## Supplementary material

Structural evolution of rayon-based carbon fibers

induced by doping boron

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**Fig. S1** A picture of the B<sub>4</sub>C/graphite crucible (BGC)

Mechanical properties of single carbon fiber were performed using a single fiber electronic tensile strength tester (LLY-06E, China). The specimens were prepared by fixing the filament on a paper holder with an instant cyanoacrylate adhesive, as reported elsewhere <sup>1</sup>. A gauge length of 20 mm and crosshead speed of 0.5 mm/min were applied for the tests. At least 50 measurements were done for each fiber specimens. All tests were finished at room temperature (23±3 °C, 50±5% relative humidity).



**Fig. S2** Mechanical properties of boron-doped RCFs treated to 2200 °C (a) tensile strength; (b) tensile modulus.



Fig. S3 Surface and cross-section morphologies by FE-SEM examination of the B1-24 (a, b) and B1-26 (c, d)



**Fig. S4** Mechanical properties of boron-undoped treated to different temperatures (a) tensile strength; (b) tensile modulus.



Fig. S5 XRD patterns of boron-undoped and boron-doped RCFs treated to 2400 and 2600 °C.



**Fig. S6** Room temperature Raman spectra of boron-undoped and boron-doped RCFs treated to (a) 2400 °C and (b) 2600 °C.



Fig. S7 TGA curves of boron-undoped and boron-doped RCFs treated to (a) 2400 °C and (b) 2600 °C

## References

1. K. Naito, Y. Tanaka, J. M. Yang and Y. Kayawa, *Carbon*, 2008, **46**, 189-195.