Artificial design for perovskite ferroelectrics using nanosheet architectonics

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Control over the emergence of ferroelectric order remains a fundamental challenge for the rational design of artificial materials with novel properties. Here, we report a new strategy for artificial design of layered perovskite ferroelectrics by the assembly of oxide nanosheets in a unit-cell-upon-unit-cell manner (Figure 1). Ferroelectricity is ubiquitous in the ABO_3 perovskite titanates, niobates, and tantalates. However, the only layered perovskites to display a ferroelectric transition has been Aurivillius compounds such as $SrBi_2Ta_2O_9$, $Bi_{4-x}La_xTi_3O_{12}$, and a few others. In these perovskites, ferroelectricity arises from a highly polarized nature of perovskite-type layers [1]. Our principal concern is artificial design of layered perovskite ferroelectrics by perovskite nanosheets as a building block. We fabricated high-quality bicolor perovskite superlattices, composed of three different perovskite nanosheets ($Ca_2Nb_3O_{10}$, $Ca_2NaNb_4O_{13}$, $Ca_2Na_2Nb_5O_{16}$). These perovskite nanosheets are Dion–Jacobson phases with different perovskite-like layers (m octahedral thick). We approached the preparation of superlattice films by a layer-by-layer assembly involving Langmuir-Blodgett deposition. The artificially fabricated superlattices [$(Ca_2Nb_3O_{10}/Ca_2NaNb_4O_{13})_n$, $(Ca_2Nb_3O_{10}/Ca_2Na_2Nb_5O_{16})_n$] are structurally unique, which is not feasible to create in the bulk form. By such an artificial structuring, we found that these superlattices possess a new form of interface coupling, which gives rise to ferroelectricity with a good fatigue-free characteristic. Considering the flexibility of self-assembled nanosheets interfaces, this technique provides a route to synthesize a new kind of layered ferroelectric oxides.
We also address SPM characterization of ferroelectric properties in individual perovskite nanosheets ($Ca_2Nb_3O_{10}$, $Ca_4Nb_3TiO_{13}$).

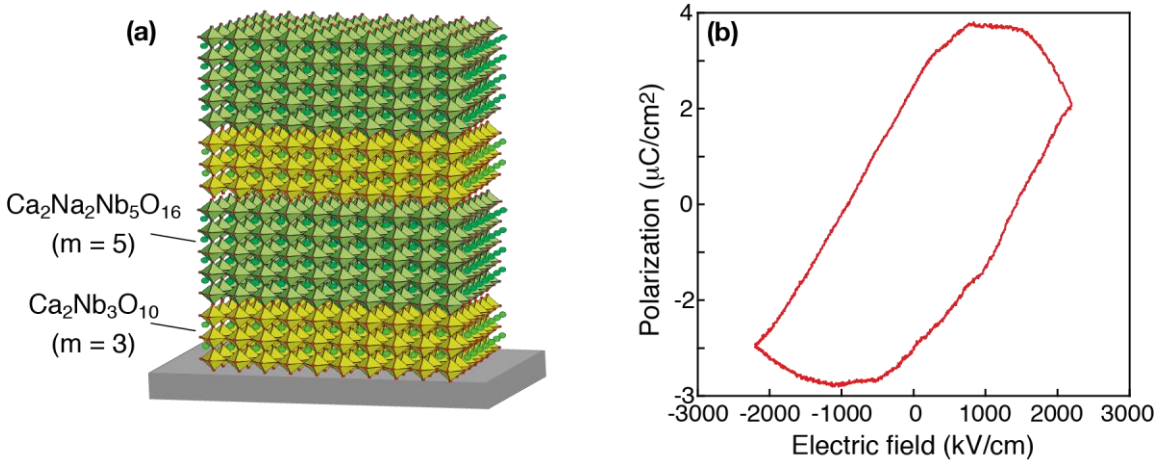

Figure 1. (a) Structural model and (b) ferroelectric property of a nanosheets superlattice $(Ca_2Nb_3O_{10}/Ca_2Na_2Nb_5O_{16})_n$ (n = 6).

Reference

[1] B. W. Li, M. Osada, T. C. Ozawa, Y. Ebina, K. Akatsuka, R. Ma, H. Funakubo, and T. Sasaki, *ACS Nano* **4**, 6673 (2010).