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Giant photoresponse in quantized SrRuO₃ monolayer at oxide interfaces

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Abstract

The photoelectric effect in semiconductors is the main mechanism for most modern optoelectronic devices, in which the adequate bandgap plays the key role for acquiring high photoresponse. Among numerous material categories applied in this field, the complex oxides exhibit great possibilities because they present a wide distribution of band gaps for absorbing light with any wavelength. Their physical properties and lattice structures are always strongly coupled and sensitive to light illumination. Moreover, the confinement of dimensionality of the complex oxides in the heterostructures can provide more diversities in designing and modulating the band structures. On the basis of this perspective, we have chosen itinerant ferromagnetic SrRuO_3 as the model material, and fabricated it in one-unit-cell thickness in order to open a small band gap for effective utilization of visible light. By inserting this SrRuO_3 monolayer at the interface of the well-developed two-dimensional electron gas system ($\text{LaAlO}_3/\text{SrTiO}_3$), the resistance of the monolayer can be further revealed. In addition, a giant enhancement ($>300\%$) of photoresponse under illumination of visible light with power density of 500 mW/cm^2 is also observed. Such can be ascribed to the further modulation of band structure of the SrRuO_3 monolayer under the illumination, confirmed by cross-section scanning tunneling

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4 **microscopy (XSTM). Therefore, this study demonstrates a simple route to design**
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6 **and explore the potential low dimensional oxide materials for future**
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Over the past decades, low dimensional materials have attracted tremendous interests in the applications of novel optoelectronics. The confinement of electrons in nanocrystals exhibits high flexibility in the energy-relaxation pathway of photoexcited electron-hole pairs.¹ Greatly enhanced photocurrent due to the generation of multiple excitons has been observed in zero-dimensional (0D) colloidal quantum-dot,²⁻⁴ and one-dimensional (1D) carbon nanotube systems.⁵⁻⁶ Recently, two-dimensional (2D) materials such as graphene and transition-metal dichalcogenide (TMD) monolayers, also become another fast-growing branch in this research field due to their extraordinary electrical and optical properties. Graphene, as a zero-bandgap material, has an extremely broad absorption spectrum from far-infrared to ultraviolet light.⁷⁻⁸ Its linear energy-momentum dispersion allows intriguing mechanisms of electron excitation by absorbing light while being placed in specific designed devices or heterostructures.^{1, 9-12} Compared to the graphene-based devices, the TMD monolayers are direct-bandgap semiconductors (1~2 eV), which possess remarkably stronger photoresponse within the visible light range,¹³⁻¹⁶ and can be complementary to the drawbacks of graphene. These studies clearly reveal that quantum confinement effect and adequate bandgap engineering can lead to superior light-dependent functionalities of the low dimensional materials than their bulk counterparts.

In addition to the low dimensional materials, transition-metal oxides, especially

the Mott insulators with narrow-bandgap, have been considered as another category of potential optoelectronic materials as well. The theoretical works proposed by Manousakis *et al.*¹⁷⁻¹⁸ have predicted that the enhancement of quantum efficiency through photo-induced carrier multiplication process may happen in those Mott insulators within the band gap range of 0.5-1 eV. However, in the bulk Mott insulators like LaVO₃, the presence of high-density charge-trapping defects and the formation of polarons usually hamper additional multiple electron-hole pairs, leading to low performance of the photo-induced transport behavior.¹⁹ Therefore, it would be intriguing if we can fabricate the high quality Mott insulator oxides in low dimensionality. On the basis of quantum confinement effect, while the size of materials is reduced to nanoscale, the energy bands become discrete and the band gap becomes wider. Hence, to explore the potential material systems, the transition-metal oxides with very small bandgap or no bandgap have been conceptually preferred. Previous reports have demonstrated that the metallic oxides, such as SrRuO₃ (SRO)²⁰⁻²² or LaNiO₃ (LNO),²³ present a metal-to-insulator transition when the thickness decreases below several unit cells, which offers the possibilities of meeting the criteria for high performance in optoelectronic devices.

In this work, the SRO monolayer has been chosen for investigating the photoresponse because it presents wide absorption spectrum in its bulk form.²⁴ By

using the merits of epitaxial oxide heterostructures, where versatile electronic reconstructions and electron-phonon interactions can be procured at the interfaces, the electronic state of the SRO monolayer can be further modulated. To achieve this purpose, a specifically designed sample architecture, similar to the cases with an inserted one-unit-cell manganite between LaAlO_3 (LAO)/ SrTiO_3 (STO) heterostructures,²⁵⁻²⁶ has been adopted as illustrated in the schematic of Figure 1a. LAO/STO is a famous system that possesses 2D electron gas (2DEG) behavior, which results from structural and electronic reconstruction at its interface.²⁷⁻³⁰ Therefore, the LAO capping layer is also expected to cause certain variation on the sandwiched SRO monolayer. Further verifications have been brought by electrical transport measurement, X-ray absorption spectroscopy (XAS) and cross-section scanning tunneling microscopy (XSTM). Excitingly, a large enhancement of photocurrent relative to dark-current (~325%) is obtained under the illumination with power density of 500 mW/cm^2 , which confirms the feasibility of creating and modulating the 2D oxide systems for designing new optoelectronic devices.

Results and discussion

The high-quality samples for investigation were fabricated using pulsed laser deposition (PLD) equipped with reflection high-energy electron diffraction (RHEED). To accurately control the thickness of the SRO monolayer in one unit cell,

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4 TiO₂-terminated (001) STO single crystal substrates with atomically flat surface were
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6 required before the growth. The preparation uses the common acid treatment method
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9 proposed by Kawasaki, *et al.*³¹ Under the optimized growth conditions (please see
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11 experimental section), the deposition of the SRO monolayer and the LAO capping
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13 layer can follow the layer-by-layer epitaxy mechanism. As shown in Figure 1b, the
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15 SRO monolayer was obtained by stopping the deposition after finishing one clear
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17 intensity oscillation in RHEED curve. The subsequent LAO capping layer was also
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19 precisely controlled in 6 unit cells from the RHEED monitoring. Here this sample is
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21 designated as LAO/SRO/STO. The morphology of the sample probed by atomic force
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23 microscopy (AFM) as the inset in Figure 1b reveals an atomically smooth surface
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25 with regular terraces and a step height of $\sim 4\text{\AA}$, confirming the layer-by-layer epitaxial
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27 growth. It is worth noting that the SRO naturally prefers to end up with SrO
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29 termination while grown on the TiO₂ terminated STO substrate, which implies that
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31 the RuO₂ plane is sandwiched between two SrO planes in this case.³² Figure 1c
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33 exhibits the typical atomic-resolution Z-contrast scanning transmission electron
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35 microscopy (STEM) image along [010] direction of the STO substrate. According to
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37 the principle in the Z-contrast image, the contrast between two A-site elements, La
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39 and Sr, can be easily distinguished due to their large difference of atomic numbers
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41 ($Z_{\text{La}} = 57$ and $Z_{\text{Sr}} = 38$, respectively). Thus, the La atoms exhibit brighter contrast than
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the Sr atoms. The resembling phenomenon can be observed at three B-site elements ($Z_{\text{Ti}} = 22$ and $Z_{\text{Ru}} = 44$, and $Z_{\text{Al}} = 13$) as well. By identifying these atoms in the Z-contrast images, the SRO monolayer has been confirmed to be coherently connected to the neighboring STO substrate and the LAO capping layer without detectable linear defects, presenting a high quality epitaxial growth of the designed heterostructure.

We have then examined the electronic transport behavior of this SRO monolayer. Similar to the studies presented in several previous studies²⁰⁻²², the resistance of this SRO monolayer presents an expectable semiconducting behavior (Figure 2a) as well. To understand the transport mechanism dominating in the SRO monolayer (Figure 2b), we firstly adopt the thermal activation model to fit the curve of temperature dependent resistance using Arrhenius equation:

$$R(T) = R_0 \exp\left(\frac{E_A}{k_B T}\right) \quad (1)$$

where T is the absolute temperature, R_0 is a prefactor that represents the value of resistance at infinite temperature, E_A is the activation energy and k_B is the Boltzmann's constant. The conduction mechanism of this model depends on the thermally excited electrons from the valence band or the impurity levels to the conduction band by overcoming the bandgap. The linear fit of $\ln(R(T))$ versus $1/T$ shows a good agreement with the experimental data in the high temperature range of

230 K - 300 K, in which the thermal activation energy E_A of ~170 meV is extracted according to the slope. However, the model quickly fails below 230K, implying that this conduction type is insufficient to be used to interpret the transport behavior of the SRO monolayer at low temperature. Therefore, the Mott variable range hopping (VRH), widely used for describing the transport behavior in many strongly correlated electron systems, has been also adopted. The temperature dependence of resistance in the Mott VRH expression can be simplified as the following equation:

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^{1/\alpha} \quad (2)$$

where prefactor R_0 is a constant derived from the electron-phonon interaction, T_0 represents the degree of charge carrier localization, determined by the density of localized states at the Fermi level ($N(E_F)$) and the localization length (ξ): $T_0 \approx 27/(\pi k_B N(E_F) \xi^2)$.³³⁻³⁵ Moreover, the energy for electron hopping is also a function of temperature, and α is the dimension of system. For a 3D or 2D system, α corresponds to 4 or 3, respectively. According to this model, the electrons near the Fermi level are localized with random potential fluctuations, and the conduction principally relies on long-distance hopping of these electrons at these localized states by receiving energy from phonons. Therefore, the hopping energy (ΔE) can be expressed as the equation (3):

$$\Delta E = \frac{1}{4} k_B T \left(\frac{T_0}{T}\right)^{1/\alpha} \quad (3)$$

This equation describes that when temperature decreases, the energy for electron hopping increases. Here a better fit at wider temperature range from 150K to 300K can be obtained when the model of 2D Mott variable range hopping (VRH) is used:

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^{1/3} \quad (4)$$

It implies that the carriers in this inserted SRO monolayer are strongly localized and confined between LAO and STO, and hence 2D hopping behavior is reasonably responsible for the transport nature. However, we still observe a deviation of the experimental data from the theoretical fitting curves below 150 K. This critical temperature is very close to the magnetic phase transition of bulk SRO. Although there is still no evidence to support the existence of phase transition in this SRO monolayer, it is believed that increasing magnetic disorder with decreasing temperature in the SRO monolayer could happen and result in the change of the electrical transport behavior. As a result, merely the 2D Mott VRH mode cannot perfectly fit the data as well, and the conduction may involve more other mechanisms at low temperature. From the analysis of the transport data, excitingly, both models reveal the similar results that a gap has now been created in the energy band of this SRO monolayer, which satisfies the first criterion for high efficient optoelectronics.

It is noteworthy that no study has experimentally revealed electrical transport behavior of the SRO monolayer thus far. The thinnest SRO film with the detectable

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4 resistance is 2 unit cells, reported by Chang, *et al.*²¹ Therefore, in order to realize how
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6 the LAO capping layer assists this SRO monolayer to acquire the measurable
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8 resistance (even though it is still very high), we performed the x-ray absorption
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10 spectroscopy (XAS) to reveal its electronic structure. Here we prepared other two
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12 samples, the SRO monolayer capped with 6-unit-cell STO layer and 100-unit-cell
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14 SRO film capped with 6-unit-cell LAO layer (termed as STO/SRO/STO and
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16 LAO/100 u.c. SRO/STO, respectively), and SRO and RuO₂ powders for comparison
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18 with LAO/SRO/STO sample. STO/SRO/STO is a very important control sample, in
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20 which the STO capping layer can not only keep the structural completeness of the
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22 SRO monolayer from the symmetry breaking effect at exposed surface, but also
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24 provide another kind of electrostatic boundary condition to the SRO monolayer
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26 compared to LAO/SRO/STO sample.²⁶ We have also found that the resistance of
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28 STO/SRO/STO is extremely high and exceeds the measurement limit of our
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30 instrument. It is consistent with the present studies mentioned above that the
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32 resistance of the SRO monolayer is hardly being detected. The corresponding
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34 evidence will be given in the latter photoresponse measurement.
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49 Figure 3a indicates the possible chemical influence on the local environment of
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51 Ru ions from the neighboring capping layers in the XAS spectra across the Ru
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53 *L*₃-edge ($h\nu \sim 2840$ eV for Ru⁴⁺) with the light polarization perpendicular to the
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surface normal ($I_{E//ab}$). All samples exhibit nearly the same position of the absorption peak, implying no obvious valence change for Ru ions for these samples. Recall that the deposited SRO monolayer naturally prefers to transform B-site termination to A-site termination.³² By following the concept from the LAO thin film grown on the SrO-terminated STO system, this top SrO plane should be oxygen-deficient and create a positive built-in electric field toward surface.³⁶ Simultaneously, it also helps to hinder the electrons transferring to the SRO monolayers, and thus maintains the valence of SRO. The retention of Ru⁴⁺ can be further confirmed by the XAS spectra across the O *K*-edge, as shown in Figure 3b and Supplementary Fig. S1, where the Ru 4*d* – O 2*p* (~529.04 eV) and Ti 3*d* – O 2*p* (~530.86 eV) hybridizations are revealed. Although the peak for the Ru 4*d* state in the SRO monolayer is very broad, its peak position still locates at nearly the same energy with that of the bulk SRO film, suggesting that no obvious oxygen deficiency occurs at this RuO₂ plane. Similar inference can be also obtained from the Ti 3*d* state, which has no obvious peak shift between the samples of the SRO monolayer and the 100-unit-cell SRO film. Because the Ti 3*d* state only reflects the oxidation for the STO substrate, the unchanged valence state of Ti ions supports that charge transfer can be effectively protected at the top SrO plane. Moreover, the spectra of STO/SRO/STO and LAO/SRO/STO both exhibit a double-peak feature, where the most intense peaks (e_g levels) and pre-peaks

(t_{2g} levels) are highlighted by the dashed lines in the figure. Compared to the reference samples, the line shape of STO/SRO/STO is closer to that of the SRO powder, whereas the line shape of LAO/SRO/STO is resembling to that of the RuO_2 powder. While the thickness of this inserted SRO layer is increased to 100 unit cells, its line shape becomes the same with that of the SRO powder again, implying that the 100-unit-cell SRO thin film maintains the bulk properties and the effect of the LAO capping layer can be ignored. The $t_{2g}-e_g$ crystal field splitting in the SRO monolayer is realized from the breaking of degeneracies of electron orbital states in Ru ions due to the produced electrostatic field while being placed in the octahedrons. Further orbital splitting of the e_g and t_{2g} states caused by the Jahn-Teller effect appears when a strain or deformation is introduced into these octahedrons. The higher the intensity ratio of main peak to pre-peak (e_g/t_{2g}) is, the less distortion the Ru octahedron has.³⁷ Therefore, in this work, the SRO monolayer possesses less lattice distortion while being covered by the LAO than the STO thin film. Such can be attributed to the relaxation by the conceivable presence of point defects like oxygen vacancies produced in the top SrO layer during high vacuum deposition process for LAO. The possible mechanism for how the lattice variation leads to the modulation of resistance has then been described in the schematic of Figure 3c. In bulk SRO, the Fermi level is located within the valence band of the Ru t_{2g} orbital that usually exhibits a low spin

states ($t_{2g}^4 e_g^0$) and results in the corresponding metallic behavior. When its dimensionality is reduced to the monolayer, we supposedly observe a band gap that will be confirmed in the following measurement of cross-sectional scanning tunneling microscopy and spectroscopy (XSTM/S). Hence, the Fermi level has then been located at gap between the Ru t_{2g} and e_g orbitals. With relaxing lattice distortion of SRO, smaller band gap between t_{2g} and e_g due to crystal field splitting is anticipated and leads to lower resistance observed in LAO/SRO/STO. From previous studies²⁵⁻²⁶, we have realized that charge transfer is originally responsible for control of transport behavior of the manganite monolayers. Nevertheless, no variation of Ru valence could be seen in the case with either the STO or the LAO capping layer, suggesting that modulation of lattice distortion should dominate the transport behavior of the SRO monolayer rather than charge transfer effect.

The band gap variation of the SRO monolayers in the cases with different capping layers can be further supported by the density-functional theory (DFT) calculations as shown in Figure 4. To investigate the properties of the SRO monolayer at the interfaces, we constructed two cases of slab models, each of which has two symmetric interfaces. The case 1 is (STO)₆-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(STO)₆, denoted as case 1 – L6. The case 2 is (LAO)_n-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(LAO)_n, in which $n = 1$ for case 2 – L1 and $n = 2$ for case 2 – L2, respectively. Figure 4 shows

the layer projected density of states in the SRO monolayer of case 1 – L6, case 2 – L1, and case 2 – L2. A band gap of around 0.4 eV is displayed in case 1 – L6, which is in good agreement with Li *et al.*'s recent predictions of the undoped SRO monolayer.³⁸ On the other hand, the band gap of the SRO monolayer in case 2 – L1 is estimated to be 0.15 eV, which is obviously narrowed compared to that in case 1 – L6. This narrowing effect is much more significant in case 2 – L2, where the SRO monolayer shows spin-polarized conducting state, as indicated by the corresponding layer projected density of states. When the unit-cell number of the LAO capping layer increases above 2 unit cells, all simulated results are almost the same with case 2 – L2. Therefore, the comparison among these three cases is enough. In experiment, although the resistance in LAO/SRO/STO is still high with presenting a semiconducting feature, we can find that it is relatively smaller than that in STO/SRO/STO. The difference between theory and experiment data may be originated from some non-perfect condition in samples such as temperature effect because all theoretic results are constructed on the calculation adopting absolute 0 K, whereas the experimental results can only be obtained at above 60 K. However, the tendency is similar for both theory and experiment, indicating that the band gap of the SRO monolayer with the LAO capping layer is intrinsically smaller than that with the STO capping layer.

The photoresponse of the SRO monolayer was then conducted by a simple e-beam lithography pattern with four square electrodes connecting to the interface. As shown in Figure 5a, the light illumination was focused on the center area between the electrodes. The change of current under the illumination is defined as photocurrent: $\Delta I = I_{\text{light}} - I_{\text{dark}}$, where I_{dark} is the dark current before illumination and I_{light} is the obtained current under the illumination. The ratio of $\Delta I/I_{\text{dark}}$ is then defined as photoresponse. Figure 5b is the current-voltage (I-V) curves (in logarithmic scale) of both LAO/SRO/STO and STO/SRO/STO samples measured in the dark and under illumination of ultraviolet light source with $\lambda = 350$ nm and power density of 0.5 mW/cm^2 . The measured dark current of LAO/SRO/STO is around one order of magnitude larger than that of STO/SRO/STO. In addition, STO/SRO/STO also presents an unstable dark current at applied voltage range below 2.5 V due to a very high resistance that is close to the instrumental measurement limit, which is ~ 1 pA. If the practical current obtained from sample is below this value, it is always presented as noisy signals even though we can still observe the “fake” current from the instrument. It implies that the practical current of STO/SRO/STO at an applied field below ~ 2.5 V is far smaller than the limit, and the observed current floats with very large fluctuations. On the other hand, the current of LAO/SRO/STO rapidly increases with applied voltage, where the measured current is always above 1 pA that only

requires the field larger than 0.15V. Therefore, such abnormal fluctuations are hardly observed in the case of LAO/SRO/STO. This result confirms that the electronic transport behavior of the SRO monolayer can be effectively improved by the LAO capping layer, which is consistent with the conclusions of XAS and theory prediction. When both samples are illuminated, their currents exhibit a large increment with nearly the same magnitude (two orders of magnitude) at all applied voltage range, implying that such an enhancement is indeed caused by this inserted SRO monolayer. Basically, this phenomenon cannot be observed if we replace the SRO monolayer by highly conductive interlayer or interface, *i.e.*, LAO/100 u.c. SRO/STO or 2DEG LAO/STO, respectively. From Supplementary Fig. S2, we have revealed that either LAO/100 u.c. SRO/STO or 2DEG LAO/STO has undistinguishable variation of current under the same illumination condition, which is in accordance with the expectation that the metallic characteristic cannot afford large photoresponse. Similar results for the 50 nm SRO thin film with a very small photoresistivity of $\sim 0.2\%$ to 2% can be obtained in our previous studies.³⁹⁻⁴⁰ These observations support that only the opened small bandgap in the SRO monolayer can originate large photoresponse in this kind of oxide heterstructures. Therefore, further exploration of the photocurrent in the semiconducting SRO monolayer at the interface between the LAO layer and the STO substrate becomes very attractive. Figure 5c shows the photocurrent of the SRO

monolayer at three typical wavelengths (UV (405 nm), green (520 nm), and red (642 nm)). Before the illumination, I_{dark} of the SRO monolayer is $\sim 1.8 \times 10^{-10}$ A operated at 5 V. Under the illumination, the power densities of all light sources were kept at 3.6 mW/cm² for comparison. Obviously, as the photon energy of light decreases, the photocurrent becomes smaller, which can be attributed to the weaker ability to generate photo-excited carriers under the light with smaller photon energy. For more practical application, we then chose the green light source (in the visible light range) to perform the power dependent measurements. At this wavelength (Figure 5d), the photocurrent increases with power density. A large photoresponse of ~ 325 % can even be obtained when the power density achieves to 500 mW/cm². It clearly reveals that this SRO monolayer has strong light-electron interaction to greatly improve its intrinsically poor transport behavior.

To explore the reason of large photoresponse of the SRO monolayer directly, the XSTM/S operated in an ultrahigh vacuum (UHV) chamber with a light source (laser diode, $\lambda = 405$ nm, power intensity = 3 mW/cm²) was used. This technique provides the local topography and the corresponding electronic information under illumination, which can reveal the photo-induced change in the band alignments of the SRO monolayer at the atomic spatial resolution. In this measurement, the 0.5 wt.% Nb doped STO substrates (Nb-STO) substrate and the protecting thick film of amorphous SRO

(a-SRO) were required to avoid crashing the tip during the scan. Therefore, the 6-unit-cell STO film was deposited on the Nb:STO substrate at first to mimic original environment of LAO/SRO/STO sample. Afterward the SRO monolayer and the LAO capping layer were sequentially grown on STO. Finally, the surface was covered by a conducting a-SRO film with the thickness greater than 500 nm for protection. After finishing the growth, the sample was transferred in an ultra-high vacuum (UHV) chamber to proceed the following cleavage and probe of the sample.⁴¹ The measurement method is schematized in Figure 6a. Before the illumination, Figure 6b displays a typically cross-sectional STM topographic image at a sample bias of +2.0 V. On the basis of the different electronic properties for STO, SRO and LAO, each region can be clearly distinguished. The Nb:STO substrate reveals atomically flat terraces, and height profile changes drastically at the interface between the Nb:STO and the STO buffer layer as indicated by a black arrow in Figure 6b. Moreover, a brighter region about 0.4 nm between the STO buffer layer and LAO, which can be identified as the SRO monolayer. The detailed information for the comparison of the photo-induced changes of the SRO monolayer can be unveiled by the spectroscopic dI/dV results shown in Figure. 6c to 6h. Excitingly, a spectacularly electronic change at the SRO monolayer has been indeed observed, in which the interface exhibits a brighter contrast while being illuminated exhibited in Figures 6c and 6d. More clear variation of the band

alignments across the SRO monolayer for these two conditions is then carried out by the quantitative analysis of the normalized dI/dV spectroscopic results, as shown in Figures. 6e and 6f, respectively.⁴² By extracting the intensity profile at the SRO monolayer, we are able to observe its energy gap directly. Before the illumination, the SRO monolayer possesses a small energy gap around 0.8 eV (Figure 6g), supporting the presence of semiconducting behavior. When the sample is irradiated, the energy gap of the SRO monolayer is reduced to 0.6 eV and the corresponding density of states (DOS) increases as well (Figure 6h). Such a reduction of energy gap under illumination is possibly from the structural variation of the SRO monolayer due to the photostriction effect and photo-excited electrons accumulated at the interface.³⁹⁻⁴⁰ Hence, the electronic conductivity of the SRO monolayer can be greatly enhanced under illumination.

Conclusions

In this work, we have demonstrated the fabrication of the complex oxide monolayers inserted in specially designed oxide heterostructures through the layer-by-layer growth mechanism and their potential in the optoelectronic devices. On the basic concept of the quantum confinement effect, we can start with a complex oxide, like SRO adopted in this study that originally possesses metallic characteristic in its bulk counterpart, and then force it to open a small bandgap and become semiconducting by limiting the

thickness in one unit cell. Compared to the van-der-Waal-based 2D materials, such kinds of complex oxide monolayers can exhibit a superior advantage that their electronic structures and physical properties are more easily modulated through the strain engineering. For example, the band gap of the SRO monolayers can be adjusted by altering different capping layer, STO or LAO, through their strong orbital-lattice coupling. The electronic transport behavior of the SRO monolayer is more improved by capping LAO than STO, which is due to the asymmetric-electrostatic-boundaries-induced lattice relaxation. As a result, we are able to first reveal the resistance of the SRO monolayer that has never been reported. Here we also examine the photoresponse of this SRO monolayer, where a considerably large enhancement under the illumination of visible light range is observed. From *real-time* observation of XSTM/S measurement, we have realized that this enhancement can be ascribed to the further reduction of energy gap during the illumination. Therefore, this study has offered a new perspective to explore the promising 2D oxide monolayers for optoelectronics.

Materials and Methods

Sample Preparation: The samples were fabricated on TiO₂-terminated STO (100) substrates using PLD. During the deposition, the stoichiometric targets of SRO, LAO, and STO were used, and the growth of monolayer and capping layers were precisely

controlled in layer by layer monitored by a RHEED. The substrate temperature and the oxygen pressure were maintained at 700 °C and 100 mTorr, respectively, for the growth of SRO and STO. However, to avoid the possible 3D growth of the LAO capping layer, the pressure decreased to 5×10^{-5} Torr to ensure the layer-by-layer growth.⁴³ After the deposition, all the films were post-annealed at the oxygen pressure of 300 Torr for 30 min, and then cooled down to room temperature.

Structure Characterization by STEM Z-contrast imaging: Structure characterization by Z-contrast imaging was carried out on a JEM-ARM200F microscope, equipped with a cold field emission electron gun, Cs-probe corrector and Cs-image corrector with a minimum probe of about 0.078 nm in diameter. The probe convergence angle and the detection angle used for imaging were 25 mrad and 92–228 mrad, respectively.

X-ray Absorption spectroscopy: The Ru L-edge XAS was performed at the 16A1 beamline in Taiwan Light Source. The fluorescence from SRO was collected using a Lytle detector. The O K-edge XAS was performed at the 2A beamline in Pohang Light Source in total electron yield mode. The direction of the incident X-rays was kept perpendicular to the sample planes so that the polarization vector would reside in the SRO plane.

Cross-Section Scanning Tunneling Microscopy and Spectroscopy: Before the STM measurements, amorphous SRO capping layers (> 500 nm) were deposited on top of all samples to prevent tip crash during the measurements. These samples were cleaved in situ in an UHV chamber whose base pressure was approximately 5×10^{-11} Torr. The cross-sectional STM topography images were obtained using constant current mode at +2.0 V. The corresponding atomically resolved spectroscopic results under illumination and dark conditions were recorded with the first derivative of tunneling current over tip-sample voltage (or differential conductivity), dI/dV . The spatial resolution is around 0.4 nm at interfaces. In order to reduce the thermal influence in our STS measurements under light illumination, we used the electronic controlled system. The thermal influence could be reduced by intermittently modulating the light output.

DFT calculation: We used first-principles calculation within the framework of density-functional theory to investigate the electronic states of the SRO monolayer. These calculations were performed using the Vienna ab initio simulation package (VASP),⁴⁴⁻⁴⁵ in which the exchange-correlation potential is treated in Perdew–Burke–Ernzerhof (PBE). Because the on-site electron-electron interactions are strong in the localized d orbitals for Ru, the Hubbard U parameters, i.e., $U = 2.5$ and $J = 0.4$ eV were applied to Ru d orbitals. These parameters have been extensively used to

investigate the electronic and magnetic properties of SRO-based interfaces.⁴⁶ The energy cutoff of 500 eV was used for the plane wave expansion of the projector augmented wave and $5 \times 5 \times 1$ Monkhorst–Pack grid is sampled for k-points in the self-consistent calculations.

Electric transport Measurements:

In order to conduct the transport measurements, four square metallic (Au/Ti) electrodes (0.3 mm^2 size) connected to the sandwiched SRO monolayer were thermally evaporated on the samples using e-beam lithography. Then gold wires were manually bonded to the electrodes using silver paste. The typical transport measurement was performed on Cryogen-free 4 K cryogenic probe station (Lake Shore Model CRX-4K) with high resistance meter (Keithley Model 6517A) for the samples. The resistance was obtained under the DC electric bias 1 V.

Photoresponse measurement:

Photoresponse of the samples was measured by a semiconductor characterization system (Keithley 4200-SCS with DC preamplifier). During the photoresponse measurements, the samples were illuminated by four kinds of single mode laser diodes: 350, 405, 520, and 642 nm, respectively (Thorlabs modulated by the ITC4001 driver). The light intensity was measured by a power meter.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Fitting results of samples across the XAS spectra of O *K* edge;

Photo-dependent I-V curves for the samples of STO/SRO/STO,

LAO/SRO/STO, LAO/100 u.c. SRO/STO, and common 2DEG system.

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Author contributions

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Notes

The authors declare no competing financial interest.

References:

- (1) Gabor, N. M.; Song, J. C. W.; Ma, Q.; Nair, N. L.; Taychatanapat, T.; Watanabe, K.; Taniguchi, T.; Levitov, L. S.; Jarillo-Herrero, P. Hot Carrier-Assisted Intrinsic Photoresponse in Graphene. *Science* **2011**, *334*, 648-652.
- (2) Sukhovatkin, V.; Hinds, S.; Brzozowski, L.; Sargent, E. H. Colloidal Quantum-Dot Photodetectors Exploiting Multiexciton Generation. *Science* **2009**, *324*, 1542-1544.
- (3) Binks, D. J. Multiple exciton generation in nanocrystal quantum dots - controversy, current status and future prospects. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12693-12704.
- (4) Rabani, E.; Baer, R. Theory of multiexciton generation in semiconductor nanocrystals. *Chem. Phys. Lett.* **2010**, *496*, 227-235.
- (5) Gabor, N. M.; Zhong, Z.; Bosnick, K.; Park, J.; McEuen, P. L. Extremely Efficient Multiple Electron-Hole Pair Generation in Carbon Nanotube Photodiodes. *Science* **2009**, *325*, 1367-1371.
- (6) Wang, S.; Khafizov, M.; Tu, X.; Zheng, M.; Krauss, T. D. Multiple Exciton Generation in Single-Walled Carbon Nanotubes. *Nano Lett.* **2010**, *10*, 2381-2386.
- (7) Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C. Graphene photonics and optoelectronics. *Nat. Photon.* **2010**, *4*, 611-622.
- (8) Zhang, B. Y.; Liu, T.; Meng, B.; Li, X.; Liang, G.; Hu, X.; Wang, Q. J. Broadband high photoresponse from pure monolayer graphene photodetector. *Nat. Commun.* **2013**, *4*, 1811.
- (9) Mueller, T.; Xia, F.; Avouris, P. Graphene photodetectors for high-speed optical communications. *Nat. Photon.* **2010**, *4*, 297-301.
- (10) Liu, M.; Yin, X.; Ulin-Avila, E.; Geng, B.; Zentgraf, T.; Ju, L.; Wang, F.; Zhang, X. A graphene-based broadband optical modulator. *Nature* **2011**, *474*, 64-67.
- (11) Winzer, T.; Knorr, A.; Malic, E. Carrier Multiplication in Graphene. *Nano Lett.* **2010**, *10*, 4839-4843.
- (12) Xia, F.; Mueller, T.; Lin, Y.-m.; Valdes-Garcia, A.; Avouris, P. Ultrafast graphene photodetector. *Nat. Nanotech.* **2009**, *4*, 839-843.
- (13) Sun, Z.; Martinez, A.; Wang, F. Optical modulators with 2D layered materials. *Nat. Photon.* **2016**, *10*, 227-238.
- (14) Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotech.* **2013**, *8*, 497-501.

- (15) Buscema, M.; Barkelid, M.; Zwiller, V.; van der Zant, H. S. J.; Steele, G. A.; Castellanos-Gomez, A. Large and Tunable Photothermoelectric Effect in Single-Layer MoS₂. *Nano Lett.* **2013**, *13*, 358-363.
- (16) Zhang, W.; Chuu, C.-P.; Huang, J.-K.; Chen, C.-H.; Tsai, M.-L.; Chang, Y.-H.; Liang, C.-T.; Chen, Y.-Z.; Chueh, Y.-L.; He, J.-H.; Chou, M.-Y.; Li, L.-J. Ultrahigh-Gain Photodetectors Based on Atomically Thin Graphene-MoS₂ Heterostructures. *Sci. Rep.* **2014**, *4*, 3826.
- (17) Manousakis, E. Photovoltaic effect for narrow-gap Mott insulators. *Phys. Rev. B* **2010**, *82*, 125109.
- (18) Coulter, J. E.; Manousakis, E.; Gali, A. Optoelectronic excitations and photovoltaic effect in strongly correlated materials. *Phys. Rev. B* **2014**, *90*, 165142.
- (19) Wang, L.; Li, Y.; Bera, A.; Ma, C.; Jin, F.; Yuan, K.; Yin, W.; David, A.; Chen, W.; Wu, W.; Prellier, W.; Wei, S.; Wu, T. Device Performance of the Mott Insulator LaVO₃ as a Photovoltaic Material. *Phys. Rev. Appl.* **2015**, *3*, 064015.
- (20) Toyota, D.; Ohkubo, I.; Kumigashira, H.; Oshima, M.; Ohnishi, T.; Lippmaa, M.; Takizawa, M.; Fujimori, A.; Ono, K.; Kawasaki, M.; Koinuma, H. Thickness-dependent electronic structure of ultrathin SrRuO₃ films studied by in situ photoemission spectroscopy. *Appl. Phys. Lett.* **2005**, *87*, 162508.
- (21) Chang, Y. J.; Kim, C. H.; Phark, S. H.; Kim, Y. S.; Yu, J.; Noh, T. W. Fundamental Thickness Limit of Itinerant Ferromagnetic SrRuO₃ Thin Films. *Phys. Rev. Lett.* **2009**, *103*, 057201.
- (22) Shen, X.; Qiu, X.; Su, D.; Zhou, S.; Li, A.; Wu, D. Thickness-dependent metal-insulator transition in epitaxial SrRuO₃ ultrathin films. *J. Appl. Phys.* **2015**, *117*, 015307.
- (23) King, P. D. C.; Wei, H. I.; Nie, Y. F.; Uchida, M.; Adamo, C.; Zhu, S.; He, X.; Bozovic, I.; Schlom, D. G.; Shen, K. M. Atomic-scale control of competing electronic phases in ultrathin LaNiO₃. *Nat. Nanotech.* **2014**, *9*, 443-447.
- (24) Lee, S.; Apgar, B. A.; Martin, L. W. Strong Visible-Light Absorption and Hot-Carrier Injection in TiO₂/SrRuO₃ Heterostructures. *Adv. Energy Mater.* **2013**, *3*, 1084-1090.
- (25) Chen, Y. Z.; Trier, F.; Wijnands, T.; Green, R. J.; Gauquelin, N.; Egoavil, R.; Christensen, D. V.; Koster, G.; Huijben, M.; Bovet, N.; Macke, S.; He, F.; Sutarto, R.; Andersen, N. H.; Sulpizio, J. A.; Honig, M.; Prawiroatmodjo, G. E. D. K.; Jespersen, T. S.; Linderroth, S.; Ilani, S.; Verbeeck, J.; Van Tendeloo, G.; Rijnders, G.; Sawatzky, G. A.; Pryds, N. Extreme mobility enhancement of two-dimensional electron gases at oxide interfaces by charge-transfer-induced modulation doping. *Nat. Mater.* **2015**, *14*, 801-806.

- (26) Liu, H.-J.; Lin, J.-C.; Fang, Y.-W.; Wang, J.-C.; Huang, B.-C.; Gao, X.; Huang, R.; Dean, P. R.; Hatton, P. D.; Chin, Y.-Y.; Lin, H.-J.; Chen, C.-T.; Ikuhara, Y.; Chiu, Y.-P.; Chang, C.-S.; Duan, C.-G.; He, Q.; Chu, Y.-H. A Metal–Insulator Transition of the Buried MnO₂ Monolayer in Complex Oxide Heterostructure. *Adv. Mater.* **2016**, 28, 9142-9151.
- (27) Ohtomo, A.; Hwang, H. Y. A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* **2004**, 427, 423-426.
- (28) Liu, Z. Q.; Li, C. J.; Lü, W. M.; Huang, X. H.; Huang, Z.; Zeng, S. W.; Qiu, X. P.; Huang, L. S.; Annadi, A.; Chen, J. S.; Coey, J. M. D.; Venkatesan, T.; Ariando Origin of the Two-Dimensional Electron Gas at LaAlO₃/SrTiO₃ Interfaces: The Role of Oxygen Vacancies and Electronic Reconstruction. *Phys. Rev. X* **2013**, 3, 021010.
- (29) Bristowe, N. C.; Philippe, G.; Littlewood, P. B.; Emilio, A. The origin of two-dimensional electron gases at oxide interfaces: insights from theory. *J Phys. Condens. Matter.* **2014**, 26, 143201.
- (30) Lee, P. W.; Singh, V. N.; Guo, G. Y.; Liu, H. J.; Lin, J. C.; Chu, Y. H.; Chen, C. H.; Chu, M. W. Hidden lattice instabilities as origin of the conductive interface between insulating LaAlO₃ and SrTiO₃. *Nat. Commun.* **2016**, 7, 12773.
- (31) Kawasaki, M.; Takahashi, K.; Maeda, T.; Tsuchiya, R.; Shinohara, M.; Ishiyama, O.; Yonezawa, T.; Yoshimoto, M.; Koinuma, H. Atomic Control of the SrTiO₃ Crystal Surface. *Science* **1994**, 266, 1540-1542.
- (32) Rijnders, G.; Blank, D. H. A.; Choi, J.; Eom, C.-B. Enhanced surface diffusion through termination conversion during epitaxial SrRuO₃ growth. *Appl. Phys. Lett.* **2004**, 84, 505-507.
- (33) Mott, N. F. Amorphous and Liquid Semiconductors Introductory talk; Conduction in non-crystalline materials. *J. Non-Cryst. Solids* **1972**, 8, 1-18.
- (34) Khondaker, S. I.; Shlimak, I. S.; Nicholls, J. T.; Pepper, M.; Ritchie, D. A. Two-dimensional hopping conductivity in a GaAs/Al_xGa_{1-x}As heterostructure. *Phys. Rev. B* **1999**, 59, 4580-4583.
- (35) Withers, F.; Russo, S.; Dubois, M.; Craciun, M. F. Tuning the electronic transport properties of graphene through functionalisation with fluorine. *Nanoscale Res. Lett.* **2011**, 6, 1-11.
- (36) Nakagawa, N.; Hwang, H. Y.; Muller, D. A. Why some interfaces cannot be sharp. *Nat. Mater.* **2006**, 5, 204-209.
- (37) Agrestini, S.; Hu, Z.; Kuo, C. Y.; Haverkort, M. W.; Ko, K. T.; Hollmann, N.; Liu, Q.; Pellegrin, E.; Valvidares, M.; Herrero-Martin, J.; Gargiani, P.; Gegenwart, P.; Schneider, M.; Esser, S.; Tanaka, A.; Komarek, A. C.; Tjeng, L.

- H. Electronic and spin states of SrRuO₃ thin films: An x-ray magnetic circular dichroism study. *Phys. Rev. B* **2015**, *91*, 075127.
- (38) Si, L.; Zhong, Z.; Tomczak, J. M.; Held, K. Route to room-temperature ferromagnetic ultrathin SrRuO₃ films. *Phys. Rev. B* **2015**, *92*, 041108.
- (39) Liu, H.-J.; Wei, T.-C.; Zhu, Y.-M.; Liu, R.-R.; Tzeng, W.-Y.; Tsai, C.-Y.; Zhan, Q.; Luo, C.-W.; Yu, P.; He, J.-H.; Chu, Y.-H.; He, Q. Strain-Mediated Inverse Photoresistivity in SrRuO₃/La_{0.7}Sr_{0.3}MnO₃ Superlattices. *Adv. Funct. Mater.* **2016**, *26*, 729-737.
- (40) Wei, T.-C.; Wang, H.-P.; Liu, H.-J.; Tsai, D.-S.; Ke, J.-J.; Wu, C.-L.; Yin, Y.-P.; Zhan, Q.; Lin, G.-R.; Chu, Y.-H.; He, J.-H. Photostriction of strontium ruthenate. *Nat. Commun.* **2017**, *8*, 15018.
- (41) Huang, B.-C.; Chiu, Y.-P.; Huang, P.-C.; Wang, W.-C.; Tra, V. T.; Yang, J.-C.; He, Q.; Lin, J.-Y.; Chang, C.-S.; Chu, Y.-H. Mapping Band Alignment across Complex Oxide Heterointerfaces. *Phys. Rev. Lett.* **2012**, *109*, 246807.
- (42) Feenstra, R. M. Tunneling spectroscopy of the (110) surface of direct-gap III-V semiconductors. *Phys. Rev. B* **1994**, *50*, 4561-4570.
- (43) Ariando; Wang, X.; Baskaran, G.; Liu, Z. Q.; Huijben, J.; Yi, J. B.; Annadi, A.; Barman, A. R.; Rusydi, A.; Dhar, S.; Feng, Y. P.; Ding, J.; Hilgenkamp, H.; Venkatesan, T. Electronic phase separation at the LaAlO₃/SrTiO₃ interface. *Nat. Commun.* **2011**, *2*, 188.
- (44) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558-561.
- (45) Kresse, G.; Hafner, J. *Ab initio* molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, *49*, 14251-14269.
- (46) Gupta, K.; Mandal, B.; Mahadevan, P. Strain-induced metal-insulator transition in ultrathin films of SrRuO₃. *Phys. Rev. B* **2014**, *90*, 125109.

Figures

Figure 1. (a). The schematic of the SRO monolayer capped with the 6-unit-cell LAO layer grown on the TiO₂ terminated STO substrates. (b) *Real-time* monitoring of RHEED intensity for the SRO monolayer and LAO capping layer. The inset in (b) shows the typical morphology of atomically flat surface. (c) The SRO monolayer sample identified by the HAADF-STEM measurement.

Figure 2. (a) A semiconducting behavior of the SRO monolayer can be observed by capped with the LAO thin layer. (b) The plot of $\ln(R(T))$ versus $(1/T)^{1/\alpha}$, where $\alpha = 1$ is the fitting result from Arrhenius equation, and $\alpha = 3$ is according to the model of 2D Mott VRH. The wider fitted range in the latter model supports that 2D transport behavior for this SRO monolayer.

Figure 3. (a) The XAS spectra across the Ru L -edges taken from the SRO monolayers with different capping layers, and the control samples of the 100-unit-cell SRO with the LAO capping layer, the standard SRO and RuO₂ powders. No obvious peak shift on the signal of e_g and t_{2g} orbitals describes no valence change of Ru ions in all samples. Higher intensity ratio of e_g / t_{2g} also indicates less distortion of Ru octahedrons. (b) The XAS spectra across O K -edge reveal the Ru 4d – O 2p (~529.04 eV) and Ti 3d – O 2p (~530.86 eV) hybridizations. The nearly unchanged peak positions between the SRO monolayer and the bulk SRO film suggests that the top SrO plane of SRO can effectively avoid oxygen deficiency at the RuO₂ plane and the neighboring TiO₂ planes inside the substrates. (c) The model of band gap modulation in the SRO monolayer due to the crystal field splitting by different capping layers.

Figure 4. The slab models of case 1 – L6 ((STO)₆-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(STO)₆), case 2 – L1 ((LAO)₁-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(LAO)₁), and case 2 – L2 ((LAO)₂-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(LAO)₂) for calculation and the respective layer projected density of states of these SRO monolayers. The Fermi level is given by the dashed line.

Figure 5. (a) The schematic of the photoresponse measurement. (b) The I-V curves for LAO/SRO/STO and STO/SRO/STO samples under the photon source of 350 nm with power density of 0.5 mW/cm². (c) The photocurrent and photoresponse of the SRO monolayer at three photon sources with 405 nm, 520 nm, and 642 nm. (D) The power dependent photocurrent and photoresponse of the SRO monolayer performed at 520 nm, where the variation of photocurrent to dark current can be as high as 325%.

Figure 6. (a) Schematic diagram of cross-sectional STM used to measure the photo-modulated electronic properties of the SRO monolayer. (b) Typical cross-sectional topography image of the SRO monolayer at sample bias of +2.0 V. (c) and (d) are STS spectroscopic dI/dV images of the SRO monolayer at sample bias of +2.0 V in dark and under illumination, respectively. (e) and (f) are band alignments and corresponding atomic-scale resolutions of electronic properties across the SRO

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monolayer extracted from (c) and (d), respectively. Further analysis of the energy gap from dI/dV curves of the SRO monolayer in dark and under illumination can be observed in (g) and (h), respectively.

Figure 1. (a). The schematic of the SRO monolayer capped with the 6-unit-cell LAO layer grown on the TiO₂ terminated STO substrates. (b) Real-time monitoring of RHEED intensity for the SRO monolayer and LAO capping layer. The inset in (b) shows the typical morphology of atomically flat surface. (c) The SRO monolayer sample identified by the HAADF-STEM measurement.

161x133mm (300 x 300 DPI)

Figure 2. (a) A semiconducting behavior of the SRO monolayer can be observed by capped with the LAO thin layer. (b) The plot of $\ln(R(T))$ versus $T^{-1/\alpha}$, where $\alpha = 1$ is the fitting result from Arrhenius equation, and $\alpha = 3$ is according to the model of 2D Mott VRH. The wider fitted range in the latter model supports that 2D transport behavior for this SRO monolayer.

119x167mm (600 x 600 DPI)

Figure 3. (a) The XAS spectra across the Ru L -edges taken from the SRO monolayers with different capping layers, and the control samples of the 100-unit-cell SRO with the LAO capping layer, the standard SRO and RuO₂ powders. No obvious peak shift on the signal of e_g and t_{2g} orbitals describes no valence change of Ru ions in all samples. Higher intensity ratio of e_g / t_{2g} also indicates less distortion of Ru octahedrons. (b) The XAS spectra across O K -edge reveal the Ru 4d – O 2p (~ 529.04 eV) and Ti 3d – O 2p (~ 530.86 eV) hybridizations. The nearly unchanged peak positions between the SRO monolayer and the bulk SRO film suggests that the top SrO plane of SRO can effectively avoid oxygen deficiency at the RuO₂ plane and the neighboring TiO₂ planes inside the substrates. (c) The model of band gap modulation in the SRO monolayer due to the crystal field splitting by different capping layers.

112x71mm (300 x 300 DPI)

Figure 4. The slab models of case 1 – L6 ((STO)6-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(STO)₆), case 2 – L1 ((LAO)₁-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(LAO)₁), and case 2 – L2 ((LAO)₂-(SRO)_{1.5}-(STO)_{5.5}-(SRO)_{1.5}-(LAO)₂) for calculation and the respective layer projected density of states of these SRO monolayers. The Fermi level is given by the dashed line.

94x50mm (300 x 300 DPI)

Figure 5. (a) The schematic of the photoresponse measurement. (b) The I-V curves for LAO/SRO/STO and STO/SRO/STO samples under the photon source of 350 nm with power density of 0.5 mW/cm². (c) The photocurrent and photoresponse of the SRO monolayer at three photon sources with 405 nm, 520 nm, and 642 nm. (D) The power dependent photocurrent and photoresponse of the SRO monolayer performed at 520 nm, where the variation of photocurrent to dark current can be as high as 325%.

127x90mm (300 x 300 DPI)

Figure 6. (a) Schematic diagram of cross-sectional STM used to measure the photo-modulated electronic properties of the SRO monolayer. (b) Typical cross-sectional topography image of the SRO monolayer at sample bias of +2.0 V. (c) and (d) are STS spectroscopic dI/dV images of the SRO monolayer at sample bias of +2.0 V in dark and under illumination, respectively. (e) and (f) are band alignments and corresponding atomic-scale resolutions of electronic properties across the SRO monolayer extracted from (c) and (d), respectively. Further analysis of the energy gap from dI/dV curves of the SRO monolayer in dark and under illumination can be observed in (g) and (h), respectively.

232x351mm (300 x 300 DPI)

80x40mm (300 x 300 DPI)