Fabrication of Necklace-like Structures via Electrospinning

Yu Jin,[†] Dayong Yang,*,[‡] Dongyang Kang,[†] and Xingyu Jiang*,[†]

[†]CAS Key Lab for Biological Effects of Nanomaterials and Nanosafety, National Center for NanoScience and Technology, Beijing 100190, China, and [‡]Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215125, China

We report a one-step method to fabricate necklace-like structures from zero-dimensional materials via electrospinning. PVA was used as polymer matrix for accomplishing necklace-like arrays of silica particles. We systemically investigated how the diameter of SiO_2 particles, the weight ratio of PVA to SiO_2, the voltage, and the relative content of $PVA/SiO_2/H_2O$ influenced the morphology of electrospun fibers. SiO_2 particles with diameter of 143 nm tended to aggregate into bunches in the fibers, while 265 and 910 nm SiO_2 particles tended to align along the fibers one by one, resembling necklaces. The content of water in the $PVA/SiO_2/H_2O$ solution showed critical influence on the diameter of fibers and consequently determined the morphology. Too thin solutions gave birth to blackberry-like structure; too condensed solution was too hard to eject from the orifice of the needle; when the ingredient was elaborately tailored, we obtained necklace-like structures. We believe that these results can serve as references to generating other complex structures involving polymers and particles via electrospinning and that these structures will be potentially useful in photoelectric devices, drug release, and optical components.

1. Introduction

Using electrospinning (ES), we report a method to prepare polymer/particle necklace-like structures. One-dimensional (1D) necklace-like nanostructures have drawn great attention in recent years because of their distinctive geometries and special physical/chemical properties.[1−5] Necklace-like single-crystalline tetragonal perovskite PbTiO$_3$ exhibited good photoelectric properties, potentially useful for transparent electrodes in display photoelectric devices of heterojunction structures.[2] Compared with separate nanosheets, 1D arrays of Li$_{1+\alpha}$V$_3$O$_8$ nanosheets showed superior electrochemical properties as positive electrode materials for lithium batteries.[5] Another similar structure, core−sheath nanofibers containing colloidal arrays in the core, could control the release of multiple reagents following a programmable manner.[1]

Many approaches were explored to fabricate necklace-like nanostructure.[3,4,6−9] Yu et al.[8] synthesized unique necklace-like Cu@cross-linked poly(vinyl alcohol) (PVA) microcables by a hydrothermal process. Yin et al.[6] combined physical confinement and capillary force to assemble spherical colloids into helical chains. Liu et al.[7] utilized template-based pulsed electrodeposition of multilayered metal nanowires into anodic aluminum oxide template and a subsequent solid-state reaction between metals and alumina to obtain noble-metal@oxide inorganic peapod nanostructures. Compared with these methods, ES is a straightforward and fast method to fabricate necklace nanostructures. ES is a well-established and widely used method for fabricating polymer fibers in the micro/nanometer scale.[10−14] Various morphologies such as fibers, spheres, core−sheath structures, and tubes were produced by ES.[15−21] Relatively few studies detailed the fabrication of necklace-like structures, although several studies pioneered such attempts. Lim et al.[9] used electrospun nanofibers as confining geometries to fabricate 1-D colloidal assemblies to show that the necklace-like morphology of the composite fibers was mainly governed by the wettability and weight ratio between the polymers and the particles. Lim et al.[22] further demonstrated that the surfaces of the composites of microspheres and ES polymers were superhydrophobic. Kanehata et al.[23] produced silica fibers composed of silica nanoparticles by ES silica nanoparticles in polymer solutions and subsequently removed polymers to yield porous inorganic nanofibers via calcination. Stoiljkovic et al.[24] obtained

*Corresponding authors: tel/fax 86-512-62872562, e-mail dyyang2008@sinano.ac.cn (D.Y.); tel 86-10-82545558, fax 86-10 62656765, e-mail xingyujiang@nanoctr.cn (X.J.).

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submicrometer polystyrene (PS) fibers composed of PS particles by ES PS particles and PVA and subsequently extracted PVA by water. All these attempts proved that ES is a useful tool to construct one-dimensional necklace nanostructures from zero-dimensional materials. There still lacks, however, a systematic investigation for the precise control of the morphology of ES necklace nanostructures.

Herein, therefore, we utilize ES to fabricate necklace-like PVA/SiO$_2$ fibers with PVA as template polymer. We systemically investigated how the diameters of SiO$_2$ particles, the weight ratio of PVA to SiO$_2$, the voltage and the relative content of PVA/SiO$_2$/H$_2$O influenced the morphology of ES mats, and finally we obtained necklace-like structures.

2. Experimental Section

Preparation and Characterization of PVA/Silica Solutions. We dissolved a measured amount of PVA (Acros Organics, 88% hydrolyzed, M_w 88 000) granules in distilled water at 50 °C, stirred it for 6 h, and obtained transparent solutions. Silica particles dispersed in water were purchased from China University of Petroleum (http://www.heavyoil.cn/). The average diameters of silica particles were 143, 265, and 910 nm, and the concentrations of silica dispersions were 12.2%, 21.6%, and 13.1%, respectively. The silica dispersion and the PVA solution were mixed in different volume ratios under vigorous shaking for at least 3 h at room temperature and ultrasonically treated for 10 min.

Electrospinning. We employed a dc high-voltage generator (Spellman, SL150) to produce voltages ranging from 0 to 50 kV. The solution was contained in a 2.5 mL syringe with a flattened metal needle. The solutions in the syringe flowed out under the force of gravity. A sheet of aluminum foil was placed under the syringe as the collector. The anode was connected with the needle and the cathode with the aluminum foil. All experiments were conducted at room temperature.

Scanning Electron Microscopy (SEM). We used SEM (Hitachi, S4800) to observe the morphology of the electrospun mats. All samples were sputter-coated with gold for 60 s (the thickness of gold coating was about 10 nm) prior to observation with SEM.

Thermogravimetric Analysis (TGA). The thermoanalyzer (PerkinElmer, Diamond) was operated in air from room temperature (25 °C) to 700 °C at a heating rate of 10 °C /min.

Transmission Electron Microscopy (TEM). TEM samples were prepared by collecting the fibers on copper TEM grids coated with a layer of amorphous carbon. Images were obtained using a transmission electron microscope (FEI, Tecnai G^2 20 ST) operated at 200 kV.

3. Results and Discussion

The process for preparing solutions is important for ES. We chose PVA as the matrix polymer for silica because of their good wettability, which facilitated the formation of necklace-like structure.[9] We mixed the silica/H$_2$O dispersion (white) and the PVA/H$_2$O solution (transparent) together (PVA:SiO$_2$ = 500:500 means a mix of 500 μL PVA solution and 500 μL SiO$_2$ solution) and stirred them vigorously to obtain a milky solution. When the PVA/SiO$_2$ solutions were kept undisturbed for more than 1 day, the solutions tended to separate into different phases. Remixing can effectively rehomogenize the mixtures. The ES setup we used composed of a high-voltage generator, a 2.5 mL plastic syringe with a flattened needle, and an aluminum foil as the collector (Figure 1). The anode was connected with the needle and the cathode with the aluminum foil. When we applied a high voltage on the PVA/SiO$_2$ solutions in the syringe, the solutions were electrified with positive charges. A charged jet ejected from the surface of the solution when the electric forces exceeded the
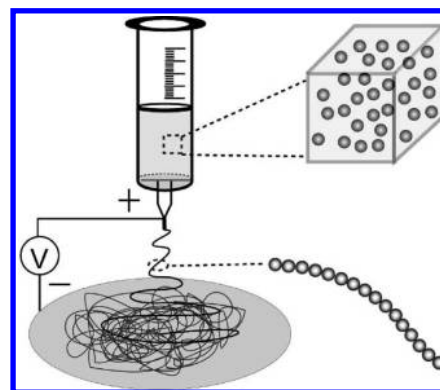

Figure 1. Schematic illustration of the setup and process for preparing necklace-like chains.
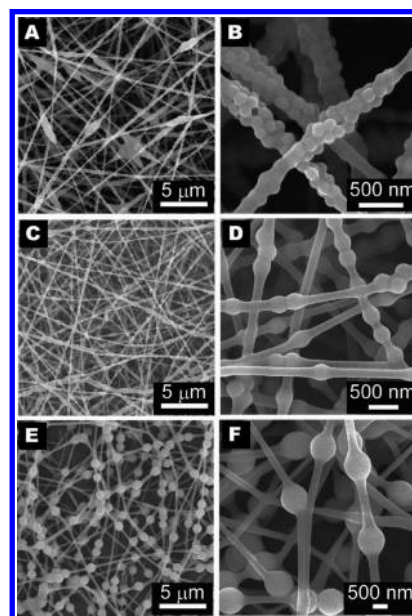

Figure 2. SEM images of electrospun PVA/SiO$_2$ fibers with different SiO$_2$ diameters: (A, B) 143 nm, PVA:SiO$_2$ = 500:500; (C, D) 265 nm, PVA:SiO$_2$ = 800:200; (E, F) 910 nm, PVA:SiO$_2$ = 500:500; work distance 10 cm, voltage 10 kV.

surface tension of the solutions. The solvent evaporated and the fibers deposited on the aluminum foil. We used SEM and TEM to observe the morphology of the electrospun mats.

We chose three representative silica dispersions with different diameters for the current study. The concentrations of silica dispersions with diameter of 143, 265, and 910 nm were 12.2%, 21.6%, and 13.1%, respectively. Because those three silica dispersions had different concentrations, we chose the concentration of PVA as 12, 10, and 12%, respectively, so as to achieve appropriate ingredient for ES. Compared with the smooth fibrous structure of pure ES PVA, the PVA solutions containing SiO$_2$ particles gave rise to different morphologies. The size of the particles influenced the morphology. As showed in Figure 2, 143 nm SiO$_2$ tended to aggregate into clusters of particles. We ascribed the aggregation to two possible reasons: (i) smaller particles (143 nm) have relatively large surface energy; (ii) the diameter of fibers is larger than the size of particles, so particles have to pack together. The 265 and 910 nm SiO$_2$ particles tended to align along the fibers one by one, and the morphology of ES fibers was similar to that of a necklace. We believe that the mats of particle bunches embedded in fibers (Figure 2A,B) can be
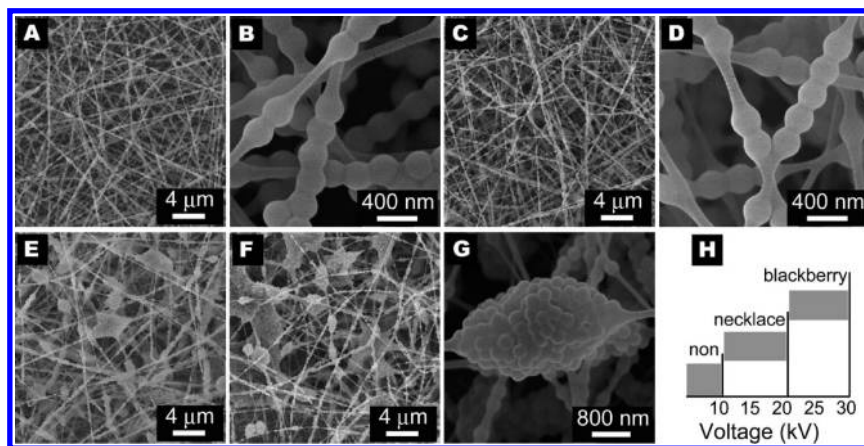
Figure 3. Influence of voltage on the morphology of PVA/ SiO$_2$ (265 nm) ES mats. (A, B) 15 kV, (C, D) 20 kV, (E) 25 kV, (F, G) 30 kV, (H) a "phase diagram" of the morphology of the composite as a function of voltage. PVA:SiO$_2$ = 700:300, work distance 10 cm.
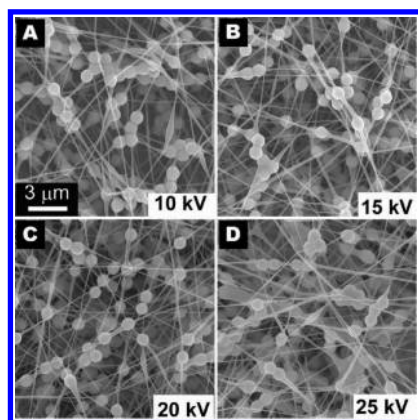

Figure 4. Influence of voltage on the morphology of PVA/SiO$_2$ (910 nm) ES mats. (A) 10 kV, (B) 15 kV, (C) 20 kV, (D) 25 kV; PVA:SiO$_2$ = 400:600, PVA 12%, work distance 10 cm. All the images share the same scale bar.

Figure 5. Influence of the volume ratio of PVA:SiO$_2$ on the morphology of PVA/SiO$_2$ (265 nm) ES mats. (A) 400:600, (B) 600:400, (C) 800:200; PVA 10%, work distance 10 cm, voltage 20 kV. All the images share the same scale bar.

potentially applied in many areas, including controlled release of drugs and the fabrication of superhydrophobic surfaces.[1,22] But here we intend to fabricate necklace-like structures, so we will focus our attention on the 265 and 910 nm SiO$_2$.

For a given solution, we can tailor the morphologies by adjusting the work distance and applied voltage. When investigating ES of PVA, PS, polycarbonate (PC), and poly-(vinylidene fluoride) (PVDF) solutions,[10,11,25,26] we found that the voltage greatly influenced the morphology when work distance was fixed. Fixing the work distance at 10 cm, we varied the voltage from 10 to 30 kV. When the applied voltage was less than 10 kV (i.e., 8 kV), the electrostatic forces could not overcome the surface tension of the polymer solutions to result in deposited mats on the collector. When the voltage was 15 and 20 kV, necklace-like structures formed (Figure 3A−D). When the voltage was between 25 and 30 kV, blackberry-like structures appeared (Figure 3E−G). We correlated voltage with morphologies (Figure 3H) and found that 10−20 kV was the optimal range of voltage for the formation of necklace-like structures. But this rule seemed only suitable for 265 nm SiO$_2$; for 910 nm SiO$_2$, voltage had little influence on the morphology (Figure 4). We should
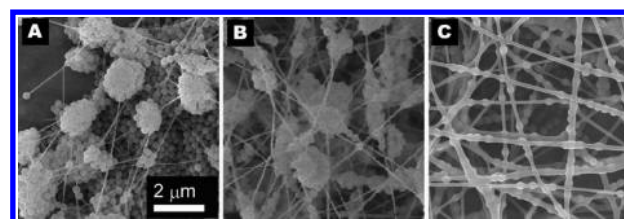
not apply the voltage−morphology relation to all different systems, and we do not understand the reasons for this phenomenon yet.

We next tested if increasing the concentrations of the particles would result in altered morphology of the necklaces, for example, to increase the compactness of the necklaces shown as those in Figure 2C−F (for both 265 and 910 nm). We assumed that if we added more particles in the solutions, the space between the beads would shrink. We changed the volume ratio between the PVA solution and the SiO$_2$ solution. In our experiments, the concentration of PVA/H$_2$O was fixed at 12% for 910 nm particles and 10% for 265 nm particles. The concentration of SiO$_2$/H$_2$O was as received from the supplier. For 265 nm SiO$_2$, we changed the volume ratio of PVA solution:SiO$_2$ solution from 400:600 to 600:400 to 800:200 (e.g., 400 μL PVA solution and 600 μL SiO$_2$ solution mixed together). When the SiO$_2$ volume was large, particles tended to aggregate to form blackberry-like structures (Figure 5A); after increasing PVA volume, more fibers appeared, but blackberry-like structures still dominated the morphology; when decreasing SiO$_2$ volume, semi-necklace-like structures formed (Figure 5C). Therefore, we should control the ratio of PVA:SiO$_2$ between 600:400 and 800:200.

Similarly, for 910 nm SiO$_2$ particles, the morphology of fibers and the number of particles in a single fiber were affected by the volume ratio of PVA:SiO$_2$ (Figure 6). But in this case, particles did not tend to aggregate to form blackberry-like structure (Figure 6B−D), which indicated that 910 nm SiO$_2$ was more suitable for forming necklace-like structures than 265 nm SiO$_2$ did. But in Figure 6B−D, the distance between particles was too large to form necklace due to the relatively small amount of SiO$_2$ particles. So for the formation of necklace, we will use the solution of PVA:SiO$_2$ = 300:700. But the solution (PVA:SiO$_2$ = 300:700) yielded particle aggregates. We reasoned that the

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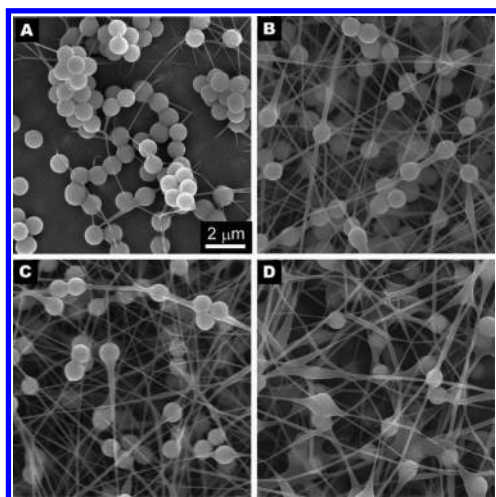(26) Liu, Y.; Yang, D.; Yu, T.; Jiang, X. *Electrophoresis* **2009**, in press (elps.200900128).

Figure 6. Influence of the volume ratio of PVA:SiO$_2$ on the morphology of PVA/SiO$_2$ (910 nm) ES mats. (A) 300:700, (B) 400:600, (C) 600:400, (D) 700:300; PVA 12%, work distance 10 cm, voltage 15 kV. All the images share the same scale bar.
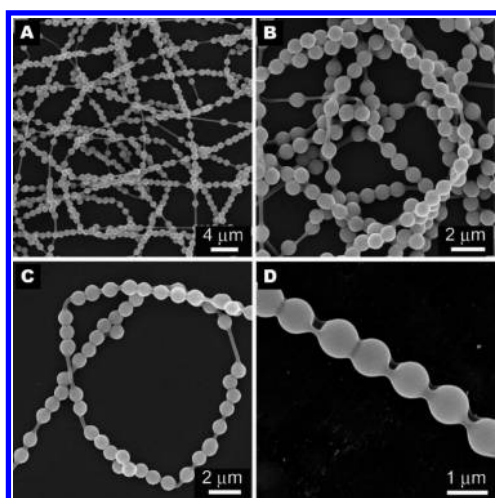

Figure 7. Necklace-like structures of PVA/SiO$_2$ (910 nm) ES mats by removing part of water in the solutions. PVA:SiO$_2$ = 300:700; PVA 12%, work distance 10 cm, voltage 15 kV.

solution (PVA:SiO$_2$ = 300:700) was too thin, and there was no sufficient polymeric chain entanglement, so the electrospun jets could not give birth to fibers. We therefore attempted to make the solution thicker.

In order to test if water removal might give us another level of control of the morphology of the composite, we heated the PVA/SiO$_2$ solution (PVA:SiO$_2$ = 300:700) at 80 °C for 3 h to yield a thickened solution. Using this solution, we obtained necklace-like structures via ES (Figure 7). In Figure 7, the gradually enlarged SEM images showed that SiO$_2$ particles stacked regularly one by one with a fiber connecting neighboring particles. In this case, we measured the weight ratio of PVA:SiO$_2$:H$_2$O by TGA and determined the ratio for forming necklace was 7:19:75 (before removing water, the ratio was 7:19:174).

We further used TEM to characterize the morphology of electrospun mats. We showed three representative images in Figure 8. It was clear that 143 nm SiO$_2$ tended to aggregate (Figure 8A), 265 nm SiO$_2$ was jacketed by fiber (Figure 8B), and only the solution of 910 nm SiO$_2$ formed necklace-like structures (Figure 8C).

Thus, we could determine the experimental parameters for fabricating necklace-like structures: diameter of SiO$_2$ = 910 nm,
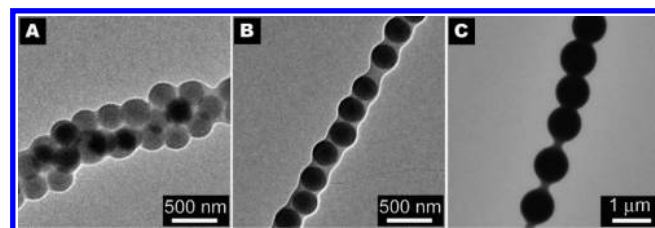

Figure 8. Representative TEM images of ES PVA/SiO$_2$ fibers with different SiO$_2$ diameters: (A) 143 nm, PVA:SiO$_2$ = 500:500, (B) 265 nm, PVA:SiO$_2$ = 700:300, (C) 910 nm, PVA:SiO$_2$ = 300:810 (after removing part of water in the solutions); work distance 10 cm, voltage 15 kV.
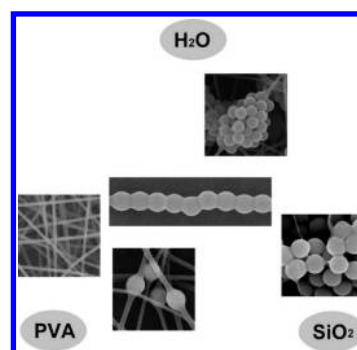

Figure 9. Phase diagram between the relative content of PVA/SiO$_2$/H$_2$O and morphology of ES mats.

PVA:SiO$_2$:H$_2$O = 7:19:75, work distance = 10 cm, and voltage = 15 kV. These conditions allow repeatable fabrication of necklace-like structures.

From the above results, we found that the weight ratio of PVA:SiO$_2$:H$_2$O was the determinant for the morphology of ES composite. In Figure 9, we sketched a three-phase diagram to illustrate the relationship between the ingredients of solutions and the morphology of the ES composite. Pure PVA yields smooth fibers (bottom left); when SiO$_2$ is the overwhelming majority, SiO$_2$ particles tend to stack together (bottom right); when water is excessive, blackberry-like structures formed (top center); as PVA is in excess, fibers strung particles (bottom); when all the ingredients are well tailored, particles stack in a line and form necklace-like structures. The content of water is related to the viscosity of the solutions, which affects the diameter of the fibers. When the content of water increased, the viscosity of the solutions decreased, resulting in the small diameter of PVA fibers. When the diameter of PVA fibers was too small to pack the SiO$_2$ particles, the particles tended to aggregate and the blackberry-structure formed. But when the content of the water was insufficient, the viscosity of the solution was too high for the polymeric solution to eject from the orifice of the needle. Only well-tailored water content yielded appropriate viscosity, thus giving birth to necklace-like structures.

4. Conclusions

We utilized ES to fabricate necklace-like structures with PVA as the template polymer. The diameters of SiO$_2$ particles, voltage, and ingredient of solutions influenced the morphology of electrospun mats. We believe that the results and rules can provide a set of references to other systems (such as other polymers and particles[27]) for the fabrication of necklace-like structures, which

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will be useful in photoelectric devices,[2,5] sensor,[28] drug release,[1] and optical components.[3]

Supporting Information Available: Representative viscosity and conductivity data of solutions. This material is available free of charge via the Internet at http://pubs. acs.org.

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