

Fabrication of Ascorbyl Palmitate Loaded Poly(caprolactone)/ Silver Nanoparticles Embedded Poly(vinyl alcohol) Hybrid Nanofibre Mats as Active Wound Dressings via Dual-spinneret Electrospinning

L. Du,^{ab} H. Z. Xu,^c T. Li,^a Y. Zhang,^{ab} and F. Y. Zou^{*ab}

^a School of Fashion Design & Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China.

^b Zhejiang Provincial Research Center of Clothing Engineering Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China.

^c Department of Bio-based Materials Science, Kyoto Institute of Technology, Kyoto 606-8585, Japan.

Corresponding author: F. Y. Zou, E-mail: zfy166@zstu.edu.cn; Fax: 86-571-86843249.

AgNO₃, which was selected as the source of Ag⁺ ions, was added to the PVA solution firstly. In this approach, the interaction of electropositive Ag⁺ ions with hydroxyl groups resulted in a stable Ag-OH chelate complex. With the adding of the reductant, the Ag⁺ ions in the chelate complex were in situ reduced by TP and would grow to AgNPs. The chelating effect between the Ag⁺ ions and hydroxyl groups in PVA and high viscosity of the PVA solution may play an important role in restricting the Ag crystal growth rate and AgNPs aggregation.^{1, 2} And therefore, we studied the chelating effects or the PVA concentration which is the dominant factor to control the size of AgNPs. Details of the series of solutions are given in Table S1.

Table S1 PVA solutions with different concentrations, AgNO₃ dose, and TP dose.

Sample Number	PVA Concentration	AgNO ₃ Dose (relative to the weight of PVA,	TP Dose (relative to the weight of AgNO ₃ ,
(A)	8	2	60
(B)	10	2	60
(C)	10	4	60
(D)	10	2	120

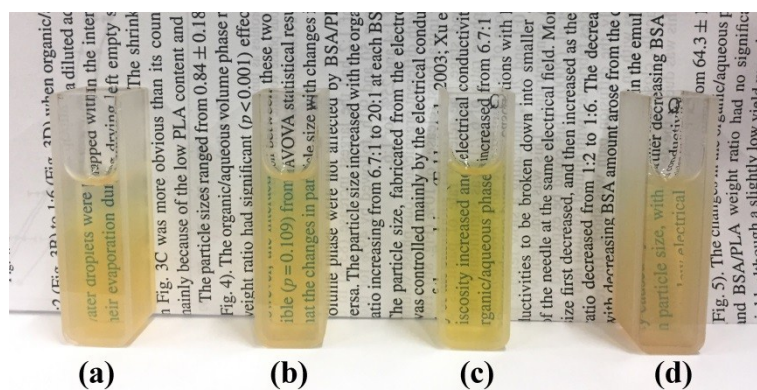


Fig. S1 Photos of 10 fold dilution different reaction solutions after 90 min.

Fig. S1 displays a photograph of glass vials containing AgNPs. The solution (C) showed clear bright yellow, and solution (A), (B) were also bright yellow but with slight turbid. However, the color of solution (D) changed to golden red. The color of the solution containing AgNPs is dependent on the particle size.³ Thus, the different solution colors are indicative of AgNPs of different sizes. The UV-vis spectra of these AgNPs/PVA precursor solutions can also provide

evidence for the formation of AgNPs with different sizes, which are shown in Fig. S2. With the increasing of the mass fraction of PVA from 8 wt% to 10 wt%, there was no dramatic UV peak shift. The two narrow UV peaks remained at around 435 nm. A red-shift can be obtained with the increased TP dose. However, with the increasing of Ag^+ , the UV peak of AgNPs moved to 430 nm and became sharper, indicating the hypsochromic shift of SPR peak. The absorption peaks move from 435 nm to 430 nm, and according to the literature, the smaller size of AgNPs could lead to hypsochromic shifts.⁴

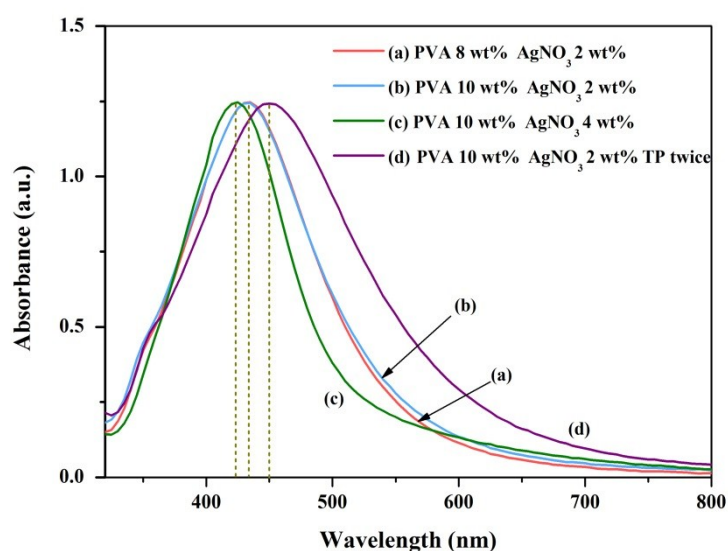


Fig. S2 UV-vis spectra of AgNPs in the different reaction systems.

The UV-vis results are according with the TEM images, which are shown Fig. S3. It is worth noting that, when the AgNPs were prepared with the excess reductant, a large average size of AgNPs (2.99 ± 0.46 nm) was observed, indicating the significant effects of the proper proportion of reductant on the size control. Meanwhile, the viscosity of PVA has no discernible effect on the size control. Although the smaller size of AgNPs could be obtained using the 4 wt% Ag^+ (relative to the weight of PVA), the excessive Ag^+ will enhance the cytotoxicity to the cells.

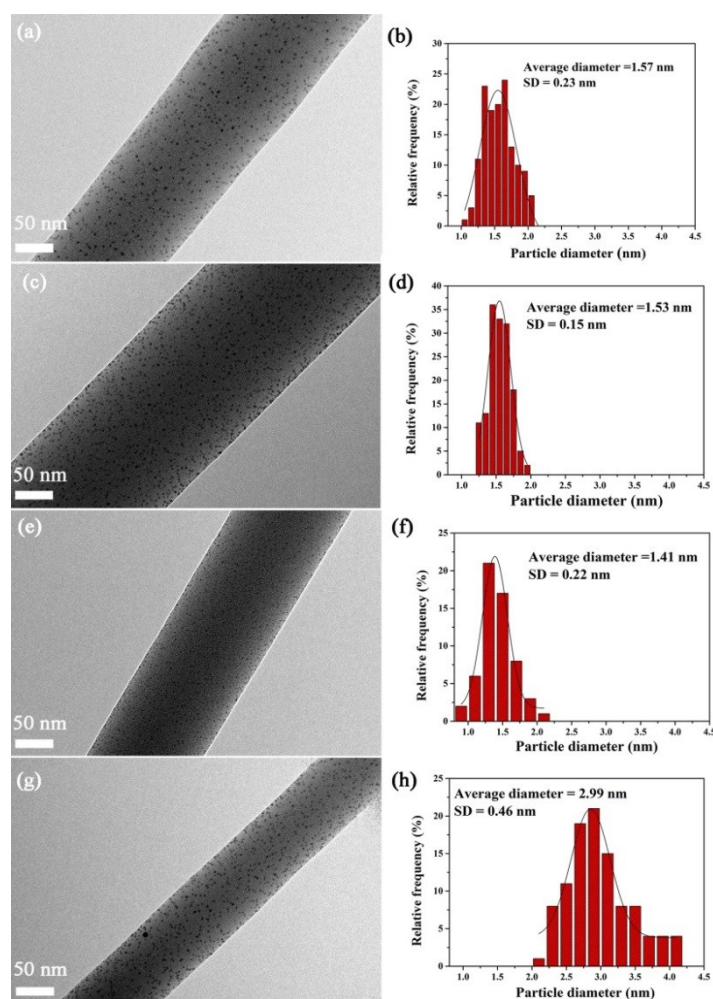


Fig. S3 TEM images of the PVA/AgNPs nanofibers with different average sizes of AgNPs by changing the solution proportioning.

Silver-ion Release Study

Silver-ion release behavior from the hybrid PVA/AgNPs was determined with atomic absorption spectroscopy (SPECTRAA 220, Varian, America). The phosphate buffered saline (PBS, pH = 5.5) was used as a releasing medium. 50 mg nanofibre mat was immersed in the 20 mL releasing medium in a 50 ml vial. The hybrid NFNs The vial was incubated at 37 °C and stirred at 100 rpm. 0.5 mL of the released solution was extracted at different time intervals, and 0.5 mL fresh medium was added to maintain a constant volume. Then the 0.5 mL taken released solution was diluted to 5 mL with fresh releasing medium solution to assess the quantity of silver-ion released. The calibration was conducted using an external standard between 1 and 1000 ppm.

Ag⁺ releasing profile in PBS solution was presented in Fig. S4. The release rate of the Ag⁺ showed an initial burst release during the first 12 hours after immersion in the releasing medium

and increased gradually thereafter. Silver ion release from AgNPs is a cooperative oxidation process requiring both protons and dissolved dioxygen.⁵ The initial burst release of Ag⁺ was possibly due to the diffusion of oxidized AgNPs that were adsorbed at the surface of the nanofibres. With the continuous swelling of PVA nanofibre, the AgNPs would have the chance to contact with the protons and dissolved dioxygen. The continuous slow and sustained release was followed. It is also remarkable to point out that about 70 % of the silver remained after 48 h, suggesting that most of the AgNPs were stable in the hybrid nanofibers mat. The rapid and constant release of the silver ion from the fibre can effectively inhibit bacterial growth at the wound site.

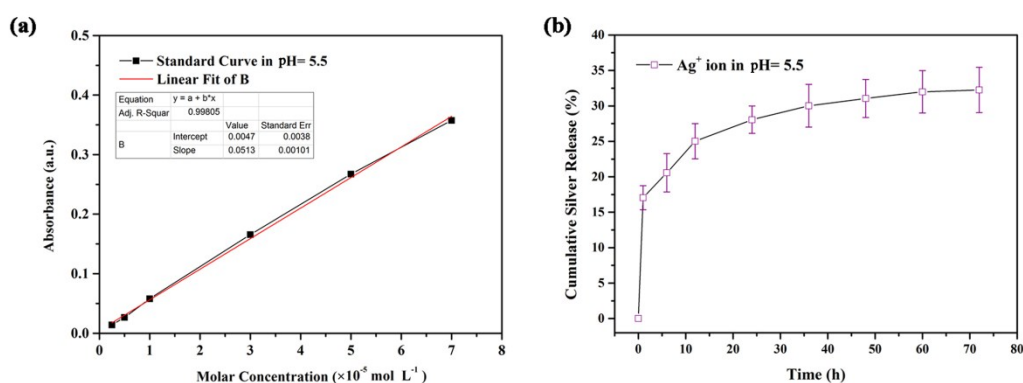


Fig. S4 (a) Standard curve at a pH of 5.5, (b) In vitro release profile of Ag⁺ from nanofibers mats as a function of time.

References

1. P. Wang, H. Zhu, S. Y. Bao, M. L. Du and M. Zhang, *J. Phys. D-Appl. Phys.*, 2013, **46**, 345303-345310.
2. H. Zhu, M. L. Du, M. L. Zou, C. S. Xu, N. Li and Y. Q. Fu, *J. Mater. Chem.*, 2012, **22**, 9301-9307.
3. K. Belser, T. V. Slenters, C. Pfumbidzai, G. Upert, L. Mirolo, K. M. Fromm and H. Wennemers, *Angew. Chem. Int. Ed.*, 2009, **48**, 3661-3664.
4. Y. Wan, Z. R. Guo, X. L. Jiang, K. Fang, X. Lu, Y. Zhang and N. Gu, *J. Colloid Interface Sci.*, 2013, **394**, 263-269.
5. J. Y. Liu and R. H. Hurt, *Environ. Sci. Technol.*, 2010, **44**, 2169-2175.