# Supplementary Information

# Enhanced photocatalysis activity of ferroelectric KNbO3 nanofibers

## compared with anti-ferroelectric NaNbO3 nanofibers synthesized by

## electrospinning

Yu Huan<sup>1</sup>, Xiaohui Wang<sup>a),1</sup>, Weichang Hao<sup>2</sup>, Longtu Li<sup>1</sup>

<sup>1</sup>State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

<sup>2</sup> Department of Physics, and Key Laboratory of Micro-nano Measurement,

Manipulation and Physics, Ministry of Education (MOE), Beihang University, Beijing 100191, China

<sup>&</sup>lt;sup>a)</sup> Author to whom correspondence should be addressed; Email: <u>wxh@mail.tsinghua.edu.cn</u>

## **Synthesis**

All the solvents and raw materials were analytically pure and used without any further purification. KNbO<sub>3</sub> nanofibers and NaNbO<sub>3</sub> nanofibers were synthesized by sol-gel based electrospinning as follows. 2.22 mmol alkali acetate (CH<sub>3</sub>COOK or CH<sub>3</sub>COONa, 99.9%) was dissolved in 4 ml 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, 98%). After stirring for 2 h at room temperature, 2 mmol niobium ethoxide  $(Nb(OC_2H_5)_5, 99.9\%)$  and 1 ml acetylacetone  $(C_5H_8O_2, 98.5\%)$  were added into the above solution in sequence. In the present study, the alkali metals were added excessively in order to compensate their volatilization. After stirring for more than 5 h, 0.5 g of polyvinylpyrrolidone (PVP, 99.9%,  $M_{\rm w} = 1300000$ ) was dissolved into the solution to form a transparent precursor with a suitable viscosity. Later, the precursor was loaded into a plastic syringe equipped with a stainless steel needle and then electrospun into nanofibers under a high voltage of 30 kV with a spinning rate of 1 mL/h in air. The distance between the needle tip and the collector was about 25 cm. During the electrospinning process, the temperature and humidity were about 20 °C and 30%, respectively. A piece of flat tinfoil foil was used to collect these bindercontained non-woven fibers. Then the binder-contained non-woven fibers were peeled off from the collector and dried at 80 °C for 5 h in a vacuum oven. Finally, the bindercontained non-woven fibers were sintered in air for 3 h at a ramp rate of 1 °C /min to obtain the KNbO<sub>3</sub> and NaNbO<sub>3</sub> nanofibers.

### Characterization

Thermogravimetric-differential scanning calorimetry analysis (TG-DSC) were carried out on STA 449 F3 (Netzsch, Germany) under a 20 mL/min air flow with heating rate of 10 °C/min. The Brunauer-Emmett-Teller (BET) specific surface area was measured using a QUADRASORB SI (Quantachrome, USA). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) were carried out on electron microscope TECNAI G<sup>2</sup> 20 (FEI, USA) at 200 kV. X-ray diffraction (XRD) was measured by Smartlab (Rigaku, Japan) using Cu Ka radiation. Scanning electron microscopy (SEM) studies were carried out on MERLIN VP Compact (Carl Zeiss, Germany). Fourier transform infrared spectra (FTIR) were recorded on a VERTEX 70V spectrometer (Bruker, Germany) using KBr pellet method in the range of 400 to 4000 cm<sup>-1</sup>. Micro-Raman spectra were measured on a Confocal LabRAM HR800 spectrometer system (JY, France) in the range of 100 to 1500 cm<sup>-1</sup>. High-resolution X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALab 250 Xi electron spectrometer (Thermo Fisher Scientific, USA ). Diffuse reflectance ultraviolet and visible (UV-Vis) spectra were obtained using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrometer (Perkin Elmer, USA) with a 150 mm Int. Sphere. Fine BaSO<sub>4</sub> powder was used as a standard, and the spectra were recorded in the range of 100 to 1200 nm. The effective piezoelectric coefficient  $d_{33}^*$  of an individual KNbO<sub>3</sub> nanofiber was measured using a scanning probe microscopy system (SPM, SPI4000&SPA300HV, Seiko, Tokyo, Japan) with a conductive Rh-coated Si

cantilever (SI-DF3), which has a spring constant of 1.9 N/m and a free resonance frequency of 28 kHz.

#### **Photocatalytic evaluation**

The photocatalytic activity of the as-prepared samples for the degradation of RhB (99.9%) in aqueous solutions was evaluated. Prior to irradiation, 0.1 g powders was mixed with RhB (100mL, with a concentration of 0.02 mM/L) in a 100-mL Pyrex flask and then sonicated in a cool water bath for 10 min. Then, the suspensionwas magnetically stirred to reach a complete adsorption-desorption equilibrium. The flask was subsequently exposed to UV-Vis light irradiation with maximum illumination time up to 240 min. During the irradiation, the suspension was magnetically stirred and the reaction temperature was kept at room temperature. The excitation source is a 300 W mercury lamp located at *ca.* 15 cm away from the flask. At certain time intervals, about 3.5 mL aliquots were sampled and centrifuged. The absorption intensity of RhB at 554 nm was measured to detect the dye concentration on a PerkinElmer Lambda 950 UV-Vis spectrometer (Perkin Elmer, USA).



Figure S1 Raman spectra in the range of 100–1200 cm<sup>-1</sup> (a) KN-NF and KN-NF calcined at different temperatures, (b) NN-NF and NN-NF calcined at different

#### temperatures

The Raman spectra of KN-NF and KN-NF calcined at different temperatures are displayed in Fig. S1a while that of NN-NF and NN-NF calcined at different temperatures are shown in Fig. S1b. As a main unit of perovskite structure, the vibrations of the NbO<sub>6</sub> octahedron are usually considered to consist of  $1A_{1g}(v_1) +$  $1E_g(v_2) + 2F_{1u}(v_3+v_4) + F_{2g}(v_5) + F_{2u}(v_6)$ ,<sup>1</sup> among which  $1A_{1g}(v_1) + 1E_g(v_2) + F_{1u}(v_3)$ belong to stretching modes and the other belong to the bending modes. In Fig. S1a, the peaks at around 260, 531 and 589 cm<sup>-1</sup> correspond to  $F_{2g}(v_5)$ ,  $E_g(v_2)$  and  $A_{1g}(v_1)$ vibrational modes of NbO<sub>6</sub> octahedron, respectively. The peak at around 833 cm<sup>-1</sup> is attributed to the combination mode of  $A_{1g}(v_1)$  and  $F_{2g}(v_5)$ , indicating the formation of the perovskite structure. When the KN-NF is calcined at 600 °C, the band is broad because of the low crystallinity. Thus, the proper calcination temperature of KN-NF is 700 °C. In the NaNbO<sub>3</sub> materials the Raman spectra in region from 90 to 170 cm<sup>-1</sup> can be related to the vibration modes of the Na<sup>+</sup> against NbO<sub>6</sub> octahedra. The peaks at ca. 249, 565 and 608 cm<sup>-1</sup> correspond to  $F_{2g}(v_5)$ ,  $E_g(v_2)$  and  $A_{1g}(v_1)$  vibration modes of NbO<sub>6</sub> octahedron, respectively. The peak at ca. 871 cm<sup>-1</sup> is attributed to the combination mode of  $A_{1g}(v_1)$  and  $F_{2g}(v_5)$ . The characteristic peaks of NbO<sub>6</sub> octahedra appear when the NN-NF calcined at 600 °C. Thus, the proper calcination temperature of NN-NF is 600 °C. As well known, the Raman spectra is very sensitive to the NbO<sub>6</sub> octahedral tilting associated with the phase transition ,which is induced due to variation in the particle size and reflects in a large change in the internal modes associated with the NbO<sub>6</sub> octahedral. It is found the bands of the nanofibers calcined at high temperature are sharper than that of the nanofibers calcined at low temperature due to the better crystallinity. It can also be seen that the intensity of Raman spectrum increases with increasing calcination temperature. Furthermore, the wavenumber of the  $v_1$  mode moves towards to higher value with increasing calcination temperature. The same change trend is observed in the  $v_5$  mode. These changes should be related with the grain growth of the nanofibers.



Figure S2 (a1) TEM image of KN-NF-700, (a2-a4) EDS mapping images of different chemical elements. (b1) TEM image of NN-NF-600, (b2-b4) EDS mapping images of different chemical elements.



Figure S3 UV-Vis spectral changes of RhB aqueous solutions as a function of irradiation time. (a) KN-NF-700, and (b) NN-NF-600. Insets illustrates photos for comparison of the RhB aqueous solutions photodegraded irradiated with the corresponding samples for 0 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min and 240 min.

The photocatalytic activity of as-prepared samples is evaluated for RhB degradation under UV-Vis light illumination. The temporal UV-Vis spectral changes

of RhB aqueous solutions in the process of photo-degradation are displayed in Fig. S3. Fig. S3 shows that with increasing irradiation time, the major absorbance decreases and the positions of major absorbance are shifted to low wavelength, suggesting that both chromophores and aromatic rings of RhB have been destroyed.<sup>2</sup> The change of relative RhB concentration as a function of irradiation time is shown in Fig. 3a.



Figure S4 XRD patterns KN-NF-700 and NN-NF-600 after photocatalytic

reactions



Figure S5 High-resolution XPS spectra of as-prepared samples in current work (a) K 2p core-level, (b) Na 1s core-level, (c) Nb 3d core-level, (d) O 1s core-level

## References

- 1. K.-i. Kakimoto, K. Akao, Y. Guo and H. Ohsato, *Jpn. J. Appl. Phys.*, 2005, **44**, 7064.
- 2. X. Zhou, H. Yang, C. Wang, X. Mao, Y. Wang, Y. Yang and G. Liu, *J. Phys. Chem. C*, 2010, **114**, 17051-17061.