Electronic Supplementary Material (ESI) for CrystEngComm.


# Revisit the calcination-induced multi-layer hollowing of electrospun solid fibers

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| Composition | EtOH | HAc | PVP | TNB | $VO(acac)_2$ | Ti:V (mole ratio) |
|---|---|---|---|---|---|---|
| Quality (g) | 5.0 | 2.0 | 1.0 | 1.0 | 0.1 | 7.97:1 |
| | 5.0 | 2.0 | 1.0 | 0.92 | 0.18 | 4.01:1 |
| Mass fraction (%) | 54.9 | 22.0 | 11.0 | 12.1 | | / |

**Table S1** The compositions of the electrospinning solution for $TiO_2$-$V_xO_y$ fibers.

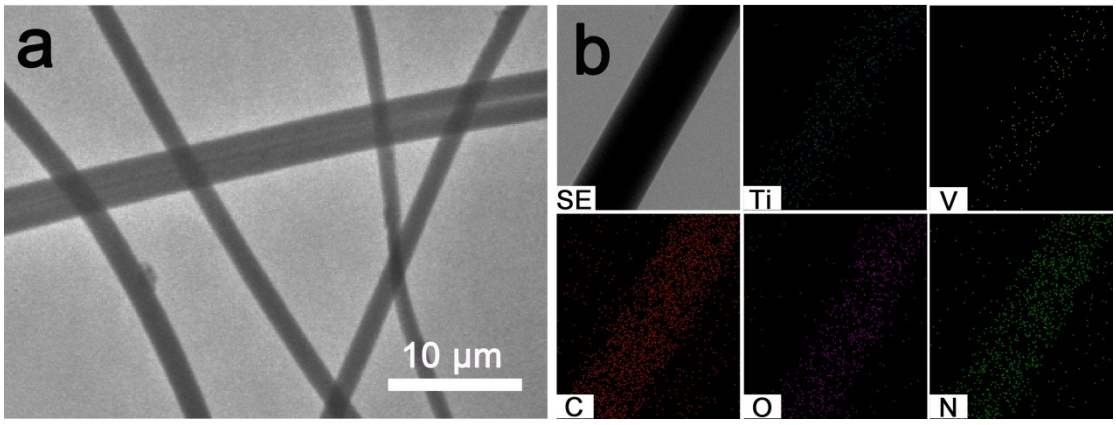


**Fig. S1** (a) TEM of the electrospun $TiO_2$-$V_xO_y$ fibers showing the uniform solid fiber. (b) The elemental mapping of Ti, V, C, O and N of the electrospun $TiO_2$-$V_xO_y$ fibers.

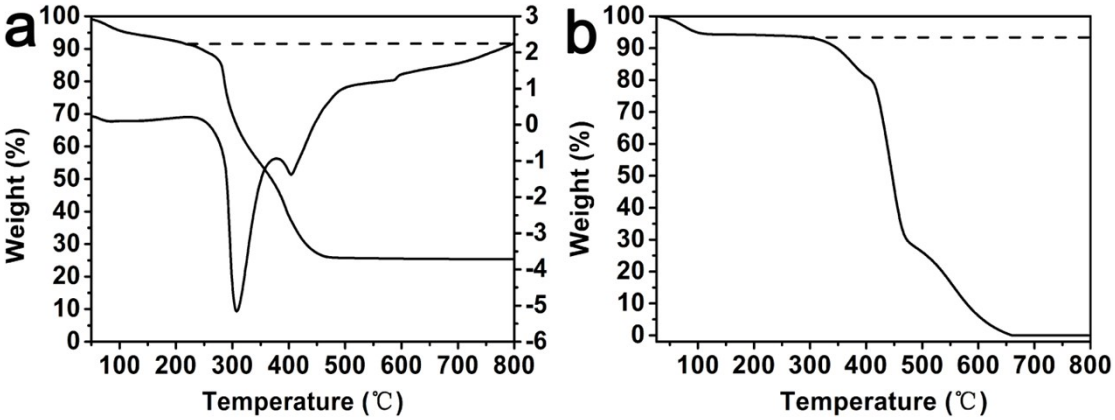


**Fig. S2** (a) TGA of the electrospun fiber of $TiO_2$-$V_xO_y$ showing two major weight-loss zones at RT-475 °C. RT-220 °C: evaporation or desorption of residue solvents, including ethanol, water, and acetic acid. 220-475 °C: a three-stage thermogravimetric process of PVP. (b) TGA of the electrospun fiber of PVP showing a similar three-stage thermogravimetric process at 320-650 °C with the corresponding temperature shifted to higher temperature range.

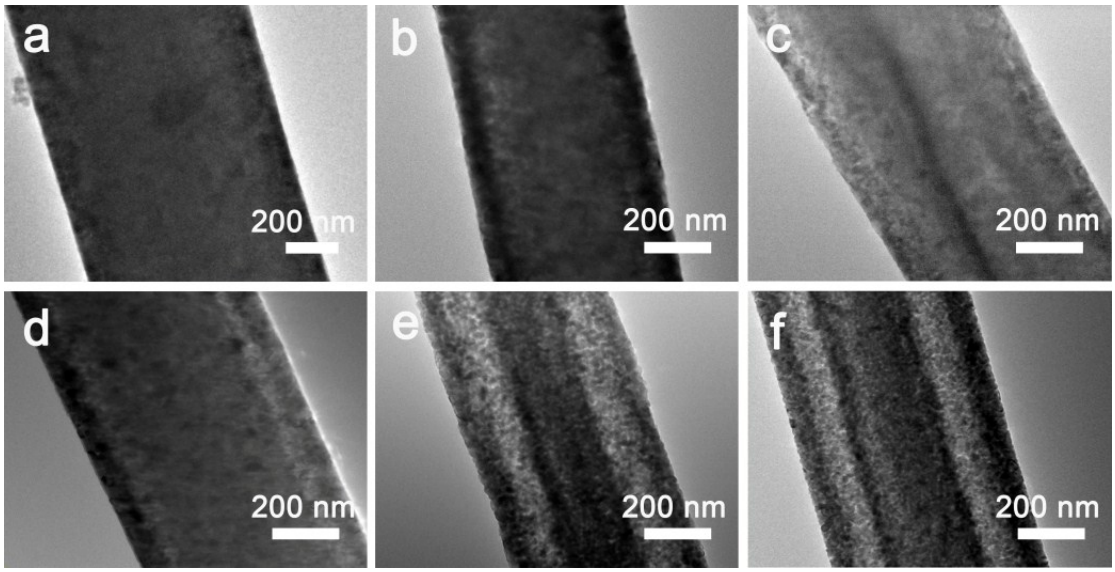


**Fig. S3** High magnification TEM showing the structural evolution of $TiO_2$-$V_xO_y$ calcined at 300 °C in air: (a) 5 min. (b) 15 min. (c) 30 min. (d) 60 min. (e) 90 min. (f) 6 h.

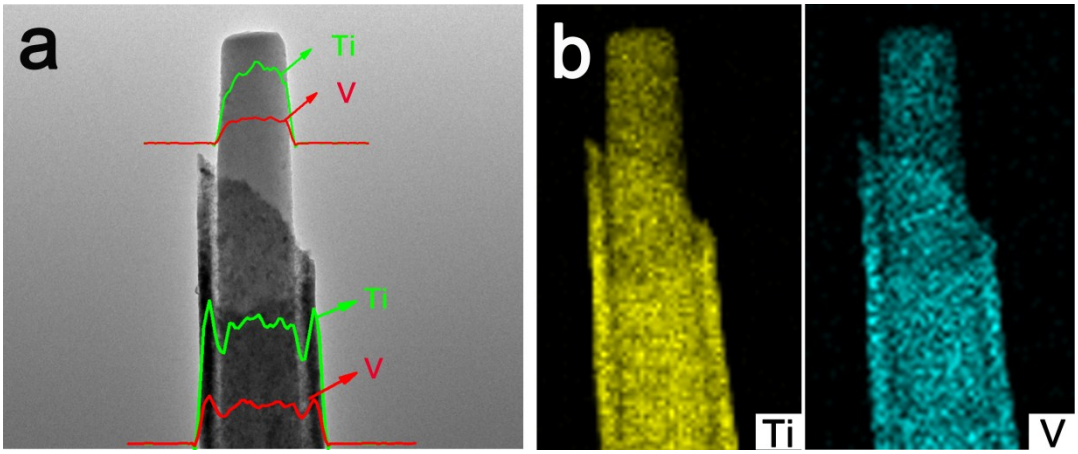


**Fig. S4** Characterizing chemical composition of the core (wire) and shell (tube): (a) Cross-sectional EDS line scan of Ti and V of the calcined fiber of $TiO_2$-$V_xO_y$ at 300 °C for 60 min in air. (b) Corresponding elemental mapping.

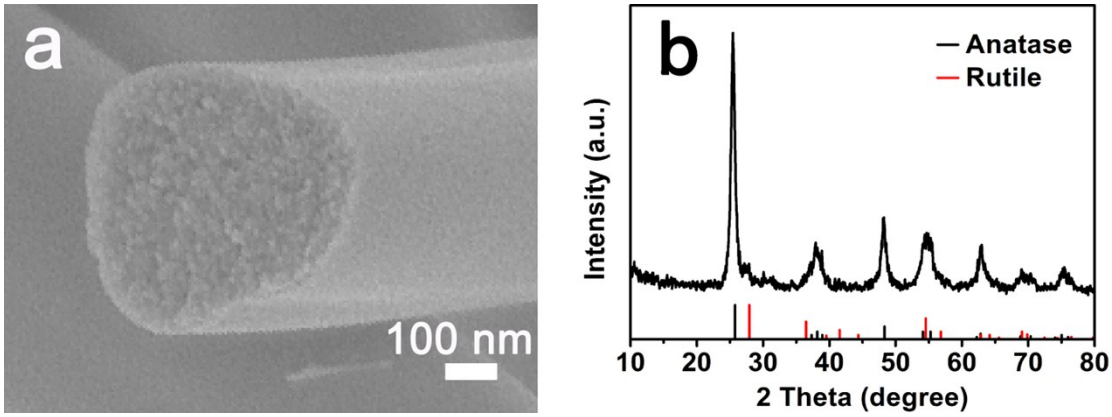


**Fig. S5** (a) High magnification SEM showing the solid fiber of pure $TiO_2$ calcined at 450 °C for 6 h in air. (b) Corresponding XRD patterns showing the anatase $TiO_2$.

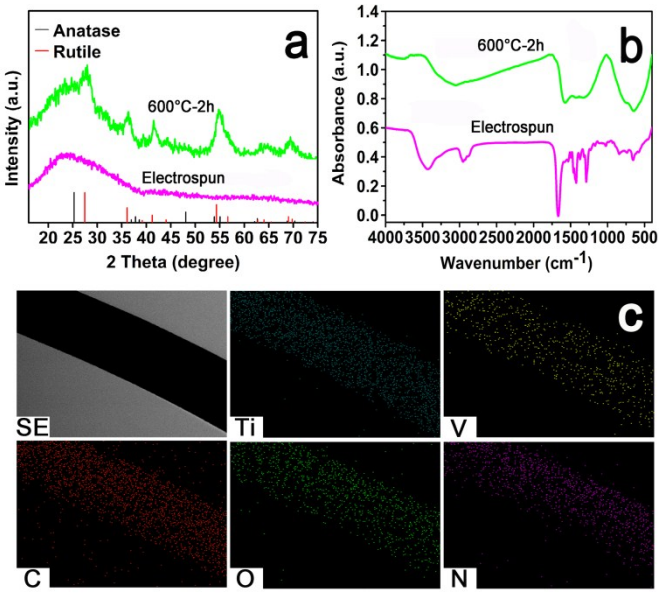


**Fig. S6** (a) XRD patterns of the electrospun fiber and the calcined fiber of $TiO_2$-$V_xO_y$ at 600 °C for 2 h in nitrogen. (b) Corresponding FTIR spectra at 600 °C for 2 h in nitrogen. (c) The elemental mapping of Ti, V, C, O and N of the calcined fiber of $TiO_2$-$V_xO_y$ at 600 °C for 2 h in nitrogen based on the EDX analysis.

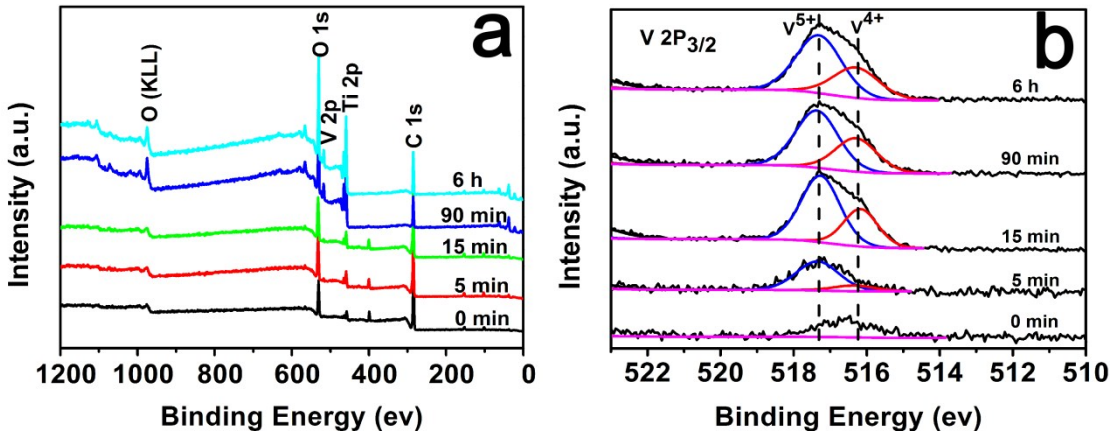


**Fig. S7** Characterizing the oxidation state of vanadium of $TiO_2$-$V_xO_y$ using XPS calcined at 300 °C in air: (a) XPS survey spectrum. (b) Deconvoluted XPS peak of V $2p_{3/2}$.

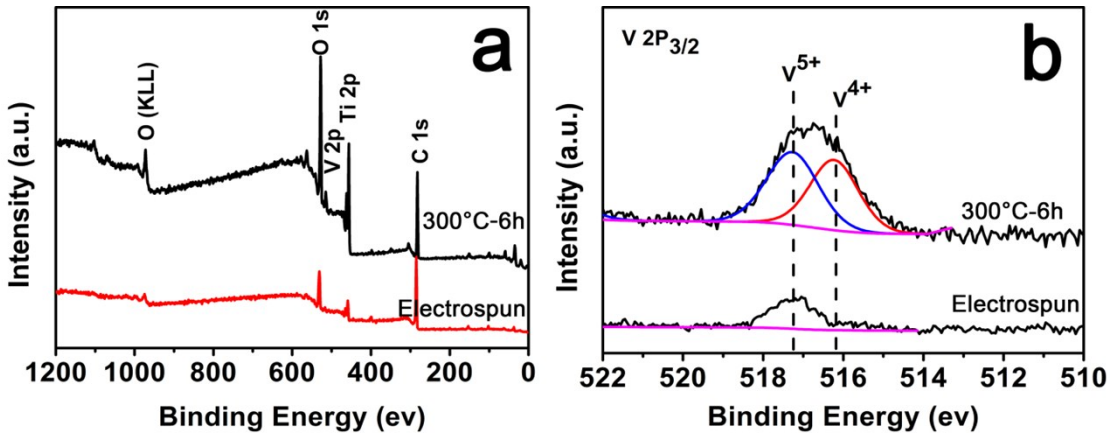


**Fig. S8** Characterizing the oxidation state of vanadium of a reference electrospun fiber of $TiO_2$-$V_xO_y$ from $NH_4VO_3$, and calcined at 300 °C for 6 h in air using XPS : (a) XPS survey spectrum. (b) Deconvoluted XPS peak of V $2p_{3/2}$.

**Table S2** The d-spacings of anatase (101) and rutile (110) of $TiO_2$-$V_xO_y$ during the calcination at 300 °C.

| Samples | d-(101) (Å) | d-(110) (Å) |
|---|---|---|
| Ti/V-300-6 h | 3.383 | 3.229 |
| Ti/V-300-90 min | 3.359 | 3.245 |
| Ti/V-300-60 min | 3.369 | 3.242 |

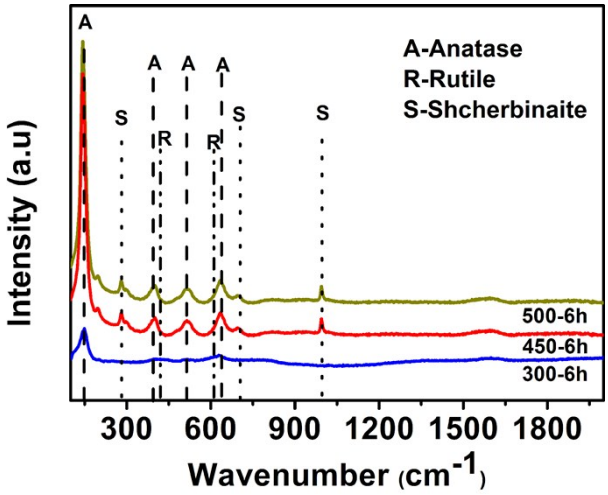


**Fig. S9** Raman spectra of the calcined fiber of $TiO_2$-$V_xO_y$ at 300, 450 and 500 °C.