

Supporting Information for:

Fabrication of Nanostructured Metal Nitrides with Tailored Composition and Morphology

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Characterization. XRD patterns of samples were recorded on a Rigaku D/max-2500 diffractometer with Cu KR radiation ($\lambda = 0.1542$ nm) at 40 kV and 200 mA. The products were characterized by TEM (FEI Tecnai F20) and SEM (JEOL 6701F) equipped with Energy Dispersive X-ray Spectroscopy detector (Oxford INCA). For the XPS analysis, a Kratos AXIS 165 multitechnique electron spectrometer was utilized. The nitrogen adsorption-desorption isotherms at 78.3 K were measured using a Quantachome AS-1 analyzer. Elements analysis was performed using a flash EA 1112 NC analyzer from Thermo Scientific. Metal elements analysis was conducted using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Shimadzu ICPE-9000).

Electrospinning of $\text{Ti}(\text{OBu})_4/\text{PVP}$ composite nanofibers. As a typical procedure, $\text{Ti}(\text{OBu})_4$ (1.5 mL) was mixed with acetic acid (2 mL) and ethanol (3 mL) under stirring. This solution was added to PVP (0.45g, $M_w \approx 1\,300\,000$, Alfa Aesar) and ethanol (7.5 mL) solution, followed by magnetic stirring for 1h. The precursor solution was then immediately delivered into a plastic syringe equipped with 23 gauge stainless steel needle. The needle was connected to a high-voltage supply (SL50P60, Spellman). A piece of grounded aluminum foil was placed 15 cm below the tip of the needle to collect the nanofibers. The voltage was set at 30 kV and the typical feeding rate for the solution was 1.0 mL/h using a syringe pump (KDS-200, Stoelting Co.).

Electrospinning of $\text{Nb}(\text{OC}_2\text{H}_5)_5/\text{PVP}$ composite nanofibers. $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (2 g, Alfa Aesar) was mixed with absolute ethanol (14 mL) under stirring. After 30 minutes, PVP (0.8g, $M_w \approx 1\,300\,000$, Alfa Aesar) was added to the above solution. The mixture was stirred for 1 hour to generate a homogeneous solution. Then the precursor solution was delivered into a plastic syringe equipped with 23 gauge needle made of stainless steel. The needle was connected to a high-voltage supply. A piece of grounded aluminum foil was placed 10 cm below the tip of the needle to collect the nanofibers. The voltage was set at 20 KV and the solution feeding rate was 1.0 mL h^{-1} .

Electrospinning of $\text{VO}(\text{OiPr})_3/\text{PVP}$ composite nanofibers. PVP (0.4 g, $M_w \approx 1$

300 000, Alfa Aesar) and (1-Hexadecyl)trimethylammonium bromide (CTAB) (0.1 g, Aldrich), which helps stabilize the spinning jet and improve the size uniformity of the resulting fibers, were added into 2-propanol (7 mL) instead of ethanol avoiding rapid hydrolysis of $\text{VO}(\text{OiPr})_3$. The mixture was stirred for 1 hour to obtain a homogenous solution. Then $\text{VO}(\text{OiPr})_3$ (1 mL, Alfa) was added into the solution, followed by magnetic stirring for about 1 hour. And then this precursor solution was immediately loaded into a plastic syringe equipped with 23 gauge needle made of stainless steel. The needle was connected to a high-voltage supply (SL50P60, Spellman). A piece of grounded aluminum foil was placed 15 cm below the tip of the needle to collect the nanofibers. The voltage was set at 30 KV and the typical feeding rate for the solution was set 1.0 mL h^{-1} .

Electrospinning of $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4/\text{PVP}$ composite nanofibers. Zirconium(IV) propoxide solution (1 mL, 70 wt%, Aldrich) was mixed with 2-propanol (12 mL) under magnetic stirring for 30 min. And then PVP (0.56 g, $M_w \approx 1\ 300\ 000$, Alfa) was added to the above solution, followed by magnetic stirring for about 2 hour. Then the precursor solution was delivered into a plastic syringe equipped with 23 gauge needle made of stainless steel. The needle was connected to a high-voltage supply. A piece of grounded aluminum foil was placed 15 cm below the tip of the needle to collect the nanofibers. The voltage was set at 30 KV and the solution feeding rate was 1.0 mL h^{-1} .

Electrospinning of $\text{Ti}(\text{OiPr})_4\text{-VO}(\text{OiPr})_3\text{-PVP}$ composite nanofibers. The respective amount of $\text{Ti}(\text{OiPr})_4$ and $\text{VO}(\text{OiPr})_3$ was dissolved in 2-propanol (10 mL) according to different Ti/V metal atomic ratio ranging from 0.5 to 1.5. PVP (0.57 g, $M_w \approx 1\ 300\ 000$, Alfa Aesar) and (1-Hexadecyl)trimethylammonium bromide (CTAB) (0.1 g, Aldrich) were added into 2-propanol (7 mL). And then this precursor solution was immediately loaded into a plastic syringe equipped with 20 gauge needle made of stainless steel. The needle was connected to a high-voltage supply (SL50P60, Spellman). A piece of grounded aluminum foil was placed 15 cm below the tip of the needle to collect the nanofibers. The voltage was set at 30 KV and the typical feeding rate for the solution was set 3.0 mL h^{-1} .

Multifluidic compound-jet electrospinning of $\text{Ti}(\text{OBu})_4/\text{PVP}$ multi-channel micro/nano tubes. Multi-channel micro/nano $\text{Ti}(\text{OBu})_4/\text{PVP}$ tubes were synthesized using a similar procedure to that reported by Zhao and co-workers.²² One to three metal capillaries were elaborately embedded in a plastic syringe and arranged at proper position and angles. The channel number is dependent on the number of inner metal capillaries. Two immiscible viscous liquids were fed into inner capillaries and a outer plastic syringe in an appropriate feeding rate, respectively. The as-prepared $\text{Ti}(\text{OBu})_4/\text{PVP}$ precursor solution with a proper concentration was loaded at outer syringe as outer liquid and the flow rate was set at 6 mL/h. Heavy mineral oil was chosen for inner fluid and pumped out separately from inner metal capillaries at a feeding rate of 0.4 mL/h using several syringe pumps simultaneously. Inner metal capillaries were connected to the cathode of high-voltage supply and a piece of aluminum foil was connected to the anode as a collecting substrate. The working voltage was set at 30 KV and the distance between the tip of nozzle and the substrate

is 25 cm. After the multifluidic compound-jet electrospinning process, a fibrous nonwoven mat was collected on Al foil. The mineral oil was extracted by immersing the mat in octane overnight and the multi-channel $\text{Ti}(\text{OBu})_4/\text{PVP}$ micro/nanotubes were obtained.

Synthesis of metal nitride materials. the as-collected electrospun precursor nanofibers or micro/nano tubes were peeled off from the aluminum foil and put into a tube furnace and were heated to desired temperature at a rate of 2 °C /min under ammonia (>99.999 % 100 sccm) gas flow and maintained for 3h. The heating temperature ranged from 400 °C to 1000 °C. The metal nitride samples were obtained as the sample was allowed to cool to the room temperature in the NH_3 gas flow.

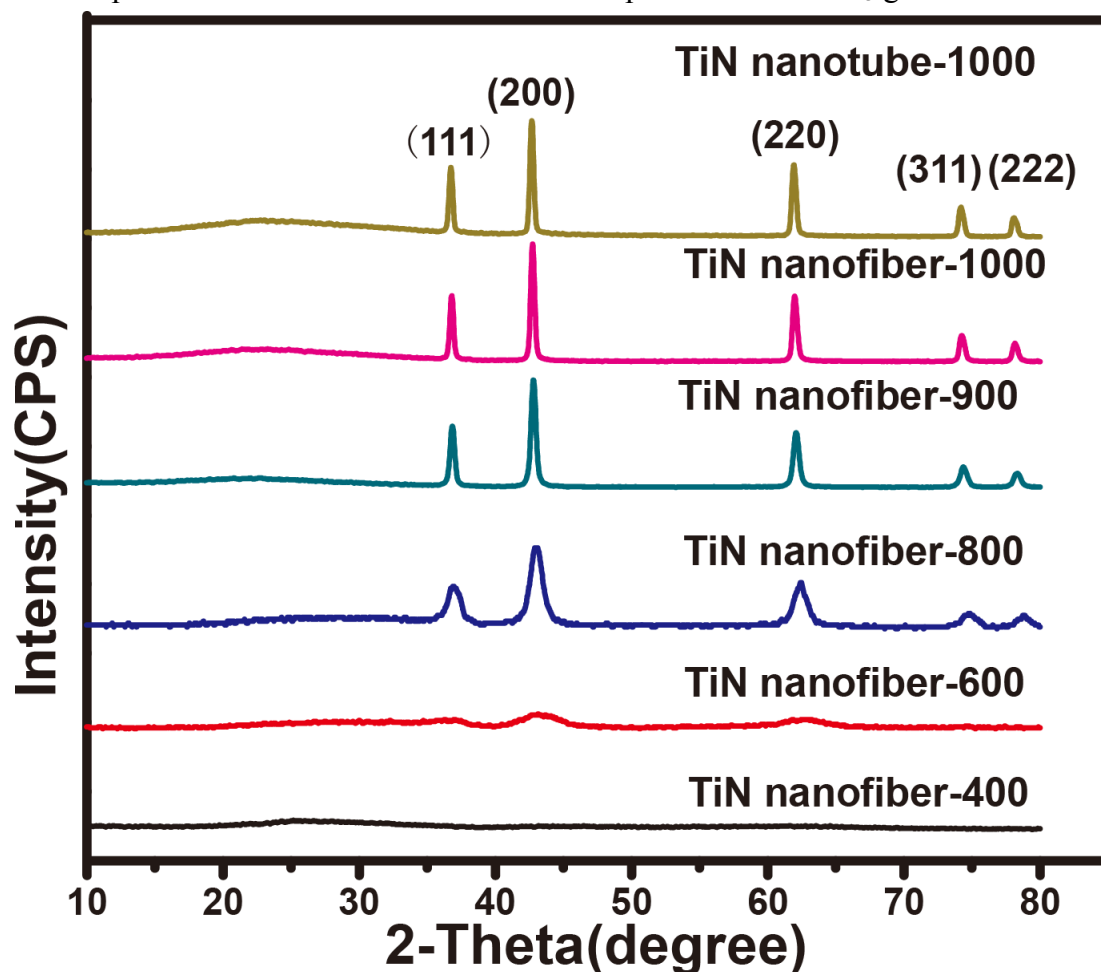


Fig. S1 Wide-angle X-ray diffraction (XRD) patterns of TiN nanofibers synthesized at different temperature ranging from 400 °C to 1000 °C as well as TiN single-channel micro/nanotubes obtained at 1000 °C.

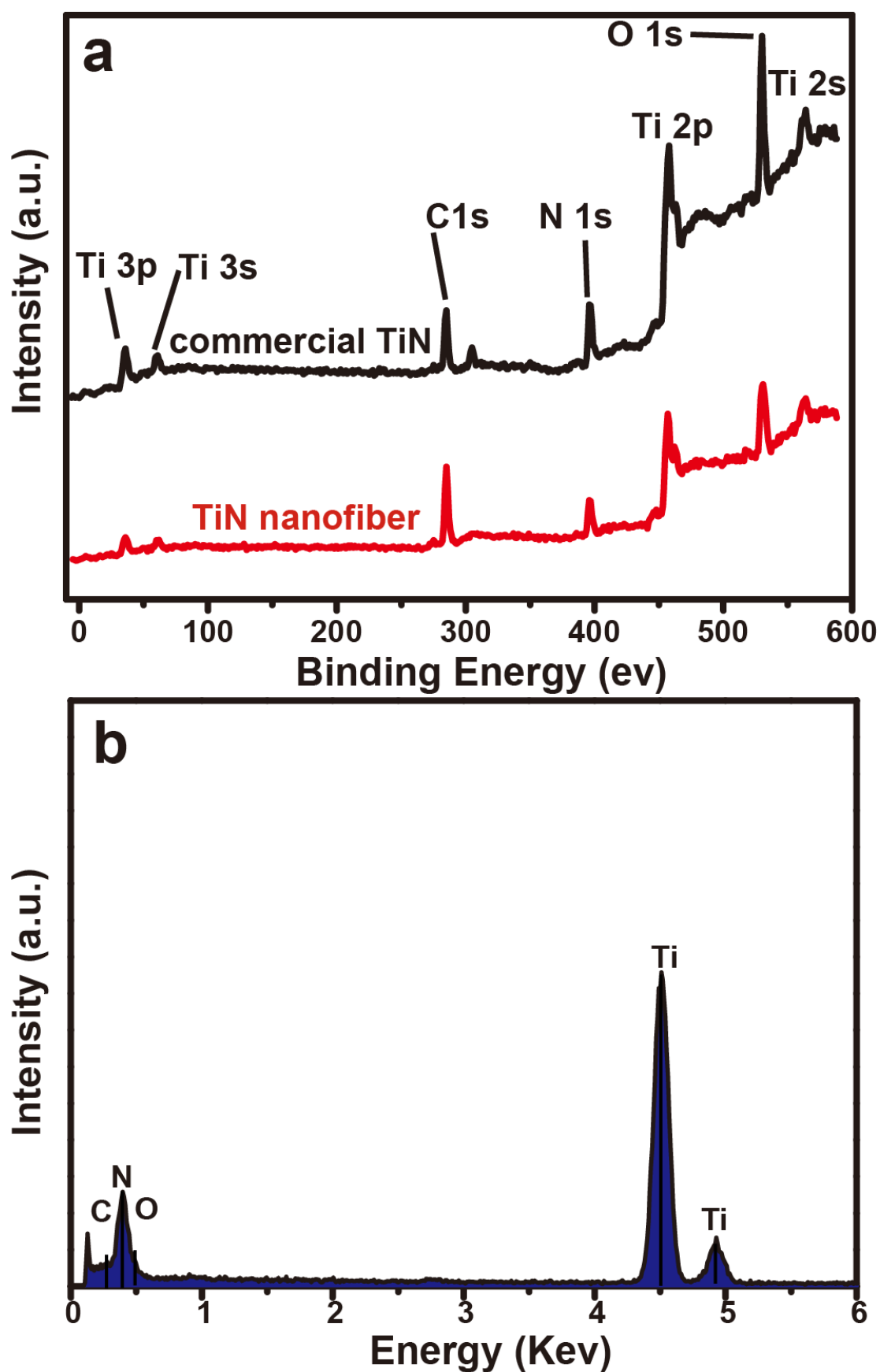


Fig. S2 a) XPS spectra of commercial TiN and TiN nanofiber-900, b) EDXA spectra of TiN nanofiber-900.

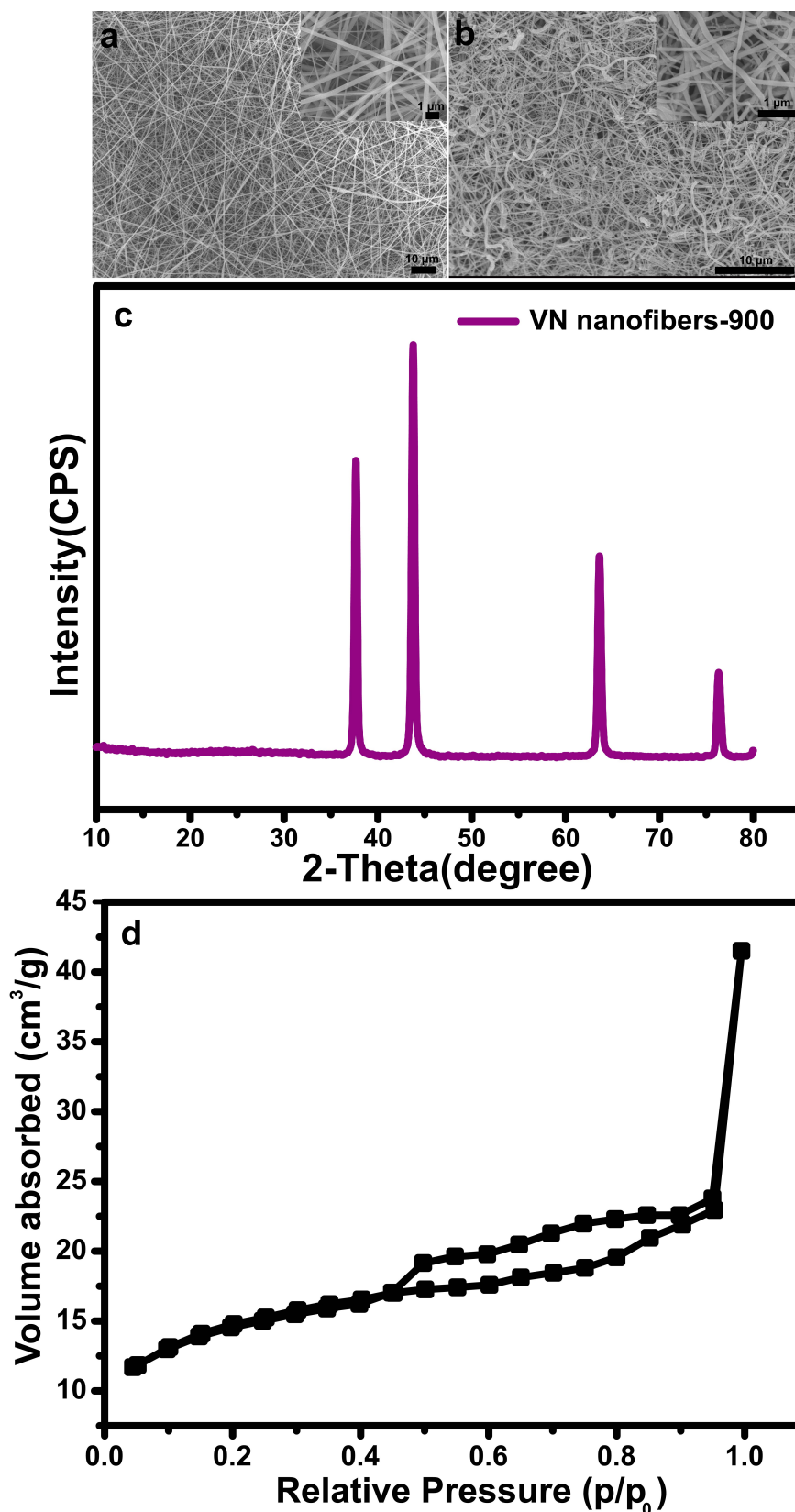


Fig. S3 a) SEM image of VO(OiPr)₃/PVP composite nanofibers. Inset: SEM image with higher magnification, b) SEM image of VN nanofibers prepared at 900 $^{\circ}\text{C}$, c) XRD pattern of VN nanofibers and d) Nitrogen adsorption-desorption isotherms of VN nanofiber-900.

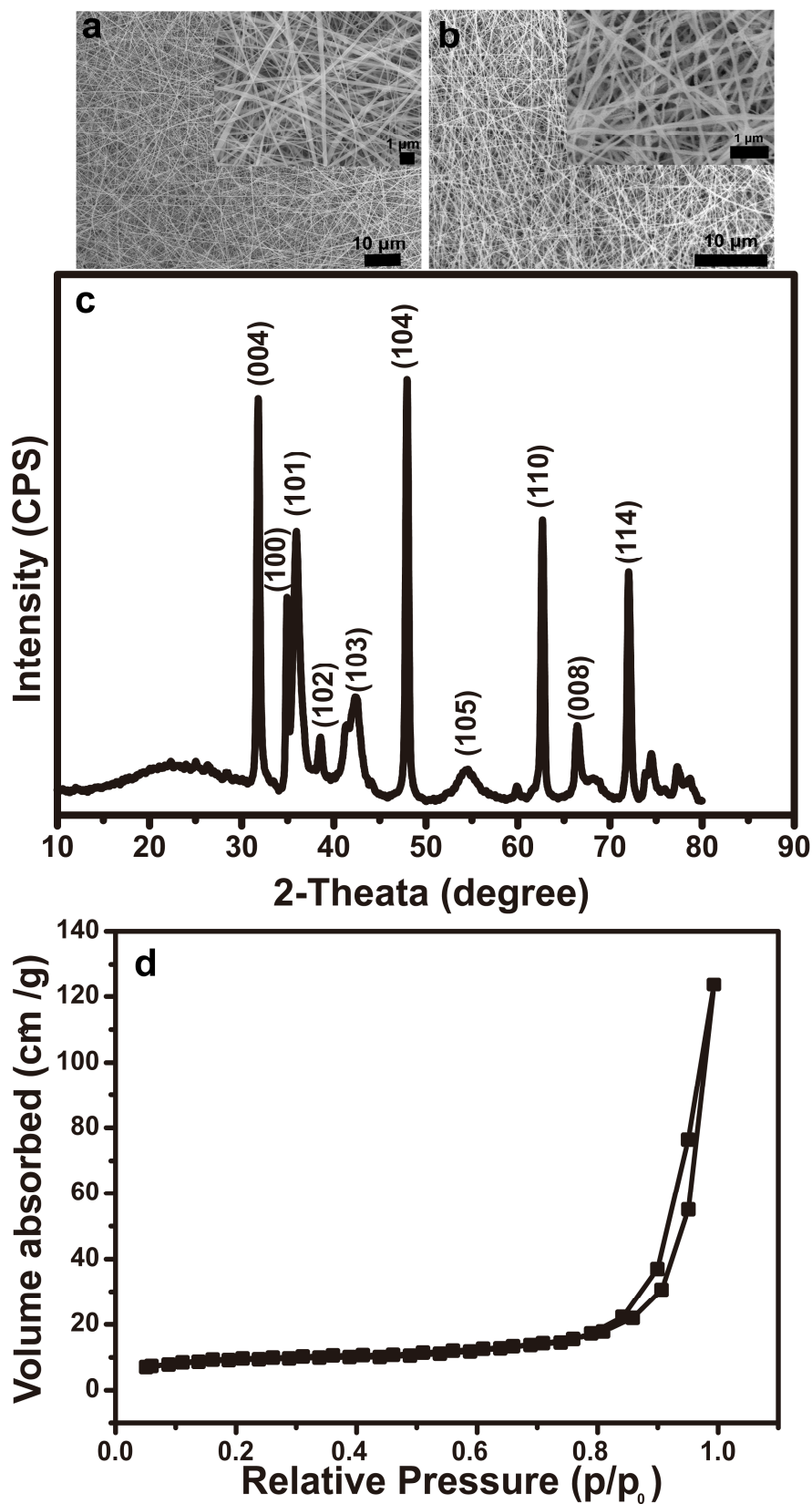


Fig. S4 a) SEM image of Nb(OC₂H₅)₅/PVP composite nanofibers. The inset is higher magnification. b) SEM image of NbN nanofibers prepared at 900 °C with higher magnification

image inset, c) XRD pattern of NbN nanofibers and d) Nitrogen adsorption-desorption isotherms of VN nanofibers.

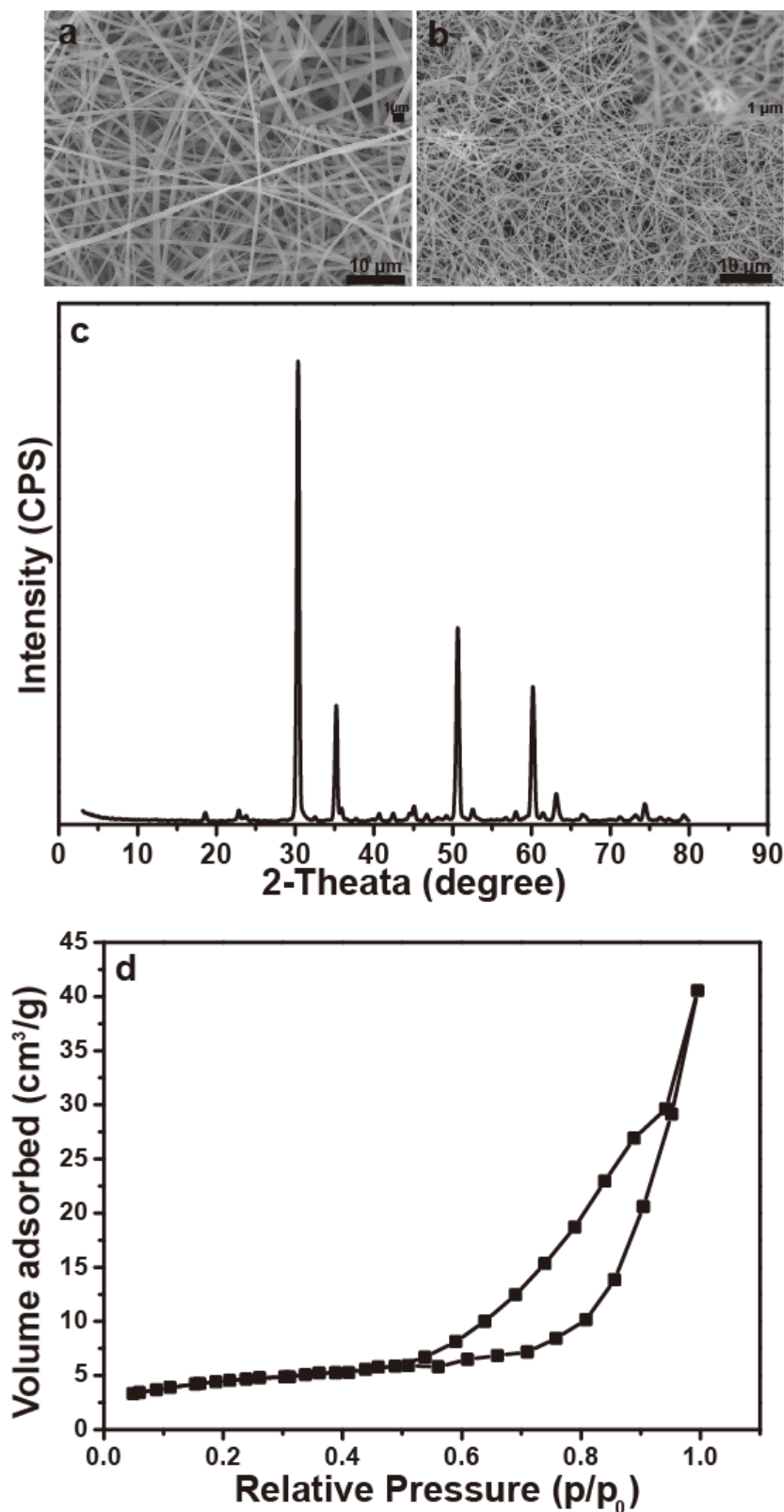


Fig. S5 a) SEM image of Zr(OCH₂CH₂CH₃)₄/PVP composite nanofibers. The inset is higher magnification. b) SEM image of zirconium oxynitride nanofibers prepared at 1000 °C with higher

magnification image inset, c) XRD pattern of zirconium oxynitride nanofibers and d) Nitrogen adsorption-desorption isotherms of zirconium oxynitride nanofibers.

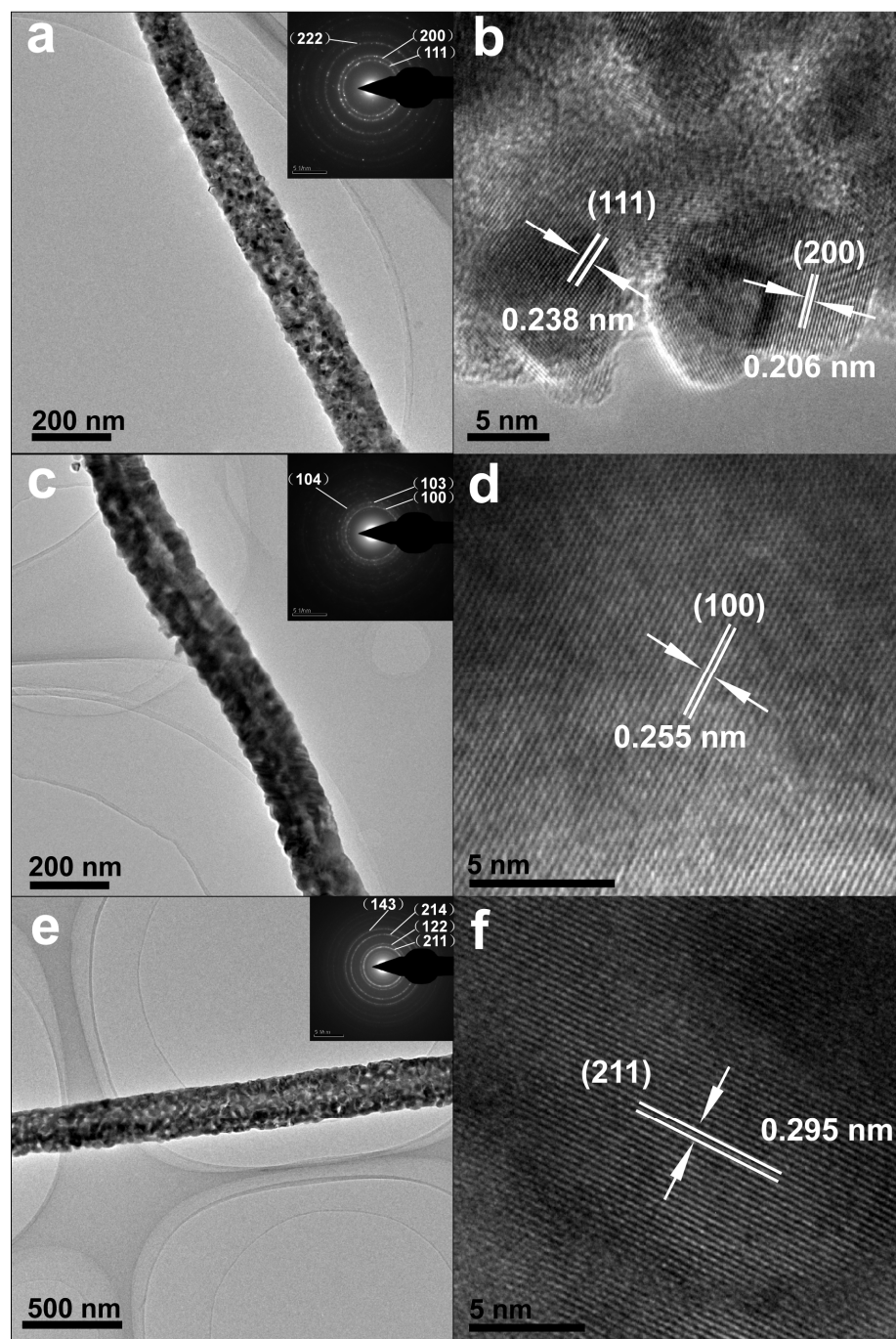


Fig. S6 a) TEM image of a single VN nanofiber; b) HRTEM image of part of VN nanofiber; c) TEM image of a single NbN nanofiber; d) HRTEM image of NbN nanofiber; e) TEM image of a single zirconium oxynitride ($\text{Zr}_7\text{O}_8\text{N}_4$) nanofiber; f) HRTEM image of part $\text{Zr}_7\text{O}_8\text{N}_4$ nanofiber; The inset in a), c) and e) is corresponding SAED pattern of VN, NbN, $\text{Zr}_7\text{O}_8\text{N}_4$ nanofibers, respectively.

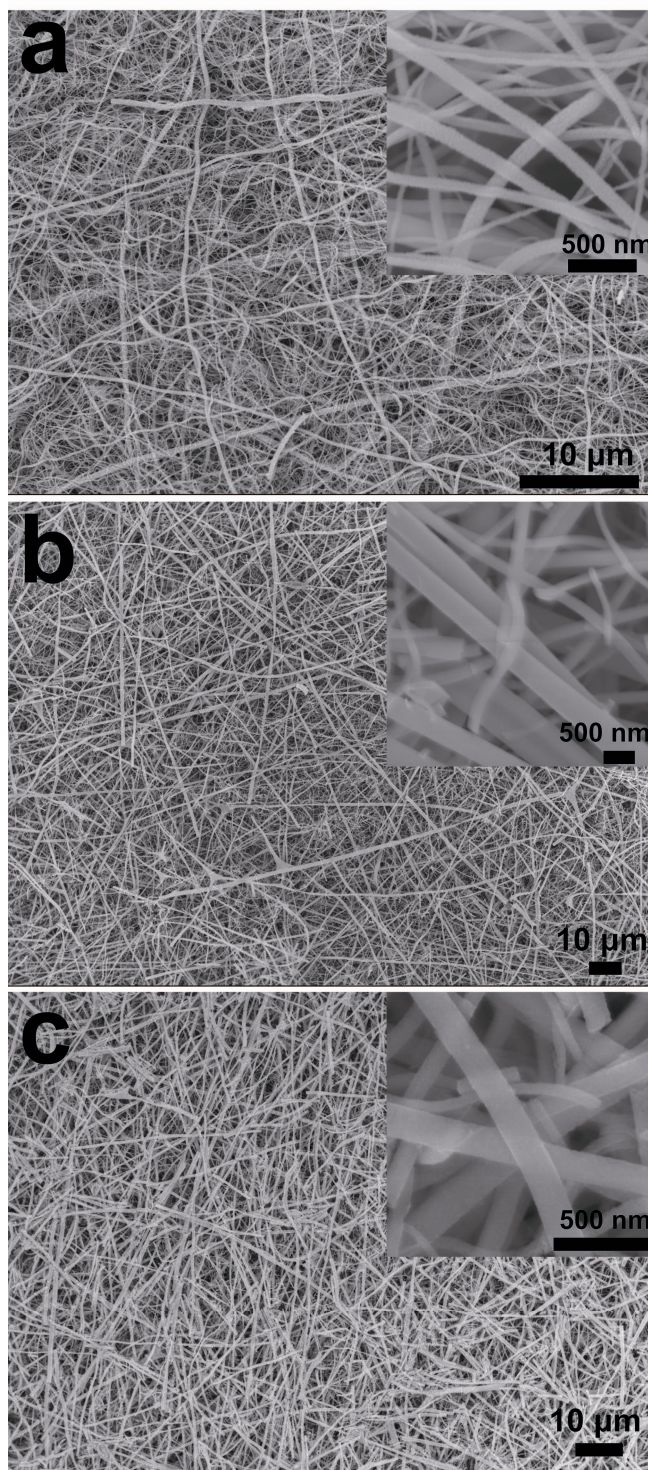


Fig. S7. SEM image of Ti-V-N nanofibers: a) TiVN-0.5, b) TiVN-1.0 and c) TiVN-1.5. (the inset is higher magnification)

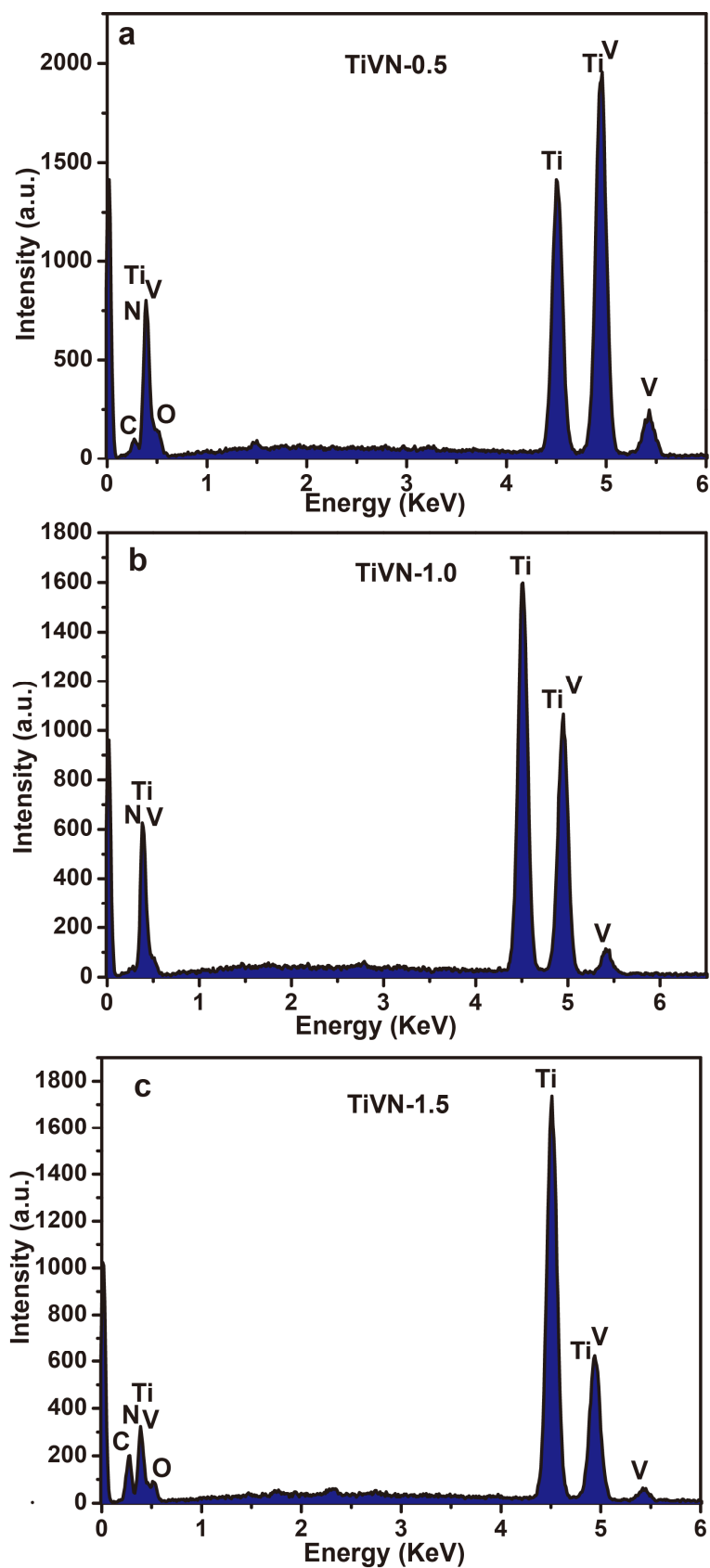


Fig. S8 EDXA spectra of various Ti-V-N nanofibers

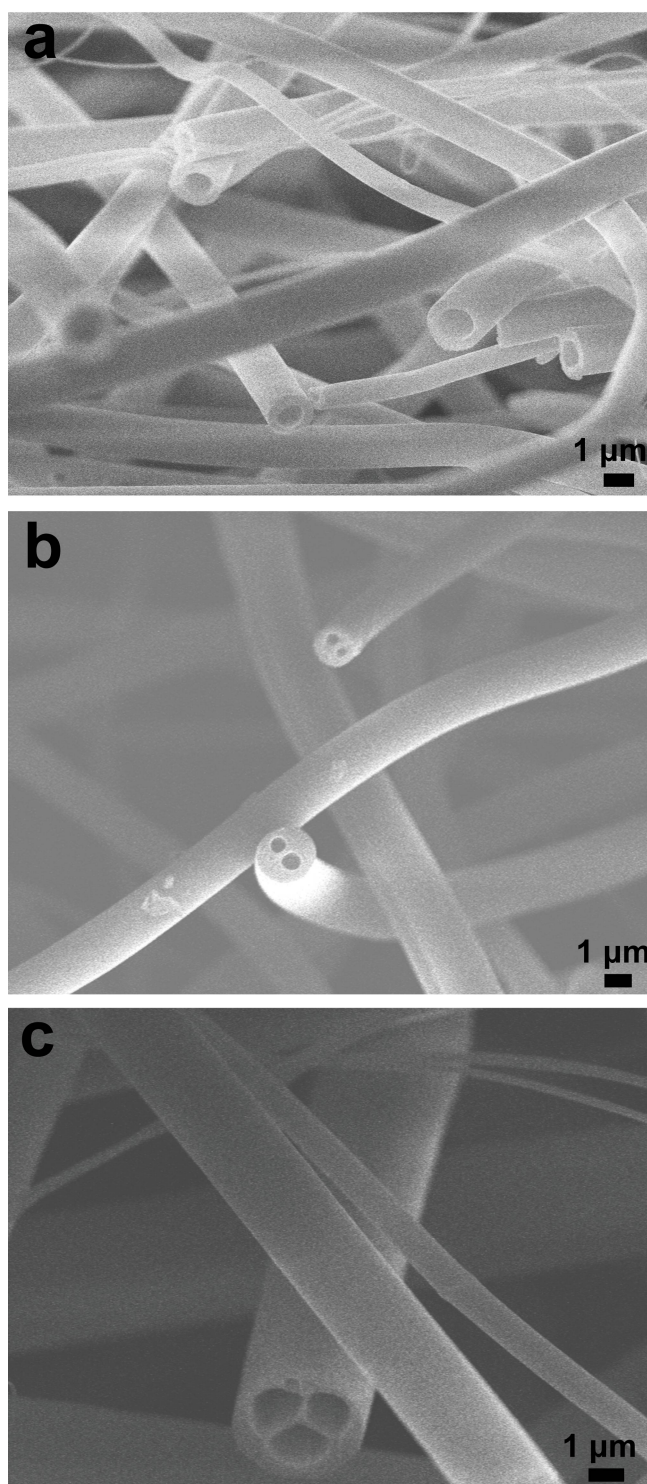


Fig. S9 a)-c) SEM images corresponding to $\text{Ti}(\text{OBu})_4$ / PVP precursor composite tubes with variable channel number from one to three, respectively.

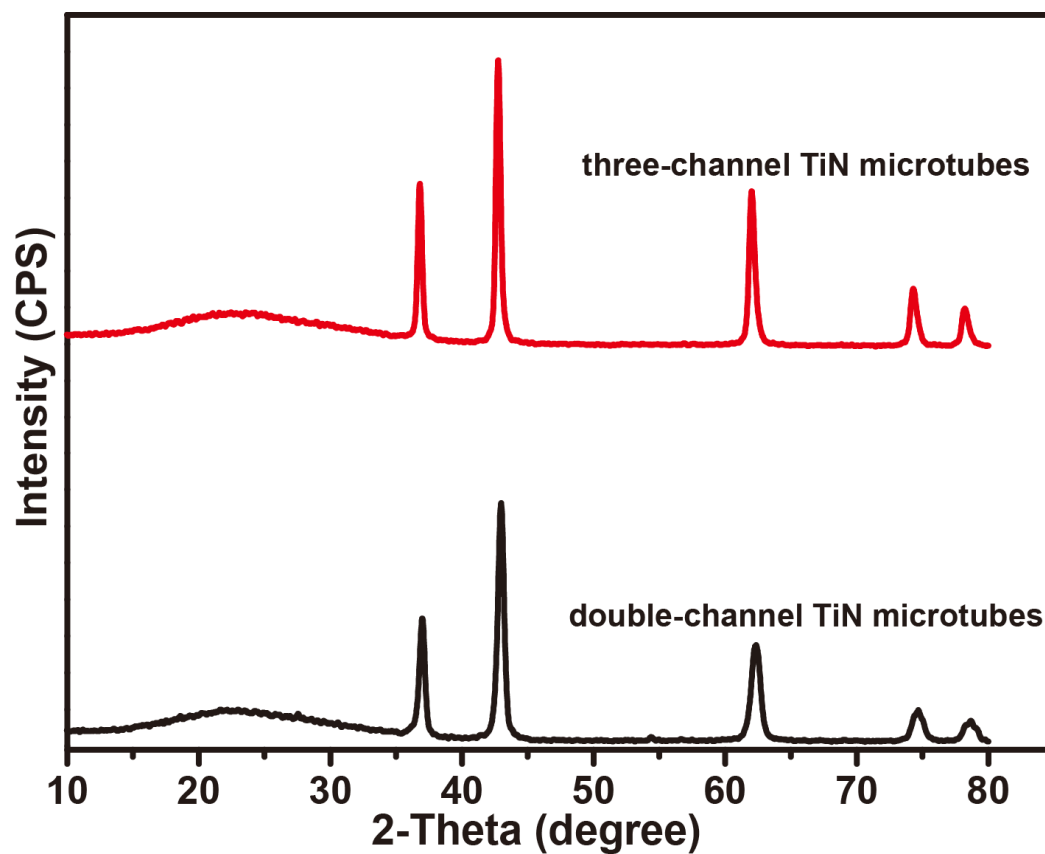


Fig. S10 XRD patterns of TiN microtubes prepared at 900 °C with two and three channels.

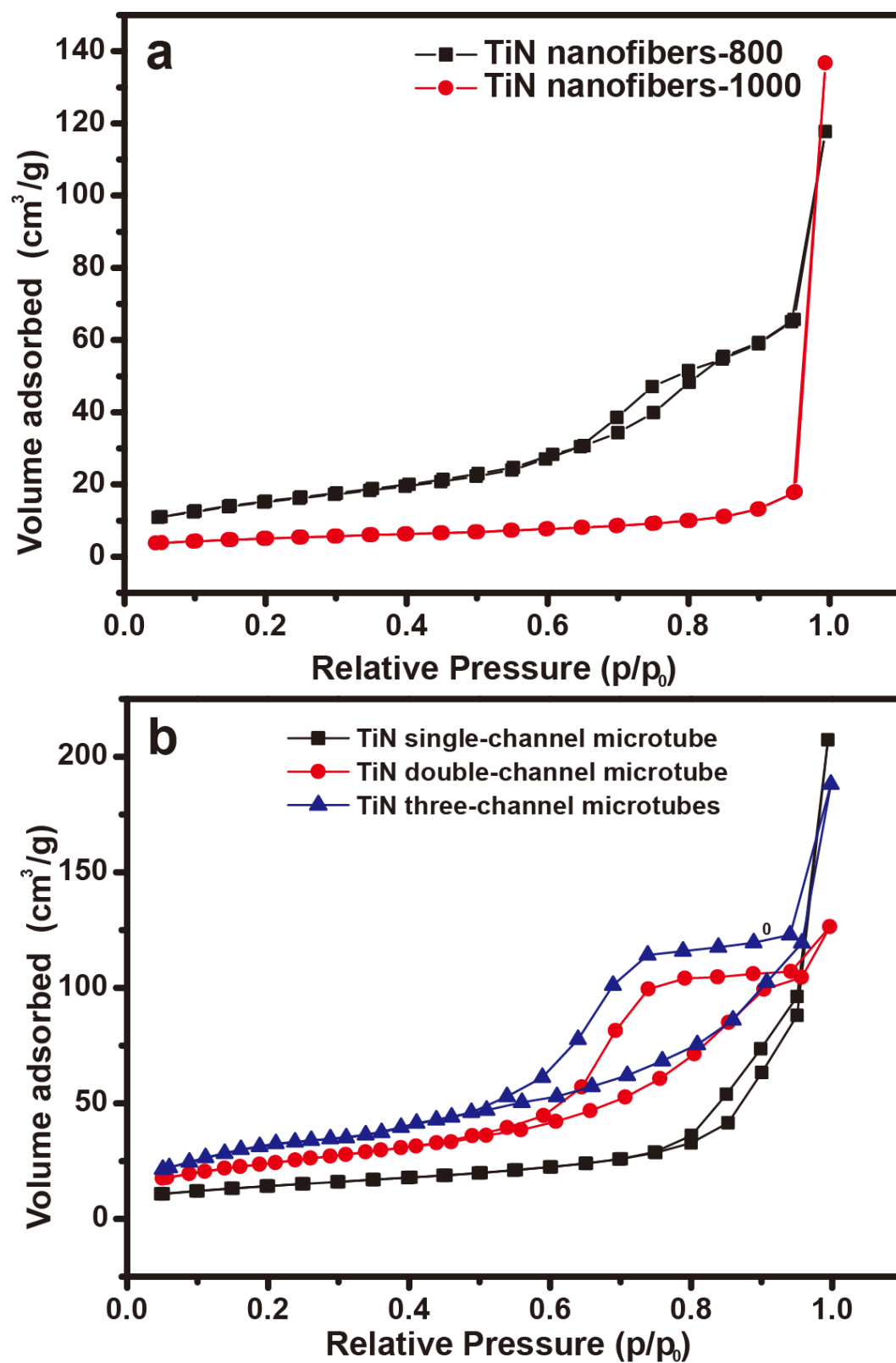


Fig. S11 a) Nitrogen adsorption-desorption isotherms of TiN nanofibers and b) Nitrogen adsorption-desorption isotherms of TiN multichannel micro/nano tubes.

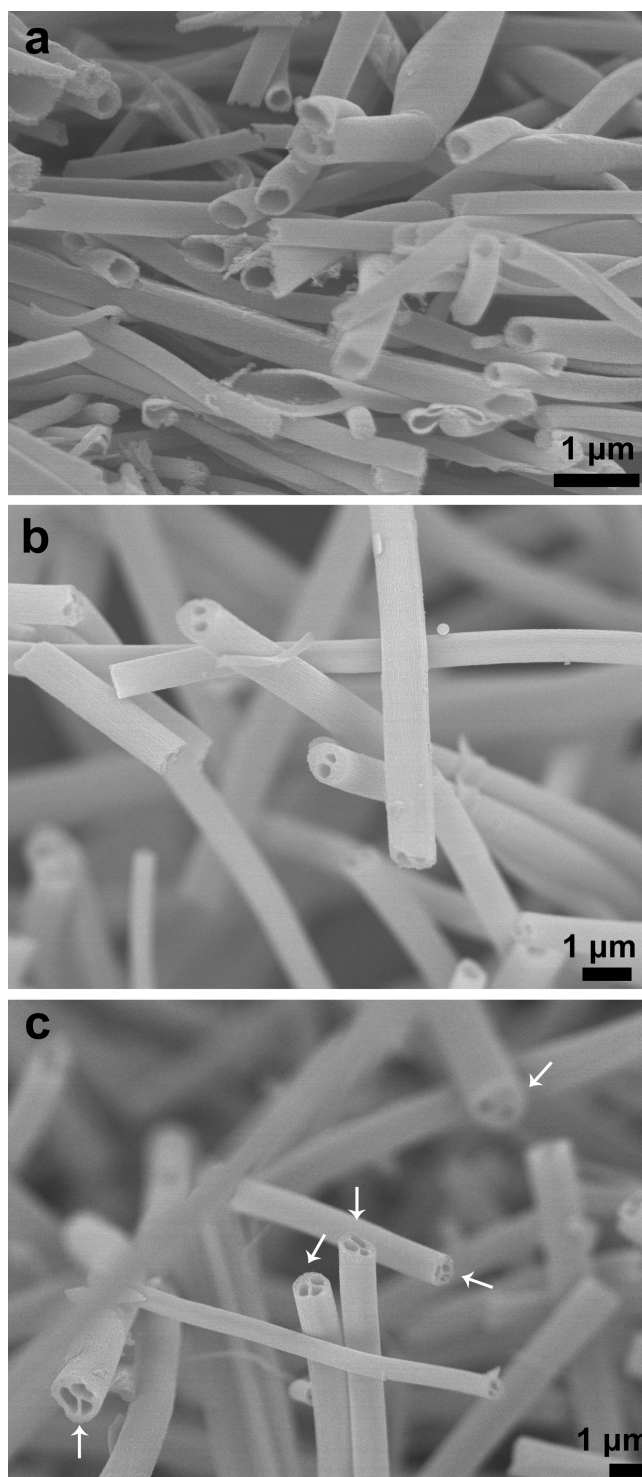


Fig. S12 a)-c) SEM images corresponding to numerous hierarchical TiN micro/nanotubes with variable channel number from one to three, respectively. All the tubes above are synthesized at 1000 °C.