Bulk photovoltaic effect enhancement via electrostatic control in layered ferroelectrics

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The power conversion efficiency (PCE) of conventional solar cells based on p-n junctions is limited by the Shockley-Queisser limit [1]. Ferroelectrics provide an alternative way to separate charge by the internal depolarization field or by the bulk photovoltaic effect (BPVE). In the BPVE, the electrons are continuously excited to a quasiparticle coherent state that has an intrinsic momentum, generating a spontaneous direct short-circuit photocurrent. Besides, BPVE is able to create an open-circuit photovoltage that is above materials' band gap, potentially enabling higher PCE. Although it has been shown that BPVE arises in noncentrosymmetric materials through the "shift current" mechanism [2–5], the effects of materials' structure and electronic structure remain unclear, and this hinders the use and optimization of bulk photovoltaics. Furthermore, ferroelectric oxides usually possess wide band gaps, which allow absorption of only a small proportion of the solar irradiation [6].

Here, we choose a recently designed visible-light-absorbing ferroelectric $Pb(Ni_xTi_{1-x}O_{3-x} (Ni-PTO) [7]$ whose electronic states near the band gap possess a diverse character that enhances the physical and chemical tunabilities, and engineer its BPVE performance via electrostatic control. We construct the Ni-PTO solid solutions as layered systems by substituting Ni for Ti and then removing the O atom that is adjacent to the Ni atom at its apical position. We show that the shift current yield of this layered material can be greatly enhanced by increasing the number of layers. This shift current enhancement is accomplished through electrostatic control of electron density delocalization. The change of covalent orbital character not only enhances the shift vector magnitude, but also changes its sign, highlighting the importance of consistency in direction of shift current from different regions of the Brillouin zone. This system can be viewed as a nanoscale composite with alternating photocurrent generating layers and insulating layers, ideal for a BPVE device. This is helpful for optimizing the performance of photovoltaics.

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FIG. 1: (Color online) The (left) shift current susceptibilities (σ_{xxZ}) and (right) Glass coefficients (G_{xxZ}) of the layered Ni-PTO with varying superlattice periodicity.



FIG. 2: (Color online) The electric field and potential inside Ni-PTO for N = 3 and 4. The Ni- $V_{\rm O}$ substitution results in adjacent planes of charge. As layers increase, stronger screening over a greater distance is required to minimize the potential changes introduced by this charge separation.

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