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Tuning Photovoltaic Performance of Perovskite Nickelates Heterostructures by Changing the A-Site Rare-Earth Element

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Supporting Information

ABSTRACT: Perovskite rare-earth nickelates (RNiO₃) have attracted much attention because of their exotic physical properties and rich potential applications. Here, we report systematic tuning of the electronic structures of RNiO₃ (R = Nd, Sm, Gd, and Lu) by isovalent A-site substitution. By integrating RNiO₃ thin films with Nb-doped SrTiO₃ (NSTO), p–n heterojunction photovoltaic cells have been prepared and their performance has been investigated. The open-circuit voltage increases monotonically with decreasing A-site cation radius. This change results in a downward shift of the Fermi level and induces an increase in the built-in potential at the RNiO₃/NSTO heterojunction, with LuNiO₃/NSTO showing the largest open-circuit voltage. At the same time, the short-circuit current initially increases upon changing the A-site element from Nd to Sm. However, the larger bandgaps of GdNiO₃ and LuNiO₃ reduce light absorption which in turn induces a decrease in the short-circuit current. A power conversion efficiency of 1.13% has been achieved by inserting an ultrathin insulating SrTiO₃ layer at the SmNiO₃/NSTO interface.

Our study illustrates how changing the A-site cation is an effective strategy for tuning photovoltaic performance and sheds light on which A-site element is the best for photovoltaic applications, which can significantly increase the applicability of nickelates in optoelectronic devices.

KEYWORDS: nickelate, oxygen vacancy, heterojunction, photovoltaic, A-site cation substitution

1. INTRODUCTION

The desire for clean, inexpensive, and efficient energy technologies has led to an extensive search for novel materials with unique properties. Perovskite oxides with the chemical formula of ABO₃, where A is a rare-earth or alkaline-earth metal ion and B is a transition metal ion, have attracted much interest because of their wide range of functional properties and rich physics. Various ABO₃-based photovoltaic devices have been proposed and investigated. For example, ferroelectric materials, such as BaTiO₃,¹ BiFeO₃,^{2–6} and Pb(Zr,Ti)-O₃,⁷ have sparked significant interest because of their switchable photovoltaic response and above-bandgap photovoltages. However, the low photocurrent and power conversion efficiency limit their applicability in solar cells. Another approach is to use perovskite oxides as the light absorbing component in a solar cell. Wang et al.⁸ have reported BiFeO₃ as an oxide dye in all-oxide photovoltaic heterojunctions, inspired by conventional dye-sensitized solar cells⁹ and recently developed hybrid perovskite solar cells.¹⁰ Large

interface areas between the light absorber and the nanostructured electron (hole)-transport material within mesoporous structures can enable effective separation and collection of photon-generated carriers, enhancing photovoltaic performance. Although this design has been successful for fabricating inorganic–organic hybrid perovskites, it precludes epitaxial heterojunction formation.¹¹ In addition, novel perovskite oxides with tunable electronic structures can be combined with appropriate substrates to form conventional p–n junction solar cells.^{12,13} Such simple heterojunctions benefit from both physical and chemical stability and make maximum use of the functionality of epitaxial layers.

Among the perovskite oxides, rare-earth nickelates (RNiO₃, RNO, where R represents a rare-earth lanthanide element) are particularly interesting.^{12,14–21} Their electronic states strongly

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Figure 1. (a) XRD θ - 2θ scans around the (002) peaks of the 30 nm thick RNO thin films prepared under 300 mTorr. The black dashed line indicates the peak originated from the STO substrate. (b, c) HAADF images of RNO/STO heterojunctions. A clear crystalline lattice is observed for epitaxial NNO layer, whereas for LNO, only the interface area shows evidence of crystallinity.

depend on the rare-earth element.^{22,23} Isovalent substitution of R ions can change the rotation, tilt, and distortion of the NiO_6 octahedra, thus affecting the structural, physical, and chemical properties of RNO.²¹ Most studies on RNO thus far have focused on the origin of the metal-insulator transition.^{16,24–32} Ramanathan et al. have explored the multifunctional applications of RNO, especially SmNiO_3 (SNO), in synaptic transistors,³³ solid fuel cells,²⁰ and electric-field sensors in salt water.³⁴ However, up until now, little is known about potential applications of RNO in optoelectric devices,^{35–39} although the bandgap of RNO can be tuned by changing the A-site cation. We have previously reported that the bandgap of NdNiO_3 (NNO) can be continuously tuned by changing its oxygen content, leading to possible applications in photovoltaic devices.^{12,13} It is thus of great scientific and technological interest to examine the effect of changing the A-site rare-earth element on photovoltaic response. To this end, we have prepared a series of Au/RNO/Nb-doped SrTiO_3 (Au/RNO/NSTO) heterojunctions and have investigated associated photovoltaic characteristics. These were then correlated with band structure evolution upon A-site substitution.

2. RESULTS AND DISCUSSION

RNO (R = Nd, Sm, Gd, and Lu) epitaxial films were grown on (001)-oriented SrTiO_3 (STO) and 0.5 wt % NSTO single crystal substrates using pulsed laser deposition (PLD). The pseudocubic lattice constants for bulk NNO, SNO, GdNiO_3 (GNO), and LuNiO_3 (LNO) are 3.81,⁴⁰ 3.784,⁴¹ 3.756,⁴² and 3.67 Å,⁴³ respectively. The lattice constant for cubic STO is 3.905 Å. Therefore, the c -axis lattice constants for RNO films should become smaller when grown on STO substrates. Figure 1a shows X-ray diffraction (XRD) θ - 2θ scans for RNO films prepared with an oxygen partial pressure ($P(\text{O}_2)$) of 300 mTorr. The (002) diffraction peaks for the films shift toward lower angles as the A-site cation is changed from Nd to Gd. The extended XRD patterns are presented in Figure S1. The calculated experimental c -axis lattice constants are 3.80 Å for NNO, 3.817 Å for SNO, and 3.858 Å for GNO, respectively. The experimental values are larger than our theoretical values for fully strained stoichiometric films (Table 1), most likely as a result of oxygen vacancies, as discussed in our previous reports.^{21,38} Smaller A-site cations result in larger lattice mismatch (Table 1) and lower oxygen vacancy formation energies,^{44,45} and are thus expected to induce more oxygen vacancies in the films. A scanning transmission electron microscopy (STEM) image for the NNO/STO interfaces is

Table 1. Pseudo-cubic Lattice Constants, a_{RNO} , for Bulk RNO with Different A-Site Cations and Their Corresponding Lattice Mismatches (ϵ) with STO Substrate with Cubic Lattice Constant of 3.905 Å, where $\epsilon = (3.905 - a_{\text{RNO}})/a_{\text{RNO}}$; Experimental c -Axis Lattice Constants (c_{expt}) and the Strained c -Axis Lattice Constants Estimated (c_{est}) from the Young's Modulus by Taking into Account Poisson's Ratio $\nu \approx 0.34$ ^{58a}

	NdNiO_3 (NNO)	SmNiO_3 (SNO)	GdNiO_3 (GNO)	LuNiO_3 (LNO)
a_{bulk} (Å)	3.810	3.784	3.756	3.670
ϵ (%)	2.493	3.198	3.967	6.403
c_{exp} (Å)	3.801	3.817	3.858	
c_{est} (Å)	3.776	3.740	3.702	3.585

^a c_{expt} is calculated using Bragg's law, $2c_{\text{expt}}\sin\theta = n\lambda$, where n is a positive integer (2) and λ is the wavelength (1.5406 Å) of the Cu K α X-ray.

shown in Figure 1b. The relatively small lattice mismatch results in an interface of excellent structural quality, as seen. The uniform atomic columns indicate high crystallinity in the as-grown NNO film. In contrast, the film quality for LNO on STO is very poor; although the film nucleates as an epitaxial film, it quickly becomes amorphous, as seen in Figure 1c. This result explains the absence of a (002) reflection for the LNO film in the θ - 2θ plot (Figure 1a). The formation of the amorphous LNO films is due to the large lattice mismatch. Lattice mismatch usually results in the accumulation of strain energy up to the critical thickness such that the total strain energy exceeds the energy associated with some structural transformation in the film. The most common structural transformations are: (1) the transition from a flat but biaxially strained film to an at least partially relaxed array of nanocrystalline islands, and, (2) the formation of misfit dislocations or structure defects throughout the film.⁴⁶ When the LNO film grows thicker than the critical thickness (~ 2 nm), the large lattice mismatch will induce more structure defects, such as oxygen vacancies, to release strain energy. Our previous investigation revealed that poor crystallinity can be induced by oxygen vacancies in GNO/NSTO heterojunctions prepared under different $P(\text{O}_2)$ values and the relative amounts of Ni^{2+} and Ni^{3+} vary accordingly.^{38,47} We think a similar phenomenon is occurring here for LNO.

Ni 2p X-ray photoelectron spectroscopy (XPS) spectra for the RNO film series is shown in Figure 2a. The Ni 2p spectra of the NiO film grown on the MgO (001) substrate was

Figure 2. (a) Ni 2p XPS of RNO thin films prepared under 300 mTorr. The dashed line indicates the binding energy for Ni³⁺ in PA-NNO. A clear shift to the lower binding energy with decreasing A-site rare earth radius indicates a decrease in formal charge. (b) Absorption spectra for RNO films prepared under 300 mTorr. The insets show schematics of the different optical transitions in nickelates.

chosen as Ni²⁺ reference. According to the previous reports,^{21,48} Ni valence is 3+ in LaNiO₃ film. However, because of the strong overlap between La 3d and Ni 2p, we cannot obtain the standard Ni 2p spectra of Ni³⁺ from LaNiO₃. Smaller A site cations (such as Nd, Sm, Gd, etc.) can induce oxygen vacancies in the nickelates thin films.²¹ Because the oxygen plasma treatment can heal these oxygen vacancies,⁴⁹ we can use the Ni 2p spectrum for the plasma annealed NdNiO₃ (PA-NNO) film as our Ni³⁺ reference. A gradual decrease in Ni cation charge from Ni³⁺ to Ni^{2+ δ} is indicated by the decrease in binding energy as R changes from Nd to Lu. This change in valence is due to an increasing oxygen vacancy concentration during the growth, culminating in LNO with the highest oxygen vacancy concentration, consistent with the XRD and STEM results shown in Figure 1. Figure 2b shows absorption spectra of the RNO film series as derived from spectroscopic ellipsometry data. The left (right) inset of Figure 2b presents a schematic of the electronic structure of nickelate in its metallic (insulating) phase based on current understanding.^{50–53} Below 3.2 eV, the electronic structure of a nickelate shows three dominant optical transitions. Features A and B are due to excitations from occupied to unoccupied antibonding e_g^* orbitals.^{50,51} Feature C is assigned to transitions from the hybridized t_{2g}^* /nonbonding O 2p to the e_g^* orbitals.^{50,52} The electronic structure of RNO is strongly dependent on the chemical identity of the A-site cation. When the A-site cation radius decreases from Nd to Lu, the tolerance factor and the Ni–O–Ni bond angle decrease, leading to a reduction of the bandwidth and an increase in U/W (where U is the Coulomb repulsion and W is initial width of the Ni 3d band). This transition in turn makes the system more

Figure 3. (a) Schematic illustrations of the Au/RNO/NSTO heterojunctions and the crystal structure of bulk RNO, here R can be Nd, Sm, Gd, or Lu. (b) $1/C^2$ versus voltage curves of the RNO (30 nm)/NSTO heterojunctions prepared under 300 mTorr oxygen pressure. The dashed lines are fittings based on linear regressions and the intercepts with the x -axis yield the V_{bi} values for the RNO/NSTO heterojunctions. (c–f) J – V characteristics of different RNO (30 nm)/NSTO heterojunctions, measured in dark and under illumination.

Figure 4. (a, b) Oxygen partial pressure dependence of V_{OC} and J_{SC} for different RNO (30 nm)/NSTO heterojunctions. (c) Calculated PCE of different RNO/NSTO heterojunctions with RNO of the same thickness prepared under different oxygen partial pressures. PCE is defined as $PCE = V_{OC}J_{SC} \times FF/P_{IN}$, where FF is the fill factor, and P_{IN} is the power density (150 mW/cm^2) of the xenon lamp. (d) J - V curves of SNO/NSTO and SNO/STO/NSTO heterojunctions with SNO layer prepared under 20 mTorr. The inset shows the calculated J_{SC} , V_{OC} , FF, and PCE for the SNO/STO/NSTO heterojunction.

insulating by increasing the bandgap.^{22,50} Moreover, an increase in oxygen vacancy concentration during growth induces a gradual decrease in Ni cation charge from Ni^{3+} to $\text{Ni}^{2+\delta}$ when the A-site cation radius decreases. Both valence and conduction bandwidths will be reduced because of the larger Ni^{2+} ionic radius and Ni–O bond length ($d_{\text{Ni-O}}$).¹² As a result, both effects mentioned above contribute to the decrease in the intensities of features A–C with decreasing A-site cation radius.

We have previously reported the photovoltaic behavior of NNO/NSTO heterojunctions using oxygen-deficient NNO thin films.¹³ Because changing the A-site cation affects the electronic structure of RNO as shown in Figure 2, it is of interest to measure the photovoltaic properties of the entire RNO family. To this end, we have prepared RNO/NSTO p–n heterojunctions as shown in Figure 3a, where R changes from Nd to Lu. For an ideal p–n junction, the reverse bias capacitance can be expressed as $1/C^2 \propto (V_{bi} + V)$, where C is the reverse bias capacitance per unit area, V_{bi} is the built-in voltage and V is the reverse bias voltage.⁵⁴ C - V curves of different RNO/NSTO heterojunctions have been measured and plots of $1/C^2$ versus V are presented in Figure 3b. Linear regression was used to deduce V_{bi} , which is the x intercept. It can be seen that V_{bi} increases with decreasing A-site ionic radius, consistent with our previous report that the Fermi level shifts to lower energy with decreasing A-site ionic radius.²¹ Figure 3c–f shows current density–voltage (J - V) curves of different RNO/NSTO heterojunctions measured in dark and under 150 mW/cm^2 xenon light illumination. Because of the metallic nature of NNO thin films prepared under 300 mTorr,¹³ the J - V curve of NNO/NSTO heterojunction shows no rectifying behavior and we did not observe any photovoltaic effect on heterojunction. Decreasing

the A-site cationic radius shifts the Fermi level to progressively lower energy²¹ and induces an increase in V_{bi} at RNO/NSTO heterojunctions, which in turn improves the rectifying properties (Figure S2). The rectifying ratio defined as the ratio of forward-to-reverse currents at $\pm 1 \text{ V}$, increases from 1.0 for NNO to 27.4 for SNO, to 37.3 for GNO, to 1162.4 for LNO. The improvement of the rectifying ratio leads to larger open-circuit photovoltage (V_{OC}).⁵⁵ On the other hand, the short-circuit current (J_{SC}) initially increases upon changing A-site cation from Nd to Sm. Beyond that, the larger bandgaps for GNO and LNO reduces the light absorption, which decreases J_{SC} .

All of the above results were obtained from RNO/NSTO heterojunctions with RNO layer prepared at $P(\text{O}_2) = 300 \text{ mTorr}$. We have shown previously that oxygen vacancies plays an important role in the electronic structures of RNO.^{12,38} Figure 4a, b shows the photovoltaic properties of RNO/NSTO heterojunctions with RNO layers prepared under different oxygen partial pressures. We have shown that when the oxygen pressure is fixed at 300 mTorr, V_{bi} increases with decreasing A-site cation radius from Nd to Lu (Figure 3b) due to the downward shift in the Fermi energy.²¹ On the other hand, for the same rare-earth element, more oxygen vacancies act as electron donors, resulting in an upward shift up of Fermi energy and smaller V_{bi} .^{13,38,47} Combining these two effects, the optimized V_{OC} increases from $\sim 0.2 \text{ V}$ for NNO prepared at 0.5 mTorr to $\sim 0.8 \text{ V}$ for LNO prepared at 600 mTorr (Figure 4a). However, the J_{SC} decreases significantly as the A-site cation changes to Gd and Lu, because the larger bandgaps reduce light absorption. The power conversion efficiencies (PCEs) of these devices are summarized in Figure 4c. The balance between V_{OC} and J_{SC} leads to a maximum PCE of $\sim 0.26\%$ for SNO/NSTO heterojunction prepared under 20

mTorr. To further improve the PCE, a p-i-n heterostructure was prepared, where i represents an ultrathin insulating STO layer. With this layer, the rectifying characteristics are much improved as shown in Figure 3d and Figure S3. Under illumination, the V_{OC} and J_{SC} simultaneously increase by about 2-fold, resulting in an increase in PCE to 1.13%. This improvement is due to the enlarged depletion layer, which reduces recombination of photogenerated carriers.^{56,57} Further experimental investigations will address how to improve the PCE by adjusting the film thickness or replacing the semitransparent Au layer with transparent ITO as the top electrode material.

3. CONCLUSION

We have found that changing the A-site rare earth cation can strongly affect the electronic structure of nickelates and can be used to tune the photovoltaic performance of RNO/NSTO heterojunctions. By controlling the oxygen content in nickelates films during growth, we can optimize the photovoltaic performance of these heterojunctions by balancing the photovoltaic parameters V_{OC} and J_{SC} . We find that decreasing the A-site element radius by transitioning from Nd to Lu increases V_{OC} from 0.2 to 0.8 V, whereas the SNO/NSTO heterojunction shows the largest J_{SC} . A PCE of 1.13% was achieved by fabricating a SNO/STO/NSTO heterojunction. Inserting an insulating STO layer enlarges the depletion region and enhances electron–hole separation. Our study further demonstrates the potential application of nickelates in optoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b01851.

Details of experiments, extended XRD of the RNO films, J – V characteristics for different RNO/NSTO heterojunctions, J – V characteristics of SNO/NSTO and SNO/STO/NSTO heterojunctions, AFM topographic images of RNO films, XPS survey spectra of RNO films, I – V curves of the RNO films grown on STO (PDF)

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Notes

The authors declare no competing financial interest.

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