Supporting Information:

Experimental section:

Materials:

Poly(vinyl pyrrolidone) (PVP) (Mw ≈ 1300000, Aldrich), Tetrabutyl titanate [$Ti(OBu)_4$] (Beijing chemical reagents company), absolute ethanol (A.R., Beijing fine chemical Co., Ltd.), acetic acid (A.R., Beijing fine chemical Co., Ltd.), hydrochloric acid (A.R., Beijing fine chemical Co., Ltd.).

Preparation of TiO_2 microfiber:

0.5 g PVP powder was added to a mixture of 7.5 g absolute ethanol and 2.0 g acetic acid in a capped bottle. The solution was stirred for 1 hour to generate a homogeneous solution. Then 2.0 g $Ti(OBu)_4$ was added to the solution, the mixture was continuous stirred for 1 hour.

About 3 mL of the precursor solution was placed in a 5-mL syringe equipped with a blunt metal needle of 0.8 mm outer diameter and 0.6 mm inner diameter. The solution feed rate is 0.8 mL h^{-1}. A stainless steel plate covered with a sheet of aluminum foil was employed as the collector. The distance between the needle tip and collector was 15 cm, and the voltage was set at 15 kV. The as-collected nanofibers were calcined at 500℃ for 2 hours.

Synthesis of hierarchical TiO_2 nanostructure:

A homogenous solution was prepared by mixing 30 mL deionized water with 30 mL HCl. Then 2.0 mL $Ti(OBu)_4$ was injected into the solution in a 100 mL Teflon-lined autoclave. After vigorous stirring for 10 minutes, a piece of electrospun film, which was cut to suitable area to fit the size of autoclave, was put into the autoclave. Then autoclave was sealed and heated to 150℃ for 1-4 hours. The as-obtained product could be directly picked up by tweezers, which leave out centrifugation process. The film is washed with deionized water and ethanol to remove any ionic residual then dried in oven at 50℃ for 4 hours for further characterization.

Characterization:

The morphologies of samples were performed on Hitachi S-4300 Scanning Electron Microscopy (SEM) and JEM-2010 Transmission Electron Microsopy(TEM). Electron diffraction spectroscopy was carried on JEM-2010TEM at 200 kV.

Samples of as prepared TiO_2 fiber and hierarchical TiO_2 structures were characterized by X-ray powder diffraction (XRD) with a Mac Science MXP-AHF18 X-ray diffractometer using CuKa radiation.

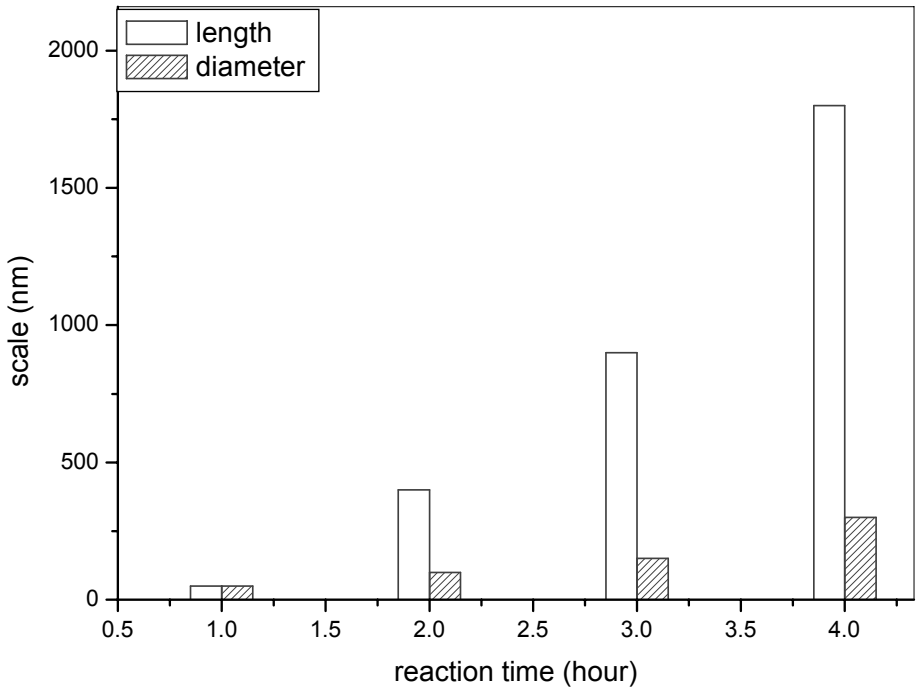

Figure S1. The correlation graph of the diameter and the length of TiO_2 nanorods of TiO_2 hierarchical nanostructure and the reaction time.

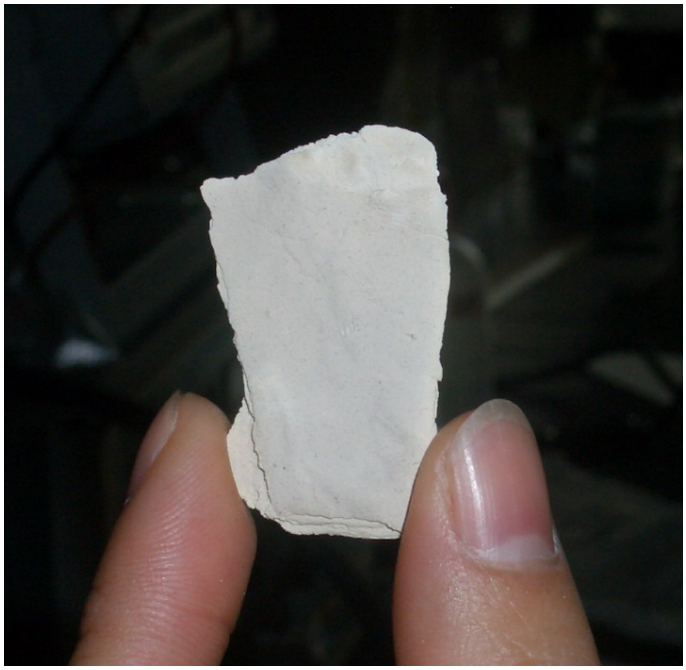

Figure S2. Photograph of self-supporting TiO_2 film prepared by combination of electrospinning method with hydrothermal approach.

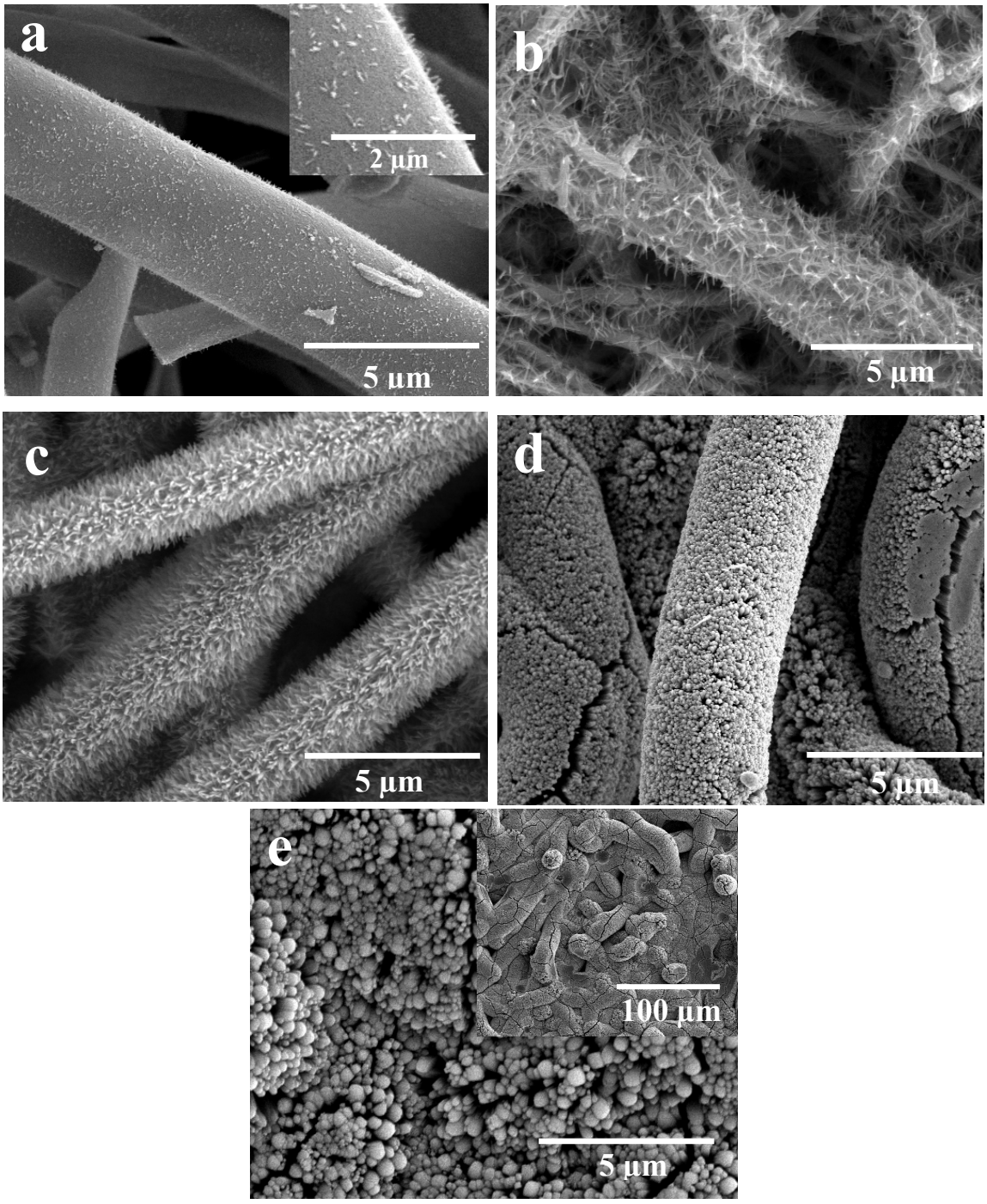

Figure S3. SEM images of hydrothermally treated TiO_2 fibers with the different quantity of $Ti(OBu)_4$ precursor a) 0.3mL; b) 0.5 mL; c) 1.0 mL; d) 3.0 mL; e) 4.0 mL.