

# Synthesis and Characterization of Flower-like Clewed PbTiO<sub>3</sub> Nanowires Prepared by Hydrothermal Method

Yunlei Zhao<sup>1,2,3</sup>, Zhiqiang Chen<sup>3</sup> and Yu Deng<sup>1,2,\*</sup>

<sup>1</sup>Modern Analysis Center, Nanjing University, Nanjing 210093, China

<sup>2</sup>Physics School, Nanjing University, Nanjing 210093, China

<sup>3</sup>Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

\*Corresponding author

**Abstract**—Flower-like clewed PbTiO<sub>3</sub> (PT) nanowires have been synthesized using hydrothermal method. The nanowire have an average length of 0.5 μm and a mean diameter of 10–20 nm, the clews have average diameters of 1 μm. With tetragonal lattice structure, the clewed PT nanowire grow along the (001) direction. The growth mechanism has been discussed. To fabricate nanowire-clew, the reaction temperature and the nonpolar surfactant are proved to be critical factors.

**Keywords**—nanowires; phonon characteristics; fabrication; characterization

## I. INTRODUCTION

Excellent physical properties are reported to be found in lead titanate (PbTiO<sub>3</sub>, PT) [1-3]. PT nanostructures are considered to be desirable materials for future application, which is due to the demand of making microelectronic and optoelectronic devices smaller and stronger in properties. In PT low-dimensional materials, excellent large pyroelectricity, giant dielectric permittivity and optical nonlinearity are all points that researchers have been interested in [3-5]. So trying to find more attractive physical properties in one-dimensional nanostructures (1DNS) could be a very meaningful project to study. However, though there are many trying these years for preparing low-dimensional materials of perovskite oxides, only a few paper mentioned about size-dependent properties and controllable growth in PT 1DNS. [6-9]. So in this paper, we would show a convenient hydrothermal method for synthesis of single crystalline PT nanorods which has a high output-rate and of low cost. Nanorods with morphology have been prepared by adding different polymer-additives, and the growth process together with structural characters of the PT nanostructures have also been studied.

## II. EXPERIMENTAL

The flower-like clewed PT nanowires were prepared by hydrothermal technique with assistance of polymer. The first step here is to prepare two different solutions in following method. One is Pb(NO<sub>3</sub>)<sub>2</sub> in water and another is Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> in alcohol. Then they were mixed together, together with a constant stirring rate for 15 min. Then we gradually add NaOH into the solution until the concentration reaches to 10 M/L. Then poly vinyl alcohol (0.8 g/L) together with poly acrylic acid (0.1 g/L) were put in as additives under stirring. Then we put the

reaction mixture into an autoclave. The autoclave was placed in an oven at 180 °C for 48 h, and cooled to room temperature in air. The obtained powders would be washed for several times and annealed at 450 °C. So that we obtained products which show a light yellow color.

X-ray diffraction (XRD) was collected with CuKα working as radiation source, elected area electron diffraction (SAED) and morphology data were performed with high-resolution transmission electron microscope (HRTEM) JEOL-2100, scanning electron microscope (SEM) was detected with Hitachi-4800, energy dispersive spectroscopy (EDS) was performed with Oxford EDX-250, and these Raman spectra were collected under back-scattering geometry on a HR-800 Raman spectrometer, using 488 nm wavelength exciting light at a power of 10 mW.

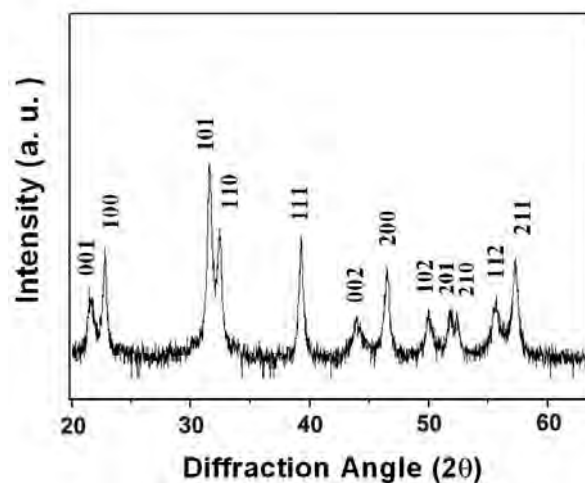


FIGURE I. THE XRD PATTERNS OF THE PT NANORODS UNDER ROOM TEMPERATURES.

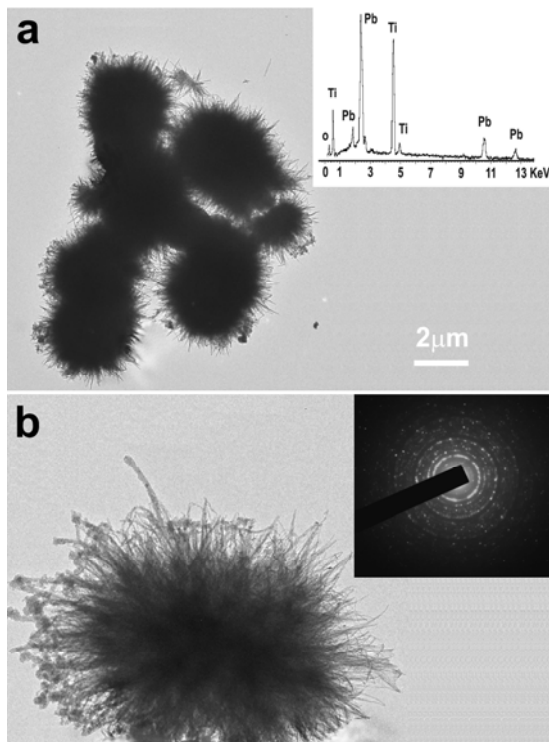


FIGURE II. (A) THE TEM IMAGE AND EDS OF THE FLOWER-LIKE CLEWED PT NANOWIRES. (B) THE SAED PATTERN OF THE FLOWER-LIKE CLEWED PT NANOWIRES.

### III. RESULTS AND DISCUSSION

Figure I shows as-prepared samples' XRD pattern. Sharp peaks here show their crystallinity are very good. And these peaks all match very well as the tetragonal (T) phase that no impurity lines were found. According to the calculation, the  $a$ ,  $b$ ,  $c$  lattice constants have been figured out [10] as  $a=b=3.91 \text{ \AA}$ ,  $c=4.12 \text{ \AA}$ , which verifies size effect is introduced to samples effectively, that caused the  $c/a$  ratio of T phase to decrease [2, 8]. According to Figure I, it could be found that both the (101) and (110) peaks shifted here in sample, which show the decreasing of the T structure here evidently [2].

Figure II(a) is the flower-like clewed PT nanowires TEM image. The nanowires are both smooth and straight, which taking a main part (>70%) in the sample. And their diameters distributes from 25 nm to 60 nm and the mean length is 3  $\mu\text{m}$ . The EDS pattern is here together in Figure II(a), which help showing nanorods are in a main part of the sample. An individual flower-like clewed PT is chosen as TEM investigation, which is in Figure II(b).

In Figure III(a), we can clearly see the curved nanowires. The HRTEM image in Figure III (b) shows the length along growth orientation is 4.0  $\text{\AA}$  as measured, which matches (001) lattice constant, shows evidence of nanorods are grown along (001) direction [2, 7]. Also, SAED in Figure III(b) confirms the conclusion. Many defects such as dislocation and amorphase in these nanowires are shown in the HRTEM image in Figure III(c).

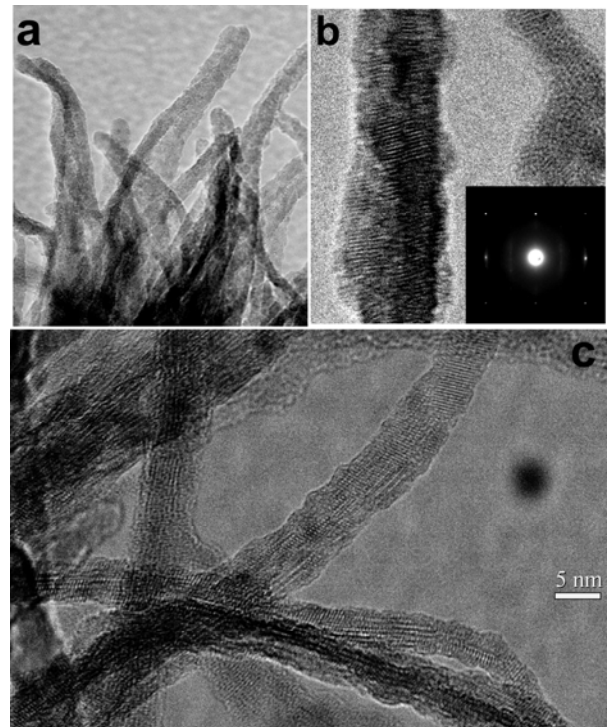


FIGURE III. (A) THE CURVED PT NANOWIRES. (B) THE HRTEM IMAGE WHICH SHOWS INTER-PLANAR SPACING ALONG GROWTH-DIRECTION. (C) THE DEFECTS SUCH AS DISLOCATION AND AMORPHASE IN THESE NANOWIRES.

Without NaOH, flower-like clewed PT nanowires cannot get produced by the hydrothermal reaction together with the polymer assisting. Figure IV(a) is the TEM image of nanowires and (b) is products no NaOH inside, while all the others are without difference. It seems like the nanoparticles are of a size of about 70nm which is different from 1DNS. Further more, it shows out that the prepared PT nanowires will dramatically appear as different morphology if polymer-additives are different. Three different additives are used here for comparison: A (0.2 g/L poly vinyl alcohol), B (0.8 g/L poly vinyl alcohol) and C (0.1 g/L poly acrylic acid and 0.8 g/L poly vinyl alcohol) for the synthesis of (c) (d) (e) nanorods here, and their SEM data finally confirmed this. It is clearly shown that A produces the short nanorods (length about 500 nm and diameter about 60 nm), B produces products are longer (length about 1  $\mu\text{m}$  and diameter about 40 nm), while C produces the longest one (length about 3  $\mu\text{m}$  and diameter about 30 nm). And Figure IV (f) and (g) are morphology of and clewed flower-like nanowires with more smooth surface.

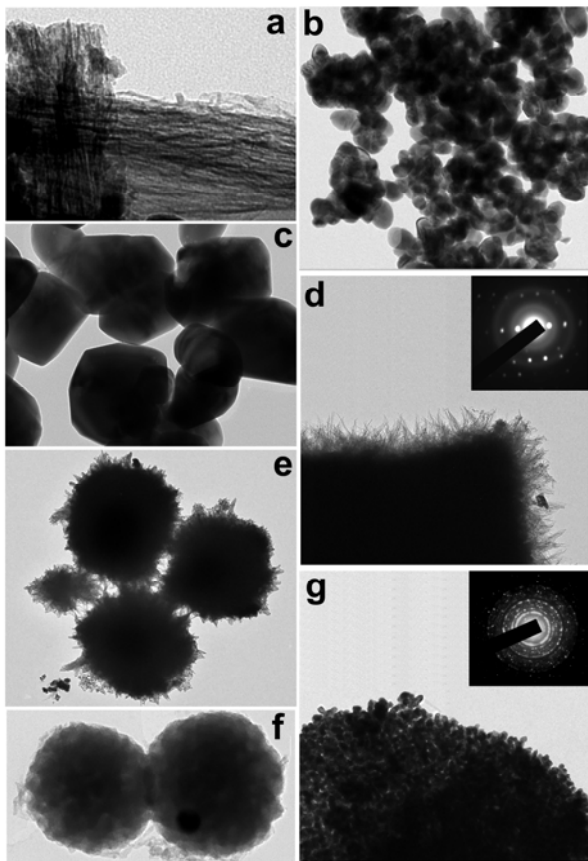


FIGURE IV. THE MORPHOLOGY OF THE AS-PREPARED SAMPLES ZT DIFFERENT SYNTHESISI CONDITIONS.

Raman spectra of flower-like clewed PT nanowires are here in Figure V. They are all compared with Burns' work [1,2]. The peak of the lowest wavenumber is the "soft mode" corresponding to E (1TO) symmetry. PT crystal ( $31\text{ cm}^{-1}$  downshift from  $82\text{ cm}^{-1}$  to  $51\text{ cm}^{-1}$ ) [11]. The reduction of tetragonality in the PT nanorods should be responsible for it, which also leads to weakening of ferroelectricity [11, 12, 18, 23]. Figure V depicts the frequency and the damping constant of E (1TO) mode as the functions of temperatures, where the damping constant dominates the shape of the Raman peak [11, 18, 23]. As temperature increasing, the mode frequency downshifts and damping constant increases. The weak soften behaviors (see Figure VI) and the large damping constant suggest that the lattice vibration of the PT nanorods is evidently softer than PT crystal [11, 12, 18, 23], which is similar to the case of PT nanoparticles and should mainly originate from the size effect [11].

There are many evidences strongly implying that the "annealing growth" mechanisms as Ostwald ripening [27, 28] are more suitable for our PT nanowires than the "growth during cooling" mechanisms as VLS theory [29]. Thus, we suggest that formation of nanorods should be attributed to three parts of modified assembling, recrystallizing and oriented attaching growth. Since the PT nanowires are formed by the point-initiated uniaxial crystal growth, the lattice of them will be rigidly arrested from expansion [26, 30, 31]. As known, in the

synthesis process the surfactants can not only enhance the surface tension of the nanostructures but also work as "surfactant template", which will also limit the lattice [2, 7, 11, 28]. The PL spectrum studies (see Figure VI) well agree with above discussions, showing the PL peak shifting due to the introduction of impurity energy levels [28].

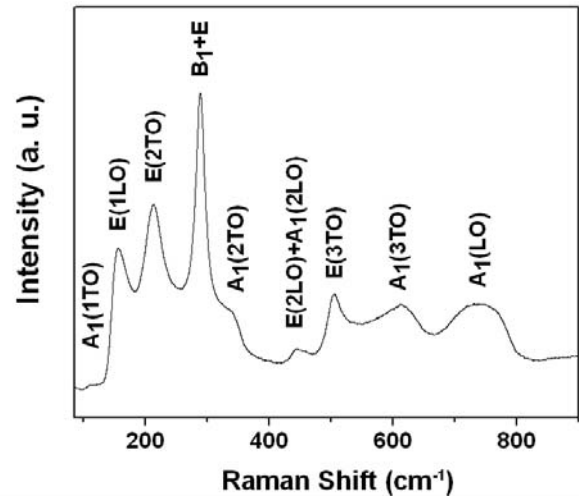


FIGURE V. THE RAMAN SPECTRUM OF THE FLOWER-LIKE CLEWED PT NANOWIRES.

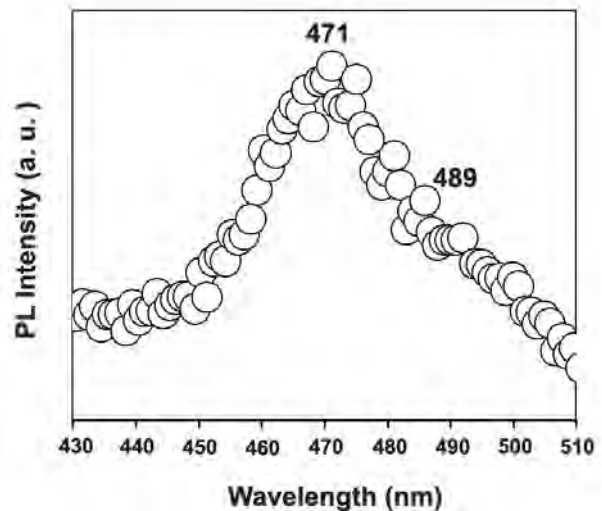


FIGURE VI. THE PL SPECTRUM OF THE FLOWER-LIKE CLEWED PT NANOWIRES.

#### IV. SUMMARY

In summary, we studied the synthesis and characterization of PT flower-like clewed PT nanowires by hydrothermal preparation. In comparison to single crystal, the decreasing of tetragonality and shrinking of cell have been detected. A weaker soften behavior of mode E(1TO) was also revealed, implying a weaker ferroelectricity. The particular properties of the PT nanorods are attributed to an enhanced size effect. Further investigation on the formation mechanism of the nanowires suggest that the point-initiated growth of nanowires and the

surfactants used in preparing process should be responsible for the enhancing of the size effect.

#### ACKNOWLEDGEMENT

The authors acknowledge the support of Natural Science Foundation of Jiangsu Province, China (Grant No.BK20151382), and NSAF (Grant No.U1530402), and Joint large-scale scientific facility funds of NSFC and CAS (Grant No: U1732120).

#### REFERENCES

- [1] Y. B. Mao, S. Banerjee, S. S. Wong, *J. Am. Chem. Soc.* 125 (2003) 15718.
- [2] J. J. Urban, W. S. Yun, Q. Gu, H. Park, *J. Am. Chem. Soc.* 124, (2002) 1186.
- [3] J. J. Urban, J. E. Spanier, L. Ouyang, W. S. Yun, H. Park, *Adv. Mater.*, 15, (2003) 423.
- [4] X. Y. Zhang, X. Zhao, C. W. Lai, J. Wang, X. G. Tang, J. Y. Dai, *Appl. Phys. Lett.* 85, (2004) 4190.
- [5] G. Xu, Z. Ren, P. Du, W. Weng, G. Shen, G. Han, *Adv. Mater.* 17, (2005) 907.
- [6] H.S. Gu, Y. M. Hu, J. You, Z. L. Hu, Y. Yuan, T. J. Zhang, *J. Appl. Physic.* 101 (2007) 024319.
- [7] S. Y. Zhang, F. S. Jiang, G. Qu, C. Y. Lin, *Materials Letters*, (2008) 48.
- [8] W. P. Chen, Q. Zhu, *Materials Letters*, 61 (2007) 3378.
- [9] X. Lu, D. Zhang, Q. Zhao, C. Wang, W. Zhang, Y. Wei, *Macromol. Rapid Commun.*, 27 (2006) 76.
- [10] W. S. Yun, J. J. Urban, Q. Gu, H. Park, *Nano Lett.* 2 (2002) 447.
- [11] K. Ishikawa, K. Yoshikawa, N. Okada, *Phys. Rev.*, B 37 (1988) 5852.
- [12] Y. Deng, Z. Yin, Q. Chen, M.S. Zhang, W.F. Zhang, *Mater. & Sci. Eng.*, B 84 (2001) 248.
- [13] M. de Keijser, G. J. M. Dormans, P. J. van Veldhoven, D. M. de Leeuw, *Appl. Phys. Lett.* 59 (1991) 3556.
- [14] S. Yakovlev, C. H. Solterbeck, E. Skou, M. Essouni, *Appl. Phys. A* 82 (2006) 727.
- [15] I.P. Batra, P. Wurfel, B. D. Silverman, *Phys. Rev. B* 8 (1973) 3257.
- [16] I.P. Batra, P. Wurfel, B. D. Silverman, *Phys. Rev. Lett.* 30 (1973) 384.
- [17] Y. Umeno, T. Shimada, T. Kitamura, C. Elsasser, *Physical Review B* 74 (2006) 174111.
- [18] G. Burns, B. A. Scott, *Phys. Rev. Lett.* 25 (1970) 167.
- [19] Y. Deng, M. S. Zhang, J. L. Wang, Q. R. Gu, *Inter. J. Modern Phys. B* 19 (2005) 2669
- [20] Z. Tomeno, Y. Ishii, Y. Tsunoda, K. Oka, *Physical Review B* 73 (2006) 064116
- [21] O. Yamaguchi, A. Narai, T. Komatsu, K. Shimizu, *J. Am. Ceram. Soc.* 69 (1986) C-256.
- [22] R. J. Nelmes, W. F. Kuhs, *Solid State Comm.* 54 (1985) 721.
- [23] R. E. Cohen, *Nature* 358 (1992) 136.
- [24] G. Burns, B. A. Scott, *Phys. Rev. B*, 7 (1973) 3088.
- [25] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata, M. Sakata, *Physical Review Letters*, 87 (2001) 217601.
- [26] Z. Y. Tang, N. A. Kotov, M. Giersig, *Science* 297 (2002) 237.
- [27] P.W. Vorhees, *Annu. Rev. Mater. Sci.* 22 (1992) 197.
- [28] W. Wang, C. Xu, G. Wang, Y. Liu, C. Zheng, *Adv. Mater.* 14 (2002) 837.
- [29] S. Sharma, M.K. Sunkara, *Nanotechnology* 15 (2004) 130.
- [30] H. L. Wang, X. D. Ma, X. F. Qian, J. Yin, Z. K. Zhu, *J. Solid State Chem.* 177 (2004) 4588.
- [31] J. D. Holmes, K. P. Johnston, R. C. Doty, B. A. Korgel, *Science* 287 (2000) 1471.