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Regulating solution epitaxy of PbTiO₃ film by Ni ions for enhanced visible-light photovoltaic current

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Abstract

The bulk photovoltaic effect of perovskite ferroelectric oxides has been widely explored because of its ability to obtain the above-bandgap photovoltage. However, the photovoltaic current in these materials remains low at the nA level in the visible-light range, severely limiting the device applications due to a wide bandgap. Herein, we report a Ni ions-assisted coprecipitation-hydrothermal method to regulate the growth of single-crystal PbTiO₃ film with a controlled thickness from 0.7 μm to 2.2 μm. The epitaxial relationship between the tetragonal perovskite film and cubic Nb:SrTiO₃ substrate has been characterized to be {001}_{film} || {100}_{substrate}. The film adopts a single-domain structure with a polarization direction pointing to the substrate. Interestingly, the film exhibits a large photovoltaic current under 405 nm irradiation, with values reaching 3.6 mA/cm², which is 3.6 times higher than those of the reported ferroelectric materials. Introducing Ni ions as an additive into the precursor solution was investigated to effectively mediate the competitive nucleation and growth processes between the film and the by-product powder, thereby enabling a tunable thickness of the films. An intriguing Ti-vacancy composition gradient was revealed throughout the film and its coupling with the spontaneous polarization generates a polarization gradient and thus a built-in electric field, accounting for the excellent photovoltaic performance reported here.

Keywords: Composition gradient, single crystal, single domain, ferroelectric photovoltaic, competition growth



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INTRODUCTION

Since the discovery of the bulk photovoltaic (PV) effect in the 1970s, ferroelectric oxides have gained substantial attention due to the distinct polarization-related charge-separation mechanism^[1]. Different from the p-n junction effect in silicon PV cells^[2,3], ferroelectric PV is a bulk phenomenon^[4,5] that exhibits unique characteristics, including above-bandgap photovoltage^[6], switchable PV current^[7] and inherent light polarization dependence^[8,9]. As a classical ferroelectric material among the ABO₃ perovskite group, lead titanate [PbTiO₃ (PTO)] possesses a high spontaneous polarization that offers various functions such as piezoelectricity^[10], ferroelectricity^[11], photocatalyst^[12], and photovoltaics^[13]. A wide bandgap of PTO (~ 3 eV), a common characteristic of many perovskite oxides, however, is not beneficial for enhancing PV current in the visible-light range toward optoelectrical devices.

Different strategies have been developed to enhance the PV current of PTO-based materials. For example, chemical doping and bandgap engineering were employed to address this issue. PTO-based multicomponent solid solution offers flexibility in chemical composition and bandgap adjustment to enhance PV current^[14-16], and further increase the current to 6.2 $\mu\text{A}/\text{cm}^2$ via designing the composition in the vicinity of the morphotropic phase boundary^[17,18]. The substitution of Ni in PTO is thought to work in conjunction with oxygen vacancies to alter the band structure and boost the PV current according to theoretical calculations^[19-21]. The preparation of films by solid-state or sol-gel methods to investigate the bandgap narrowing effect in Ni-doped films has been conducted to verify theoretical calculations^[22-24] and boost the PV current up to ~ 15.8 $\mu\text{A}/\text{cm}^2$ ^[24]. Furthermore, the combination of PTO with a p-n junction realizes the coupling of bulk and junction PV effects, improving the separation of photogenerated carriers and suppressing their non-radiative recombination, thereby increasing the current to 210 $\mu\text{A}/\text{cm}^2$ ^[25]. Nonetheless, the studies mentioned above were subjected to polycrystalline films or ceramics, where the defects such as grain boundaries and inconsistent grain sizes could be a center to trap photogenerated carriers and thus increase their recombination, leading to a low PV current. Consequently, constructing efficient channels for the separation and transport of photogenerated carriers in single-phase ferroelectric oxides is particularly desired.

In this work, we developed a high-quality single-crystal PTO film assisted by Ni ions on 0.7 wt.% Nb:SrTiO₃ (NSTO) substrate via a coprecipitation-hydrothermal method. Ni ions as an additive effectively regulated the competitive growth of film and by-product powder in the hydrothermal process. The epitaxial relationship of the film with a thickness ranging from 0.7-2.2 μm has been identified to $\{001\}_{\text{PTO(Ni)}} \parallel \{100\}_{\text{NSTO}}$. A combined characterization reveals that the introduction of Ni ions also contributes to the generation of a Ti-vacancy composition gradient throughout the film. Moreover, the piezoelectric force microscope (PFM) result confirms that the film adopts a single-domain structure with a polarization direction pointing to the substrate. The coupling between the composition gradient and spontaneous polarization generates a polarization gradient and further a built-in electric field that contributes to improved PV performance in the visible-light range. The PTO(Ni) film demonstrates a large PV current of up to 3.6 mA/cm^2 at 405 nm and a 3.6-fold enhancement in photoresponsivity compared with pure PTO film. These findings may trigger interest in developing wide-bandgap ferroelectric oxides for passive visible light detection.

MATERIALS AND METHODS

Materials

Lead nitrate (Pb(NO₃)₂, $\geq 99.0\%$), nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O, $\geq 98\%$], tetrabutyl titanate [Ti(OC₄H₉)₄, TBOT, $\geq 98\%$], potassium hydroxide (KOH, $\geq 85\%$), ethylene glycol monomethyl ether (CH₃OCH₂CH₂OH, $\geq 99\%$), ammonium hydroxide (NH₃·H₂O, 25%-28%), acetone (CH₃COCH₃, $\geq 99.5\%$),

and ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. Single-crystal 0.7 wt.% NSTO substrates with dimensions $10 \times 10 \times 0.5 \text{ mm}^3$ and (100) orientation were obtained from Shanghai Institute of Optics and Mechanics.

Film preparation

The films were synthesized by a coprecipitation-hydrothermal method as follows: NSTO substrate was cleaned ultrasonically with acetone, ethanol, and deionized water before use and then placed in a Teflon holder for drying. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and TBOT were dissolved into ethylene glycol monomethyl ether for the preparation of Ni-Ti-Pb mixed solution. The amount of TBOT was 5 mmol and the Ni/Ti molar ratio was set at 0:100, 1:100, 3:100, 5:100, and 10:100 for film at 0%, 1%, 3%, 5%, and 10% Ni, respectively. The Pb/Ti molar ratio was set at 1.25:1. The mixed metal solution was dripped into excess ammonia water at room temperature. Fine Ni-Ti-Pb coprecipitate could be precipitated in the ammonia solution. After filtering, the Ni-Ti-Pb coprecipitate was added to a 4.5 mol/L potassium hydroxide solution. After 2 h of continuous stirring at room temperature, the NSTO substrate was placed in the solution of the autoclave before hydrothermal treatment at 210°C for 12 h. NSTO substrate was maintained horizontally 15 mm above the bottom of the autoclave. The resultant products, including film and powder, were washed with water and ethanol several times and subsequently dried at 60°C in the air.

Characterization

The structures of the sample were characterized by scanning electron microscope (SEM, Hitachi SU-70 Analytical FESEM), X-ray diffraction (XRD, Thermo ARL X'TRA powder diffractometer, Cu $K\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$), piezoelectric force microscope (PFM, Asylum Research, Cypher S and MFP-3D), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). An integrated focused ion beam (FIB, Helios Nanolab 600) and SEM (Hitachi S4700) was used to extract thin-film lamellae from the PTO(Ni)/NSTO sample, and Pt and C layers were deposited on the film surface to protect from damage and increase the conductivity, respectively. Subsequent cross-sectional observations of the film were carried out using an aberration-corrected transmission electron microscope (FEI Titan G2 80-200 Chemi STEM). The variations in composition across the thickness of PTO(Ni) films were characterized by time-of-flight secondary-ion mass spectrometry (TOF-SIMS, IONTOF GmbH TOF.SIMS 5-100).

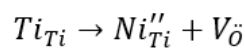
Photovoltaic measurement

Photovoltaic properties of PTO and PTO(Ni) films were collected using optical units from Thorlabs and source measure units (Keithley 2450). The light from a monochromatic laser passes through a reflector and is vertically incident on the calibration detector (Optical power and energy meter consists of PM100USB and S130VC) or the sample surface. A diaphragm is used to control the on/off state of the light path. Top electrodes (diameter: $\sim 1 \text{ mm}$, thickness: $\sim 40 \text{ nm}$) were deposited on the film surface by direct current (dc) sputtering (SD-3000). The films were irradiated with light from 405 nm (MDL-III-405) and 375 nm (MDL-III-375) lasers.

RESULTS AND DISCUSSION

To study the effect of Ni ions on the growth of single-crystal PTO films, different Ni ion concentrations (0, 1, 3, 5 and 10 at.%) were used under the hydrothermal reaction condition. One can identify the epitaxial relationship of $\{001\}_{\text{PTO(Ni)}} \parallel \{100\}_{\text{NSTO}}$ by the X-ray diffraction (XRD) pattern of the tetragonal PTO(Ni) (JCPDS 70-0746) film and cubic NSTO (JCPDS 35-0734) substrate [Supplementary Figure 1A and B]. XRD patterns of the films indicate no slight peak shifts, in contrast to the pronounced peak shift in the by-product powders [Supplementary Figure 1C and D]. This suggests that Ni ions are predominantly localized within the by-product powder rather than the film lattice. We also performed the Rietveld refinement of XRD patterns of by-product powders with different Ni ion concentrations of 0%, 1%, 3%, 5%, and 10% in

Supplementary Figure 2A-E. One can observe that all peaks have been well refined. The refined lattice parameters are listed in **Supplementary Table 1**, which are comparable to those of literature values^[26]. Specifically, the refined lattice parameter c decreases from 4.168 to 4.151 Å as the Ni ion concentration increases from 0 to 10%, while a increases slightly from ~ 3.904 to 3.907 Å. The unit cell volumes are found to decrease with increased Ni ion concentration. It could be due to the larger radius of Ni^{2+} than that of Ti^{4+} . We argue that the introduction of Ni ions is highly likely to play a key role in regulating the nucleation and growth control of the PTO film, rather than merely acting as a doping effect. The morphological changes of films and by-product powders are illustrated in **Figure 1A-O**, while the corresponding schematic diagrams of the growth are shown in **Figure 1P-T**. As **Figure 1A** shows, many fibrous crystallites formed on the substrate in pure PTO condition, with a length and width of ~ 40 nm and ~ 5 nm, respectively. Homogeneous nucleation of particles in the solution is preferred for film growth. In the absence of Ni ions (pure PTO), particle nucleation occurs with a small critical size after a relatively short period (~ 30 min). As the Ni ion concentration increased, the crystallites on the substrate began to extend in the plane, forming a discontinuous film. A possible explanation for this is that when Ni ions were introduced into the coprecipitation process, they could easily enter the lattice of PTO and substitute for Ti ions during the hydrothermal reaction, generating oxygen vacancy defects for a charge balance.



The substitution of Ni ions and the resulting oxygen vacancies may create a more complex hydrothermal environment where a larger critical nucleation size in homogeneous nucleation is needed to ensure stability. The defects might also hinder the diffusion of ions involved in the reaction, causing a slower consumption rate of raw materials. As a result, the epitaxial growth of the film is promoted by increasing critical nucleation size and slowing raw material consumption. When the Ni ion concentration increased from 1% to 3%, the in-plane size of the discontinuous film also increased from ~ 0.8 µm to 5-15 µm [**Figure 1B and C**]. A critical point was achieved when the concentration of Ni ions was 5%, where a large-area smooth film with some holes was formed [**Figure 1D**]. Ultimately, a dense and high-quality PTO(Ni) film was fabricated with the assistance of a 10% Ni ion concentration [**Figure 1E**]. Correspondingly, the film thickness increased gradually from 0.7 µm to 2.2 µm [**Figure 1F-J**], accompanied by the size of the by-product powder increasing from 40 nm to 40 µm [**Supplementary Figure 3**]. The morphology of the particles developed from a fibrous to a regular cubic shape [**Figure 1K-O**]. It is evident that the introduction of Ni ions effectively regulates the growth of both the films and the by-product powders, as illustrated in **Figure 1P-T**. Moreover, as shown in **Supplementary Table 2**, energy dispersive spectroscopy (EDS) analysis revealed that Ni ions are mainly concentrated in the powders, which significantly decreases the concentration of Ni ions in the solution. Therefore, Ni ions are also not likely to enter the film. Additionally, electronic polarization screening at the PTO/NSTO interface is crucial for reducing the interface energy, thereby enabling the solution epitaxy of PTO films^[13,27]. The introduction of Ni ions will increase the interfacial lattice mismatch^[19] and raise the interface energy, which is not favorable thermodynamically.

Time-dependent experiments in **Supplementary Figure 4** also illustrate the growth of PTO assisted by Ni ions. During the initial 2 h of the reaction, there are almost no particles observed on the substrate. When the reaction time was prolonged to 4 h, a few particles of ~ 100 nm were formed. A continuous film with some holes and cracks has been obtained after a reaction of 6 h. Subsequently, the film became smooth and flat after about 12 h. As the reaction time is prolonged, PTO particles coarsen to a continuous film that subsequently undergoes a layer-by-layer-like growth without phase transition [**Supplementary Figure 4I**]. The epitaxial relationship between the film and the substrate is characterized to be $\{001\}_{\text{PTO(Ni)}} \parallel \{100\}_{\text{NSTO}}$

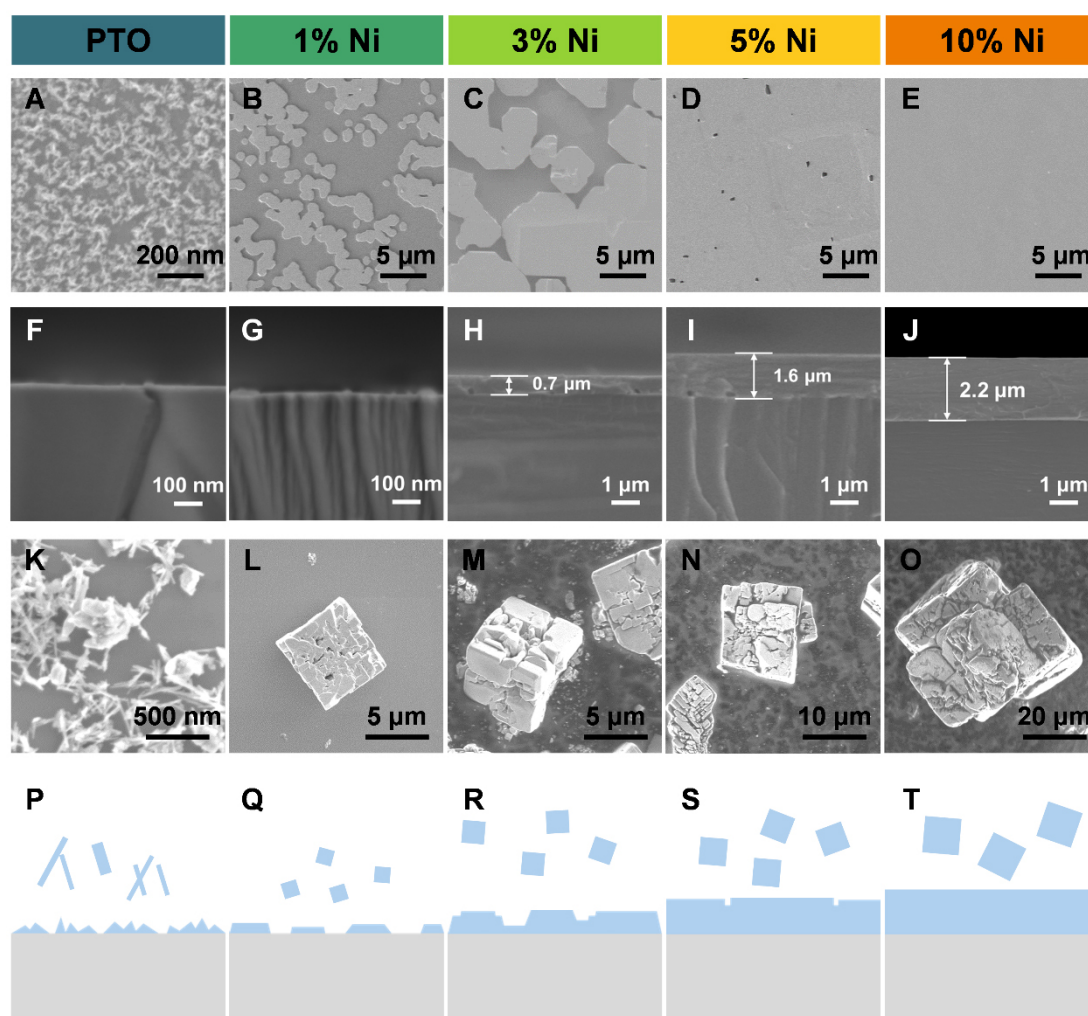


Figure 1. Ni ions-assisted growth of PTO films and by-product powders on NSTO substrate. SEM images of PTO films synthesized via coprecipitation-hydrothermal method from precursor solutions with different Ni ion concentrations of (A) 0%; (B) 1%; (C) 3%; (D) 5%; and (E) 10%. SEM images of by-product powders synthesized from precursor solutions with different Ni ion concentrations of (F) 0%; (G) 1%; (H) 3%; (I) 5%; and (J) 10%. Cross-sectional SEM images of films synthesized from precursor solutions with different Ni ion concentrations of (K) 0%; (L) 1%; (M) 3%; (N) 5%; and (O) 10%. (P–T) The corresponding schematic diagrams of the growth models. PTO: PbTiO_3 ; NSTO: Nb:SrTiO_3 ; SEM: scanning electron microscope.

consistently. From [Supplementary Figure 4J](#), it was observed that components of by-product powders transform from incompletely reacted precursor materials, such as $\alpha\text{-PbO}$ (JCPDS 05-0561), Pb_2O (JCPDS 75-0201), and TiO_2 (JCPDS 21-1276 and JCPDS 21-1272), to the final tetragonal phase PTO. Notably, there are no diffraction peaks indicative of nickel oxides throughout this process. We have further confirmed Ni ions in the powder rather than in the film for the 10% Ni ion concentration sample by using XPS. A distinct Ni $2p$ signal can be observed in the powder [[Supplementary Figure 5A](#)], which can be deconvoluted into four peaks^[28], corresponding to the Ni $2p_{3/2}$ (855.55 eV) and Ni $2p_{1/2}$ (873.25 eV) peaks and their associated satellite peaks at a binding energy of 861.45 eV (Ni $2p_{3/2}$) and 879.51 eV (Ni $2p_{1/2}$), respectively. However, the Ni signal on the film surface is almost undetectable from the background signal [[Supplementary Figure 5B](#)]. Therefore, it can be concluded that Ni ions influence the competition for the nucleation of materials in the precursor solution and on the substrate, promoting the nucleation and growth of crystalline particles on the substrate to form a continuous film. Specifically, the concentration of dissolved raw materials in a closed hydrothermal system was high to easily reach supersaturation, which promoted the homogeneous

nucleation of particles to occur predominantly in the competitive growth of film and powder. This would lead to a rapid decrease in the concentration of Pb ions in the solution^[13]. Accordingly, the introduction of Ni ions also affected the dissolution equilibrium of Ti in the particles, resulting in a decrease in Ti concentration. Consequently, the heteroepitaxy of PTO on the substrate was suppressed kinetically at this stage [Supplementary Figure 4I]. As the reaction continued, the incompletely reacted precursor materials, such as lead oxide and titanium oxide particles, gradually dissolved, causing a slow increase in the concentration of materials. The heteroepitaxy of PTO film on the substrate thus occurred with Pb- and Ti-vacancies at the interface when the condition was closer to a thermodynamic equilibrium state. As the heteroepitaxy continues, the formation of vacancies gradually becomes more difficult due to an increased concentration of Pb ions and Ti ions in the solution. Ultimately, a Pb-vacancy and Ti-vacancy gradient structure forms along the thickness direction of the film. Meanwhile, Ni ions may accumulate in the powder by substituting Ti [Supplementary Figure 1B and Supplementary Figure 4J].

The film obtained from precursor solutions with 10 at.% Ni ion concentration was chosen for microstructure investigation, named as PTO(Ni) film. Figure 2A shows the SEM image of PTO(Ni) film, where the surface of the film is smooth and continuous, with a root-mean-square roughness (R_q) of ~ 0.19 nm [Supplementary Figure 6]. Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of PTO(Ni) film shows a sharp interface and a flat surface, and the thickness was determined to be ~ 2.2 μm [Figure 2B]. The presence of four peaks at an interval of exactly 90° confirms the single-crystal character of PTO(Ni) film by the in-plane XRD off-axis ϕ scan [Supplementary Figure 7A]. Additionally, we chose three regions at different distances from the interface, marked as 1, 2, and 3 in a circle, for selected area electron diffraction (SAED) analysis [Supplementary Figure 7B-E]. The distinct and intense diffraction spots in the SAED patterns further support the single-crystal nature of PTO(Ni) film. The atomic-scale cross-sectional HAADF-STEM image of the PTO(Ni)/NSTO interface is shown in Figure 2C. The interface is atomic-scale smooth without significant elemental interdiffusion.

Furthermore, a composition distribution of PTO(Ni) film can be investigated by TOF-SIMS analysis [Figure 2D]. PTO(Ni) film exhibits a notable composition gradient of Pb and Ti. Off-axis X-ray reciprocal space mapping (RSM) about the 103-diffraction condition of PTO(Ni) film and NSTO substrate supports that the film is *c*-axis oriented without forming *a*-domains [Supplementary Figure 7F]. The 103-diffraction peak of film distinctly extends in Q_z , reflecting a gradual change in the lattice spacing of (103) planes, arising from the composition gradient. The presence of Pb-vacancy is attributed to the spontaneous formation during the epitaxial growth process of PTO crystals^[13,29]. Usually, the decrease in Ti ions may be associated with the introduction of Ni ions and its subsequent occupation of Ti lattice sites. However, the actual Ni ion concentration in the film is substantially lower than our designed concentration based on the XRD results from both films and by-product powders [Supplementary Figure 1]. In addition, electron energy-loss spectrum (EELS) collected at different regions of the film demonstrates a typical four-peak profile at the Ti $L_{2,3}$ edges [Figure 2B and E], suggesting that no detectable Ti^{3+} is present near the interface^[30,31] to screen the positively charged polar surface of the film. The O *K* edge [Supplementary Figure 8] indicates that no clear oxygen vacancies have been determined due to the fact that peak 2 is lower than peak 1 at the interface and NSTO interior^[32]. Thus, the Ni^{2+} ions and oxygen vacancies are not detectable in the film based on the above results. The out-of-plane PFM phase image supports that the film adopts a single-domain structure [Figure 2F]. The polarization direction can be determined to be downward, as all Ti atoms shift upward relative to Pb^[11]. Therefore, the PTO(Ni) film retains a similar polarization shielding mechanism to the pure PTO film^[13].

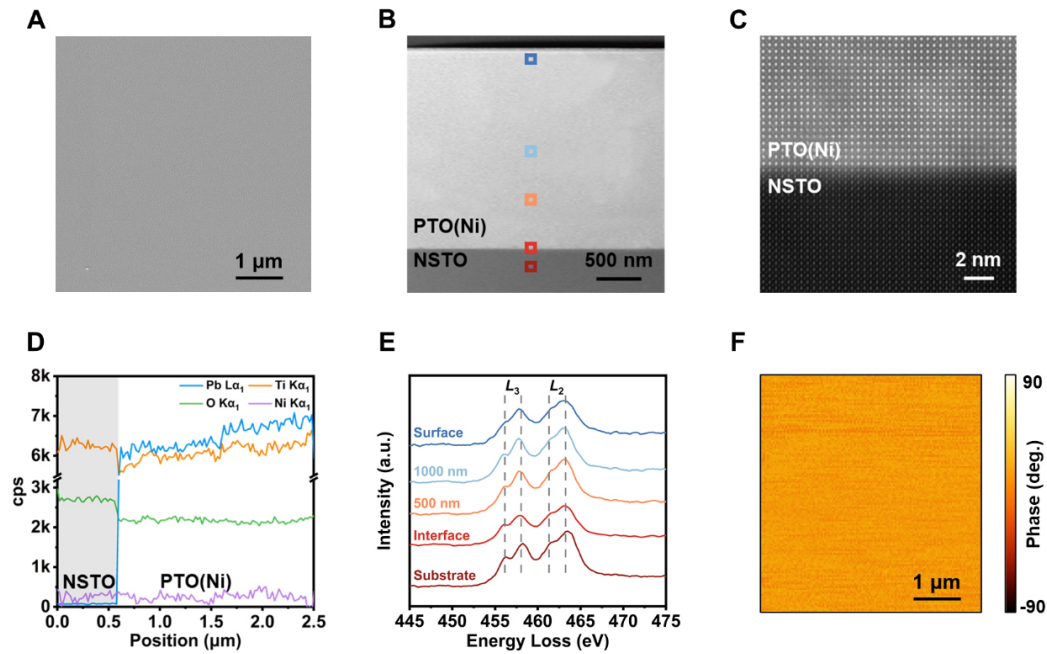


Figure 2. Characterization of PTO(Ni) film on NSTO substrate. (A) SEM image of PTO(Ni) film; (B) Cross-sectional HAADF-STEM image of PTO(Ni) film; (C) Atomic-scale cross-sectional HAADF-STEM image of PTO(Ni)/NSTO interface; (D) TOF-SIMS spectra of PTO(Ni) film; (E) Ti $L_{2,3}$ spectra perpendicular to the interface corresponding to the boxes in (B); (F) Out-of-plane PFM phase image of PTO(Ni) film. PTO: PbTiO_3 ; NSTO: Nb:SrTiO_3 ; SEM: scanning electron microscope; HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy; TOF-SIMS: time-of-flight secondary-ion mass spectrometry; PFM: piezoelectric force microscope.

For PTO, the displacement of Ti ions is directly proportional to the magnitude of polarization, and the direction of displacement is opposite to the direction of polarization^[11]. Herein, the displacements of Ti ions were measured at different areas in Figure 3A using atomic-level HAADF-STEM images [Figure 3B–F]. From Figure 3G, the out-of-plane displacements of Ti ions are suppressed near the interface ($\delta_c = 0.00781 \pm 0.035 \text{ \AA}$ at the interface) and gradually increase when moving away from the interface throughout the whole film thickness ($\delta_c = 0.190 \pm 0.054 \text{ \AA}$ at the surface). The displacements of Ti ions always remain lower than those of bulk PTO ($> 0.3 \text{ \AA}$)^[27,33]. These results imply that PTO(Ni) film exhibits a polarization gradient from the interface to the surface. In theory, the polarization gradient (∇P) of ferroelectrics is a function of composition c , mechanical strain δ , and temperature T , that is, $\nabla P \propto \nabla c, \nabla \delta, \nabla T$ ^[34–37]. The polarization gradient structure in PTO(Ni) film was proposed to arise from a coupling between the composition gradient with the polarization vector ($\nabla P \propto \nabla c$), where the contribution from temperature gradient (∇T) and strain gradient ($\nabla \delta$) were ignored due to the solution environment and a very low in-plane lattice mismatch between PTO ($a = 3.899 \text{ \AA}$) and the NSTO ($a = 3.904 \text{ \AA}$)^[38] substrate. The coupling of the composition gradient (∇c) and the spontaneous polarization (P) results in the polarization gradient. Additionally, Supplementary Figure 9 exhibits a typical “butterfly shape” and typical hysteretic character with a 180° phase contrast. Compared to that of pure PTO film^[13], the amplitude and phase curves of PTO(Ni) film become more asymmetric, identifying a built-in electric field existing in the film due to the polarization gradient. Based on the above-mentioned results and discussions, one can infer that the polarization gradient of PTO(Ni) film is proposed to derive from the coupling of the compositional change [Figure 2D] and the spontaneous polarization, which in turn generates a built-in electric field, as shown in Figure 3H.

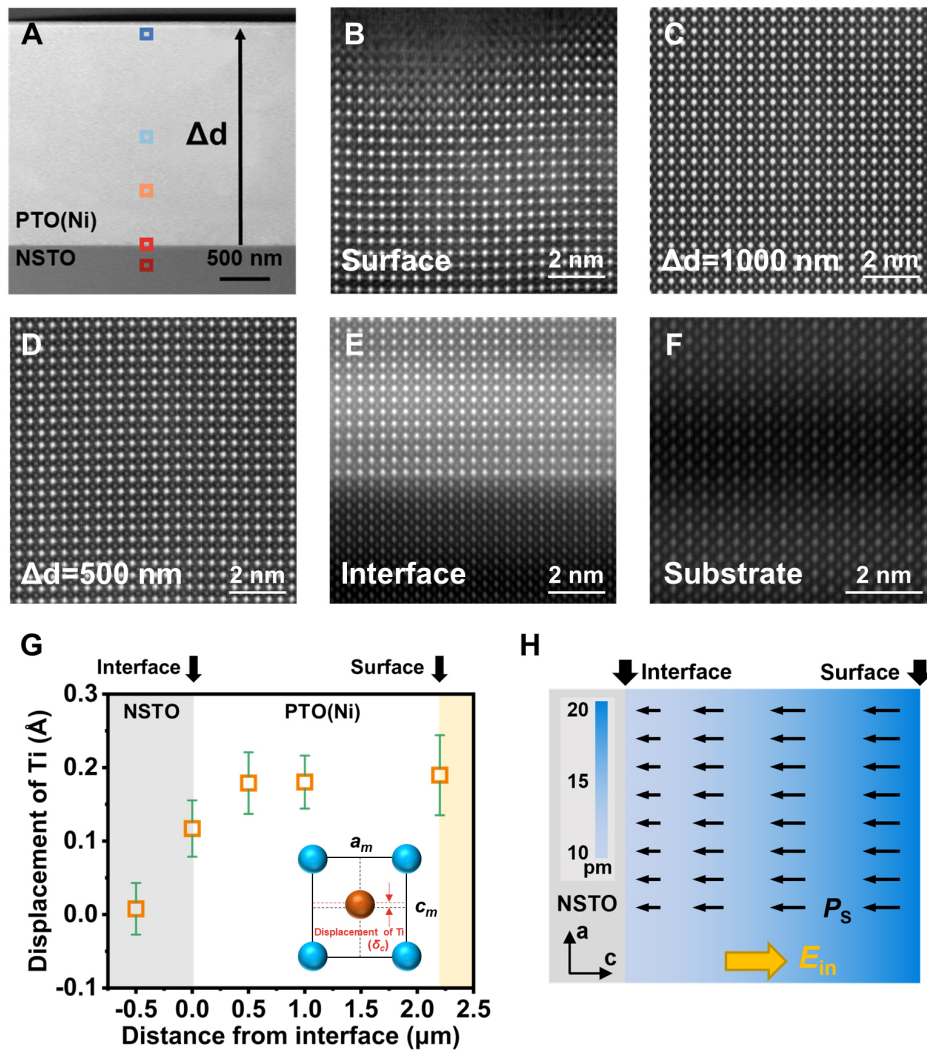


Figure 3. The polarization gradient characterization of PTO(Ni) film. (A) Cross-sectional HAADF-STEM image of PTO(Ni)/NSTO heterostructure, where Δd represents the distances from the interface; (B-F) Atomic-scale cross-sectional HAADF-STEM images of regions with different Δd in PTO(Ni) film: (B) $\Delta d \approx 2,200$ nm; (C) $\Delta d \approx 1,000$ nm; (D) $\Delta d \approx 500$ nm; (E) $\Delta d \approx 0$ nm; (F) $\Delta d \approx -500$ nm, corresponding to boxes in (A); (G) Experimentally extracted off-center displacements of the Ti ions as a function of the distance from the interface according to B-F. Insets are the schematic illustrations of the average displacement measurement of Ti^{4+} relative to the center of the four nearest Pb^{2+} in each of the corresponding regions, where the δ_c denotes the off-center displacements of Ti^{4+} along the c -axis. Error bars are indicative of the standard deviations (s.d.) of the displacements; (H) Schematic illustration of the polarization gradient throughout PTO(Ni) film. P_s denotes the spontaneous polarization, and E_{in} denotes the built-in field. PTO: PbTiO_3 ; HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy; NSTO: Nb:SrTiO_3 .

We prepared pure PTO film^[13] with a thickness of ~ 2.3 μm via a direct hydrothermal method [Supplementary Figure 10] and have conducted PV performance tests on both the pure PTO and PTO(Ni) films [Section Characterization and Supplementary Figure 11]. As a comparison, the PV current density-voltage (J - V) curve under 405 nm laser irradiation is illustrated in Figure 4A for both the PTO film and the PTO(Ni) film. The PTO(Ni) film demonstrates a remarkable PV current of up to 28.6 μA ($J_{sc} \sim 3.6$ mA/cm^2), which is 3.6 times that of pure PTO film ($J_{sc} \sim 1.0$ mA/cm^2). Similarly, the PTO(Ni) film also achieves a ~ 1.28 -fold enhancement in PV current under 375 nm laser irradiation [Figure 4B]. Furthermore, the PV current in the PTO(Ni) film is proportional to the light intensity, arguing that the PTO(Ni) film still exhibits a bulk PV effect [Figure 4C]^[39,40]. Additionally, the PTO(Ni) film maintains good stability and rapid

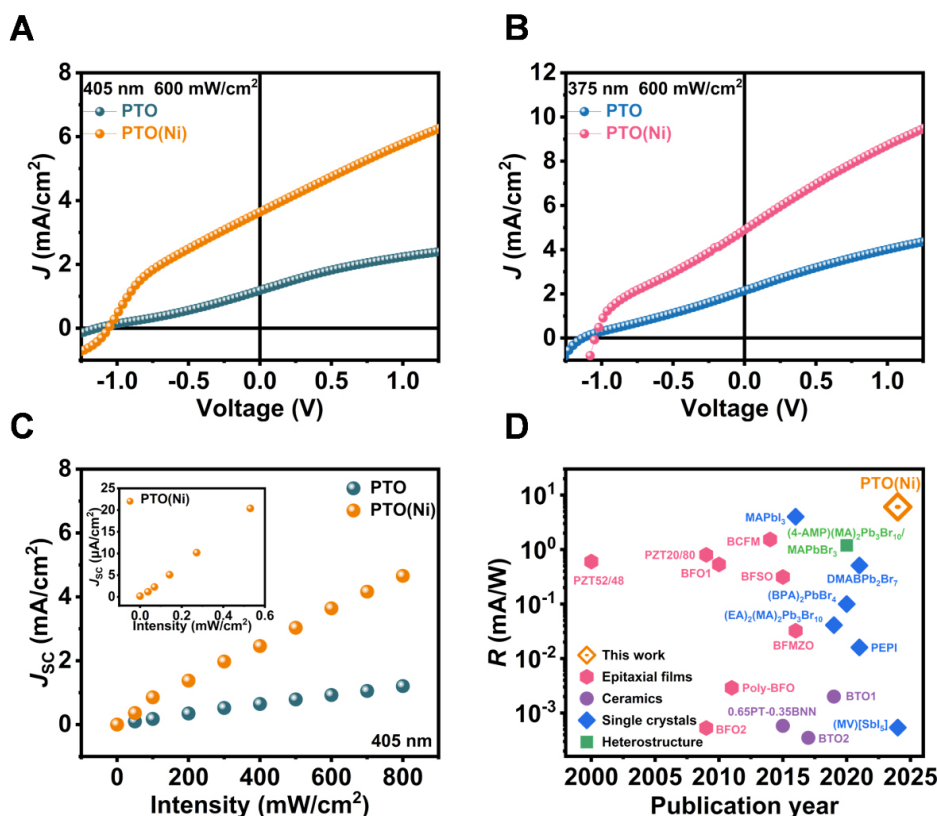


Figure 4. PV performance between pure PTO and PTO(Ni) film. J-V curve of pure PTO and PTO(Ni) film under the irradiation of 600 mW/cm² I_{light} from (A) 405 nm and (B) 375 nm laser; (C) Short-circuit current density (J_{sc}) of pure PTO and PTO(Ni) film at various light intensities. The inset depicts the excellent response of PTO(Ni) film at low light intensities (0.3–4.22 mW/cm²); (D) Photoresponsivity (R) of PTO(Ni) film (this work) compared with previously reported perovskites under blue light. The pink hexagons, purple circles, blue diamonds, and green squares represent epitaxial films, ceramics, single crystals, and heterostructure, respectively. PV: photovoltaic; PTO: PbTiO₃.

optical switching [Supplementary Figure 12]. A sharp peak value of the photovoltaic current [Supplementary Figure 12A and B] is most likely related to the pyroelectric effect^[4]. By using a weak light intensity (0.3–4.22 mW/cm²), the PV effect of the PTO(Ni) film is still detectable (1.2–20.3 μA/cm²), with the film maintaining a stable dynamic photoresponse and good retention [Supplementary Figure 12C and D and the inset of Figure 4C]. To evaluate the PV performance of PTO(Ni) film, the photoresponsivity ($R = J_{sc}/I_{\text{light}}$) has been calculated and compared with previously reported perovskites under blue light [Figure 4D and Supplementary Table 3]^[14,41–57]. Obviously, the photoresponsivity of PTO(Ni) film has improved to 6.066 mA/W, which is the highest one and about 3 times higher than that of CH₃NH₃PbI₃ single^[50], one to two orders of magnitude higher than that of (4-AMP)(MA)₂Pb₃Br₁₀/MAPbBr₃ heterostructure^[47], Bi_{0.88}Ce_{0.12}Fe_{0.9}Mn_{0.1}O₃ film^[52], Bi(Fe_{0.6}Sc_{0.4})O₃ film^[51], BiFeO₃ film^[54], Pb(Zr,Ti)O₃ films^[55,57], and (C₄H₉NH₃)₂(NH₂CHNH₂)-Pb₂Br₇ single crystal^[46]. Such a large enhancement in PV performance could be ascribed to the built-in electric field based on the detailed structural characterization of PTO(Ni) film. According to first-principles calculations, the Ti-vacancy exhibits two distinct transition levels (0.68 and 0.45 eV above the valence band maximum) in the bandgap, depending on the charge state. This results in PTO exhibiting more favorable p-type conduction^[58]. Therefore, the presence of Ti-vacancy also likely plays a significant role in the remarkable PV current in the visible-light range.

CONCLUSIONS

In summary, a single-crystal, single-domain PTO(Ni) film on an NSTO substrate was successfully prepared using a coprecipitation-hydrothermal method. The introduction of Ni ions into the precursor solution effectively regulated the competition growth of the film and the by-product powder, enabling the formation of a Ti-vacancy composition gradient. The coupling of the composition gradient with spontaneous polarization generates a polarization-gradient structure, largely enhancing the visible-light PV current up to 3.6 mA/cm². These findings may establish a unique low-temperature solution-based method, assisted by ions, to prepare single-crystal, single-domain films with gradient structures, thus opening new avenues for the growth of other ferroelectric oxides. Moreover, it may spark interest in developing PTO as a potential material for passive visible light detection devices and novel ferroelectric-based optoelectronic devices^[59].

DECLARATIONS

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Authors' contributions

Materials synthesis, Photovoltaic measurement: Sun, Y.; Chen, J.; Fu, Y.
Mechanism explanation, data acquisition and analysis: Zhang, R.; Chen, J.; Lin, C.; Ren, Z.; Tian, H.
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Availability of data and materials

The data supporting the findings of this study are available within this Article and its [Supplementary Materials](#). Further data are available from the corresponding author upon reasonable request.

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Conflicts of interest

The authors declared that there are no conflicts of interest.

Content of Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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