containing silane coupling agent

measured by impedance tube for the comparison with those of silica fibers. Since the silica fibers are much more resistant at high temperature compared to PVP fibers, it is adequate to use the inorganic fibers in construction engineering. In this study, the thickness of the samples was fixed as 1 or 2 cm depending on the frequency ranges, and the sound absorption coefficients were measured as a function of the frequency of incident waves. As displayed in the dashed line of Fig. 4(b), the sound absorption coefficient of PVP fiber was measured and the maximum absorption coefficient was slightly higher than 0.9 at the frequency of about 1.15 kHz. Although the absorption coefficients were recorded as relatively high values at high frequency region, the PVP fibers were contracted due to their hygroscopic nature after a few weeks, indicating that the polymeric fibers are inadequate sound absorbers. When the sample holder was filled with non-porous silica fibers, the absorption coefficients were decreased, indicating that the air cavities in the samples were not sufficient for the absorption of incident sound wave, as shown in the dotted line of Fig. 4(b).

The sound absorption coefficient of the macroporous silica fibers having air cavities with 700 nm was also measured as displayed in the solid line of Fig. 4(b). Although the measured values are similar with the PVP fibers, the absorption coefficients at high frequency from 1.2 to 1.4 kHz were increased compared to the results from PVP fibers. The sound absorption coefficient of silica fibers was also compared with commercial sponge, implying that inorganic fibers are less effective to absorb sound waves in the frequency range from 1 to 2.5 kHz compared to the well-known material like sponge. However, the sound absorption coefficient of silica fibers is higher than that of sponge from 4 to 5.1 kHz, implying that the porous inorganic fibers can be used to augment sponges, similarly with glass fibers with excellent thermal resistance [9]. Though the introduction of meso- or micropores in sound absorbing materials may enhance the sound absorption coefficient, the macropores in this study can be effective choice, since the size of macropores can be easily decreased to increase the sound absorption coefficient by changing the size of templates [10,11].

TABLE 1

The Thermal Conductivity Data of Macroporous Silica Fibers

Apparent Density	Heat Capacity	Thermal Diffusivity	Thermal Conductivity
0.138 g/cm^3	1.082 J/(g·K)	0.048 m^2/s	0.007 W/(m·K)

Besides the sound absorption coefficients, the thermal conductivity of the macroporous silica fibers was measured by LFA (Laser Flash Analysis) method from the following equation [12].

$$\alpha = \frac{k}{\rho C_P} \tag{1}$$

The apparent density, heat capacity, and the thermal diffusivity of the porous silica fibers are summarized in Table 1, and the final value of the thermal conductivity was 0.007 W/(m · K), indicating that the porous fibers can be also applied as efficient sound absorbers with low thermal conductivity. The porosity of the silica fibers can be estimated from the apparent density ρ using the following equation.

$$Porosity = \left(1 - \frac{\rho}{\rho_b}\right) \times 100(\%) \tag{2}$$

Since the bulk density of silica ρ_b is 2.65 g/cm^3, the porosity of the porous silica fibers can be calculated as 94.8%, implying that abundant air voids exist in the sample to induce extremely low thermal conductivity and excellent sound absorption property. There exist macropores with 700 nm in diameter in the silica fibers since polystyrene nanospheres with the same diameter were used as templates to form the pores by thermal decomposition. In this study, it is thought that the macropores of each fiber and the space between the fibers are ascribed to the extremely high porosity of the sample.

Since the electrospinning process can be used for the fabrication of porous fiber networks, the resulting fibrous structure is applicable to prepare superhydrophobic surfaces after proper treatment of the fibrous materials with hydrophobic chemicals like silane coupling agents. In this study, the fluorine-containing silane coupling agent, HDFTHDTS, was used to prepare superhydrophobic surfaces with the aid of lotus effect. The water droplets showed high static contact angle, as displayed in the inset photograph of Fig. 4(b). Thus, the infiltration of humidity can be prevented for the porous fibers and the deterioration of thermal insulating properties can be avoided to maintain low thermal conductivity of the porous materials. The sound absorbing ability can be also maintained using the porous fibers with superhydrophobic surface, since the infiltration and condensation of water vapor into the porous region of the fiber network can be also prevented due to water-repelling surface property and the air voids can be maintained for the absorption of sound waves.

4. Conclusions

Macroporous silica fibers were fabricated by the colloidal templating after self-assembly by electrospinning. Stable operation during continuous production of the fibrous materials was possible using rotating drum for the collection of the fibers. The resulting silica fibers were modified by hydrophobic silane coupling agent to prepare superhydrophobic surfaces with excellent water repelling property. The sound absorption coefficient of the macroporous silica fibers was comparable to commercial sponge, showing the absorption coefficient larger than 0.9 in the high frequency region of the incident sound waves.

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