

Exploration of the novel stacked structure and one-step fabrication of electrospun silica microbelts with controllable wettability

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A fairly general and direct synthesis for the preparation of silica microbelts with a novel stacked structure and controllable wetting behavior by using a combination of sol-gel chemistry and electrospinning techniques was explored successfully. The formation mechanism of the stacked structure and the potential application of the silica microbelts were confirmed.

1. Introduction

For their unique properties and versatile applications, one-dimensional structures, such as fibers, belts, tubes *et al.*, have attracted considerable attention¹ and several methods for their fabrication have been demonstrated and developed in recent years. Electrospinning, based on strong mutual electrical forces, provides a highly effective way to process solutions into continuous one-dimensional structures with diameters ranging from a few nanometers to several micrometers.² Because of the requirements on the viscoelastic behavior of a solution, this technique is widely used to deal with organic polymers with high molecular weights.^{3–5} Efforts have been made to fabricate ceramic fibers based on conventional sol-gel precursor solutions.^{6–8} Wettability is an important feature of materials, as it plays a critical role in many practical applications.^{9,10} The advantages of electrospinning are that it enables the fabrication of functional fibers with controllable wetting behaviour. Researchers have described two different strategies to make hierarchically roughened superhydrophobic electrospun nonwoven mats by decorating micrometer-scale fibers with nanometer-scale pores or particles.⁴ Recently, multifunctional superhydrophobic fabrics were produced successfully by creating hierarchical electrospun fibrous structures from methyltriethoxysilane with a low surface energy.¹¹

Silica is of great importance in the chemical sciences, technology and solid state physics for its mild reactivity and good chemical properties. The multifunctional unmodified or modified silica fibers can possess a combination of properties. For example, ceramic silica hybrid nanofibers were prepared for use in biomedical applications by the electrospinning of solutions containing a biocompatible polymer and modified silica precursors.¹² Zhu and co-authors synthesized a silica fiber with a highly ordered mesoporous structure and long continuous fibrous property on a large-scale by employing electrospinning.¹³

After condensation of the sol-gel precursor the surface hydroxyl (–OH) groups or non-polar (–OR) groups on the backbone will determine the wetting behaviour of the final product. The silica produced from the single tetraethoxysilane (TEOS) sol-gel precursor has hydrophilic hydroxyl groups on its backbone. Trimethylchlorosilane (TMCS) is the most common surface modification reagent used to introduce the hydrophobic –Si–(CH₃)₃ group for modifying the wettability, but multiple chemical modifications always require a complicated experimental procedure.¹⁴ More recently, we successfully explored a one-step synthesis of a hydrophobic silica aerogel *via in situ* surface modification at ambient pressure by using TEOS and TMCS as co-precursors.¹⁵ In this paper, we describe a fairly general and direct synthesis for the preparation of silica microbelts with a novel stacked structure and controllable wetting behavior by using a combination of sol-gel chemistry and electrospinning techniques. The silica microbelts were fabricated from two different sols: a single TEOS precursor and TEOS and TMCS co-precursors.

2. Experimental section

The silica sol for use in electrospinning was prepared by hydrolyzing the single TEOS precursor and TEOS and TMCS co-precursors. TEOS (98%) and TMCS ($\geq 99\%$) were purchased from Sigma-Aldrich Chemical Company. Ethanol (99.7%) and HCl (36.38%) were supplied by Beijing Chemical Company. All of the reagents were directly used without further dilution. In a typical experiment for the preparation of hydrophilic microbelts, only TEOS was mixed with ethanol, water and HCl solution (molar ratio

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in the solution; TEOS : ethanol : H₂O : HCl = 1 : 3.1 : 1 : 7 × 10⁻⁴). Both TEOS and TMCS were mixed with ethanol, water and HCl solution (molar ratio in the solution; TEOS : TMCS : ethanol : H₂O : HCl = 1 : 0.9 : 3.1 : 1.5 : 7 × 10⁻⁴) to produce the hydrophobic microbelts. All the mixtures were refluxed at 70–80 °C for about 3–4 h and the solvent was removed by distillation to obtain the silica sols which exhibited viscoelastic behaviour.

In order to favor the formation of a silica microbelt, a small amount of polyethylene oxide (PEO, *M_n* = 900 000) (Changchun Jinghua Company) should be added into the sols. The silica sols with 0.5, 1.3 and 2.5 wt% PEO content were prepared and kept under stirring for 24 h to get a completely dissolved solution, which was for use in electrospinning. Here, both needle (Beijing Future Material Sci-tech Company) and roller electrospinning (Nanospider, Elmarco) were conducted. For the needle electrospinning, the flow rate was 0.05 mL min⁻¹, the needle to collector distance was 15 cm, and the voltage was 13 kV. For the Roller electrospinning, the applied voltage between the collector and electrode was kept at 30 kV. The electrode-to-collector distance was 20 cm, and the electrode rotation rate was 3 rpm. Two different collective substrates were used (non-conductive: flexible paper with resistivity 2 × 10⁴ ohm m⁻¹; conductive: aluminum foil). The collected products were dried at room temperature.

The SEM (scanning electron microscope) images were collected using a JHelios Nano Lab 600i. The measurements of the static contact angles of the samples were performed on a SL200B contact angle meter. ²⁹Si MAS NMR (nuclear magnetic resonance) spectra were recorded on a Varian Infinity Plus 400 NMR spectrometer, fitting the samples in a 7 mm ZrO₂ rotor. The spinning speed was 8 kHz. The infrared spectra of the products were recorded on a Nicolet Impact 410 FTIR spectrophotometer. X-ray diffraction patterns were obtained with a Siemens D5005 diffractometer using Cu-Kα radiation (λ = 1.5418 Å).

3. Results and discussions

The electrospun silica microbelts were prepared using both needle and roller electrospinning. In our experiments, silica sols with 0.5 wt% polyethylene oxide (PEO) were found to give the best results. Fig. 1 shows the SEM images of the electrospun silica microbelts obtained by needle and roller electrospinning.

According to the results, needle electrospinning is more likely to produce a continuous structure than roller electrospinning in our system. As shown in Fig. 1 a to f, each individual microbelt from the TEOS single precursor (Fig. 1 a, b and c) and the TEOS and TMCS co-precursors (Fig. 1 d, e and f) produced by needle electrospinning remains as a continuous structure with a uniform width of about 1 μm. The belts produced by needle electrospinning show a rather narrow width distribution. While the widths of the microbelts from the TEOS single precursor (Fig. 1 g and h) and the TEOS and TMCS co-precursors (Fig. 1 i and j) produced by roller electrospinning show a wide distribution, also the belt widths prepared by roller electrospinning are generally larger than those produced by needle electrospinning. Microscale silica microbelts with stacked structures were observed in Fig. 1 g and

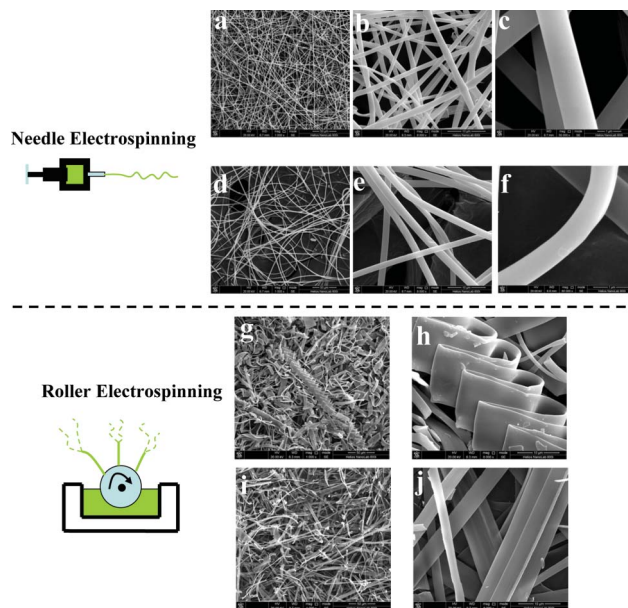


Fig. 1 SEM images of the electrospun silica microbelts on the non-conductive substrate with 0.5 wt% PEO in the sols. a)–c): Needle-spun microbelts from the TEOS single precursor, scale bar: 50 μm, 10 μm and 1 μm, respectively; d)–f): needle-spun microbelts from the TEOS and TMCS co-precursors, scale bar: 50 μm, 10 μm and 1 μm, respectively; g) and h): roller-spun microbelts from the TEOS single precursor, scale bar: 50 μm and 10 μm, respectively; i) and j): roller-spun microbelts from the TEOS and TMCS co-precursors, scale bar: 50 μm and 10 μm, respectively.

h. It should be noted that the appearance of a stacked structure in the roller-spun microbelts from the TEOS single precursor is not a unique case. Helical silica nanosprings have been synthesized using the chemical vapor deposition technique and the helical structure is present in the middle of a straight nanowire.¹⁶ The author claimed a 10–15% ratio between the helical nanostructures and the straight ones, which is higher than the ratio between the stacked structures and the straight ones in our products on the non-conductive substrate. Using the electrospinning technique, uniform microscale polymeric helical structures can be produced although the mechanism is currently not very clear. The viscoelastic contraction upon partial neutralization of the charged fibers, solution concentration, and process parameters were found to affect the formation of such helical structures.^{17,18} It is believed that it will be more energetically favorable for the microbelt to form a stacked structure compared to a helical structure. Although the PEO content in the sols is very low, its presence is necessary and must be controlled precisely. The sols were electrospun into small droplets without PEO. If the PEO content is a little higher, it becomes difficult to form individual structures as displayed in Fig. 2.

Although a few helical structures were confirmed, it is still a challenge to fabricate one-dimensional structures with excellent flexibility, which can be used in nano-engineering applications.^{19,20} To our best knowledge, there are no similar reports on the formation of one-dimensional stacked structures of ceramic materials. Compared to polymeric systems, it will be much more difficult to fabricate microscale ceramic stacked

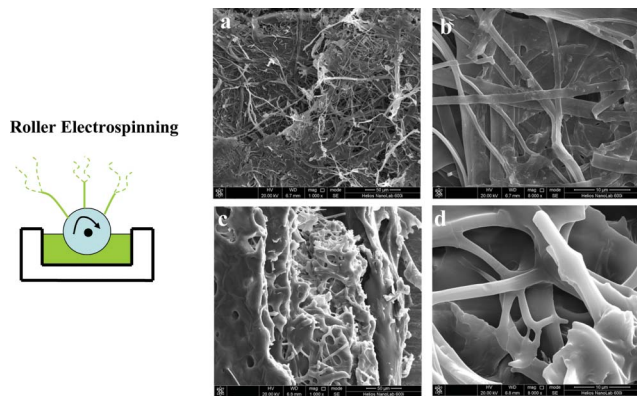


Fig. 2 SEM images of electrospun silica by roller electrospinning with a higher PEO content in the sols from the TEOS single precursor on the non-conductive substrate; a) and b): 1.3 wt%; c) and d): 2.5 wt%; scale bar: 50 μm and 10 μm , respectively.

structures directly. In order to explore the actual formation mechanism of the stacked structure, we use two different collective substrates (non-conductive and conductive). The experimental results reveal that the formation mechanism of the stacked structure will depend on the substrate. When a non-conductive substrate is used, the ratio of the stacked structures is very low as shown in Fig. 1 g and h. If a conductive substrate is used, the ratio of the stacked structures increases a lot as displayed in Fig. 3 a and b. In Fig. 3 a, the length of some of the microbelts with perfect stacked structures even exceeds 1 mm. The process of electrospinning, in which the silica sols were electrospun, causes the microbelts to carry a charge which stabilises them. Once the charged ceramic microbelts touch the conductive substrate, the charges transfer and the microbelts become unstable. Finally the microbelts spontaneously contract into the stacked structures by undergoing a structural rearrangement as we have observed.¹⁷

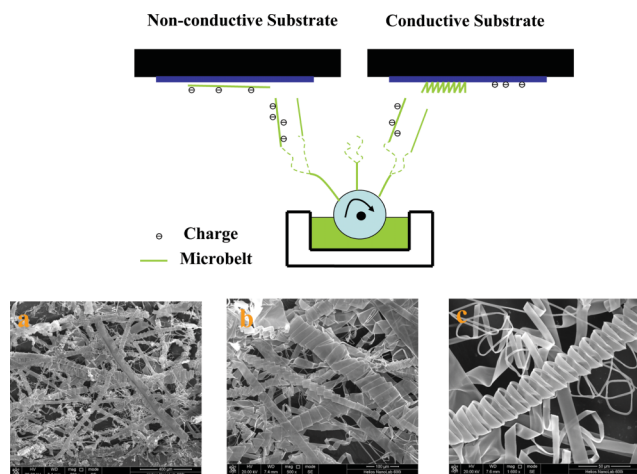


Fig. 3 Illustration of the formation mechanism of the stacked structure (top); SEM images of the electrospun silica microbelts from the TEOS single precursor on the conductive substrate with 0.5 wt% PEO in the sols (bottom: a, b and c; scale bar: 400 μm , 100 μm and 50 μm , respectively).

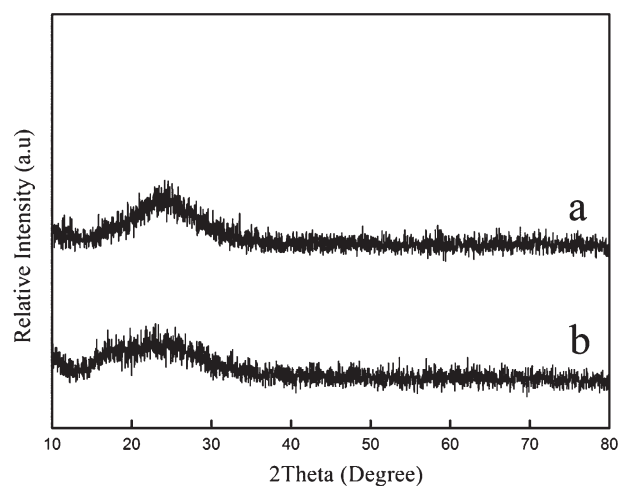


Fig. 4 X-ray diffraction pattern of the silica microbelts produced from the TEOS single precursor (a) and the TEOS and TMCS co-precursors (b).

The X-ray diffraction results and FTIR spectra are shown in Fig. 4 and Fig. 5, respectively. Only a diffuse peak emerges at about $20\text{--}30^\circ$ in the X-ray diffraction pattern, which reveals the typical amorphous structure of the prepared silica microbelts from both the TEOS single precursor and the TEOS and TMCS co-precursors. The bands at 1170 , 1080 and 450 cm^{-1} for the Si–O–Si bonds are present in the infrared spectra. In Fig. 5 b, the bands located at 2970 and 1260 cm^{-1} belong to the $-\text{CH}_3$ of the hydrophobic $-\text{Si}-(\text{CH}_3)_3$ groups. Due to the presence of PEO, we can not confirm the successful grafting of $-\text{Si}-(\text{CH}_3)_3$ groups on the silica backbone from the TEOS and TMCS co-precursors from the FTIR spectra.

A droplet of water was placed on the membrane surface and the contact angles were determined and are displayed in Fig. 6 a and b. The contact angle of the sample prepared from the TEOS single precursor is 25° , which indicates its hydrophilic nature. The hydrophobic behavior of the electrospun microbelt produced from

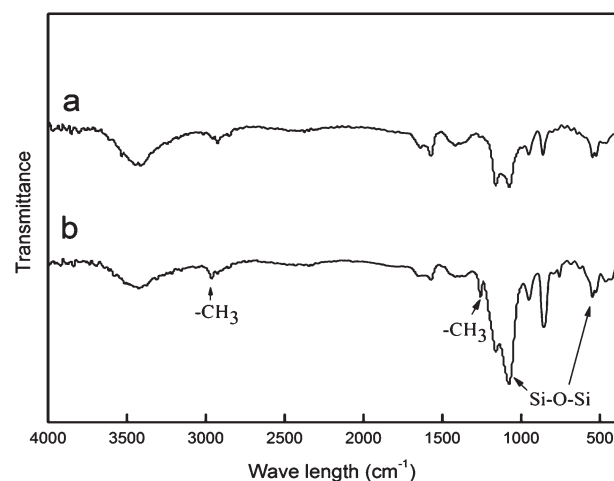


Fig. 5 The FTIR spectra of the silica microbelts prepared from the TEOS single precursor (a) and the TEOS and TMCS co-precursors (b).

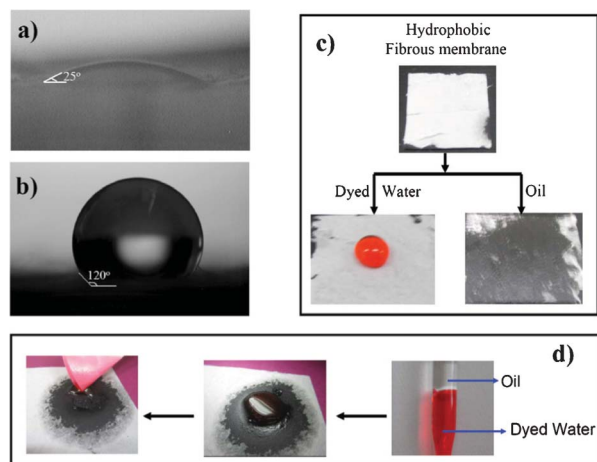


Fig. 6 Water droplet images and contact angle of the TEOS single precursor (a) and the TEOS and TMCS co-precursor (b) fibrous membrane; comparison of dyed water and oil droplet profiles on the hydrophobic fibrous membrane; water beads up on the surface, while oil diffuses into the membrane (c); an illustration of the separation of dyed water and oil (d).

the TEOS and TMCS co-precursors is confirmed by its 120° contact angle. Interestingly, the electrospun fibrous membrane was found to have the ability to separate water and oil as illustrated in Fig. 6 c and d. Although the mechanical properties of electrospun fibrous membranes should improve in the future, such selective behaviour makes it a potential candidate for the removal of oil

spills in the sea. Fig. 7 a and b display the ^{29}Si NMR spectra of the silica microbelts produced from the TEOS single precursor and the TEOS and TMCS co-precursors, respectively. The signals in the range of -80 to -120 ppm are attributed to the ^{29}Si nucleus in a tetrahedral oxygen environment, conventionally indicated by the Q_n notation.^{21,22} The chemical shifts at around -92 , -100 and -110 ppm in the spectra of the microbelts produced from the TEOS single precursor (Fig. 7 a) are assigned to the Q2-Si, Q3-Si and Q4-Si sites, respectively.^{23,24} The additional signal in Fig. 7 b at around 15 ppm clearly confirm the presence of the hydrophobic $-\text{Si}(\text{CH}_3)_3$ groups on the silica backbone. The ^{29}Si NMR results are in good agreement with the wettability measurements.

4. Conclusions

In summary, we describe a novel route for the preparation of novel stacked structures and a one-step fabrication of electrospun silica microbelts with controllable wettability by a combination of sol-gel chemistry and electrospinning techniques. Such fairly general and direct syntheses broaden the field and the potential applications of one-dimensional silica in different environmental conditions by controlling the hydroxyl groups and non-polar groups on the backbone. Experimental results reveal that perfect one-dimensional stacked structures can form on a conductive substrate and an exploration of the one-dimensional stacked structure formation mechanism was also conducted.

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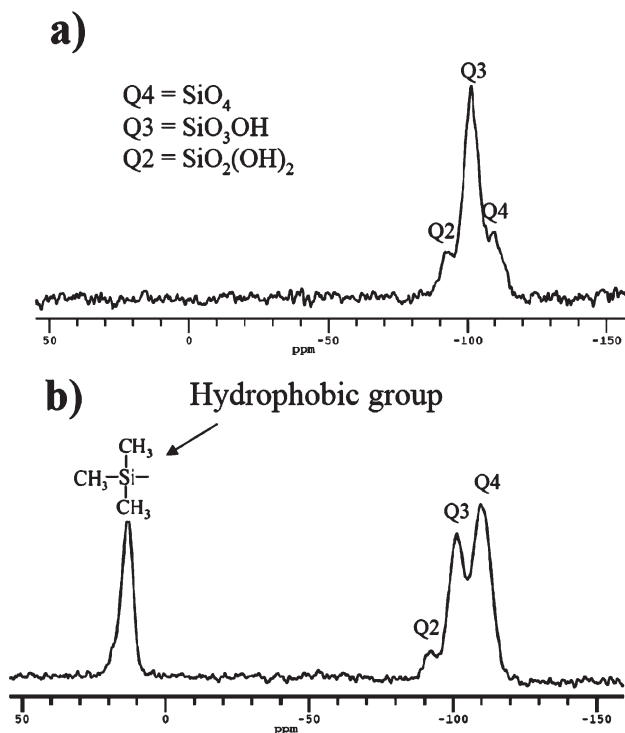


Fig. 7 ^{29}Si NMR spectra for the silica microbelts produced from the TEOS single precursor (a) and the TEOS and TMCS co-precursors (b).

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