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ARTICLE TYPE

Length-controlled synthesis and the photoluminescence of pre-perovskite PbTiO₃ nanofibers

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A novel approach that combines modified sol-gel process with PVA-assisted hydrothermal reaction at 200 °C for 12 h has been developed to prepare single-crystal pre-perovskite PbTiO₃ nanofibers with good dispersity and length control. By increasing the dosage of triethanolamine (TEA) solution into Ti precursor to modify the sol-gel process, the length of the nanofibers in the prepared samples decreased from about 35-90 μm to 5-12 μm, whereas corresponding diameter remained in the certain range of 100-300 nm basically. Besides, the dispersity of the samples, as well as the diameter uniformity of a single nanofiber, was improved significantly. In particular, a broad green photoluminescence (PL) emission (~550nm) was observed in the nanofibers at room temperature. It is interesting to find that no obvious size effect has been detected on the green PL emission.

Introduction

Perovskite-type oxides have already attracted great attention due to their exceptional properties, which are of great importance to the development of electronic devices.¹ In the past decade, one-dimensional (1D) perovskite nanomaterials, with large surface area and size-dependent effect, have become a highly attractive area for many researches. Such materials exhibit unique thermal, mechanical, optical and electric properties, compared with bulk materials², leading to potential applications in nonlinear optical probe³, nanogenerator device⁴ and so on. Therefore, different approaches have been used to synthesize 1D nanostructure of perovskite-type oxides⁵, such as template method⁶, hydrothermal method⁷, solid-phase reaction⁸ and electrospinning method⁹. Among them, polymer-assisted hydrothermal method developed by our group has been demonstrated to be effective to synthesize single-crystal perovskite ternary compound nanostructures (PbZr_xTi_{1-x}O₃ (PZT), etc.)¹⁰⁻¹². When this method was applied to synthesize PbTiO₃ nanomaterials, a new tetragonal structure of single-crystal nanofiber--pre-perovskite phase was discovered by Ren et al^{13,14}. In particular, pre-perovskite PbTiO₃ nanofibers characterized by a 1D columned structure, has been determined to have a direct-band structure with a gap of 3.20 eV, emitting strong green and near infrared photoluminescence (PL) emission at room temperature¹⁵.

In our previous study, the size of pre-perovskite PbTiO₃ nanofibers could be modified by changing the growth dynamics through the molecular ratio of Pb/Ti¹⁶. However, the dispersity of the samples and the diameter uniformity of a single nanofiber were not achieved, and the aggregation became serious gradually as the size of the nanofibers decreased, which possibly influenced

the assignment of intrinsic properties, such as PL property. Organic molecular modification is a very effective way to tailor the hydrolysis-condensation process, stabilization of complexes, particle-surface and crystal growth, which has been widely used in sol-gel process¹⁷⁻¹⁹, hydrothermal reaction¹⁰ and other aqueous solution method^{20,21}. Recently, acetylacetonate (acac) molecules were introduced into the sol of tetrabutyl titanate to tune the hydrolysis-condensation process by Chao et al²². It is found that the size of amorphous particles decreased and the corresponding dispersity also increased, which played an important role in mediating the growth of the PbTiO₃ nanocrystals on the substrates. Encouraged by previous work, in order to regulate the size of pre-perovskite PbTiO₃ nanofibers and enhance dispersity as well as uniformity, we introduced different amount of triethanolamine (TEA) solution into Ti precursor to modify the sol-gel process and subsequent crystal growth during the PVA-assisted hydrothermal reaction to achieve length-controlled PbTiO₃ nanofibers. This approach effectively improved the dispersity of the nanofibers and the diameter uniformity of a single nanofiber. Moreover, the effect of length on the green PL emission of pre-perovskite PbTiO₃ nanofibers was discussed.

Experimental details

Synthesis: 0.005 mol Ti(OC₄H₉)₄ was dissolved into 10 ml 2-methoxyethanol to prepare Ti precursor, into which TEA solution (w=25%) was added then. The mixed solution was stirred for 16 h slowly, and developed into gel in the end. The amount of TEA solution added into Ti precursor was assigned as 0 ml (marked sample-1), 0.1 ml (marked sample-2), 0.5 ml (marked sample-3) and 1.0 ml (marked sample-4), respectively. Meanwhile, 0.0055 mol Pb(NO₃)₂ was dissolved into 10 ml water, which was acted as Pb precursor. Finally, KOH (1.37 g), Polyvinyl Alcohol (PVA) (2

g/L) and precursors were added into a 50 ml stainless-steel Teflon autoclave. During the whole process, KOH acted as mineralizer and PVA was surface modification agent. After being kept in an oven for 12 h at 200 °C to perform hydrothermal reaction, the autoclave was cooled down to room temperature naturally. Then the resultant was filtered and washed several times using deionized water and ethanol, in order to remove impurity, organic molecules and so on. Finally, the products could be received just after being air-dried at 80 °C for 12 h, presented as powders.

Characterization: Powder X-ray diffraction (XRD) pattern was collected on a Thermo ARL X'TRA powder diffractometer with Bragg-Brentano geometry by Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with 0.82 \AA resolution at room temperature without any pretreatment. By utilizing MDI Jade 5.0, the full width at half maximum (FWHM) of the XRD diffraction peaks were calculated. The morphology, size and dispersity of the prepared samples were detected by a Hitachi field-emission scanning electron microscopy (SEM) instrument Model S-4800 at 5 kV. High-resolution transmission electron microscopy (HRTEM) images were taken by a transmission electron microscope (TEM) (JEOL-2010) with an accelerating voltage of 200 kV. The molecule structures of compositions were identified by Fourier transform infrared (FTIR) (Nicolet 5700). To study the luminescence property, photoluminescence (PL) spectrum was excited by the 410 nm exciting light of Xenon lamp via fluorescence spectrophotometer (FLSP920).

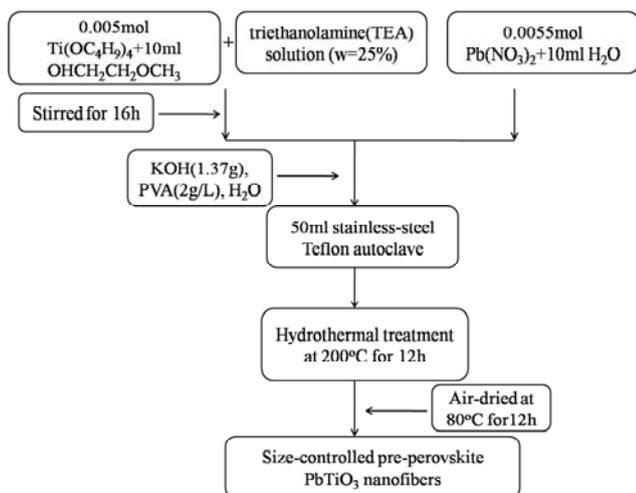


Fig.1 The flowchart for the synthesis of pre-perovskite PbTiO₃ nanofibers by the modified sol-gel process and the PVA-assisted hydrothermal reaction

Results and discussion

As shown in Fig.2, the XRD patterns of four samples are presented. All the diffraction peaks of four samples are consistent with those of the pre-perovskite PbTiO₃ phase¹³. Obviously, the intensity of some diffraction peaks, such as (200), (310), (330) and (600), increases after adding 0.1 ml TEA solution, which indicates TEA solution is conducive to oriented growth of PbTiO₃ nanofibers (sample-2). However, when the amount of TEA solution was increased thereafter, the diffraction peaks decrease gradually (sample 2-4), along with the broadening of diffraction peaks. The full width at half maximum (FWHM)

values of diffraction peaks (200), (330) and (002) are listed in Tab.1. Accompanied with the increase of the dosage of TEA solution, the FWHM values of diffraction peaks (200), (330), and (002) increase accordingly. On the basis of Fig.2, it suggests that the crystal size of PbTiO₃ nanofibers decreases.

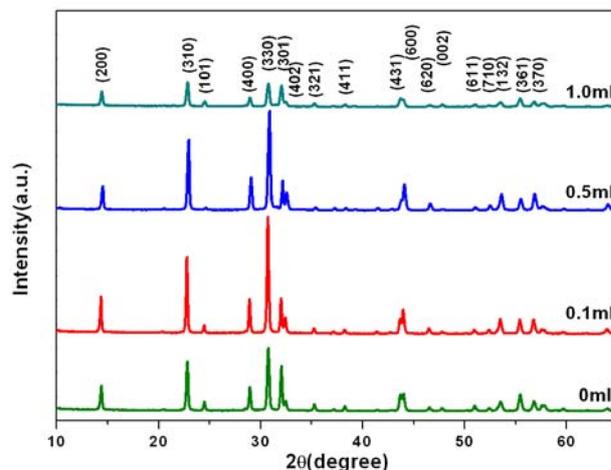


Fig.2 XRD patterns of pre-perovskite PbTiO₃ nanofibers (sample 1-4) by adding different amount of TEA solution.

Tab.1 The FWHM of (200), (330), (002) diffraction peaks of pre-perovskite PbTiO₃ nanofibers (sample 1-4).

Sample	1: 0 ml	2: 0.1 ml	3: 0.5 ml	4: 1.0 ml
(200)	0.181	0.148	0.185	0.204
(330)	0.191	0.170	0.201	0.259
(002)	0.158	0.175	0.210	0.215

The morphology, size and dispersity of pre-perovskite PbTiO₃ nanofibers were examined via scanning electron microscope (SEM). SEM images of four samples are displayed in Fig.3 ((a) - (d)), in which the sizes of these nanofibers are measured and the results are plotted in Tab.2. The corresponding length and diameter distribution histograms of sample 1-4 are displayed in Fig.4 ((a)-(h)). With increasing the dosage of TEA solution, the length of the nanofibers decreases from about 35-90 μm in sample-1 to 5-12 μm in sample-4. The proportion of the nanofibers with the diameter in the range of 100-300 nm has been determined to be 63.8%, 84.0%, 95.4% and 91.6%, respectively. It is clear that the length of pre-perovskite PbTiO₃ nanofibers is regulated effectively and the diameter basically remains in the same range of 100-300 nm. As a comparison, the length of the nanofibers of sample-4 is about 1/7 of that of sample-1, accompanied by the change of the aspect ratio from 225-350 in sample-1 to 42-60 in sample-4. From the SEM images, without adding TEA solution, aggregation phenomenon of nanofibers is serious. After introducing the TEA solution into Ti precursor, the dispersity of the samples, as well as the diameter uniformity of a single nanofiber, is improved significantly.

HRTEM images in Fig.3 (e) and (f) were obtained from an individual nanofiber of sample-1 and sample-4, respectively. The insets in (e) and (f) show the selected area electron diffraction pattern. It is proved that the pre-perovskite PbTiO₃ nanofiber is a single crystal. Furthermore, the interplanar spacing are 0.877 nm

and 0.871 nm, which correspond to the (110) plane of pre-perovskite PbTiO_3 ¹³. Combined with all the above findings, well-crystallized single-crystal and length-controlled pre-perovskite PbTiO_3 nanofibers have been synthesized successfully, and the growth direction is proved to be [001] axis.

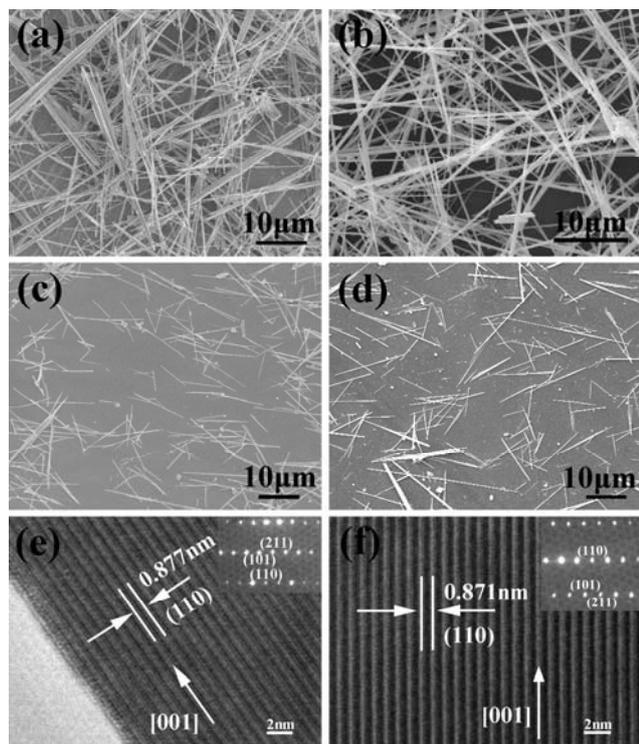


Fig.3 SEM images of pre-perovskite PbTiO_3 nanofibers. (a)- (d): sample 1-4, respectively. High-resolution TEM (HRTEM) images of pre-perovskite PbTiO_3 nanofibers, (e): sample-1, (f): sample-4. The insets in (e) and (f) show the selected area electron diffraction pattern.

Tab.2 Average scope of the length, diameter and aspect ratio of nanofibers derived from SEM results.

Sample	1: 0 ml	2: 0.1 ml	3: 0.5 ml	4: 1.0 ml
Length (μm)	35-90	20-50	10-20	5-12
Diameter (nm)	100-400	140-500	100-400	120-200
Aspect ratio	225-350	100-143	50-100	42-60

In the case of sol-gel, hydrolysis of titanium alkoxide occurred firstly when TEA solution was added. In fact, this process is very complex and an inorganic three-dimensional (3D) network is formed²³. Meanwhile, the complexing reaction, hydrolysis and dehydration polycondensation²⁴ would take place on the premise that TEA exists, affecting the network structure of Ti gel.

When the different amount of TEA solution was added into Ti precursor and stirred slowly for 16 h, the amorphous powder precursors were formed by freeze-drying at $-50\text{ }^\circ\text{C}$ for 36 h to study the effects of TEA solution on the Ti precursor. The surface absorption of the amorphous powder precursors were characterized by FTIR.

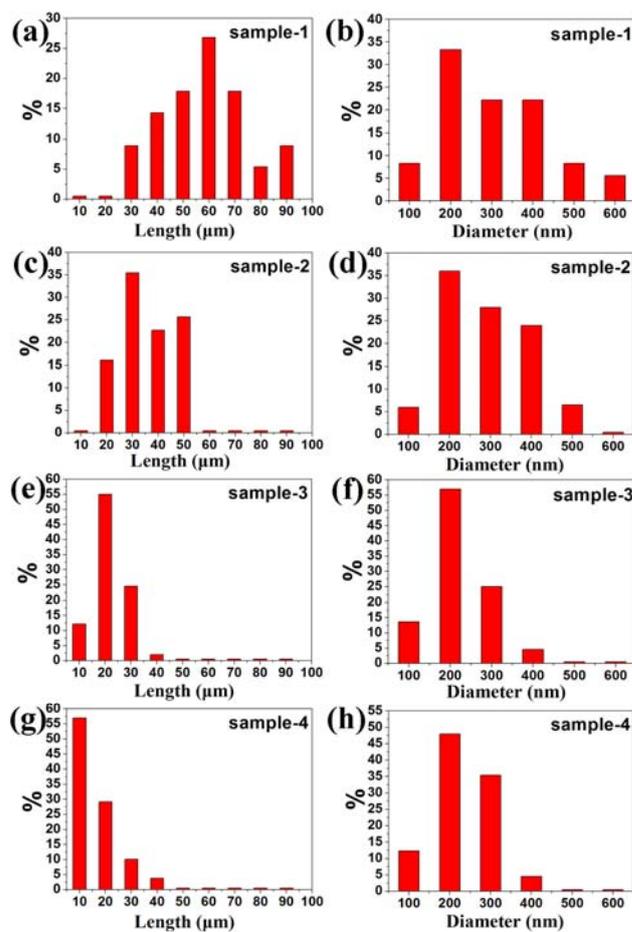


Fig.4 Length and diameter distribution histograms of sample 1-4, respectively

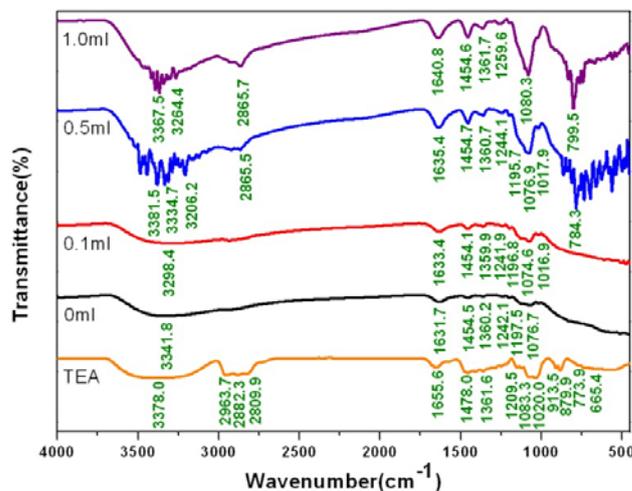


Fig.5 FTIR spectra of the amorphous powder precursors prepared by the sol-gel and subsequent freeze-drying process (the bottom curve represents the FTIR spectrum of pure TEA, the upper ones show the FTIR spectra of modified amorphous precursor in sample 1-4).

The absorption spectra of the amorphous powder precursors and TEA are displayed in Fig.5. The bands between 3500 and 3000 cm^{-1} can be assigned to the stretching modes of $-\text{OH}$ group of water and TEA. The bands ranging from 1200 to 1470 cm^{-1} and sharp bands around 2865 cm^{-1} are corresponding to the

stretching and bending vibrations of aliphatic $-CH_3$ and $-CH_2-$ groups²⁵. The peak located in 1640 cm^{-1} in the absorbed spectra should belong to the presence of moisture in the sample²⁶. The bands at 1076 cm^{-1} and 1017 cm^{-1} are due to the C-O group vibrations of isobutoxy groups and TEA^{21, 27}. C-H out-of-plane bending falls in the FTIR values of $773\text{--}913\text{ cm}^{-1}$ ²⁸. As shown in Fig.5, the FTIR spectrum of sample-3 (0.5ml) shows a slight difference from sample-1 (0ml) and sample-2 (0.1ml), but it is similar to that of sample-4 (1.0ml). This could be attributed to the fact that the complexing reaction, hydrolysis and dehydration polycondensation between TEA solution and Ti precursor would take place vigorously when the more TEA solution was added (such as more than 0.1ml). Meanwhile, the increasing dosage of TEA solution contributes to the intensity of bands at 3347 cm^{-1} , 2865 cm^{-1} , 1635 cm^{-1} , 1454 cm^{-1} , 1360 cm^{-1} , 1076 cm^{-1} , 784 cm^{-1} . As a comparison of the four spectra (sample 1-4), the bands of 1640 cm^{-1} , 1080 cm^{-1} , 799 cm^{-1} are obviously shifted to high wave numbers, implying that TEA experienced chemical reaction with $Ti(OC_4H_9)_4$.

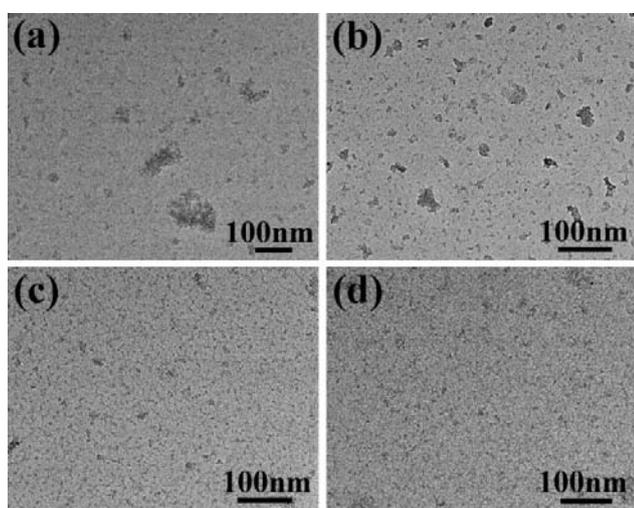


Fig.6 TEM images of the amorphous powder precursors prepared by the modified sol-gel process and the freeze-drying treatment. (a)-(d): sample 1-4, respectively.

Furthermore, TEM was used to study the morphology and dispersity of the amorphous powder precursors. From the TEM images in Fig.6, without adding the TEA solution, small amorphous particles with a diameter of $\sim 3\text{ nm}$ aggregate into 40-100nm blocks (Fig.6 (a)). With increasing the dosage of the TEA solution, it presents clearly that the size of the aggregated blocks decreases significantly and the dispersity of small amorphous particles highly improved (Fig.6 (b-d)). Especially in Fig.6 (d), the small amorphous particles present excellent dispersity and size uniformity. The results from the above FTIR spectra and TEM images strongly suggest that TEA solution can effectively modify the Ti precursor, leading to the good dispersity and uniformity of initial reactants. Therefore, it is suggested that the number of crystal nucleation of pre-perovskite $PbTiO_3$ nanofibers (the molecular ratio of $Pb/Ti = 1.1$) increase during the hydrothermal reaction, which suppresses the growth rate of the nanofibers. As a result, the length of the nanofibers decreased and the dispersity was enhanced, as well as the diameter uniformity of a single nanofiber.

A schematic diagram is provided to illustrate that different dosage of TEA solution results in different types of nanofibers accordingly, as displayed in Fig.7. Without the introduction of TEA solution into Ti precursor, the initial reactants were aggregated with a large size (Fig.7 (a)), which resulted in the aggregation and large size of the nanofibers, as shown in Fig.3 (a). When the dosage of TEA solution was increased, the chemical reaction between TEA solution and Ti precursor became vigorously, and this might have a strong effect on the three-dimensional (3D) network of Ti gel, giving rise to small-sized and homogeneous reactants with the significantly improved dispersity (Fig.7 (c)). And then the number of the crystal nucleation increased during the hydrothermal reaction, which suppressed the growth rate of the nanofibers. As a result, the length of the obtained nanofibers decreased and the dispersity improved, as shown in Fig.3 (d).

According to previous study, the pre-perovskite $PbTiO_3$ nanofiber is metastable phase and grow along $[001]$ with the outer surface enclosed by $\{110\}$. It is revealed that Pb-O covalent bonding is the key point to stabilize the one-dimensional (1D) structure of pre-perovskite $PbTiO_3$ nanofibers¹³. Besides, the Pb^{2+} excess is beneficial to synthesize and stabilize the nanofibers. Increased Pb/Ti ratio gives rise to a smaller diameter of the nanofibers and makes them stable because the high concentration of Pb^{2+} in the solution significantly prohibits the re-dissolution of the resulting nanofibers¹⁶. It is concluded from the above results that the amount of Pb has a decisive impact on the diameter of the nanofibers, where the enclosed surface $\{110\}$ is supposed to be Pb-O termination. Therefore, if the amount of Pb remains unchanged, the diameter of the nanofiber would be kept in a certain range.

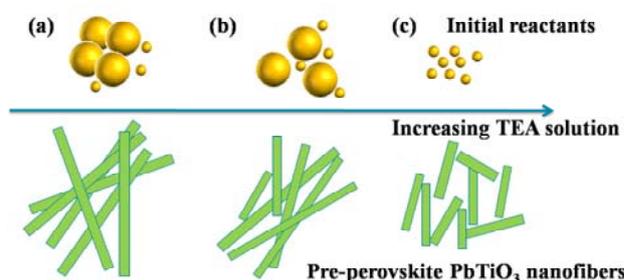


Fig.7 Schematic illustration of different dosage of TEA solution into Ti precursor, which will grow into pre-perovskite $PbTiO_3$ nanofibers of different sizes via hydrothermal reaction (the yellow particles: initial reactants; the green fibers: pre-perovskite $PbTiO_3$ nanofibers).

To get rid of the impact of surface modification agents (such as PVA molecules), all the samples were washed by acetone, after which the photoluminescence (PL) measurements were taken with 410 nm excitation source of Xenon lamp at room temperature. Fig.8 presents that there is a broad green emission band at the wavelength of 530-550 nm in each curve within the scan range of 430 nm~790 nm. The upper inset in Fig.8 shows that the nanofibers in sample-1 present obvious green light. According to previous study¹⁵, the green emission is intrinsically structural related and caused by self-trapped exciton (STE) effect of highly distorted TiO_6 octahedron. As for STE, in the pre-perovskite $PbTiO_3$ nanofibers with a direct band structure, the excited electron and remaining hole could generate a local

deformation of the lattice, and thus localize themselves into a state below conduction band and above valence band. With increasing the dosage of TEA solution, the emission peak of 550nm exhibits no obvious shift as shown in Fig.8, indicating that the role of crystal structure and electronic band structure is much stronger than that of the size.

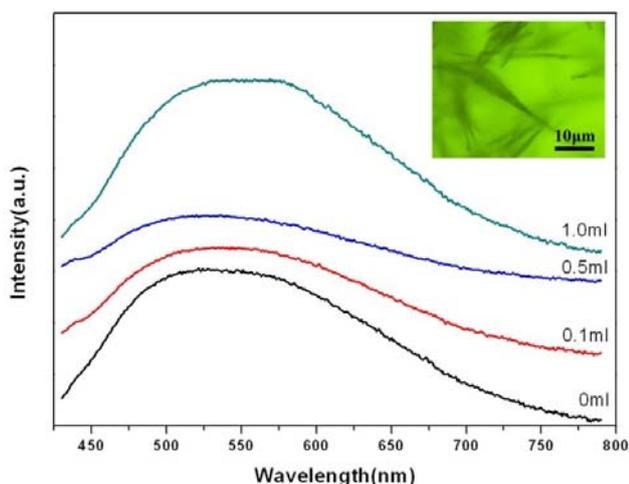


Fig.8 PL spectra of sample 1-4 excited by 410 nm wavelength Xenon lamp at room temperature. The upper inset shows that the nanofibers in sample-1 present obvious green light.

Conclusions

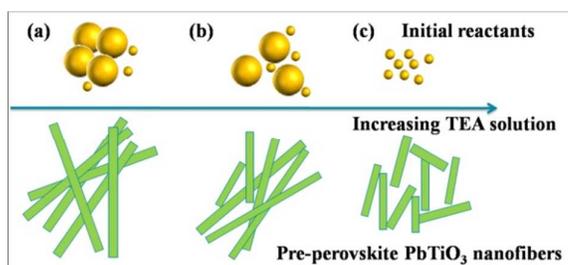
By adjusting different dosage of TEA solution, Ti precursor was modified effectively in the sol-gel process. Combined with PVA-assisted hydrothermal reaction, length-controlled single-crystal pre-perovskite PbTiO_3 nanofibers have been successfully synthesized. The length of the nanofibers ranged from 35-90 μm to 5-12 μm , accompanied by a change of the aspect ratio from 225-350 to 42-60. Also, the dispersity of the prepared samples and the diameter uniformity of a single nanofiber were improved gradually. All the results indicated that the chemical reaction of TEA solution with $\text{Ti}(\text{OC}_4\text{H}_9)_4$ could decrease the size of the initial reactants and improve their dispersity. Such reactants may play an important role in increasing the number of crystal nucleation of pre-perovskite PbTiO_3 nanofibers during the hydrothermal reaction, resulting in the decreased size and good dispersity of the nanofibers. In particular, such nanofibers presented a strong green emission (~ 550 nm) at room temperature, whereas there was no peak shift for the emission with decreasing the lengths of the nanofibers. The novel method that combines modified sol-gel process with PVA-assisted hydrothermal reaction could be extended to other 1D perovskite oxide materials for tailoring their crystal growth. Moreover, the as-prepared single-crystal pre-perovskite nanofibers may be ideal objects to understand intrinsic optical properties of perovskite-related oxides as well as optoelectronic nanodevices.

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Notes and references

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[Highlights]

The introduced TEA solution modified the sol-gel process and the length of the nanofibers decreased during the subsequent hydrothermal reaction.