A Teaching Procedure about Accurate Nanofabrication in Practice Education to Graduate Students

Hai-Peng LI, Xian-Ying WANG, Shi-You ZHENG, Ding WANG, Lai-Qiang LI, Xiao-Hong CHEN, Hao SUN, Yun TANG and Deng-Guang YU

School of Materials Science and Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China.

Keywords: Practice education, Nanofabrication, Teaching procedure, Electrospinning, Mathematical model.

Abstract. The suitable methods and procedures are very important for teaching the graduate students to learn how to begin their scientific research. In this paper, a teaching procedure was suggested about how to conduct accurate nanofabrication using electrospinning for improving the practice capability of graduate students. This procedure is useful for them to grasp the advanced nanotechnologies and advanced nanomaterials, to culture scientific research interests, and to deeply learn the related theories and mechanisms through self-promotion. The suggested procedure exhibits an approach for effective conducting practice education (particularly about the practice teaching of advanced technologies) to graduate students.

Background

The grasp of advanced modern technologies is very important for the graduate students majoring in natural science to deepen learning, to expand their knowledge and capabilities for their future career [3-4]. Advanced technologies not only can act as a useful platform to train their ability about scientific research, but also can provide an effective manner for fostering their creative learning and promote them to better integrate theory with practice. However, how to effectively transfer the related knowledge and particularly the practices associated with these advanced technologies to the graduate students often cudgel their supervisors’ brains: how to explain the related theories, how to carry out the experiments, and how to promote them to do innovative thinking? Thus, a suitable teaching procedure proceeding in an orderly way and step by step should be very important for them.

Figure 1. A schematic diagram showing the double-circle procedure for teaching the graduate students about accurate nanofabrication in practice education.
After many years’ studies about fundamental knowledge and also basic theories in their undergraduate studies, the graduate students are often keen to carry out scientific experiments, particularly when many undergraduate students have experienced the cognitive practices in their undergraduate courses. However, the systematic implementations of an advanced technology often mean a series of knowledge and separate experiences (accumulated in the undergraduate experiments) need to be combined together. Thus, the start point is a very important step because of “well begun, half done”.

Taking experiments about nanofabrications using the advanced coaxial electrospinning as examples, here we demonstrate that a double-circle teaching procedures for conducting practice teaching to the graduate students majoring in materials sciences and engineering. A schematic diagram is shown in Fig. 1 with an emphasis on the repeating of the starting step about nanofabrications. CIRCLE I shows a routine and systematic procedure for developments of novel nanoproducts: studying basic theories in classroom, doing cognitive practices about advanced nanotechnologies, conducting experiments about nanofabrications, carrying out a series of characterizations on the nanoproducts. CIRCLE II exhibits the most important step about nanofabrications, where repeated attempts and tests are inevitable: creating the junior samples, evaluating the key properties (e.g. the diameter of nanofibers here), and designing the improvement measures to repeat the experiments.

**Modified Coaxial Electrospinning**

Taking modified coaxial electrospinning as the model advanced nanotechnology, a teaching procedure about accurate nanofabrication in practice education to graduate students is developed. A schematic diagram of the modified coaxial electrospinning process with a solvent as the sheath fluid is shown in Fig. 2. As an advanced method for creating nanofibers, traditional coaxial electrospinning has the capability, flexibility, and utility for producing core/sheath nano- and micro-structures through a concentric spinneret that can accommodate two different liquids [1-8]. It was once regarded as one of the most significant breakthroughs in the electrospinning field, and has been applied broadly in controlling the secondary structures of nanofibers, encapsulating drugs and biological agents into polymer nanofibers, preparing nanofibers from materials that lack filament-forming properties, and enclosing functional liquids within an existing fiber matrix [9–17].

![Figure 2](image.png)

**Figure 2.** A schematic diagram of the modified coaxial electrospinning. $F_s$ represents shell fluid flow rate. When $F_s=0$ mL/h, it is a traditional one-fluid electrospinning; When $F_s>0$ mL/h, it is a double-fluid modified coaxial electrospinning.

The common sense is that sheath fluids utilized in the traditional coaxial processes must have enough viscosity to overcome the interfacial tension caused by “viscous dragging” and “contact friction” between two solutions for a successful working process [18,19]. However, a modified
coaxial electrospinning was firstly reported by Yu and his co-workers [20], which is characterized by unspinnable sheath fluids such as pure solvents, mixed solvents, solutions with small-sized molecules, and dilute polymer solutions [21-23]. The modified coaxial process is not only useful in generating novel core-sheath nanostructures and nanocoating, but is also very useful in accurate manipulation of nanofibers’ diameters. The modified coaxial system consists of four elements. Compared with the one-fluid electrospinning, it has an additional syringe pump and a concentric spinneret to lead the two working fluids. Shown in Fig. 2, Fs represents shell fluid flow rate. When Fs=0 mL/h, it is a traditional one-fluid electrospinning; When Fs>0 mL/h, it is a double-fluid modified coaxial electrospinning.

Accurate Nanofabrication of Electrospun Nanofibers

It is not easy for a traditional single-fluid electrospinning to manipulate the resultant nanofibers’ diameters in a controllable manner because of the mutual influences of many factors during the electrospinning processes. The advanced modified coaxial electrospinning shows its advantages in manipulating the nanofibers’ diameters through the variations of sheath fluids’ properties (such as components and compositions of the mixed solvents, solvents with different boiling points, surface tensions and conductivities). For example [24], the different boiling points can be taken as the key factor in the generation of ethyl cellulose (EC) nanofibers. Shown in Fig. 3, as solvent boiling point increases: methanol (65 °C) < ethanol (78 °C) < DMF (155 °C), the resultant nanofibers diameter decreases: methanol (670 ± 130 nm) > ethanol (410 ± 110 nm) > DMF (300 ± 140 nm). Provided the boiling point of the gas (the single fluid electrospinning for preparation of F1 nanofibers was conducted in the open atmosphere) is the ambient temperature (21 °C), an inverse relationship between solvent boiling points and diameters of nanofiber can be described as

\[ D (\text{nm}) = 841 - 3.71T (\degree C) \]

with a correlation coefficient of 0.9753 (Figure 2(e)), where D is the nanofibers’ diameter and T is the temperature of solvent boiling point. These results demonstrate that boiling points play a key role in controlling the diameter of nanofibers. Based on this example, the graduate students can significantly deepen their learning about the advanced nanotechnology, tell clearly the subtle differences between different kinds of electrospinning processes, and how to carry out experiments to realize the accurate nanofabrications. Certainly, this experience can also provoke the students’ interests about the practices of advanced technologies, provoke them to carry out more experiments, lead them to do researches and investigations in a more innovative manner.

![Figure 3. Nanofiber diameters’ distributions: (a) none; (b) methanol; (c) ethanol; (d) FDMF; and (e) the relationships between the EC nanofibers’ diameter and the sheath boiling point [24].](image-url)
The above-mentioned example can be taken as a template to a series of other polymers and composite. For instance [25], with a co-dissolving solution consisting of poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) in a mixture of dichloromethane (DCM)/N,N-dimethylformamide (DMF) as the core working fluid, a series of solvent mixtures with a varied compositions could be exploited as the sheath fluids to fabricate nanofibers and meanwhile accurately manipulate their diameters. With the ratios of DMF increased from 0% to 20%, 40%, 60%, and to 80%, the resultant composite nanofibers had an average diameter and distribution of 610 ± 150 nm, 460 ± 110 nm, 270 ± 80 nm, 220 ±50 nm, and 180 ±50 nm, respectively (Fig. 4a to 4e). The trend is obvious that the more the DMF the smaller the nanofibers’ diameters. To disclose the trend and find the inner relationship between the nanofibers’ size and the sheath solvent compositions in a quantitative manner, both linear equation and exponential equation were exploited to fit the statistical data. The results were shown in Fig. 4f (linear equation) and 4g (exponential equation). The linear equation is $D=557-530V_r$ with a correlation coefficient of $R^2=0.9023$, reflecting a poor linear relationship between them. However, the regressed exponential equation $D=162V_r^{-0.61}$ gives a correlation coefficient value of $R^2=0.9922$, suggesting a fine relationship. Thus, the exponential equation was better than the linear one in reflecting the influence of sheath solvent compositions on the nanofibers’ diameters, and it could be effectively utilized to accurately predict the diameter of electrospun nanofibers. These examples clearly taught the students that the fundamental mathematic equations and models can be utilized to summarize and deduce the protocols for accurate nanofabrication of electrospun nanofibers using the modified coaxial electrospinning.

Figure 4. The average diameter and distribution of the prepared nanofibers under the volume ratio of DMF in the mixture with dichloromethane: (a) 0%; (b) 20%; (c) 40%; (d) 60%; (e) 80%. (e) and (f) different equations were exploited to fit the statistical data about diameters: linear equation; and exponential equation, respectively [25].
Deepen Learning about Microfabrication Mechanism

The repeated experiments for accurate nanofabrications during the CIRCLE II directly represent the improvements of the students’ practice skills. However, to train them in a systematic way, the CIRCLE II must go back to CIRCLE I to finish the whole teaching procedure. In CIRCLE I, the integration of theory with practice is the key content. Thus, based on the above examples, the students can be taught to think about the mechanisms about accurate nanofabrications, the common contents among different specific examples. From the results about EC and PCL/PTMC composite nanofibers, it is clear that the solvent DMF in the sheath fluid always played the key roles in reducing the nanofibers. A microformation mechanism was shown in Fig. 5. DMF has a high boiling point of 153 °C, meaning very difficult to be exhausted during the electrospinning processes. The more DMF in the sheath fluid, the more difficult it was exhausted during the electrospinning. Thus in turn, the longer time period the fluid jets were subjected to the electrical force drawing and the nanofibers with smaller diameters were generated. When excessive DMF was added into the sheath mixture, non-linear morphologies were generated because the DMF made the polymeric fluids lose their resistances to the electrical drawing.

![Figure 5](image_url)

**Figure 5.** The suggested mechanisms about the influences of DMF contents in the sheath solvent mixtures on the formation of polymeric nanofibers using modified coaxial electrospinning.

Summary

A teaching procedure with two circles was developed for graduate students to learn how to begin their scientific researches. The teaching procedure was suggested with the accurate nanofabrication using modified coaxial electrospinning as the teaching materials, which was useful for improving the practice capability of graduate students. Meanwhile, the developed procedure should promote the graduate students to grasp the advanced nanotechnologies and advanced nanomaterials in a more effectively manner, to culture their scientific research interests, and to deepen learning about the related theories and mechanisms. The suggested procedure paves a way for conducting other practice educations (particularly about the practice teaching of advanced technologies) to graduate students.

Acknowledgements

The financial supports from the following projects are appreciated: the Shanghai Education Science Research Project (C17058), the National Natural Science Foundation of China (No. 51373101), the 2017 Graduate curriculum reform project in USST, and the College Student Innovation Project of USST (Nos. XJ2017286, SH2017189-190-191).

References

[1] D.G. Yu, K. White, N. Chatterton, Y. Li, L. Li, X. Wang, Structural lipid nanoparticles self-assembled from electrospun core-shell polymeric nanocomposites, RSC Adv., 5 (2015) 9462-9466.
[2] U.E. Illangakoon, D.G. Yu, B.S. Ahmad, N.P. Chatterton, G.R. Williams, 5-Fluorouracil loaded Eudragit fibers prepared by electrospinning, Int. J. Pharm., 495 (2015) 895-902.

[3] X.Y. Li, Z.B. Zheng, D.G. Yu, X.K. Liu, Y.L. Qu, H.L. Li, Electrospayed spherical ethyelcellulose nanoparticles for an improved sustained-release profile of anticancer drug, Cellulose, 24 (2017) 5551-5564.

[4] D.G. Yu, J.J. Li, M. Zhang, G.R. Williams, High-quality Janus nanofibers prepared using three-fluid electrospinning, Chem. Commun., 53 (2017) 4542-4545.

[5] D.G. Yu, X.Y. Li, X. Wang, J.H. Yang, S.W.A. Bligh, G.R. Williams, Nanofibers fabricated using triaxial electrospinning as zero order drug delivery systems, ACS Appl. Mater. Interfaces, 7 (2015) 18891-18897.

[6] Y.H. Wu, D.G. Yu, X.Y. Li, A.H. Diao, U.E. Illangakoon, G.R. Williams, Fast-dissolving sweet sedative nanofiber membranes, J. Mater. Sci., 50 (2015) 3604-3613.

[7] G. Chen, Y. Xu, D.G. Yu, D.F. Zhang, N.P. Chatterton, K.N. White, Structure-tunable Janus fibers fabricated using spinnerets with varying port angles, Chem. Commun., 51 (2015) 4623-3626.

[8] D.G. Yu, C. Yang, M. Jin, G.R. Williams, H. Zou, X. Wang, S.W.A. Bligh, Medicated Janus fibers fabricated using a Teflon-coated side-by-side spinneret, Colloid. Surface. B, 138 (2016) 110-116.

[9] C. Yang, D.G. Yu, D. Pan, X.K. Liu, X. Wang, S.W.A. Bligh, G.R. Williams, Electrospun pH-sensitive core-shell polymer nanocomposites fabricated using a tri-axial processes, Acta Biomater., 35 (2016) 77-86.

[10] M. Jin, D.G. Yu, X. Wang, C.F.G.C. Geraldes, G.R. Williams, S.W.A. Bligh, Electrospun contrast agent-loaded fibers for colon-targeted MRI, Adv. Healthcare Mater., 5 (2016) 977-985.

[11] M. Jin, D.G. Yu, C.F.G.C. Geraldes, G.R. Williams, S.W.A. Bligh, Theranostic fibers for simultaneous imaging and drug delivery, Mol. Pharm., 13 (2016) 2457-2465.

[12] X. Wang, X.Y. Li, Y. Li, H. Zou, D.G. Yu, J.S. Cai, Electrospun acetaminophen-loaded cellulose acetate nanofibers fabricated using an epoxy-coated spinneret, E-polymers, 15 (2015) 311-315.

[13] X. Wang, D.G. Yu, X.Y. Li, S.W.A. Bligh, G.R. Williams, Electrospun medicated shellac nanofibers for colon-targeted drug delivery, Int. J. Pharm., 490 (2015) 384-390.

[14] Y.H. Wu, C. Yang, X.Y. Li, J.Y. Zhu, D.G. Yu, Medicated nanofibers fabricated using NaCl solutions as shell fluids in a modified coaxial electrospinning, J. Nanomater., 2016 (2016) Article ID 8970213.

[15] Y.H. Wu, D.G. Yu, J.J. Li, Q. Wang, H.P. Li, X.Y. Li, Medicated multiple-component polymeric nanocomposites fabricated using electrospraying, Polym. Polym. Compos., 25 (2017) 57-62.

[16] B. Sanchez-Vazquez, A.J. Amaral, D.G. Yu, G. Pasparakis, G.R. Williams, Electrospayed Janus particles for combined photo-chemotherapy, AAPS PharmSciTech, 18 (2017) 1460-1468.

[17] Y.H. Wu, H.P. Li, X.X. Shi, J. Wan, Y.F. Liu, D.G. Yu, Effective utilization of the electrostatic repulsion for improved alignment of electrospun nanofibers, J. Nanomater., 2016 (2016) Article ID2067383.

[18] Y.Y. Yang, M. Zhang, Z.P. Liu, K. Wang, D.G. Yu, Meletin sustained-release gliadin nanoparticles prepared via solvent surface modification on blending electrospray, Appl. Surf. Sci., 434 (2018) 1040-1047.

[19] Y. Xu, J.J. Li, D.G. Yu, G.R. Williams, J.H. Yang, X. Wang, Influence of the drug distribution in electrospun gliadin fibers on drug-release behavior, Eur. J. Pharm. Sci., 106 (2017) 422-430.
[20] Z.P. Liu, Y.Y. Zhang, D.G. Yu, D. Wu, H.L. Li, Fabrication of sustained-release zein nanoparticles via modified coaxial electrospraying, Chem. Eng. J., 334 (2018) 807-816.

[21] Q. Wang, D.G. Yu, S.Y. Zhou, C. Li, M. Zhao, Fabrication of amorphous electrospun medicated-nanocomposites using a Teflon-based concentric spinneret, e-Polymer, 18 (2017) DOI: https://doi.org/10.1515/epoly-2017-0110.

[22] Y.H. Wu, D.G. Yu, H.P. Li, X.Y. Wu, X.Y. Li, Medicated structural PVP/PEG composites fabricated using coaxial electrospinning, e-Polymers, 17 (2017) 39-44.

[23] Q. Wang, D.G. Yu, L.L. Zhang, X.K. Liu, M. Zhao, Electrospun hypromellose-based hydrophilic composites for rapid dissolution of poorly water-soluble drug, Carbohydr. Polym., 174 (2017) 617-625.

[24] D.G. Yu, X.Y. Li, W. Chian, Y. Li, X. Wang, Influence of sheath solvents on the quality of ethyl cellulose nanofibers in a coaxial electrospinning process, Bio-med. Mater. Eng., 24 (2014) 695-701.

[25] Z.B. Zheng, C. Li, Y.C. Deng, Y.L. Qu, D. Wu, D.G. Yu, The Influence of sheath solvent compositions on the diameters of electrospun PCL/PTMC nanofibers, Adv. Eng. Res., 110 (2017) 196-202.