Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Materials for

Realizing Single-Crystalline Vertically-Oriented and High-Density Electrospun Nanofibril Bundles by Controlled Postcalcination

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Materials and Methods

1. Electrospinning synthesis of as-electrospun composite fibers

$SrCO_3$ NFBs have been fabricated by the electrospinning technique and subsequent calcinations. The chemicals were commercially available (Sinopharm Chemical Reagent Company) and used as received without further purification. For a typical procedure, 2.0 g polyvinyl alcohol (PVA1788, M_w ca. 66000 or *M*w = 996 kg/mol) powders were dissolved in 12.9 ml deionized water in one vial, and stirred at 343 K for 1 h, a viscous colorless solution of PVA was obtained. Meanwhile predetermined amounts of 1.2 g strontium acetate ($Sr(Ac)_2 \bullet 0.5\ H_2O$, purity of 99.9 %) powders was dissolved with 2.4 ml deionized water in another separate vial and slowly added to the PVA solution at rate of one drop/sec with constant stirring at 343 K for 3 h. The transparent buffer solution was maintained at 298 K for 5 h with magnetic stirring and then left for more than 15 hours to ensure complete dissolution and eliminate the air bubbles. The electrospinning was then undertaken using a home-made vertical needle-collector setup, and by employing the following conditions: a controlled flow rate at ~ 0.1 mL/h, applied voltage ~ 12.0 kV and tip-collector distance ~ 16 cm.

2. Multi-step atmospheric calcination of the SC $SrCO_3$ NFBs based on the calorimetry analysis

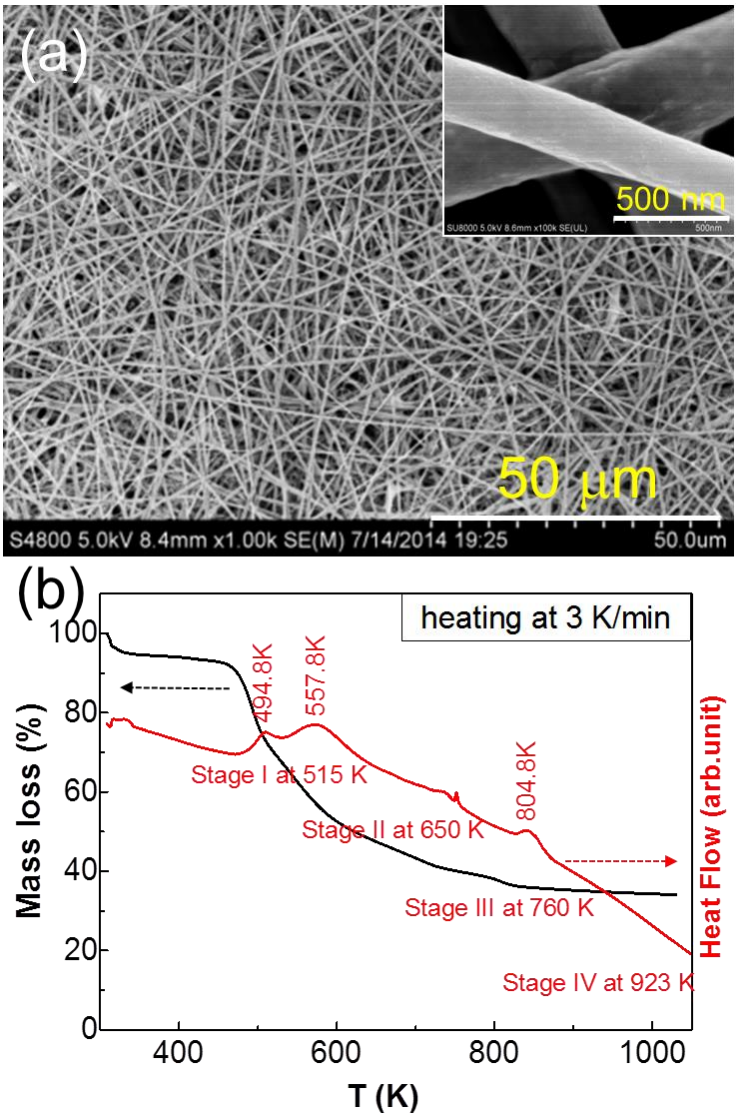

Figure S1 (a) SEM images of the strontium carbonate/PVA composite fibers with diameters of approximately ~ 400-600 nm, and a length of several hundred micrometers. Inset, SEM image with higher magnification. (b) Differential thermal analysis (DTA)-thermogravimetric analysis (TGA) curves of the as-electrospun composite fibers. Four stages were observed, and the first peak is responsible for the onset of PVA decomposition. The optimal calcination conditions for electrospun nanofibers was found via a two-step process in sequence: first sintering the as-electrospun PVA-containing composite fibers at a heating rate of 3 K/min under static atmosphere ambient to 646 K for 1 h, and subsequently sintering to 743 K for 1 h at the same heating rate and naturally cooling.

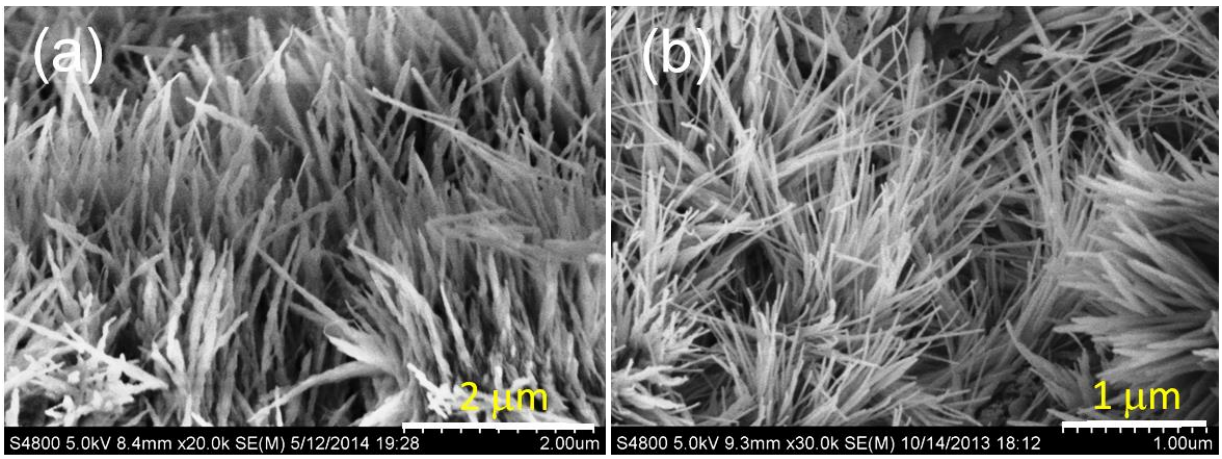

Figure S2 More SEM images of the as-calcined $SrCO_3$ NFBs.

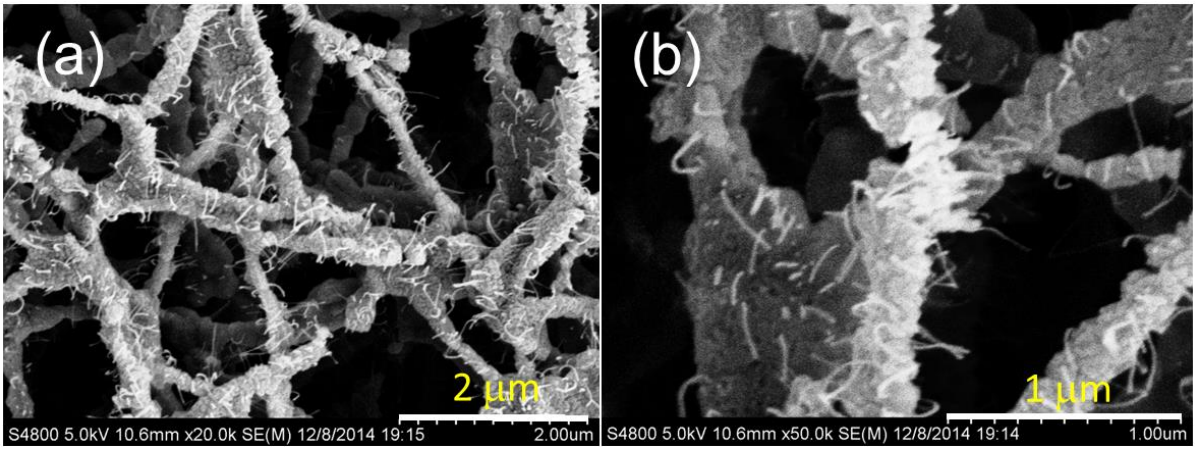

Figure S3 The SEM images show that the early stage of the optimal as-calcined product as follows: first sintering the as-electrospun PVA-containing composite fibers at a heating rate of 3 K/min under static atmosphere ambient to 646 K for 5 minutes, and subsequently sintering to 743 K for 5 minutes at the same heating rate and naturally cooling, reveals that the urchin-like nanostructures were formed.

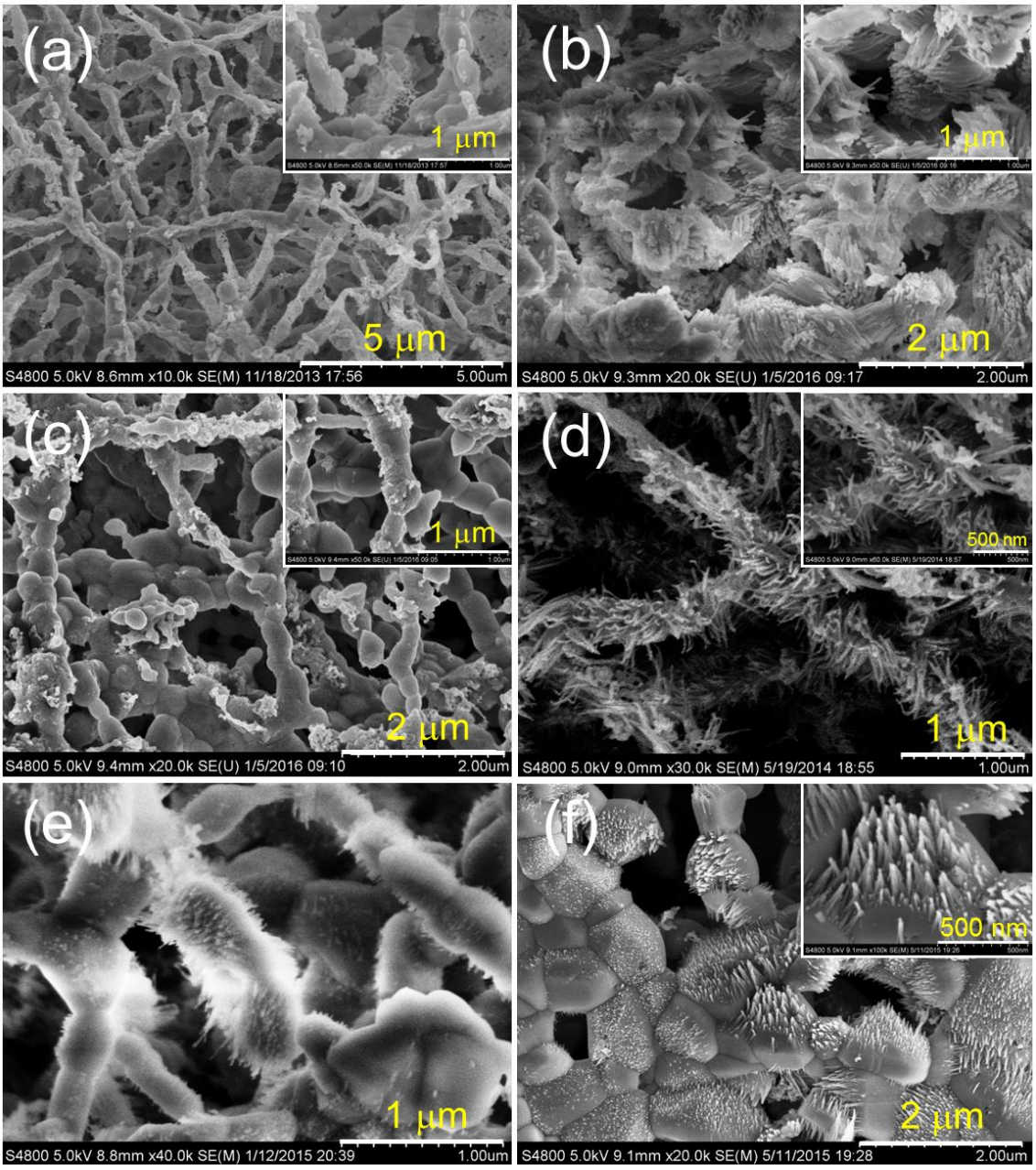

Figure S4 (a)-(f) SEM images of six unsuccessful schemes by one-step calcination cases. The effect of post-calcinations parameters on electrospun nanofibers was found very crucial. (a) At 1 K/min to 650℃ for 1h, (b) At 3 K/min to 650℃ for 2h, (c) At 3 K/min to 650℃ for 5min, (d) At 3 K/min to 600℃ for 2h, (e) At 5 K/min to 650℃ for 1h, (f) At 3 K/min to 725℃ for 1h and subsequently naturally cooling. Insets: SEM images with higher magnification. The as-calcined SC vertically-oriented electrospun $SrCO_3$ NFBs product is sensitive to the calcination parameters.

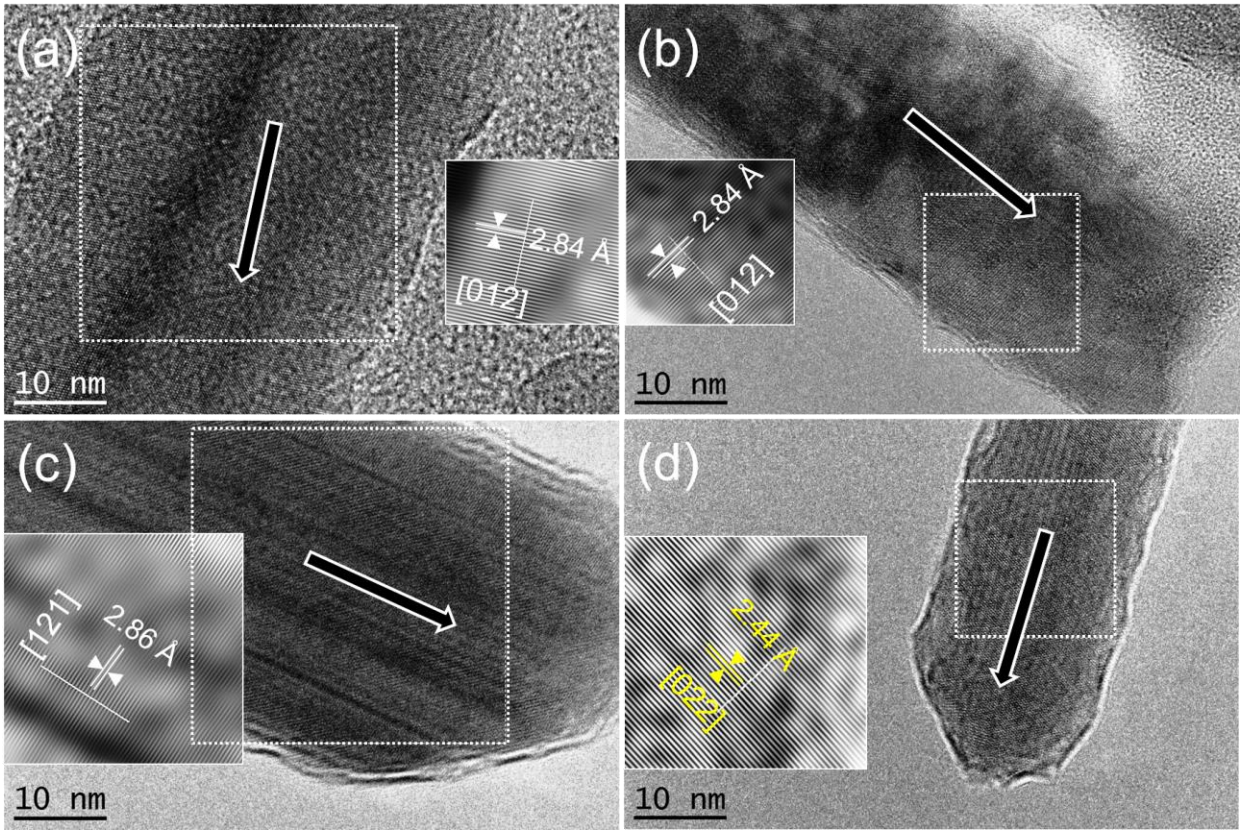

Figure S5 (a)-(d) More HRTEM images of the as-calcined $SrCO_3$ NNs. The white arrows guide the growth direction. Inset in (a), (b), (c) and (d), corresponding enlarged simulated HRTEM image of the white dotted box area shown in (a), (b), (c) and (d), indicates that the [012], [012], [121], and [022] growth direction of the as-calcined SC $SrCO_3$ NN, respectively.

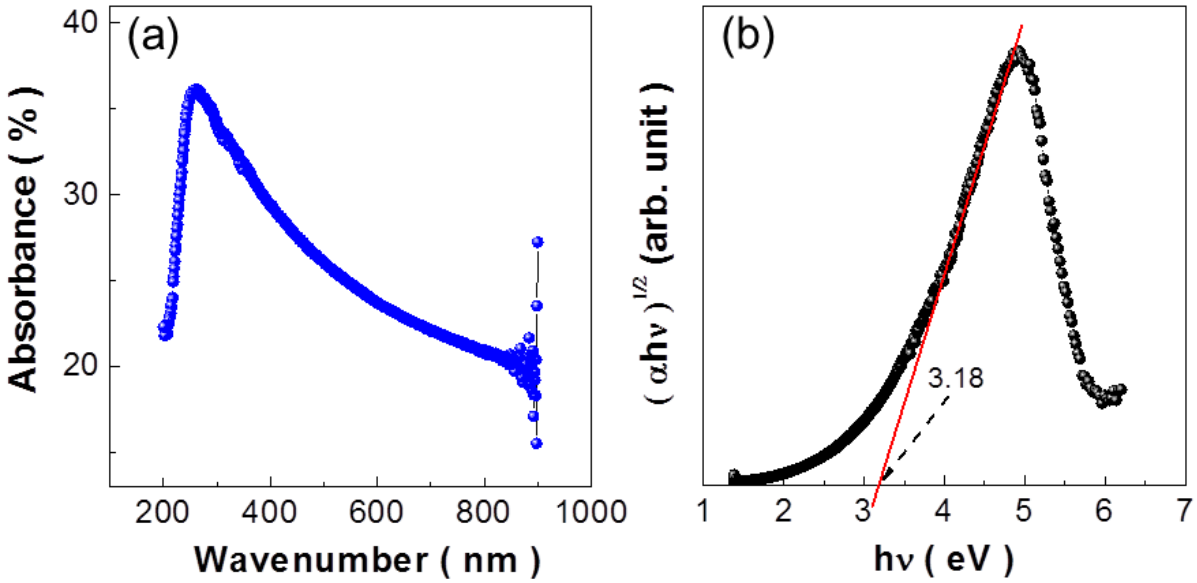

Figure S6 (a) Ultraviolet–visible absorbance (Agilent Technologies, Cary-5000) of the as-calcined $SrCO_3$ NFBs. (b) The optical band gap of the as-calcined $SrCO_3$ NFBs.

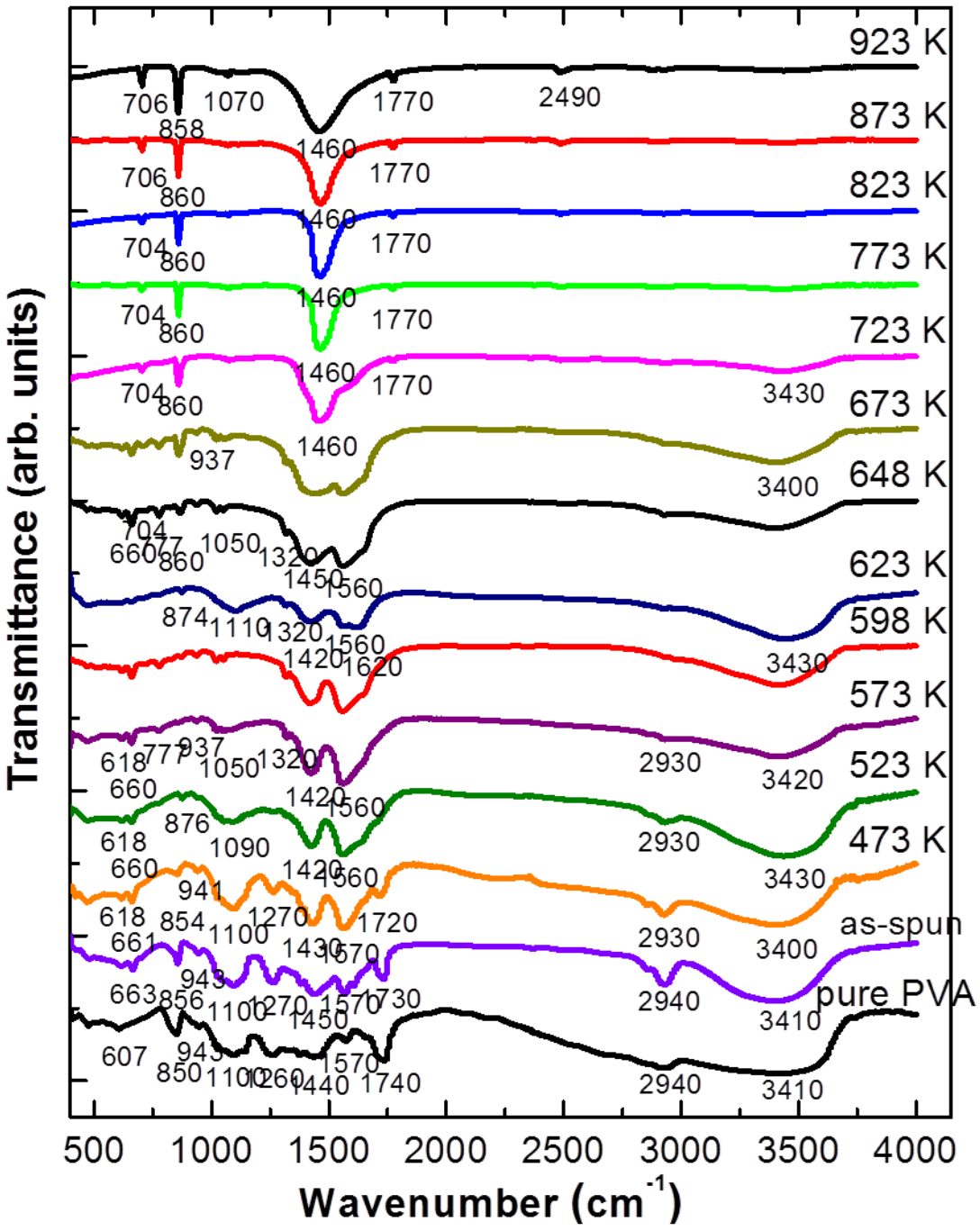

Figure S7 Sequential FTIR curves showing the crystallization of as-electrospun composite nanofibers and the as-calcined $SrCO_3$ NFBs. The FTIR measurements showed that the absorption bands of pure PVA, the as-spun composite fibers, and calcined at 473 K were very similar with characteristic peaks at 620 cm^{-1} (the out of plane bending C-OH), 860 cm^{-1} (the out of plane bending $[CO_3]^{2-}$ and C-C stretching), 940 cm^{-1} (the out of plane bending C-OH and C-C stretching), 1100 cm^{-1} (the out of plane

wagging vibration CH_2, C-OH stretching and C-C stretching), 1260 cm^{-1} (the out of plane wagging vibration CH_2), 1450 cm^{-1} (the in-plane bending vibration C-OH), 1460 cm^{-1} (the asymmetric $[CO_3]^{2-}$ stretching), 1770 cm^{-1} (the C=O stretching), and 2490 cm^{-1} (O–H stretching). When calcined at 573 - 598 K, the peak at 777 cm^{-1} (the out of plane wagging vibration CH_2) indicates the appearance of long chains of $-(CH_2)_n-$, and the formation of the vibrations in $[CO_3]^{2-}$ when further calcined at 573 - 598 K. When calcined at 723 K, the vibration in C-C bond cleavage is significant, showing that the long-range chain of PVA is broken. The absorption bands of samples calcined at 723 K, 773 K, 823 K, 873 K were very similar that there is only exists the vibrations in $[CO_3]^{2-}$, and absence of C-OH, O-H, and $-(CH_2)_n-$ is remarkable. The peak at 3400-3420 cm^{-1} (the O–H stretching vibration of residual water) was detected until 673 K. When calcined at 923 K, the sample had characteristic peaks at 706 cm^{-1} (the in-plane bending $[CO_3]^{2-}$), 858 cm^{-1} (the out of plane bending $[CO_3]^{2-}$ and C-C stretching), 1070 cm^{-1} (the symmetric $[CO_3]^{2-}$ stretching), 1460 cm^{-1} (the asymmetric $[CO_3]^{2-}$ stretching), and 1770 cm^{-1} (the C=O stretching), which indicated that $SrCO_3$ crystals were formed. The peak at 2490 cm^{-1} is probably due to the adsorbed H_2O in KBr matrix during the FTIR sample preparation.

References

Spectral Database for Organic Compounds,
http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi