

Light-controlled resistive switching memory of multiferroic BiMnO₃ nanowires array

Bai Sun, and Chang Ming Li*

Institute for Clean Energy & Advanced Materials (ICEAM), Southwest University, Chongqing
400715, China

Faculty of Materials and Energy, Southwest University, Chongqing 400715, China
Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energies,
Chongqing 400715, China

Supplementary Information

1. Experimental details

1.1 Materials preparation

In this work, the BiMnO₃ nanowires array was directly grown on a Ti substrate by a hydrothermal process. All chemicals used in this work were analytical reagent grade and commercially available from Sigma, and were used without further purification. Detailed experimental procedures are as follows: First, a small amount of Bi(NO₃)₃·5H₂O (0.025 mol) and MnCl₂·6H₂O (0.025 mol) were dissolved in 50 ml acetone (99.8%) under stirring until completely dissolved, followed by addition of 200 ml deionized water under stirring. Then a concentrated ammonia was added in until the pH value of the mixed solution reached 13~14. After stirring continuously for 2 hour, the sediment was centrifuged out and washed with distilled water several times until the pH became 6.5~7.5. The co-precipitate was redispersed in 40 ml of distilled water, followed by addition of 4.0 g of NaOH under vigorous stirring for 30 min. Next, 0.5 g cationic

surfactant cetyltrimethylammonium bromide (CTAB) was added in under stirring continuously for 1.0 hour. Finally, the solution was transferred to a 50 ml sealed Teflon-lined steel autoclave. Ti substrates were sequentially cleaned by acetone, ethanol, deionized water and ultrasonication, followed by drying in air. The clean Ti substrate was placed in an autoclave to heat at 120°C for 150 hours. After the autoclave was cooled to room temperature, the Ti substrate was rinsed with deionized water and subsequently dried at 50°C for overnight.

1.2 Materials characterization

The microstructures of as-prepared BiMnO₃ nanowires were characterized by X-ray diffraction (XRD, Shimadzu XRD-7000 X-ray diffractometer) with Cu K α radiation. The surface morphology of BiMnO₃ nanowires array grown on Ti substrate was characterized using scanning electron microscopy (SEM, JSM-6510). The size, crystal structure, selected area electron diffraction (SAED) and the energy dispersive X-ray spectroscopy (the upper limit of impurity volumes that the EDX technique can detect is ~0.01%) spectra of the BiMnO₃ nanowires were examined by transmission electron microscopy (TEM-2100) at an acceleration voltage of 200 kV. Ultraviolet-visible (UV-vis) spectroscopy was realized with a Cary 5G (USA) equipment. Magnetic properties of BiMnO₃ nanowires were characterized by a Quantum Design SQUID MPMS XL-7 (SQUID). The measurement of ferroelectric hysteresis loops (P–E) of BiMnO₃ nanowires was performed by a Precision Premier Workstation ferroelectric test system (Radiant Technology, USA). In the test of P–E hysteresis loops and resistive switching characteristics, where Ag and Ti was used as two electrodes, and the Ag electrodes with area of ~1 mm² was prepared by silver glue.

1.3 Performance test

In the performance test of resistive switching device, the current density-voltage (J-V) and

resistance-cycle number characterizations curves were tested using the electrochemical workstation CHI-660D. In this experiment, we used an ordinary filament lamp with various power densities as light source, and the white-light power density was measured by an irradiatometer. The wavelength range of white-light is 400~760 nm.

2. Optical properties of BiMnO₃ nanowires

The UV-vis absorption spectrum of as-prepared BiMnO₃ nanowires without the Ti substrate is shown in Fig. S1.

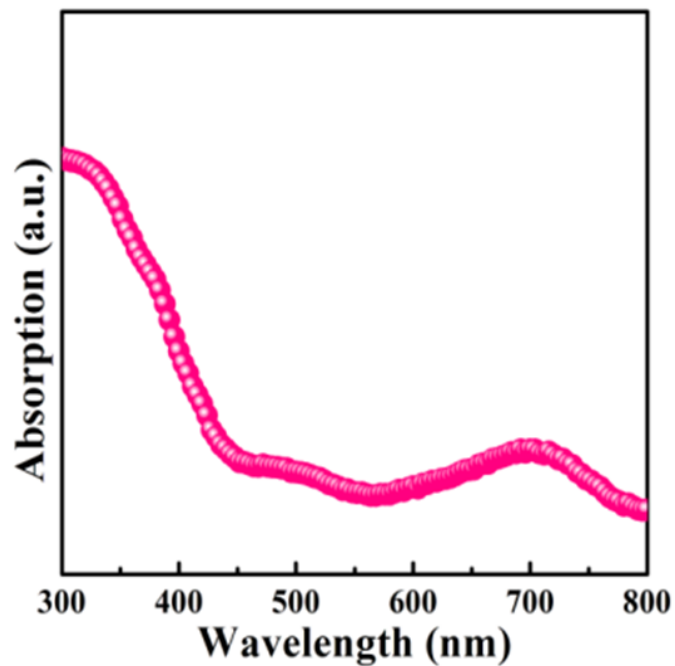


Fig. S1 The UV-vis absorption spectrum of as-prepared BiMnO₃ nanowires.

3. The ferroelectricity of BiMnO₃ nanowires

3.1 Ferroelectric measurement

The ferroelectric polarization-electric field (P-E) loops is a definitive way to evaluate the

ferroelectric response in ferroelectric materials. Fig. S2 (a) shows a schematic diagram of the circuit used for the P–E hysteresis loops measurements, where the Ag and Ti act as two electrodes. We measured the P–E hysteresis loops of the Ag/BiMnO₃/Ti structure in the dark and under white-light illumination with various power densities at room temperature. We firstly measured the P–E hysteresis loops in the dark, and then we gradually increased the light power density and measured the P–E hysteresis loops. In previous report, the origin of the ferroelectric polarization in BiMnO₃ is attributed to nonrelativistic,¹ which is also suitable for our sample. From the Fig. S2 (b), we can see that the white-light-induced changes P_s and P_r are nearly linear to the light power densities. In previous reports, the magnetic field and pressure can slightly change the ferroelectric hysteresis loops, and the relative changes in the saturated ferroelectric polarization and the remanent ferroelectric polarization were less than 20% at room temperature.^{2,3} Therefore, the great changes in the saturated ferroelectric polarization and the remanent ferroelectric polarization induced by white-light in the BiMnO₃ nanowires at room temperature are remarkable, which demonstrates the potential application for light-controlled nonvolatile memory devices.

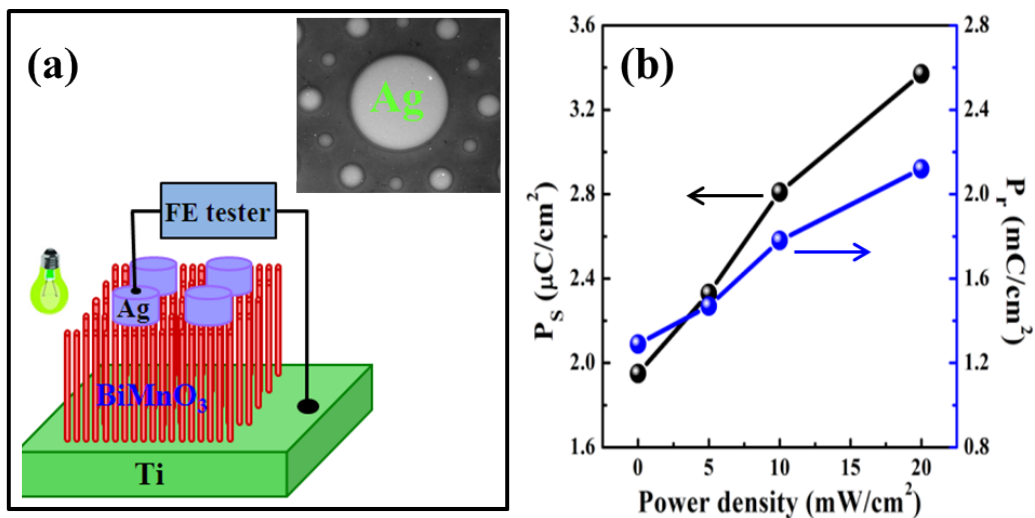


Fig. S2 (a) A schematic diagram of the circuit used for the P–E hysteresis measurements. (b) The white-light power density-dependent P_s of the saturated ferroelectric polarization and P_r of the remanent ferroelectric polarization.

3.2 The mechanisms of white-light controlled ferroelectricity

The possible mechanisms of the light-induced ferroelectricity change include increased conductivity (namely increased current density), a photovoltaic effect and ferroelectric domain mobility under white-light illumination. The current-voltage characteristic curves of the Ag/BiMnO₃/Ti structure in the dark and under white-light illumination at room temperature show that the current under white-light illumination is 15% higher than that in the dark. Therefore, increased conductivity cannot be the dominant origin for the light-induced ferroelectricity change because the saturated ferroelectric polarization and the remanent ferroelectric polarization increase by about 70% under white-light illumination. Generally, the photovoltaic effect is unidirectional, and not the dominant origination because the light-induced ferroelectricity change is symmetrical. In a previous report, the light induced change in ferroelectric polarization in ferroelectric compounds was explained by the trapping of photogenerated charges at domain boundaries.^{2,3} The observed remarkable improvement in the ferroelectric polarization of the BiMnO₃ nanowires array should be attributed to trapping of the photo-generated charge at the domain boundaries, which enhanced ferroelectric domain mobility. In addition, since the ferroelectric polarization should decrease with increasing temperature, therefore, the white-light-induced improvement in the ferroelectric polarization of the single-crystalline BiMnO₃ nanowires is unlikely to originate from a light-induced temperature increase.

Reference

1. I. V. Solovyev, and Z. V. Pchelkina, *Physical Review B*, 2010, **82**, 094425.
2. D. Dimos, W. L. Warren, M. B. Sinclair, B. A. Tuttle and R. W. Schwartz, *J. Appl. Phys.*, 1994, **76**, 4305.
3. A. L. Kholkin, S. O. Iakovlev and J. L. Baptista, *Appl. Phys. Lett.*, 2001, **79**, 2055.